

Reactor Boiler and Auxiliaries - Course 133

UPGRADING REQUIREMENTS AND PROCESSES

The following terms are in common usage in the heavy water upgrading field:

- Heavy Water - A mixture of ordinary water (H_2O) and heavy water (D_2O) in which the deuterium isotope predominates or is at least present in considerably greater amounts than found in ordinary water.
- Isotopic Purity - The weight % of D_2O in a D_2O - H_2O mixture.
- Upgrading - Any process which increases the fraction of D_2O in a quantity of heavy water. "Upgrading" and "reconcentration" are used interchangeably in the field.
- Downgraded Heavy Water - Heavy water in which the proportion of D_2O is lower than "reactor grade".
- Reactor Grade - A term applied to heavy water in which the fraction of D_2O is equal to or greater than an arbitrary value based on an economic study of a given reactor system.

Heavy water which has become downgraded by the addition of H_2O contains highly valuable D_2O . Restoring downgraded heavy water to "reactor grade" (usually ≈ 99.8 wt % D_2O) may cost less than the lost fuel burnup that would result if it were re-used in its downgraded condition. In the operation of a CANDU-PHW reactor, high purity D_2O is essential if good neutron economy is to be maintained. The addition of 0.25% H_2O to pure D_2O more than doubles the neutron capture cross section of the material. Consequently, the isotopic purity of the moderator should be kept at "reactor grade". In NPD, for example, a 1% decrease in D_2O isotopic purity would cost an estimated \$175,000 annually in loss of fuel burnup.

Downgrading of Heavy Water

While high purity heavy water is most desirable in a heavy water moderated and cooled reactor system, it is very difficult to maintain this purity because of the ease with which heavy

water downgrades when it contacts ordinary water. Although heavy water systems are designed to avoid mixing of heavy and light water, heavy water can become downgraded by several means, some of which are:

1. Sampling heavy water for chemical control.
2. Collecting heavy water in an open vessel when draining a piece of equipment, such as a pump, for maintenance work.
3. Opening a piece of equipment, allowing the light water moisture in the air to contact (and downgrade) residual heavy water on the exposed internal surfaces.
4. Spilling heavy water due to equipment failure. Downgrading results due to contact of the heavy water with light water moisture contained in the air or on surfaces.
5. Failure of a heavy water heat exchanger. Either outright loss of heavy water to the light water coolant or downgrading of the heavy water may result.
6. Deuteration and dedeuteration of new and spent ion exchange resins.

The formation of tritium (${}^3_1\text{H}$) by neutron capture in D_2O which has been irradiated complicates the problem of handling downgraded D_2O , and may be a factor in determining where the upgrading will be done - either on-site or at a distant upgrading unit. Ideally, on-site upgrading could eliminate the tritium problem by the use of a closed "in-line" upgrading unit. However, several factors must be considered, to determine whether on-site upgrading is more economical than some alternate scheme. Some of these factors are:

1. The cost of shipping and handling the downgraded D_2O .
2. The savings in rem of ${}^3_1\text{H}$ uptake by the elimination of handling, if an "in-line" unit is used.
3. The additional D_2O needed for station inventory.
4. The cost of modifications to an existing station to install an on-site unit.

Upgrading Processes

The processes that are used for upgrading heavy water are the same as those used for producing heavy water from natural water. However, the selection of an upgrading process is easier

than a production process because the downgraded water normally has a much higher isotopic purity than ordinary water, the starting point for a production process. An upgrading unit is the final stage of a long, tapered production plant, and therefore the economic prospects of a process depend on the capital operating and maintenance costs, hydrogen-deuterium separation ability and the ease with which the isotopic purity of the feed may be changed. All these factors must be carefully weighed in each case.

The separation factor (γ) is the best single measure of the ease or difficulty of a separation, and is the relative volatility of the gas and liquid, as:

$$\gamma = \frac{\left(\frac{y}{1-y}\right)_{\text{gas}}}{\left(\frac{x}{1-x}\right)_{\text{liquid}}} = \frac{\left(\frac{\text{atom fraction H}_2}{\text{atom fraction D}_2}\right)_{\text{gas}}}{\left(\frac{\text{atom fraction H}_2}{\text{atom fraction D}_2}\right)_{\text{liquid}}}$$

at any point in the process. In gaseous diffusion separation, it is equal to $(M_1/M_2)^{1/2}$, where M_1 and M_2 are the masses of the isotopes undergoing separation.

