March towards self-reliance in heavy water and specialty materials

J. Srivastava[1,*], S. K. Nayak[2] and U. Kamachi Mudali[3]

[1]Heavy Water Board, Vikram Sarabhai Bhavan, Mumbai 400 094, India
[2]Principal Residence, KBP College-Vashi, Sector 15-A, Vashi, Navi Mumbai 400 703, India
[3]Vellore Institute of Technology, Bhopal 466 114, India

The Heavy Water Board (HWB), an industrial unit of the Department of Atomic Energy (DAE), Government of India is engaged in the production of heavy water and specialty materials required by DAE for supporting the Indian Nuclear Power Programme (INPP). HWB through its four operating plants has ensured self-sufficiency in the availability of heavy water for pressurized heavy water reactors and has also exported heavy water. The mandate of HWB has been enlarged to include the production of specialty materials for DAE. This includes the development of technology for the production of solvents required in pursuit of a closed nuclear fuel cycle, development and deployment of technology on an industrial scale for the production of special materials such as nuclear-grade sodium, enriched boron compounds and boron carbide pellets for fast breeder reactors. Development and deployment of new processes, technologies, systems and equipment in areas of relevance to DAE, viz. recovery of value metals like cobalt, gallium, rare earth materials, etc. from the secondary resources is also a part of the enlarged mandate of HWB. The Board is also deploying spin-off technologies and providing consultancy services in the field of energy conservation, engineering and project management.

Keywords: Boron isotopes, heavy water, non-nuclear applications of heavy water, oxygen-18, sodium, solvents, tributyl phosphate.

Heavy water production for PHWRs

Bhabha's vision

THE Board of Research in Atomic Energy (now called the Board of Research in Nuclear Sciences) is the agency of the Department of Atomic Energy (DAE), Government of India (GoI) for funding extramural research. In his capacity as chairman of the Board, Homi Bhabha[1] wrote to the then Prime Minister Jawaharlal Nehru in April 1948:

> 'Government should explore immediately the possibility of utilizing cheap hydro-electric power in India for manufacturing Heavy Water, on one hand for our own requirement in pile, and on the other hand for sale to other countries'.

With this vision, a successful journey aimed at the production of heavy water in India began with the setting up of the first plant at Nangal, Punjab (Figure 1).

Beginning at Nangal

Heavy water is essential for Pressurized Heavy Water Reactors (PHWRs). The production of heavy water had to be taken up on a large scale to match the projected nuclear power programme. To start with, two industrially viable processes, viz. electrolysis and distillation of water were selected for producing heavy water indigenously by the DAE in 1954. The economics of the electrolysis process was analysed considering heavy water being the main product and also the by-product of a fertilizer plant based on electrolytic hydrogen. India's first heavy water plant (HWP) with 14 Te/annum capacity was set up at Nangal. The first drop of heavy water was produced on 9 August 1962.

Of late, the distillation of hydrogen has become an obsolete method for industrial-scale production of heavy water due to technology shift in the production of hydrogen in fertilizer plants.

Research and development at BARC

Heavy Water & Stable Isotope Production (HW & SIP) Section as part of the Chemical Engineering Division

Figure 1. Heavy water plant, Nangal.

*For correspondence. (e-mail: ce@mum.hwb.gov.in)

(CED) at the Atomic Energy Establishment, Trombay, later renamed as Bhabha Atomic Research Centre (BARC), launched an indigenous effort by setting up pilot plants based on water distillation and dual temperature H_2S–H_2O exchange process for collection of data. Subsequently, a core group was constituted for working on process development, generating flow sheets, sizing of equipment and carrying out test-loop studies for establishing the suitability of materials and components for the H_2S–H_2O-based process[2]. Several studies were carried out, viz. measurement of surface tension, foaming characteristics of water saturated with H_2S, corrosion behaviour, effluent treatment, etc. Monitoring methods for H_2S and procedure for pre-conditioning of carbon steel by the formation of protective sulphide film were developed[3]. Various analytical methods for the analysis of deuterium were developed and standardized.

