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PRELIMINARY ANALYSIS OF CHLORIDE REMOVAL FROM DAREX DISSOLVER SOLUTION BY DISTILLATION

J. S. Watson
M. E. Whatley

ABSTRACT

The removal of chloride from the Darex solutions resulting from the dissolution of stainless steel fuel elements in aqua regia can be effected by continuous distillation in a tower. A preliminary steady-state analysis of this operation, incorporating the continuous dissolver as a source of metal salts in the reflux stream, showed that process objectives could best be met by feeding strong nitric acid into the center region of the tower rather than into the reboiler of the still. If more than about four theoretical stages are available in both the top and bottom sections of the tower, distillation pinch points for nitric acid are realized, and the overhead acid composition is insensitive to an increase in the number of stages. Since, at high acid concentrations, HCl is much more volatile than HNO_3, the bulk of the chloride will be removed in the top few stages and the rest of the tower can be analyzed as an HNO_3—metal nitrates—water system. Vapor-liquid equilibrium data for this system were only partially available from previous work, and the necessary supplementary data were obtained experimentally.

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1.0 INTRODUCTION

In the continuous Darex "head-end" process for reprocessing stainless steel clad reactor fuels,[1] the fuel elements are dissolved by an aqua regia solution 5 to 6 M in nitric acid and approximately 2 M in hydrochloric acid. In order to avoid excessive corrosion in the subsequent process steps, the chloride must be removed from the solutions.

The chloride may be distilled from the solution. The relative volatility of HCl increases as the nitric acid concentration increases, and at about 8 M HNO_3, chloride decomposition becomes important. When a continuous distillation column is used, the nitric acid profile is a decisive parameter in estimating chloride removal.

The minimum nitric acid addition to the system is that necessary to replace the acid consumed by dissolution and the free acid carried away with the bottoms product. Most consideration has been given to addition of azeotropic (15.3 M) or more concentrated nitric acid to the bottom of the column or directly to the reboiler. This has been shown experimentally to give low nitric acid concentrations at the top of the column and results in distillation of the chloride at the top, and decomposition at the bottom. The chloride is essentially all recovered overhead and can be reused to make aqua regia for further dissolution. Only a small amount of hydrochloric acid is lost to decomposition. A significant amount of nitric acid must be added to the overhead stream. It is likely, when strong acid is used, that the product solution from the reboiler will be high in acid and that some nitric acid will be wasted.

A better acid profile in the column can be obtained by adding all of the nitric acid feed near the center of the column. The nitric acid concentration still will decrease toward the top of the column for chloride distillation from the solution. However, around the feed plate the nitric acid concentration will be relatively constant at high values. Because of distillation pinches this region can be made essentially any length to afford enough residence time in the high nitric acid concentrations for sufficient residual chloride decomposition to occur. This system can be operated such that all of the nitric acid is fed to the column and aids in chloride removal. The reboiler acid concentration can be maintained at a desired level even though higher than azeotropic concentration is used for feed. The overhead concentration will be higher than necessary and water must be added to adjust to 5 or 6 M for use in the dissolver.

2.0 PROPOSED ANALYSES

A detailed analysis of even the steady-state conditions which can exist in a Darex distillation is impossible at the present time unless simplifications are made. The equilibrium relationships for HCl-HNO_3 volatility in the presence of stainless steel are scarcely known and reliable data which will apply in a column are difficult to obtain.

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However, as noted earlier, much can be inferred about the fate of chloride in the system from the nitric acid profile in the column.

For this study, estimation of nitric acid profiles was considered a suitable objective. To further simplify the problem the effect of the chloride on the nitric acid volatility was ignored. In other words, the system was approximated by the much simpler system of nitric acid—stainless steel nitrate distillation. This is a reasonable approximation since after the first stage or two from the top, the chloride should be only a trace component.

3.0 NITRIC ACID FEED TO THE REBOILER

In the first system proposed, nitric acid was fed to the reboiler and to the recycle aqua regia going to the dissolver. The mixed acid in the overhead from the column was experimentally found to be too dilute for use directly in the dissolver. This stream was maintained 5 M by adding a controlled amount of more concentrated acid, R, before going to the dissolver. The reboiler can be used to concentrate the metals and thereby, according to the over-all nitrate balance about the system, increase the metal loading to acid concentration ratio so that, after dilution, the solution will be more desirable feed for solvent extraction.

A simplified flowsheet for such a chloride removal system is shown in Fig. 1. The important variables are shown on the figure and can be most conveniently expressed in the following units.

L = liquid rate in the column, moles of volatile component (water plus nitric acid) per unit time

V = vapor rate in the column, moles per unit time

F = acid feed rate to reboiler, moles per time

R = acid feed rate to the top of the column, moles per time

P = product rate, moles of volatile component per time

x_F = reboiler feed composition, mole fraction nitric acid

x_R = overhead feed composition, mole fraction nitric acid

x_P = product acid composition, moles of nitric acid in the product per mole of volatile component

