

Editorial

Technological revolution is the enormous force resulting from man's awesome and far-reaching ability to exploit and manipulate the surrounding environment and resources to his advantage. Discovery and exploitation of various forms of energy are closely linked with the advancement of civilization. Demonstration of nuclear chain reaction is a tribute to the extraordinary intelligence and perseverance of a few scientists that resulted in the construction of nuclear reactors for energy production. While the nuclear fuel is the heart of a reactor, moderator plays a significant role in sustaining the chain reaction. Materials like ordinary water, heavy water and graphite are good moderators with heavy water being the best. In 1932, Urey's experimental diligence resulted in concentrating deuterium in the form of its oxide, heavy water. Although D₂O was first used in studying the fate of biochemical constituents in vivo, its importance as moderator in nuclear reactors led to technological innovations in enrichment methods to enable to produce large quantities of D₂O. Foresight and relentless efforts by our scientists and engineers culminated into setting up of heavy water plants in India. Today India is self sufficient and one of the major producers of D₂O in the world. This thematic bulletin on "Heavy Water" describes various aspects of heavy water production, its quality control and safety related issues.

I am extremely thankful to Dr. D.G. Pradhan, Senior Chief Chemist, Heavy Water Board (HWP) for accepting to be the guest editor of this issue. He chose the experts who not only contributed their articles in time but also have been very cooperative in making the articles technically simple. I thank all of them for the same. I take this opportunity to record our gratitude to Shri H.S. Kamath, Chairman and Chief Executive, HWP for his encouragement and guidance in bringing out this issue.

A.V.R. Reddy

CONTENTS

From the Secretary's Desk	ii
Dr. M.V. Ramaniah Memorial Award	iii
Dr. Tarun Datta Memorial Award	iv
Prof. H.J. Arnika Memorial Award	vi
Announcements	vii
Focus	1
Guest Editorial	3
Properties and Advances in Use of Heavy Water	5
<i>D.G. Pradhan</i>	
Heavy Water Production by Ammonia-Hydrogen Exchange Process - Success of Monothermal Route in India	12
<i>M. Bhaskaran</i>	
Heavy Water Production by NH₃-H₂ Exchange Process - Experience and Limitations of Bi-thermal Route	17
<i>P.R. Mohanty</i>	
Development of H₂S-H₂O Exchange Process based Heavy Water Technology	25
<i>V.K. Khilnani and R.R. Sonde</i>	
Heavy Water Production by Cryogenic Distillation Process employed in HWP, Nangal	31
<i>Arjun Singh</i>	
The Quality Requirement of Heavy Water	36
<i>C. Mohapatra and R.V. Gupta</i>	
Chemistry in Effluent Treatment at Heavy Water Plants	44
<i>J. Nageshri, N.L. Malaikar, S.K. Gupta and S.G. Belokar</i>	
Literature Update	51
<i>A.V.R. Reddy</i>	

From the Secretary's Desk



Dear Members,

Greetings to you all!

The vision and enthusiasm of a few individuals, matched with determined perseverance and deep commitment for a technologically strong India, provided the much-required spark that saw our country emerging as one of the developed Nations in harnessing nuclear energy. Thanks to their firm conviction and confidence in Indian capabilities, that today our country ranks among those, which have mastered the entire gamut of intricate nuclear technologies in planning, designing, constructing and commissioning of our nuclear power reactors and associated infrastructure including a strong human resource base.

While formulating the blue print of the nuclear programme of India, Late Dr. Homi Bhabha clearly spelt out the first stage with natural uranium fueled, D₂O moderated reactors. The advancement of technology for D₂O production from a mere 150 ppm of D₂O to nearly 100%, ran parallel with the designing of PHWRs. Today our country not only meets the requirements of D₂O for our indigenous PHWRs but also gains as a potential exporter of this commodity.

IANCAS compliments Dr.D.G.Pradhan for his scrupulous effort as the guest editor for this issue on "Heavy Water" and we trust that this bulletin will offer good reading not only to the academics but also to the members of the DAE family.

Announcement inviting the nominations for Annual Tarun Dutta Memorial Award-2001 is given in this issue. I request the members to give wide publicity to this. The award for the best thesis is named after Prof.H.J.Arnikaar as IANCAS-Prof.Arnikaar Best Thesis Award. The announcement inviting applications from the recent Ph.D. awardees for the award of 2001 is enclosed. It is with pleasure, the citations given to all the IANCAS Award recipients for the year 2000 are included in this issue.

Members are requested to update their addresses to facilitate prompt communication and receipt of the bulletins.

IANCAS is grateful to BRNS for encouraging and supporting the publication of these thematic bulletins with generous grants.

G.A. Rama Rao



FOCUS

Shri H.S. Kamath

*Chairman & Chief Executive
Heavy Water Board*

To meet the demand of heavy water for Pressurised Heavy Water Reactors (PHWR) indigenously, India embarked on heavy water production programme in late sixties. This programme has gone through challenging phases associated with development of any new technology. The late sixties and early seventies were exciting periods when various alternate manufacturing processes available either in the laboratory or in plant scale were evaluated to choose the best options suitable for the Indian scenario. Concerted efforts were needed for the choice of technologies since required information was not forthcoming from the developed countries monopolising the technology. India decided to go for two different technologies for the production of heavy water. Hydrogen Sulphide-Water exchange process was developed in-house while the Ammonia-Hydrogen exchange process was of a foreign origin and this was not a fully proven technology when it was imported. The first phase of the Heavy Water Programme saw the plants being set up based on both the processes. However, since both the technologies were being tried for the first time in India, the plants faced several problems. Thus the period from late seventies to late eighties was the gestation period to overcome, with tremendous amount of grit and determination, technological problems in both the processes. A large number of process modifications had to be done during construction and pre-commissioning. It was only in the late eighties the Heavy Water Board had a real turnaround with the commissioning of the second generation Heavy Water Plants at Thal, Hazira and Manuguru; commencing an upward trend in terms of production of heavy water.

The new generation plants at Manuguru, Thal and Hazira took care of the problems faced in the previous heavy water plants at Kota, Baroda and Tuticorin. It is creditable that HWB could assimilate and master both the technologies and today India is perhaps the only country in the world producing heavy water based on both the processes.

The period of the nineties has been a period of consolidation for the HWB. While the present HWP's can support a PHWR programme of the size of 6000 MWe, the D₂O required in excess of 6000 MWe has to be supplied by setting up new HWP's based on either of the technologies developed. Expansion of HWP(Manuguru) would be an alternative proposition as it would utilise the existing infrastructure. The process package for an additional stream has been worked out.

Plants based on NH₃-H₂ exchange process are linked to the fertilizer plants for supply of feed synthesis gas. With the fertilizer technology shifting from high to low pressure, this linkage may not remain viable due to throughput consideration. With this in view, HWB is presently developing an alternative process of NH₃-H₂O exchange front end plant to make these plants completely independent of the fertilizer plants. A technology demonstration plant at Baroda is being set up.

The focus of the HWB at present is on energy conservation and energy management to bring down the energy consumption to as low as can be reasonably achieved. The specific energy consumption has been brought down by about 13% during 1999-2000 and by about 6.5% during the year 2000-01. This has resulted in considerable saving of natural resources and substantial reduction in cost of production of D₂O.

Along with energy conservation measures, HWB is introducing quality systems in the plants by getting accreditation to ISO quality standards. HWPs at Tuticorin and Manuguru have implemented ISO 9001 and ISO 14001. Work on implementation of these standards is in progress in other plants. In the area of safety, HWPs have been performing well.

Thrust areas of HWB for the next few years will be to make the HWPs further more energy-efficient and provide services to other industries in the field of technical strength achieved. Diversification into production of important metal extractants to meet in-house requirements of the department is another area requiring effort of HWB. In addition to meeting the requirement of D₂O of our Department, HWB has successfully executed export order of 116 MT D₂O to South Korea based on the strength of superior quality. Some of the future orders for export demand production of high isotopic concentration of better than 99.95%, a challenge to be met by HWB.

This special issue of IANCAS Bulletin highlights the complexities of heavy water production processes which India has assimilated with success. The invited articles cover all the important facets of heavy water production and use as contributed by all the technique developers of HWB.

Guest Editorial
D.G. Pradhan



I am happy that IANCAS is bringing out this thematic bulletin covering all aspects of heavy water (D_2O) production and use. Seven articles on these aspects have been written and I thank the authors for timely contribution of their articles.

Use of D_2O as moderator and coolant in the pressurized heavy water reactors in harnessing nuclear energy for peaceful purposes gave impetus for its large scale production. India has acquired industrial experience of almost all D_2O production processes, developed so far, by constructing, commissioning and successfully operating a number of Heavy Water Plants (HWPs) based on cryogenic distillation of hydrogen and isotopic chemical exchange involving hydrogen sulphide, water, ammonia and synthesis gas ($N_2 + 3H_2$).

While the D_2O production process is governed by certain differences in the properties between hydrogen and its compounds compared to those of deuterium and its compounds, the amount of heavy water to be produced is dictated by the advances in the application of D_2O . Dr. D.G. Pradhan's article deals with the important properties and uses of heavy water with a brief account of natural abundance of deuterium and isotope effect as the basis for the D_2O production.

Favorable reaction kinetics in the exchange reaction either due to inherent nature of the labile bonds being broken/formed or by the use of catalyst and appreciable change of equilibrium constant with change in temperature, have resulted in preeminence of isotopic chemical exchange process in D_2O production. Physical processes such as distillation and laser separation methods are also important. Heavy water is essentially separated from a large amount of feed with low natural abundance of deuterium (about 1 part in 7000 parts) and enriched in a cascade having a number of enrichment stages. Based on the manner of providing reflux, two configurations have evolved - monothermal and bithermal. While the H_2S - H_2O system, occupying the center stage of global D_2O production, is adopted in bithermal mode, the NH_3 - H_2 exchange system has been exploited in both the configurations.

Development of H_2S - H_2O technology in India has been described by Shri V.K. Khilnani and Dr. R.R. Sonde. D_2O Production is an energy intensive process as expenditure on energy constitutes about 70% of the total cost. Bithermal NH_3 - H_2 exchange process is attractive due to low energy consumption, but several limitations enumerated in his article by Shri P.R. Mohanty have yet to be satisfactorily addressed. On the other hand, the success of monothermal NH_3 - H_2 exchange process in India has been described by Shri M. Bhaskaran.

Cryogenic distillation of hydrogen is an important process of separation of both deuterium and tritium, but requires proper quality control failing which impurities like O_2 and N_2 shall solidify at liquid hydrogen temperature in the distillation tower. The oxygen required for burning deuterium to D_2O is also to be made free from moisture, methane etc. to avoid degradation of isotopic purity. Shri Arjun Singh described cryogenic

process of D₂O production highlighting certain special features.

Separation factor for isotope separation is a key parameter in defining process attractiveness. Water distillation process, though disadvantageous from separation factor point of view, is invariably used for final enrichment of D₂O nuclear grade from about 10-30% D₂O due to simplicity of operation having low potential for loss by leakage. Chemistry control of feed to distillation tower is important as any contamination with trace amounts of oil, H₂S, NH₃ etc. can deteriorate the packing used in the tower reducing the number of theoretical trays drastically. Quality of D₂O produced from the plants depends upon several factors. Analysis and quality control measures adopted have been described by Shri C. Mohapatra and Shri R.V.Gupta.

Along with the separation factor, energy consumption is of equal importance for D₂O production, which depends upon the degree of energy recovery by maintaining clean contact surface. This calls for appropriate quality control of utilities like cooling water, steam and refrigerant. Corrosion control measures adopted are of prime importance in the HWP's handling huge quantities of toxic, inflammable and hazardous chemicals which again calls for proper quality control of the process fluids and utilities so that contact material and the protective layers remain intact. The special gas liquid contacting devices like sieve and ejector trays used for intimate mixing of gas and liquid streams should not get blocked with deposits formed by reaction of sub-ppm level impurities like oxygen, carbon monoxide and carbon dioxide with H₂S and highly reactive potassium amide catalyst. Understanding of process chemistry as well as maintaining proper quality of feed and various utilities by proper control measures are pre-requisites for successful operation of HWP's to produce D₂O in safe, economic and sustained manner. Environmental impact of operating plants and chemistry of effluent treatment in HWP's are described in an article by S/Shri J. Nageshri, N.L.Malaikar, S.G.Belokar and S.K.Gupta.

I take this opportunity to thank Dr. A.V.R.. Reddy, Editor, IANCAS, for requesting me to be the guest editor. I am extremely thankful to Shri H.S. Kamath, Chief Executive and Chairman, Heavy Water Board for his guidance and providing the 'focus' to this issue.

Properties and Advances in Use of Heavy Water



Dr. D.G. Pradhan, Sr. Chief Chemist of Heavy Water Board, joined Department of Atomic Energy through 10th Batch of Training School. He obtained his M.Sc. from Utkal University, Orissa in 1965 and Ph.D. in 1971 for his research on "Hydrogen Isotope Effect" at Bhabha Atomic Research Center. He joined Heavy water Plant, Talcher in 1973 and was closely associated with commissioning of the plant and subsequent operation as Technical Service Manager before leaving for HWB central office during 1995. He has more than 30 years of R & D experience on Hydrogen Isotope Chemistry and a large number of publications to his credit.

Introduction

Hydrogen, the lightest element, is the most abundant matter in the universe and each of its isotopes has a name. Hydrogen, having one proton in the nucleus has the symbol H, Deuterium, having one neutron and a proton in the nucleus, is given the symbol D, which is a stable isotope, whereas radioactive isotope, Tritium, with two neutrons and a proton in the nucleus, has the symbol T. It undergoes beta decay to ^3He with a half life of 12.26 years. Oxides of these isotopes, H_2O , D_2O and T_2O are known as water, heavy water and tritiated water respectively.

Discovery of deuterium was reported in December 1931 based on the spectroscopic analysis of 2 mL of liquid obtained by a Raleigh distillation of 6 liters of liquid hydrogen at triple point [1]. Electrolysis of water was reported [2] to be another method of concentrating deuterium and ^{18}O . Fractional distillation of water [3] was also used for concentrating deuterium and ^{18}O . As soon as 0.3 mL of nearly pure D_2O was accumulated, measurement of some of the physical properties of heavy water was undertaken to study the plausible differences in equilibrium and thermodynamic properties of isotopes in chemical reactions [4]. The initial studies on separation and properties of heavy water led to vigorous research on characterization of the

differences between light and heavy water resulting in avenues for heavy water in nuclear, chemical and biological applications. Some of the important properties and uses of heavy water are discussed in this article.

Natural Abundance of Hydrogen and Oxygen Isotopes in Water

Accurate measurement of D and ^{18}O in water is required for studies in geochemistry, hydrology, environment and biochemistry. There is considerable variation in the D and ^{18}O content of natural water due to fractionation during evaporation, condensation and ice precipitation. Formation of rain or snow is not a simple process and many different phenomena occur which may affect isotopic composition of water reaching the ground. Factors such as relative humidity, wind velocity and direction and altitude of condensation should be considered. It is, therefore, expected to have variation in D and ^{18}O content with the place and time of collection of the sample.

In general, ocean water density is found to be more than that of fresh water partly due to higher D content and partly due to higher ^{18}O content. Atmospheric oxygen has a higher ^{18}O content than that of ordinary water which has been suggested to be due to enrichment of ^{18}O in the stratosphere by

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random exchange between O_2 and CO_2 . The exchange reaction between $H_2^{18}O$ and $^{16}O_2$ could not explain the result and the hypothesis that O_2 of atmosphere comes entirely from photosynthesis is not tenable from a study of isotope exchange reaction with ^{18}O , which shows that most of the oxygen obtained during photosynthesis comes from water and not from CO_2 which has higher ^{18}O content due to exchange reaction



The ratio of isotopes ^{16}O , ^{17}O and ^{18}O has been found to be $(506 \pm 10) : (0.204 \pm 0.008) : 1$ in nature. Natural abundances of H_2O , D_2O and T_2O are in the ratio of about $1 : 1.5 \times 10^{-4} : 2 \times 10^{-16}$.

Basic Formalism for Hydrogen Isotope Separation

The basis of isotope separation is the mass difference between the isotopes. In the case of hydrogen isotopes, the relative mass difference is highest. The effect of mass of a particular isotope on chemical and physical properties as well as on reaction rate constitutes the subject matter of isotope effect. The origin of such an effect lies in the fundamental motion of atoms and sub-atomic particles in a molecule viz. translational, rotational, vibrational and electronic. The energy of a molecule depends upon the magnitude of these motions which in turn depends upon the temperature along with mass, bond length, electronic state and vibration of atoms in the molecule. As the temperature is reduced, magnitude of various motions reduces. At absolute zero temperature, the molecules possess certain amount of energy known as the Zero Point Energy (ZPE) which depends upon vibrational frequency (ν_0) at that temperature

$$ZPE = \frac{1}{2} h\nu_0 \quad (2)$$

where h is the Planck's constant. The frequency of vibration depends upon mass. Lower frequency

resulting from higher mass reduces ZPE for the heavier isotope.

The mode of vibration depends upon the number of atoms in the molecule and there are three normal modes of vibration for water molecule as shown in Fig. 1. Frequency of these vibrations and the ZPE differ from H_2O to HDO to D_2O as given in Table 1.

TABLE 1. Frequency of Vibration and ZPE for H_2O , HDO and D_2O

Mode of vibration	Frequency (in cm^{-1})		
	H_2O	HDO	D_2O
Bending	1594.59	1402.20	1178.33
Symmetric Stretching	3656.65	2726.73	2671.46
Antisymmetric Stretching	3755.79	3007.47	2788.05
ZPE	4634.32	4032.23	3388.67

Separation of Hydrogen Isotopes

Separation of Hydrogen Isotopes; D from H, T from H and T from D, is of great importance to the nuclear industry. Large quantities of D_2O are required for nuclear power reactors fueled with natural uranium as moderator and coolant. Additionally, with the development of nuclear industry, T separation has also become very important. H and D occur in nature and T is formed by neutron capture by D and also in the fission of uranium. In D_2O reactors, concentration of T in D_2O increases gradually, which must be removed to reduce the radiation exposure. The aqueous waste from fuel reprocessing plants of the water cooled reactors also contains appreciable quantities of T as HTO.

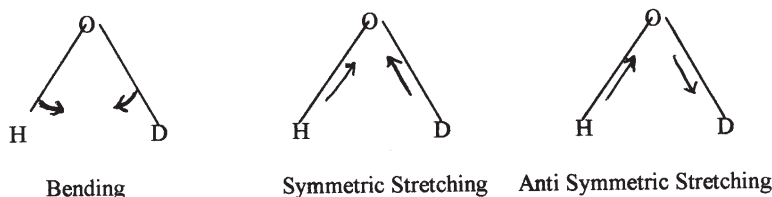


Fig. 1 Different modes of vibration for water.

Almost all heavy water production today is based on isotopic chemical exchange process though physical processes such as distillation, selective absorption and laser separation methods are important. Heavy water is separated and enriched in manufacturing processes which necessitates processing of large quantities of feed in cascades having a number of enrichment stages as the abundance of D is low in the source material such as water, hydrogen, ammonia and hydrocarbons. T separation similarly involves isotopic chemical exchange, electrolysis, distillation and use of membranes and lasers.

Isotope Effect

For a chemical reaction to take place, the reactant molecules have to acquire certain minimum amount of energy called the Activation Energy. The energy level of T and D containing reactants is lower than that of H-containing reactants. The reactants combine to form a loosely bound activated complex having almost the same potential energy for H, D and T-containing molecules. Hence the activation energy of T and D containing molecules is more than that of H-containing molecules. Thus, the T and D containing molecules react slower than the H-containing molecules and this is called normal kinetic isotope effect i.e. $k_H > k_D > k_T$, where k is the rate constant of a chemical reaction. Since k is energy dependent, normal isotope effect generally decreases with rise in temperature. Some of the observed isotope effects are given in Table 2.

TABLE 2. Hydrogen isotope effect at various temperature

Type	Observed ratios	Temperature (°C)
k_{C-H}/k_{C-D}	8.2	0
- do -	6.9	25
- do -	4.6	100
- do -	2.1	500
k_{N-H}/k_{N-D}	9.2	25
k_{O-H}/k_{O-D}	11.5	25
k_{C-H}/k_{C-T}	16.0	25

It is also, however, possible that the reactants combine to form a strained transition complex

increasing the potential energy difference between H- and D- containing molecules further, in which case D-containing molecules react faster than the H-containing molecules giving rise to inverse isotope effect. Isotopic substitution at positions other than the bonds being broken/formed lead to secondary isotope effect. In addition to kinetic isotope effect, there are thermodynamic or equilibrium isotope effect, solvent isotope effect and biological effect.

