

Historical Perspective

A.K. Tyagi

Foundation of India's Atomic Energy Programme:

Evolution of Atomic Energy Programme in India is an ever-inspiring story of sustained efforts made by Indian scientists and engineers towards progress, prosperity, self-reliance and security of our nation. The saga of nuclear science and technology development in India is based on the objective of peaceful utilisation of energy embedded in tiny but mighty atoms. Within a year of India's independence, the Atomic Energy Programme was formally seeded by setting up the Atomic Energy Commission (AEC) on August 10, 1948 through the vision of Dr. Homi Jahangir Bhabha; father of the Indian Atomic Energy Programme. The early activities directed towards unfurling the fundamental science of atomic energy (mostly covering physics, chemistry and mathematics), were cradled in makeshift laboratories and facilities. One such example is an old and defunct textile mill at the Cadell Road in Mahim area of Bombay (presently known as 'Veer Sawarkar Marg' in Mumbai). The programme's humble beginning was enriched with the great vision, determination and multi-faceted capabilities of the founding father Dr. Bhabha along with a small team of eminent Indian scientists, mostly handpicked by him. At the same time, the programme faced challenges such as limited finances, at large non-existing indigenous technologies and dearth of trained scientific human resource. The former factors triumphed over the latter and the journey soon witnessed setting up of the Department of Atomic Energy (DAE) on August 3, 1954 followed by formally establishing Atomic Energy Commission (AEC) in DAE through a resolution passed by the Government of India in 1958. Beginning from the inception of programme in 1948, the year 2023 marks the completion of 75 years of AEC, which coincides with the conclusion of year-long nationwide celebrations ('Azadi ka Amrit Mahotsav') of 75 years of India's independence. It also overlaps with the onset of next 25 years of Government of India's vision ('Azadi ka Amrit Kaal') to make India a developed nation standing as a global leader.

Initial years:

The Atomic Energy Act was enacted in 1948 and the Atomic Energy Commission, led by Dr. Bhabha, initiated its work with Dr. K. S. Krishnan and Dr. S. S. Bhatnagar as members. The early focus was on surveys of minerals for the Atomic Energy Programme. In June 1949, Dr. Jagdish Shankar (the first chemist in Atomic Energy Establishment) and Dr. Braham Prakash were recruited for Chemistry and Metallurgy programmes. Experts like Dr. V. T. Athavale and Shri. D. V. Bhatnagar joined thereafter and initiated the work from the premises of NPL, New Delhi and by Dec. 1949, the activities were shifted to Bombay. Dr. Shankar played a crucial role in establishing research facilities and expanding the scientific

staff in the 1950s. This included recruitment of three additional chemists namely, Dr. A. K. Sundaram, Dr. M. D. Karkhanavala, and Shri T. K. S. Murthy. This expansion facilitated new research in polarography, spectrophotometry, solvent extraction, and ion exchange, supplementing mineral analysis. The experimental facilities grew with the acquisition of X-ray diffraction unit in 1954 and a spectrograph for spectrochemical analysis. Dr. Karkhanavala oversaw these facilities.

Subsequently, Dr. Shankar's visits to atomic energy laboratories in the United Kingdom and France catalyzed the initiation of various activities within the Chemistry Division. These activities included ore dressing, ore extraction, chemical engineering, physical chemistry, solid state chemistry, radiochemistry, and later, the preparation of pure materials. With establishment of the Department of Atomic Energy (DAE) in August 1954 with its headquarters in Bombay (now Mumbai), Chemistry Division became among the first scientific Divisions in the DAE. The expanded research programmes introduced novel approaches using solvent extraction and ion exchange with radioactive indicators.

Acknowledging the importance of bolstering Analytical Chemistry, reorganization occurred in 1956, transferring part of the Physical Chemistry Section, engaged in electrochemistry, spectrophotometry, and spectrochemical analyses, to the Analytical Chemistry Section. Simultaneously, the Pure Materials Section received further reinforcement for preparing high-purity materials. The Division's activities in spectroscopic research expanded when Prof. R. K. Asundi, a renowned spectroscopy specialist from the Banaras Hindu University joined Chemistry Division. He later became an advisor to the Department of Atomic Energy.

