Radiation Chemistry Research

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Preamble:
This article details evolution of radiation chemistry research at Chemistry Group. It describes development of various facilities and their applications in understanding radiation chemistry of water, aqueous solutions and polymers to address the need of nuclear establishments of DAE. Several societal and medical applications of radiation chemistry are also discussed.

Brief historical perspective:

Radiation chemistry research in the Department of Atomic Energy, India, has a long history since late 1950s and early 1960s. During that period, intense basic and applied research was being pursued related to nuclear reactors. There was an interest in using organic solvents as primary coolants in nuclear reactors. Main interest in organic coolants was due to the fact that they are less corroding than water, and thus carbon steel components can be used in lieu of corrosion resistant materials required for water. In addition, other envisaged advantages were high boiling points and higher heat capacities. In this regard, polybiphenyls were considered as prospective solvents. It was important to study radiation effects on these solvents. Thus in initial period, studies were mainly carried out to examine the radiation stability of these solvents at high radiation doses, and to check the evolution of hydrogen and lower hydrocarbons, as part of a project named as NUHMOC. However, euphoria over use of organic solvents as primary coolants was short-lived. Lot of work was carried out on compounds like terphenyl and valuable data were collected. Interest in organic coolants tapered due to their radiation instability and increased viscosity because of polymeric compounds formations. Subsequently, studies were carried out on radiation effects on greases, lubricants and transformer pump oils used in the vicinity of radiation environment and useful data were generated for the safety of reactor personnel. Since the radiation stability of these solvents was not adequate to be used for the proposed purpose, radiation chemistry research changed focus from organic solvents to water for nuclear applications.

Radiation chemistry research at Trombay began with the commissioning of Apsara reactor, way back in 1956. The main motivation was to study the radiation chemistry of water used as reactor coolants / moderators for performance of research and power reactors. To carry out radiation chemistry research, Radiation Chemistry Section was created in Chemistry Division in 1958, and included in Radiation Chemistry & Chemical Dynamics (RC&CD) Division in 1999, which was renamed as Radiation & Photochemistry Division (RPCD) in the Chemistry Group in the year 2005.

Development for supporting radiation chemistry research:

Research in radiation chemistry at BARC started in 1950s, and almost a decade later, photochemical research was also initiated to complement the radiation chemistry research. During the study of Cobalt-60 gamma radiolysis of various aqueous and organic systems, a strong need was visualized to investigate a chemical reaction in real time to understand its dynamics. Under IAEA arrangement, a well-timed visit by Prof Edwin J. Hart from Argonne National Laboratory, USA, to BARC during the year 1971 proved really fruitful. Edwin, co-discoverer of hydrated electron (e^-_{aq}), brought with him a mini flash photolysis unit for the photo-generation of electrons and introduced BARC researchers to the realm of time resolved studies in photochemical research. The type of work carried out with this unit was reactions of e^-_{aq} with a variety of organic, inorganic compounds and monomers. Later Chemistry Group, BARC developed indigenously one microsecond flash photolysis system, especially to be used for radioactive samples.

Research in Radiation Chemistry led to development of several facilities. Lot of emphasis was given to develop suitable analytical techniques, such as Gas Chromatography for detection and estimation of volatile products, during earlier time. It is worth mentioning that pioneering development of Gas chromatograph (GC) took place in then Atomic Energy Establishment Trombay (AEET), and technology was transferred to several private companies, such as AIMIL Industries, M/s Toshniwal Bros Pvt Ltd and M/s Associated Instrument Mfg. Ltd. Those companies in turn supplied Gas Chromatographs to few premier scientific institutions in India. Subsequently, GC was coupled with mass spectrometer (MS) to increase the accuracy of product identification.

