

**A Perspective on Separation Science and Technology**

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**Abstract**

Separation science plays a critical role in our society. Chemical separations are essential in providing the foods and services that are needed to maintain our standard of living and quality of life. Without separations, access to such necessities as medicines, clean water, safe food, and energy sources would not be possible. A focus on separation science is also needed to reduce the adverse effects of industrial activities, and to develop a sustainable chemical enterprise that can drive the economy. The goal of a separation process can vary from dividing a complex mixture into several fractions to extracting a single chemical from a highly dilute solution. The scale of a separation process can vary from less than a microgram to mega tons of material. The constant pressure to produce higher-purity products (> 99.999%) creates a demand for new separation processes / technologies. An attempt has been made in this article to highlight the challenges and directions of future developmental activities. The importance of separation science in contemporary scientific pursuits like desalination, production of oxygen and Super Critical Fluid Extraction are highlighted. Some examples from the author's work related to gas chromatography and separation of radionuclides using designer ligands are also discussed.

**Introduction:** The critical essential elements impacting the rapid growth of our country are Health, Energy, Environment, Water and Security. Cross functional discipline of Separation Science and Technology plays a pivotal role in meeting the mammoth challenges in these areas.

In the coming decades, health and hygiene is going to be vital for India with growing urbanization. Bulk drugs and proprietary pharmaceuticals would require modern separation science to provide breakthrough and make these drugs available at affordable price. The enzymatic based separation process, ion exchange resins integrated into nano synthesis of the bulk drugs and drug delivery system will change the fundamentals of health services in future.

Providing affordable energy in abundance which does not pose environmental hazards will be the major challenge facing India with a population of more than 1.3 billion. The future of energy and environment

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in India depends on a) energy conservation and conversion of waste to energy; b) clean coal technology along with nuclear technology and c) renewable energy technologies like solar-biomass-wind-geothermal. All these technologies use advanced separation science and technology.

Namami Gange and Jal Shakti Abhyan aims at providing clean, potable water to every citizen in the country. Developments in membrane science, nano-bio technology, nano coated impregnated resins are critical to ensure water availability in desired quality and quantity in the coming years.

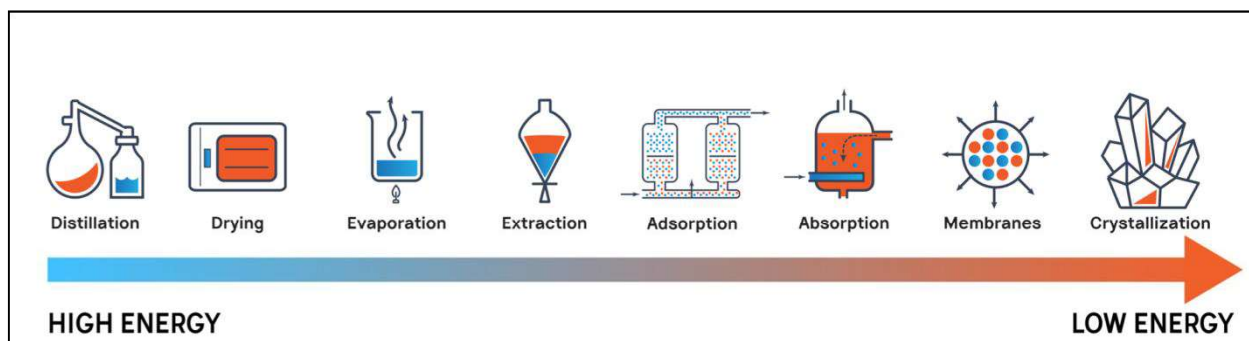
Finally, security is assuming a major challenge for India due to changing global geo politics. High technology and sophisticated surveillance systems are essential features of future security systems. Need for high purity electronics / nuclear materials will form essential part of future security/ strategic systems. Many processes in the electronics, solar energy and nuclear industry have much higher purity requirements than in past decades. Uranium concentration in seawater is extremely low (parts per billion), but resource is large (more than 4 billion tons) and required purity level  $> 99.99\%$ . Radionuclides like Sr-90, Cs-137, Mo-99 are present at trace concentrations in competition with bulk ions at 100,00-fold higher concentrations in matrices like High Level Nuclear Waste / Special Target Dissolver Solutions and need to be recovered at  $>5$  N purity. Rare earths recovery and purity at  $>5$  N level is essential for the development of high technology materials with desired optical, magnetic and nuclear properties.