General Properties of Heavy Water

Compounds of hydrogen, deuterium and tritium differ in their physical properties as the mass differences of isotopes of hydrogen differ greatly. Several methods of separation and concentration of hydrogen isotopes and numerous methods of analysis are based on these differences in physical properties. However, many of the physical and chemical properties of heavy water are almost identical to those of light water but for a striking difference with respect to the life process. While water is necessary for life, heavy water is poisonous to all, but for the very lowest forms of life.

Certain forms of algae and similar elementary bodies grow in heavy water, but when mammals are fed considerable quantities of D_2O , undesirable physiological effects occur. Germination of seeds gets delayed and impaired in D_2O and growth of plants is affected considerably on continuous watering with D_2O .

Some of the important physical properties of heavy water are given in Table 3.

Chemical and Radiochemical Properties of Heavy Water

The differences in thermodynamic and nuclear characteristics between H_2O and D_2O cause slight difference in chemical behaviour. Solubility of some salts are lower in D_2O by as much as 30% at low temperature [5] and ion exchange equilibrium are slightly displaced. Fig. 2 shows changes in entropy, enthalpy and free energy of transfer of NaCl in D_2O - H_2O system which can be explained on the basis of hydrogen-bonded water structure; (deuterium-bonded structure is relatively stable) and solvent isotope effect. The difference between heats

TABLE 3. Physical Properties of Heavy Water

Molecular Weight	20.03382 on physical scale and 20.02836 on chemical scale (^{16}O , ^{18}O : ^{17}O =506:1:0.2)
Specific Gravity	1.10775 at 25°C
Temperature of Maximum Density	11.23±0.02°C
Melting Point	3.82°C
Boiling Point	101.431±0.003°C
Critical Temp.	371.2°C(374.2°C for H_2O)
Critical Pressure	218.83 atm. (220.29 for H_2O)
Vapor Pressure	$\log(\text{pH}_2\text{O}/\text{pD}_2\text{O})=(-30.77\pm0.18)/T+(14603\pm70)/T^2$ & $\text{pHDO}/\text{pD}_2\text{O}=(\text{pH}_2\text{O}/\text{pD}_2\text{O})^{1/2}$
Molar Volume, Solid at T_m	19.679(19.65 for H_2O)
Liquid at T_m	18.118(18.018 for H_2O)
Liquid at 25°C	18.134(18.069 for H_2O)
Surface Tension(z)	$z=1-0.00501\Delta S$ where $\Delta S=S_{25}-1$
Viscosity	8.93×1.232 mili poise at 25°C(8.93 mili poise for H_2O)
Refractive Index(n) & Molar Refraction (R)	$n_{\text{D}_2\text{O}}=1.3283$ at 5893°A(0.0047 units less than that of H_2O) $R_{\text{D}_2\text{O}}=3.679$ (3.712 for H_2O)
Velocity of Sound	1398 meters/sec. at 25°C(1496 meters/sec. for H_2O)

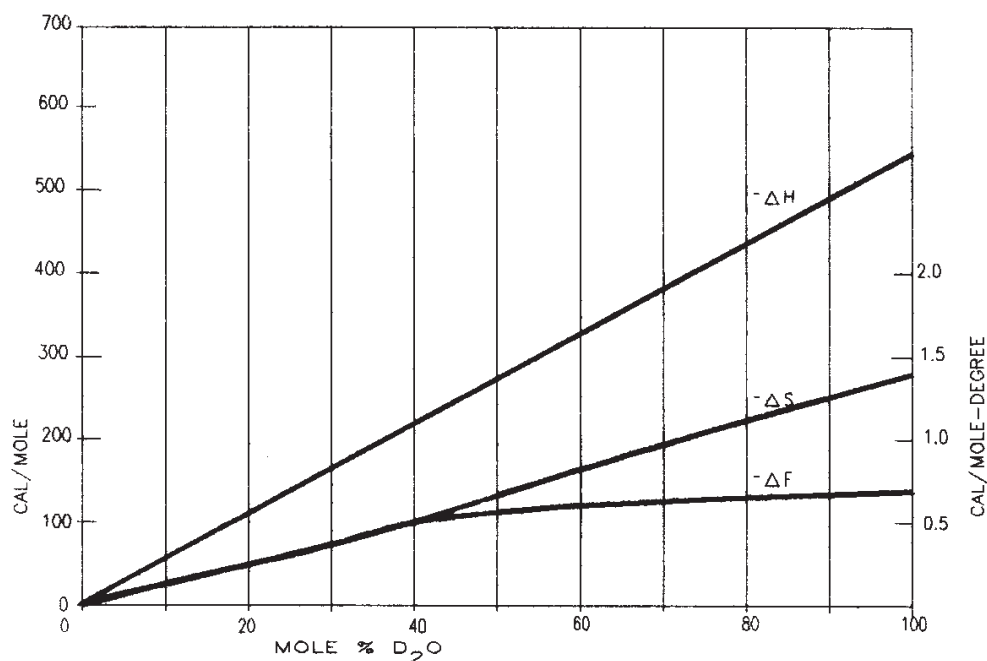


Fig. 2 Enthalpy, free energy and entropy of transfer of NaCl from D_2O to H_2O in D_2O - H_2O mixtures

of solution of alkali ion in heavy and light water increases with cation radius, heats of solution being higher in D₂O. Neutral heavy water has a pD of 7.4 as D₂O ionises to a lesser extent than H₂O. Acids dissociate to a lesser degree in D₂O than in H₂O.

The radiolysis of D₂O is similar to that of H₂O. It is negligible in low conducting water but rapidly increases linearly with increase in ionic concentration. But net decomposition is lower for D₂O than for H₂O. The recombination of D₂ and O₂ is not complete even at higher temperature and O₂ level builds up undesirably in He system of reactors. A small amount of H₂ added directly to primary system acts as a catalyst in the recombination reaction and O₂ concentration quickly reduces to undetectable levels. There is a preferential combination of O₂ with H₂ compared to D₂ [6].

Nuclear Properties of Heavy Water

Presence of one additional neutron in the nucleus of hydrogen in heavy water considerably reduces the neutron absorption capacity of heavy water compared to that of water. It is also a good scatterer of neutrons. D₂O thus is a good moderator for neutrons. Some of the important neutron absorption/scattering related properties are given in Table 4.

Tritium and deuterium are used in nuclear fusion. A few MeV deuterons are also used as projectiles in the nuclear reactions.

Uses of Heavy Water

Nuclear

Boiling water reactors (BWR) and pressurized water nuclear reactors (PWR) use H₂O as coolant and moderator and partially enriched uranium in ²³⁵U as fuel. On the other hand, the inherent advantage of D₂O with low neutron absorption and effective moderation facilitates use of natural uranium in Pressurized Heavy Water Reactors (PHWR). The Canadian design of heavy water power reactors, the CANDU design, requires 0.85 te of D₂O per electrical MWe of installed capacity. D₂O is not consumed by reactor operation and hence the demand for D₂O is set by the rate at which new PHWRs are built. Less than 1% of the inventory per year is needed to replace losses by leakage [7].

General

Heavy Water is used as a source for the preparation of a large number of compounds labeled with deuterium either by direct synthesis or chemical exchange process. These labeled deuterium compounds are used as tracers for studying reaction mechanism, deuterated solvents for Nuclear Magnetic Resonance (NMR) application and several value added products.

Study of isotope effect including solvent isotope effect has emerged as one of the finest tools for elucidation of reaction mechanism and optimized production of a particular compound in competitive reactions[8]. Deuterium isotope effect has been utilized for developing (i) lubricants by replacement of H with D to last substantially longer as oxidation rate is slowed down, (ii) medicines which are

TABLE 4. Nuclear Properties of heavy water

Properties	Value
Neutron macroscopic absorption cross section at 2200 m/sec (Σ_a, cm^{-1})	0.00004
Thermal neutron macroscopic absorption cross section ($\Sigma_{tr}, \text{cm}^{-1}$)	0.395
Thermal neutron diffusion area (L^2, cm^2 for 0.13% H ₂ O) content	13,500
Corrected for H ₂ O absorption	25,000
Average cosine of neutron scattering angle (μ)	0.15
Epithermal neutron macroscopic scattering cross section (Σ_s, cm^{-1})	0.349
Epithermal neutron macroscopic slowing-down cross section ($\frac{1}{\beta} \Sigma, \text{cm}^{-1}$)	0.178

effective at lower dose levels and reduced administered frequency rates due to reduction of metabolic loss of the medicines unrelated to drug action, (iii) long lasting anti malarial drugs with deuterium substitution, (iv) increasing stability of vaccines including polio vaccine in heavy water medium and (v) manufacture of deuterated polymers/optical fibers with superior properties.

The climatic condition of rainfall during past could be found out from the measurement of the ^{18}O and D-content of wine, which preserves soaked water of the grapes in bottles year-wise. The rise and fall of temperatures over the past 7,50,000 years in Tibet was revealed in a thousand-foot-long ice core, the longest ever retrieved from the mid-latitudes. Samples of the ice core were cut from various levels, and content of a particular oxygen isotope in each sample was measured. Evaporating water leaves behind ^{18}O and D; larger amounts of these indicate higher temperature of that period.

Biological Application of Heavy Water

A hypothesis put forward by Gilbert N. Lewis that D_2O would not support life and would be lethal to higher organisms was experimented with germination of tobacco seeds [9] and some inconclusive test on warm blooded animals like a mouse. It could be shown that tobacco seeds, which germinate infallibly in four days in ordinary water, did not germinate in three weeks in D_2O . If the seeds were then removed from D_2O and placed in ordinary water, germination took place in an abnormal way after about one week leading to a thin and sickly growth.

Green algae could be grown in pure D_2O [10] whose morphology differs significantly from that grown in H_2O . E.-Coli (Stain K-12) could also be grown in fully deuterated media, but at a rate, of about five times slower than that in ordinary water. Starting with algae grown in pure D_2O , a number of deuterated species could be prepared through biosynthesis.

Replacement of protium by deuterium results in variation of rates and equilibrium of chemical reactions and pH/pD of physiological solutions, viscosity of the medium, structure of nucleic acids etc.. Although there are efforts, the effect of D on the

growth of simple and higher organisms is yet to be fully understood.

Though studies prior to 1960 were unanimous in concluding that D is toxic and that high concentration of D are incompatible with continued life, it is by no means true for all living organisms. Many important classes of organisms survive complete replacement of H by D. Some variety of algae, bacteria, yeast moulds and Euglena can be grown in pure D_2O whereas embryo plants can be grown only up to a D_2O concentration of about 50% and mammals can tolerate up to about 30% D_2O . When content of body water of mice reaches 20%, severe physiological effects manifest whereas 50% D_2O is lethal. Similar results are found in dogs.

When Poliomyelitis virus, which is a small RNA virus, is grown in 20-30% D_2O , its proliferation is enhanced, whereas Simian virus 40, a DNA virus multiplies less in D-media. Western equine encephalitis, a large RNA bearing virus was inhibited by D_2O indicating that the nucleic acid portion of the virus does not necessarily determine the response of the virus to D_2O [11].

Panel discussion during the technical committee meeting on "Modern Trends in the Biological Application of Stable Isotopes" held in Leipzig from 14-18 February 1977 under IAEA, Vienna dealt with the question of whether ethical considerations (possible toxic effects) are likely to restrict the use of stable isotopes in medicine. The only possible problem that could be identified was in relation to the use of deuterium which, in high concentration is toxic due to hydrogen bond effects in DNA and to other processes.

References

1. H.C. Urey, F.G. Brickwedde and G.M. Murphy, Phys. Rev. 39 (1932) 164 and ibid 40 (1932) 1.
2. E.W. Washburn and H.C. Urey, Proc. Nat. Accd. Sci 18 (1932), 496 and G.N. Lewis and R.T. Macdonald, J. Chem. Phys. 1 (1933) 341 and J Am. Chem. Soc. 55 (1933) 1297.
3. G.N. Lewis and R.E. Cornish, J. Am. Chem. Soc. 55 (1933) 2616.

4. G.N. Lewis and R.T. Macdonald, J. Am. Chem. Soc. 55 (1933) 3057 & 4130
5. V.M. Vdovenko, Y.V. Gurikov and E.K. Legin Soviet J. At., Energy 19 (1965) 1393, 1397.
6. R.V. Dalin, USAEC Report BNWL SA 107, July 20, 1965.
7. H.K. Rae, Separation of Hydrogen Isotopes, ACS Symposium Series 68, 1978.
8. D.G. Pradhan, Indian Journal of Chemistry, 9(1971), pp.318-321, 831-834, 835-836, 10(1972) pp. 502-504, 562-563, 11 (1973), 894& 1155 etc.
9. G.N. Liews, J. Am. Chem. Soc., 55 (1933) 3503 & Science, 79 (1934) 151.
10. J.J. Katz, American Scientists 48 (1960) 544
11. Isotope Effects in Biological Systems, Isotope Effects in Chemical Reactions, ACS Monograph Ed. C.J.Collins&N.S.Bowman, Van Nostrand Reinhold Co., Newyork, 1970, p 286-363.

Heavy Water Production by Ammonia - Hydrogen Exchange Process: Success of Monothermal Route in India

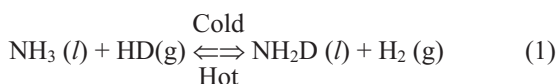


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Introduction

Heavy Water Plants are inherently complex due to very low abundance level of deuterium and are capital and energy intensive. Among the successful commercial processes for heavy water production, chemical exchange process is the widely used one. While hydrogen sulphide-water system is having over 90% share in the world's heavy water production, alternate process based on the ammonia-hydrogen exchange system was developed in the late 60's for commercial production.

Deuterium exchange reaction between different chemical species is due to the isotope effects. The ammonia-hydrogen exchange process is based on deuterium transfer reaction between liquid ammonia and gaseous hydrogen.



However, this process did not get importance as a commercial process, as the rate of reaction was extremely small. In 1950, Clays, Wilmarth and Dayton showed that the rate of the above reaction could be enhanced using potassium amide dissolved in ammonia as a catalyst. Though the homogeneous potassium amide did improve the rate of reaction, the rate was still far less compared to that of hydrogen

sulphide-water process and needed improved gas-liquid contactors for mass transfer.

When ammonia (l) and hydrogen (g) having different isotopic concentrations are brought into contact, deuterium accumulates in the liquid phase based on the equilibrium conditions. The separation obtained is governed by the separation factor, which is defined as the ratio of the deuterium content in the liquid phase to that in the gaseous phase.

$$\text{Separation factor, } S = (D/D+H)_l / (D/D+H)_g \quad (2)$$

The separation factor for the ammonia-hydrogen exchange process is 2/3 of the equilibrium constant and it decreases with increase in temperature.

A large number of separation contacts between liquid ammonia and gaseous hydrogen are essential for obtaining the desired level of separation. The chemical exchange process based on the continuous countercurrent contact of the liquid and gas needs provision of a reflux stream to the column. In the monothermal mode of the chemical exchange process, the reflux is provided by a phase converter, which changes the component completely into the other by chemical reaction. Ammonia-hydrogen exchange process is fairly easy to adopt to monothermal operation as the heat of formation of ammonia from hydrogen and nitrogen is relatively low and the conversion of nitrogen and hydrogen

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into ammonia and its decomposition is an established process.

Basic Scheme of Ammonia – Hydrogen Exchange Process

A schematic of monothermal $\text{NH}_3\text{-H}_2$ exchange process is shown in Fig. 1. Feed gas containing deuterium is brought into contact with liquid ammonia in an extraction tower wherein deuterium exchange reaction takes place and the deuterium laden liquid is enriched further in the enrichment tower. The reflux requirement of the enrichment tower is met with decomposition of the liquid ammonia into hydrogen and nitrogen in an ammonia-cracking unit. The deuterium depleted feed gas is taken out of the extraction tower and sent to the feed gas generation unit after reflux liquid ammonia is generated in an ammonia synthesis unit. A low temperature of around -25°C is employed for the exchange reaction in order to have a good separation factor. The separation factor at -25°C is over 5.

Dependence on Fertilizer Ammonia Plant

Monothermal $\text{NH}_3\text{-H}_2$ process needs hydrogen as feed gas and the success of a commercial process depends on the availability of the same. Large-scale fertilizer plants producing ammonia have hydrogen as a mixture of hydrogen and nitrogen in the approximate stoichiometric ratio of 3:1 used for the synthesis of ammonia and this is an ideal feed gas. Hence all the monothermal ammonia-hydrogen exchange process plants depend on the fertilizer ammonia plants and are connected to them. The dependence of the monothermal $\text{NH}_3\text{-H}_2$ plants on the fertilizer ammonia plants limits the choice of location and production capacity.

Prototype Plant

Development of $\text{NH}_3\text{-H}_2$ monothermal process was originally carried out as a prototype plant in France in 1968 with a capacity of 20 tonnes/year. The plant was linked to the 650 te/ day ammonia plant and the exchange tower operated at -25°C and 350 kg/cm^2 pressure. The exchange section produced liquid ammonia stream with 1.3% deuterium and the final enrichment was done by distillation of ammonia. The operational data

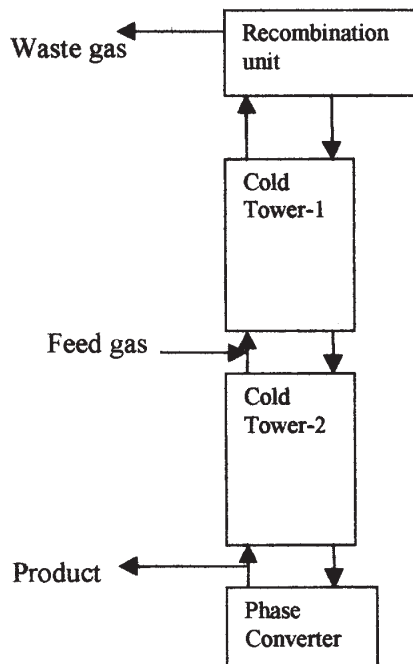


Fig. 1 Monothermal $\text{NH}_3\text{-H}_2$ exchange process

generated from this plant formed the basis for the subsequent plants based on this process. Together with the $\text{H}_2\text{S-H}_2\text{O}$ process, which was the dominant one world over, the evolving new process based on the ammonia-hydrogen exchange was also selected for commercial production of heavy water by India. A consortium named GELPRA led by M/s Sulzer got involved in setting up of two plants at Baroda and Tuticorin based on the monothermal process in the beginning of 70s.

Monothermal $\text{NH}_3\text{-H}_2$ Exchange Process.

It is essential that the exchange reaction be carried out at low temperatures in order to have a large separation factor. The separation factor depends not only on temperature, but also is a function of deuterium content of the system and solubility of hydrogen in liquid ammonia. This is so, as the exchange reaction takes place in the bulk liquid phase containing homogeneous potassium amide catalyst. Apart from using potassium amide catalyst for enhancing the rate, a large interfacial contact area for gas- liquid is essential in order to

increase the yield. Special mass transfer stages having large interfacial area of gas-liquid contact help reduce the tower volume. Potassium amide dissolved in liquid ammonia catalyses the exchange reaction.

Monothermal NH₃-H₂ exchange plants in India

Out of the seven heavy water plants based on chemical exchange process in India, four are based on the monothermal NH₃-H₂ exchange process and has a combined capacity of over 250 tonnes per annum. The plants based on the process are located at Baroda in Gujarat, Tuticorin in Tamil Nadu, Thal in Maharashtra and Hazira in Gujarat. The commissioning dates of these plants are given in Table 1 below.

TABLE 1. Location and Commissioning dates of monothermal NH₃-H₂ plants in India

Location	Commissioning Date
Baroda	July 1977/January 1980
Tuticorin	July 1978
Thal	October 1986
Hazira	February 1991

Continuous analysis of the problems encountered in the initial phase and their rectification not only removed the process and equipment related problems but also resulted in improved operability of the plants. The confidence gained at Baroda and Tuticorin enabled HWB to take up setting up of two more plants having double the capacity at Thal in Maharashtra and Hazira in Gujarat in 1980s. These plants were set up with total indigenous efforts. The plants at Thal and Hazira were twin stream heavy water plants with integrated ammonia synthesis unit and common utility systems and were linked to the fertiliser plants of RCF at Thal and Kribhco at Hazira.