In 1957, Dr. V. K. Iya joined the Chemistry Division after being selected by Dr. Bhabha himself. Dr. Iya made significant contributions towards the production of phosphorus (^{32}P) and sulfur (^{35}S) isotopes using neutron irradiation facilities at the Apsara Reactor. In 1957, the isotope preparation programme was formally established as a separate Isotope Division and in the same year, the Radiochemistry Laboratory was established at Trombay for research on radioactive materials. Team of scientists from the Radiochemistry Section of Chemistry Division, led by Dr. H. D. Sharma, was transferred to this new laboratory, later named the Radiochemistry Division. The remaining programmes continued in the Radiation Chemistry Section of Chemistry Division. Concurrently, programmes related to analytical chemistry culminated into formation of the Analytical Division in 1956. Even Spectroscopy Division headed by Dr. R. K. Asundi, was carved from the Chemistry Division in 1956. The Analytical Division significantly enhanced its spectroscopy work by recruiting spectroscopy specialist like Dr. N. A. Narasimhan, which led to the expansion of research activities from spectrochemical analysis to atomic and molecular spectroscopy. In 1958, the Physical Chemistry Section of the Chemistry Division was renamed as Solid State Studies Section. Modern equipment such as thermogravimetric balance and an indigenously built electron microscope were setup in the Division.

Between 1958 and 1959, organizational restructuring saw the Ore Dressing Section becoming a part of the Metallurgy Division, while the Ore Extraction and Chemical Engineering Sections formed the Chemical Engineering Division. This phase witnessed the birth of several new Divisions crucial to atomic energy programme within a decade from the inception of Chemistry Division, thereby becoming 'the cradle of Chemical Research in the Indian Atomic Energy Programme'. Post-reorganization, the Division encompassed Solid-

State Studies Section, Pure Materials Section, and Radiation Chemistry Section, a setup that endured for decades. The Radiation Chemistry Section expanded its scope over time, leading to the creation of the Water Chemistry Division in 1984, eventually renamed as the Applied Chemistry Division in 1989. New sections namely, Physical Chemistry Section and Chemical Dynamics Section emerged in the 1980s and 1990s. The National Centre for Compositional Characterisation of Materials (NCCCM) was established at Hyderabad in 1993 to cater to the needs of advanced chemical characterisation. All these developments have led to the evolution of today's Chemistry Group, which continues to make significant and relevant contributions to the Atomic Energy Programme and frontier areas of chemistry.

Chemistry catering to the needs of department:

After summarizing the structure and growth of chemical research within the Atomic Energy Programme, it is worthwhile to mention some of the significant research conducted during this period. The pursuit of the programme's immediate goals led to the investigation and identification of local mineral resources critical for fission-based nuclear energy technologies, encompassing uranium, thorium, zirconium, nuclear-pure graphite, beryllium, and cadmium. India faced financial constraints and limited global accessibility to these minerals post-World War II, necessitating chemical characterization and processing of these materials to extract the required 'Nuclear Materials.' This became a pivotal responsibility for the chemistry community during its formative years and, research on 'Chemistry of Nuclear Materials' commenced along with the onset of Indian Atomic Energy programme.

The initial chemistry activities centred on Analytical Chemistry; specifically involving the estimation of uranium in monazite sand samples. Dr. Bhabha presented this work at an International Conference organised by the International Atomic Energy Agency (IAEA). The methodology used was developed by a team of dedicated scientists spearheaded by Dr. V. T. Athavale and was considered confidential at that time. However, it met with scepticism from the conference delegates. Dr. Bhabha staunchly defended the approach and the data it produced, which were later validated and acknowledged. As a result of this work, shipment of monazite sand to European countries was promptly halted, leading to the establishment of the Indian Rare Earths Limited on August 18, 1950. Another milestone event involved the preparation of kilogram quantities of high-purity uranyl nitrate through diethyl ether extraction in 1955. This year also marked the first 'International Conference on the Peaceful Uses of Atomic Energy' held in Geneva (August, 1955) with Dr. Bhabha as President, where a technical paper was presented from the Chemistry Division on ion exchange recovery of uranium as a carbonate complex. In addition to this, separation of zirconium and hafnium was also among the success stories of the Chemistry Division in 1955. Chemistry fraternity made another impactful contribution to the Indian Atomic Energy Programme when fungal contamination was discovered within the coolant circuitry of the CIRUS reactor, constructed in collaboration with Canada. To address this issue, the coolant channels underwent a cleansing process using potassium dichromate solution. Unfortunately, radiation exposure led to chromium activation, which got deposited over the channel walls. The challenge of chromium build-up in these channels was entrusted to chemists, who ingeniously solved it by introducing required quantities of complexing agents into the channels, in-turn effectively eliminating the chromium deposits. These were few early important inputs from the Chemistry Division. Concurrently, a dedicated recruitment programme was initiated by Dr.