Given the importance of separation science, the U.S. Department of Energy, the National Science Foundation, and the National Institute of Standards and Technology asked the National Academies of Sciences, Engineering, and Medicine to develop a research agenda for fundamental research in separations to transform the field and provide opportunities for a paradigm shift. Important findings of the committee are summarized in the report published in 2019 [1]. Highlights of this report are

- 1) Important advances have occurred in the last 30 years in molecular modeling and simulation, machine learning and data analytics, analytical techniques, and characterization. These advances tantalize us with the prospect of a greatly improved theoretical and mechanistic understanding of separation processes, improved modeling and prediction of chemical behaviors, and the exploration and development of new chemicals, materials, and approaches.
- 2) Thus, separation science is poised for a paradigm shift in which the brightest minds in chemistry, chemical engineering, materials science, and other fields will be vying to achieve the breakthroughs in the next generation of separation science, and conventional separation technology will be replaced with high-throughput, energy-efficient, and exquisitely selective separation systems.

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**Membrane-based separations for Desalination:** Fig.1 shows that various chemical separation processes have vastly different energy requirements. Sea is perhaps an infinite source of an essential life sustaining constituent like water. However, prohibitive cost involved in distillation was responsible for little headway in exploiting fruits of desalination to reach general public. Reverse-osmosis Membrane technology, though developed in mid 20<sup>th</sup> century has been employed on large scale only in last two decades. It has major advantage of substantially lower energy requirement (only twice the thermodynamic minimum energy) as compared to evaporation. Thousands of facilities now use this technology worldwide. Additional improvements in the technology will need to focus on such issues as the longevity of membranes particularly with respect to fouling, pretreatment, and post-treatment conditions



**Fig.1: Energy Requirements of Different Separation Processes**

**Production of Oxygen:** Recent COVID epidemic brought to focus the need to produce and distribute medical oxygen in large scale at competitive cost. It is produced industrially by three processes viz. Cryogenic Distillation, Membrane Separation, Pressure Swing Adsorption

- **Cryogenic Distillation (Fig.2)** : It is a leading leading process for producing >99% oxygen in bulk. It Involves liquifying air and distilling the liquid air to separate the Oxygen, Nitrogen, and Argon. It Can be sold in a liquid form. 1 L of liquid Oxygen = 860 L of gaseous Oxygen. Major drawbacks of this process are, use of large bulky equipment, substantial energy requirement and the possibility of liquid oxygen evaporating back into the atmosphere over time