Monothermal NH₃-H₂ Exchange Plant Scheme

Ammonia synthesis gas (syngas) is generated by steam reformation of hydrocarbons-naphtha, natural gas etc. in the front end of the ammonia plant and is subsequently sent to the ammonia synthesis loop consisting of ammonia converter, waste heat recovery and cooling section and the liquid ammonia

separation unit of the ammonia plant. Nitrogen and hydrogen combine to form ammonia in the ammonia converter under high pressure and the syngas produced at the generation section is compressed to the required pressure. The feed gas to heavy water is tapped from the discharge of the syngas compressor. After recovery of deuterium in heavy water plant, the syngas is returned to the fertilizer plant for production of ammonia. Fig. 2 depicts a typical interlinking of the ammonia plant with heavy water plant. Table 2 indicates the heavy water plants with the operating pressures of the ammonia plants to which the plants are interlinked.

The syngas from ammonia plant contains moisture and other oxygenated impurities like CO and CO₂ at trace levels. Though an elaborate purification system is provided in the heavy water plant, it is important that the gas generation section is designed and operated to have minimum levels of CO/CO₂ impurity. By ultramethanation, these impurities in ammonia plant are maintained at about 1 ppm.

TABLE 2. HWP – Ammonia Plants and Operating Pressures

Sl. No	Heavy Water Plant	Fertiliser Plant	Operating Pressure, kg/cm ²
1	Baroda	GSFC	650
2	Tuticorin	SPIC	250
3	Thal	RCF	200
4	Hazira	KRIBHCO	200

The level of deuterium in the synthesis gas varies widely depending on the process employed in the ammonia plant. The deuterium concentration of the hydrocarbon and the steam carbon ratio employed in the reformation process affect the deuterium level in the feed syngas due to the in-situ deuterium shift reaction between hydrogen to water. It is hence important to recover and recycle all the steam condensate produced from the process as the deuterium gets accumulated in the water phase. It has been the experience that with effective utilization of the deuterium rich condensate, deuterium concentration level of 115 ppm is possible to be achieved in the feed synthesis gas. The various

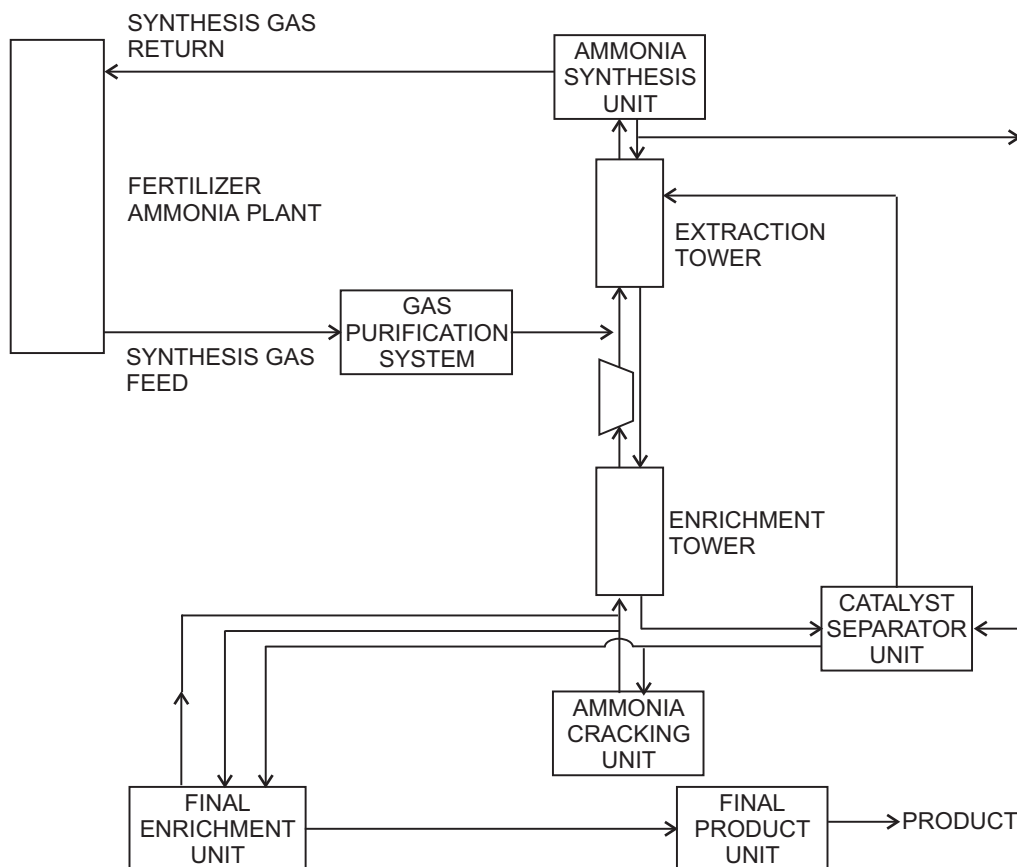


Fig. 2 Integration of HWP with Ammonia Plant and HWP Flow Scheme

sections provided in the process scheme are (i) Syngas pressure boosting, (ii) Drying and purification of gas, (iii) Extraction of deuterium into liquid ammonia containing potassium amide catalyst, (iv) Synthesis of ammonia from nitrogen and hydrogen, (v) Enrichment of ammonia containing catalyst, (vi) Decomposition of ammonia in an ammonia cracker, (vii) Final enrichment of ammonia, (viii) Heavy water Production and (ix) Heavy water upgradation.

The auxiliary units include amide catalyst preparation section, natural gas handling, effluent water circulation and gas vent system, fire water system while the utilities include cooling water, ammonia refrigeration section, nitrogen generation and instrument air.

After removing impurities, the gas is cooled to -25°C and sent to the deuterium extraction tower. The deuterium-laden ammonia is further enriched and is sent to the catalyst removal unit for preparing the liquid ammonia for cracking. The deuterium enriched ammonia containing catalyst is heated after reducing the pressure to 25 kg/cm^2 and the liquid ammonia containing less than 1 ppm K^+ is sent to the ammonia cracker operating at 130 kg/cm^2 pressure.

Liquid ammonia is cracked into the components in a fired furnace having high nickel alloy tubes filled with special grade iron based catalyst which is resistive to nitration on exposure to high ammonia concentration. The heat requirement for the cracking of ammonia is supplied by burning naphtha/natural gas.

In order to achieve a closed loop for the system with respect to ammonia, generation of ammonia is required which will be matching to the amount cracked. The ammonia is added to the extraction tower. The feed gas together with the gas coming out of the enrichment tower is sent to the extraction tower which in turn is sent to ammonia synthesis unit. The ammonia synthesis unit comprises mainly of ammonia converter, heat recovery unit and cooling system for condensing the ammonia synthesized. As the ammonia requirement for the process is about 20% of the syngas sent from the extraction tower to the synthesis unit, the same can be generated through a once through loop converter. The ammonia converter loop in a typical ammonia plant is operated in a recirculating mode in order to convert the syngas produced in the generation section completely. While the cracking process is endothermic, the ammonia synthesis process is exothermic. The heat recovery is done by generation of steam, which find utility for various heating requirements. A small quantity of enriched ammonia and syngas is withdrawn from the enrichment section and further contacted for final concentration. The unit is almost same as that of the first enrichment section except for the small size. The synthesis gas enriched to 50 to 60% deuterium in the unit is burned with air to produce off-grade heavy water, which is further distilled to nuclear purity.

The process employs ejector trays for efficient liquid-gas contacting. The gas is sent through a number of nozzles and the ejector action of the high-speed gas draw the liquid ammonia containing amide catalyst into a reaction chamber. Liquid is

dispersed as fine droplets and the enhanced area improves the total exchange. At the end of the reaction chamber, the liquid is separated and added to the liquid pool and the gas depleted in deuterium enters the stage above. The high energy requirement for the gas liquid contactor is reflected in the high pressure drop in the ejector stage and necessitates the liquid to be pumped to the stage below. Thus, a typical exchange tower has a number of ejector trays and each have two numbers of canned motor pumps.

Operation of the plant with various pressure and temperature levels demand complex control. Thus extensive instrumentation is one of the basic features of the plant. Though the earlier plants were having conventional instrumentation, the newer plants have state of the art instrumentation with distributed digital control system.

Changes in the Ammonia Plant and Effects on HWP

Technology of ammonia production world over has undergone tremendous changes and the operation pressures have drastically fallen. It is not commercially attractive to operate monothermal plants connected to ammonia plants operating at lower pressures. HWB has embarked on process development for operation of the heavy water plants independent of ammonia plants. A process for developing water-ammonia exchange process for deuterium transfer is being developed presently. In this process, deuterium from water will be transferred to ammonia and the ammonia will be processed further for enrichment of deuterium in the monothermal ammonia-hydrogen exchange route.

Heavy Water Production by NH_3 – H_2 Exchange Process - Experience and Limitations of Bi-thermal Route



Shri P.R. Mohanty obtained his B.Sc. (Engg) in Chemical Engineering in 1976 from REC, Rourkela and graduated from BARC Training School in 20th batch during 1976-77 standing first amongst the Chemical Engineers. He joined Heavy Water Plant, Talcher and at present is the Production Manager of the plant. He has about 20 years experience in the field of commissioning, operation, performance studies and trouble shooting at HWP, Talcher. Since last four years he is closely associated with development of technology and production of Organophosphorus Solvents like D2EHPA and TBP.

Introduction

After the first successful separation of Deuterium by fractional evaporation of hydrogen in 1932 by Urey, Brickwedde and Murphy [1], many methods were explored for production of heavy water, but a few could only be adopted on industrial scale. Among them, Chemical exchange process has become the forerunner in the field. Owing to extremely low natural abundance ratio of deuterium to hydrogen and the requirement of high purity for nuclear grade heavy water, provision of hundreds of individual separative elements in series becomes necessary in multi contact operation, apart from the need to process very large quantity of the dilute feed. A reflux to enable continuous counter current flows is provided in two configurations; the mono-thermal and bi-thermal process.

In the mono-thermal process, the liquid feed to cold exchange tower flows down counter current to the gas, where deuterium is transferred from gas to the liquid and hence the liquid gets successively enriched. At the bottom of cold exchange tower, the liquid is completely converted to gas and thus provides the necessary reflux. The manner of providing such reflux is called chemical refluxing. The bi-thermal scheme depends on the fact that the equilibrium constant of isotope exchange reaction is

a function of temperature and in general decreases with increase in temperature[2]. While the cold enrichment column performs similar duty as in mono-thermal case, the reflux is provided by a hot column instead of the phase converter of mono-thermal scheme. Thus this refluxing is referred to as thermal refluxing.

To effect the deuterium exchange reaction, the systems adopted on industrial scale are $\text{H}_2\text{S} - \text{H}_2\text{O}$ and $\text{NH}_3 - \text{H}_2$ apart from $\text{H}_2\text{O} - \text{H}_2$ [3]. The $\text{H}_2\text{S} - \text{H}_2\text{O}$ exchange process in bi-thermal configuration occupies the center stage of heavy water production meeting over 90% of global requirement. The $\text{NH}_3 - \text{H}_2$ exchange has, however, evolved in both mono-thermal and bi-thermal configuration.

An industrial scale plant based on bi-thermal $\text{NH}_3 - \text{H}_2$ exchange process developed by Friedrich Uhde GmbH was set up by the Department of Atomic Energy at Talcher in the State of Orissa. The plant was integrated with the NH_3 plant of Fertilizer Corporation of India Ltd. to meet its requirement of feed hydrogen, utilities etc. The plant was commissioned during mid eighties and was in operation till mid nineties after which the operation was suspended due to unsatisfactory operation of the fertilizer plant and consequent limitation of feed and utilities.

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Before discussing various limitations of the process identified during the course of operation of the plant and experimental studies undertaken in that regard, it is felt appropriate to briefly discuss general characteristics of the process and the pilot plant studies carried out for process development.

General Characteristics of Bi-thermal NH₃-H₂ Exchange Process

Equilibrium Constant

The isotopic exchange between NH₃ and H₂ in its general form involves seven isotopic species, viz. NH₃, NH₂D, NHD₂, ND₃, H₂, HD and D₂ and twelve different reactions are possible. The most predominant reaction in the low concentration range encountered in the first stage of a cascade is given as :



The equilibrium constant is related to temperature by the well-known equation

$$\delta (\ln K_1) / \delta (T) = \Delta H^\circ / RT^2 \quad (2)$$

with the symbols having their usual meaning. The equilibrium constant 'K₁' increases with decrease of temperature.

Jacob Bigeleisen [4] has given equation (3) for the equilibrium constant K₁ in the temperature range of 200 – 500K.

$$K_1 = A e^{B/T} \quad (3)$$

Where, A = 0.955, B = 512, T = Temperature in K.

The reaction (1) is extremely slow and hence requires a catalyst to attain a practical rate. It has been the general observation that the exchange of deuterium between hydrogen and any hydrogen bearing solvent (like NH₃) is usually catalyzed by the anion of the solvent (NH₂⁻) [5]. Alkali metal amide like KNH₂ has been found to be most suitable for use as homogeneous catalyst in liquid NH₃. The exchange reaction in this case can be described as :



The equilibrium constant K₂ for this reaction is given as [5]

$$\text{Log}_{10} K_2 = -0.0667 + 237/T \quad (5)$$

Where T is temperature in K

Separation Factor

The more commonly used term, separation factor 'α', defined as the abundance ratio of the desired species in the two phases and related to the equilibrium constant K₂ by the ratio of replaceable hydrogen atoms in hydrogen and ammonia molecule is given as

$$\alpha = 2/3 K_2 \quad (6)$$

Recovery

The theoretical recovery of deuterium (R) in a bi-thermal hot-cold pair is given as

$$R = 1 - (\alpha_h / \alpha_c) \quad (7)$$

Where α_c & α_h are separation factors at cold and hot temperatures respectively. The ratio (α_c/α_h) becomes effective separation factor α_{effective} for the bi-thermal process. Thus, with a pair of hot and cold columns the maximum recovery can be 77% while operating between the freezing point and critical temperature of NH₃. With the practical limitation of the lower value of cold tower temperature and upper limit for hot tower temperature due to economic reasons, the maximum achievable recovery does not exceed 45%, which is very low. In order to increase recovery to a level so as to make the process economical, a stripping system consisting of a pair of hot and cold columns is combined with the enrichment system.

Exchange Rate

On account of the low solubility of hydrogen in liquid ammonia and the consequent small liquid phase driving force, the rates of HD absorption per unit surface area of liquid ammonia, even when enhanced by a rapid exchange reaction are low. This poses a serious challenge for the practical gas-liquid contactor. Higher rates of HD absorption per unit area can be achieved by higher hydrogen pressure, improved chemical kinetics, tower volume etc.

Higher Hydrogen Pressure

Liquid phase driving force increases with increase of hydrogen partial pressure. The upper

limit of pressure is, however, decided by engineering considerations and the overall economics.

Improved Chemical Kinetics

Study of catalytic activities [5] of alkali amides for isotopic exchange between molecular hydrogen and liquid ammonia has established that the activity is only due to the free NH_2^- ions present and the reaction is first order with respect to catalyst concentration. The general nature of variation of rate constant with catalyst concentration $[\text{KNH}_2]$ at cold tower temperature is shown in Fig. 1.

The rate constant rises rapidly at lower catalyst concentration and thereafter flattens out due to solvation of the NH_2^- ions, thereby limiting the concentration of free NH_2^- ions responsible for the catalytic activity. The concentration of the catalyst is, therefore, decided on the above basis to achieve highest rate at minimum catalyst inventory.

Improved Liquid Phase Mass Transfer Coefficient

In the case of bi-thermal process using sieve plate column, the exchange rate is primarily controlled by physical absorption of HD which is a diffusion-controlled process. Under such a situation, one of the ways is to increase the interfacial area per unit contactor volume by reducing the perforation size in the sieve tray and incorporating other features (normally proprietary in nature) to improve turbulence and tray hydraulics.

The overall exchange rate is also strongly influenced by the temperature since increase in temperature not only improves the kinetics of exchange reaction but also improves the rate-controlling step, i.e., liquid phase driving force (due to increase in solubility of hydrogen in liquid ammonia with rise in temperature).

The general nature of empirical relations of over-all exchange rate with pressure and temperature for the hot and cold columns are

$$(K)_{\text{cold}} = A_1 P \{B_1 + C_1 (0.1T + D_1)^m\} \quad (8)$$

$$(K)_{\text{hot}} = A_2 P \{B_2 + C_2 (0.1T + D_2)^n\} \quad (9)$$

Where "K" is overall exchange rate in K.mol/hr.m^3 of contactor volume, P =Pressure in atm., T is

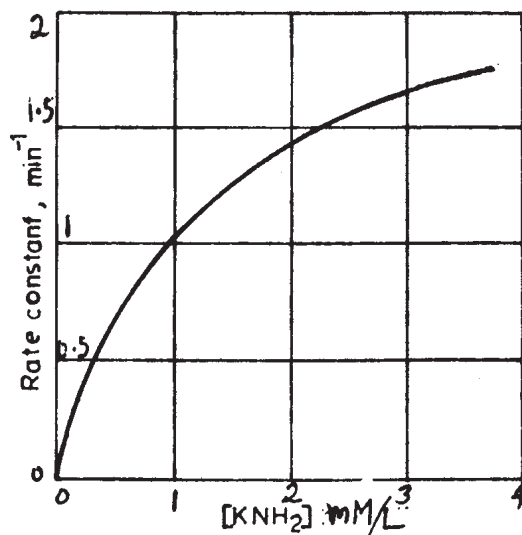


Fig. 1 Variation of reaction rate with KNH_2 concentration

temperature in K and A,B,C,D, m and n are empirical constants applicable to the specific tray geometry hydraulic characteristics.

Tower Volume

The tower volume for a given enrichment duty is given as [5].

$$V = G R T N / P K_G a \quad (10)$$

Where V is the tower volume, G is gas flow, R is gas constant, T is temperature in K, N is number of theoretical stages, P is pressure, K_G is over all mass transfer coefficient and 'a' is interfacial area per unit volume. Compared to mono-thermal process N is larger for the bi-thermal process owing to its operation closer to the equilibrium line and 'a' is smaller by about an order of magnitude. Primarily on account of these factors, the tower volume in bi-thermal case is 4 – 5 times larger as compared to mono-thermal case.

Lower Energy Consumption

The energy consumption in a chemical exchange process is quite a complex function of several interdependent parameters like the separation factors, pressure and temperatures, manner of providing reflux - chemical or thermal and

flow rates. In spite of larger gas flows and tower volumes as well as elaborate heat exchange loops for optimum heat recovery between hot and cold streams, the energy consumption for bi-thermal process is about half of mono-thermal process[6]. This offers a distinct advantage for the bi-thermal process over the mono-thermal.

Pilot Plant Studies

Pilot plant studies were carried out [7] in Germany to establish exchange rate as function of pressure, temperature and catalyst concentration, vapour pressure data of NH_3 in N_2/H_2 at increased pressure and temperature range of interest, equilibrium constant for the isotope exchange reaction, effect of homogeneous and heterogeneous additives on reaction rates, reaction of oxygen bearing impurities with KNH_2 and development of computer programme for process optimization and analytical methods for KNH_2 and NH_2D . Further studies focused on design of complete enrichment cascade, measurement of enrichment factors in case of departure from optimum operation, long duration

tests and gas purification test. Based on these studies design of industrial scale plant was made.

For a commercial Heavy Water Plant to be integrated with an ammonia Plant of 1000 MT per day capacity, the gas throughput would be of the order of 1,00,000 to 1,20,000 NM^3/h corresponding to annual capacity of 60-65 MT of D_2O . Test results with a larger pilot plant were reported to have confirmed the earlier studies and indicated remarkable increase of exchange efficiency up to 40%. With the extended technical knowhow M/s Friedrich Uhde GmbH designed a production plant, which was set up at Talcher in Orissa by the Department of Atomic Energy.