y_T = overhead composition, mole fraction nitric acid

y_D = composition of dissolver feed, mole fraction nitric acid

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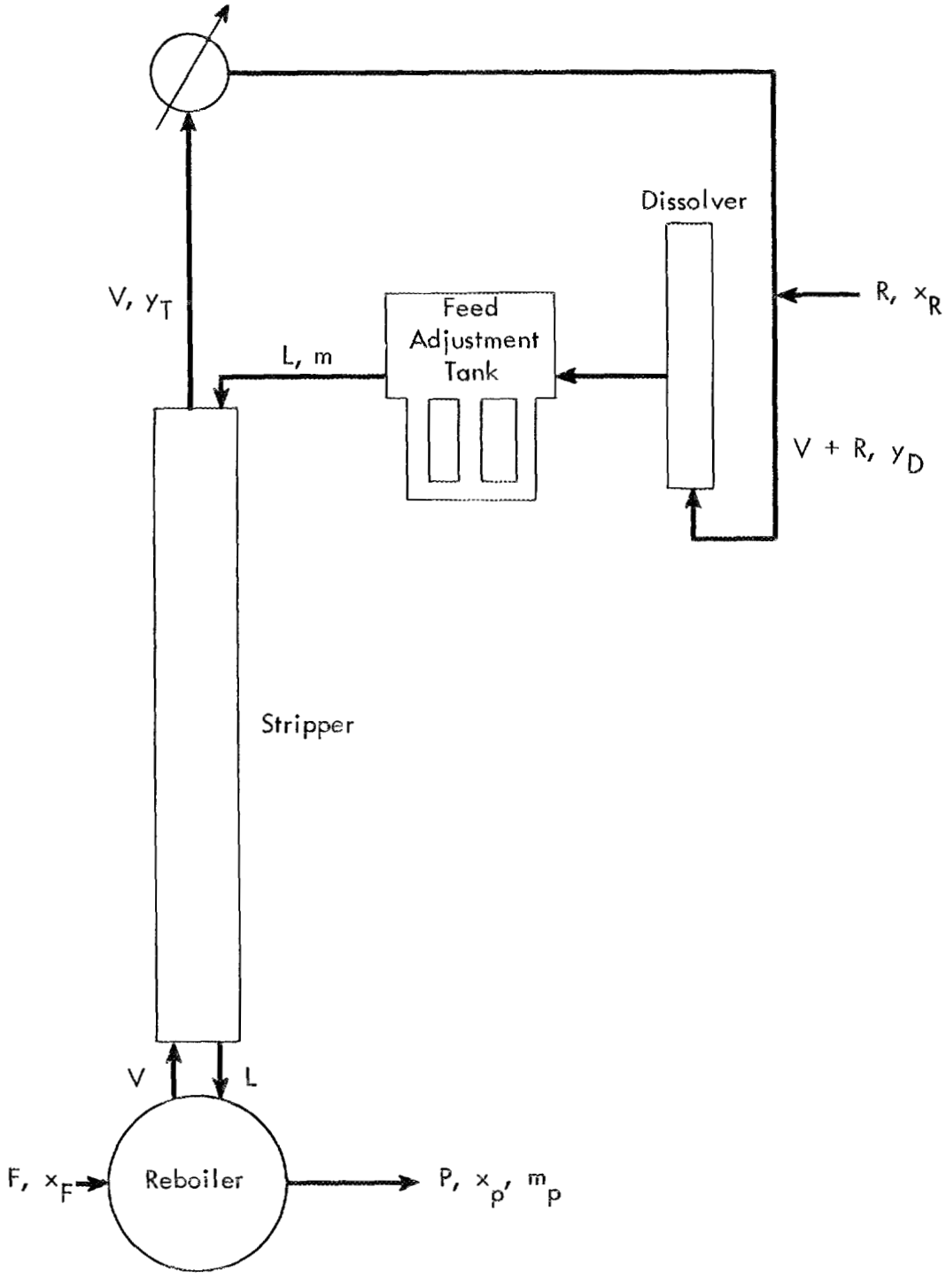

Fig. 1. Darex chloride removal system with acid feed to the reboiler.

m = metal loading of liquid stream from the dissolver, equivalents of metal per mole of volatile component

m_P = metal loading of the product, equivalents of metal per mole of volatile component

If one assumes constant molal overflow, the metal loading, m, expressed as equivalents of metal per mole of volatile components will be constant throughout the column. One can define an equilibrium curve for a constant metal loading based only on the volatile components. Such plots are shown in Fig. 2 as reported by Johnson, O'Connell, and Sabo.[2]

If one neglects water formation and nitrate losses from decomposition in the dissolver, five independent material balances may be made about the system. The over-all material balance is

$$F + R = P(1 + m_P) \tag{1}$$

The over-all nitrate balance about the system is

$$Fx_F + Rx_R = P(x_P + m_P) \tag{2}$$

The material balance about the acid adjustment stream, R, and the dissolver may be written

$$V + R = L(m + 1) \tag{3}$$

The nitrate balance around this same region may be written

$$Vy_T + Rx_R = L(1 + m)y_D \tag{4}$$

And finally the metal balance around some point in the column and the reboiler is

$$Lm = Pm_P \tag{5}$$

These material balances can be used to express, under steady-state conditions, all flow rates proportional to the acid feed rate to the bottom of the column. For the usual case where the two acid streams, F and R, have the same composition

$$V = F \frac{m_P(1 + m)}{m(1 + m_P) + (m - m_P)\left(\frac{y_P - y_T}{x_F - y_D}\right)} \tag{6}$$

