Mathematical Model of Heavy Water Extraction and Distillation

M. P. BURGESS

E. I. duPont de Nemours and Company, Aiken, South Carolina

A mathematical model of the heavy water production facility at the Savannah River Plant, an installation of the U.S. Atomic Energy Commission at Aiken, South Carolina, operated by E. I. du Pont de Nemours and Company, was developed because measured production rates, even when averaged over one-month periods, are inadequately precise for process control. With this model the instantaneous steady state production rate for any set of process conditions is calculated with precision. Therefore the model is used to establish process set points for achieving production goals, to study the effect of important process variables on these goals, and to evaluate proposed changes of equipment. In fact, with only minor changes in the computer program, several features of a newly designed heavy water plant are being evaluated.

Heavy water is extracted from natural water and concentrated from 0.015% to 10 to 20% by dual temperature exchange with hydrogen sulfide gas (GS process). The solution is then concentrated to nearly 100% D_2O by continuous vacuum distillation. The processes are shown schematically in Figure 1, and were described in detail by Bebbington (*1*).

Extraction of heavy water from natural water requires that certain process variables be set and controlled within a few percent of optimum. But the effects of their setting and variation are difficult to assess because the in-process inventory of deuterium oxide is about 100 times the daily production, and the concentrations of deuterium oxide in the several bubble-tray towers are difficult to measure with sufficient precision. The only realistic measure of production rate is based on monthly inventories (lb. D_2O) of heavy water in drums and estimates of deuterium oxide in process. Daily average production rates, calculated from monthly inventories and estimates of material in process, are unsatisfactory for evaluating small changes in process variables.

During design of the GS process prior to 1952, equations were developed to describe material flow rates, operating conditions, and equilibrium constants (*1*). Equations were computed manually, and tray-to-tray problems were solved with McCabe-Thiele diagrams. Approximations, frequently graphical, had to suffice; no attempt was made to close the overall material balances or to determine optimum liquid-to-gas ratios in the towers. Many of those design equations were used in the mathematical model described in this paper; however they were solved numerically on a digital computer, with the model programmed in Fortran IV for the IBM 360/65 computer. An exact solution of simultaneous equations is not possible by either method of calculation because material-balance equations depend on tray-to-tray calculations with curved equilibrium lines to define many of the terminal concentrations. Each solution requires a series of nested successive approximations in which the guesses for values of implicit variables are improved with each loop until the overall material balances are ultimately closed to within some acceptable tolerance.

A decidedly important advantage of using a computer for the calculations is that iterations can be performed so rapidly that closing material balances is practical; whereas time-consuming manual computations—frequently with scant data—gave only approximations to closed material balances.

ALGORITHM

Calculations, either manual or by computer, start with specifying the desired product concentration from the distillation process and temporarily estimating a GS process drawoff concentration from the problem conditions. Figures 2 and 3 are flowsheets of the calculation procedures; each step of process is separately explained in the ensuing discussion.

Vacuum Distillation

Because deuterium oxide is less volatile than hydrogen oxide, it can be concentrated from about 10 to nearly 100% economically by vacuum distillation. At the Savannah River Plant distillation columns comprising 444 bubble trays are connected in series to achieve this deuterium enrichment. This equipment is designated as *DW* in Figure 1. Tray-to-tray calculations in the model of this process start with the tray at which product is drawn off and proceed sequentially through the columns to the tray at which distillate is drawn off.

The calculations are based on a two-component system, hydroxen oxide-deuterium oxide as discussed by Bebbing-

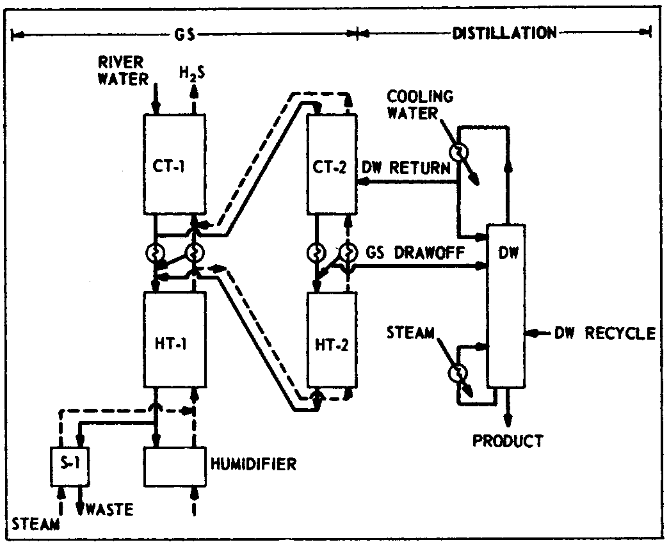

Fig. 1. GS and distillation processes.