Bhabha in 1957, known as the BARC Training School, aimed to nurture highly talented and educated individuals. Chemistry discipline attracted the second-highest number of trainees in the inaugural batch of BARC Training School. Over the past 66 years, this training program has produced some of the finest scientists in the country, which also include globally renowned chemists.

Chemist fraternity continued to serve the department as evident from the succeeding discussion. 'Dhruva', the 100 MWth indigenous research reactor at Trombay attained criticality on August 08, 1985. During its commissioning and initial operating phase, a problem of large amplitude flow-induced vibrations was encountered in the fuel assembly, which led to excessive wear of fuel rod aluminum cladding. As a result of this, aluminum turbidity developed in the heavy water system. The task of purifying the heavy water inventory was entrusted to the Chemistry Group (then known as Chemical Group), where extensive efforts were undertaken leading to successful removal of the turbidity using a special acrylic type weakly acidic magnesium-magnesium oxide loaded sorbent material. A centrifuge-separator was also employed for this purpose. This work stands among the hallmark contributions of chemistry programme towards research reactors.

Tarapur Atomic Power Station unit 3 and 4 (TAPS-3&4) are India's first two 540 MWe indigenous PHWRs. During the first approach to criticality for both units, controlled injection of gadolinium nitrate in conjunction with boric acid in moderator system was used for reactivity control purpose, wherein accurate trace analysis (< 30 ppb) of gadolinium is needed. For this requirement, a UV-visible spectrophotometry-based rapid analysis method was developed by Chemistry Group; verified with ICP-AES technique and demonstrated at TAPS 3&4 site for Gd-estimation up to 25 ppb in association with RRSD, BARC and NPCIL. This method was successfully used during the first approach to criticality of both, TAPS-4 and TAPS-3 on 06.03.2005 and 21.05.2006, respectively.

A follow-up requirement in PHWRs is removal of gadolinium from the moderator system. An iso-pH regime is desired both, in the moderator system as well as at the outlet of ion exchange column. A methodology towards this requirement was developed in Chemistry Group for TAPS-3&4. Leach-out characteristics of nitric acid from a weak base anion exchange resin was evaluated as a function of nitric acid loading at fixed flow rate(s). Based on the results of these studies, column configuration consisting of strong acid cation topped mixed bed (strong acid cation and weak base anion) followed by 5% nitric acid loaded weak base anion exchange column was recommended. With this configuration, nitric acid could be leached-out by the bottom layer of 5% nitric acid loaded weak base anion exchanger during the initial Gd-removal phase. As a result, column outlet pH could be maintained to avoid Gd-precipitation and material compatibility of system components was not compromised. Functioning of this triple layer bed was successfully demonstrated in TAPS-3 (May 2008).

Thorough understanding of water chemistry under extreme conditions of temperature, pressure, radiation and inclusions (chemical / physical) is another core expertise at the Chemistry Group. Decades of R&D efforts and applications of the knowledgebase so evolved has led to eleven successful chemical decontamination campaigns undertaken by the Chemistry Group at seven Indian PHWRs for removal of iron (several hundred kg / campaign) and active contaminants (up to hundreds of curies / campaign) such as ⁶⁰Co,

Sb (^{124}Sb and ^{125}Sb), etc. Sustained and continuing efforts such as these amply exhibit the notable contribution of the Chemistry Group towards the Indian Nuclear Programme.

Removal of suspended turbidity from the coolant circuitry of NPPs is yet another challenging requirement. On the basis of electro-sorption of suspended particles on high surface area fibrous electrode (graphite), an electrochemical filter has been indigenously developed at Chemistry Group. It houses series of electrode pairs inside the filter assembly for turbidity removal. This filter assembly was successfully applied for removal of indium turbidity from the moderator system of RAPS-1 (December 2001). It was also successfully used for removing microbial population from the RAPS-2 tritium monitoring facility, which thereby improved the sensitivity of plastic scintillators. The filter design was scaled-up and a pilot plant system was fabricated to work with higher flow rates. This filter was successfully used for (i) removal of iron turbidity from the active process cooling water of KGS-1 (April 2007) and (ii) removal of iron, silica and microbial turbidity from the open storage pond at WSCD, Kalpakkam. These examples are testimonies of the role of water chemistry-based technologies for our indigenous nuclear programme.