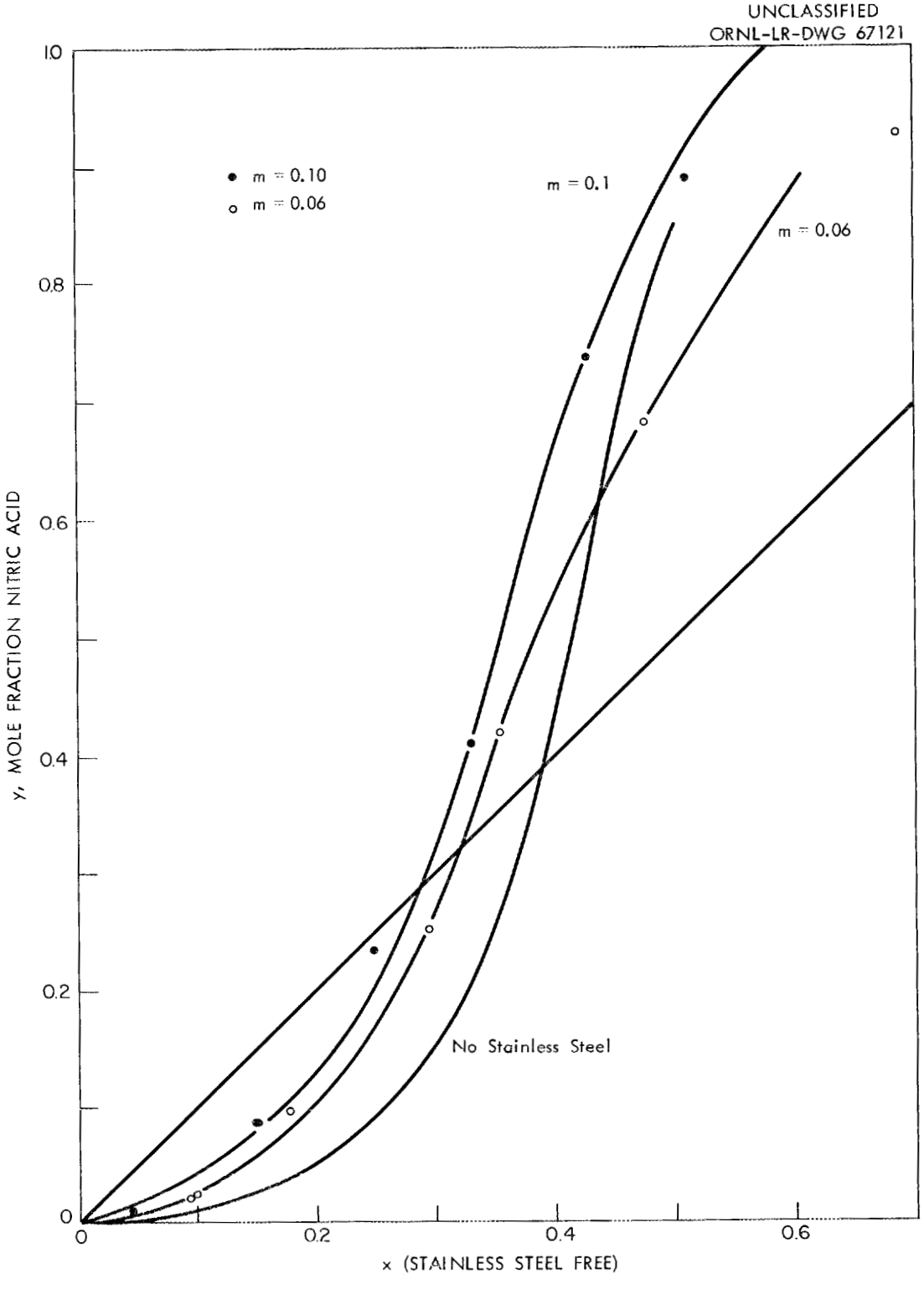

Fig. 2. Nitric acid volatility from stainless steel nitrate solutions (from Johnson, O'Connell, and Sabo).

$$L = F \frac{m_P(x_F - y_T)}{m(1 + m_P)(x_F - y_D) + (m - m_P)(y_D - y_T)} \tag{7}$$

$$R = F \frac{m_P(1 + m)(y_D - y_T)}{m(1 + m_P)(x_F - y_D) - (m - m_P)(y_D - y_T)} \tag{8}$$

and

$$P = F \frac{mm_P(x_F - y_T)}{m_P m(1 + m_P)(x_F - y_D) + m_P(m - m_P)(y_D - y_T)} \tag{9}$$

The operating line is obtained by making a nitric acid balance about the section of the column above some plate m.

$$y_n = \frac{L}{V} x_{n+1} + \frac{L}{V} m - \frac{R}{V} x_F \tag{10}$$

The slope and intercept of the operating line can easily be obtained from Eqs. 6, 7, and 8. Note that

$$\frac{L}{V} = \frac{x_F - y_T}{(1 + m)(x_F - y_D)} \tag{11}$$

and

$$\frac{R}{V} = \frac{y_D - y_T}{x_F - y_D} \tag{12}$$

If one sets out to calculate the nitric acid profile in a column using these assumptions, the acid feed rate to the reboiler, F; the feed composition, x_F; the required dissolver feed composition, y_D; the metal loading in the stream from the dissolver, m; and the desired metal loading in the product, m_P, should all be known. Then Eqs. 1 and 2 may be used to obtain the free nitric acid composition of the product

$$x_P = \frac{x_F}{1 + m_P} - m_P \tag{13}$$

Equations 6 through 9 and the equilibrium relations may be used to calculate all of the remaining flow rates and the overhead acid composition, y_T. The overhead composition cannot be expressed in a simple explicit form but must be found by trial and error. One must

first assume a value for y_T, evaluate the operating line and proceed to make the stagewise calculation to obtain a value of y_T to be used as a basis for a new assumption, and so forth.

It is possible, especially for a relatively short column with few stages or for a high feed composition, to find that the only acceptable value for y_T is greater than y_D. (This corresponds to requiring a negative value for R according to Eq. 8.)

4.0 INTERMEDIATE ACID FEED WITH WATER OVERHEAD ADJUSTMENT

An alternate method of operating the chloride distillation column which offers several advantages over the other systems involves adding all of the acid feed to some point near the center of the column (see Fig. 3). This system will be run with a nitric acid concentration overhead higher than that required in the dissolver so only water addition is required to adjust the dissolver feed. This system utilizes the feed acid for chloride removal as well as any system which still gives good chloride removal since all of the acid is added to the column and none in the overhead.

The important variables are shown (Fig. 3) and in most cases have the same meaning as in the previous case. The only two differences are: (1) x_R is zero since only water is added to the overhead stream and (2) the liquid rate, L_L, and the metal loading, m_L, in the column below the feed point is less than the liquid rate, L, and the metal loading, m, above the feed point.

Using these variables, independent material balances may be made. The over-all material balance is

$$F + R = P(1 + m_P) \tag{14}$$

The over-all nitrate balance is

$$Fx_F = P(x_P + m_P) \tag{15}$$

The material balance about the top of the column is

$$L(1 + m) = V + R \tag{16}$$

The nitric acid balance around the top of the column may be written

$$Vy_T = (V + R)y_D \tag{17}$$

and the metal balance between some point in the upper portion and the reboiler is

