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The steady-state and dynamic simulation of cascade distillation system for the production of oxygen-18 isotope from water[☆]

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ABSTRACT

Accurate simulation of water distillation system for oxygen-18 (¹⁸O) isotope separation is necessary to guide industrial practice, since both deuterium (D) and oxygen-18 isotope get enriched and interfere with each other. In the present work, steady-state and dynamic distillation models are established based on a classic method and a cascade distillation system with 5 towers is introduced to test the models. The theoretical expressions of separation factor $\alpha_{H/D}$ for protium/deuterium and separation factor $\alpha_{^{16}O/^{18}O}$ for oxygen-16/oxygen-18 were derived, with the existence of deuterium and oxygen-18, respectively. The results of the steady-state simulation by the classical method proposed in the present work agreed well with the results of the lumping method. The dynamic process could be divided into 5 stages. Impressively, a peak value of product withdraw was observed before the final steady state, which was resulted from the change of ¹⁶O/¹⁸O separation factor and isotope distribution. An interesting low concentration zone in the towers of T2–T5 existed at the beginning of the dynamic process and it required industrial evidence.

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1. Introduction

The global demand for the high-purified ¹⁸O water has been increasing with the rapid development of Positron Emission Tomography/Computed Tomography (PET/CT) technology, which has great potential for excellent early diagnosis of cancer [1–3]. Generally, ¹⁸O water is manufactured by water distillation [4], O₂ cryogenic distillation [5,6] and NO cryogenic distillation [7], among which the water distillation is so widely applied that it contributes to more than half of the world's production. Superior advantages over other separation process are obtained for the water distillation: (1) the low-cost and easily available feedstock of water, (2) little negative influence on environment, and (3) low-risk operation for safe process. But there exist some drawbacks, typically that the single-stage separation factor (α) of 1.006 between oxygen-16 (¹⁶O) and ¹⁸O is extremely small and the natural abundance of ¹⁸O is only 0.204%. So, appropriately designed processes, especially cascade process, are required for efficient separation.

Nevertheless, more than 2000 theoretical plates are needed to produce 98% ¹⁸O water through multi-tower cascade operation,

and a great deal of energy consumption is observed for the continuous vaporization of water [8–10]. Additionally, it takes really a long period to achieve stable operation for a well-designed water distillation cascade, as the initial abundance of ¹⁸O is very small. Thus, the real cascade experiments for process optimization are high-cost and difficult to be carried out to observe the isotopic distribution in separation systems. However, better understanding of stable production and start-up procedure will significantly benefit the production design and cost control. Therefore, steady-state and dynamic simulation for the water distillation cascade process is important for this promising industry.

The general theory of isotope separation in columns only solved the two-component separation problem in order to calculate the theoretical number of the columns [11]. Fraenkel *et al.* developed a plate-by-plate calculation method for the separation of ¹⁶O and ¹⁸O under steady-state conditions [12]. Other researchers employed Aspen Plus to resolve steady-state simulation of ¹⁶O/¹⁸O separation [13,14]. However, all these methods mentioned above ignored the deuterium (D) influence on ¹⁶O/¹⁸O separation. In fact, the real isotope system of ¹⁸O water is far more complex.

There are nine kinds of isotopic variants of water molecules [15], as shown in Table 1. Because the concentration of ¹⁷O remains very low in ¹⁸O production system, it is ignored in the

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Table 1
Nine kinds of isotopic variants of water molecule

¹⁶ O labeled water	¹⁷ O labeled water ^①	¹⁸ O labeled water ^②
H ₂ ¹⁶ O	H ₂ ¹⁷ O	H ₂ ¹⁸ O
HD ¹⁶ O	HD ¹⁷ O	HD ¹⁸ O
D ₂ ¹⁶ O	D ₂ ¹⁷ O	D ₂ ¹⁸ O

① ¹⁷O will not be discussed in the present work because it difficult to get enriched in a system designed for ¹⁸O production [16].

② The natural concentration of ¹⁸O is 0.204%.

present work. Thus, six main kinds of isotopic variants of water molecules are discussed here. Although the natural D abundance is about 0.015%, which is one order of magnitude lower than that of ¹⁸O, large amount of D isotope get enriched in the product, because the typical α for protium/deuterium (H/D) is 1.04 and the effective separation factor, defined as $(\alpha-1)/\alpha$, is much higher than that of ¹⁶O/¹⁸O. Literatures available indicated that the D isotope will significantly reduce the separation factor of ¹⁶O/¹⁸O as described in Eq. (1), which might significantly increase theoretical plates [17,18]. Therefore, the separation of deuterium should be also considered to modeling the real distillation system.

$$\left(\alpha_{D_2^{16}O/D_2^{18}O}-1\right)/\left(\alpha_{H_2^{16}O/H_2^{18}O}-1\right)=0.825\pm0.022 \quad (1)$$

Currently, to our best knowledge, there is no literature available for the dynamic simulation for ¹⁸O production through water distillation. The researchers in Japan had development a dynamic model for the O₂ cryogenic distillation process. The systems are quite different because only O isotopes exist in O₂ distillation system, without complex isotope exchange reactions. However, there are mainly six kinds of isotopic molecules in H₂O, leading to complex isotope exchange reaction network [19]. Thus, the dynamic simulation for water distillation is much more complex and further work is required obviously.

In the present work, theoretical α expression of ¹⁶O/¹⁸O and H/D is derived for the simulation with the existence and effect of ¹⁸O and D. The equilibrium vapor concentration of ¹⁸O and D is also obtained. Both steady-state and dynamic simulation models are established for the cascade separation system with five columns. Our previous work realized the steady-state simulation for the distribution of ¹⁸O and D in water distillation system via lumping method [20], and the present steady-state result is compared with that of lumping method. This work provides a new approach for simulation of the ¹⁸O separation via water distillation.

2. Model and Method

Herein, a classical method is applied to obtain the equations, such as mole balance, liquid-vapor equilibrium, and separation factors, for the steady-state and dynamic models. This classical method involves much less assumptions than lumping method as reported in our previous work. The detailed description on the models is presented as follow.

2.1. The steady-state model

Under steady-state conditions, the fraction and flow rate at certain point keep consistent in the separation system. As shown in Fig. 1, a typical theoretical plate contains mole flow rate (L and G) and fraction (x and y) in liquid (downward) and

vapor (upward) streams, as well as isotope exchange between the two streams. The mole balance from the n -th theoretical plate to the product flow is expressed as below [21]:

$$G_n y_n^{18O} = L_{n-1} x_{n-1}^{18O} - P x_p^{18O} \quad (2)$$

$$G_n y_n^D = L_{n-1} x_{n-1}^D - P x_p^D \quad (3)$$

$$G_n = L_{n-1} - P \quad (4)$$

where L_{n-1} and G_{n+1} are the mole flow rates of liquid and vapor into the n -th theoretical plate and L_n and G_n are the mole flow rates of corresponding outlet streams, while P is the product flow rate; x_{n-1} , y_n , and x_p are the mole fraction of the liquid stream L_{n-1} , vapor stream G_n and product P , respectively. In addition to these balance equations, phase equilibrium equations are required to determine all the variables.

