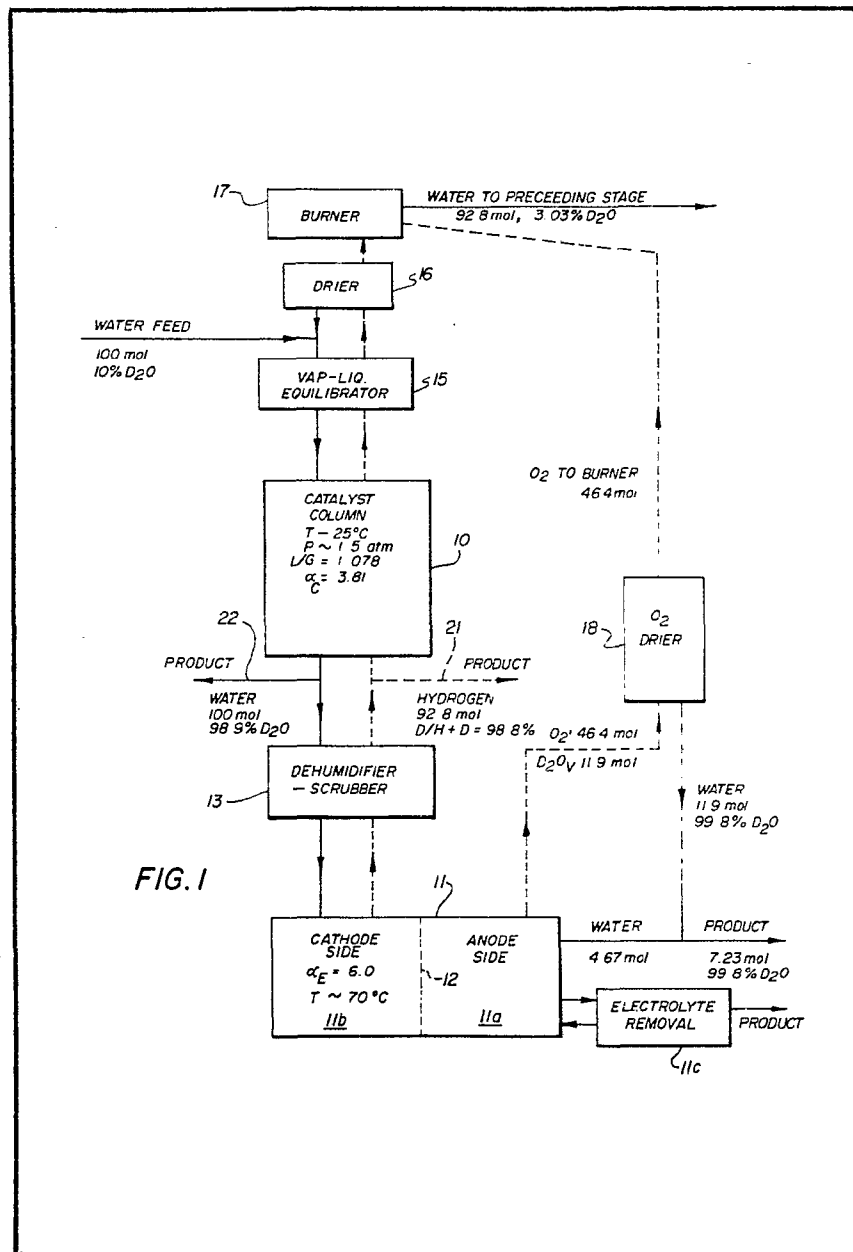


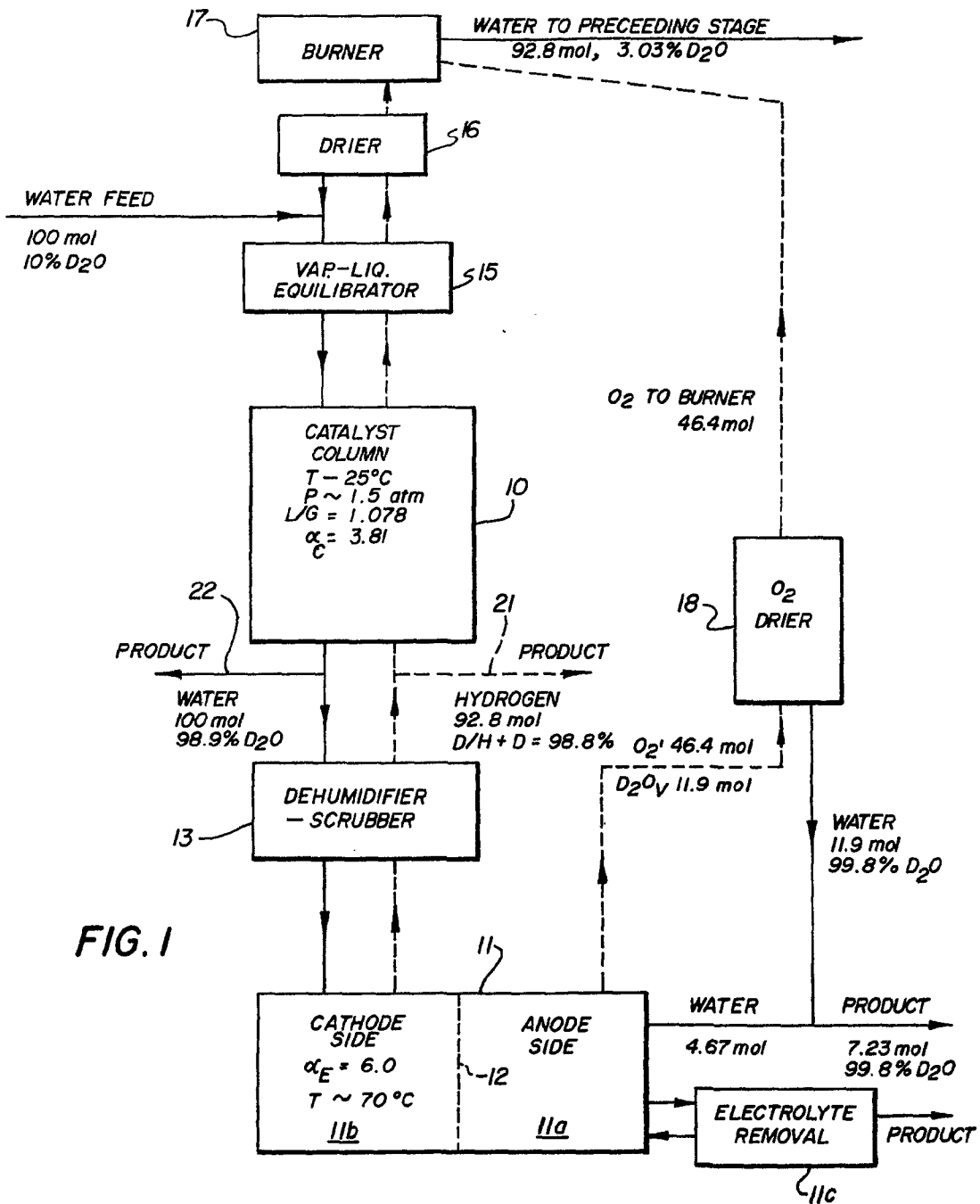
- (21) Application No 7906508
- (22) Date of filing 23 Feb 1979
- (23) Claims filed 23 Feb 1979
- (30) Priority data
- (31) 908226
- (32) 22 May 1978
- (33) United States of America (US)
- (43) Application published 5 Dec 1979
- (51) INT CL² C01B 4/00 5/02
- (52) Domestic classification C1A VD
- (56) Documents cited GB 864026 GB 800730 GB 726771 GB 581908 GB 435450
- (58) Field of search C1A
- (71) Applicant Atomic Energy of Canada Limited, 275 Slater Street, Ottawa, Ontario, Canada
- (72) Inventors John P. Butler, Martin Hammerli
- (74) Agent D. Young & Co.