Description of Plant

The plant as shown on the simplified flow diagram (Fig. 2) consists of five essential sections, the gas purification section with transfer columns, the first stage with stripping system, the second and third stages and lastly, the final concentration section comprising the $\text{NH}_3\text{-H}_2\text{O}$ exchange and the water distillation section. The plant is integrated with a 900

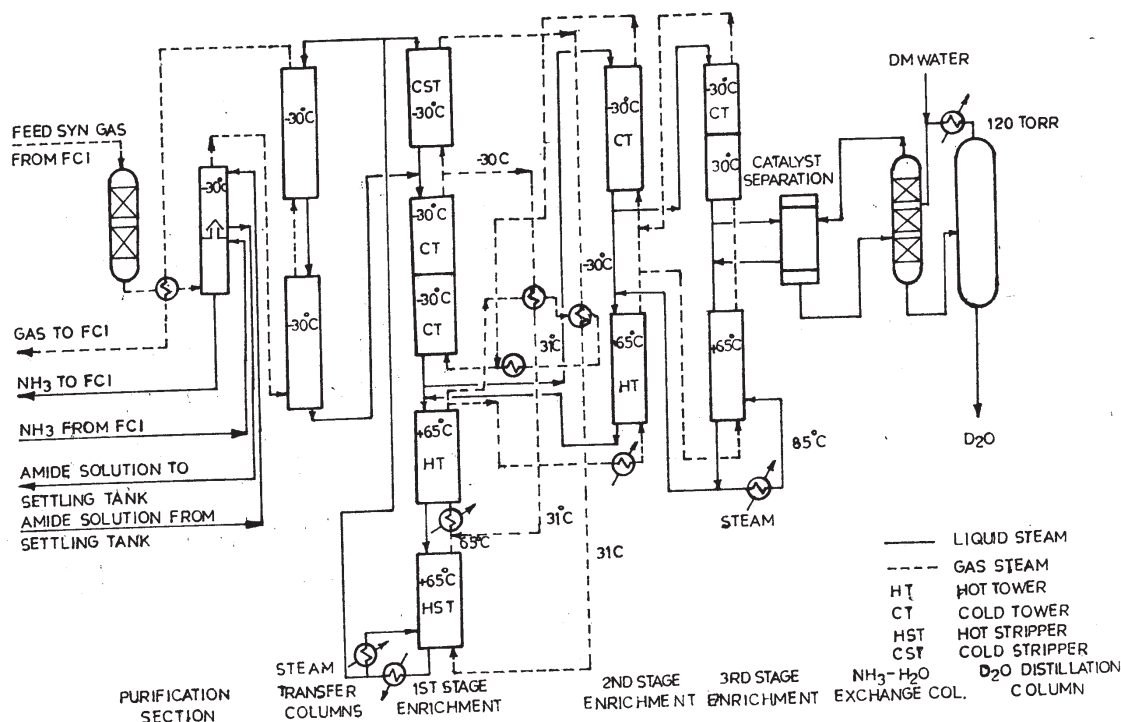


Fig. 2 Schematic process flow diagram of HWP Talcher

TPD ammonia plant of FCIL for supply of hydrogen feed, liquid NH_3 and other utility streams. An important plant section not shown on the flow diagrams is the refrigeration unit. The refrigeration compressor with two different temperature levels is driven by a steam turbine of the extraction condensing type. Back pressure steam is used for process heating and saturating the gas.

Gas Purification and Transfer Section

The synthesis gas from the NH_3 plant passes through a gas purification section in which all oxygen-bearing compounds such as H_2O , CO_2 , CO and O_2 and traces of oil are removed as these impurities react with potassium amide, forming compounds insoluble in liquid ammonia which clog the sieve trays. Purification is achieved by passing the gas successively through active carbon bed, deoxo catalyst, cold ammonia wash section and potassium amide scrubber [8]. The purification and transfer sections are operated in conjunction with the ammonia plant at 220 atm. pressure, whereas the first, second and third enrichment stages are independent of ammonia plant and operate at 300 atm. pressure. The purified gas passes through the transfer columns operating at -30°C where the deuterium of the gas is transferred to the counter current ammonia containing the catalyst KNH_2 and the depleted syngas is returned to the ammonia synthesis unit. In washing trays at the top of the transfer column, entrained potassium amide is removed. The enriched ammonia leaving the bottom of the transfer column is pressurized to the pressure level of first stage and fed there for further enrichment.

First Stage and Stripping Section

The first stage consists of the bi-thermal section proper and the stripping system operating at temperature levels of -30°C and 65°C for the cold and hot columns/stripper. The operation of the individual sections of the first stage could be best explained with the aid of the McCabe-Thiele diagram given in Fig 3.

Here, $N(A)$ is the concentration of the liquid ammonia fed from the bottom of the transfer column to the top of the cold column of the enrichment system. In the cold column, deuterium is transferred

from the gas to the liquid (from A to B). At the bottom of the cold column, a part of deuterium-bearing ammonia is removed and transferred to the next stage and a corresponding stream is returned with a lower deuterium concentration. The concentration changes from $N(B)$ to $N(C)$ and operating point shifts to 'C'. We then follow the working line of the hot column CD as far as to the bottom of the hot column. Here the split gas stream joins which means a change in the slope of the working line for the stripping column (DE). In the hot stripping column deuterium continues to be transferred to the gas and the lowest deuterium concentration $N(E)$ is finally reached at the bottom of the hot stripping column. Prior to entering the cold stripping column, a part of the ammonia is removed and fed to the top of the transfer column. This alters the slope of the working line again and in the cold stripping column we come back to the feeding point along the line EA. This diagram also shows that the slope of the working line is limited by the slope of the two equilibrium lines at the temperature of hot and cold column. In the first stage there are two

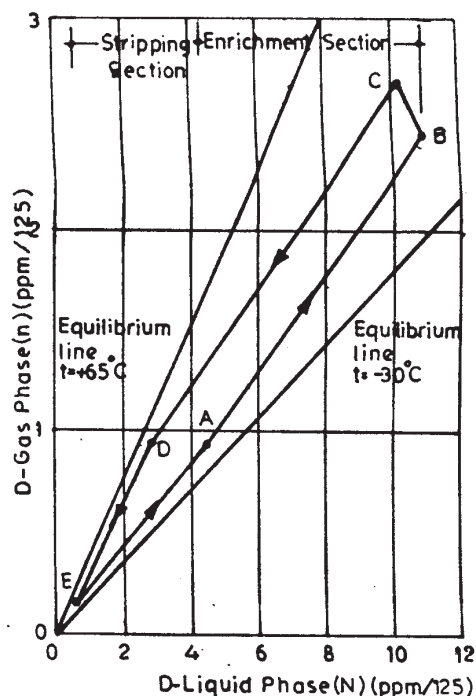


Fig. 3 McCabe thiele diagram for 1st stage

superimposed gas cycles to provide different slopes of operating lines for the enrichment column pair and stripping column pair. However, only one circulating compressor is sufficient as the different pressure drops in both cycles can be used for controlling the gas rates. The counter current liquid circulation is maintained with the help of individual pumps.

As the entire gas and liquid streams are in close circulation between hot and cold columns and vice-versa, the heat recovery by optimum heat exchanger arrangement is of paramount importance in order to reduce energy consumption. The general arrangement of heat exchangers is shown on an enthalpy – temperature plot in Fig.4.

Second and Third Stage

The arrangement of the second and third stage in respect of the gas/liquid counter flows is similar to the first stage except for the strippers, which are provided in first stage only. The heat exchange arrangement in second and third stages hot columns is similar to first stage hot column and hot stripper respectively. Due to smaller size and flow rates in third stage, the gas cooling is effected by direct contact cooling at bottom of cold column.

In each stage the deuterium content is increased by a factor of around 9. Liquid which has been enriched to about 17% deuterium is then taken out between the hot and cold column of the third and last stage and sent to final concentration section after removal of dissolved KNH_2 .

Final Concentration Section

The final concentration section comprises of $\text{NH}_3\text{-H}_2\text{O}$ exchange followed by vacuum distillation of water. Enriched ammonia from third stage after removal of catalyst is fed into the $\text{NH}_3\text{-H}_2\text{O}$ exchange column, where it transfers its deuterium to H_2O . This column is arranged in three sections, middle being for exchange. The lower section is used for stripping ammonia from water and upper section for water from ammonia. Enriched water from $\text{NH}_3\text{-H}_2\text{O}$ exchange is taken to vacuum distillation column for production of nuclear grade heavy water.

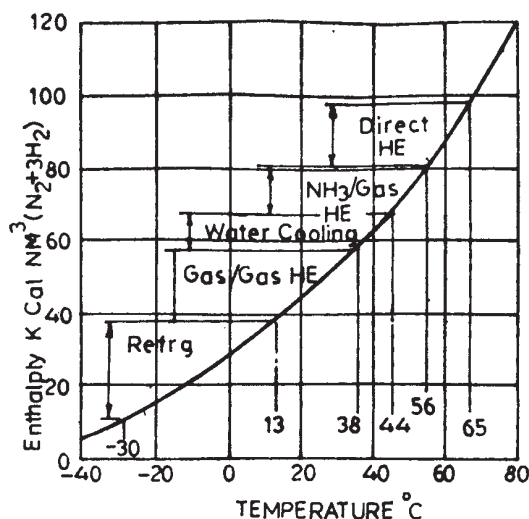


Fig. 4 Enthalpy - temperature diagram for syn. gas

Operating Experience

Formation of Solid Deposits during Heating of Amide Solution

Experience [9] with heating of potassium amide solution in 1st and 3rd stages has shown that beyond a temperature of 65°C, particularly with steam temperature above 100°C, severe fouling of heat transfer surface occurs within a short duration. In order to understand this phenomenon, an experimental set up was installed in the plant to simulate these conditions using an autoclave along with heaters in gas and liquid loop, filters and necessary instrumentation. Observations from the plant were confirmed in this experimental set up. Chemical analysis of the deposits on heat exchanger surface indicated high percentage of KNH_2 along with some KOH (possibly due to exposure of sample to air), iron and other reactive compounds of potassium which violently react with water. It was further revealed that the rate of fouling sharply increases beyond amide temperature of 70°C and heating steam temperature of 100°C and hence its severity could be reduced by limiting these temperatures. While the heating of gas streams at inlet to hot columns of 1st and 2nd stages did not pose

much problem in the heaters as such, it led to another serious limitation in the exchange columns, which will be discussed in the next section.

Formation of Solid Deposits while Contacting Unsaturated Gas with Potassium Amide Solution

While contacting unsaturated gas with hot amide solution, formation of solid particles has been noticed. They tend to accumulate in the column and clog the fine holes of the sieve trays, increase the ΔP across the column and thereby pose serious limitation on gas handling capacity of the trays. From the operating experience, it is observed that severity of this problem is strongly influenced by the extent of unsaturation, dry bulb temperature of the gas, temperature of the liquid. The solid deposits so formed were found to contain mainly KNH_2 with traces of other compounds of potassium, but were almost insoluble in liquid ammonia. Further, no deposition was found to occur when saturated gas is contacted with amide solution. Observations however point to sudden loss of ammonia from the solution in the process of humidification leading to formation of solid particles which were not dissolving in liquid ammonia.

Higher Foam Height on Exchange Trays and limitation on Gas throughput in Columns

Exchange columns are provided with proprietary sieve trays of very small hole diameter (1.2 mm) for effecting counter current gas liquid contacting. The tray spacings are maintained between 250 mm to 300 mm to accommodate the desired numbers within reasonable column height. Experience gained during operation of these columns indicate that notwithstanding the limitations described above, gas throughput beyond 65-70% of design resulted in excessive liquid carryover, specially in hot section of the plant. However, operation of the columns with pure ammonia and gas at design temperature, pressure and flow rates has been found to be quite stable and satisfactory without any liquid carry over or excessive pressure drop in any column. The proprietary trays, however, had the provision to adjust the heights of outlet weir on the trays, in case need is felt. Accordingly, based on the observations of foam height studies, the weir heights were

reduced and about 10% improvement in gas throughput could be achieved without sacrificing exchange rate.

Differential Catalyst Concentration in Enrichment Stages

Due to the arrangement of heat exchangers in the gas circuit from hot column to cold column and the provision for separating the condensed ammonia from the gas, a substantial quantity of condensed ammonia directly enters the sump of cold columns of first and second stages, thus diluting the catalyst concentration there. Since the liquid feed to second and third stage cold columns are drawn from these sumps respectively, the catalyst concentration reduces progressively from first to third stage. As a result of this, the catalyst concentration in third stage hot column attains a value of $1/4^{\text{th}}$ of first stage cold column. This poses certain limitation in the exchange rate, especially in third stage. It can be suitably overcome by re-engineering of the system.

Tray Efficiency

The over all tray efficiency for the exchange process is a function of hydraulic parameters, geometric parameters, physical property parameters and kinetic parameters. Due to the combined effect of limitations of temperature, gas flows, tray hydraulics and catalyst concentration (in third stage), the observed tray efficiencies were far from design intent, specially in the hot section. However, once these limitations are overcome, the tray efficiency is expected to improve.

Large Plant Volume

In view of the general characteristics of the bi-thermal process, the plant volume is quite high (app. 700 M^3). Such high volume implies large inventory of potassium amide solution and synthesis gas. Accordingly, the start up time for such a cascade for hydraulic stabilization and building up necessary deuterium profile is quite high, in the order of 5-6 days. It, therefore, becomes very essential to avoid any kind of interruption, either due to power or feed or utilities. Such interruptions pose a serious constraint on overall productivity of the plant. Other operational requirements like water washing of the plant to remove solid deposits formed and

subsequent drying of the system prior to charging catalyst solution takes a long duration of time in spite of various engineering controls and thus reduces available time for production.

Overall impact on Plant Performance

On account of the various limitations and their interrelated and cumulative effects, the enrichment ability of the cascade has been greatly impaired making the plant performance far from satisfactory.

Conclusion

While the remedial measures for some of the limitations have already been identified, it is expected that the available operating data, suitably augmented with additional experimental and process modeling inputs can be very helpful in arriving at possible solutions for rest of the limitations and then the inherent benefit of low energy consumption and simplicity of operation of the bi-thermal $\text{NH}_3\text{-H}_2$ exchange process can be derived.

References

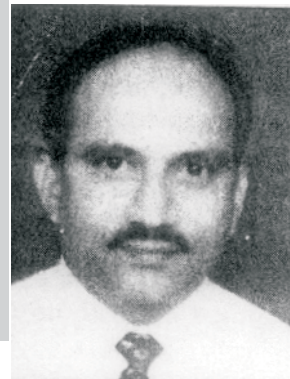
1. H.C.Urey, F.G. Brickwedde, G.M.Murphy, Phys. Rev, 39 (1932) 164.
2. D.G. Pradhan, in this issue.
3. M.Benedict, T.H.Pigford, "Nuclear Chemical Engineering", McGraw Hill Book Co Inc, New York.
4. Jacob Bigeleisen, "Concentration of D by chemical exchange process – equilibrium in exchange of D between H_2 and NH_3 ", Report BNL-118 (1951).
5. Robert Delmas, "Isotopic exchange between molecular hydrogen and liquid ammonia catalysed by Alkali Amides", Ph.D Thesis, Report CEA-R3377.
6. H.K.Rae, "Selecting Heavy Water Process", ACS Symposium series, 68 (1978).
7. E.Nitschke, S.Walter, I.P.Grutzenbach and U.Schindewolf, "Investigation on Deuterium exchange in the Ammonia/Hydrogen system in the pilot plant at Gewerkschaft Victor", Report by Friedrich Udhe GmbH.
8. R.Bhattacharya, P.R.Mohanty, B.L.Pandey, "Operating experience of gas purification system of Heavy Water Plant, Talcher", Proceedings of SCOPEX-92, Feb 27,28,1992, BARC, Mumbai.
9. Internal Reports of Heavy Water Board – Unpublished.

Development of H₂S – H₂O Exchange Process Based Heavy Water Technology



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Introduction

The process of heavy water extraction from the naturally occurring deuterium sources like water and natural gas depends principally on the difference in the separative potential between hydrogen and deuterium bearing species. Deuterium was first separated by the fractional evaporation in 1932 by Urey, Brickwedde and Murphy. Over the next few years, number of processes including electrolysis, water distillation and hydrogen distillation were investigated as potential separation methods. However, during World War II in the USA, due to the strategic importance of heavy water, a very large effort was put in to evaluate and develop methods for large scale production of heavy water. Throughout fifties and sixties a number of methods were

considered and investigated in the laboratory and in pilot plants, but only a handful could be converted into feasible technologies. Subsequent to the World War II, major research and development to investigate heavy water processes was carried out in those countries that built prototype Pressurised Heavy Water Reactors (PHWRs) viz. Canada, France, Germany, India, Sweden and United Kingdom. India is pursuing this route for production of large quantities of heavy water.

Around 1950, to meet the need of heavy water requirement in USA, the Girdler-Sulphide Corporation (a subsidiary of Dupont) was assigned the task of developing the H₂S-H₂O exchange process which later came to be known as GS process.

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Plants were later constructed based on this process both in USA and Canada. In India, development of $\text{H}_2\text{S}-\text{H}_2\text{O}$ process was taken up in the late sixties to meet the large requirements of nuclear programme in India.

Development of Process

The production of heavy water is an expansive proposition due to the very low value of natural abundance of deuterium in hydrogen bearing compounds. It ranges from 120 ppm in natural gas to about 150 ppm in water. The reactor grade heavy water is 99.75 mol % D_2O , which means the enrichment of over 7000 times. Therefore, an industrial heavy water plant is required to handle large amount of feed material and also requires a large number of contacting stages. The combination of large feed processing and requirement of a large number of separative elements result in heavy water plants being very large as compared to most of the other chemical plants. The designer has to trade and optimise the plant volume, energy consumption and ease of operation.

The designs of the isotopic separation plants are based on the theory of cascade having a continuous reduction in the boil-up rate along the column. The ideal cascade results in minimum volume of the system with number of stages. At the other extreme, in conventional distillation process, the boil-up rate is kept constant throughout the column and the entire operation takes place in a single stage. The squared-off cascade is employed in isotopic separative plants, where the change in the boil-up rate is affected only after some portion, where constant boil-up has taken place. This arrangement of the cascade makes the system complex compared to conventional system with single stage operation, but results in a considerable saving in terms of capital and energy cost.

The relative tower volumes decrease by 30% for a two stage cascade and further 10% decrease is achieved for a three stage cascade. A single stage Heavy Water Plant would contain an inventory equal to annual capacity while in the case of the two stage cascade, the inventory would be reduced by an order of 8 and for three stage cascade, it would be further reduced by a factor of two. Addition of further stages does not give the benefits in proportion to the

complexities arising due to increased staging. First stage handles a very large gas and liquid flow rates, and therefore requires tall columns in parallel. Thus, an optimally designed Heavy Water Plant consists of parallel series towers which makes the topology of the plant complex.

Chemical Exchange

The separation between two isotopes is achieved through a chemical reaction of two components, each component being predominant in one of the phases, having the natural isotopic composition. The isotopic composition in the two chemicals differ slightly from one another under equilibrium conditions. The simple process separation factor is the ratio of equilibrium constant to the value the equilibrium concentration would have if there were equi-partition. The selection of the two chemicals for isotopic exchange reactions would be a compromise on the separation factor on one hand and the rate of reaction on the other. For separation of hydrogen and deuterium, water - hydrogen exchange reaction has a large separation factor but a poor rate while water - hydrogen sulphide exchange reaction has a low separation factor but a rapid rate.

In $\text{H}_2\text{S}-\text{H}_2\text{O}$ isotopic exchange process, the reflux is provided in a way completely different than the distillation process. The hot tower of bithermal process is analogous to an imperfect reboiler and, provides gas to the cold tower at a considerably lower deuterium concentration than is achieved by a phase converter in the monothermal process. As a consequence, the bithermal process requires much longer cold tower making the process more complex. The counter current H_2S gas and water flows, if appropriately controlled, cause a net transport of deuterium up the hot section and down the cold section to provide enriched water and enriched gas at the centre of the column. The enriched stream at this point is withdrawn as feed for the subsequent section causing a net extraction of deuterium from the feed liquid.

Development of $\text{H}_2\text{S}-\text{H}_2\text{O}$ technology in India went through various stages viz. Process Development, Pilot Plant Studies, selection of material of construction, Finalisation of Flow Sheet and finally setting up of the plant at commercial

scale. The first plant based on H_2S - H_2O exchange process was set up at Kota. The capacity and the configuration of cascade was decided based on the available industrial infrastructure. Subsequently one more plant of double the capacity of Kota was set up at HWP, Manuguru with a number of the modifications, based on the operational / commissioning experience of HWP, Kota. Today both the plants are running above their design capacity.

System Features

The enrichment ratio for the three stage Heavy Water Plant has been optimised to give overall minimum cascade volume. The flow sheet adopted for our plants has used the combination i.e. the 'D' transport in the 1st and 2nd pair of 1st stage by liquid stream, and from 3rd pair onwards through liquid and gas route. Fig. 1 shows a single pair of cold and hot towers of the first stage with associated waste stripper and the external heat recovery exchangers. Each of the cold and hot towers contains two sections, one in which deuterium exchange takes place, designated as the mass transfer section and the second, in which direct contact heat exchange takes place between the gas and liquid phase, designated as the heat transfer section. The raw water is the feed. It is treated in a process feed water treatment plant where the water is partially demineralised, deaerated and fed to the purge tower.