Firstly, the physical and chemical properties of the six different types of isotopic water are almost the same [22]. Thus, the ideal gas and ideal liquid assumption are reasonable for this separation system [23]. According to the Dalton's law of partial pressure and Raoult's law, we obtain:

$$p_M = y_M \cdot p_{\text{total}} \quad (5)$$

$$p_M = x_M \cdot p_M^* \quad (6)$$

where p and p^* is the vapor pressure and saturated vapor pressure, while the subscript M and total refers to certain isotopic variant and the systems, respectively. The saturated vapor pressure of H₂¹⁶O, H₂¹⁸O, D₂¹⁶O and D₂¹⁸O at different temperature is available from literatures [20,24]. However, it's impossible to directly measure the saturated vapor pressure of pure HD¹⁶O and HD¹⁸O, and special calculation method is required to obtain these parameters. Herein, geometric mean rule is applied for this purpose and it is expressed as [25]:

$$p_{HD^{16}O}^* = \sqrt{p_{H_2^{16}O}^* \cdot p_{D_2^{16}O}^*} \quad (7)$$

$$p_{HD^{18}O}^* = \sqrt{p_{H_2^{18}O}^* \cdot p_{D_2^{18}O}^*} \quad (8)$$

Based on this rule, the saturated vapor pressure of all variants is available for the simulation.

Secondly, a complicated reaction network of reversible isotope exchange exists in liquid phase [26]. We assume that the distribution of D and ¹⁸O atoms among the six isotopic variants of water molecule is random [25,27], and then, the mole concentration of each isotopic variant is determined by the mole concentration of H, D, ¹⁶O and ¹⁸O.

$$x_{H_2^{16}O} = x_H^2 \cdot x_{^{16}O} \quad (9)$$

$$x_{HD^{18}O} = 2x_H \cdot x_D \cdot x_{^{18}O} \quad (10)$$

The rest equations for other isotopic variants are similar to Eqs. (9)–(10), except for the subscript. Considering the normalization of mole concentration, only two variables are required for the mole fraction of the six variants at certain stage and the number of variables is significantly reduced.

$$x_{^{16}O} + x_{^{18}O} = 1 \quad (11)$$

$$x_H + x_D = 1 \quad (12)$$

Finally, the separation factors play a key role in the separation performance. Based on the ideal consumption, they can be simply defined as the ratio of saturated vapor pressures:

$$\alpha_{\text{H}_2^{16}\text{O}/\text{HD}^{16}\text{O}} = \frac{p_{\text{H}_2^{16}\text{O}}^*}{p_{\text{HD}^{16}\text{O}}^*} = \frac{p_{\text{H}_2^{16}\text{O}}^*}{\sqrt{p_{\text{H}_2^{16}\text{O}}^* \times p_{\text{D}_2^{16}\text{O}}^*}} = \sqrt{\frac{p_{\text{H}_2^{16}\text{O}}^*}{p_{\text{D}_2^{16}\text{O}}^*}} \quad (13)$$

$$\alpha_{\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}} = \frac{p_{\text{H}_2^{16}\text{O}}^*}{p_{\text{H}_2^{18}\text{O}}^*} \quad (14)$$

$$\alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}} = \frac{p_{\text{D}_2^{16}\text{O}}^*}{p_{\text{D}_2^{18}\text{O}}^*} \quad (15)$$

Considering Eqs. (5) to (15), the equilibrium mole fraction of ^{18}O and deuterium in vapor phase can be calculated and the expressions are as below:

$$y_{^{18}\text{O}} = x_{^{18}\text{O}} \cdot \frac{\left(x_{\text{H}} \alpha_{\text{H}_2^{16}\text{O}/\text{HD}^{16}\text{O}} \cdot \sqrt{\frac{\alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}}{\alpha_{\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}}}} + x_{\text{D}} \right)^2}{x_{^{16}\text{O}} \cdot \alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}} \cdot \left(x_{\text{H}} \cdot \alpha_{\text{H}_2^{16}\text{O}/\text{HD}^{16}\text{O}} + x_{\text{D}} \right)^2 + x_{^{18}\text{O}} \left(x_{\text{H}} \alpha_{\text{H}_2^{16}\text{O}/\text{HD}^{16}\text{O}} \cdot \sqrt{\frac{\alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}}{\alpha_{\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}}}} + x_{\text{D}} \right)^2} \quad (16)$$

$$y_{\text{D}} = x_{\text{D}} \cdot \frac{x_{^{16}\text{O}} \cdot \alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}} \left(x_{\text{H}} \cdot \alpha_{\text{H}_2^{16}\text{O}/\text{HD}^{16}\text{O}} + x_{\text{D}} \right) + x_{^{18}\text{O}} \left(x_{\text{H}} \cdot \alpha_{\text{H}_2^{16}\text{O}/\text{HD}^{16}\text{O}} \cdot \sqrt{\frac{\alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}}{\alpha_{\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}}}} + x_{\text{D}} \right)}{x_{^{16}\text{O}} \cdot \alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}} \cdot \left(x_{\text{H}} \cdot \alpha_{\text{H}_2^{16}\text{O}/\text{HD}^{16}\text{O}} + x_{\text{D}} \right)^2 + x_{^{18}\text{O}} \left(x_{\text{H}} \cdot \alpha_{\text{H}_2^{16}\text{O}/\text{HD}^{16}\text{O}} \cdot \sqrt{\frac{\alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}}{\alpha_{\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}}}} + x_{\text{D}} \right)^2} \quad (17)$$

The detailed derivation is shown in Appendix Eqs. (A1)–(A12). In Eq. (16), the separation factors only depend on the temperature T , and compared with Eqs. (11) and (12), it can be simplified as:

$$y_{^{18}\text{O}} = f(T, x_{\text{D}}, x_{^{18}\text{O}}) \quad (18)$$

Similarly, the Eq. (17) can be also simplified as:

$$y_{\text{D}} = g(T, x_{\text{D}}, x_{^{18}\text{O}}) \quad (19)$$

The simultaneous equations consist of Eqs. (2)–(4), (18) and (19) indicate that only liquid mole flow rate and the temperature are required to resolve all the equations at all theoretical plates when the product and feedstock conditions are given. Additionally, as the enthalpy of different isotopic water is almost the same, constant mole flow assumption is reasonable.

2.2. The dynamic simulation model

The steady state is not established immediately but over a long start-up period or equilibrium time (isotope accumulation period). According to the mole balance in Fig. 1, the change rate of mole fraction of ^{18}O and D at different time t in the liquid phase is:

$$\frac{dx_n^{^{18}\text{O}}}{dt} = \frac{L_{n-1}x_{n-1}^{^{18}\text{O}} + G_{n+1}y_{n+1}^{^{18}\text{O}} - L_nx_n^{^{18}\text{O}} - G_ny_n^{^{18}\text{O}}}{H_n} \quad (20)$$

$$\frac{dx_n^{\text{D}}}{dt} = \frac{L_{n-1}x_{n-1}^{\text{D}} + G_{n+1}y_{n+1}^{\text{D}} - L_nx_n^{\text{D}} - G_ny_n^{\text{D}}}{H_n} \quad (21)$$

where H_n is the liquid holdup of the n -th theoretical plate.