It was envisaged that the final enrichment in the HWP would be carried out by the distillation process. To start with a 1″ diameter column and later a 4″ diameter column with Dixon ring packing were set up and operated. A special type of ordered packing was developed by the Heavy Water Division (HWD), BARC[4]. The development of packing made of phosphor–bronze wire mesh with corrugation led to a sizable reduction in the plant volume and capital cost.

Pursuing multiple technologies with success

On 1 May 1969, a separate unit, viz. 'Heavy Water Projects Board' for the production of heavy water was established. It was subsequently rechristened 'Heavy Water Board' for building new HWPs.

Indigenous development became successful by setting up a pilot plant based on water distillation and dual temperature H_2S–H_2O exchange process for collection of data. The first H_2S–H_2O-based HWP was set up at Kota, Rajasthan, considering its proximity to the nuclear power plants RAPP I and II, available source of water from the Rana Pratap Sagar reservoir and required land.

Monothermal ammonia–hydrogen exchange technology was pursued as another successful method for large-scale heavy water production from 1957 to 1960. Gujarat State Fertilizer Co (GFSC), Baroda had a single-stream ammonia plant. In 1968, it was decided to integrate a HWP with the GFSC plant at Baroda. Construction of the plant was started in 1970 and it produced heavy water in July 1977.

The setting up of a HWP at Tuticorin, Tamil Nadu, was considered based on monothermal ammonia–hydrogen-based technology integrated with the fertilizer plant of SPIC, Tuticorin, which was commissioned in 1978.

With the technological breakthrough, a bithermal ammonia–hydrogen exchange process was developed by UDHE, Germany, which was found to be a potential candidate based on its lower specific energy requirement. The bithermal ammonia–hydrogen technology for the production of heavy water was integrated with the Talchar plant, Odisha of the Fertilizer Corporation of India (FCI). The plant was commissioned in 1984. However, the fertilizer plant could not carry out satisfactory sustained operations at a reasonable load. Also, the syngas supplied to the HWP did not meet the purity requirements. Therefore, the plant could not be operated on a sustained basis at the rated capacity.

Having adequate experience in operating, commissioning, technological improvements, and stabilizing the operations of HWPs, the HWB was well equipped for setting up two mono-thermal ammonia–hydrogen-based plants, one at Thal and the other at Hazira, Gujarat and one bithermal H_2S–H_2O-based plant at Manuguru, Telangana. A captive power plant (CPP) was considered for the Manuguru plant of capacity 3 × 30 MW turbogenerators to meet the power and steam requirement of HWP.

From construction to consolidation

Industrial plants set up at Baroda and Tuticorin based on ammonia–hydrogen monothermal exchange process have led to the successful indigenous deployment of second-generation plants at Thal and Hazira. Hydrogen sulphide–water bithermal exchange process (Girdler sulphide process) was indigenously developed starting from laboratory studies to a pilot plant, and a breakthrough was achieved by setting up the first industrial plant at Kota. The consolidation of the process could be achieved by setting up a second-generation plant at Manuguru. A brief about all the plants starting with the plant at Nangal follows.

Nangal plant: This plant was completely manually operated. With time, the demand for power in the region increased, and the electrolysis plant at Nangal continued to be operated at a reduced load. An increase in power tariff and low deuterium concentration in the feed gas resulted in an increased cost of production of heavy water at the Nangal plant. The plant was running and contributing till August 2002, when it was finally decommissioned and dismantled.

Kota plant: This is the first indigenous plant (Figure 2). It is based on H_2S–H_2O bithermal chemical exchange process

Figure 2. Heavy water plant, Kota.

and is a first-generation, sulphide-based HWP. The feed water requirement of the plant is met by drawing water from the Rana Pratap Sagar reservoir. The plant is fully dependent on Rajasthan Atomic Power Station (RAPS) for its steam and power requirements.