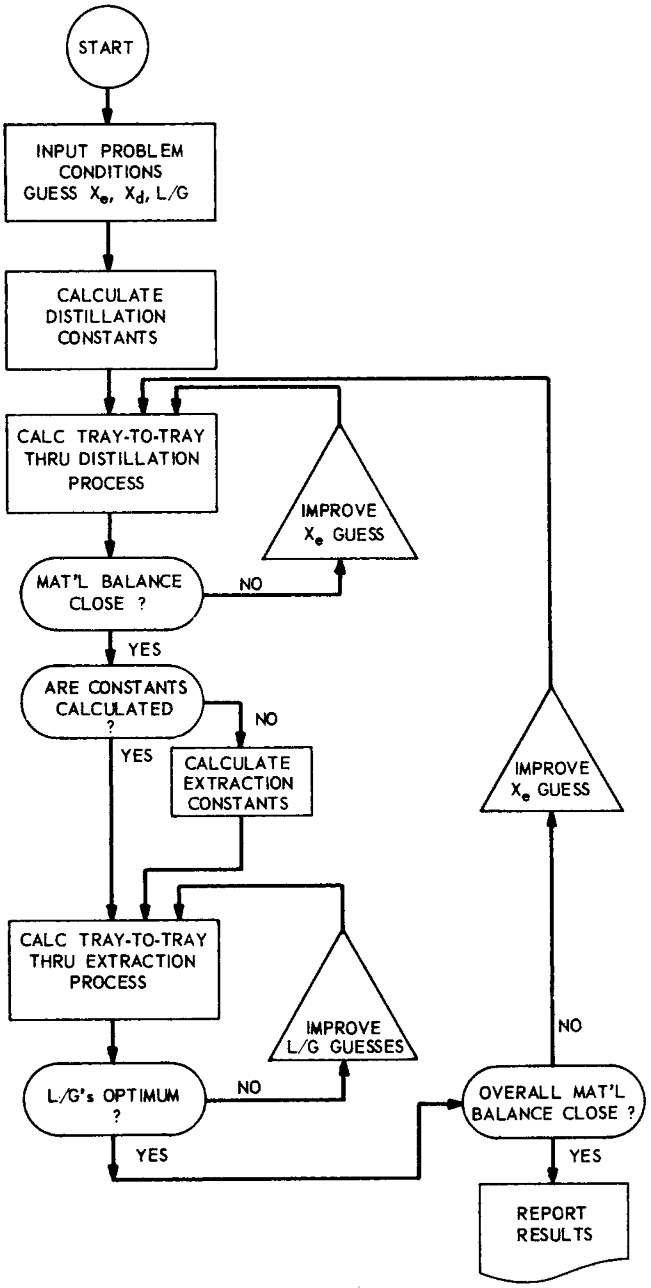

Fig. 2. Program procedure.

ton (*2*), although a three-component system, hydrogen oxide-hydrogen deuterium oxide-deuterium oxide, really exists. Comparative calculations with both systems were made in a previous study and the separative work performed and concentration gradients agreed sufficiently well that the simpler binary system continued in use.

The problem conditions for the distillation process are the product concentration, the head pressure and boilup rate of each column, and the distillate drawoff rate. From these, a number of problem constants are calculated before starting the tray-to-tray iterations. The pressure over each tray is calculated tray-to-tray, starting with each column head pressure, using equations given by Robinson and Gilliland (*3*). The correlating factor for pressure drop through the bubble cap was changed from the 6.0 suggested by Robinson and Gilliland to 5.50 to bring into agreement the overall measured and calculated column pressure differentials.

The pressure at each tray was converted to the corresponding temperature (τ) for saturated steam with the Keenan and Keyes (*4*) equation by successive approximation (see Loop Closure, below). The relative volatility (α) of hydrogen oxide (H_2O) to hydrogen deuterium oxide (HDO) is then calculated for the conditions over each tray with the equation (*5*)

$$\alpha = 0.86211 \; e^{65.43/\tau}$$

where τ is in degrees Kelvin. Typical results from the tray-to-tray calculation of pressure, temperature, and α are shown in Figure 4.

The Murphree tray efficiency was estimated for each column from the physical data at the temperature and pressure at the top of each column. The calculation method is described in the worksheet appended to the *AIChE Bubble-Tray Design Manual* (*6*). Tray efficiencies calculated by this method were found in good agreement with the results of plant tests in 1961, as illustrated in Figure 5.

To begin the tray-to-tray calculations, the product concentration X_b (the D_2O concentration of liquor collected in the base of the first column) is fixed and the distillate concentration X_d is taken as 0.6 of the assumed GS process drawoff concentration X_e, for the initial estimate. Then the distillate rate D and GS process product drawoff rate F_e are calculated from material balances around the distillation columns:

$$B = \frac{D(X_e - X_d) + F_r\,(X_r - X_e)}{X_b - X_e}$$

$$F_e = B + D - F_r$$

The vapor flowing to the bottom tray of each column is assumed to be in equilibrium with the liquor collected in