Radiation chemistry research:

Radiation Chemistry research in Chemistry Group involves investigation of effects of radiation, generally gamma rays and electrons, on aqueous and non-aqueous solutions, polymers, and other materials of importance. Kinetics and spectroscopic properties of intermediates, reactive species and stable products have been measured to understand a reaction in detail. Knowledge gained on fundamental aspects of interaction is propelled the applications of radiation chemistry in addressing social and health issues. Measurements in steady-state, using Cobalt-60 Gamma source, and time resolved (ms, μs, ns time domain) radiolysis, employing a linear electron accelerator (7 MeV LINAC) in a pulse radiolysis set up, were performed with advancement in instruments. Dr. R.M. Iyer, Dr. J.P. Mittal and Dr. P.N. Moorthy played significant roles in initiating and sustaining radiation chemistry research at Chemistry Group. They encouraged their younger colleagues to take up challenging problems in this research area.

Cobalt-60 gamma source and nanosecond LINAC facility:

In 1970s, initial radiation chemical studies at Chemistry Group, BARC, were performed using Cobalt-60 gamma source. In this direction, radiation polymerization studies have been carried out, one major objective was on the initiation and mechanism of polymerization. Radiation induced polymerization has several advantages over conventional methods. Several investigations were performed on radiation effects on natural as well as synthetic polymers. Degradation studies of resins and other unwanted products were also investigated using Co-60 gamma radiation. Studies on wood polymer composites with the aim of extending shelf life of soft wood under harsh atmospheric conditions were pursued. Work was also carried out on hydrogels for burn wound healing applications, and subsequently its efficacy was demonstrated.

After the development of pulse radiolysis technique in early 1960s, a few of BARC scientists got trained in pulse radiolysis technique at reputed laboratories in UK and USA, like University of Newcastle upon Tyne, Brookhaven National laboratory, University of Notre Dame, where they performed pioneering studies on effects of radiation interactions. These scientists had prolonged research stays at different laboratories, and worked with established professors carrying out research in the field of radiation chemistry. They provided much required boost to the research in radiation chemistry after they returned to BARC, fully trained and bubbling with enthusiasm.

After extensive studies using gamma source, it was realized to provide radiation chemistry research a quantum jump by time resolved studies to characterize reactive species using pulse radiolysis studies. In 1986, nanosecond electron pulse radiolysis facility was commissioned at Chemistry Group BARC and housed in the basement of Modular Laboratories at BARC Trombay campus, and till date it continues to be a work-horse of Radiation Chemistry research at Chemistry Group. The pulsed linear electron accelerator (LINAC) of 7 MeV energy capable of giving electron pulses of 5, 10, 25, 100 and 500 ns as well as 2 microseconds was procured from Radiation Dynamics, UK and was coupled with indigenously developed optical detection technique. Subsequently, computer program was developed in-house to acquire optical signal from oscilloscope to personal computer for processing spectral and kinetic data. Some radiation chemists were very enthusiastic, and first they learnt the computer programming, and then used their knowledge to develop and subsequently upgrade the program to suit the emerging requirement. In due course of time, a conductivity measurement facility was also developed and coupled with LINAC for detecting radical ionic species. This became a national facility of its kind in India, and since then for last 37 years it has been a workhorse for carrying out pulse radiolysis experiments and also for irradiation of samples at higher absorbed doses. Till date more than 50 PhDs have been awarded and more than 800 scientific papers have been published in various national and international journals of repute, employing this facility.

Fig. 1: 7 MeV pulse linear electron accelerator (LINAC) facility at Chemistry Group

The pulse radiolysis studies using LINAC facility provided a paradigm shift in understanding a reaction. Detailed kinetics of various steps, characterization of transients and intermediates could be investigated. This led to understanding of the mechanism of radiation induced polymerization. Based on these studies, a correlation between polymerization kinetics and the nature of transients / intermediates could be established.

Radiation effects on various catalytic materials were investigated and with the help of suitable reactions changes in efficiency of catalysts were measured. Studies were carried out at lower temperatures in glasses of acidic/alkaline water as well as alcohols and other organic compounds to investigate reactions of radiolytic species, such as solvated electrons using spectrophotometry techniques.

Development of hydrogels containing curcumin, silver nanoparticles or other biologically important reagents were also carried out. Polymeric beads were made for the extraction of gallium from Bayer's liquor as well as removal of toxic heavy metal ions from water.