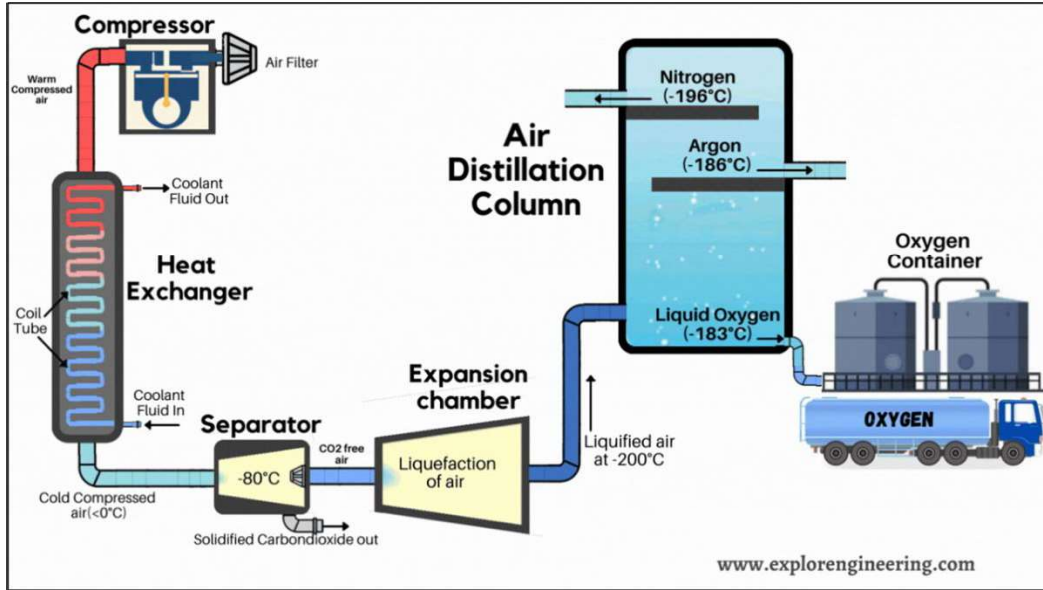


Fig.2: Schematic of Cryogenic Distillation Process for production of Oxygen

- **Membrane Separations:** In view of the energy intensive Cryogenic Distillation process, membrane based separations are preferred. Permeable materials are used to selectively separate Oxygen, Nitrogen, and Argon. Pressurized air is passed through the membrane and is separated by permeability characteristics of each component in relation to the membrane porosity. Membranes require a large surface area to achieve high product flow rates. Large pressure is however a safety hazard.
- **Pressure Swing Adsorption:** Pressure swing adsorption (PSA) is a technique used to separate some gas species from a mixture of gases (typically air) under pressure according to the species' molecular characteristics and affinity for an adsorbent material. It operates at near-ambient temperature and significantly differs from the cryogenic distillation commonly used to separate gases. Selective adsorbent materials (e.g., zeolites, (molecular sieves), activated carbon, etc.) are used as trapping material, preferentially adsorbing the target gas species at high pressure. The process then swings to low pressure to desorb the adsorbed gas as shown in Fig.3.

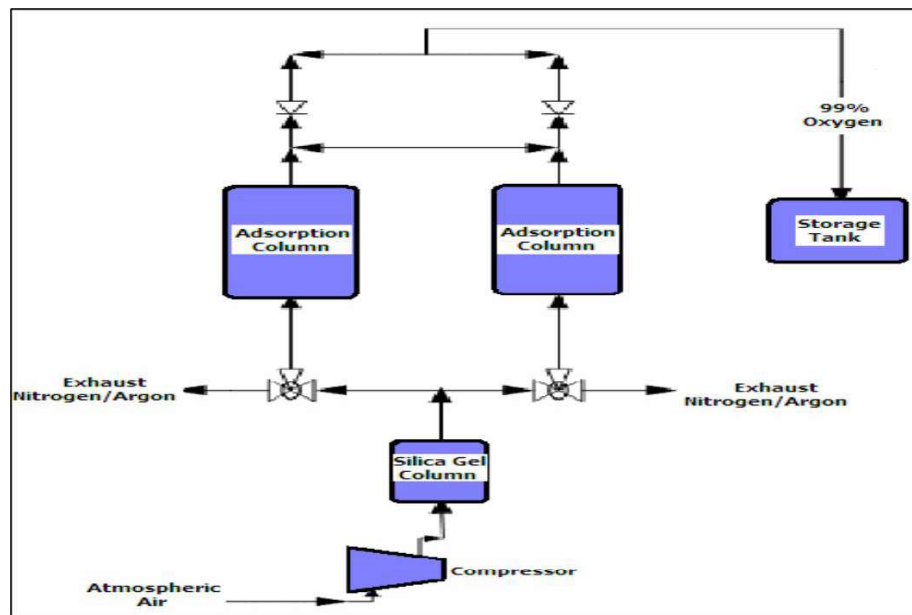
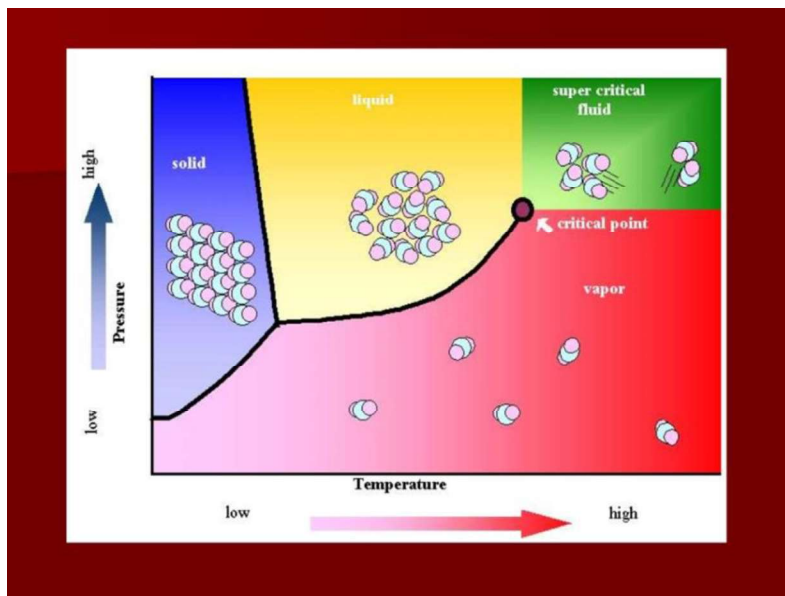