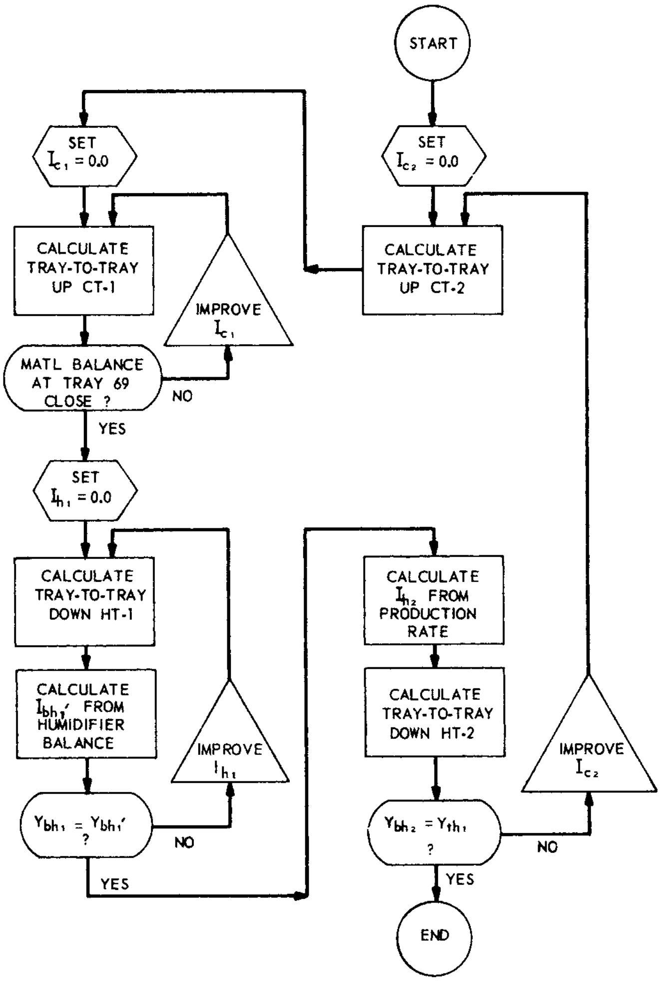

Fig. 3. The GS process subprogram procedure.

the base of that column, and its concentration is calculated with the equilibrium equation below. Then the vapor and liquid D_2O concentrations leaving each tray are calculated with successive solutions of these equations:

$$X_n = a + b\ Y_n$$

$$Y_n^* = \frac{X_n}{\alpha_n\,(1 - X_n) + X_n}$$

$$Y_{n+1} = Y_n - E_{mv}\,(Y_n - Y_n^*)$$

The constants a and b in the operating line equation are determined for each column material balances through the column and around the bottom of the system. The vapor from the last tray is totally condensed, so the value of Y_{n+1} is compared with the previous estimate of X_d. If the absolute difference is not within a preset tolerance, such as 0.0001 Y_{n+1}, the guess for X_d is improved (as discussed under Loop Closure) and the tray-to-tray calculation is repeated.

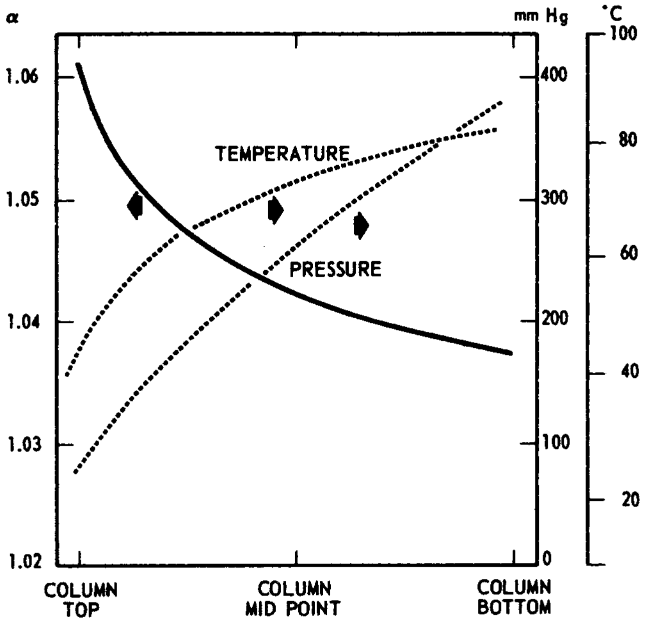

Fig. 4. Typical separation factors (α) in the distillation towers.

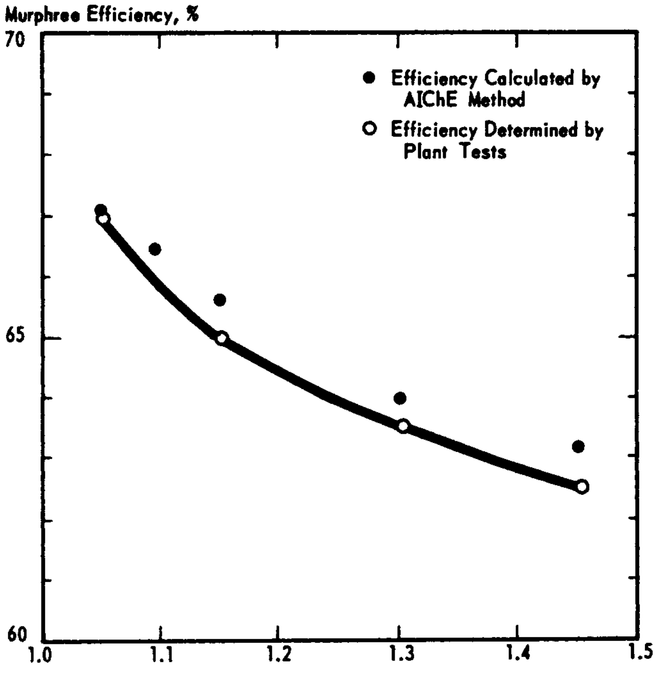

Fig. 5. Tray efficiencies in vacuum distillation.