The relative volatility (γ) increases with falling pressure and temperature; for constant pressure the size of the plant is proportional to $(\gamma - 1)^2$, and the steam consumption, if using distillation, proportional to $(\gamma - 1)$. It therefore pays to operate at as low a pressure as possible. On the other hand, the volume of steam to be handled increases with falling pressure, so that a compromise has to be made to obtain the optimum operating point.

Several methods have been used for the separation of hydrogen and deuterium, and some of these have been listed in Table I. The processes can be broadly put into three classifications:

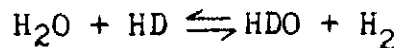
- (a) high energy,
- (b) large volume,
- (c) low energy coupled with low volume.

Although the value of γ is of great importance, since it determines plant size (approximately proportional to $1/(\gamma - 1) \ln \gamma$, flow rates, etc), there is no correlation between γ and the economic prospects of a process. The energy consumption, plant size and cost have to be carefully weighed in each case.

TABLE IHydrogen-Deuterium Separation Processes

	γ	$1/(\gamma - 1)\ln\gamma$
High Energy Requirement		
gaseous diffusion	1.20	26.3
thermal diffusion	1.05	400
electrolysis of water	10	0.0485
Large Volume Requirement		
water distillation	1.05	400
ammonia distillation	1.03	1110
freezing of water	1.02	2500
Low Volume, Low Energy		
hydrogen distillation	1.4	7.35
chemical exchange		
H ₂ O/H ₂	3	0.454
H ₂ O/H ₂ S	2	1.43
NH ₃ /H ₂	6	0.111

Of the chemical exchange processes, the H₂O/H₂ reaction appears to be the most attractive for H and D separation. It offers a relatively high γ , good opportunities for heat recovery and can utilize inexpensive equipment capable of high through-put rates, such as conventional sieve-plate towers for gas-liquid contacting. In comparison with distillation, the plant volume is smaller because γ is much larger. The reaction



however, requires a catalyst - Pt on colloidal charcoal, and because of the low solubility of H₂ in H₂O, practical exchange rates can only be obtained at high pressure. Efficient homogeneous catalysts for this exchange reaction have not yet been found. Moreover, while the mass transfer aspects of the H₂/H₂O process have not been extensively studied, it is likely that the catalyst problem will introduce complications, and more development work is required before the process could be used for up-grading.

Up to the present time, the GS (Girdler-Spevack) process (H₂O/H₂S exchange) is mostly used for initial concentration to about 10 - 20%. The H₂/NH₃ process also appears promising.

However, for D₂O upgrading, where the feed D₂O isotopic purity is relatively high, the economic aspects and H₂O-removal ability of what is in effect the final stage(s) of a production plant are of prime importance; water distillation or electrolysis generally proves to be best suited to this application, for the following reasons:

1. Distillation and electrolysis are less complicated, and more reliable than, for example, the GS process. This becomes particularly noticeable in the relatively small units used in final enrichment since the cost of final enrichment (capital and operating) accounts for only 2 to 4% of the total cost, if starting with natural water. Costs are no longer proportional to plant size in this application.
2. Processing can be performed under vacuum, preventing losses due to leaks, outleakage of $^1\text{H}^2$ and resulting in an improved γ at decreased pressure.
3. The water can be used directly, in the case of distillation, and an easily removeable electrolyte (KOH) can be added for electrolytic upgrading.
4. The required H₂O removal capability can be obtained most economically without an excessively large installation.

ASSIGNMENT

1. Suggest ways by which reactor grade D₂O may become downgraded during the day-to-day operation of a nuclear station.
2. Of the many hydrogen-deuterium separation processes available, which generally prove to be most suitable for D₂O upgrading and why?
3. The presence of tritium complicates the handling of irradiated, downgraded D₂O. Suggest ways in which this hazard may be minimized when filling drums of downgraded water for shipment, and how the hazard could be largely eliminated at a station.

R. Popple