$$Lm = Pm_P \tag{18}$$

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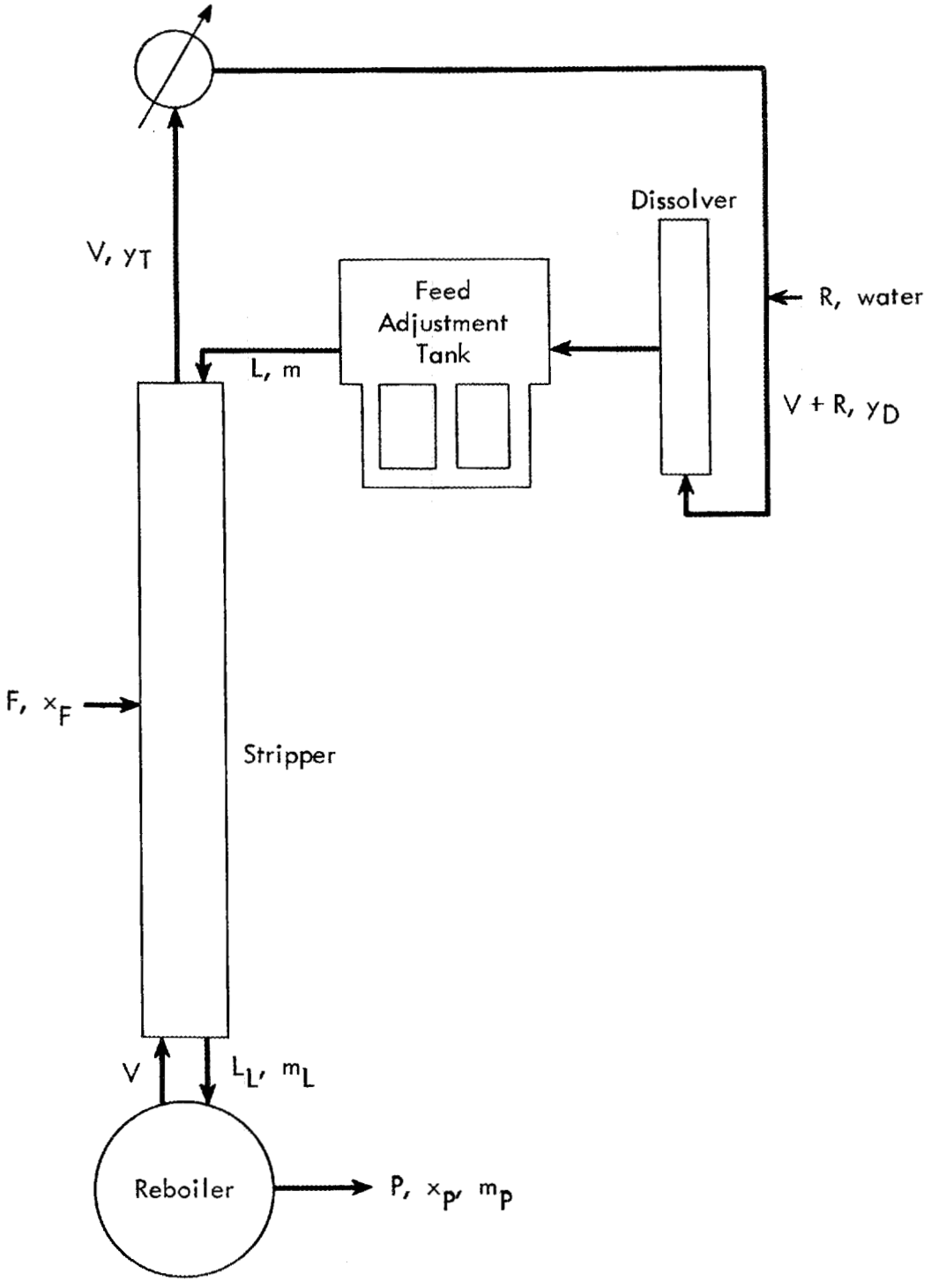

Fig. 3. Darex chloride removal system with all acid fed to the center of the column.

Because of the acid feed to the column the liquid rate and metal loading in the lower portion of the column will be changed.

$$L_L = L + F \tag{19}$$

and

$$L_L m_L = Lm = Pm_P \tag{20}$$

As in the previous case, Eqs. 14 through 18 may be used to express all flow rates under steady state condition proportional to the feed rate, F. Because the two input streams, F and R, do not have the same composition the acid to metal ratio in the product which one desires for satisfactory solvent extraction feed depends upon the relative values of R and F as well as upon the controlled metal loading in the reboiler. In this case it is convenient to specify the acid to metal loading ratio, k, in the product.

$$k = \frac{x_P}{m_P} \tag{21}$$

Then the flow rates may be written

$$R = F \frac{x_F}{m} \left(\frac{1 + m}{1 + k}\right)\left(1 - \frac{y_D}{y_T}\right) \tag{22}$$

$$L = F \frac{x_F}{m(1 + k)} \tag{23}$$

$$V = F \frac{x_F}{m} \left(\frac{1 + m}{1 + k}\right)\left(\frac{y_D}{y_T}\right) \tag{24}$$

Also the acid and metal loading in the product can be found to be

$$x_P = km_P = \frac{kx_F}{(1 + k - x_F) + R(1 + k)} \tag{25}$$

The operating line for the upper portion of the column is

$$y_n = \left(\frac{L}{V}\right) x_{n+1} + \frac{L}{V} m \tag{26}$$

where according to Eqs. 23 and 24

$$\frac{L}{V} = \frac{y_T}{y_D(1 + m)} \tag{27}$$

The operating line for the section below the feed plate intersects the upper operating line at the feed composition, x_F, and has a slope

$$\frac{L_L}{V} = \frac{x_F + m(1 + k)}{x_F(1 + m)\ \frac{y_D}{y_T}} \tag{28}$$

Both operating lines depend upon y_T, and again one must evaluate y_T by trial and error. Since water is to be added to the top of the column, it is necessary that y_T be greater than y_D. Again one is faced with limitations on the acid feed composition. If one tries a feed too dilute, the overhead composition will be less than y_D and R will appear to be negative.

5.0 AVAILABLE EQUILIBRIUM DATA

The principal reason for restricting the present study and not considering chloride volatility and its effect upon nitric acid volatility was lack of vapor-liquid data on stainless steel—nitric acid—hydrochloric acid—water systems. However, once the problem was restricted to the much simpler system involving only nitric acid—water distillation from stainless nitrate solutions, the necessary data were relatively easy to obtain.