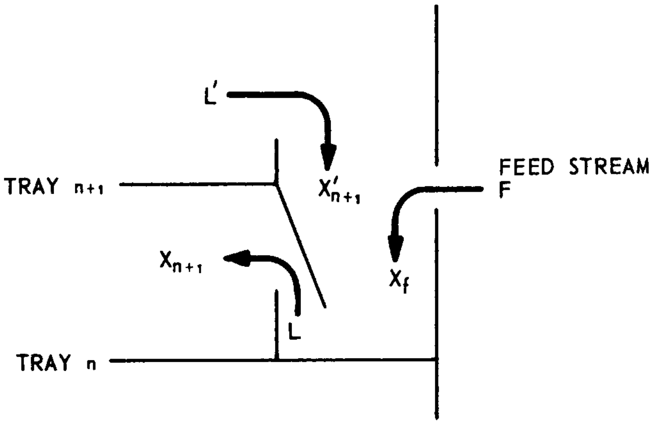

Fig. 6. Mixing feed in a downcomer.

During each tray-to-tray calculation, the trays receiving recycle F_r and feed from the GS process F_e are normally determined automatically. Each X_n is compared with the next feed concentration X_f, and when X_n is less than X_f, the X_n and liquid rate are adjusted with these equations.

$$L' = L - F$$

$$X_n' = (L\ X_n - F\ X_f)/L'.$$

It is assumed that each feed stream is preheated to the bubble point, enters the column in the tray downcomer, and is perfectly and immediately mixed with the liquor in the downcomer. The terms are shown in Figure 6.

Once the best feed trays have been determined by this procedure, the problem can be repeated, and the nearest actual feed trays specified as data input. A slight mismatch of the process and feed water concentrations at the feed tray causes a slight decrease in concentration capacity. The extent of this decrease is occasionally of interest.

GS Process

Water flows countercurrent to a hydrogen sulfide gas stream in bubble-cap towers operated at such rates, temperatures, and pressures that the deuterium concentrates at the junction between the cold and hot towers. The equipment consists of eight two-stage units:

The first stage has one cold tower operated at about 35°C. and one hot tower at about 140°C. These are designated at CT-1 and HT-1 in Figure 1.

The second stage has a pair of cold towers in series and a pair of hot towers in series, designated as CT-2 and HT-2 in Figure 1.

Clarified river water is fed to the top tray of each CT-1 and the CT-1 effluent is heated and fed to the top of HT-1. The HT-1 effluent is steam-stripped of the dissolved hydrogen sulfide and then pumped to the waste via a heat recovery system.

Process gas is circulated through the first stage with a blower located at the discharge of CT-1. The gas is heated and humidified in the bottom ten trays of HT-1 by direct contact with heated waste water and also at the tray 13 with direct injection of the steam-stripper off-gas.

Both gas and liquid streams transport deuterium from the cold tower-hot tower junction of the first stage to the second stage as shown in Figure 1. A liquid drawoff from the cold tower-hot tower junction of the second stage is stripped of H_2S and fed to the distillation columns. The more dilute distillation condensate is returned to tray 39 of CT-2.

Several problem constants for this process need only be calculated on the first of the many passes through this routine. These include all of the physical properties of the hydrogen sulfide-water system, the total gas and liquid flow rates, and the estimated steam input. These data are functions of the problem conditions, including the gas flow rate and the liquid-to-gas flow ratios in the first and second stages.

Because the gas flow rates are limited by the plant blower capacity, they are stated as problem conditions. The other flows are calculated with these equations developed from material balances (*1*):

$$L_{c1} = R_{c1}\ G_{c1}$$

$$L_{h1} = \rho_1\ L_{c1} - \eta_1 G_{c1}$$

$$G_{h1} = L_{h1} + G_{c1} - L_{c1} + B - F_r$$

$$L_{c2} = R_{c2}\ G_{c2}$$

$$L_{c2b} = L_{c2} + D$$

$$L_{h2} = \rho_2\ L_{c2b} - \eta_2 G_{c2} - \tau_2\, F_e$$

$$G_{h2} = G_{c2} + L_{h2} - L_{c2}$$

where, for the appropriate stages

$$\rho = \frac{\dfrac{1}{1 + S_c} - \dfrac{H_h}{1 + H_h}}{\dfrac{1}{1 + S_h} - \dfrac{H_h}{1 + H_h}} \qquad \eta = \frac{\dfrac{H_c}{1 + H_c} - \dfrac{H_h}{1 + H_h}}{\dfrac{1}{1 + S_h} - \dfrac{H_h}{1 + H_h}}$$

$$\tau = \frac{\dfrac{1}{1 + H_h}}{\dfrac{1}{1 + S_h} - \dfrac{H_h}{1 + H_h}}$$

The steam input to the stripper supplies the unrecovered heat from the hot tower effluent. Plant performance has shown that 30% of the heat needed to increase the enthalpy of first stage water and gas from cold tower to hot tower conditions of temperature and pressure must normally be supplied by this addition of steam. The enthalpies of the gas and liquid are calculated for this estimate from equations previously reported (*7*).

The Murphree tray efficiencies used in the tray-to-tray calculations were assumed constant through each extraction tower. Values for the first stage hot and cold towers were determined experimentally and values for the second stage were estimated (*8*).