Several studies have been carried out using this 7 MeV linear electron accelerator (LINAC) facility and some of those are mentioned below.

- Pulse radiolysis of neat water was investigated, and all the transients (both oxidizing and reducing) and stable products were characterized, and the G-values of these products were measured. After gaining sufficient knowledge on radiolysis of water, pulse radiolysis of several organic compounds of importance were also investigated in aqueous solution.

- Dyes have been subjected to many radiolytic studies. Spectral and kinetic parameters of redox species formed in dyes of relevance in photogalvanic cells have been generated. Excited states and charged species formed upon radiolysis of laser dyes and other compounds in hydrocarbon solvents were probed. It is worth mentioning that the excited triplet states of coumarin dyes and a number of biphenyl derivatives were characterized. Dye molecules have been also investigated for their mineralization.
- Redox parameters of a variety of antioxidant compounds (both natural as well as synthetic) have been determined in order to understand their efficacy. A good number of pulse radiolysis studies on curcumin and its derivatives have been carried out, and redox potentials were measured.
- Kinetics of noble metal nanoparticles formation and subsequent reactions, as well as that of semiconductor particles have been studied.
- The mechanism of radiation induced polymerization has been established, and radiation effects on polymers have been understood.
- Large number of studies on corrosion inhibitors and components of dilute chemical decontamination formulations coupled with electrochemical investigations helped to get better understanding of the formulations.
- In recent past, using pulse radiolysis technique it was possible to get insights into radiolytic processes taking place in CO_2 gas (having ethylene impurity) used in annular space tubes of pressure tubes in nuclear reactors. These processes were found to have some role in nodular corrosion of the Zr-2.5 Nb pressure tubes.
- Apart from mechanistic studies on nanoparticle formation, synthesis of nanoparticles on a few gram scales were carried out using high radiation doses.
- Radiation chemical studies were also performed on C_{60} and its derivatives in both aqueous as well as organic solvents for the investigation of their radicals and triplet states.
- Using high dose rates available with accelerator, studies on radiation effects on semiconductors used in radiation environment and space applications were also investigated.
- Radiation chemical studies of a good number of compounds were studied for their radioprotector usages during radiation therapy. Radiation chemical studies of selenium based organoselenium compounds have been performed quite extensively, and diselenodipropinoic acid (DSePA) has been proven as a suitable candidate for radiation protection and cancer therapy.

Current radiation chemistry research:

Apart from those mentioned above, in-depth studies have been carried out on the radiation-induced synthesis of various nanoparticles like CdSe, CdS, ZnSe, ZnS, ZnO, SnO_2, UO_2, VO_2, SiO_x, SnSe, Se, and other metallic nanoparticles in aqueous as well as other media. The radiation effect on different novel solvents, room temperature ionic liquids (RTILs) and deep eutectic solvents (DESs), are being investigated thoroughly for their possible usage in nuclear fuel cycle. The role of RTIL and DES in the formation of semiconductor and/or metallic nanoparticles has been studied. Their stability towards the radiation dose was investigated. The LINAC facility has been extensively used for the kinetics and dynamics studies of different transient species formed during the irradiation of a sample as well as for irradiation of samples either for the synthesis of various nanoparticles or degradation of organic compounds like pesticides, textile dyes, drugs and others. Reaction mechanism of formation of nanoparticles or degradation of organic compounds could be elucidated using the time-resolved transient absorption studies.

The Chemistry Group scientists and engineers gathered enough expertise not only in radiation chemistry research, but also in instrumentation. In order to meet the growing demand on the research in the field of radiation chemistry in India, in particular from non-DAE organizations, expertise gained proved useful in setting up another 7 MeV LINAC facility at Savitribai Phule Pune University through a special BRNS project. Researchers from Savitribai Phule Pune University, other universities across India as well as from BARC performed pulse radiolysis experiments using that facility at Pune. The advantage of that facility over the existing facility at BARC, Trombay, was the improved signal-to-noise ratio, fast data acquisition and stable dose.