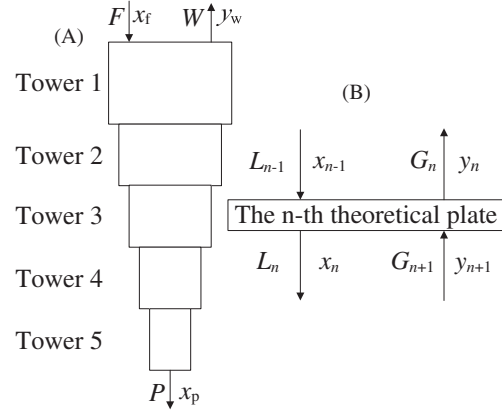


Fig. 1. Schematic diagram of the cascade system and the material streams at n -th theoretical plate for the mole balance calculation.

Assuming that the liquid inside the overhead tank is homogeneous, change rate of mole fraction of ^{18}O and D in the liquid phase is:

$$\frac{dx_{\text{tank}}^{^{18}\text{O}}}{dt} = \frac{L_o(x_i^{^{18}\text{O}} - x_o^{^{18}\text{O}})}{H} \quad (22)$$

$$\frac{dx_{\text{tank}}^{\text{D}}}{dt} = \frac{L_o(x_i^{\text{D}} - x_o^{\text{D}})}{H} \quad (23)$$

where the subscript i and o refers to inlet and outlet for the tank. To keep a stable prolonged continuous operation, L_o is 1.1 times the flow rate of the next distillation tower, and this will be discussed later.

To run the dynamic simulation, the liquid flow in each theoretical plate and in overhead tank is constant, but production P depends on the ^{18}O mole fraction of the product (stream leaving the last theoretical plate). Meanwhile, the vapor flow rate leaving the n -th theoretical plate G_n is determined by Eq. (4).

Before the product ^{18}O concentration reaches 98%, production flow rate P is 0. A PID algorithm is adopted in the dynamic simulation to determine P after the product ^{18}O concentration reaches 98% by Eq. (24):

$$P_t = P_{t-1} + K(x_{p,t}^{^{18}\text{O}} - 98\%) + Di(x_{p,t}^{^{18}\text{O}} - x_{p,t-1}^{^{18}\text{O}}) \quad (24)$$

where K and Di is the proportion coefficient and differential coefficient, respectively; t and $t-1$ refers to the t -th and the $(t-1)$ -th day. The PID parameters are optimized as 0.011574 and 0.11574 for K and Di , respectively.

Because the mole concentration change rate of ^{18}O and D at each theoretical plate varies significantly, the dynamic model may suffer from a stiff differential equation group. To achieve better stability, accuracy and efficiency, transformation is introduced [28]:

$$z_n^{^{18}\text{O}} = \ln \frac{x_n^{^{18}\text{O}}}{1-x_n^{^{18}\text{O}}}, z_n^{\text{D}} = \ln \frac{x_n^{\text{D}}}{1-x_n^{\text{D}}} \quad (25)$$

$$\frac{dz_n^{^{18}\text{O}}}{dt} = \frac{x_n^{^{18}\text{O}}}{1-x_n^{^{18}\text{O}}} \frac{dx_n^{^{18}\text{O}}}{dt}, \frac{dz_n^{\text{D}}}{dt} = \frac{x_n^{\text{D}}}{1-x_n^{\text{D}}} \frac{dx_n^{\text{D}}}{dt} \quad (26)$$

The change rate of substitution variable z is comparable and the non-stiff differential equations are easy to be resolved by ordinary integration algorithm.

2.3. Cascade process

To compare the steady-state and dynamic simulation, an open cascade process consisting of 5 distillation towers (T1 to T5) is designed for oxygen-18 production. As shown in Fig. 2, the feed-stock is directly fed into the top of T1, of which the liquid flow rate equals the feed, and pumps (P1 to P4) and condensers (E1 to E5) are used to connect the streams between towers. The vapor stream from the later tower is condensed in condenser, and subsequently, it goes back to the bottom of the former tower. To keep a stable and prolonged continuous operation, the flow rate, pumped to the overhead tank (V2 to V5), is 1.1 times of that in the next tower and the overflowing of 10% is mixed with the condensed stream back to the former tower. The final product is obtained at the bottom of T5 and its isotopic concentrations are the same with that at the last theoretical plate. The operation conditions, such as pressure, flow rate and liquid hold up, at each theoretical plate of each tower or in the overhead tank, are listed in Table 2. The pressure drop of each theoretical plate is equal, and then the pressure is determined. The temperature is estimated according to the empirical correlation between temperature and saturated vapor pressure of water.

In this cascade process, 2043 theoretical plates are used and each theoretical plate has 2 independent variables, *i.e.*, the concentration of ^{18}O and D, according to Eqs. (2)–(4), (18) and (19). So, there're totally 4086 variables in the steady state

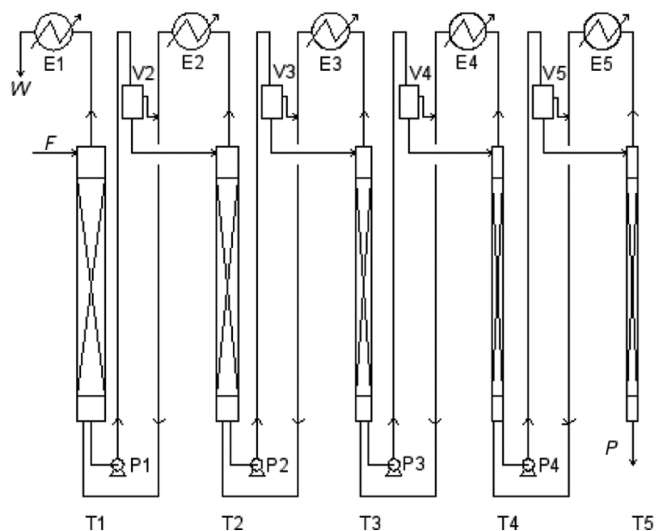


Fig. 2. Process flowchart of water distillation system consisting of five columns for ^{18}O water production.

Table 2
Process operation conditions of each tower and overhead tank

Towers or tanks	Top pressure/kPa	Bottom pressure/kPa	Theoretical plate number	Liquid flow rate/kmol·h ⁻¹	Liquid hold up ^① /kmol
T1	13.3	24.0	206	28.01	0.09527
T2	13.3	26.7	337	14.41	0.04141
T3	13.3	33.3	377	4.574	0.01122
T4	13.3	40.0	413	1.3065	0.003897
T5	13.3	53.3	710	0.3140	0.0005750
V2				15.85	0.7205
V3				5.031	0.2287
V4				1.437	0.06532
V5				0.3454	0.01570

^① The liquid hold up refers to the mole of liquid in each plate or tank.

simulation and Levenberg–Marquardt method is adopted to solve the simultaneous equations [29].

As for the dynamic simulation, the initial concentration of ^{18}O and D in each theoretical plate and overhead tank is 0.204% and 0.015%, respectively. Beside 2043 theoretical plates, 4 overhead tanks also have 8 independent variables. So, there're 4094 variables in the dynamic simulation. Herein, Adams–Bashforth–Moulton PECE Method is applied to solve the ordinary differential simultaneous equations [30].

The equations are resolved using MATLAB 2014a on a quad-core Intel CPU i7-2600 with a clock speed of 3.4 GHz and 12 GB of RAM.