The most immediately pertinent data of this type was obtained by Johnson, O'Connell, and Sabo[2] especially for this study. These authors determined the vapor composition, y, in mole fraction as a function of x, the moles of nitric acid per mole of volatile component in the liquid, for two values of metal loading, m, which might be found in a column (see Fig. 1). Note that the effect of higher m is to shift the equilibrium curve plotted in these units to the left.

Johnson, O'Connell, and Sabo also evaluated the vapor composition coming from more concentrated metal solutions such as one might find in the reboiler or product. These data are shown in Figs. 4 and 5 with y plotted as a function of the molar concentration of acid and metal. Along with these data, some results from more dilute solutions obtained by Clark and Godbee[3] are shown. As they appear these are not in their most useful form since the parameters are molar concentrations rather than the mole fraction units (x, y, and m). To use these figures to obtain the vapor composition leaving the reboiler, one must first convert the reboiler compositions to molarity. The density of stainless steel—nitric acid solutions can be obtained from the original data of Johnson, O'Connell, and Sabo and fit to the relation

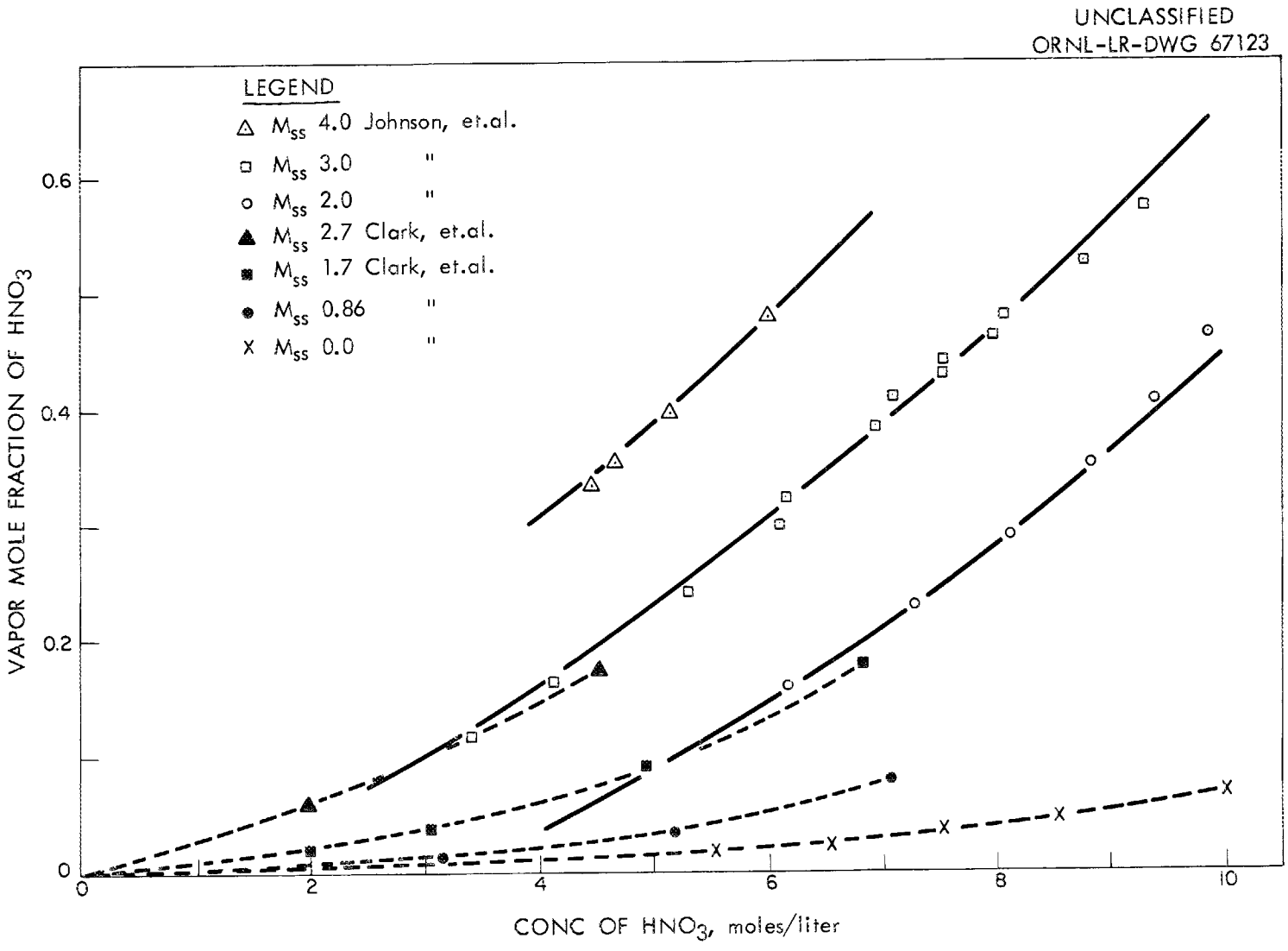

Fig. 4. Nitric acid volatility from concentrated stainless steel nitrate solutions.