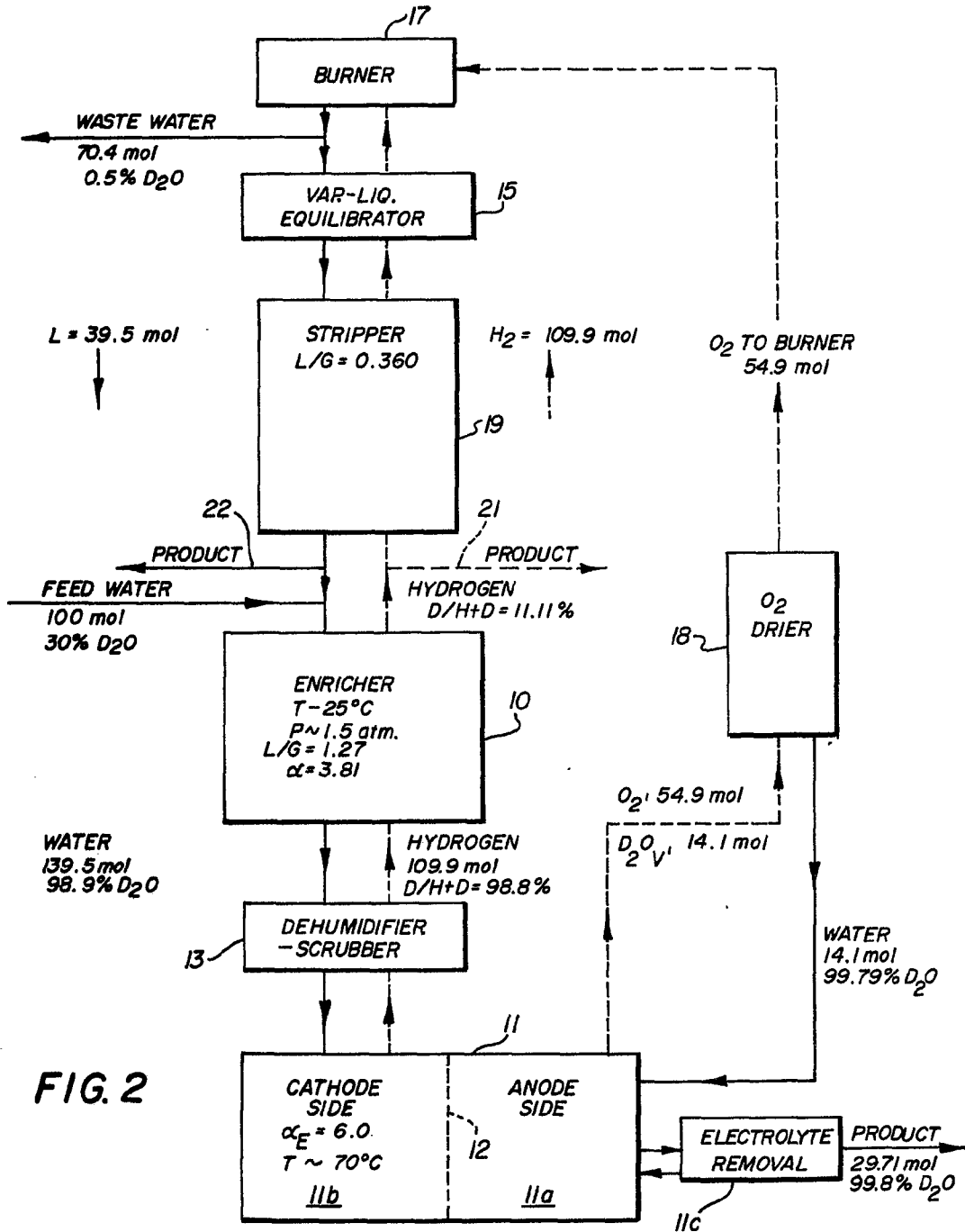
(54) **Method and Apparatus for Enrichment or Upgrading Heavy Water**

(57) A method and apparatus for upgrading and final enrichment of heavy water comprising means for contacting partially enriched heavy

water feed in a catalyst column with hydrogen gas (essentially D₂) originating in an electrolysis cell so as to enrich the feed water with deuterium extracted from the electrolytic hydrogen gas and means for passing the deuterium enriched water to the electrolysis cell.







SPECIFICATION

Method and Apparatus for Enrichment or Upgrading Heavy Water

This invention relates to apparatus and method
5 involving a combined electrolysis catalytic
exchange process for heavy water, D₂O upgrading
and final enrichment.

At the present time heavy water is produced
primarily by one or more stages of the Girdler-
10 Sulphide (GS) process which enriches water in
the range of 5—30% D₂O concentration followed
by final enrichment by water distillation processes
or by cascaded electrolysis systems. These final
stages raise the D₂O concentration to about
15 99.8%.

It is an object of the present invention to
provide a process and apparatus for deuterium
enrichment as a final stage in a heavy water plant.