3. Results and Discussion

3.1. Steady-state simulation

Given the product mole flow rate P to be $0.284531 \text{ mol} \cdot \text{h}^{-1}$, the mole concentration of ^{18}O and D at each theoretical plate is obtained based on the steady-state model in Section 2.1. The isotopic mole concentration at the bottom of each tower is listed in Table 3 and the results of lumping method, realized by Aspen Plus [20], are contained for comparison. It is obvious that the isotope distribution simulated via classical method agrees well with that by lumping method. Because of the less assumption in classical method than lumping method, the former should be more accurate.

The concentration distribution of ^{18}O and D isotopes in each theoretical plate are present in Fig. 3. A typical distribution curve is observed: the ^{18}O is enriched significantly from T3 and its concentration reaches

Table 3
The ^{18}O and D mole concentration at the bottom of each tower obtained from steady-state model and lumping method

Tower	Classical method in the present work		Lumping method	
	$^{18}\text{O}/\%$	D/%	$^{18}\text{O}/\%$	D/%
T1	0.406	0.0290	0.407	0.0285
T2	1.60	0.0917	1.61	0.0921
T3	9.20	0.322	9.24	0.323
T4	50.3	1.31	50.3	1.35
T5	98.0	70.8	98.0	70.9

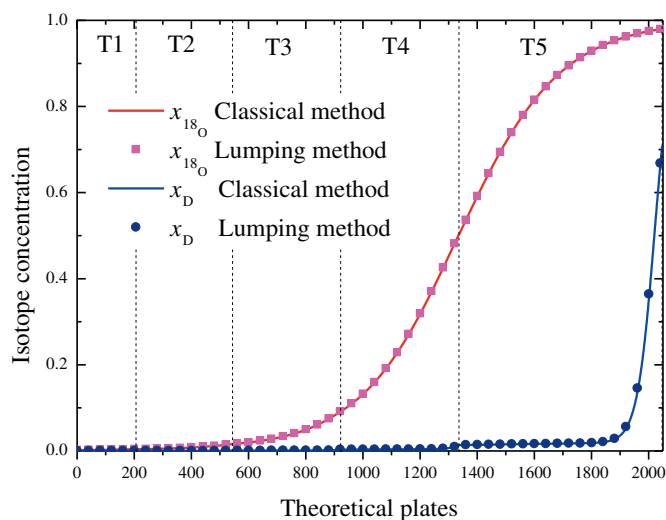


Fig. 3. Isotope distribution at each theoretical plate.

98% at the bottom of T5. On the contrary, the D concentration increases slightly before T5 and it increases rapidly near the bottom of T5. This difference may result from the lower initial D concentration, but higher D separation factor than that of ^{18}O . At the beginning of the distillation, the low natural abundance is the main resistance. When the concentration increases to a considerable value, the separation factor plays a key role for further enrichment. Thus, the increase of ^{18}O concentration is much flatter than that of D isotope.

3.2. Dynamic simulation

Before the analysis of dynamic simulation, some variables should be defined. Relative extraction ratio η is used to measure the ability for isotopes extraction from the inlet stream at the top of each tower:

$$\eta_I = \frac{j_I}{j_{I,\max}} \quad (27)$$

where I refers to different isotopes, ^{18}O and D. The isotope transfer rates are defined as:

$$j_I = Lx_{If} - Gy_I \quad (28)$$

$$j_{I,\max} = Lx_{If} - Gy_I^* \quad (29)$$

where x_{If} is the feed mole fraction to the tower, y_I^* is in equilibrium with x_{If} at certain conditions and y_I is the outlet vapor mole fraction, which is in equilibrium with the outlet liquid mole fraction leaving the first theoretical plate of the tower. Generally, at stable state, η is between 0 and 1, as y_I gradually decrease to y_I^* when the theoretical plates increase to infinite. Another important variable is product withdraw and it is expressed as the mole flow rate of isotope in product:

$$\text{WD}_I = P \times x_p^I \quad (30)$$

When the distillation process reaches stable state, WD_I should be equal to j_I of each tower.

3.2.1. Global isotope distribution

The isotope distribution at each plate in a time period of 1000 days is present in Fig. 4. It takes 171 days to reach the desired ^{18}O mole fraction of 98% at the last theoretical plate, and subsequently, the PID control Eq. (24) is applied to slowly increase the product flow rate to maintain the ^{18}O concentration in the product. During this unsteady period, significant changes in ^{18}O and D concentration distribution of T3 to T5 are observed.

The ^{18}O concentration in T3 and T4 increases and reaches maximum directly following that in T5; after a long time at high concentration level, a considerable decrease is observed for T3 and T4; and subsequently, both towers remain constant. The T1 and T2 towers may experience similar increase and decrease procedure, but it is difficult to be observed because of the rather low concentration. Differently, the D concentration in T5 increases rapidly to about 100% at the bottom of the tower and that in T4 also increases quickly after the T5 reaches the highest concentration. Then, the D concentration in T4 gradually decreases to a very small value and remain constant. After that, D concentration in T5 suffers from a rapid decrease, and subsequently, a slight increase to reach the steady condition. T1, T2 and T3 seem to be more stable after a sharp increase at the beginning.

Totally, about 800 days are required to approach final steady state for all towers and it is really a long time for industry. However, it is only about 400 days for the product flow rate to reach 95% of the designed value and significant amount of product is obtained during the start-up period. Additionally, a detailed video of isotope distribution at different time is attached as an accessory.

3.2.2. Explanation of the concentration distribution

The isotope distribution evolution is mainly influenced by isotope transfer rate j into the towers and product withdraw WD leaving the systems. Furthermore, j comes from the bottom of the previous tower or the feedstock (Fig. 2), and WD is determined by Eq. (30). Because the PID control Eq. (24) is applied, the product ^{18}O concentration is limited to $(98 \pm 0.04)\%$ and the increase trend of ^{18}O concentration results in the increase of product flow rate. Generally, this increase trend exists before the steady state and is enhanced by the improved separation factor of ^{18}O . In fact, the separation factor of $^{16}\text{O}/^{18}\text{O}$ and H/D can be expressed as:

$$\alpha_{^{16}\text{O}/^{18}\text{O}} = \alpha_{\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}} \cdot \alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}} \cdot \lambda_D^2 \quad (31)$$

$$\alpha_{\text{H}/\text{D}} = \frac{\lambda_D \cdot x_{^{16}\text{O}} \alpha_{\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}} \alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}} + x_{^{18}\text{O}} \cdot \sqrt{\alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}}}}{\lambda_D \cdot x_{^{16}\text{O}} \alpha_{\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}} \alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}} + x_{^{18}\text{O}} \cdot \sqrt{\alpha_{\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}}}} \quad (32)$$

where:

$$\lambda_D = \frac{x_{\text{H}} \cdot \alpha_{\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}} + x_{\text{D}}}{x_{\text{H}} \cdot \alpha_{\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}} \cdot \sqrt{\alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}}} + x_{\text{D}} \cdot \sqrt{\alpha_{\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}}}} \quad (33)$$

The effect of D concentration is observed in parameter λ_D and its value decrease with the x_{D} , which should be responsible for the interesting change of isotope distribution.