Baroda plant: Due to drastic changes in the operation of the fertilizer plant by GFSC, the production of heavy water at Baroda become uneconomical. Hence the decision was taken to shut down the HWP at Baroda. Subsequently, a pilot plant based on a water–ammonia front-end process was incorporated with water as feed to study the feasibility of the process.

Tuticorin plant: Additional cracker tubes have been employed to enhance capacity instead of elevated temperature, which has helped in minimizing cracker tube failures under carbide precipitation at grain boundaries of Inconel-625 at high temperature. To monitor the cracker tube temperature profile, a modified temperature measurement scheme was adopted.

Talcher plant: FCI's fertilizer plant suffered due to power supply problems. During the initial operation of the HWP, frequent failures of various components were observed. Remedial actions could not be taken systematically due to the lack of a stable power supply from FCI. Finally, heavy water was produced at Talcher in 1984.

Thal plant: This is a two-stream plant based on monothermal NH_3–H_2 exchange. It is linked to the two-stream ammonia plants of M/s RCF Ltd, Thal, Maharashtra. The plant suffers due to the purity of feed gas and lower hydrogen content in the synthesis gas from the associated fertilizer plant. However, with proper monitoring and suitable measures, this plant produces at the rated capacity.

Hazira plant: This is a two-stream HWP based on the monothermal NH_3–H_2 exchange process. The plant is linked to the two-stream ammonia plants of M/s KRIBHCO Ltd, Hazira, Gujarat. It shows satisfactory performance owing to the high purity of feed gas. Full capacity utilization of the plant is achieved by improving on-stream hours, feed processing rate, etc.

Manuguru plant: This plant is based on H_2S–H_2O bithermal chemical exchange process (Figure 3). It is a second-generation sulphide-based plant with two streams. Based on the experience gained at Kota, some process modifications were carried out to improve the performance. It has been provided with a CPP for the supply of steam and power. The plant draws water from the nearby Godavari River. It was commissioned in December 1991 and achieved stable operation within a year. It has the inherent advantage of getting uninterrupted supply of steam and power, barring in-house trips of CPP.

Export of heavy water

After achieving self-sufficiency and securing domestic requirements, the HWB started exporting heavy water. The Board established itself as a global supplier in the international market through export to the Korean company Korea Electric Power Corporation (KEPCO) for use in its PHWRs. The quality of heavy water was much appreciated by South Korea. HWB has exported 227 Te of heavy water in a decade by executing as many as 15 export orders, meeting the required specifications by the users and following the regulatory guidelines.

In 2007, for the first time, HWB supplied high-quality heavy water to M/s Spectra Gases, USA, for the preparation of deuterated compounds (non-nuclear applications). Subsequently HWB executed export to CIL, USA and Sigma–Aldrich, USA (Figure 4).

In 2021, HWB executed two export orders to South Korea and Japan for non-nuclear applications.

Figure 3. Heavy water plant, Manuguru.

Figure 4. Export consignment of heavy water.

Present scenario in heavy water production

Efforts were made to reduce the cost of production of heavy water to the maximum possible extent. This was achieved through process intensification, re-optimization of operating parameters, energy audits, use of energy-efficient equipment, integration of heat transfer loops, etc. All the above efforts have resulted in a reduction of over 30% in specific energy consumption for all the plants (Figure 5). Simultaneously, it has also reduced specific CO_2 emissions (Figure 6).

Beginning with the plant at Nangal set up in 1962, a total of eight HWPs were built in India to meet its requirements. Initially, the supply lagged the demand, but during the 1990s, supply overtook and surpassed the demand. The H_2S–H_2O exchange process-based plants, being independent, account for the major production today. Despite four plants going off the line over time, heavy water production has been increasing and specific energy consumption improving continuously. All the plants are certified for IS: 9001(QMS), IS: 14001(EMS) and OHSAS 18001/IS: 18001. As a result, HWB's safety record is the best among the chemical industries in India.

Environment management system

HWPs consume large amounts of power, water and chemicals. Therefore, conservation of natural resources, energy and environmental protection was given due importance right from the beginning. Reduce, reuse and recycle of natural resources is an ongoing process. In all the plants, green belts are developed. Some of the important achievements in this field are as follows.