The purge tower maintains the purity of the circulating H_2S gas. The deuterium transport takes place from gas to liquid in the mass transfer section of the cold tower. At the bottom of the mass transfer section of the cold tower, a direct contact heat transfer section is provided. In this section, the cold liquid from the mass transfer section of the cold tower is allowed to counter contact the hot gas from the mass transfer section of the hot tower, thereby cooling and dehumidifying the gas before entering the mass transfer section of the cold tower. The hot liquid from cold tower is fed to mass transfer section of hot tower where deuterium transport takes place from liquid to gas. Thus the bottom of mass transfer section of hot tower contains liquid depleted in deuterium to that of the feed. To extract maximum heat from the gas, a recirculation flow is maintained in the heat transfer section. The recirculation flow rate is controlled to maximize the heat recovery from

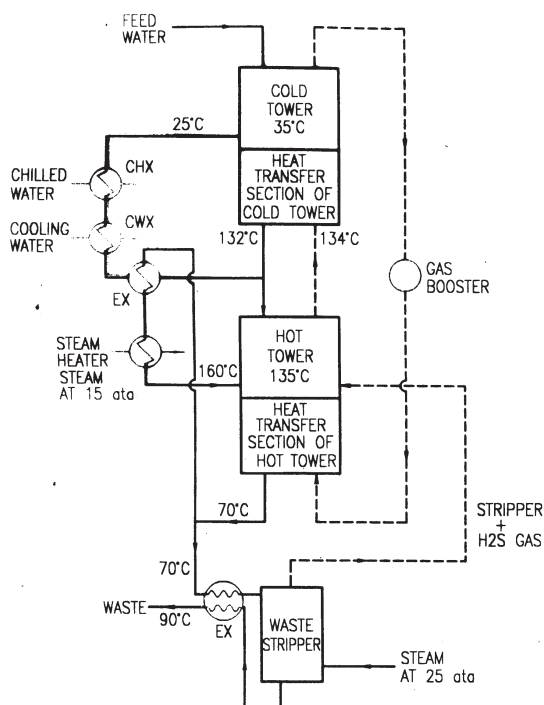


Fig. 1 A single pair of cold-hot towers

the gas to the liquid both in the direct contact heat recovery as well as in the external heat recovery system. Heat is also added through the stripped stream from the waste stripper. The waste stripper is provided to strip the hot tower bottom liquid of its dissolved H_2S before discharging it as effluent. Steam is used to strip the liquid and the steam along with the stripped gas is fed back to the heat transfer section of the hot tower. The gas thus remains in a closed loop with a compressor provided to overcome the pressure drop in the loop.

Design and Operating Variables

The complexity also increases due to number of design and operational variables which have impact on the deuterium extraction system volume and energy consumption for the cascade. The key parameters are briefly described in the following.

The Temperatures and Pressures of Operation of the Cold and the Hot Columns

The process recovery is defined as $(K_c - K_h)/K_c$, where K_c and K_h are the equilibrium constants of the isotopic exchange reaction occurring at the cold and at the hot temperatures respectively. For maximum extraction of the deuterium, the cold tower and the hot tower should be operated at lowest and highest possible temperatures. The temperatures of the cold tower and hot tower were fixed as 35°C and 135°C respectively. The lowest possible operating temperature at a given pressure gets fixed as the ice like substance formation takes place below which the system is inoperable. At higher temperatures which is governed by steam economy, the vapour pressure of water increases exponentially with rise in temperature at the operating pressure, leading to excess energy consumption. Thus, the choice of operating pressure, and the temperatures are inter related. The system pressure has been fixed at 20 kg/cm²(g). Theoretically maximum possible value of deuterium recovery is 19.6%. By this approach 99.9% of the theoretical value is achieved.

Number of Trays in Each Section

The number of trays provided is dictated by the desired enrichment in each of the stages. Typically number of mass transfer trays is around 60 in a stage in each column.

Liquid to Gas Ratios

The cascade with coupled hot-cold columns, with limitations in the choice of the temperatures of operation, results in a very narrow operating regime between the equilibrium lines for cold and hot towers.

Recirculation Rates in the Heat Transfer Section

The direct contact heat transfer sections in the cold and the hot columns are provided with liquid recirculation, the quantity of which is fixed to extract maximum heat while maintaining minimum ΔT between gas and liquid streams. The gas flow rates getting fixed from capacity considerations, the recirculation rates are thus fixed to maximise the heat recovery.

Heat Exchanger Net-Work Design

The external heat recovery network consists of process to process heat recovery exchangers, cooling water, chilled water exchangers and the steam heaters. The network design is fixed based on the optimised plant pinch temperature difference of 15°C. The hot utility levels have been optimised with reference to the extraction temperature in the case of steam and the cold utility levels have optimised w.r.t total cost minimisation.

Purging and Stripping Section

The purity of recirculating gas is maintained by taking a small bleed from recirculating gas from top of the cold tower and fed to purge tower, where it comes in contact with feed liquid. The H₂S gets dissolved in feed and the inerts are vented. Similarly the H₂S is stripped off from the effluent in the waste stripper and sent back to system.

Important parameters for the optimised cascade are:

- (i) The tower volume is 80 m³, heat exchange area is 140 m², steam consumption is 11000 tonnes and the power consumption is 1400 MWhr per tonne of heavy water for a typical 100 tonnes / annum capacity plant.
- (ii) The hydrogen sulphide gas hold up of the plant is approximately 200 tonnes and therefore requires elaborate safety systems. Important engineered safety systems are : (a) Design of the plant in a modular fashion with quick isolation arrangement with provision of gas dumping safely through flare stack, (b) Close vent and drain systems, (c) Selection of suitable materials of construction with elaborate quality surveillance, (d) Fail-safe instrumentation system along with voting and stand-by logic in crucial areas, (e) Stand-by flare system, (f) Effluent treatment plant, (g) Extensive gas detection and alarm systems and (h) Breathing air system and sheltering system.
- (iii) The design of heat cycle for Captive Power Plant is based on extraction-condensing type of turbines with an intermediate steam generating facility to generate the secondary process steam. This is to avoid the sulphide

contamination of the boiler condensate under single failure condition of the equipment.

- (iv) Large size utility systems like demineralisation plant with vacuum deaeration facility and a chiller plant capable of generating 13,000 tonnes of refrigeration.
- (v) A captive H₂S generation plant.

Development of Technology

The process package contains design basis, internal mass and flow diagrams, energy balances, sizing and design of the equipment. The high efficiency trays of different configurations were used in the same column to handle varying flow rates. The X-flow trays with inlet active area promoters were used for mass transfer application while the multi-downcomer trays were used for heat transfer application, where the liquid rates are three times higher compared to that of rates in mass transfer section.

Material of Construction

H₂S gas is not only toxic and flammable but is highly corrosive in the presence of water. The results of the R&D efforts on a test loop, in addition to available guidelines, were utilised for selection and development of specifications for the material. These then are translated into the actual fabrication by close interaction with the industry. The fabrication procedures were also established based on the mock up tests.

Safety System

The crucial considerations for design of safety system is integrity of the pressure boundaries under varying loads, close vent and drain system to ensure zero discharge at all normal operating conditions, discretisation of the cascade to limit the inventory exposure even under worst conditions. The safety interlock system is provided with sufficient back-up and fail-safe features to take care of different emergency situations. A highly reliable gas monitoring system gives alarms in the control room and field when the gas concentration exceeds 1 ppm. The plant is divided into number of zones based on the H₂S hold up and the wind direction and number of H₂S monitors are strategically located.

Operational Experience

Problems faced at Kota, were generally in auxiliary systems like H₂S generation plant, the effluent disposal unit and the control supply system (UPS). There were also some equipment failures during the pre commissioning activity. All these problems and the cautious approach taken during the commissioning and initial start up due to handling of large inventory of H₂S for the first time resulted in long stabilisation time for Kota. The subsequent plant took less time and could achieve the design production levels in a short time primarily due to expertise gained from the first plant. Some of the areas emphasised in the second plant were :

Reduction in Equilibrium Time and Fast start up

If the plant is designed as single stage, it would take approximately one year to achieve the first drop of heavy water which gets reduced to approximately one month by designing the cascade in three stages. If one further analyses the equilibrium time distribution over the different stages, the equilibrium time for the third stage comes to approximately 20 days. Having optimised the cascade from other considerations, it was decided to trade the optimisation of the third stage w.r.t steam economy vs the production. This was carried out by making the gas circulation loop independent and thus making possible the third stage operation independent. This has reduced the non- productive time between successive shut downs.

Increased throughput

The production is directly proportional to the feed processing capacity of the system. The uncertainty is always there with the stable operating range of the exchange columns, which fixes the processing capacity. The operational parameters for the exchange columns were analysed and it was established that these columns could be loaded at higher flooding velocities compared to design value. This has resulted in increase in the operating ranges thereby increasing the production by almost 10%.

Changes in the Operating Parameters

Changes in the primary parameters like temperature and pressure have direct effect on the production and/or energy consumption. At HWP,

Kota the quantity of steam available was less compared to design requirement to maintain the required temperature levels. In-house developed dedicated simulator for this process helped in fixing the operating parameters for maximising the production under constrained conditions.

Waste Heat Recovery Systems

Elaborate heat recovery networks are employed to optimise the energy requirement. Almost all types of heat exchange methods like direct heat transfer and indirect heat transfer utilising the various types of the equipment are employed. New generation equipment like plate type exchangers have been employed in utilising the low grade heat economically. Efforts are also being made to generate the refrigeration utilising the low grade heat.

Minimising the Effluents

The schemes of recycling the treated effluents in the plant are aimed to achieve the target of zero discharge. The cooling tower with recirculation provision is used to bring down the temperature of the effluent before discharging. This has helped in reducing the dischargeable effluents leading to less water intake. A plant was set up based on development work to process H₂S contaminated oil to enable to reuse/ dispose the same.

Conclusion

Today the H₂S-H₂O based heavy water production technology is a matured technology in India. All the plants based on this technology are operating close to or above their design capacities with exemplary safety. Having mastered the technology, efforts are now on to reduce the capital as well as operating cost for the future generation plants. Number of R&D activities connected to efficiency improvement in both mass transfer and heat transfer equipment are planned.

Bibliography

1. H.K. Rae, "Selecting Heavy Water Processes", ACS symposium series, Washington, 68 (1978).
2. M. Hammerili, W.H. Stevens and J.P. Butler, "Separation of Hydrogen Isotopes", American Chemical Society symposium series, Washington, 68 (1978) p.110.
3. R.R. Sonde, "Mathematical Modelling and Simulation of Heavy Water Cascade", Ph.D. Thesis, IIT, Mumbai (1996).
4. R.R. Sonde, 1994, "Assimilation of Heavy Water Technology in India", Facets of Nuclear Science and Technology, Published by DAE, 1996, pp 39-53.
5. B. Linhoff, , "Pinch Analysis", Chemical Engineering Progress, (1994) p. 33-57.
6. R.K. Bhargava, "Heavy water - an Indigenous Success Story", The Hindu Survey of Indian Industry, (1996).

Heavy Water Production by Cryogenic Distillation Process Employed in HWP, Nangal



Shri Arjun Singh after completing the 5 years integrated course in B.Sc.(Chemical Engineering) in 1972, joined the 16th batch of BARC Training School. In 1973 he joined the Heavy water Plant (Talcher), a bi-thermal ammonia-hydrogen exchange process plant, where he was actively associated in the project coordination, commissioning, testing and plant operation activities till 1989. Then he joined the Heavy Water Plant (Nangal), a cryogenic distillation plant, as in-charge of the plant carrying responsibility of operation, quality control, safety and coordination with fertilizer officials. At present he is working in the Central Office of HWB.

Introduction

The process employed in Nangal heavy water plant is the liquefaction and distillation of hydrogen. In the hydrogen gas, the deuterium isotope may be present in two different species i.e. HD and D₂ depending upon the isotopic concentration. Separation of such species depends upon their difference in vapor pressures at boiling points. The boiling points of HD and D₂ and H₂ can be known from the vapor pressure (P) and temperatures (T) relations given below:-

$$\text{Log } P_{H_2} = 4.6633 - 44.791 / T + 0.020230 T \quad (1)$$

$$\text{Log } P_{HD} = 5.04964 - 55.2495 / T + 0.01429 T \quad (2)$$

$$\text{Log } P_{D_2} = 4.7459 - 38.5951 / T + 0.02650 T. \quad (3)$$

The ratio of vapor pressure of two different species of hydrogen viz. P_{H_2} / P_{HD} or P_{HD} / P_{D_2} is known as separation factor (α). In the case of hydrogen isotopes, the separation factor at the boiling point is slightly above unity, rendering the separation of hydrogen isotopes an extremely difficult process.

The separation factors for H₂ / HD and HD / D₂ systems at a particular temperature T are given by equations (4) and (5) respectively.

$$\begin{aligned} \text{Log } \alpha_{H_2/HD} &= \text{Log } [H_2] / [HD] = \log P_{H_2} / P_{HD} \\ &= -0.3863 + 10.5204/T + 0.00544 X T. \end{aligned} \quad (4)$$

$$\begin{aligned} \text{Log } \alpha_{HD/D_2} &= \text{Log } [HD] / [D_2] = \log P_{HD} / P_{D_2} \\ &= +0.3037 + 3.3456/T - 0.01171 X T. \end{aligned} \quad (5)$$

There are five distinguishable molecular species of hydrogen and deuterium i.e. para-H₂, ortho-H₂, HD, ortho-D₂ and para-D₂. Vapor pressure of these species varies with temperature as shown in Fig. 1.

The distillation of hydrogen is carried out in the conventional sieve tray columns in three steps.

- Step -1, where the HD concentration is increased up to 2-4% in the hydrogen gas in the Triple Column.
- Step -2, where the HD concentration is further improved up to 98% in the HD-column.
- Step -3, where the HD and D₂ are separated by the distillation in the D₂-column.

Step-1 is performed in three stages of cascade system where the feed gas enters into stage-1 and the rich liquid is fed from stage 1 to stage 2, and from stage 2 to stage 3. The three sections of the distillation columns are stacked one above another, the combination is called the "Triple Column".

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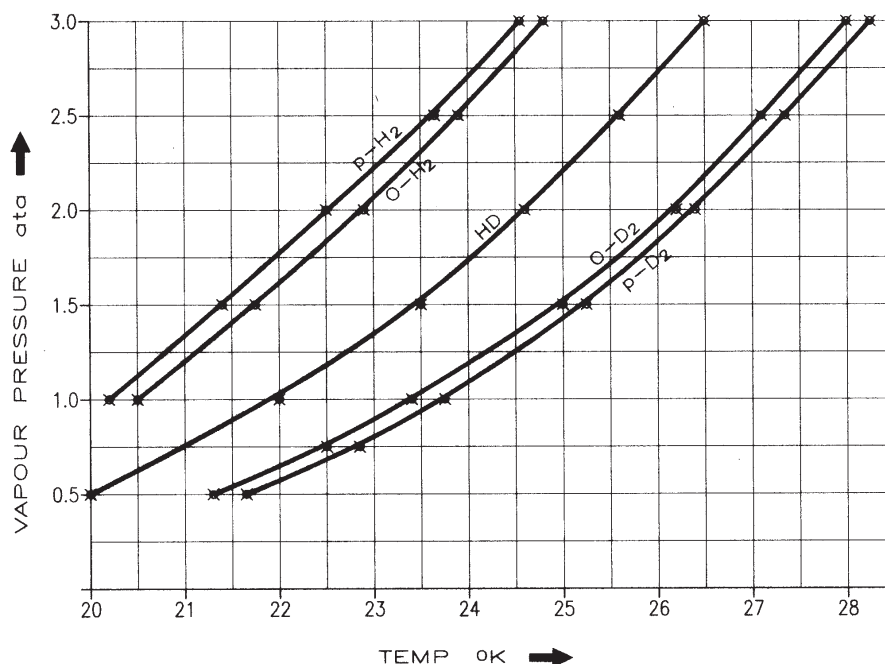


Fig. 1 Vapour pressure curves for H₂, HD, D₂

The first two steps of the isotope separation are to increase the concentration of the HD in hydrogen for which the separation factor is very low (1.749) at the boiling point (BP) of equilibrium hydrogen (20.27 K). It, however, improves at temperatures below the boiling point, as shown in Table 1, but it calls for operation at sub-atmospheric pressures which is not preferred due to possible problems of ingress of atmospheric air.

TABLE 1. Theoretical Separation Factor for H₂ / HD System

Temperature, K	Theoretical Separation Factor
22.5	1.598
20.33	1.75
19.97	1.78
19.33	1.83
19.17	1.85
18.95	1.87
17.48	2.04

Process Descriptions

The Enrichment

About 9000 NM³/h hydrogen gas is obtained from a naphtha reformation plant (a unit of the fertilizer plant) for distillation. After extraction of the deuterium, the depleted hydrogen gas (containing < 5 ppm D) is returned to the ammonia plant for production of fertilizer (Fig. 2)

The feed hydrogen gas (containing 125 ppm D) at a pressure of 4.0 kg/cm² is passed through Deoxo Unit in HWP for removing oxygen, if any, and then through water cooler to achieve lowest possible temperature of hydrogen gas. This gas is then sent to cold box, where it is pre-cooled first in the warm regenerators up to 73 K and then in vacuum liquid N₂ evaporator at 65 K and finally in the cold regenerators to a temperature of 28 K. Ultimately, the liquefaction takes place nearly at 20 K. At this low operating temperature of 20 K, all the known gases except the helium and hydrogen solidify. It is, therefore, essential that all the impurities present in the feed gas be removed to such an extent (less than 1

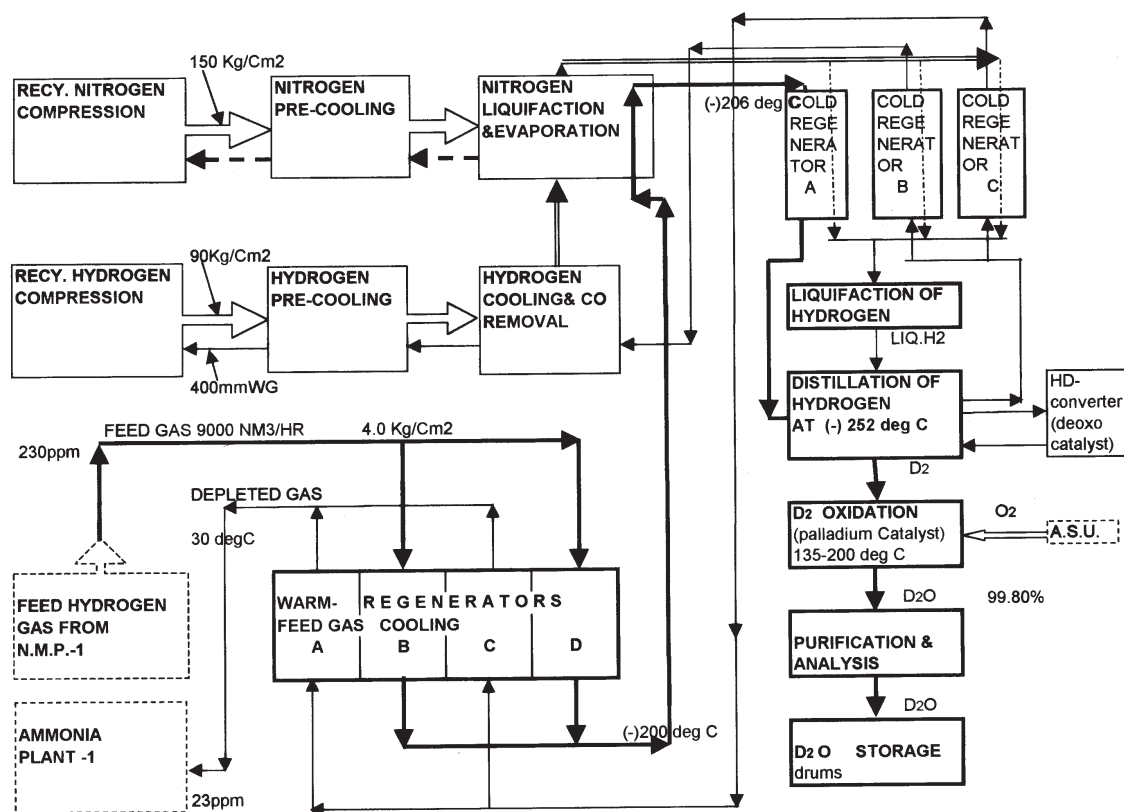


Fig. 2 Block diagram of heavy water plant, cryogenic process

ppm) so that they do not choke the equipment during the liquefaction process. Incidentally, while cooling the feed hydrogen gas, in the warm and cold regenerators, the impurities i.e. CO, CO₂, and CH₄ are eliminated by solidification due to their low partial pressures. The gas after expanding through an expansion valve enters the pressure column operating at 3.5 kg/cm². The enriched liquid from the bottom of pressure column is sent as feed to the medium pressure (MP) column operating at 1.6 kg/cm². Enriched liquid from MP column is sent as feed to low pressure (LP) column operating at 0.7 kg/cm². Liquid from low-pressure column, which contains about 4% HD is sent to HD-column also operating at 0.7 kg/cm². The depleted hydrogen gas from the top of low-pressure column is passed through the cold regenerator/warm regenerators for exchanging cold with the incoming hot gas and then routed to the ammonia plant.