Three Mile Island accident in March, 1979 and Chernobyl accident in April, 1986 brought forth the safety concerns due to hydrogen produced under LOCA conditions in nuclear reactors. Over a period, Chemistry Group has worked on noble metal-based supported catalysts for room temperature initiation of hydrogen-oxygen reaction at varying hydrogen concentration in presence of different chemical species likely to be present under the accident conditions. Employing an innovative approach for electroless deposition of noble metal on SS wiregauze, a catalyst with controlled surface morphology was developed to deliver the required performance. A prototype device based on this catalyst, in-collaboration with RSD, was supplied to NPCIL in 2011 and found acceptable for installation in PHWRs. Considering the NPCIL requirement of 1180 such devices, the commercial production had been achieved with ECIL, Hyderabad. Currently all operational PHWRs have been retrofitted with Passive Catalytic Recombiner Devices (PCRDs) with this indigenously developed safety feature. In June 2023, KAPS-3 became first PHWR to be commissioned with pre-fitted PCRDs. It is a perfect demonstration of a basic research leading to deployment of technology of relevance.

Envisioning the potential of fission-based nuclear energy from uranium and thorium, Dr. Bhabha shaped India's 'Three-stage Nuclear Programme' based on the 'Closed Fuel Cycle' model. This approach entails extracting Actinides (U and Th) from natural sources, fabricating them into suitable chemical fuel forms, and irradiating the fuel in a nuclear reactor to produce power and valuable radioisotopes; an initial phase termed the 'Front End' of nuclear fuel cycle. Following this, spent nuclear fuel (SNF) is securely stored and chemically treated to retrieve fissile isotopes (Pu, minor actinides, ^{233}U), depleted uranium and / or thorium as well as fission products that are useful for non-power applications (medical, industrial, technological, etc.). The minimal high-level nuclear waste (HLW) produced is vitrified in a stable glass matrix, a domain in which the chemistry fraternity at BARC has played a leading role. Entire nuclear fuel cycle involves complex physico-chemical interactions among fuel components, radiation, coolant, and structural materials, demanding a thorough understanding to ensure reactor safety and assess fuel performance. The Chemistry Group has also played a pivotal role in evaluating the temperature and composition dependent physico-chemical properties of nuclear materials since its inception. Some of these

activities include high temperature thermophysical, thermodynamic and transport properties of (i) uranium and thorium-based oxide fuels (and SIMFUELS) for development of Indian PHWR and AHWR programmes, (ii) thorium and uranium-based metallic alloy fuels for futuristic advanced reactors, (iii) fluoride-based salts for Molten Salt Reactors, (iv) indigenous development of red mud-based sacrificial core-catcher ceramics for containment of molten corium under a severe accident scenario, (v) radiation sensors and detectors for application under extreme radio-chemical environments, etc. Apart from experimental investigations, Chemistry Group traditionally has rich expertise in theoretical and computational research also, which has considerably added to various research activities.

Alongside nuclear materials research, the DAE has emphasized the development of high-purity materials across various domains from its inception. This activity began in the Pure Materials Section of the Chemistry Division, focusing initially on rare earth separation technology. Subsequently, two important committees namely, Bhabha committee (1966) and Kalam committee (1993) highlighted India's requirement for ultrapure semiconductors, particularly in electronics for indigenous development of critical key technologies as safeguard against technology denials. This impelled indigenous development of processes achieving 5N (99.999%) purity for various elements. Presently, production of detector grade germanium for indigenous development of high-purity germanium (HPGe) detectors has been achieved at the Chemistry Group. This is the highest purity level achieved in India till date.

Radiation chemistry stands as a pivotal research field within India's atomic energy R&D landscape, primarily led by BARC. Initially, radiation chemists were tasked with understanding the stability of organic coolants under radiation and, creating high-specific-activity cobalt (^{60}Co) through nuclear transformation for cancer radiotherapy. In the late 1950s, BARC focused on understanding the decomposition products and pathways of organic coolants, followed by exploring radiation-induced polymerization, grafting, and biodegradable detergent production in the 1960s. In 1986, Chemistry Group achieved a milestone by installing a 7 MeV linear electron accelerator along with an indigenous optical pulse radiolysis setup, establishing it as a national facility. The efforts also extended to exploring atmospheric photochemical processes, analysing volatile organic compounds' tropospheric lifetime, global warming potential, and ozone depletion potential. The latest addition, a single-molecule fluorescence spectroscopy and imaging facility, enables actinide chemistry studies under normal laboratory conditions without the limitations of high activity handling.

The year 2024 marks 75 years of 'Chemistry Programme' in DAE which is a unique occasion to reflect back and compile the contributions of the programme to meet Department's objectives thus far. In the spirit of celebrating the completion of '75 years of Chemistry Programme in DAE', and, with the intent of re-dedicating ourselves with greater commitment in the service of nation, it is planned to pen-sketch the evolutionary journey of different subject areas that constitute overall research at the 'Chemistry Group' of BARC.

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