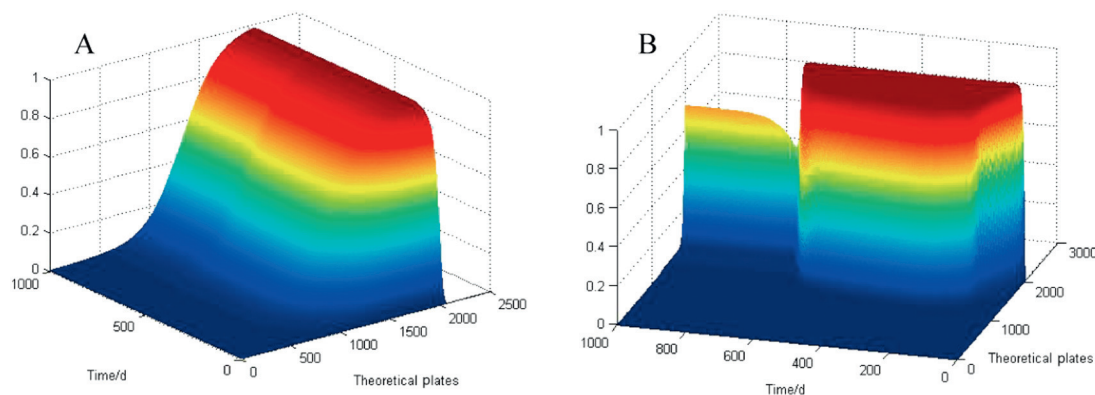


Fig. 4. Concentration distributions of ^{18}O (A) and D (B) at each plate during 1000 days.

Firstly, the isotope transfer rate at feedstock position and product withdraw of ^{18}O and D is shown in Fig. 5A, and the relative extraction ratio at feedstock position is represent in Fig. 5B. Due to the perfect ability for D separation, the η_D and j_D is almost constant along the simulation period. According to the value of transfer rate and product withdraw, five stages are divided as listed in Table 4.

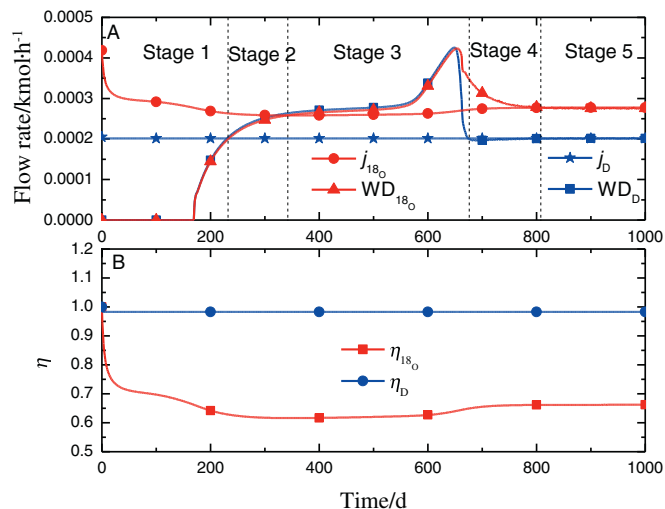


Fig. 5. Isotope extraction and withdraw at different times.

Table 4

The standard to divide the simulation period into five stages

Stage	^{18}O	D	Time region/d
1	$WD < j$	$WD < j$	0–231
2	$WD < j$	$WD > j$	232–341
3	$WD > j$	$WD > j$	342–675
4	$WD > j$	$WD < j$	676–808
5	$WD \approx j$	$WD \approx j$	809–1000

The isotope concentration at the bottom of each tower for ^{18}O and D is exhibited in Figs. 6 and 7, respectively. In stage 1, isotopes are accumulated in the towers and significant increase of ^{18}O and D concentration is observed until stage 2. The D concentration at T4 reaches the maximum when entering stage 2, and

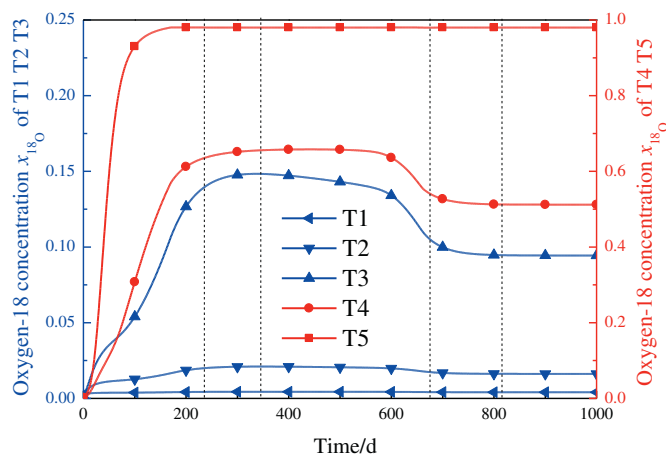


Fig. 6. Oxygen-18 concentration at the bottom of each column versus time.

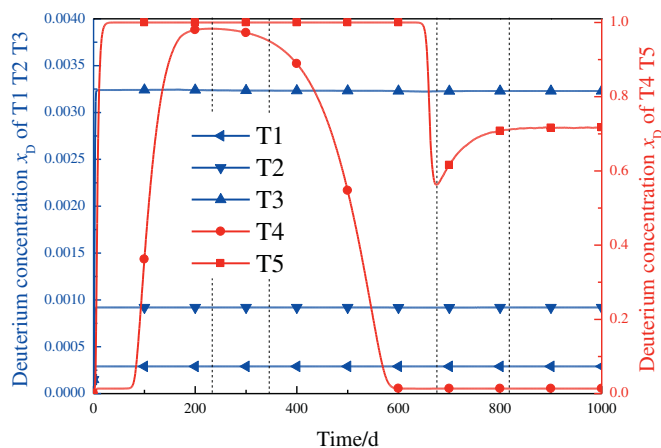


Fig. 7. Deuterium concentration at the bottom of each column versus time.

subsequently, decreases because of WD_D is larger than j_D , while the ^{18}O concentration continue to increase. Early in stage 3, ^{18}O concentration decreases very slowly, due to the close value of $WD_{^{18}\text{O}}$ and $j_{^{18}\text{O}}$. Meanwhile, the D concentration in T4 still decrease rapidly. Later in stage 3, two opposite forces exist to affect the increase trend of ^{18}O concentration in the product. 1) The decreased D concentration results in larger λ_D and then, higher separation factor of $^{16}\text{O}/^{18}\text{O}$ is obtained, according to Eq. (31) and (33). Thus, increase trend of ^{18}O concentration is strengthened. 2) The ^{18}O concentration at the bottom of T4 decrease in stage 3, resulting in decreased isotope transfer rates into T5. Then, there is no enough isotope in the tower to support the product withdraw and the increase trend of ^{18}O concentration is weakened. The increased separation factor forces the WD of ^{18}O and D to increase quickly and further decrease the D concentration. However, the separation factor is limited due to the finite value of λ_D and the weakened isotope transfer becomes significant to decrease the WD. Therefore, a peak value of WD is observed near 650 days, and then, WD_D decreases until the end of stage 3. The ^{18}O concentration and WD slowly decrease to realize a steady state in stage 4. But the D concentration in T5 slightly increases, because of a quite small value of WD_D lower than j_D . In fact, a video attachment is available and it will exhibit the evaluation process much clear and comprehensible.