Advancement in radiation chemistry research:

To keep pace with current research in radiation chemistry, radiolysis experiments are planned to be monitored in picoseconds time domain. The department needs these studies even at high temperature and pressure to meet nuclear reactor requirement.

Ultrafast studies:

It was realized that several chemical processes were fast enough to be investigated by nanosecond LINAC. Therefore, an effort was made to build a picosecond electron accelerator facility based on femtosecond laser driven radiofrequency photocathode (RF PC) electron gun at BARC Trombay for the pulse radiolysis experiments in the sub-nanosecond time scale in order to understand the radiolytic effects in the early time scale. In this project, RRCAT Indore was involved for the supply of various components required for the accelerator. However, due to the complex nature of the facility, it is still under developmental stage. Efforts are also being made to use this facility to generate nanosecond electron pulse with sufficient charge for the pulse radiolysis experiments using a thermionic gun instead of RF PC.

Meanwhile, another picosecond source of electrons has been developed. Multiphoton ionization of water molecules was used for in-situ generation of ultrashort electron pulse in aqueous media. A laser beam (800 nm; 50 fs; 200 μJ) on being tightly focused into water, leads to absorption of multi photons by water molecules and induces photoionization with the ejection of an electron. The electron, thus generated, was monitored in situ using the pump-probe technique. The formation of the electron was further confirmed by its absorption spectra covering the spectral range of 400-1100 nm region. The semi-dry electron was observed in NIR spectral region and the solvated electron with a peak at 720±10 nm was formed within the instrument response time (~1.5 ps). The electron spectra thus generated match well with the electron spectra generated using 7 MeV LINAC. The electron thus generated in water undergoes fast decay (~7 ps) due to the recombination reaction. The reaction of in situ generated electrons with strong oxidizing agent methyl viologen (MV) was investigated, and the formation of reduced MV was observed within 1.5 ps. The present setup can be used to study the time-resolved reaction of a solute with the electron in an aqueous solution with a resolution of less than 2 ps.

High temperature high pressure (HTHP) studies:

A high temperature high pressure set up was coupled in the year 2013 with the existing 7 MeV LINAC facility at Chemistry Group in order to perform radiation chemical experiments at HTHP conditions. These experiments are important for understanding the radiation chemical reactions occurring inside the moderator system in nuclear reactor as well as to understand the chemical reactions taking place at the geothermal vent conditions under Deep Ocean. The latter work is expected to contribute towards the understanding the formation of early life on the earth. Experiments were performed with the samples containing gadolinium nitrate or boric acid, neutron poisons in the nuclear reactor system, at different temperatures and pressures. The yields of H_2 and H_2O_2 formed during the radiolysis at HTHP were measured. Transient absorption spectra and kinetics at HTHP conditions were also monitored for other compounds of interest. It is also planned to investigate the radicals, formed during electron beam irradiation, by coupling the LINAC system with a laser-based Raman spectrometer.