The HD liquid from the bottom of low-pressure column is sent to HD-column, where it is fractionally distilled. The bottom product of HD column contains more than 95% HD. The top product of HD-column, which is a mixture of H₂ and HD, is fed back to the low-pressure column. The HD gas from bottom of HD-column, after passing through the heat exchangers, is compressed to 0.80 kg/cm² and passed through a catalyst bed. The catalyst helps hasten the equilibrium reaction,



to generate a mixture of gases containing 22.5% D₂, 27.5% H₂ and 50% HD. This is an exothermic reaction evolving heat of about 110 cal/mole and is carried out at a reasonable rate in the presence of a catalyst at a temperature of around +30°C. The gas mixture coming out of the catalyst bed is passed

TABLE 2. Boiling Points of Different Species of Hydrogen

Gases →	Normal H ₂ 75% o-H ₂	Equilibrium H ₂ 0.21% o-H ₂	Normal D ₂ 66.67% o-D ₂	Equilibrium D ₂ 97.8% o-D ₂	HD
BP (K)	20.50	20.27	23.57	23.52	22.13

through heat exchangers for pre-cooling and fed to the D₂-column. However, due to small volume of gas to be cooled, this operation does not appreciably alter the total heat balance of the system. In D₂-column, final fractional distillation is carried out and, the bottom of D₂-column, a product containing more than 99.98% D₂ is obtained. The overhead product from this column is fed back to the HD column.

D₂ Oxidation

The D₂ gas produced in the distillation process described above and having isotopic purity of more than 99.98% D, is catalytically oxidized to produce D₂O. The oxidation of deuterium gas is carried out by passing the mixture of deuterium and the oxygen gas in the molar ratio of 1:125 through a platinised catalyst bed. Excess of oxygen is necessary to safeguard against flame burning of D₂ gas at the mixing zone which some times happens during the start up due to the presence of catalyst dust. The catalyst dust activates the auto-ignition of hydrogen even at much below the auto-ignition temperature (650°C). Since the explosive limit of D₂ in oxygen is 5% to 95%, an explosive mixture is formed at the mixing zone. The D₂ oxidation reaction is exothermic and in this case it is observed that for every 1% rise in D₂ concentration in the D₂ / O₂ mixture, there is a rise in catalyst bed temperature of the order of 80°C. The heat of the reaction keeps the catalyst bed temperature in the range of 167-200°C with the oxygen recirculation rate of 135-150 NM³ /h.

The oxygen and D₂ vapor mixture coming out of the catalyst bed is cooled up to 10°C for partial condensation of D₂O, which is then withdrawn from the system at the bottom of the separator. The oxygen gas for the oxidation is drawn from an air separation plant; hence it contains some amount of nitrogen and argon as inert impurities. In order to avoid the build up of inert impurities in the close loop

circulation of oxygen, it is essential to allow certain amount of bleed from the system which causes some loss of D₂O. Such a bleed of gas is preferred from a point in the system where the D₂O concentration is the minimum. The purged gas is passed through a bed of silica gel where D₂O vapor is adsorbed to be recovered later. The quality control of D₂O product is carried out by passing the D₂O through a mixed ion exchange bed and measuring its isotopic purity, conductivity and pH by the on-line analyzers.

Special Features of the Plant

- The triple column and the HD-column are fitted with sieve trays of conventional design whereas the D₂ column is fitted with bubble cap trays.
- Maintaining the low temperature at a level of liquefaction temperature of hydrogen is an essential requirement in this plant. It is achieved in a three-tier refrigeration system comprising of an ammonia cycle, a nitrogen cycle and a hydrogen cycle. The ammonia cycle is used to pre-cool the nitrogen and the hydrogen gases before they are further cooled up to the liquefaction temperatures. In order to take advantage of Joule-Thomson effect by expansion of hydrogen, it is necessary that hydrogen gas be cooled below the inversion temperature (-83°C). Above this temperature if the hydrogen gas is throttled, it gets heated up and below this temperature it cools down. Nitrogen refrigeration cycle is to cool the hydrogen gas below its inversion temperature.
- Hydrogen exists in two molecular states, namely, ortho-hydrogen (o-H₂) and para-hydrogen (p-H₂). Normal hydrogen is a mixture of 75% o-H₂ and 25% p-H₂ by volume. The equilibrium (catalyzed) mixture of o-H₂ and p-H₂ at any given temperature is called "equilibrium hydrogen" (e-H₂). At the normal

boiling point of hydrogen (20.5 K), o-H_2 has a composition of 0.21% o-H_2 and 99.79% p-H_2 . The boiling points of normal and equilibrium forms of hydrogen and deuterium including that of HD is given in the Table 2.

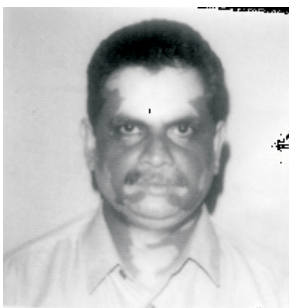
Conversion of o-H_2 to p-H_2 evolves heat of the order of 169.34 cal/g at BP. If this heat is absorbed at a temperature of liquid nitrogen bath at reduced pressure in the presence of a catalyst (hydrous ferrous oxide) then the hydrogen liquefaction rate is enhanced at the boiling point. Otherwise, this heat causes evaporation of liquid hydrogen (partially) resulting into very slow liquid formation and liquid build up in the system. Therefore, the specific energy requirement to produce a unit of liquid hydrogen increases substantially. This is the case in Nangal plant where the ortho to para conversion catalyst has not been employed in the design.

Added to this, no amount of perfection in insulations provided to the cold equipment can prevent ingress of heat from the surroundings. Thus, the heat of ortho-para conversion and the ambient heat ingress into the system are the two detrimental factors to the rate of liquid- H_2 formation, liquid build up in the columns and the maintenance of low temperatures at the level of boiling point of hydrogen. If the ortho- H_2 is not converted to para- H_2 before liquefaction, the resultant liquid will be ortho- H_2 . When this liquid is stored, the auto conversion from ortho to para - H_2 takes place with evolution of heat (169.34 cal/g), which is more than the heat of vaporization (106.6 cal/g). Around 1% of the stored liquid- H_2 will evaporate per hour due to the release of heat of conversion. Due to this, in

Nangal plant, whenever the plant trips on power failure, the liquid hydrogen starts evaporating and within a short period of 6-8 hours the entire liquid holdup is evaporated. Thereafter, bringing the plant to normal operation takes another 4-5 days to build up the required liquid holdup and required deuterium concentration profile in the distillation columns.

- (d) The Nangal plant requires electrical energy as major input and very small quantity of cooling water, steam, hydrogen gas, nitrogen gas, oxygen gas and lubricant oil. Thus, it is a very clean process and an environmentally benign process with no pollutants and no discharge of effluents.
- (e) This becomes an energy attractive process, if the hydrogen gas is produced by the fertilizer plant for their own consumption. Such a hydrogen distillation plant needs total electrical energy in the range of only 14 GJ/ Kg D_2O .
- (f) This plant produces D_2O of very high isotopic purity as the isotopic separation is carried out of pure hydrogen. Also D_2 gas of high isotopic purity (~100% D) can be produced. Depending on the purity level of the oxygen gas (used for oxidation of D_2) a very high purity of D_2O (~99.99%) can be produced in this plant.
- (g) In this plant it is possible to produce heavy water with any desired concentration of ^{18}O by suitably administering the oxygen in the oxidation step.
- (h) This process is also capable of producing almost deuterium free hydrogen gas (<5 ppm D) in the top reject of the triple column, which can be oxidized to get deuterium free water.

The Quality Requirement of Heavy Water



Shri C. Mohapatra joined 26th Batch of BARC Training School during 1982-83 after completing M.Sc. (Chemistry) from Sambalpur University, Orissa. Before joining Heavy Water Plant, Manuguru, Shri Mohapatra worked for three years at Heavy Water Division, BARC. At present, he is the Chief Chemist of Heavy Water Plant, Manuguru.

Shri R.V. Gupta did B.E. In Chemical Engineering. He joined BARC Training School and was subsequently deputed to Heavy Water Plant, Kota. He worked in production group in various capacities and played an important role in successful commissioning of the plant, which was first of its kind in India. Later, he took-up the responsibility as Production Manager at Heavy Water Plant (Manuguru). He was instrumental in successful commissioning of the plant. He was also Convener (Chairman) of optimisation Committee for HWP(M), which carried out various process restructuring as well as other measures to optimise plant operation. Presently he is working as Senior Deputy General Manager (O&M), Heavy Water Plant, Manuguru.



Introduction

The method used in extracting deuterium from water having about 150 parts per million (ppm) to 99.8 mole % purity at HWP, Manuguru is carried out in a primary plant based on $H_2S - H_2O$ bithermal isotopic exchange process and the secondary plant which upgrades the resulting 15% D_2O by distillation under vacuum. Considerable effort resulted in a high quality product in terms of isotopic and chemical purity. Several methods have been used for quantifying different constituents of heavy water.

FTIR spectrophotometric method has been adopted for analysis of isotopic purity and tritium has been analysed using scintillation counter. Chemical constituents such as chloride in trace level

have been analysed by ion chromatographic technique and other parameters by usual methods applicable to water analysis.

Heavy Water Quality Requirement

The quality requirement of heavy water depends on its ultimate use. Heavy water is mainly used as the moderator or as cooling fluid in PHWRs. The quality has been specified in ASTM D-2032-68 and summarized in Table 1. Heavy water quality is classified as

- (i) Isotopic purity (tritium and deuterium)
- (ii) Chemical purity (Conductivity, Turbidity, Chemical Oxygen Demand, Chloride and pH)

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TABLE 1. Various Quality specifications of heavy water

Parameters	Units	ASTM D-2032-68	Nuclear Power Corp. India Specs.	Export to South Korea	
				As per Contract No. PWB-P-94E F3	As per Contract No. C00NWS100 12-012
1. D ₂ O Content	mole %	≥ 99.75	≥ 99.78	≥ 99.75	≥ 99.75
2. Tritium Activity	GBq/kg	-	-	< 1.0	<0.0037
3. Chemical Oxygen Demand (KMnO ₄ Consumption)	ppm	< 10	< 10	< 10	< 10
4. Specific Conductivity at 25° C	μS/cm	< 15	< 2	< 15	< 15
5. Turbidity	NTU	< 5	< 5	< 5	< 5
6. Chloride	ppm	< 0.1	< 0.2	< 0.1	< 0.05
7. pH	N/A	-	5.5 ~ 8.0	6.0 ~ 8.0	6.0 ~ 8.0

Tritium is heavier isotope of hydrogen and is radioactive. It is normally present in heavy water used in a nuclear reactor. When tritium activity is less than 74 kBq/L, heavy water is classified as the virgin heavy water.

Significance of Specification

- (1) The moderator and heat transport heavy water D₂O content should be at least 99.75 mole percent. This allows the reactor to operate with the required fuel burn up. Higher D₂O content enhances fuel economy and fuel burn up.
- (2) Specific conductivity is a measure of the amount of ionic impurity in the heavy water. Normally less than 15 μS/cm water is used. Higher conductivity will affect water quality by making system corrosive or scaling in addition to enhancing radiolytic decomposition of heavy water.
- (3) The chemical oxygen demand (COD) analysis is referred to as KMnO₄ demand which determines the total organics in water. Presence of organics may cause excessive deuterium (D₂) accumulation in cover gas system. Control of organics in D₂O has been found to assist the control of deuterium production in moderator system.

- (4) The turbidity of water is a measure of the amount of suspended solids in the water. High levels of suspension cause deposits (scaling or fouling) in the reactor system resulting in higher radiation fields. Water of less than 5 Nephelometric Turbidity Units (NTU) is visually clear and is acceptable.
- (5) The chloride concentration is important as this ion at high temperature leads to the phenomenon of stress corrosion cracking and increases radiolytic decomposition rate.
- (6) The pH of pure heavy water is 7.4, but due to ingress of CO₂ it remains at less than 7.

Method of Analysis and Quality Assurance

Sampling of Heavy Water

Heavy water is usually shipped in 200 kg quantities in SS drums. The exchange reaction is rapid with atmospheric water vapour and hence care must be taken to avoid excessive contact with humid air while collecting samples of D₂O for analysis. Contact with air, which can be avoided either by collecting the heavy water under vacuum or by collecting it under inert atmosphere of N₂ or helium, may bring down the pH of heavy water from 7.4 to 5 and increase the conductivity to 1 μS/cm due to

absorption of CO₂ from atmospheric air. A minimum amount of 500 g of D₂O sample should be drawn by inserting the free end of the sampling tube to half depth of D₂O storage drum.

IR method of D₂O analysis (Isotopic purity)

The isotopic analysis of heavy water by IR Spectrophotometric method is based on absorption of IR radiation by different water species (H₂O, HDO and D₂O). Water/heavy water is a non linear triatomic molecule with 3N-6 degrees of molecular vibrations. For water (H₂O) or heavy water (D₂O) it is 3. IR active vibrational modes are as follows:

	Symmetric cm ⁻¹	Antisymmetric cm ⁻¹	Bending cm ⁻¹
μ _{OH}	3652	3758	1596
μ _{OD}	2671	2754	1187

Water - heavy water mixture is in equilibrium as follows:



The frequency of radiation to be selected for the analysis depends on heavy water concentration of the sample. When a sample has concentration more than 99% D₂O (Mixture of D₂O and HDO), μ_{O-H} is chosen. Due to intermolecular hydrogen bonding in HDO molecule, absorption is observed at 3400 cm⁻¹ instead of 3600 - 3758 cm⁻¹. An FTIR spectrometer is used for obtaining IR frequency and monitoring absorbance. A linear relationship is observed between concentration of D₂O and absorbance at 3400 cm⁻¹.

Conditions

(i)	Instrument used	Mattson Genesis II FTIR Spectrometer
(ii)	μ cm ⁻¹	3400
(iii)	Sample cell	CaF ₂ window, 0.2 mm cell path length
(iv)	Sample requirement	2 mL

(v)	Standards	in the range of 99 - 99.9 % D ₂ O (Obtained from HWD, BARC)
(vi)	Room temperature	25°C
(vii)	Humidity	10 % RH

FTIR instrument is checked for its wavelength and absorbance accuracy (Fig. 1). The absorption spectra of D₂O standards (background subtracted) are recorded (Figs. 2a & 2b). Background spectrum is obtained for water vapour and CO₂ (Fig. 3) and a calibration graph is prepared. Samples from each drum of D₂O are analysed by comparison against calibration graph. The accuracy and precision obtained is of the order of ± 0.01 % D₂O.

Chloride analysis by Ion Chromatography

The corrosive inorganic anions such as chloride, nitrite, phosphate (ortho) and sulphate can be determined down to 0.5 ppb in 15 minutes using preconcentration by ion chromatographic technique. A heavy water sample containing mixture of anions is injected into CO₃²⁻/HCO₃⁻ eluent stream and passed through a series of ion exchangers (concentrator, guard and separator column). The anions are concentrated and then separated based on their relative affinities for styrenedivinylbenzene based low capacity pellicular anion exchange resin capable of resolving F⁻, Cl⁻, NO₂⁻, PO₄³⁻ and SO₄²⁻. The separated anions are directed to suppressor where these anions are converted to their respective acids which are highly conductive. At the same time carbonate-bicarbonate eluent is converted to weakly conductive carbonic acid (H₂CO₃) which increases the Signal/Noise ratio. The conductivities of separated acids are then measured. The retention times form the basis for their identification as compared to standards. Fig. 4a represents the chromatogram of deionised water where as Fig. 4b represents the sequence of elution of different anions present in Heavy Water sample. Quantification is by measuring peak area with an integrator. An accuracy of 5 ppb is easily achieved with a precision of 0.5 ppb.

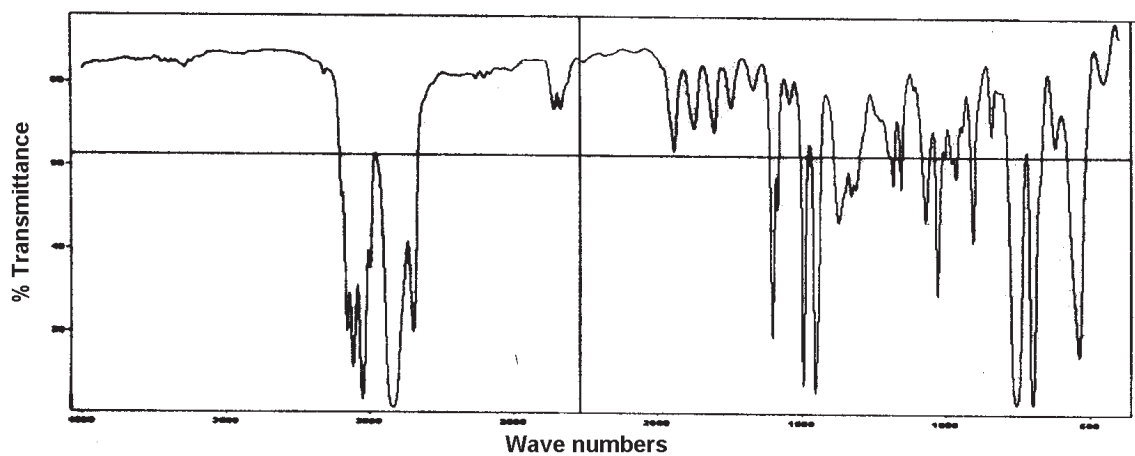


Fig. 1 Wavelength accuracy check by Polystyrene film

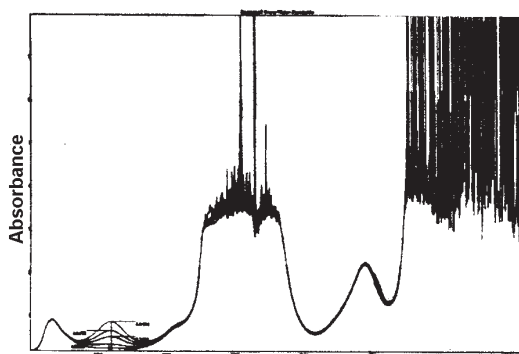


Fig. 2a Spectra of D₂O standards

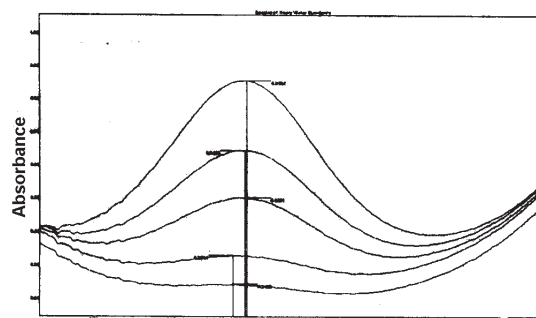


Fig. 2b Absorption peaks of D₂O standards

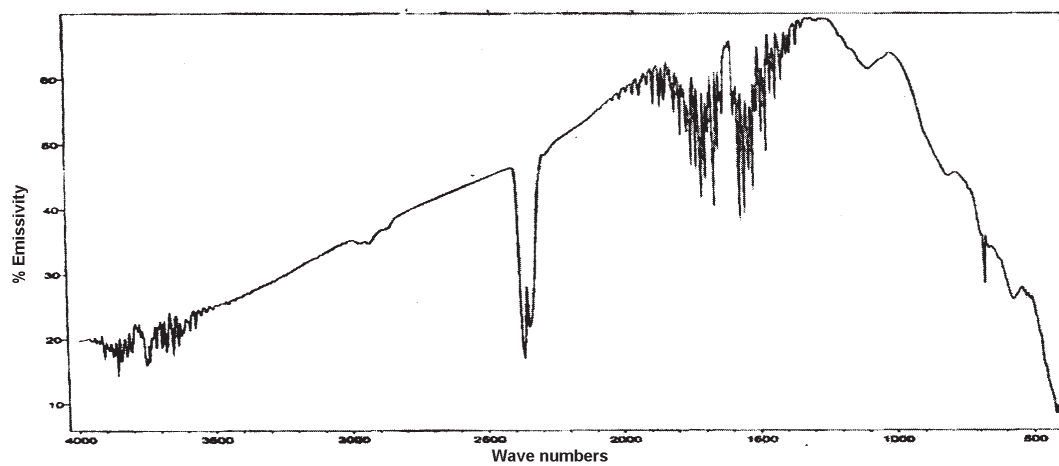


Fig. 3 Background spectrum

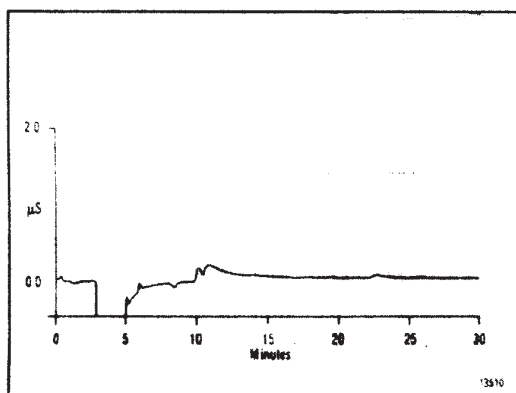


Fig. 4a Chromatogram of blank

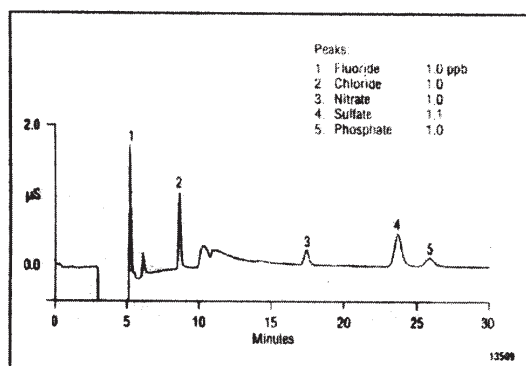


Fig. 4b Chromatogram of sample

Conditions

For obtaining reliable, consistent and accurate results, the eluent free from ionic impurity is required. Chemicals and deionised water used to prepare eluents must be of highest purity. The deionised water used to prepare eluent is with a specific resistance of 18 MΩ-cm. The deionised water free of ionised impurity organics, micro organisms and particulate matter is used.