Flue gas conditioning: At HWP, Munuguru, Telengana (HWPM) injection of ammonia at the inlet of electrostatic precipitator (ESP) of the coal-fired boilers reduced the resistivity of fly ash in flue gas, thereby increasing the efficiency of the ESP. This technology was developed in-house and successfully implemented in January 1999 for the first time in the country on a commercial basis (Figure 7).

Conservation of water: Water consumption in HWPs has been reduced by 60% through recycle and reuse of liquid effluent.

Harnessing solar energy: HWB indigenously developed a solar energy-based steam generator and installed it at HWP, Kota. A grid-interactive 12 MWp solar photovoltaic power plant has been installed at HWPM (Figure 8). This fulfills the requirement of the RPRO (Renewable Power Purchase Obligation) Regulations-20.

Ageing management

All HWPs follow a defined ageing management programme (AMP) for assessment of the ageing characteristics,

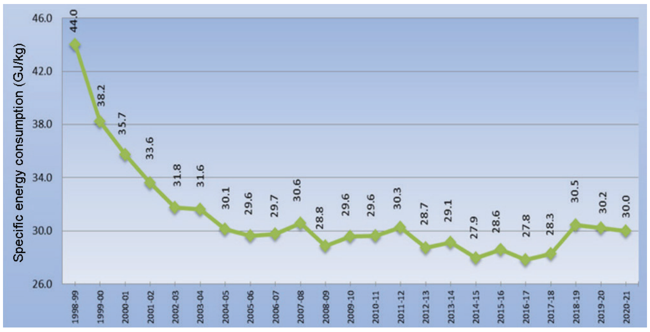

Figure 5. Specific energy consumption.

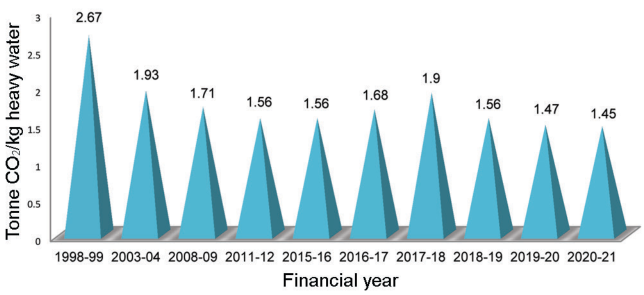

Figure 6. Specific CO_2 emissions.

Figure 7. Effect of ammonia flue gas conditioning.

Figure 8. Solar plant.

factors influencing the ageing process, and their consequences on safety margins and reliability. In HWPs, the following programmes contribute to AMP.

(i) Good maintenance practices.
(ii) In-service inspection and surveillance.
(iii) Control of plant parameters within operating limits and conditions.
(iv) Feedback from operating experiences.
(v) Review and updating of operating procedures.
(vi) Repair and replacement of aged/outdated equipment.

Production of specialty materials

HWB has now diversified into activities like industrial production of other nuclear materials required for the nuclear power programme. These include the production of sodium and ^{10}B-enriched boron carbide for fast breeder reactors, nuclear-grade solvents used in the front-end and back-end of the nuclear fuel cycle, and rare metal recovery from secondary sources by solvent extraction. It is a natural extension of the use of the knowledge of chemical engineering and expertise in operations acquired in the production of heavy water by the HWB.

Production of nuclear-grade solvents for closed nuclear fuel cycle

Various organophosphorous and amide-based nuclear-grade solvents were identified as essential inputs to the front-end and back-end of the nuclear fuel cycle, for recovery and separation of rare earth and other valuable metals, for fuel processing or reprocessing of spent fuel. In consonance with the pressing need for various nuclear solvents in the nuclear power programme, the task of extending the new processes for solvent synthesis and production from laboratory/bench scale to production scale was taken up in the mid-nineties by HWB as an in-house activity.

