ADDENDUM - 2

PROPOSAL FOR ENRICHMENT OF DEUTERIUM IN WATER

The present investigation has shown that highest enrichments were obtained if the feed water concentration is continuously increased and maintained the same as the cell water concentration at any time. This would require arrangements, such that there is a differential rise in concentration from one stage to another, as a result requiring infinite number of stages for finite enrichment. However, in order the plant to be workable, only a finite number of stages can be employed. These number of stages have been computed by making use of the data collected during present investigation.

The method considered makes use of electrolysis which yields hydrogen, which in turn is contacted with lean water from earlier stages over a catalyst. In this manner, hydrogen is partially stripped of its deuterium content without necessitating its being burnt to water. Any hydrogen having more than $(1/K)$ of natural abundance of deuterium can be employed, because deuterium from such hydrogen will be transferred to natural water ($K$ is the equilibrium constant at the exchange temperature).

The flow sheet for such a method has been presented in Figure 2.1. The water of natural abundance is taken in the cells of stage $(n-5)$ and is electrolysed. The hydrogen thus obtained
is not passed through catalytic exchange tower, because it has been considered to be too lean in deuterium content for recovery. The slightly concentrated water from this stage goes to the next stage. A part of feed to this stage is obtained from catalytic exchange stage (n-4). In this catalytic exchange tower, water of natural deuterium abundance has been contacted with hydrogen from stage (n-4) to n. A part of the water is fed to cells of stage (n-4) whereas the rest goes to the next exchange tower (n-3), where it undergoes exchange reaction with hydrogen of stages (n-3) to n. This process is continued till the end of the cascade, where the product of required enrichment is withdrawn.

The calculations have been carried out by taking the following considerations into account:

1. During most of the runs, the separation factor ranged from 7 to 9. Thus a separation factor of 8.0 has been taken for the calculations. Because of such high separation factor, it is not necessary to recover deuterium from the off gas of the first stage.

2. At each mixing point, the deuterium concentration in both the streams is the same.

3. The flows of water and hydrogen in the exchange towers is so arranged that there is no net transport of deuterium in them.
This requires that:

\[ L x = G y \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (2.1) \]

where \( y \) = atom fraction of deuterium in hydrogen,
\( x \) = atom fraction of deuterium in water,
\( L \) = downflow of water and
\( G \) = upflow of hydrogen at the top or bottom of a column.

4. The plant is operated in such a manner that the electrolytic cells and exchange tower change the deuterium fraction of their feeds by the same ratio. The exchange towers are run at 70° C., when the D ratio of 2.8 is obtained. The separation by electrolysis is \( \sqrt{x} = \sqrt{8} = 2.8 \). The reflux ratio is accordingly arranged so that the cells yield a concentration ratio of 2.8.

5. The calculations are started from the last stage.

6. For each stage, the calculations are conducted in the following steps:

(a) Calculate the concentration of the feed to the stage cells from the concentration of the upflow product stream by the relationship:

\[ \frac{\text{D fraction in the outgoing product}}{\text{the stage}} = \frac{2.8}{2.8} = 2.8 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (2.2) \]
(b) Calculate the off gas concentration from the stage from the knowledge of separation factor and product concentration.

(c) Calculate the reflux ratio required for bringing about the required separation in the stage by the following relationship:

\[ R = \frac{\text{Moles of off gas}}{\text{Moles of product}} = \]

\[ \frac{\text{D fraction in the product from the stage} - \text{D fraction in feed to the stage}}{\text{D fraction in in-feed} - \text{D fraction in off gas from the stage}} \]

\[ \ldots \ldots \ldots \ldots \ldots \text{(2.3)} \]

(d) Calculate the moles of off gas \( G' \) by multiplying the product moles \( P \) by the reflux ratio \( R \). Thus,

\[ G' = PR \ldots \ldots \ldots \ldots \ldots \text{(2.4)} \]

(e) Apply equation (2.1) to calculate \( L \).

(f) Calculate the amount of feed required from earlier stage by material balance.

(g) Check the calculations by trying a D-balance across a stage.

CALCULATIONS FOR PRODUCING 10 MOLES PER HOUR OF WATER CONTAINING 7.26% D

Let the last stage be called Stage n

Calculations for stage n:

Concentration of product = 7.26% D
Rate of product for stage n = 10 moles/hr.