In summary, D concentration significantly influence the ^{18}O separation through the effect on separation factor of $^{16}\text{O}/^{18}\text{O}$ and a product withdraw peak value is observed before the final steady state. The isotope transfer rate into the towers and product withdraw leaving the systems are coupled to determine the isotope concentration during the start-up procedure.

3.2.3. Low concentration zone in towers

At the beginning of start-up procedure, as shown in Fig. 8, the ^{18}O relative extraction ratio η for T2–T5 exceed 1, namely $y < y^*$ according to Eq. (27) to (29). Clearly in Fig. 9, low concentration zones, namely that ^{18}O concentration in the middle is low than both the top and bottom of the towers, in T4 and T5 at the 10th day as an example are observed on the isotope concentration distribution curve, when the relative extraction ratio is larger than 1. In fact, the low ^{18}O concentration in the middle of the towers will results in vapor stream with low ^{18}O concentration; and this vapor stream rises upward to the top to exchange with the liquid stream. At the top of the towers, ^{18}O concentration of vapor stream $y_{^{18}\text{O}}$ will be smaller than $y_{^{18}\text{O}}^*$, when the ^{18}O concentration in low concentration zones are small enough. Thus, that the relative extraction ratio is larger than 1 is obtained according to Eq. (27) to (29),

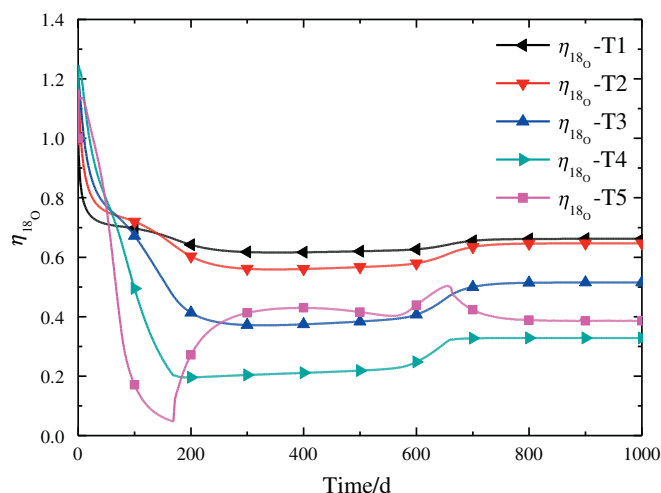


Fig. 8. The change of isotope relative extraction ratio of each tower at different time.

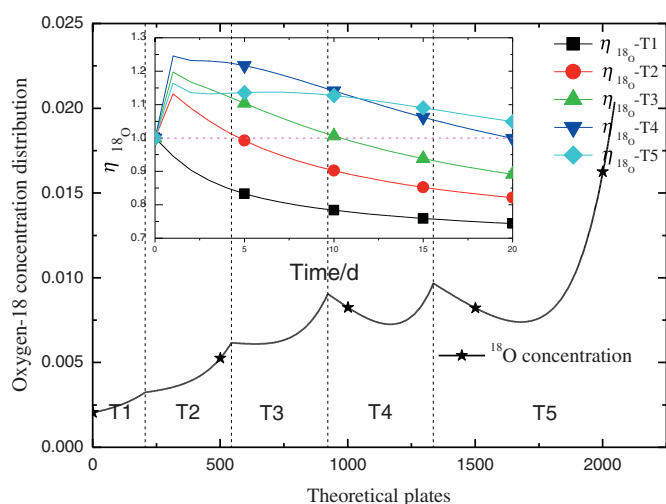


Fig. 9. Relative extraction ratio at the beginning of the simulation and ^{18}O distribution at the 10th day.

indicating that the outlet liquid concentration of the first theoretical plate in the tower is smaller than the feed concentration to the tower x_{Mf} . However, this valley does not exist in T1 and its relative extraction ratio is smaller than 1.

One possible explanation for the low concentration zone is presented here: When there is no additional feed at the top of the tower, i.e., in the case of total reflux, the separation effect will result in that ^{18}O concentration gradually decreases with time in the upper part of tower and increases in the bottom part. However, when a liquid stream with high ^{18}O concentration, accumulated in the previous tower, is fed at the top, the mixture effect will increase the concentration at this point, but it takes some time to transfer the enriched isotope to the middle of the tower. Thus, a low concentration zone is formed if the stream fed in is concentrated enough.

Meanwhile, this phenomenon is observed only at the beginning of the start-up procedure and in the latter towers (T2, T3, T4 and T5). Nevertheless, special attention should be paid to proof the existence of the low concentration zone when a new industrial production line goes to operation.

4. Conclusions

The steady-state and dynamic simulation models of ^{18}O isotope water separation in a cascade system are established and the effect of Deuterium isotope is presented. The steady-state simulation results indicate that the classical method and the lumping method corroborate mutually. The dynamic process of the example, which is significantly influenced by the D concentration, can be divided into 5 stages. The method shows prospective application of simulation and optimization of the oxygen-18 water, heavy water and deuterium depleted water production system.

Nomenclature

Di	differential coefficient
G_n	mole flow rate of gas, $\text{kmol} \cdot \text{h}^{-1}$
H_n	liquid hold up, kmol
j_I	isotope transfer rate of ^{18}O or D, $\text{kmol} \cdot \text{h}^{-1}$
$j_{I,\max}$	maximum isotope transfer rate of ^{18}O or D, $\text{kmol} \cdot \text{h}^{-1}$
K	proportion coefficient
L_n	mole flow rate of liquid, $\text{kmol} \cdot \text{h}^{-1}$
P	production rate, $\text{kmol} \cdot \text{h}^{-1}$
P_t	production flow rate at the t -th day, $\text{kmol} \cdot \text{h}^{-1}$
p_M	partial pressure of molecule M
p_M^*	saturated vapor pressure of molecule M
p_{total}	total pressure
WD_I	product withdraw of ^{18}O or D, $\text{kmol} \cdot \text{h}^{-1}$
x_{If}	mole percent of ^{18}O or D in the feed stream to the 1st tower
x_i^D	mole percent of D of the inlet stream of the tank
$x_i^{18\text{O}}$	mole percent of ^{18}O of the inlet stream of the tank
x_{Mn}	mole percent of molecule M in liquid phase
$x_n^{18\text{O}}$	mole percent of ^{18}O in the liquid stream leaving the n -th theoretical plate
x_n^D	mole percent of D in the liquid stream leaving the n -th theoretical plate
x_o^D	mole percent of D of the outlet stream of the tank
$x_o^{18\text{O}}$	mole percent of ^{18}O of the outlet stream of the tank
$x_o^{18\text{O}}$	mole percent of ^{18}O or D in the product stream
$x_p^{18\text{O}}$	mole percent of ^{18}O in the product stream
y_I	mole percent of ^{18}O or D in the vapor stream leaving the 1st tower
y_I^*	mole percent of molecule M in equilibrium with x_{If}
y_M	mole percent of molecule M in the vapor phase
y_n^D	mole percent of D in the vapor phase leaving the n -th theoretical plate
$y_n^{18\text{O}}$	mole percent of ^{18}O in the vapor phase leaving the n -th theoretical plate
$\alpha_{D_2^{16}\text{O}/D_2^{18}\text{O}}$	separation factor for $D_2^{16}\text{O}$ and $D_2^{18}\text{O}$
$\alpha_{H_2^{16}\text{O}/HD^{16}\text{O}}$	separation factor for $H_2^{16}\text{O}$ and $HD^{16}\text{O}$
$\alpha_{H_2^{16}\text{O}/H_2^{18}\text{O}}$	separation factor for $H_2^{16}\text{O}$ and $H_2^{18}\text{O}$
$\alpha_{H/D}$	separation factor for H and D
$\alpha_{^{16}\text{O}/^{18}\text{O}}$	separation factor for ^{16}O and ^{18}O
η_I	relative extraction ratio of ^{18}O or D