Research activities, including laboratory-scale process development for synthesis of solvents, viz. tributyl phosphate (TBP), di-2 ethyl hexyl phosphoric acid (D2EHPA), tri-octyl phosphine oxide (TOPO), tri-alkyl phosphine oxide (TAPO), di-nonyl phenyl phosphoric acid (DNPPA), *N*,*N*-di-hexyl octanamide (DHOA), tri-iso-amyl phosphate (TiAP), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A), etc. were done at BARC and Indira Gandhi Centre for Atomic Research, Kalpakkam, Tamil Nadu[5]. Further, revalidation of the process at bench scale and pilot scale was taken up by HWB. Subsequently, industrial-scale production facilities were set up by HWB at the HWPs in Talcher and Baroda.

HWB has set up three industrial-scale solvent production facilities, viz. TBP facility at HWP in Talcher, versatile solvent production plant at HWP in Talcher for the production of D2EHPA, TOPO, TAPO and DNPPA, and TBP plant at HWP in Baroda with higher capacity.

Based on the projected demand of the nuclear power programme, a multi-product solvent production plant (SPP) at HWP in Tuticorin for the production of DHOA, TiAP and PC88AA along with a higher capacity of TBP is being set up.

Development of novel solvents

1,3-Dioctyloxycalix[4] arene-crown-6 (CC6) solvent, also known as calix crown-6, has been identified as one of the potential candidates for selective separation of ^{137}Cs from high-level waste of spent fuel and making cesium pencils out of the radioactive waste, at Waste Immobilized Plant (WIP) in Trombay, Maharashtra. This solvent has been developed by the Nuclear Recycle Group (NRG), BARC at a laboratory scale[6]. Scaling-up for higher production was taken up at HWP in Talcher, and trial runs yielded a few kilograms of CC6, which has been handed over to NRG, BARC.

Boron isotopic enrichment and production of enriched boron compounds for fast breeder reactors

The prototype fast breeder reactor (PFBR) being set up at Kalpakkam requires ^{10}B-enriched boron carbide for control safety rod (CSR) and diverse safety rod (DSR) sub-assemblies. HWB has successfully demonstrated and deployed the technology for the production of ^{10}B-enriched boron carbide complying with CSR and DSR specifications. Considering the urgent need for supply to PFBR, HWB has installed an enrichment facility at HWP in Talcher and elemental boron, B_4C conversion, and pelletization facilities at HWP in Manuguru. The initial requirement of enriched boron carbide has already been met successfully.

Enrichment of boron-10: HWB has pursued two routes for the enrichment of boron – (i) Exchange distillation of boron tri-fluoride di-ethyl ether complex [$BF_3.O(C_2H_5)_2$] at HWP in Talcher. This method is presently being used for the enrichment of ^{10}B. (ii) Boric acid enrichment by ion exchange displacement chromatography at HWP in Manuguru.

The ^{10}B-enriched compound is converted to potassium fluoro-borate KBF_4 and electrowinned for the production of ^{10}B-enriched elemental boron (Figure 9). Boron carbide is synthesized from elemental boron by high-temperature reaction with carbon (Figure 10) and formed into pellets using a hot press (Figure 11).

Production of nuclear-grade sodium for fast reactors

For meeting the demand of nuclear-grade sodium for future Fast Breeder Reactors (FBRs) and making the FBR programme successful, and self-reliant, setting up of a 600 metric tonnes per annum nuclear-grade Sodium Metal Production (SMP) facility has been envisioned with various in-stage milestones like the development of cell technology at various capacities, prototype cell development and finally setting up of the industrial-scale facility.

Sodium metal production technology involves molten salt electrolysis of eutectic mixture for sodium production followed by purification to nuclear grade. Test cells of 50 and 500 A rating, closed-type, were taken up for the development of design and operating data. Subsequently, a 2 kA test cell has been set up, commissioned and operated at the HWP in Baroda (Figure 12). Based on operating experience and various modifications incorporated on the 2 kA cell, a 24 kA single cell design has been finalized and installed at HWP in Baroda, which would serve as a prototype cell in setting up multiple 24 kA cells for 600 MTPA nuclear-grade sodium plant.