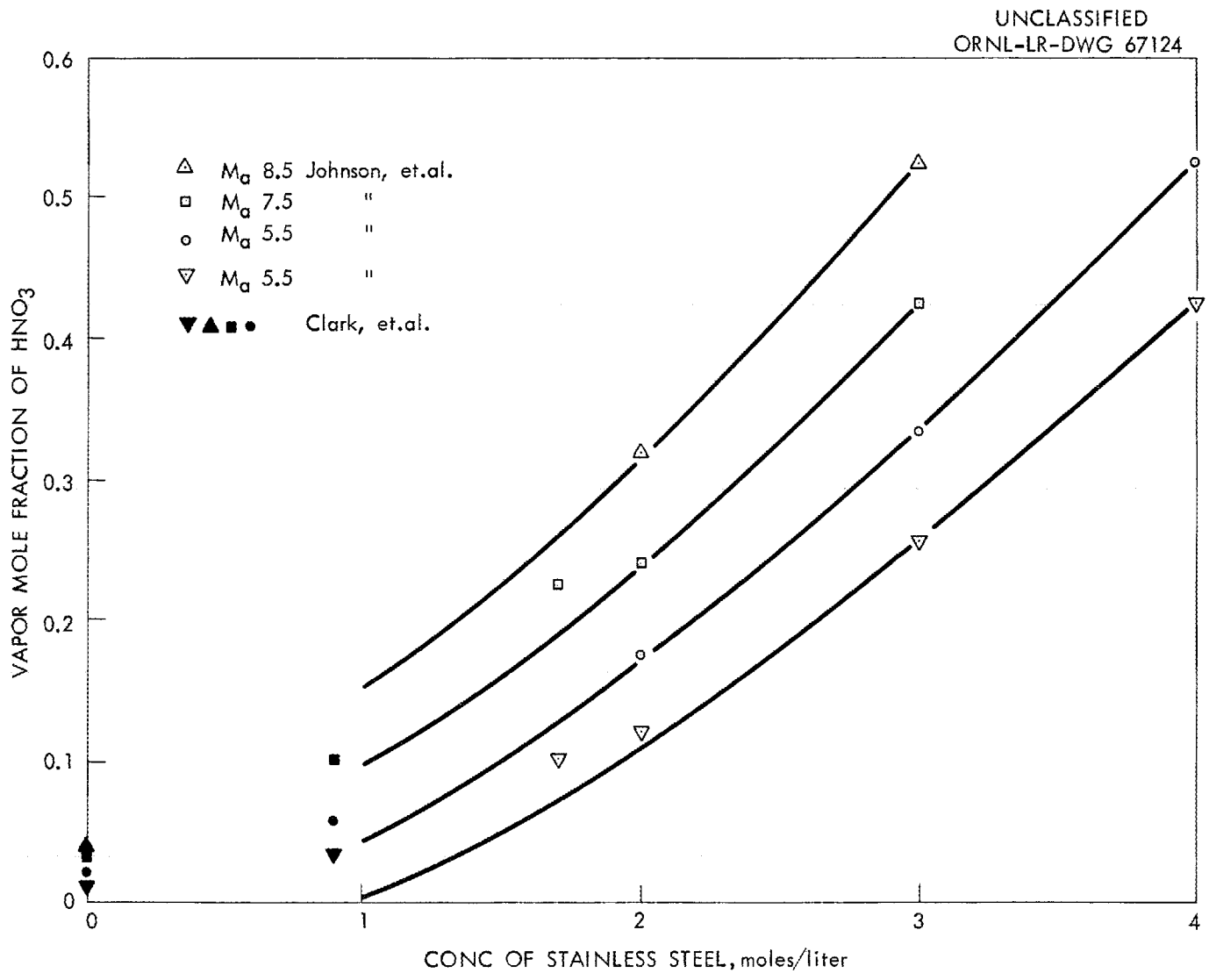

Fig. 5. Nitric acid volatility from concentrated stainless steel solutions.

$$\rho = 1.000 + 0.169\ \underline{M}_{SS} + 0.0195\ \underline{M}_{H^+} \tag{29}$$

If this relation is assumed, one can calculate the molar concentration in the solutions from the relations

$$\underline{M}_{SS} = \frac{55.5m}{2.85 + 4.22m + 4.05x + 0.14mx} \tag{30}$$

$$\underline{M}_{H^+} = \frac{157x + 5.0mx}{2.85 + 4.22m + 4.05x + 0.14mx} \tag{31}$$

6.0 EXAMPLE McCABE-THIELE CALCULATIONS OF NITRIC ACID PROFILE WITH INTERMEDIATE FEED POINT

The calculation of the nitric acid profile in an intermediate feed Darex system will be illustrated with a specific example. The parameters were chosen to be reasonably close to the values which one would expect to use.

Assume that one has a very large column with essentially an infinite number of stages in both sections, a dissolver which delivers a solution having a metal loading of $m = 0.1$, a feed composition $x_F = 0.384$ (azeotrope), a product acid to metal ratio of unity in the product, and a dissolver feed of composition 0.118 (5 $\underline{M}$).

One can normalize all flow rates in terms of the feed rate by dividing Eqs. 22, 23, and 24 by F. Then the actual throughput does not need to be specified.

Let

$$L' = \frac{L}{F}$$

$$V' = \frac{V}{F}$$

and

$$R' = \frac{R}{F}$$

As noted earlier, obtaining y_T is a trial and error procedure. Several trials were made choosing values for y_T which were too high, but the ends of the column were matched reasonably well when y_T was assumed to be 0.121. Then the slope of the upper operating line was found to be from equation

$$\text{slope (upper)} = \frac{0.121}{0.118(1 + 0.1)} = 0.93$$

The intercept of the upper operating line with the y axis was

$$\text{intercept (upper)} = \text{slope x (m)} = 0.093$$

Similarly the slope of the lower operating line was from equation

$$\text{slope (lower)} = \frac{0.384 + 0.1(1 + 1)}{0.384(1 + 1)\ \frac{0.118}{0.121}}$$

$$= 1.42$$

The water addition rate (in units of F) was relatively small.

$$r = \frac{0.384}{0.1}\ \frac{1 + 0.1}{1 + 1}\ 1 - \frac{0.118}{0.121}$$

$$= 0.053$$

Then the free acid composition of the product or reboiler solution was found to be

$$x_P = \frac{(1)(0.384)}{(1 + 1 - 0.385) + 0.053(1 + 1)} = 0.224$$

Since k = 1.0, this is also the metal loading one would set for the reboiler control. The metal loading in the lower section of the column was

$$m_m = (0.1)\left(\frac{\frac{0.384}{0.1(1 + 1)}}{\frac{0.384}{0.1(1 + 1} + 1}\right) = 0.066$$

Note that experimental data are available for a loading curve where m = 0.060 but not for m = 0.066. For illustration, this curve is close enough, so the 0.06 curve will be used for the lower section of the columns.