(i)	Instrument used	Dionex DX-100 Ion Chromatograph
(ii)	Sample volume	20 mL
(iii)	Concentrator column	TAC-1
(iv)	Guard column	IonPac AG4A
(v)	Separator column	IonPac AS4A
(vi)	Eluent	1.8 mM Na ₂ CO ₃ , 1.70mM NaHCO ₃
(vii)	Eluent flow rate	~2 mL/min
(viii)	Suppressor column	Anion Micro membrane (AMMS)
(ix)	Regeneration	Membrane Auto regeneration accessory (ASRS)
(x)	Background Conductivity	15 - 20 μS/cm
(xi)	Detector	Electrical conductivity
(xii)	Integrator	PC data station using Winchrome EX software

Electrical Conductivity of D₂O

Exposure of a pure heavy water sample to the atmosphere may cause change in conductivity / resistivity, due to loss or gain of dissolved gases. The carbon dioxide normally present in air increases the conductivity to 1 μS/cm. Chemically pure inert gas nitrogen is used to blanket the surface of sample to avoid ingress of CO₂. The apparatus consists of a measuring circuit, conductivity cell and temperature compensator.

Conditions

(i)	Instrument used	Denver Model 30 Digital Conductivity Meter
(ii)	Volume of sample	50 mL
(iii)	Standards	0.0001N KCl = 14.94 μS/cm

(iv)	Temperature	25°C
(v)	Cell Constant	0.1 cm ⁻¹

Accuracy and precision of the measurement is 20 % relative error.

Turbidity measurement

Turbidity in water causes light to get scattered rather than transmitted in straight line. The comparison of the intensity of scattered light by a sample with that of a standard suspension forms the basis of measurement. Formazine polymer is used as the reference standard suspension. Correlation of turbidity with weight concentration of suspended matter is difficult because the size, shape and refractive index of suspended matter affect the scattering of light. Turbidity meter is a device which is capable of measuring scattered light intensity at 90° to the path of incident light and expressed as NTU.

Conditions

(i)	Instrument used	Systronics make Model-132 Digital Turbidity Meter
(ii)	Standards	(a) Turbidity free water is prepared by passing distilled water through a 0.2 µm membrane filter (b) Formazine polymer is prepared by mixing a solution of hydrazine sulphate in hexamethyl-inetetramine. Then a stock solution of 400 NTU is diluted to 40 NTU by using turbidity free water.
(iii)	Light source	Tungsten filament lamp operated at temperature between 2000 and 3000 K.
(iv)	Sample tube	Colourless glass with a provision to take a sample of 25mL.

Once the meter is calibrated with turbidity standards, samples are analysed and turbidity readings are

obtained directly from the readout system. 20% precision is obtained in the range of 2 NTU.

Chemical Oxygen Demand

The chemical Oxygen demand is defined as the amount of oxygen consumed under specific conditions in the oxidation of organic matter contained in heavy water sample. The commonly used oxidizing agent is potassium permanganate. This test is called catchall analysis. In this analysis, a measured amount of heavy water is refluxed with acidified potassium permanganate. The consumption of potassium permanganate is calculated after correcting for blank.

pH measurement

The principle of electrometric pH measurement is determination of the activity of the hydrogen ions by using pH meter consisting of a potentiometer, a combined electrode (Glass-Calomel) and a temperature-compensating device. There are two controls: intercept (buffers) and slope (temperature). The intercept control shifts the response curve laterally to pass through the iso-potential point with no change in slope (Fig.5a). This permits bringing the instrument on scale (0 mV) with pH 7 buffer for that has no change in potential with temperature. Whereas the slope control rotates the e.m.f / pH slope about the iso-potential point (0 mV/pH 7) (Fig.5b). To adjust slope for temperature without disturbing the intercept, a buffer is selected that brackets the sample with pH 7 buffer and adjusts the slope control to pH of this buffer. Then only the instrument indicates correct mV/pH at the test temperature and pH of various samples are measured reliably.

Tritium analysis

A sample is refluxed with alkaline permanganate to mask most of the quenching material, radioactive iodine and carbon. Complete transfer of tritiated water is assured by distillation to near dryness. An aliquot of distillate is mixed with scintillation solution and the beta activity is measured using an anticoincidence liquid scintillation spectrometer. The spectrometer is calibrated with standard solutions of tritiated water. Then background and unknown samples are counted alternatively.

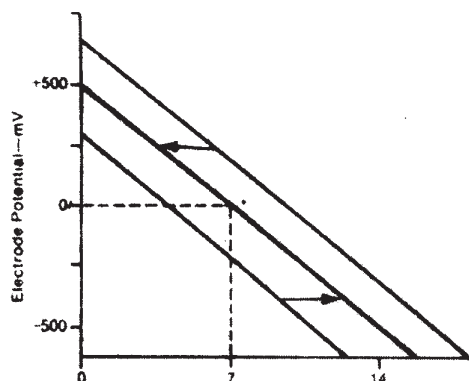


Fig. 5a Intercept control - pH

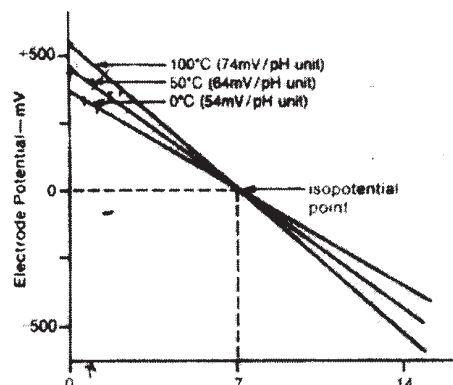


Fig. 5b Slope control - pH

Table 2. Heavy water analysis Report:

Sl. No.	Drum No.	% D ₂ O Content (mole %)	Tritium Activity (μCi/Kg)	PH (at 25°C)	Conductivity (μS/cm)	Turbidity (NTU)	Chemical Oxygen Demand (ppm)	Chloride (ppm)
Specifications		≥ 99.75	< 1000	6.0 - 8.0	< 15	< 5	< 10	< 0.05
1	HWB-7572	99.81	*<0.315	6.4	0.43	0.2	0.68	0.004
2	HWB-7597	99.82	*<0.315	6.2	0.23	0.2	0.43	0.002
3	HWB-7603	99.81	*<0.315	6.3	0.27	0.2	0.92	0.002
4	HWB-7632	99.82	*<0.315	6.3	0.25	0.1	0.74	0.004
5	HWB-7654	99.81	*<0.315	6.2	0.31	0.1	0.15	0.004

*analysed at BARC, Mumbai.

Inspection Report

Sl. No.	Drum No.	% D ₂ O Content (mole %)	Tritium Activity (μCi/Kg)	PH (at 25°C)	Conductivity (μS/cm)	Turbidity (NTU)	Chemical Oxygen Demand (ppm)	Chloride (ppm)
Specifications		≥ 99.75	< 1000	6.0 - 8.0	< 15	< 5	< 10	< 0.05
1	HWB-7572	99.81	< 0.315	6.3	1	1	1	0.02
2	HWB-7597	99.82	< 0.315	6.2	1	1	1	0.02
3	HWB-7603	99.82	< 0.315	6.3	1	1	1	0.02
4	HWB-7632	99.82	< 0.315	6.3	1	1	1	0.02
5	HWB-7654	99.82	< 0.315	6.2	1	1	1	0.02

Methods used to Achieve the Required Quality

Method used to produce nuclear grade heavy water is based on vacuum distillation which is designed to take up 15% heavy water from exchange unit and enrich it to 99.8% isotope purity. Unit has four distillation columns, each having a production capacity of 50 tons per year of nuclear grade heavy

water at a feed concentration of 15%. Feed is passed through activated charcoal bed in which oily substances will be adsorbed and this is transferred to evaporator tank after dosing KMnO₄ solution to oxidize organic matter and any oxidizable impurities. The vaporized feed is condensed in a cooling water exchanger and cooled feed is passed through ion exchange column to remove the ionic impurities. The feed, free from impurities, is fed to

distillation columns, which operates at sub atmospheric pressure for enriching to nuclear grade concentration.

The nuclear grade heavy water is again distilled to remove chemical impurities and put into a storage tank. The nuclear grade heavy water from final product storage tank is further treated to remove any trace level impurities using a mixed bed of nuclear grade ion exchange resin. Then the heavy water is drawn into a pre-cleaned and dried stainless steel drum under nitrogen atmosphere.

This process ensures the quality of product, which is free of undissolved solids, organics, dissolved solids and gases. Each drum is sampled for analyzing the impurities present. Some analysed data are presented in Table 2 in comparison with inspection report.

Conclusions

The product quality control is given prime importance at Heavy Water Plant, Manuguru. All the supplies to in-house Nuclear Power Stations and the export orders to Walsong, South Korea had met with their stringent quality specifications without any

rejection. The entire consignments of 116 MT to South Korea were accepted with excellent remarks.

Bibliography

1. Analytical procedures (1966) for the Heavy Water and Helium Systems of the NRX and NRU Reactors - part I: AECL-2596.
2. Standard Methods for examination of Water & Waste Water, APHA, Sixteenth Edition (1985).
3. Standard Test Method for Anions in water by chemically suppressed Ion Chromatography by American Society for Testing and Materials, ASTM D 4327 - 97.
4. Standard Test Method for tritium in water by American Society for Testing and Materials, ASTM D 4107 - 98.
5. Production of Heavy Water Part-I by James O.Maloney, George F.Quinn, and Harold S. Ray & Part-II by Maxwell L. Eidinoff, George G. Joris, Ellison Taylor, Hugh S. Taylor, and Harold C. Urey.
6. Kirshenbaum, I.; Physical Properties and analysis of Heavy Water, McGraw Hill Book Company, INC. (NY) (1951)

Chemistry in Effluent Treatment at Heavy Water Plants



Shri Jagdish Nageshri graduated in Chemical Engineering in 1982 from Gujarat University and also obtained Advance Post Diploma in Management with specialisation in finance and production / operations. He graduated from 28th batch of BARC training school and won Dr. Homi Bhabha prize for standing first among the in-plant trainees. Since 1985 he was actively involved in Operations Management, process modifications and trouble shooting of a very high pressure Ammonia-Hydrogen isotopic exchange unit and related R&D activities at Heavy Water Plant, Baroda. At present, he is looking after Health, Safety, Environment & HRD related activities of all Heavy Water Plants. He is life-member of Institution of Engineers (India).

Shri N.L. Malaikar obtained his M.Sc in Inorganic Chemistry in 1982 from University of Bombay. After graduating from 27th batch of BARC Training School, he joined Heavy Water Board in 1984 & was involved in R&D activities for development of catalyst used in Water-Hydrogen exchange method of Heavy Water production. Since 1990, he is working in Safety, Health & Training group of Heavy Water Board. His main areas of interest include the surveillance of Safety, Health & Environment activities of Heavy Water Plants (HWPs). He is a member of Safety Audit team of HWPs to evaluate the effectiveness of the Safety activities & programmes of HWPs.



Shri S.K. Gupta, after completing his B.Tech. in Chemical Engineering from H.B.T.I., Kanpur in 1969, joined Heavy Water Board through 13th batch of BARC Training School. He was posted for one year at H.W.P, Nangal during 1971 and thereafter he was associated in construction, commissioning and operation of HWP, Tuticorin up to 1989 as Technical Services Manager. He then joined HWP, Hazira, where he worked as Manger (process), Deputy General Manager and General Manager up to 2000. At present he is the General Manager (Safety, Health, Training and Environment) at Heavy Water Board Central Office.

Shri S. G. Belokar is a graduate Chemical Engineer and has been working in Heavy Water Plants since 1981 in Technical Services, Project Execution, Operation, Safety and Environment sections. He is also Fire and Safety professional. Presently he is working as Manager (Safety, Health and Training) at corporate office of Heavy Water Board, Mumbai.

Introduction

Out of seven heavy water plants, two are producing heavy water by Hydrogen Sulphide – Water (H_2S-H_2O) bithermal chemical isotopic exchange process and other five are producing heavy water by Ammonia-Hydrogen (NH_3-H_2) chemical isotopic exchange process. A coal based captive power plant is also set up at Heavy Water Plant

(Manuguru) for in-house reliable supply of steam and power. H_2S-H_2O based plants handle bulk quantities of H_2S gas at 20 kg/cm^2 which is highly toxic, corrosive and flammable, and other hazardous chemicals such as chlorine, acids, alkalis and various fuels like coal, furnace oil and LPG. The NH_3-H_2 based plants handle ammonia, synthesis gas (N_2+3H_2) and KNH_2 at very high pressures and temperatures ranging from -30°C to 600°C as well as

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K-Metal, hexane, natural gas/naphtha, chlorine, sulphuric acid and various hazardous industrial chemicals. Various effluents are generated in these plants. The highest priority of HWB is the environmental protection and safety of the plant and personnel. Therefore, various chemical treatments of effluents have been adopted to minimise the pollution within the plant and protect the surrounding environment with an aim to recycle back for zero effluent discharge from the plant. The chemistry of effluent treatment is discussed in this article.

The major effluents generated in Heavy Water Plants are as follows :

- (i) Gaseous effluents such as H₂S, NH₃ and flue gas consisting of Solid Particulate Matters (SPM), SO₂, NO_x, etc.
- (ii) Liquid effluents such as process effluent containing dissolved H₂S from exchange units, sour oil, Na₂SO₄ solution (by-product), water treatment plant effluents, cooling water system effluent and ammonical water
- (iii) Solid effluent such as coal ash

The limits for effluents specified by various State Pollution Control Boards are given in Tables 1 and 2.

TABLE 1. Gaseous Effluents at the discharge of Stack

Parameter	Limits
SPM	115 mg/Nm ³
SO ₂	800 mg/Nm ³
NO _x	800 mg/Nm ³

Treatment of Gaseous Effluents

In H₂S-H₂O Based Plants

The gaseous effluents from these plants are mainly H₂S gas from exchange unit and flue gas from the captive power plant. The toxic effects of H₂S on human beings are given in Table 3

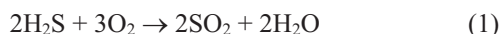
During normal operation of the plant H₂S gas is in a closed loop and very small quantity is released from purge tower and during decontamination of the equipments and piping for maintenance. During

Table 2. Liquid Effluents after treatment

Parameter	Limits
pH	5.5 – 9.0
Suspended Solids	100 mg/L
Free Ammonia	5 mg/L
Ammonical Nitrogen	50 mg/L
Total dissolved solids	2100 mg/L
COD	250 mg/L
BOD	30 mg/L
Oil and Grease	10 mg/L
Sulphides as S ²⁻	2 ppm
Sulphates as SO ₄ ²⁻	1000 mg/L
Chlorides as Cl ⁻	1000 mg/L

emergency or abnormal situation, or during dumping of towers, H₂S might be released through safety valves. In order to release the gas safely under any situation, a closed drain and vent system is provided.

There are two flare stacks of 126 metres height of which one flare stack is always kept in line and the other is a standby. To safeguard the plant personnel and general public, the H₂S gas is released/dumped through the flare stacks. The three pilot burners at the tip of the stacks are provided to burn and convert the H₂S gas to less toxic SO₂ as given below



SO₂ is not flammable. Hot SO₂ gas rises upto 1000 metres height during dumping of H₂S gas. This provides dispersion of SO₂ over a very large area.

The Flue gas of Captive Power Plant passes through the electrostatic precipitators and finally released through the 110 metre high stacks. The dosing of ammonia (NH₃) at the inlet of each electrostatic precipitators has resulted in better efficiency of Electrostatic Precipitators and the Solid Particulate Matters (SPM) level in flue gas is brought down much lower than the prescribed limits of 115 mg/Nm³. This technology is developed and engineered by Heavy Water Board [1]. SO₂ and NO_x are well within the limits prescribed.

TABLE 3. Toxic Effects of Hydrogen Sulphide

Concentration ppm	Effects
0.001	Odour threshold for very sensitive individuals.
0.13	Odour threshold for most persons.
10	Eye irritation after several hours' of exposure.
10	TLV (occupational exposure limit).
15	TLV-STEL for 15 min.
50	Irritation of the eyes and respiratory tract, conjunctivitis, keratitis and photophobia after several hours.
100	Sense of smell lost after a few minutes (olfactory paralysis). Rhinitis, bronchitis and pulmonary edema from repeated or prolonged exposure. Haemorrhage and death possible within 48 hours. Slight systemic effects.
250	Haemorrhage and death within a few hours. Symptoms of CNS depression; headache, nausea, sensory and motor impairment, possibly leading to unconsciousness.
300	IDLH (concentration considered to be of immediate danger to life and health).
500	Acute systemic effects dominate. CNS stimulation; increased respiration rate followed by respiratory arrest and possible death within few minutes.
1000	Death with a breath of one or two.

In NH₃-H₂ Based Plants

There are two types of gaseous emission in the process: Process ventings and Flue gases emissions.

Process Ventings

Large quantities of highly flammable and explosive chemicals i.e. synthesis gas, ammonia and potassium amide solution are handled in ammonia based HWP's. Ammonia and synthesis gas constitute a major portion of gaseous effluent. The ammonia is toxic and its threshold limit value (TLV) is 25 ppm (18 mg/Nm³) in air. The toxic effects of ammonia are given in Table 4 [2].

In these plants, all the vents, safety valves and rupture discs discharges are connected to the 65 metre high stacks provided with seal pots for process venting during emergency situation or decontamination of the equipments. The stacks are continuously purged with steam or nitrogen in order to avoid the formation of explosive mixture in the stack. The continuous supply of nitrogen to stack is

always maintained even during emergency situation like power failure from emergency nitrogen storage.

Flue Gas Emission

These stacks are provided for main cracker and mini cracker furnaces for venting of flue gas. The vent gases from all the stacks are periodically analysed for NO_x, SO₂, SPM and NH₃ and controlled. On-line NO_x monitors are installed to analyse flue gases from the cracker furnace. Fixed hydrogen and ammonia monitor are also installed in plant area to monitor the leakage, if any.

Treatment of Liquid Effluents***In H₂S-H₂O Based Plants***

The process effluent contains the dissolved H₂S gas which is removed by stripping and chlorination. Schematic diagram of Effluent Treatment Scheme for HWP(H₂S-H₂O based) is given in Fig. 1.

TABLE 4. Toxic effects of Ammonia

Ammonia concentration in Air	Physiological Effects
20 ppm	First perceptible odour
40 ppm	A few individuals may suffer slight eye irritation.
100 ppm	Noticeable irritation of eyes and nasal passage after a few minutes of exposure.
400 ppm	Severe irritation of throat, nasal passages and upper respiratory tract.
700 ppm	Severe eye irritation, no permanent effect if the exposure is limited to less than half an hour.
1700 ppm	Serious coughing, Bronchial spasms, less than half an hour of exposure may be fatal.
5000 ppm	Serious Oedema, Strangulation, Asphyxia, Fatal almost immediately.