Fig.3: Schematic of Pressure Swing Method for the production of Oxygen

**Supercritical Fluid Extraction (SFE):** A supercritical fluid is any substance above its critical temperature and pressure. It can diffuse through solids like a gas and dissolve materials like a liquid (Fig.4). Additionally close to the critical point, small changes in pressure and temperature result in large changes in density, allowing many properties to be tuned. It can replace hazardous organic solvents in industrial processes. Non flammable and non toxic Carbon dioxide is the most common SCE due to its favorable properties like its low critical temperature (31.9<sup>0</sup>C) and moderate critical pressure (73 bar). It has lower viscosity but larger diffusivity than liquid solvents. Carbon dioxide (CO<sub>2</sub>) is sometimes modified by co-solvents such as ethanol or methanol.

- Supercritical fluid extraction (SFE) is the process of separating one component (the extract) from another (the matrix) using supercritical fluids as the extracting solvent. Extraction is usually from a solid matrix, but can also be from liquids. SFE can be used as a sample preparation step for analytical purposes, or on a larger scale to either strip unwanted material from a product (e.g. decaffeination) or collect a desired product (e.g. essential oils).
- Applications of SFE are increasing in the areas like Decaffeination of tea, Extraction of flavors from herbs , Extraction of fats and oils (Eucalyptus/Soyabean/Ginger), Dealcoholisation of alcoholic beverages, Extraction of aromas from different flowers / juices , Extraction of antioxidants such as vitamin E and C, Extraction of bioactive components with added value for human health, such as catechin,  $\alpha$ -tocopherol, resveratrol, and various natural pigments.



**Fig.4: Molecular Characteristics of Supercritical Fluid**

**Tailoring of molecules for challenging separations in the backend of Nuclear Fuel Cycle:** Important advances in separation technologies have occurred in applications in which the exquisite selectivity and the ability to manage extremely complex feeds with high radiation fields and highly corrosive conditions are critical. It is characterized by designer solvents that use highly specific properties tailored to catch target component and reject almost all competing ions and deliver a nearly pure product.

**Separation of U-233 from irradiated Th :** Pure Thorium does not undergo fission with thermal neutrons, in practice, seeds are needed to start energy production. Any fissile material ( $^{233}\text{U}$ ,  $^{235}\text{U}$  or  $^{239}\text{Pu}$ ) can be used as seed. It is necessary to produce sufficient amount of Pu-239 / U-233 prior to the exhaustion of naturally occurring fissile U-235. In Th fuel Cycle, focus is on production of U-233 and its subsequent separation from the source material, Th-232 and activation / fission products. Branched extractant molecules like Tri-sec-butyl phosphate / Tri-ethyl hexyl phosphate/ N,N di (2-ethylhexyl) isobutyramide offer interesting possibility to enhance the S.F. values of U(VI) over Th(IV). This is explained as due to the fact that inner coordination sphere of Th(IV) accommodates four bidentate nitrate ions vis-vis two bidentate in case of U(VI), there is more steric constraint to accommodate solvating extractant molecules in the former case. Data in Table 1 shows that N,N di (2-ethylhexyl)isobutyramide is a Promising Amides as alternate to TBP in THOREX process recommended for the recovery of U-233 from irradiated Th-232 [2]