(a) D concentration in feed = 2.59% D
(b) Off gas concentration = 0.0906% D
(c) Reflux ratio $R = \frac{0.0725 - 0.0259}{0.0725 - 0.00906} = 2.768$

(d) $G_n = 2.768 \times 10 = 27.68$ moles/hr.
(e) Water entering: $L_x = G_y$
   $L = \frac{27.68 \times 0.00906}{0.0259} = 9.7$ moles/hr.

(f) Amount of feed i.e. the product of stage (n-1) = $10 + 27.68 - 9.7 = 27.98$ moles/hr.

(g) Checking the D balance of stage n:

$10 \times 0.0725 + 27.68 \times 0.00906 - 37.68 \times 0.0259$

Output D

= $0.72 + 0.26 - 0.97 = 0.00$

Calculations for stage(n-1):

The concentration of product going out = 2.59% D
Amount of product going out = 27.98 moles/hr.
(a) Feed concentration = $\frac{2.59}{2.2} = 0.925\% \text{ D.}$

(b) Concentration of off gas = $\frac{2.59}{8} = 0.324\% \text{ D.}$

(c) Reflux ratio, $R$, = $\frac{0.00925 - 0.00324}{0.00925 - 0.00324} = 2.77$

(d) Rate of off gas, $G_{(n-1)} = 27.98 \times 2.77 = 77.50 \text{ moles/hr.}$

(e) Water entering stage $(n-1)$,

$$G^* y = L x.$$  

The $G$ for this stage is not equal to $G'$ from this stage alone, but the sum of $G'$ from stages $n$ and $(n-1)$. Thus,

$$G = G_n + G'_{(n-1)} = 77.68 + 77.50 = 105.2 \text{ moles/hr.}$$

$$L = \frac{105.2 \times 0.00324}{0.00925} = 36.84 \text{ moles/hr.}$$

Out of these 36.84 moles/hr., 9.7 moles/hr. have to go for stage $n$. Therefore, the amount of water for stage $(n-1) = 36.84 - 9.7 = 27.14 \text{ moles/hr.}$

(f) Feed from earlier stage,

$$= 27.98 + 77.50 - 27.14 = 78.34 \text{ moles/hr.}$$

(g) Checking D balance for stage $(n-1)$,

Input = $105.48 \times 0.00925$; Output = $27.98 \times 0.0259 + 77.5 \times 0.00324$

Difference = 0.00

Calculations for stage $(n-2)$:

Concentration of product = 0.925\% D

Amount of product = 78.38 moles/hr.
(a) Feed concentration = 0.330% D.
(b) Concentration of off gas = 0.116% D.
(c) Reflux ratio, R, = 2.77
(d) $G'_{(n-2)} = P \cdot R = 78.38 \times 2.77 = 217.1 \text{ moles/hr.}$
(e) $G = G'_n + G'_{(n-1)} + G'_{(n-2)} = 322.3 \text{ moles/hr.}$

\[
L = \frac{322.3 \times 0.00116}{0.00330} = 125.0 \text{ moles/hr.}
\]

L to stages n and (n-1) = 36.84 moles/hr.
Therefore, L to this stage = 125.0 - 36.84 = 88.16 moles/hr.
(f) Amount of feed from stage (n-3),
\[
= 78.38 + 217.1 - 88.16 = 207.32 \text{ moles/hr.}
\]

(g) Checking D balance for stage (n-2),
Input = 295.45 \times 0.0032 = 0.97
Output = 78.38 \times 0.00925 + 217.1 \times 0.00116 = 0.72 + 0.26
Difference = 0

Calculations for stage (n-3):

Concentration of product \ensuremath{\text{from the stage}} = 0.330\% D.

Amount of product = 207.32 moles/hr.

(a) Feed concentration = 0.118\% D.
(b) Off gas concentration = 0.0413\% D.
(c) Reflux ratio, R, = 2.77
(d) $G'_{(n-3)} = 207.32 \times 2.77 = 574.3 \text{ moles/hr.}$
(e) $G = G'_n + G'_{(n-1)} + G'_{(n-2)} + G'_{(n-3)}$
\[
= 896.6 \text{ moles/hr.}
\]
Gy = Lx

L = \( \frac{896.6 \times 0.00413}{0.00118} \) = 313.8 moles/hr.