It is another object of the invention to provide a
20 process and apparatus for continuous on-line
enrichment of the heavy water in moderator and
heat transfer systems in heavy water nuclear
reactors to maintain the deuterium concentration
at greater than 99.8%.

It is another object of the invention to provide a
25 process and apparatus for enrichment of heavy
water, that has been downgraded with natural
water (to typically 20—40% D₂O) during the
course of operating a heavy water nuclear reactor,
30 and to produce a heavy water product with a
deuterium concentration of about 99.8%. This
process is referred to as upgrading hereafter.

These and other objects of the invention are
achieved by a method comprising contacting
35 partially enriched heavy water feed in a catalyst
column with hydrogen gas (essentially D₂)
originating in an electrolysis cell so as to enrich
the feed water with deuterium extracted from the
electrolytic hydrogen gas and passing the
40 deuterium enriched water to the electrolysis cell.

The objects of the invention are also achieved
by apparatus for enriching and upgrading heavy
water comprising a catalyst isotope exchange
45 column with hydrogen gas and liquid water
passing therethrough in counter-current isotope
exchange relationship, an electrolysis cell having
an anode side and a cathode side and a separator
therebetween, a dehumidifier-scrubber, means for
50 passing the liquid water enriched in deuterium
from the catalyst column through the
dehumidifier-scrubber to the electrolysis cell,
means for passing the hydrogen gas evolved in
the cathode side of the cell through the
dehumidifier-scrubber to the catalyst column, said
55 dehumidifier-scrubber adapted to adjust the
humidity of the deuterium gas to the conditions
prevailing in the catalyst columns, to bring the
deuterium concentration of the water vapour in
the gas stream in isotopic equilibrium with the
60 liquid water from the enricher, and to transfer any
entrained electrolyte in the deuterium gas to the
down-flowing water stream, means for passing
the hydrogen gas from the catalyst column to an
output, means for introducing an input water feed

to the upper portion of the catalyst column, and
means for taking a product enriched in deuterium
from the system. The preferred arrangement
further comprises a gas drier to remove the water,
means for returning a portion of this water to the
70 cell and means for taking the remaining portion as
a deuterium product output, means for sending
the dried oxygen to a burner, and a burner for
recombining the hydrogen and oxygen to produce
deuterium depleted water. For purposes of
75 upgrading, the system further comprises a
stripper containing a catalyst positioned between
the enricher column and the burner which
promotes isotopic exchange between hydrogen
gas and liquid water to further reduce the
80 deuterium content of the depleted hydrogen. In
the upgrading application a portion of the
deuterium depleted water stream from the burner
is used as feed water to the stripper and the
remaining portion goes to waste.

85 In the drawings which illustrate embodiments
of the invention,

Figure 1 is a flow diagram of the process for
use as the final enrichment stage at a D₂O plant,
and

90 Figure 2 is a flow diagram of the process for
upgrading the heavy water in a nuclear reactor.

The drawings indicate examples of the
important parameters of the processes as follows:

- a) liquid and gas flow rates in mols
- 95 b) D₂O concentrations as percentages
- c) liquid/gas molar flow rates (L/G) as a ratio
- d) Temperature (T) in °C
- e) pressure (P) in atmospheres (atm)
- f) catalyst separation factor (α_c) as a ratio
- 100 g) electrolysis separation factor (α_e) as a ratio,

It should be pointed out that the specific
concentrations and molar flows given in the
figures are by way of example only and can be
varied according to design considerations.

105 Referring to figure 1, the chief elements of the
apparatus are an enricher 10 and an electrolyser
11. The enricher is an exchange column
containing a packed catalyst bed in which
hydrogen gas and liquid water pass in
110 countercurrent isotope exchange relationship. The
catalyst must be wet-proofed, hydrophobic and of
course active in the presence of liquid water. The
preferred catalyst material is a Group VIII metal
having a liquid-water-repellent organic polymer or
115 resin coating thereon selected from the group
consisting of polyfluorocarbons, hydrophobic
hydrocarbon polymers of medium to high
molecular weight, and silicones, and which is
permeable to water vapor and hydrogen gas.
120 These types of catalyst are described in U.S.
Patent No. 3,981,976 and in a paper entitled
"Novel Catalysts for Isotope Exchange between
Hydrogen and Liquid Water" published in the ACS
Symposium Series No, 68, of the American
125 Chemical Society.