Calculations up both cold towers are again tray-to-tray starting with the liquid concentration leaving the bottom tray and the gas concentration entering the tray. The gas concentration that would be in equilibrium with the liquor leaving tray *n* is

$$Y_n^* = X_n/[\beta_c + (1 - \beta_c)\ X_n]$$

Then, from the definition of Murphree efficiency, the actual gas concentration leaving the tray is

$$Y_n = Y_{n-1} - E_{mv}\ (Y_{n-1} - Y_n^*)$$

and from a material balance around the tower and through the tray is

$$X_{n+1} = \frac{G}{L}\, Y_n + I_c$$

Calculation down the hot towers is similarly tray-to-tray with these solutions for each tray:

$$X_n^* = Y_n\ \beta_h/(1 - Y_n + Y_n\ \beta_h)$$

$$X_n = X_{n-1} - E_{ml}\ (X_{n-1} - X_n^*)$$

$$Y_{n+1} = \frac{L}{G}\ (X_n - I_h)$$

The following number of trays and tray efficiencies were used:

Tower	Active trays	Murphree efficiency, %
CT-1	69	59
HT-1	60	71
CT-2	167	55
HT-2	139	71

The second stage efficiencies appeared to be too high, based on a comparison of calculated and observed concentration gradients in the GS process towers, and subsequent refinement was planned.

The overheads from the distillation towers were assumed to be equally distributed among the eight GS process units in the model and fed continuously into the downcomer onto tray 39 of each CT-2. A material balance around the downcomer was used to adjust the value of X_{40} and the intercept I_{c2} as follows:

$$X_{40} = (L_{c2b}\ X_{40'} - D\ X_d)/L_{c2}$$

$$I_{c2} = X_{40} - \frac{G_{c2}}{L_{c2}}\ Y_{39}$$

These tray-to-tray calculations are straightforward but too few material balances could be made to define the starting X and Y concentrations and the operating line intercept on the X axis, so the intercept values had to be obtained by the following iterative procedure.

Step 1. Temporarily assume that the intercept value of the CT-2 operating line is zero. The starting concentrations for the CT-2 calculation are obtained from the drawoff concentration X_e. The drawoff liquor is condensate assumed to be in equilibrium with the gas entering tray 1 of CT-2 at the CT-2 temperature and pressure. Then, where $n = 1$

$$Y_e = X_e/[\beta + (1 - \beta)\ X_e]$$

$$X_n = \frac{G_{c2}}{L_{c2b}}\ Y_e + I_{c2}$$

Calculating tray-to-tray up CT-2 leads to the feed liquor concentration X_{167}, which, from the flow diagram, equals the CT-1 effluent concentration X_{bc1}.

Step 2. The operating line intercept on the X axis of the CT-1 is set to zero temporarily, and where $n = 1$

$$Y_{n-1} = \frac{L_{c1}}{G_{c1}}\ (X_{bc1} - I_{c1})$$

Calculation then proceeds tray-to-tray up CT-1 through tray 69. Because this top tray receives clarified river water as feed, a material balance around tray 69 must therefore account for the H_2S dissolving in this water and the off gas flow must be adjusted accordingly:

$$G_{tc1} = G_{c1} - \frac{L_{c1}\ S_c}{1 + S_c}$$

and

$$X_{fw} = \frac{G_{tc1}\ Y_{70} + L_{c1}\ X_{69} - G_{c1}\ Y_{69}}{L_{c1}/(1 + S_c)}$$

The D_2O concentration of natural water is fixed as a problem condition (0.000147 mole fraction) and if the calculated X_{fw} does not agree with this concentration, the intercept guess for CT-1 is improved and this step is repeated.

Step 3. The concentration Y_{th1} of the gas leaving the top of HT-1 is calculated from a material balance around the gas heat exchangers shown in Figure 1 between the CT-1 and HT-1. The gas concentration leaving these exchangers is

$$Y = \frac{Y_{bc1}\, G_{c1} - Y_{tc2}\, G_{c2}}{G_{c1} - G_{c2}}$$

and the condensate concentration from the exchangers is

$$X = \frac{Y\, \beta_c}{1 - Y + Y\, \beta_c}$$

Then, by material balance, the condensate rate is

$$L = G_{h1} - G_{c2} - G_{h2} - G_{c1}$$

and

$$Y_{th1} = \frac{Y_{bc1}\, G_{c1} + L\, X - Y_{tc2}\, G_{c2}}{G_{h1} - G_{h2}}$$

Step 4. To begin calculations down HT-1, the operating line intercept is temporarily set to zero; then for $n = 1$

$$X_n = \frac{G_{h1}}{L_{h1}}\, Y_{th1} + I$$

Calculations then proceed tray-to-tray down the tower until $n = 60$. X_{bh1} and Y_{bh1} are set equal to X_{60} and Y_{60}.

Step 5. Note in Figure 1 that the gas leaving the top of CT-1 is circulated through a humidifier and mixed with the stripper off-gas in this model before entering the bottom tray of HT-1. From a material balance around the humidifier

$$Y_{bh1}' = \frac{G_{tc1}\, Y_{tc1} + G_s\, Y_{s1} + L_m\, X_{bh1}}{G_{h1}}$$

where

$$L_m = G_{h1} - G_{tc1} - S_{tm}$$

$$G_s = S_{tm} + (L_{h1} - L_m)\, S_{h1}$$

$$Y_s = Q\, X_{bh1}$$

Q was developed from definitions of equilibrium concentrations of H_2O, H_2S, HDO, and HDS as follows:

Calculation of the deuterium concentration in the off-gas was simplified with these assumptions: (1) the deuterium distribution is at equilibrium in the system at the temperature in the stripper, (2) the stripper liquid feed is at stripper temperature, so that none of the steam fed to the system condenses within the stripper, (3) the relative volatility of HDS with respect to H_2S equals the relative volatility of HDO with respect to H_2O, and (4) all of the dissolved H_2S is stripped from the effluent and returned to the HT-1.