Acknowledgements

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Appendix

A.1. The derivation of vapor phase equilibrium mole fraction for ^{18}O

The Dalton's law gives the vapor-phase ^{18}O fraction as below:

$$y_{^{18}\text{O}} = \frac{p_{\text{H}_2^{18}\text{O}} + p_{\text{HD}^{18}\text{O}} + p_{\text{D}_2^{18}\text{O}}}{p_{\text{total}}} \quad (\text{A1})$$

Then,

$$y_{^{18}\text{O}} = \frac{p_{\text{H}_2^{18}\text{O}} + p_{\text{HD}^{18}\text{O}} + p_{\text{D}_2^{18}\text{O}}}{p_{\text{H}_2^{16}\text{O}} + p_{\text{HD}^{16}\text{O}} + p_{\text{D}_2^{16}\text{O}} + p_{\text{H}_2^{18}\text{O}} + p_{\text{HD}^{18}\text{O}} + p_{\text{D}_2^{18}\text{O}}} \quad (\text{A2})$$

The Raoult's law is applied to exhibit the relationship with liquid phase:

$$y_{^{18}\text{O}} = \frac{x_{\text{H}_2^{18}\text{O}} \cdot p_{\text{H}_2^{18}\text{O}}^* + x_{\text{HD}^{18}\text{O}} \cdot p_{\text{HD}^{18}\text{O}}^* + x_{\text{D}_2^{18}\text{O}} \cdot p_{\text{D}_2^{18}\text{O}}^*}{x_{\text{H}_2^{16}\text{O}} \cdot p_{\text{H}_2^{16}\text{O}}^* + x_{\text{HD}^{16}\text{O}} \cdot p_{\text{HD}^{16}\text{O}}^* + x_{\text{D}_2^{16}\text{O}} \cdot p_{\text{D}_2^{16}\text{O}}^* + x_{\text{H}_2^{18}\text{O}} \cdot p_{\text{H}_2^{18}\text{O}}^* + x_{\text{HD}^{18}\text{O}} \cdot p_{\text{HD}^{18}\text{O}}^* + x_{\text{D}_2^{18}\text{O}} \cdot p_{\text{D}_2^{18}\text{O}}^*} \quad (\text{A3})$$

where, p^* is saturated vapor pressure and that of HD^{16}O and HD^{18}O is determined via geometric mean rule. Thus, it can be further expressed as:

$$y_{^{18}\text{O}} = \frac{x_{\text{H}_2^{18}\text{O}} \cdot \frac{p_{\text{H}_2^{18}\text{O}}^*}{p_{\text{D}_2^{18}\text{O}}^*} + x_{\text{HD}^{18}\text{O}} \cdot \frac{p_{\text{HD}^{18}\text{O}}^*}{p_{\text{D}_2^{18}\text{O}}^*} + x_{\text{D}_2^{18}\text{O}}}{x_{\text{H}_2^{16}\text{O}} \cdot \frac{p_{\text{H}_2^{16}\text{O}}^*}{p_{\text{D}_2^{16}\text{O}}^*} + x_{\text{HD}^{16}\text{O}} \cdot \frac{p_{\text{HD}^{16}\text{O}}^*}{p_{\text{D}_2^{16}\text{O}}^*} + x_{\text{D}_2^{16}\text{O}} \cdot \frac{p_{\text{D}_2^{16}\text{O}}^*}{p_{\text{D}_2^{16}\text{O}}^*} + x_{\text{H}_2^{18}\text{O}} \cdot \frac{p_{\text{H}_2^{18}\text{O}}^*}{p_{\text{D}_2^{18}\text{O}}^*} + x_{\text{HD}^{18}\text{O}} \cdot \frac{p_{\text{HD}^{18}\text{O}}^*}{p_{\text{D}_2^{18}\text{O}}^*} + x_{\text{D}_2^{18}\text{O}}} \quad (\text{A4})$$

and,

$$y_{^{18}\text{O}} = \frac{x_{\text{H}_2^{18}\text{O}} \cdot \frac{p_{\text{H}_2^{18}\text{O}}^*}{p_{\text{D}_2^{18}\text{O}}^*} + x_{\text{HD}^{18}\text{O}} \cdot \sqrt{\frac{p_{\text{H}_2^{18}\text{O}}^*}{p_{\text{D}_2^{18}\text{O}}^*}} + x_{\text{D}_2^{18}\text{O}}}{x_{\text{H}_2^{16}\text{O}} \cdot \frac{p_{\text{H}_2^{16}\text{O}}^*}{p_{\text{D}_2^{16}\text{O}}^*} + x_{\text{HD}^{16}\text{O}} \cdot \sqrt{\frac{p_{\text{H}_2^{16}\text{O}}^* \cdot p_{\text{D}_2^{16}\text{O}}^*}{p_{\text{D}_2^{16}\text{O}}^*}} + x_{\text{D}_2^{16}\text{O}} \cdot \frac{p_{\text{D}_2^{16}\text{O}}^*}{p_{\text{D}_2^{16}\text{O}}^*} + x_{\text{H}_2^{18}\text{O}} \cdot \frac{p_{\text{H}_2^{18}\text{O}}^*}{p_{\text{D}_2^{18}\text{O}}^*} + x_{\text{HD}^{18}\text{O}} \cdot \sqrt{\frac{p_{\text{H}_2^{18}\text{O}}^*}{p_{\text{D}_2^{18}\text{O}}^*}} + x_{\text{D}_2^{18}\text{O}}} \quad (\text{A5})$$