The electrolyser 11 is any type of electrolysis
cell incorporating a separator 12 between the
anode compartment 11a and the cathode
compartment 11b. For economic reasons, it is

preferable that the cell used has a low water and/or electrolyte inventory.

The electrolytic hydrogen produced in the electrolytic cell which is depleted in deuterium relative to the electrolyte by virtue of the kinetic isotope effect inherent in the hydrogen evolution reaction, passes upwards (dotted lines) through a dehumidifier-scrubber 13 and through the catalyst column 10 where it steadily loses most of its remaining deuterium as it moves up the column in countercurrent flow with an input water feed (solid lines) introduced above the column and trickling down through the column, through the dehumidifier-scrubber to the electrolysis cell. The dehumidifier-scrubber adjusts the humidity of the deuterium gas to the conditions prevailing in the catalyst columns, to bring the deuterium concentration of the water vapour in the gas stream in isotopic equilibrium with the liquid water from the enricher, and to transfer any entrained electrolyte in the deuterium gas to the down-flowing water stream. The hydrogen gas after passing through the catalyst column passes to vapor-liquid equilibrator 15 which serves to bring the deuterium concentration of the water vapor in the gas stream in isotopic equilibrium with liquid water input (e.g. 100 mol., having a D_2O concentration of 10%). The hydrogen gas from the vapor-liquid equilibrator passes to drier 16 which serves to remove water vapor in the hydrogen since the atom fraction, $D/(H+D)$ is higher than the hydrogen and then to the burner 17 where it is burned (recombined with oxygen) to produce a water output that is returned to a preceding stage of the overall heavy water plant. Water from drier 16 is combined with the input feed water and returned to the vapor-liquid equilibrator.

The oxygen gas, O_2 and water vapor H_2O_v , from the anode side of the electrolysis cell 11 is passed to drier 18 that removes the water and the heavily deuterated liquid water is returned to the cell. A fractional output is taken as product. The drier could be for example a condenser involving a packed column, molecular sieve, etc.,. The oxygen output, O_2 , may be used in the conversion of the hydrogen output to water.

In Figure 1, the product is withdrawn from the water vapor removed from the oxygen. It could also be withdrawn from the electrolyte after removal of the electrolyte material such as KOH, or the liquid water from the bottom of the exchange column. If the latter is done, however, more enrichment is required in the catalyst exchange column.

Figure 2 shows the process as adapted for upgrading heavy water e.g. from a heavy water nuclear reactor. The example shown is for a 30% D_2O feed. Other concentrations could equally well be accommodated. For example, a 10% feed would be applied at an intermediate point in the stripper column 19 and similarly a 60% D_2O feed could be fed into the catalyst column 10. The system is essentially the same as described in Figure 1, but there are some differences. No drier

is needed before the burner because the hydrogen and the water vapor have approximately the same deuterium concentration. The stripper column is required when it is not convenient to feed the hydrogen at 11% deuterium or the water produced from this hydrogen back to a heavy water plant. The stripper column is also required if the heavy water feed to the plant contains tritium since environmental considerations may not permit tritiated water to be added to a heavy water plant. The L/G ratio in the stripper will be in the range of about 0.3 to 0.8 the specific value depending primarily on the chosen ratio of the deuterium concentrations of the hydrogen at the top of the enricher and the water feed. In the example chosen, the L/G ratio in the stripper is 0.36. Because a stripper column is required, the downgraded heavy water feed (about 30% D_2O) must be electrolysed more than once and in the example shown it is about 1.1.

In the above description of the figure 1 version of the apparatus, the enriched product is shown as taken from the liquid returning from the oxygen drier 18. Alternatively an output could be taken from the cell 11 and this would probably require an electrolyte removal device 11c. Output product could also be taken from the hydrogen gas stream (line 21) or the water stream (line 22). These output possibilities are also shown in figure 2.