These definitions are needed:

Stripper off-gas D concentration

$$Y = [\mathrm{HDS}]_g + [\mathrm{HDO}]_g$$

Stripper feed concentration

$$X_{bh1} = [\mathrm{HDS}]_l + [\mathrm{HDO}]_l$$

$$\text{Equilibrium constant } K_x = \frac{[\mathrm{HDO}]\,[\mathrm{H_2S}]}{[\mathrm{HDS}]\,[\mathrm{H_2O}]}$$

Relative volatility

$$\alpha = \frac{[\mathrm{HDO}]_g\,[\mathrm{H_2O}]_l}{[\mathrm{H_2O}]_g\,[\mathrm{HDO}]_l} = \frac{[\mathrm{HDS}]_g\,[\mathrm{H_2S}]_l}{[\mathrm{H_2S}]_g\,[\mathrm{HDS}]_l}$$

Solubility: S = moles H_2S/mole of H_2O liquid. Note also that $G[\mathrm{H_2S}]_g = L[\mathrm{H_2S}]_l$, where G is the off-gas rate, L is the stripper liquid feed rate $(L_{h1} - L_m)$, and subscripts g and l refer to gas and liquid phases.

By combining

$$[\mathrm{HDS}]_g \sim \frac{\alpha\, L\, X_{bh1}}{G(1 + K_x/S)}$$

and

$$[\mathrm{HDO}]_l \sim \frac{K_x\, X_{bh1}}{S + K_x}$$

From assumption (4) and the definition of S

$$[\mathrm{H_2S}]_g = \frac{L\,(S)}{G\,(1 + S)}$$

$$[\mathrm{H_2S}]_l = \frac{S}{1 + S}$$

Then, by substituting these into the equation for α and rearranging

$$[\mathrm{HDO}]_g = \frac{\alpha \left[1 - \dfrac{L\,S}{G(1+S)}\right]\left[\dfrac{K_x\, X_{bh1}}{S + K_x}\right]}{\left[\dfrac{1}{1+S}\right]}$$

$$\alpha_s = 1.1596\ e^{-65.43/T}$$

$$K_x = 1.010\ e^{233/T}$$

The equations for α_s and K_x are from Bebbington (*1*) where T is the temperature in degrees Kelvin in the stripper, calculated from the Keenan and Keys (*3*) equation for the temperature of saturated steam at HT-1 pressure.

The equation $Y = [\mathrm{HDS}]_g + [\mathrm{HDO}]_g$ is combined with the preceding equations for $[\mathrm{HDS}]_g$ and $[\mathrm{HDO}]_g$ and the result rearranged to the following equation for Q.

$$Q = \left[\frac{\alpha_s\, S_{h1}\,(1 + S_{h1})}{S_{h1} + K_x}\right]\left[\frac{K_x}{S_{h1}} + \frac{(L_{h1} - L_m)(1 - K_x)}{G_s\,(1 + S_{h1})}\right]$$

The Y_{bh1} calculated in step 4 and the Y_{bh1}' calculated above are compared and if not in agreement, the guess for the HT-1 operating line intercept is improved and these steps 4 and 5 repeated.

Step 6. To start calculation down HT-2, the off gas and liquid feed concentrations are calculated from material balances around the heat exchangers. Then

$$Y_{th2} = \frac{G_{c2}\, Y_{bc2} + X_e\,(G_{h2} - G_{c2})}{G_{h2}}$$

The calculated production rates of the two extraction stages P_1 and P_2 must be equal, and to ensure this, the intercept of the HT-2 is calculated as a function of the first stage production rate. From material balances and tower operating line equations

$$P_1 = L_{c1}\, I_{c1} - L_{h1}\, I_{h1}$$

and

$$P_2 = L_{c2}\, I_{c2} - L_{h2}\, I_{h2}$$

then

$$I_{h2} = (L_{h1}\, I_{h1} - L_{c1}\, I_{c1} + L_{c2}\, I_{c2})/L_{h2}$$

Now, where $n = 1$

$$X_n = \frac{(G_{h2})}{(L_{h2})}\, Y_{th2} + I_{h2}$$

and calculation can proceed tray-to-tray through the 139 trays. From Figure 1 the concentration of gas entering the bottom tray of HT-2 must equal the Y_{th1} calculated in step 3. If these are not in agreement, the guess of I_{c1} in step 1 is improved and the entire calculation is repeated.

Step 7. When all concentrations coupling the tower-to-tower calculations are in agreement, material balances are made independently around all important junctions as a check. The total moles of liquid and of D_2O in and out of each stage and around the interstage heat exchangers should agree to some acceptable limit, such as $< 0.01\%$.

Loop Closure

The Newton-Raphson method explained by McCracken (9) was used to close the Keenan and Keyes equation for the temperature of saturated steam. The principle of this method was used to close the loops containing tray-to-tray calculations, where the function could not be written as a single equation. All such loops were closed with these steps:

1. A reasonable first guess of an undefined variable X_1 (such as an operating line intercept on the X axis) was made and the tray-to-tray calculation performed resulting in definition of a second variable Y_1 which is required by problem conditions to equal a predefined value Y^*.

2. The value of X_1 was varied proportional to $\Delta Y = Y_1 - Y^*$ to form a second guess X_2, and the tray-to-tray calculation repeated to get Y_2.