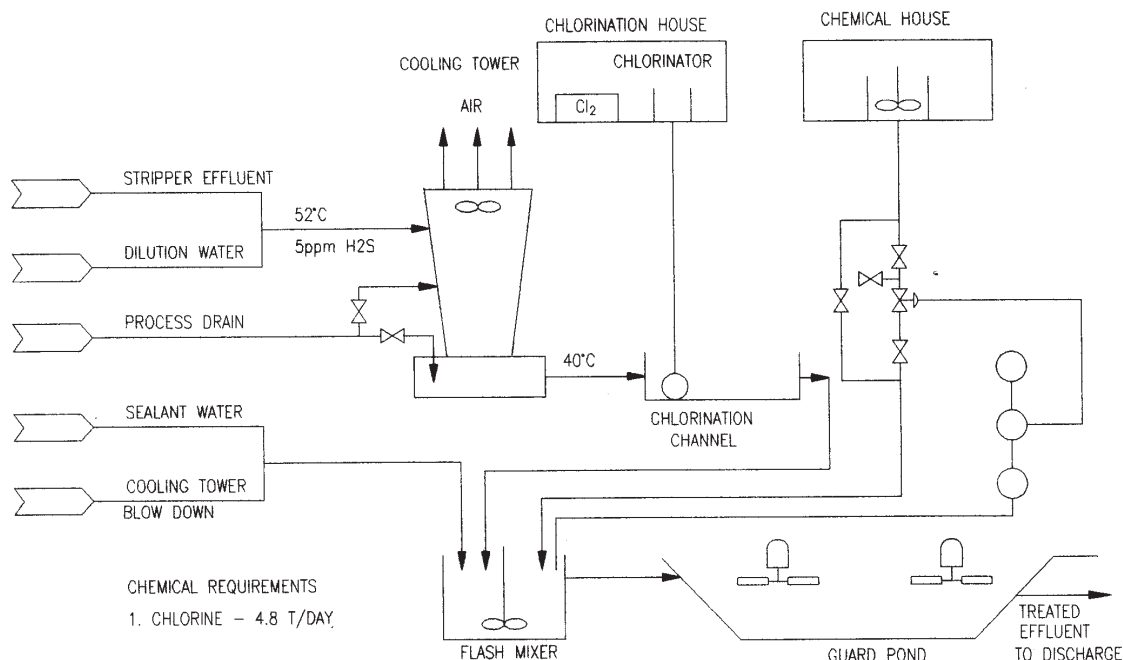


Fig. 1 Schematic diagram of Effluent Treatment Scheme for H₂S-H₂O based HWP

Stripping and Dilution of Effluents

Dissolved H₂S gas is stripped out in the waste stripper upto 1 ppm by steam. Heat of the effluent from stripper is recovered in heat exchangers with incoming feed of waste stripper. The temperature of the effluent is 90°C. Further it is mixed with double

the quantity of raw water and sent to effluent cooling tower for bringing down it's temperature to 40°C .

Chlorine Treatment for oxidation of undissociated H₂S to sulphates

When Chlorine is added to the water, chlorine reacts with water to form hypochlorous acid (HOCl) and hydrochloric acid (HCl)

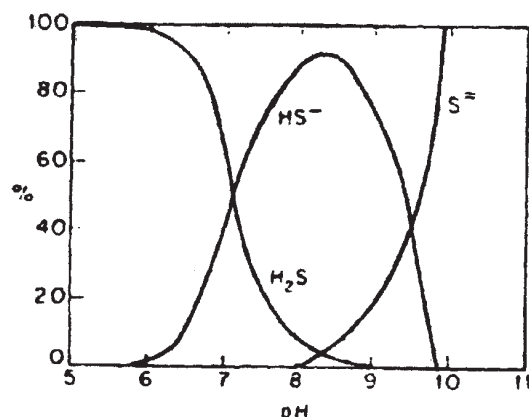


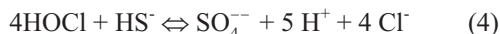
Fig. 2 Effect of pH on hydrogen sulphide-sulphide equilibrium [3]



Hypochlorous acid (HOCl) being unstable, dissociates into hydrogen ions (H^+) and hypochlorite ions (OCl^-).



Chlorination is done by dosing chlorine solution, into the effluents in the chlorination channel. This results in oxidation of sulphides to sulphates.



pH Control

Dissolved H_2S in water dissociates as per the reactions given below



The process effluent contains undissociated hydrogen sulphides alongwith a small quantity of dissociated sulphides. The chemical equilibrium constant (K) for the reaction (5) is given below:

$$\text{Log} [\text{HS}^-] - \text{log} [\text{H}_2\text{S}] = \text{pH} - \text{pK} \quad (7)$$

Where pK is the negative logarithm of the equilibrium constant K. Thus, the portion of H_2S and HS^- in the dissolved sulphide fraction in water are primarily a function of pH when pK is constant. The toxicity of sulphide in water is derived mainly from

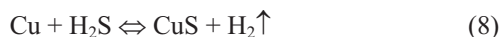
undissociated H_2S and not from the hydrosulphide (HS^-) or sulphide (S^{2-}) ions. The effect of pH in hydrogen sulphide-sulphide equilibrium is shown in Fig. 2.

At pH levels, below 6, the equilibrium shifts rapidly towards the formation of unionised or undissociated H_2S and is about 80%. At pH = 9, about 99% sulphide is present in the form of HS^- , it is evenly distributed between HS^- and H_2S at pH 7 and at pH=5, about 99% is present as H_2S . In well aerated water, H_2S gets oxidised to sulphates or elemental sulphur by chemical or biological process..

It is recognised that the hazards from the hydrogen sulphide to aquatic life is often localised and transient. The toxicity of H_2S to fish is mainly because of the substantial reduction in hatchability of fish eggs. The water containing concentrations of 2.0 $\mu\text{g/L}$ of undissociated H_2S would not be hazardous to most fish and other aquatic life. Hence the pH is maintained at 9, by addition of sodium hydroxide to keep the undissociated H_2S at less than 2 $\mu\text{g/L}$.

Sour Oil Treatment

The sour oil is generated in the H_2S gas booster seal oil system. This sour oil contains dissolved H_2S gas. In order to remove the dissolved H_2S gas, it is heated with steam and purged with nitrogen. Then it is treated in a chemical reactor containing copper powder to remove the traces of residual H_2S as copper sulphide.



The treated oil is filtered and centrifuged to remove the water and reused.

Na_2SO_4 solution

During H_2S generation, Na_2SO_4 solution is generated as a by-product due to the following reaction.



The sodium sulphate solution is treated to remove impurities such as unreacted sodium sulphide and it is then concentrated in the falling film

evaporators upto 25% w/v and then spray dried to get Na_2SO_4 powder.

Water Treatment Plant Effluents

Process Feed Water and Boiler Feed Water are treated to remove dissolved minerals and dissolved gases such as CO_2 and O_2 . During the regeneration of cation beds with HCl, acidic effluents are generated and during the regeneration of anion beds, alkaline effluents are generated. The quantity of effluents is more from cation beds as compared to the anion beds due to removal of carbon-dioxide in the atmospheric degassers between cation and anion beds. Both the effluents are mixed in the neutralisation pit and the resulting solution is acidic. The acidic effluent is neutralised and the pH is maintained between 5.5 to 9.0 by adding lime. Bio-chemical Oxygen Demand (BOD) of the effluent is maintained by surface aeration method at the guard pond before discharging to the river.

Liquid Effluents from Ammonia based HWPs

The liquid effluents from ammonia based HWPs, are normally ammonia and potassium amide solutions. All the process drains, resulting from draining/washing of pumps, equipments for maintenance, constitute liquid effluent. To avoid the localised contamination of the atmosphere, these process drains are connected to the drain header where water is recirculated continuously from effluent water reservoir. The effluent water reservoir is a covered underground effluent pit of 500 m^3 capacity. A part of the effluent from the effluent pit is preheated and fed to the ammonia stripping column to strip out the ammonia from the effluent water and released to the environment in the controlled manner. Thus, the ammonical nitrogen in the effluent is being maintained below the limits. The effluent after stripping of ammonia is neutralised and sent to delay pond for disposal. Two on-line analysers are installed to monitor the liquid effluents for pH and ammonical nitrogen continuously. A schematic diagram for effluent treatment and disposal for $\text{NH}_3\text{-H}_2$ based plant at Hazira is given in Fig. 3.

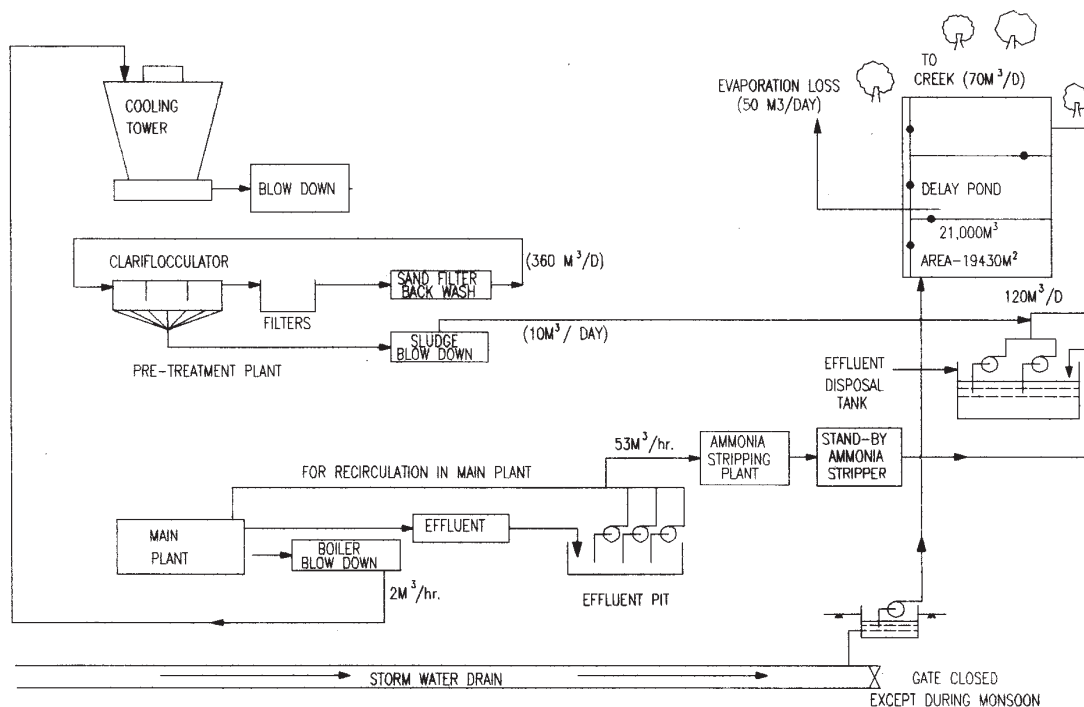


Fig. 3 Schematic Diagram of Effluent Treatment & Disposal at HWP ($\text{NH}_3\text{-H}_2$ Based)

Solid Effluent

Coal Ash

Ash generated in Captive Power Plant is transported as ash slurry (bottom ash slurry and fly ash slurry) from the plant through ash slurry pipe lines to the ash pond which is about 2 kilometres away from the plant site. Ash slurry is discharged into the ash pond where ash settles down and clean water is released to the nearby nallah.

Conclusion

The quality of effluent released at all Heavy Water Plants is well within the limits specified by the respective State Pollution Control Boards (SPCBs). Moreover, the quantity of liquid effluent is being reduced by recirculation. About 83% of liquid effluents discharge is reduced by recycling. Heavy

Water Plants are aiming to achieve zero liquid effluent discharge in near future.

References

1. Performance Enhancement of Electrostatic Precipitator (ESP) by Ammonia Injection in the Flue gas – A case study by Dr. R.R.Sonde & Prabir Saha, Heavy Water Board, Mumbai. Paper presented at CHEMCON – 2000 organised by IChE at Calcutta.
2. Preprint Vol. of National Symposium on Commissioning and Operating Experiences in Heavy Water Plant & Associated Chemical Industries. (Feb.27-28, 1992) at BARC (IS-4544(1968) Code of Safety for Ammonia including Amendment – 1, 1976).
3. Chemistry of Environmental Engineering by Clair N. Sawyer, Perry L. Mc.Carty & Gene F. Parkin. Mc.Graw Hill International Editions. – Fourth Edition 1994.

Heavy Water and Literature Update

Harold C. Urey, an American chemist, got interested in isotopes around 1929 in addition to his main research areas of kinetics, quantum mechanics and molecular spectra. In order to obtain experimental evidence for the possible existence of heavy hydrogen isotope, he planned a series of experiments on the assumption that the mass difference in the two hydrogen isotopes should lead to detectable changes in the wavelengths of lines in the spectrum of atomic hydrogen (isotope shift in line spectra, e.g., in Balmer series). He also felt that there was a need to preconcentrate the heavy hydrogen isotope, deuterium to get a good signal. On the basis of theoretical calculations of the vapour pressures of hydrogen and deuterium, Urey believed that deuterium would concentrate in the residual liquid when liquid hydrogen is evaporated. He could obtain spectral evidence for the existence of deuterium. But the intensity of the spectral lines obtained from the preconcentrated samples (at 25K) and commercial samples was comparable. This observation puzzled Urey as it was essentially a negative result on his belief of enrichment by evaporation. However, he could enrich deuterium when he repeated evaporation experiments at a reduced temperature of 14K. Urey announced his discovery of deuterium in 1932. The entire experimental investigations took only six months from conception to the announcement. Urey won the Nobel Prize in 1934 for his discovery of deuterium. Gilbert N. Lewis, an American chemist, first separated deuterium oxide (heavy water) from ordinary water in 1932. Urey and E. Washburn showed that deuterium could be concentrated in the form of heavy water by the electrolysis of ordinary water.

Deuterium has one proton and a neutron in its nucleus. Deuteron is having a loosely joined structure with an average binding energy of 1.11 MeV. It is a useful target material to produce neutrons by photo nuclear reactions. Deuteron is also used as a projectile in nuclear reactions. Although ordinary water is an attractive moderator of neutrons

in a reactor, deuterium in the form of heavy water is a very effective moderator due to the low neutron absorption cross section of deuterium. D_2O is as well a good reflector of neutrons. The greatest advantage of using D_2O as the moderator is that the reactor can operate with natural uranium as the fuel material. The abundance of D is about 150 ppm and D_2O of nearly 100% is required to use in nuclear reactors. To prepare nearly 100% D_2O , special enrichment methods involving a large amount of input feed are needed. Most of these methods are energy intensive. Isotope separation or enrichment is achieved by exploiting small differences in physical and chemical properties due to mass differences between two isotopes or species containing the isotopes. Isotope separation methods include electromagnetic, physical, chemical, electrochemical and photochemical methods. Heavy water is produced, mainly, by the following enrichment methods : distillation of water, electrolysis of water, ammonia-hydrogen exchange process, deuterium exchange between water and hydrogen sulphide (GS process).

Since the discovery of deuterium and heavy water, a lot of R&D was focused in the production of heavy water to meet the needs of reactors. It is difficult to list all the important literature. An attempt is made to list a select few literature on the production of heavy water and related issues. A few web sites are listed at the end.

1. K. Cohen, "The Theory of Isotope Separation", McGraw Hill (New York) 1951.
2. J. O. Maloney et al., "Production of Heavy Water" McGraw-Hill, New York, 1955.
3. Gamma scanning of large towers in GS process. M.J. Fulham and V.G. Hulbert, Chemical-Engineering-Progress-USA. 71(6) (Jun 1975) 73.
4. Heavy water production using hydrogen-water exchange. W.H. Stevens and F.P. Blackstein, AECL—4606 (1972).

Dr. A.V.R. Reddy, Head, Nuclear Chemistry Section, Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085; E-mail : avreddy@magnum.barc.ernet.in

5. The possible separation of deuterium of tritium from hydrogen using laser radiation pressure, D. Pooley and A.M. Stoneham, Report AERE-R—8194 (1975).
6. On-line heavy-water monitors based on the absorption of infrared energy, V.H. Allen and J.G. Bayly, IEEE-Transactions-on-Nuclear-Science NS-23(1) (Feb 1976) 317.
7. Heavy water production by isotopic exchange between hydrogen and methylamine., M. Bricc, J. Ravoire, M. Rostaing, E. Roth, and B. Lefrancois, Separation of hydrogen isotopes., H.K. Rae, (ed.) p.71-76. (1978) Washington.
8. Photochemical deuterium separation: problems and prospects J.B. Marling, I.P. Herman, Lawrence Livermore Lab., UCRL—81087 (1978).
9. Hydrogen isotopic separation by water distillation method. M. Asahara, Proc. Institute of Physical and Chemical Research symposium for separation of deuterium and tritium. Wako, Saitama (Japan). 4 Dec 1980.
10. Separation of hydrogen isotopes by isotopic exchange reaction of water-hydrogen system, S. Isomura, H. Kaetsu and R. Nakane, Institute of Physical and Chemical Research symposium for separation of deuterium and tritium. Wako, Saitama (Japan). 4 Dec 1980.
11. F. G. Brickwedde, "Harold Urey and the Discovery of Deuterium", Physics Today, September 1982.
12. Improving sieve tray performance with knitted mesh packing, D.A. Spagnolo and K.T. Chuang, Industrial and Engineering Chemistry: Process Design and Development USA. 23(3) (1984) 561.
13. Attenuation of californium-252 neutrons in water and heavy water moderators, R.M. Megahid, Arab J. of Nuclear Sciences and Applications. 20(2). (1987)209.
14. Electrochemical processes in heavy water production, K. Ram Mohan, Symposium on electrochemistry in nuclear technology. Kalpakkam (India). 10-11 Dec 1986, Transactions of the Society for the Advancement of Electrochemical Science and Technology. 23(1) (Jan-Mar 1988). 1.
15. Production of heavy water and concentration of heavy water in seawater distillation process, Y. Shindo and T. Hakuta, Nippon-Kaisui-Gakkai-Shi 43(4). (Nov 1989) 191.
16. Hydrogen isotope enrichment by hydrophobic Pt-catalyst in Japan and Western countries., M. Shimizu, S. Kiyota and R. Ninomiya, International symposium on isotope separation and chemical exchange uranium enrichment. Tokyo (Japan). 29 Oct - 1 Nov 1990.
17. D₂O production by laser-induced selective multiphonon decomposition, M. Ivanco, G.A. McRae and R.D. McAlpine, Proc. Annual conference of the Canadian Nuclear Society. Saint John, NB (Canada). 7-10 Jun 1992. V. 1. P.740.
18. Deterministic severe accident criteria as severe accident design criteria and policy for the new production reactor-heavy water reactor, P.T Rhoads, Nuclear Safety. 34(1) (Jan-Mar 1993) 13.
19. Heavy water: A distinctive and essential component of CANDU. A.I. Miller and H.M. van Alstyne, Proceedings of an IAEA technical committee meeting on Advances in heavy water reactors held in Toronto, Canada, 7-10 June 1993. p. 248.
20. A painless approach to use distributed digital-control system for Heavy Water Plant-Tuticorin., V.S. Potti, S. Krishnan, V.C. Rao and D.S Lamba, Proc. ACE-94: advances in chemical engineering in nuclear and process industries. Mumbai (India). 9-11 Jun 1994.
21. The first in the world plant for heavy water production by the method of water-hydrogen sulfide dual temperature isotopic exchange., A.M. Rozen, Atomnaya-Ehnergiya78(3). (Mar 1995)217.
22. Heavy water: properties, production and analysis, S.M. Dave, H.K. Sadhukhan and O.A. Novaro, Mumbai (India). Quest Publications. 1997.

23. Quality of protective films formed by electrochemical methods in the D₂O production facilities, M. Radulescu, I. Parvan, A. Dinu and V. Cotoian, Proc. Scientific Symposium on Advances in Cryogenics and Isotope Separation Caciulata - Valcea (Romania) (1997) 70.
 24. Analysis of human errors in operating heavy water production facilities, I. Preda, R. Lazar and C. Croitoru, *ibid*, p. 36.
- Some web1. sites**
1. www.nucleartourist.com/type/candu.html
 2. www.sno.phy.queensuea/sno/d20.html
 3. www.heavywaterboard.org
 4. www.fas.org/nuke/intro/nuke.heavy.html
 5. www.nrc.gov/NRC/EDUCATE
 6. www.isis-online.org/pub
 7. www.physicstoday.com
 8. www.physlink.com/ae365.cfm
 9. www.sumeria.net/health/heavywtr.html
 10. www.sciencenet.org.uk
 11. www.world-nucleus.org/coreissue/2000
 12. www.ansto.gov.au/ansto
 13. www.risoe.dk/rispub/NUA/heavy-water.html