The saturated vapor pressure is related to the separation factor based on ideal consumptions and Eqs. (13)–(15) will be applied here:

$$\frac{p_{\text{H}_2^{18}\text{O}}^*}{p_{\text{D}_2^{18}\text{O}}^*} = \frac{\alpha_{\text{H}_2^{16}\text{O}/\text{HD}^{16}\text{O}}^2 \cdot \alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}}}{\alpha_{\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}}} \quad (\text{A6})$$

$$\frac{p_{\text{H}_2^{16}\text{O}}^*}{p_{\text{D}_2^{18}\text{O}}^*} = \alpha_{\text{H}_2^{16}\text{O}/\text{HD}^{16}\text{O}}^2 \cdot \alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}} \quad (\text{A7})$$

$$\frac{\sqrt{p_{\text{H}_2^{16}\text{O}}^* \cdot p_{\text{D}_2^{16}\text{O}}^*}}{p_{\text{D}_2^{18}\text{O}}^*} = \alpha_{\text{H}_2^{16}\text{O}/\text{HD}^{16}\text{O}} \cdot \alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}} \quad (\text{A8})$$

thus:

$$y_{^{18}\text{O}} = x_{^{18}\text{O}} \cdot \frac{\left(x_{\text{H}} \alpha_{\text{H}_2^{16}\text{O}/\text{HD}^{16}\text{O}} \cdot \sqrt{\frac{\alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}}}{\alpha_{\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}}}} + x_{\text{D}} \right)^2}{x_{^{16}\text{O}} \cdot \alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}} \cdot \left(x_{\text{H}} \cdot \alpha_{\text{H}_2^{16}\text{O}/\text{HD}^{16}\text{O}} + x_{\text{D}} \right)^2 + x_{^{18}\text{O}} \left(x_{\text{H}} \alpha_{\text{H}_2^{16}\text{O}/\text{HD}^{16}\text{O}} \cdot \sqrt{\frac{\alpha_{\text{D}_2^{16}\text{O}/\text{D}_2^{18}\text{O}}}{\alpha_{\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}}}} + x_{\text{D}} \right)^2} \quad (\text{A9})$$

A.2. The derivation of vapor phase equilibrium mole fraction for D

Similarly, Dalton's law and Raoult's law are used for the derivation:

$$y_{\text{D}} = \frac{p_{\text{HD}^{16}\text{O}}/2 + p_{\text{D}_2^{16}\text{O}} + p_{\text{HD}^{18}\text{O}}/2 + p_{\text{D}_2^{18}\text{O}}}{p_{\text{total}}} \quad (\text{A10})$$

And,

$$y_D = \frac{x_{HD^{16}O} \cdot p_{HD^{16}O}^*/2 + x_{D_2^{16}O} \cdot p_{D_2^{16}O}^* + x_{HD^{18}O} \cdot p_{HD^{18}O}^*/2 + x_{D_2^{18}O} \cdot p_{D_2^{18}O}^*}{x_{H_2^{16}O} \cdot p_{H_2^{16}O}^* + x_{HD^{16}O} \cdot p_{HD^{16}O}^* + x_{D_2^{16}O} \cdot p_{D_2^{16}O}^* + x_{H_2^{18}O} \cdot p_{H_2^{18}O}^* + x_{HD^{18}O} \cdot p_{HD^{18}O}^* + x_{D_2^{18}O} \cdot p_{D_2^{18}O}^*} \quad (A11)$$

Replacing the saturated vapor pressure with separation factor gives the formation:

$$y_D = x_D \cdot \frac{x_{16O} \cdot \alpha_{D_2^{16}O/D_2^{18}O} (x_H \cdot \alpha_{H_2^{16}O/HD^{16}O} + x_D) + x_{18O} \left(x_H \cdot \alpha_{H_2^{16}O/HD^{16}O} \cdot \sqrt{\frac{\alpha_{D_2^{16}O/D_2^{18}O}}{\alpha_{H_2^{16}O/H_2^{18}O}}} + x_D \right)}{x_{16O} \cdot \alpha_{D_2^{16}O/D_2^{18}O} \cdot (x_H \cdot \alpha_{H_2^{16}O/HD^{16}O} + x_D)^2 + x_{18O} \left(x_H \cdot \alpha_{H_2^{16}O/HD^{16}O} \cdot \sqrt{\frac{\alpha_{D_2^{16}O/D_2^{18}O}}{\alpha_{H_2^{16}O/H_2^{18}O}}} + x_D \right)^2} \quad (A12)$$

A.3. The derivation of separation factor for H/D and $^{16}O/^{18}O$

According to the definition of separation factor, the $\alpha_{H/D}$ is expressed as below:

$$\alpha_{H/D} = \frac{x_D y_H}{x_H y_D} \quad (A13)$$

and,

$$\alpha_{H/D} = \frac{x_{HD^{16}O}/2 + x_{D_2^{16}O} + x_{HD^{18}O}/2 + x_{D_2^{18}O} y_{H_2^{16}O} + y_{HD^{16}O}/2 + y_{H_2^{18}O} + y_{HD^{18}O}/2}{x_{H_2^{16}O} + x_{HD^{16}O}/2 + x_{H_2^{18}O} + x_{HD^{18}O}/2 + y_{HD^{16}O}/2 + y_{D_2^{16}O} + y_{HD^{18}O}/2 + y_{D_2^{18}O}} \quad (A14)$$

Replacing the vapor mole fraction gives the formation:

$$\alpha_{H/D} = \frac{x_H \cdot x_{16O} \cdot p_{H_2^{16}O}^* + x_D \cdot x_{16O} \cdot p_{HD^{16}O}^* + x_H \cdot x_{18O} \cdot p_{H_2^{18}O}^* + x_D \cdot x_{18O} \cdot p_{HD^{18}O}^*}{x_H \cdot x_{16O} \cdot p_{H_2^{16}O}^* + x_D \cdot x_{16O} \cdot p_{D_2^{16}O}^* + x_H \cdot x_{18O} \cdot p_{H_2^{18}O}^* + x_D \cdot x_{18O} \cdot p_{D_2^{18}O}^*} \quad (A15)$$

And finally:

$$\alpha_{H/D} = \alpha_{H_2^{16}O/HD^{16}O} \frac{(x_H \cdot \alpha_{H_2^{16}O/HD^{16}O} + x_D) \cdot x_{16O} \cdot \alpha_{H_2^{16}O/H_2^{18}O} \cdot \alpha_{D_2^{16}O/D_2^{18}O} + x_{18O} \cdot \sqrt{\alpha_{D_2^{16}O/D_2^{18}O}} (x_H \cdot \alpha_{H_2^{16}O/HD^{16}O} \cdot \sqrt{\alpha_{D_2^{16}O/D_2^{18}O}} + x_D \cdot \sqrt{\alpha_{H_2^{16}O/H_2^{18}O}})}{(x_H \cdot \alpha_{H_2^{16}O/HD^{16}O} + x_D) \cdot x_{16O} \cdot \alpha_{H_2^{16}O/H_2^{18}O} \cdot \alpha_{D_2^{16}O/D_2^{18}O} + x_{18O} \cdot \sqrt{\alpha_{H_2^{16}O/H_2^{18}O}} (x_H \cdot \alpha_{H_2^{16}O/HD^{16}O} \cdot \sqrt{\alpha_{D_2^{16}O/D_2^{18}O}} + x_D \cdot \sqrt{\alpha_{H_2^{16}O/H_2^{18}O}})} \quad (A16)$$

Similarly, separation factor of $^{16}O/^{18}O$ is derived

$$\alpha_{^{16}O/^{18}O} = \frac{\alpha_{H_2^{16}O/H_2^{18}O} \cdot \alpha_{D_2^{16}O/D_2^{18}O} \cdot (x_H \cdot \alpha_{H_2^{16}O/HD^{16}O} + x_D)^2}{(x_H \cdot \alpha_{H_2^{16}O/HD^{16}O} \cdot \sqrt{\alpha_{D_2^{16}O/D_2^{18}O}} + x_D \cdot \sqrt{\alpha_{H_2^{16}O/H_2^{18}O}})^2} \quad (A17)$$

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