3. After these, successive guesses of X are improved with these equations:

$$X_{n+1} = X_n - \Delta Y/\text{SLOPE}$$

where

$$\Delta Y = Y_n - Y^*$$

$$\text{SLOPE} = (\Delta Y_n - \Delta Y_{n-1})/(X_n - X_{n-1})$$

The overall plant material balance involving the GS process feed and waste and the DW process recycle and product streams was closed by adjusting the drawoff concentration X_e. The function of X_e and the material balance were modeled with a quadratic equation. In the program three solutions of X_e and the residuals (R) in the overall material balances were obtained and used to find the constants of the polynomial:

$$X_e = a + b\ R + c\ R^2$$

The next guess of X_e was set to equal a; that is, where the residual $R = 0$. This process was repeated always using the last three pairs of X_e, R data in the polynomial solution to find the next X_e for trial until R was acceptably small (such as $0.0001\ \Delta Y$).

Finding the best liquid-to-gas ratios also required a polynomial equation. The production rate in the GS process is quite sensitive to both the first and second stage liquid-to-gas ratios and it goes through a maximum as each ratio is increased from 0.4 to 0.6. A typical curve is shown in Figure 7. The ratios which resulted in the maximum production rate were determined as follows:

Step 1. Make a reasonable guess at the best ratio R_{c2} for the second stage and calculate through both stages of the GS process to obtain the corresponding production rate.

Step 2. Repeat step 1 with a 2% greater ratio and again with a 2% lower ratio than the guess.

Step 3. Use the three pairs of ratio-production rate data to determine the constants in the polynomial [ratio $= a + bP + cP^2$] and solve the equation for the production rate P where the first differential of the polynomial is zero, that is

$$\text{ratio} = -b/2c$$

Step 4. Repeat steps 1, 2, and 3 using the last three data pairs in step 3 to find a better guess of the ratio until the last two production rates are essentially unchanging.

Step 5. Repeat steps 1 through 4 for the first stage liquid-to-gas ratio R_{c1} while keeping the second stage ratio at optimum.

Step 6. Repeat steps 1 through 5, keeping each stage at its optimum ratio while the other is again adjusted. This repetition has not improved the calculated production rate significantly in problems to date but it gives assurance that the maximum was obtained.

Report

So very many calculation results occur in the course of each problem solution that the user cannot practically examine each of them. Only final data are reported. Even these are somewhat voluminous but worth examining in detail to ensure that no simulation inadequacy or programming error escapes notice. These data are printed after each solution:

1. all problem conditions, whether directly input or calculated from input data

2. each tray liquid, vapor, and equilibrium concentration that was calculated during the last pass through each tower

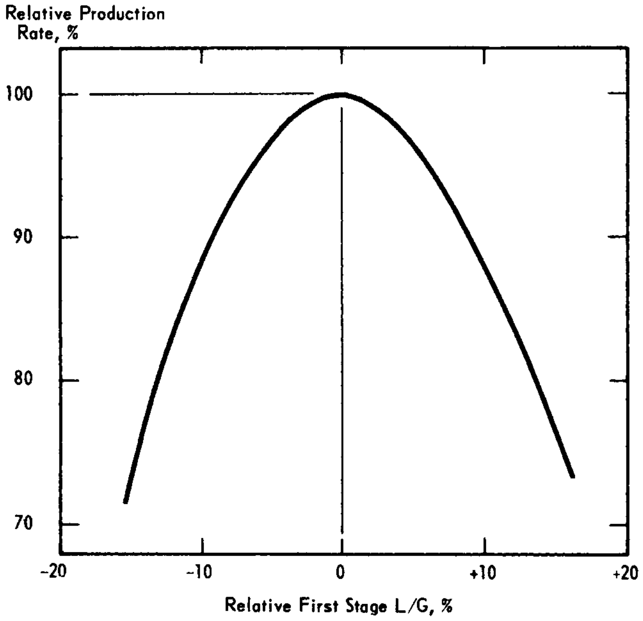

Fig. 7. Importance of liquid-to-gas (L/G) ratio in the GS process.

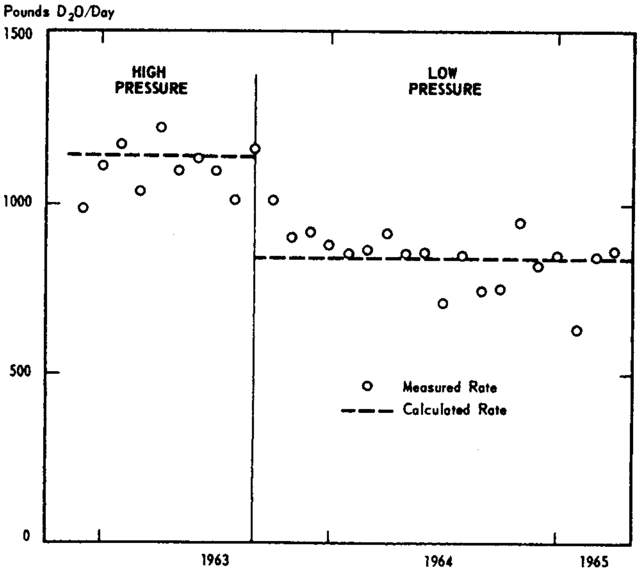

Fig. 8. Two measured and calculated production rates.