Out of these, 125 moles for stages (n-2) to n. Therefore, the moles for stage (n-3) = 313.8 - 125.0 = 188.8 moles/hr.

(f) Feed from stage (n-4) = 207.32 + 574.3 - 188.8
= 592.8 moles/hr.

(g) Deuterium Balance:

\(
\text{ut} = 781.6 \times 0.00118 = 0.92 \\
\text{Output} = 207.32 \times 0.0033 + 574.3 \times 0.00043
= 0.68 + 0.24 = 0.92 \\
\text{Difference} = 0.00
\)

Calculations for stage (n-4):

Concentration of the product from this stage = 0.118% D.

Amount of product = 592.8 moles/hr.

(a) Concentration of feed to this stage = 0.0421% D.

(b) Concentration of off gas = 0.0148% D.

(c) Reflux ratio, R, = 2.77

(d) \( G'(n-4) = 592.8 \times 2.77 \) = 1642.1 moles/hr.

(e) \( G = G'(n-4) + G'(n-3) + G'(n-2) + G'(n-1) + G_n \)
= 2638.7 moles/hr.

\[
L = \frac{2538.7 \times 0.000148}{0.000421} = 892.5 \text{ moles/hr.}
\]
Out of this the flow to stages (n-3) to n = 313.8 moles/hr.

Amount going to stage (n-4) = 893.5 - 313.8
= 578.7 moles/hr.

(f) Feed from earlier stage = 592.8 + 1642.1 - 578.7
= 1656.2 moles/hr.

(g) Deuterium Balance:
Input = 2234.9 x 0.000421 = 0.94
Output = 592.8 x 0.00118 + 1642.1 x 0.000148
= 0.70 + 0.24 = 0.94
Difference = 0.00

Calculations for stage (n-5):
Concentration of product = 0.0421% D
Amount of product = 1656.2 moles/hr.

(a) Feed concentration = 0.0150% D.

(b) Concentration of off gas = 0.00526% D.

(c) Reflux ratio, R, = 2.77

(d) \( \theta_{(n-5)} = 1656.2 \times 2.77 = 4587.7 \) moles/hr.

The off gas does not pass through any tower. But the total gas produced = 4587.7 + 2538.7 = 7126.4 moles/hr.

(f) Feed to call = 1656.2 + 4587.7 = 6243.9 moles/hr.

(g) Deuterium Balance:
Input = 6243.9 x 0.000150 = 0.94
Output = 1656.2 x 0.000421 + 4587.7 x 0.000526
= 0.70 + 0.24 = 0.94
Difference = 0.00
Thus, starting from last stage \( n \), we have come to stage \( (n-5) \), which requires water of normal concentration as its feed.

Considering \( (n-5) \)th stage as stage (1), the total number of stages is 6. The values of various requirements and flow rates are summarised below.

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final product rate</td>
<td>10.0 moles/hr</td>
</tr>
<tr>
<td>Concentration of final product</td>
<td>7.25% D</td>
</tr>
<tr>
<td>Fresh water for cells</td>
<td>6243.9 moles/hr</td>
</tr>
<tr>
<td>Fresh water for exchange towers</td>
<td>892.5 moles/hr</td>
</tr>
<tr>
<td>Total fresh water requirement</td>
<td>7136.4 moles/hr</td>
</tr>
<tr>
<td>Total hydrogen produced</td>
<td>7126.4 moles/hr</td>
</tr>
<tr>
<td>Concentration of this hydrogen</td>
<td>0.00526% D</td>
</tr>
<tr>
<td>Number of stages</td>
<td>6</td>
</tr>
<tr>
<td>Number of exchange towers</td>
<td>5</td>
</tr>
</tbody>
</table>

First stage does not require a corresponding exchange tower.

The amounts of flow through various streams to and from the different stages have been given in the flow sheet also (Figure 2.1), apart from being given in the calculations for individual stages.

Though the calculations have been presented for producing water of 7.25% D concentration, the procedure can be employed for finding the requirements of a plant for the product of any desired concentration.
FLOWSHEET FOR DEUTERIUM ENRICHMENT BY ELECTROLYSIS CUM CATALYTIC-EXCHANGE METHOD.

M/H = Moles/hour.