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**Table 1: Role of the structure of Alkyl group in Dialkyl Amides on the Separation Factor of U(VI) over Th(IV)**

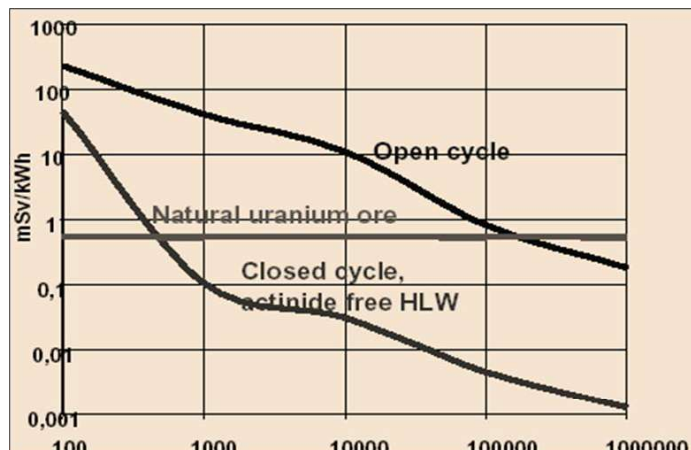
Amide	R1	R2=R3	D <sub>U</sub>	D <sub>Th</sub>	S. F.
D2EHIBA	(CH <sub>3</sub> ) <sub>2</sub> CH	CH <sub>2</sub> CH(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	3.7	1.0x10 <sup>-2</sup>	370
D2EHPVA	(CH <sub>3</sub> ) <sub>3</sub> C	CH <sub>2</sub> CH(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	2.9	8.0x10 <sup>-3</sup>	362
DIB2EHA	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(C <sub>2</sub> H <sub>5</sub> )	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	4.7	1.3x10 <sup>-2</sup>	361
DOIBA	(CH <sub>3</sub> ) <sub>2</sub> CH	C <sub>8</sub> H <sub>17</sub>	5.8	1.4x10 <sup>-2</sup>	414
DO2EHA	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(C <sub>2</sub> H <sub>5</sub> )	C <sub>8</sub> H <sub>17</sub>	6.6	1.9x10 <sup>-2</sup>	347
D2EHPRA	C <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> CH(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	9.7	0.1	97
D2EHBA	C <sub>3</sub> H <sub>7</sub>	CH <sub>2</sub> CH(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	8.4	6.0x10 <sup>-2</sup>	140
D2EHAA	CH <sub>3</sub>	CH <sub>2</sub> CH(C <sub>2</sub> H <sub>5</sub> )(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	19.1	1.1	17
DHOA	C <sub>7</sub> H <sub>16</sub>	C <sub>6</sub> H <sub>13</sub>	12.4	0.6	21
DHDA	C <sub>9</sub> H <sub>19</sub>	C <sub>6</sub> H <sub>13</sub>	11.6	0.5	23
DBDA	C <sub>9</sub> H <sub>19</sub>	C <sub>4</sub> H <sub>9</sub>	11.5	1.0	12
DHHA	C <sub>5</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>13</sub>	12.8	0.8	16
TBP	-	-	40	4	10

**Role of Actinide Partitioning in reducing radio-toxicity:** Long lived minor actinides like Am-241, Am-243, Cm-244 are responsible for the radiotoxicity of high level liquid waste generated post fuel reprocessing aimed at quantitative recovery of U and Pu. Fig. 5 shows that the removal of long lived actinides reduces the radiotoxicity of the high level waste in about 300 years (instead of waiting for million years) to the background level of natural uranium ore. Designer ligand like TODGA are capable of separating minor actinides from short lived fission products and inactive structural elements [3].