Figure 6 shows the two equilibrium curves for m = 0.1 and m = 0.06 along with the operating lines which have just been evaluated. A horizontal line was drawn from the y axis at the assumed value for the overhead vapor composition y_T. The intersection of this line with the upper operating line represents on the x axis the composition of the liquid entering the top plate or leaving the dissolver. The intersection of the horizontal line with the upper equilibrium curve represents on the x axis the liquid leaving the top stage in the column. Succeeding vertical and horizontal "steps" between the equilibrium curve and operating line will give the vapor and liquid leaving successive stages below the top of the column but above the feed

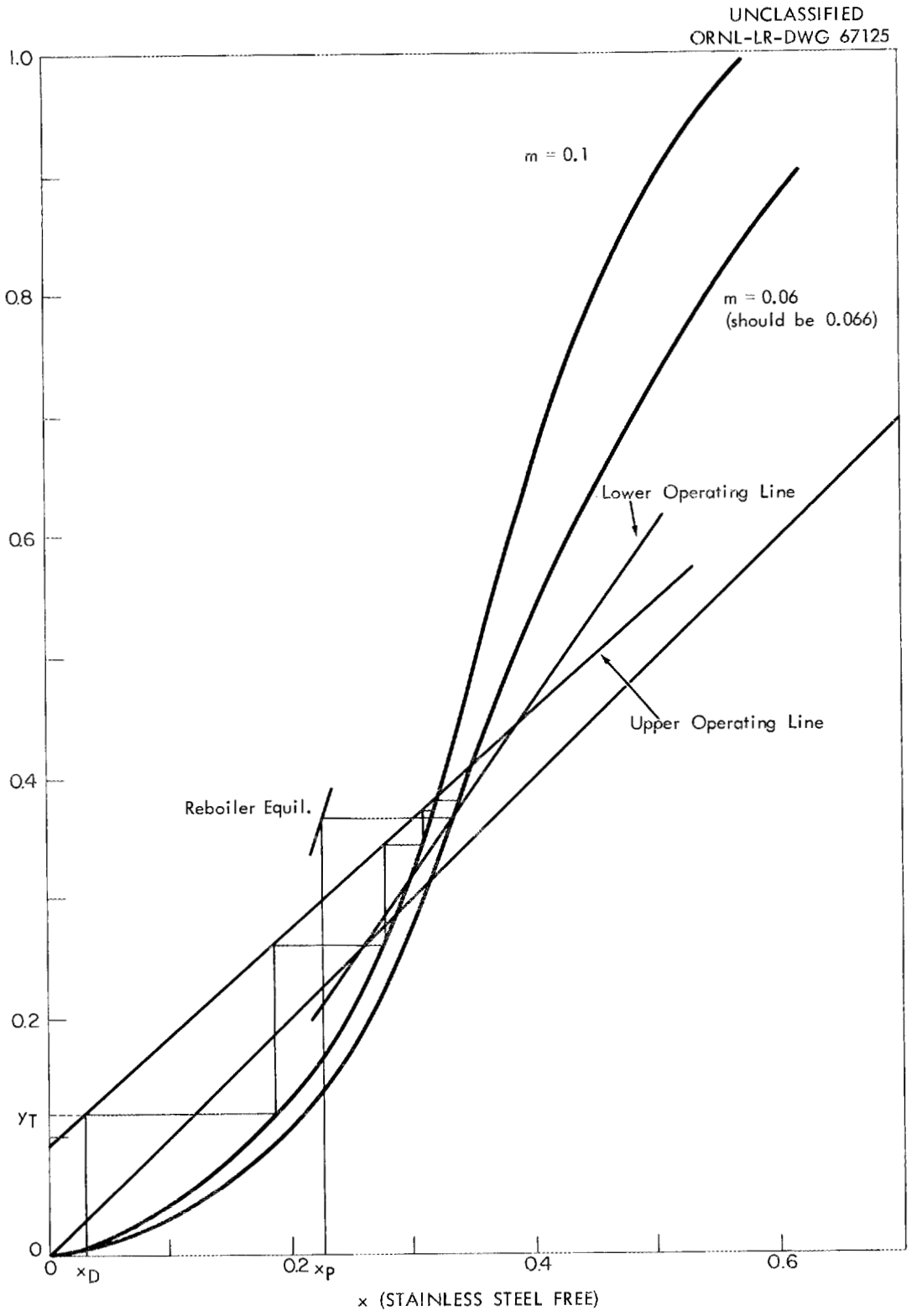

Fig. 6. Example McCabe-Thiele diagram.

point. These steps will work toward the pinch point at which the upper operating line and equilibrium curve intersect.

Eventually one reaches the last stage above the feed point. A number of streams in the stages around the feed point are shown and labeled in Fig. 7. The portion of the x-y diagram around the feed point is magnified in Fig. 8. The liquid composition of the plate below the feed point is determined by constructing a horizontal line to the lower rather than the upper equilibrium curve. The composition of the vapor entering the stage below the feed point from two stages below the feed point is evaluated by constructing a vertical step to the lower operating line. A number of successive steps are then made between the lower equilibrium curve and operating line which correspond to the number of stages in the lower portion of the column. Again note that if one has a large number of stages in the lower portion of the column, the number of stages does not significantly affect the x-y diagram since the steps go into a pinch at the intersection of the lower equilibrium curve and operating line.

After one reaches the last stage of the column and determines the vapor entering the bottom stage from lower operating line, the liquid composition in the reboiler must be found from another equilibrium curve since the metal loading in the reboiler is higher than in the column. We have already established from the over-all material and nitrate balances that the nitric acid composition of the reboiler must be 0.224 and the metal loading 0.224. If from the equilibrium relations of the system one does not find that the vapor composition from this solution is 0.365, then the overhead composition, y_T, has been assumed to have the wrong value. From Eqs. 30 and 31 one finds that in the reboiler

$$\underline{M}_{SS} = \frac{(55.5)(0.224)}{0.285 + (4.22)(0.224) + (4.05)(0.224) + (0.14)(0.224)}$$

$$= 2.73$$

and

$$\underline{M}_{H^+} = \frac{(157)(0.224) + (5.0)(0.224)}{0.285 + (4.22)(0.224) + (4.05)(0.224) + (0.14)(0.224)(0.224)}$$

$$= 7.52$$

From these values, one can determine from Fig. 5 that the composition of the vapor from the reboiler is approximately 0.370. This is essentially the same value obtained by stepping down the column from the assumed overhead composition. If the two values had not agreed one would assume another value for y_T and start again.