Figure 9. Electrowinning cell.

While developing the prototype cell, the HWP in Baroda has installed a sodium purification unit based on technology provided by IGCAR. Subsequently, the HWP in Baroda has produced 3 MT nuclear-grade sodium metal and supplied it to IGCAR (Figure 13).

Production of ^{18}O-enriched water

^{18}O-enriched water, a specialty material finds a wide spectrum of applications in the field of nuclear medicine and biomedical research. The present requirement is >95% Isotopic Purity (IP) (^{18}O) water for carrying out PET scanning for the detection and staging of cancer in patients.

The HWB has adopted the heavy water distillation process (under vacuum) for the enrichment of ^{18}O. Being the

Figure 10. High vacuum induction furnace.

Figure 12. Sodium cell (2 kA).

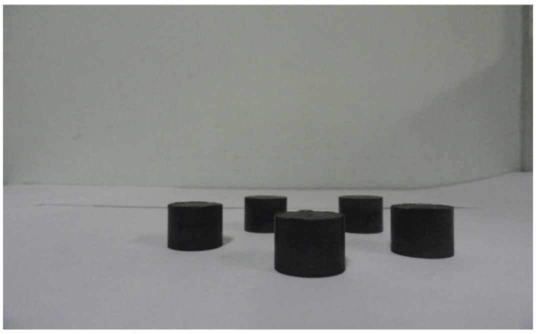

Figure 11. B4C pellets.

Figure 13. Supply of nuclear-grade sodium to IGCAR.

first of its kind for HWB and DAE, a tedious technology development cycle from the literature survey to commercial production had to be followed.

Work started in 2008–2009 by establishing a glass column set up at Tuticorin to generate hydraulic and mass transfer performance data (Figure 14). The packing of different types and configurations was manufactured for performance evaluation. Finally one structured and one random packing were selected to be deployed on an industrial scale.

Subsequently, a single prototype column was set up at Tuticorin to validate the data and sort out issues with respect to hydraulics, internal reflux/adiabatic operation, pumping, operability and controlling issues. The prototype column was operated for a year and also utilized for upgradation of the off-grade ^{18}O-water to the desired IP. The off-grade ^{18}O-water available from various hospitals/institutions was upgraded to the desired concentration. The upgraded ^{18}O-water was tested for its intended use Fluoro Deoxy Glucose (FDG) and quality was accepted for application by Radiation Medicine Centre.

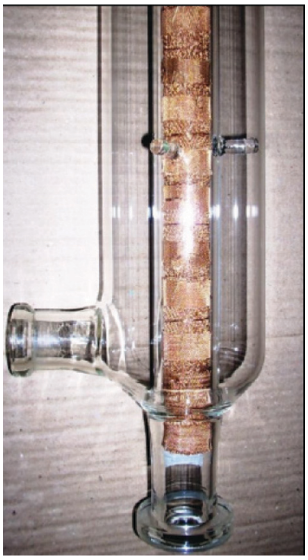

Figure 14. Glass column.

An industrial plant with ten-stage cascade was finalized to achieve reasonable inventory built (Figure 15). The product of this cascade is $D_2{}^{18}O$, which needs to be split and recombined with pure hydrogen at the back-end to give the desired product form, $H_2{}^{18}O$ (Figure 16). The facility faced several down times, but the ^{18}O inventory build-up continued. The first milestone of enrichment of 10% (first product) was achieved in January 2017.

The back-end systems of splitting and recombining were successfully commissioned. Based on requirement/demand, these units will be operated in campaign mode.

Recently, in January 2022, the first drop of ^{18}O-enriched water has been produced at HWP in Manuguru with IP >95.5%.

Thus, in a short span of 10 years HWB has developed the technology and successfully implemented it on an industrial scale and achieved production, which will have a positive impact on societal healthcare.