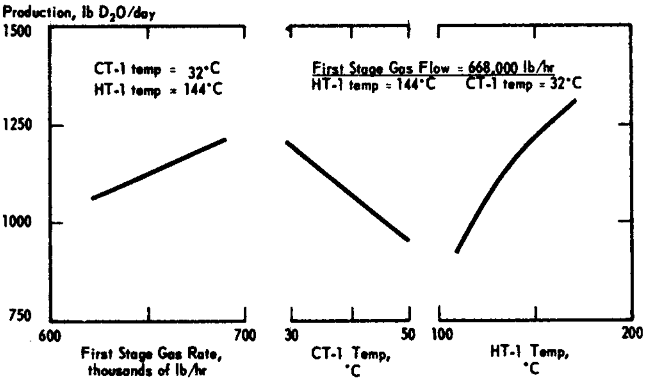

Fig. 9. Effect of some process variables on production rate.

3. the terminal results from each important iteration to exhibit closure

4. material balance data around the entire plant, around the distillation tower, around the GS process towers, and around a number of sensitive areas within the extraction towers

5. all calculated final liquid-to-gas ratios and

6. the calculated production rates of each stage and of the entire plant

Typical Results

The only plant event with a significant and measurable change in production rate occurred in 1963 to 1965. The operating pressure in the GS process towers was decreased 50 lb./sq.in., and the attainable gas flow rates and process temperatures changed accordingly. The daily production rate calculated from monthly data are shown in Figure 8. The large variation in the daily rate and the long time required to work off the greater in-process inventory illustrates the difficulty in optimizing the process from experimental results. The conditions for the two periods of time were imposed on this mathematical model and the calculated results are superimposed on the plant data in Figure 8. The agreement gave credence to the computer program.

Other typical results shown in Figure 9 have no comparative plant data but the results agree generally with plant experience and some manual calculations. The program was therefore accepted for guiding plant operation.

ACKNOWLEDGMENT

Information in this article was developed during the course of work under Contract AT (07-2)-1 with the U.S. Atomic Energy Commission.

NOTATION

1. The GS process towers are defined with these mnemonics:
   - CT-1 = the first stage cold tower
   - CT-2 = the second stage cold tower
   - HT-1 = the first stage hot tower
   - HT-2 = the second stage hot tower
2. All tray numbers proceed serially up the towers.
3. Deuterium concentrations are molar concentrations overall:

X = liquid-phase concentration, including deuterium in the form HDO and D_2O as well as dissolved HDS and D_2S

Y = gas- or vapor-phase concentration including deuterium in the form HDS and D_2S as well as water vapor in the form HDO and D_2O (see subscripts)

4. Flow rates are all in total moles of fluid per hour.

B = product drawoff rate from the distillation columns

D = distillate drawoff rate

F = feed to the distillation columns (see subscripts)

G = gas-phase flow in the GS process towers (see subscripts)

L = liquid phase flow in GS process towers

P = production rate in moles of deuterium oxide per hour

R = ratio of L/G in GS process towers or residual in iterative procedures

S_{tm} = steam input to the GS process towers

5. Constants and properties of the systems

E_{mv} = Murphree vapor phase efficiency (See reference *10* for discussion)

E_{ml} = Murphree liquid-phase efficiency

H = humidity, moles of water per mole of hydrogen sulfide gas

I = value of the operating line intercept where $Y = 0$

K_x = equilibrium constant in terms of concentration in the liquid phase, that is

$$= \frac{[\mathrm{HDO}]\,[\mathrm{H_2S}]}{[\mathrm{H_2O}]\,[\mathrm{HDS}]}$$

S = solubility, moles of hydrogen sulfide per mole of water liquid

T = temperature, °C. unless stated as °K.

α = relative volatility of water and hydrogen deuterium oxide which is assumed to be also equal to that of hydrogen sulfide and hydrogen deuterium sulfide

β = the overall separation factor calculated from

$$= \frac{(1 + H)\,(S + K_x)}{\alpha(1 + S)\,(1 + HK_x)}$$

Subscripts

b = bottom of a GS process tower or distillation column

c = GS process cold tower

e = GS process product drawoff stream

h = GS process hot tower

m = liquid makeup stream, to the HT-1 humidifier

n = tray number

r = recycle stream to the distillation columns

s = stripper off-gas to HT-1

1 = GS process 1st stage

2 = GS process 2nd stage

$*$ = equilibrium concentration

LITERATURE CITED

1. Bebbington, W. P., and V. R. Thayer, *AEC Res. Develop. Rept. DP-400,* E. I. du Pont de Nemours & Co., Aiken, S.C. (1959). A condensed version was published in *Chem. Eng. Progr.,* CEP, **55**, (9), 70-78 (1959).
2. *Ibid.,* 98-99.
3. Robinson, C. S., and E. R. Gilliland, "Elements of Fractional Distillation," McGraw-Hill, New York (1950).
4. Keenan, J. H., and F. G. Keyes, "Thermodynamic Properties of Steam," Wiley, New York (1958).
5. FIAT, "Review of German Science Physical Chemistry," 22-23, (1939-1946).
6. *Bubble Tray Design Manual,* AIChE, New York (1958).
7. Burgess, M. P., and R. P. Germann, *AIChE J.,* **15** (2) (Mar. 1969).
8. Proctor, J. F., *Chem. Eng. Progr.,* **59** (Mar. 1963).
9. McCracken, D. D., "A Guide to Fortran IV Programming," Wiley, New York (1965).
10. Gerster, J. A., "Perry's Chemical Engineers Handbook," p. 13-51 (1963).

Manuscript received October 13, 1969; revision received March 9, 1970; paper accepted April 3, 1970.