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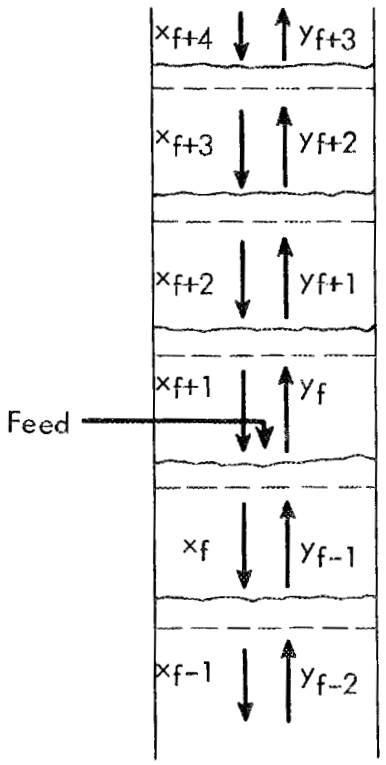

Fig. 7. Internal column streams near the feed point.

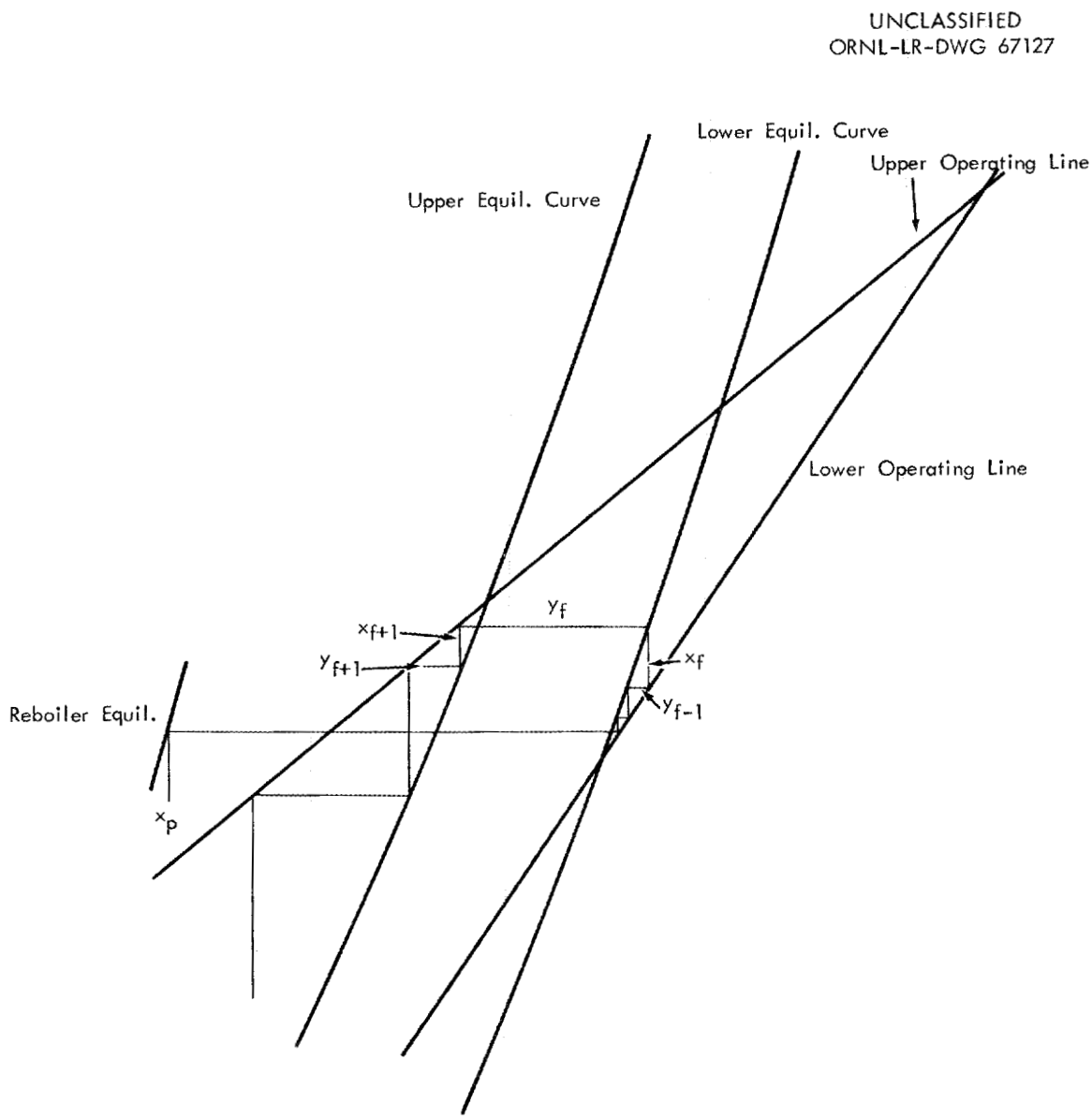

Fig. 8. McCabe-Thiele diagram near the feed point.

7.0 CONCLUSIONS AND RECOMMENDATIONS

The feasibility of operating a Darex chloride distillation system by feeding all of the nitric acid used in the process into a central feed point on the column has been calculated with simplifications. This system promises to better utilize the nitric acid for chloride removal and yet still give good chloride recovery in the overhead. The system was discussed using a nitric acid feed of 15.3 M and shown to give the desirable greater than 5 M overhead with the assumption of no nitrate decomposition or water formation. In an actual system with nitrate losses and water formation, an acid feed greater than 15.3 M will probably be required to give an overhead greater than 5 M.

Because of its promise of better chloride removal, this system is recommended for a Darex head end facility. The problem will be better described by taking into account nitrate losses and water formation. The restrictions of the present discussion caused by failure to account for the presence of chloride and especially its effect on nitric acid volatility will be much more difficult to evaluate.

The studies presented here, even with their limitations, are adequate to establish the soundness of the intermediate feed systems. The effects of the inaccuracy in the assumptions used can be corrected in the pilot plant by simply manipulating setpoints on controllers.

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