Non-nuclear applications of heavy water/deuterium

The non-nuclear applications of heavy water include metabolism studies, NMR solvents, deuterated drugs/active

Figure 15. Industrial plant for production of O-18 water.

Figure 16. Re-combination unit.

pharmaceutical ingredients, optical fibres, semiconductors, etc.

Development of deuterated compounds by HWB: HWB as a part of its diversification programme has taken up the development of D-labelled compounds, including NMR solvents. Presently, all the compounds are being imported into the country. The HWP in Baroda undertook the task of setting up a facility for in-house development of methods for deuterium labelling of hydrogen-bearing compounds like $CDCl_3$, DMSO-d6, acetone-d6, acetonitrile-d3, benzene-d6, etc. Till now, this facility is being utilized for the synthesis of deuterated NMR solvents under applied R&D. An augmented facility for the production of $CDCl_3$, DMSO-d6, acetone-d6, and acetonitrile-d3 is being set up at HWP in Baroda.

Deuterium depleted water: Deuterium depleted water (DDW) is another field that is gaining prominence due to reported benefits for its application in therapeutics, mainly in cancer treatment as adjuvant therapy. DDW with various deuterium contents is available in the international markets. HWB, being the largest producer of heavy water, has the capability of producing large quantities of DDW and supplying the same at various concentrations ranging between 30 and 120 ppm for societal purposes.

Concluding remarks

India is one of the largest producers of heavy water globally and is the only country using multiple technologies for its production. HWB has over the past few decades mastered the highly complex and energy-intensive technology of heavy water production through multiple processes, including H_2S–H_2O and NH_3–H_2 isotopic exchange processes. This has resulted in India moving from a situation of scarcity to a surplus concerning the production of heavy water. Performance indicators of operating HWPs like productivity, specific energy consumption, capacity utilization, safety and environmental performance, and human resource development have reached the zenith. Presently, HWB is capable of designing, constructing and operating HWPs on its own.

HWB has a strong presence in all the stages of India's nuclear power programme. It is actively contributing to the nuclear fuel cycle by a sustained supply of nuclear materials like heavy water for PHWRs, organo-phosphorus solvents for the front-end and back-end of the nuclear fuel cycle, ^{10}B-enriched boron for FBR, etc. HWB is also working in other areas of nuclear energy like augmenting nuclear fuel from secondary non-conventional resources like phosphoric acid, and the development of advanced technology for nuclear, societal and environmental applications.

1. Bhabha, H. J., Note on the organization of atomic research in India. 26 April 1948; reproduced in *Nuclear India*, November–December 2008, vol. 43, nos 5–6, pp. 3–5.
2. Sharma, S. and Mukherjee, S. P., A dream comes true – the saga of heavy water production in India. Department of Atomic Energy, Government of India, February 2009, pp. 29–30.
3. Dalvi, M. S., Kini, R. A., Tangri, V. K. and Sadhukhan, H. K., Development of a pre-conditioning procedure for corrosion control in H_2S–H_2O service. In Proceeding of the National Symposium on Heavy Water Technology, April 1989, pp. 163–166.
4. Sadhukhan, H. K., Varadarajan, T. G., Chandrasekharan, T., Nair, N. K. and Sethuram, N. P., Development of tower internals for heavy water upgrading based on distillation technique. In Proceeding of the National Symposium on Heavy Water Technology, Mumbai, April 1989, pp. 414–424.
5. Marwah, U. R., Sharma J. N., Sakhalkar, P. M., Bose, D. K. and Gupta, C. K., BARC process helps in industrial-scale production of D_2EHPA. *BARC Newsl.*, July 1999, No. 186, pp. 6–10.
6. Sharma, J. N., Process development for separation of cesium from acidic nuclear waste solution using 1,3-dioctyloxycalix[4] arene-crown-6 + isodecyl alcohol/*N*-dodecane solvent. *BARC Newsl.* (*Founder's Day Special Issue*), 2015, pp. 39–45.

doi: 10.18520/cs/v123/i3/322-329