95 Claims

1. Apparatus for enriching and upgrading heavy water comprising:

- a) a catalyst isotope exchange column enricher with hydrogen gas and liquid water passing therethrough in counter-current isotope exchange relationship,
- b) an electrolysis cell having an anode side and a cathode side and a separator therebetween,
- c) a dehumidifier-scrubber,
- d) means for passing the liquid water enriched in deuterium from the catalyst column through the dehumidifier-scrubber to the electrolysis cell,
- e) means for passing the hydrogen gas evolved in the cathode side of the cell through the dehumidifier scrubber to the catalyst column, said dehumidifier-scrubber adapted to adjust the humidity of the depleted hydrogen gas to the conditions prevailing in the enricher, to bring the deuterium concentration of the water vapor in the gas stream in isotopic equilibrium with the liquid water from the enricher, and to transfer any entrained electrolyte in the hydrogen gas to the downflowing water stream,
- f) means for passing the hydrogen gas from the catalyst column to an output,
- g) means for introducing an input water feed containing a minor proportion of heavy water to the upper portion of the catalyst column,
- i) means for taking the oxygen gas evolved in the anode side of the electrolysis cell and highly deuterated water vapor from the cell and passing it through the gas drier to remove the water,
- j) means for returning this water to the cell,

- k) a burner for recombining the output hydrogen and oxygen,
 l) means for passing the dried oxygen gas to the burner, and
 5 m) means for taking a product enriched in deuterium from the system.
 2) Apparatus as in claim 1 wherein the means for taking a product enriched in deuterium is means for taking a proportion of the water from
 10 the oxygen gas drier.
 3. Apparatus as in claim 1 wherein the means for taking a product enriched in deuterium is means for taking a product from the anode side of the cell.
 15 4. Apparatus as in claim 1 wherein the means for taking a product enriched in deuterium is means for taking a proportion of the hydrogen gas stream flowing upward in the system.
 5. Apparatus as in claim 1 wherein the means
 20 for taking a product enriched in deuterium is means for taking a proportion of the liquid water stream flowing downward in the system.
 6. Apparatus for upgrading heavy water as in claim 1 further comprising a stripper containing a
 25 catalyst positioned between the burner and the enricher to further reduce the deuterium content in the gas stream and transfer deuterium to the countercurrent liquid water stream.
 7. Apparatus as in claim 1 further comprising a
 30 vapor-liquid equilibrator positioned between the enricher and burner for bringing the deuterium concentration of water vapor in the gas stream into isotopic equilibrium with liquid water from the input feed or the burner.
 35 8. Apparatus according to claim 1 substantially as hereinbefore described with reference to Fig. 1 or Fig. 2 of the accompanying drawings.
 9. A method of upgrading or enriching heavy water which comprises i) passing a low grade
 40 heavy water stream through an enrichment column in countercurrent contact with a stream of electrolytic hydrogen gas, said column containing an isotope exchange catalyst;
 ii) recovering from said column an output
 45 hydrogen stream depleted with respect to deuterium and a partially enriched heavy water stream;
 iii) electrolysing the partially enriched heavy water stream to provide said stream of
 50 electrolytic hydrogen gas; and
 iv) withdrawing an enriched heavy water product stream.
 10. A method according to claim 9, wherein, before passage to the electrolytic cell the partially
 55 enriched heavy water stream from the enrichment column is passed through a dehumidifier/scrubber in countercurrent contact with the electrolytic hydrogen gas stream from the electrolytic cell prior to passage of the said gas stream to the
 60 enrichment column.
 11. A method according to claim 9 or 10, wherein the hydrogen output from the enrichment zone is passed to a burner and burned therein to produce a substantially deuterium free product
 65 water stream.
 12. A method according to claim 11, wherein prior to burning the output hydrogen stream is equilibrated with an input water stream to the enrichment zone.
 70 13. A method according to any one of claims 9—12, wherein on exiting from the enrichment zone the output hydrogen stream is passed through a stripping column in countercurrent contact with an input water stream to the
 75 enrichment column, said stripping column containing a further quantity of said isotope exchange catalyst.
 14. A method according to claim 12 or 13, as dependent on claim 11, wherein said input water stream is at least part of the water stream
 80 produced by the burner and recycled to the enrichment zone concurrently with the low grade heavy water feed.
 15. A method according to any one of claims 9—14, wherein an anodic gas stream from the electrolytic cell containing oxygen and deuterated water vapour is passed to a drier from which a condensed electrolyte is recovered for recycle to the electrolytic cell.
 85 16. A method according to claim 15, wherein part of said electrolyte recycle stream is recovered as said enriched heavy water product stream.
 17. A method according to claim 15 or 16, wherein the oxygen output from the drier is used
 95 as combustion oxygen to burn the hydrogen output stream from the enrichment column.
 18. A method according to claim 9, substantially as hereinbefore described with reference to Fig. 1 or Fig. 2 of the accompanying
 100 drawings.