### Wealth from Waste:

- Recovery of Sr-90, Cs-137 and PGMs (Platinum Group Metals) from HLW is essential not only for the ease of surveillance of the vitrified blocks, but also for their many possible applications. The extraction of Sr-90 and Cs-137 from simulated HLW solution was achieved using crown ether (DTBCH18C6), Chlorinated dicarbollide (CCD) and Calixcrown. Ru-106 is recovered from HLW using solvent extraction / ion exchange and oxidation / electrochemical methods.
- Till date, more than 3 lakh curies of <sup>137</sup>Cs of desired quality has been recovered from HLLW and about 250 numbers of Cesium glass pencils have been produced successfully for deploying them for blood irradiation and grain irradiation with enhanced safety and security [4].

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**Fig.5: Radiotoxicity Profile of the Spent fuel over million years with and without actinide partitioning**

Eleven numbers of indigenously developed Ru-106 eye plaques of different geometry configurations (six numbers of round geometry plaques and five numbers of notch configuration plaques) have been supplied to various hospitals of country including AIIMS-New Delhi, Centre for Sight – Hyderabad, Shankara Eye Hospital – Bengaluru.

### **Chromatography: A powerful Analytical technique with diverse Applications**

Chromatography is an important part of science encompassing physical chemistry, chemical engineering, biochemistry, and is cutting through different fields. While it is primarily considered a laboratory method, the amounts handled by chromatography cover many orders of magnitude. It was gas chromatography which initiated the development of microsyringes, with capacities of less than one microliter ( $10^{-3}$  g) and today, we routinely determine amounts in the picogram ( $10^{-12}$  g), and even to the femtogram ( $10^{-15}$  g) level. On the other hand, industrial plants were constructed in the former Soviet Union in the 1970s, using gas chromatography columns of 15–200 cm diameter, for the production of 200–1200 metric tons/year of pure compounds.

Today, chromatography is an essential analytical tool that is used extensively by chemists, biologists, forensic scientists and environmental scientists all over the world. It comes in wide ranging forms like Paper Chromatography (PC), Thin Layer Chromatography (TLC), Gas Solid Chromatography (GSC), Gas Liquid Chromatography (GLC), High Performance Liquid Chromatography (HPLC), Ion Chromatography (IC), Extraction Chromatography (EC), Size Exclusion Chromatography (SEC), Capillary Electrophoresis (CE) and Supercritical Fluid Extraction Chromatography (SFEC), all designed to meet specific requirements. Nobel Prize for Chemistry was awarded in 1952 to **Archer J. P. Martin and Richard L.M.Synge** for their pioneering work in Partition Chromatography.



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### Analysis of bonding/cover gas in fuel pin:

Apart from the composition of fuel, the composition of the bonding material (filling or cover gas) influences the thermal behaviour of the fuel pin. Inert gases like Ar and He are used as cover gas for the fuel pin. Helium is preferred as bonding gas for the advantage of its having high thermal conductivity and thus the efficiency in heat transfer from the fuel to the cladding. Helium is used for filling the fuel pins of both Pressurized Heavy Water Reactor (PHWR) and Fast Reactors. The helium gas cylinders are subjected to quality check for the impurities such as oxygen, argon and nitrogen which would reduce the thermal conductivity of the gas. The quality of the helium gas is checked by Gas Chromatographic technique prior to its filling in the fuel pins. The accepted purity is better than 99.99%. Special attention is given to the tubing used to connect the source and the gas chromatograph to eliminate any contamination of the carrier gas .

The pins containing mixed oxide or mixed carbide are thus filled with qualified helium gas and the end plugs are sealed. The dimensions of the fuel pin vary depending upon the nature of reactor and fuel. The fuel pin is checked for the purity of the gas as a part of quality assurance for its certification for loading in to the reactor. The fuel pin is punctured under vacuum and the gas is collected in a calibrated volume container. The pressure as read on the manometer after puncturing the fuel pin helps in deriving the volume of the bonding space. The initial pressure usually is maintained at 1.2-1.5 atm considering its subsequent dilution to 10-15 times with the release of fission gases inside the reactor. However, the purity of the helium at 95% for oxide fuel and 99% for carbide fuel (excluding hydrogen), is an important specification. The purity affects the thermal conductivity of the fuel and thus the performance of the fuel particularly during the initial stages of operation of the reactor.