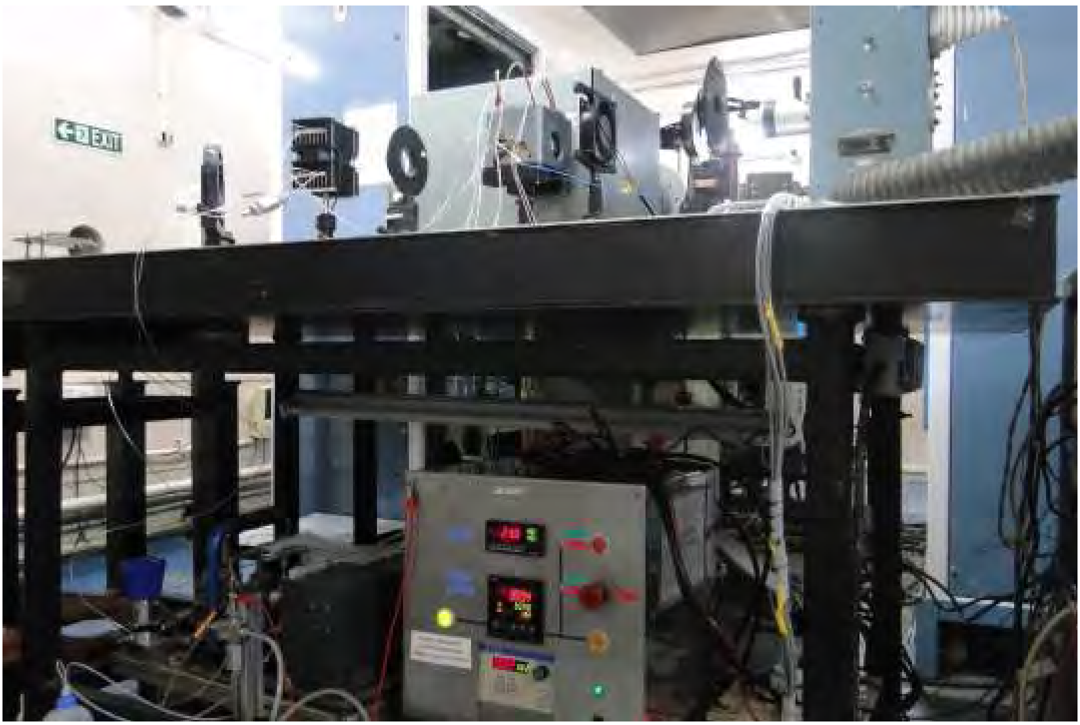

Fig. 2: High temperature high pressure set up installed at LINAC facility (bottom: control panel with pressure, temperature and flow display; top: optical cell inserted with four heating cartridges)

Addressing nuclear power plant problem:

Kakrapar Atomic Power Station (KAPS) had to shut down its plant in 2016 due to leakage in pressure tubes. Subsequent investigation showed higher density of nodules at the inlet end of the Annulus Gas Monitoring System (AGMS) on all the pressure tubes. It was found that the gas mix (CO_2 + O_2) used in the AGMS had several impurities, mainly ethylene, from the CO_2 cylinder.

Chemistry Group analyzed the content of the CO_2 gas cylinders from KAPS, and confirmed quantitatively this impurity. To understand the tentative mechanism of the observed nodular corrosion, the radiolysis of gas mixture (CO_2 + O_2 + ethylene) was investigated by LINAC irradiation, followed by product analysis by GC/GC-MS. Based on these experiments, a tentative mechanism was proposed as follows: Radiolysis of CO_2 leads to the formation of CO and O. Subsequently, O interacts with O_2 to form ozone, which adds to the C=C bond of ethylene (impurity) leading to formation of ozonides. Further oxidation produces several oxidizing species (peroxy-radicals, peroxides, formic acid, acetic acid, etc.), which attack the surface of the pressure tube leading to the growth of nodules over days to months.

Maintenance of LINAC:

Over the last more than sixty years, Radiation Chemistry Research has been actively pursued and contributed immensely in many related fields at Bhabha Atomic Research Centre, Trombay. It has been possible mainly because of the 7 MeV LINAC facility. Since the set-up has become very old (almost 37 years), its maintenance is a challenge. However, it is still being used extensively by several users, primarily because of services rendered by dedicated LINAC maintenance team.

Way forward:

A new Cobalt-60 gamma source (5000 Ci) is going to be installed at Radiation & Photochemistry Division, Chemistry Group, to boost various radiolytic experiments. Sincere efforts are being made to complete the project on picosecond 9 MeV RF-PC gun based LINAC, and investigate its feasibility for pulse radiolysis experiments. Simultaneously, some modifications will be carried out to use this facility for nanosecond pulse radiolysis experiments as well. Alternatively, picosecond electron generated from multiphoton ionization of water will be employed to investigate fast radiolytic process. Another new nanosecond 9 MeV LINAC system with various modern facilities is planned to be developed at RPCD for radiation chemical studies. Emphasis will be given for the radiation chemical studies of various unexplored systems like, CO_2, molten salts, exotic solvents like Cyrene, DES and nuclear paints etc.