Considering the pressure and volume of the gas available in the fuel pin of FBTR, a sub ambient atmospheric technique is needed to be employed in the analysis. The volume of the gas in the fuel pin in carbide fuel pins with stainless steel cladding is around 2 ml and the pressure of the gas comes down to 8-10 cm when released in to the sample loop of the gas chromatography. Whenever a low pressure sample travels through the column , equilibrium concentrations of major impurities like oxygen and nitrogen in the solid adsorbent ( molecular sieves 5A) and in the carrier gas undergo change. This results in a bias in the concentrations of these constituents as observed in the chromatogram. The bias is inversely proportional to the pressure of the sample. Hence a correction is required to be applied during analysis of sub atmospheric sample. Therefore a blank run is necessarily to be made at the same pressure for determining the correction to be applied to the actual sample for these impurities. This technique,

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sometimes referred to as Vacancy Chromatography was successfully used in the standardization of the gas chromatographic procedure for the quality control of FBTR fuel pins [5].

### Summary:

Although chemical separations are integral to overwhelmingly large number of industrial processes, they are not always considered during product development. That inattention results in industrial processes that are inefficient, cost prohibitive and have adverse environmental effects. A focus on separation science is needed to overcome such issues and ultimately to improve human health, and to develop a sustainable chemical enterprise that can drive the economy. Energy-intensive separations are reported to account for 80% of industrial separations. Some separation processes generate large waste streams with heavy metals and other contaminants that are expensive to manage. There is need to curtail the use of Volatile Organic Compounds (VOCs) and replace them with more sustainable environmentally friendly solvents.

Designing Separation Systems with High Selectivity, Capacity, and Throughput are necessary to meet the challenges. Advances in materials science, systems-engineering approaches, external stimuli (Electric Fields, Magnetic Fields, Field-Flow Fractionation, Photoregulation), instrumentation and characterization (Spectroscopic Techniques, Imaging Techniques, Scattering Techniques) and in data science and analytics have contributed to the development of novel separation processes. An important role has been played by the development of new materials like Room Temperature Ionic liquids, Metal-organic frameworks (MOFs): Selective adsorbents, Two-dimensional materials such as zeolites, graphene, graphene oxide and polymeric brushes ( Promising Membrane Materials), composites containing selective extractants (Magnetic Assisted Chemical Separations), Supercritical Fluid Extraction and Tailoring of ion specific molecules / extractants.

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### Biosketch of Prof. V.K. Manchanda



Prof. Manchanda's work in the area of complex / separation chemistry, CQC nuclear materials and novel materials as radiation sensors is recognized internationally. He has about 1100 publications (about 400 in International peer reviewed journals of repute). He has appeared in the list of top 2% scientists published by Stanford University in 2020. He is serving on the Advisory Board of 'Radiochimica Acta' (Degruyter, Munchen, Germany) and has served as Associate Editor of 'Frontiers in Energy Research : Nuclear Energy' as well as on the Editorial Board of 'Solv. Ext. Ion Exch.' (Taylor and Francis Group), well known International Journals in the areas of Radiochemistry, Energy Research and Separation Science respectively. He was awarded Fulbright Fellowship to pursue post-Doctoral studies in Texas, USA. As a Ph.D. / M. Phil. Guide of University of Mumbai, HBNI, Mumbai and SKKU, South Korea, he has guided 20 students. He was responsible for initiating BRNS supported symposium series on Separation Science and Technology. He is the Founder President of Separation Scientists and Technologists (ASSET) and is the past President of Indian Association of Nuclear Chemists and Allied Scientists (IANCAS). He has worked as Scientific Officer at Radiochemistry Division, BARC, Mumbai, India for 42 years (including as HOD from 2003 to 2011). He was invited to join Dept. of Energy Science, SKKU, Suwon in South Korea as WCU Professor where he taught and guided Ph. D. students till 2014. He is the recipient of OUTSTANDING RADIOCHEMIST AWARD for 2017. He is currently Vice President of Indian Nuclear Society.