

ORNL-TM-1730

CFSTI PRICES

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

H.C. \$93.00; MN .65

CONSIDERATIONS OF LOW PRESSURE DISTILLATION AND ITS APPLICATION
TO PROCESSING OF MOLTEN-SALT BREEDER REACTOR FUELS

L. E. McNeese

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

MARCH 1967

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION



THE UNIVERSITY OF CHICAGO
DIVISION OF THE PHYSICAL SCIENCES

REPORT OF THE COMMITTEE ON THE
PROGRESS OF THE PHYSICAL SCIENCES

FOR THE YEAR 1954



CHICAGO, ILLINOIS
1955



CONTENTS

| | Page |
|---|------|
| Abstract | 1 |
| 1. Introduction | 1 |
| 2. Distillation at Low Pressure | 2 |
| 2.1 Equilibrium Distillation | 3 |
| 2.2 Molecular Distillation | 3 |
| 2.3 Mean Free Path | 4 |
| 2.4 Langmuir Vaporization Rate | 5 |
| 2.5 Probable Operating Mode for MSBR Processing | 10 |
| 3. Relative Volatility | 11 |
| 3.1 Relative Volatility for Equilibrium Distillation | 12 |
| 3.2 Relative Volatility for Molecular Distillation | 14 |
| 3.3 Comparison of Experimental and Calculated Relative Volatilities for Rare Earth Fluorides | 16 |
| 4. Separation Potential of Various Distillation Methods | 16 |
| 4.1 Continuous Distillation | 16 |
| 4.2 Semicontinuous Distillation with Continuous Feed | 19 |
| 4.3 Semicontinuous Distillation with Rectification | 21 |
| 4.4 Batch Distillation | 28 |
| 4.5 Semicontinuous Distillation Followed by Batch Distillation | 29 |
| 4.6 Comparison of Methods Considered | 32 |
| 5. Prevention of Buildup of Nonvolatiles at a Vaporizing Surface by Liquid Phase Mixing | 36 |
| 6. Conclusions and Recommendations | 41 |
| References | 43 |

Q

11

C

CONSIDERATIONS OF LOW PRESSURE DISTILLATION AND ITS APPLICATION
TO PROCESSING OF MOLTEN-SALT BREEDER REACTOR FUELS

L. E. McNeese

ABSTRACT

Distillation at low pressure was examined as a method for removing rare earth fluorides from the fuel stream of a molten-salt breeder reactor. It was concluded that distillation allows adequate rare earth fluoride removal with the simultaneous recovery of more than 99.5% of the fuel salt. Characteristics of equilibrium and molecular distillation were noted and expressions for the relative volatility of rare earth fluorides were derived for these types of distillation.

Expressions for the separation potential of several modes of distillation were derived and reported rare earth fluoride relative volatilities were shown to allow a great deal of latitude in still design and operational mode. It was concluded that a single contact stage such as a well mixed liquid pool provides adequate rare earth fluoride removal and that rectification is not required.

The buildup of rare earth fluorides at the vaporization surface was shown to seriously reduce the effectiveness of a distillation system. Liquid circulation was shown to be an effective means for preventing buildup of rare earth fluorides at vaporization surfaces.

1. INTRODUCTION

The molten-salt breeder reactor (MSBR) is a reactor concept having the possibilities of economic nuclear power production and simultaneous breeding of fissile material using the thorium-uranium fuel cycle.¹ The reactor will be fueled with a mixture of molten fluoride salts which will circulate continuously through the reactor core where fission occurs and through the primary heat exchanger where most of the fission energy is removed. The reactor will employ a blanket of molten fluorides containing a fertile material (thorium)

in order to increase the neutron economy of the system by the conversion of thorium to fissile uranium-233. A close-coupled processing facility for removal of fission products, corrosion products, and fissile materials from these fused fluoride mixtures will be an integral part of the reactor system.

It has been proposed that the rare earth fluorides (REF) and fluorides of Ba, Sr, and Y be removed from the fuel stream by vacuum distillation. The purpose of this report is to examine various factors pertinent to such an operation and to compare several methods for effecting the distillation.

2. DISTILLATION AT LOW PRESSURE

The vaporization of a liquid is normally carried out under conditions such that the liquid and vapor phases are essentially in thermodynamic equilibrium. This condition may cease to exist if the distillation pressure is reduced sufficiently, and phenomena peculiar to low pressure distillation may be observed.

In discussing distillation at low pressure, it is convenient to make a distinction between two modes of distillation: equilibrium distillation and molecular distillation. During equilibrium distillation, a kinetic equilibrium exists at the liquid-vapor interface owing to the presence of a vapor atmosphere above the liquid which has the net effect of immediately returning most of the vaporizing molecules to the liquid surface. In contrast, molecular distillation is carried out in the absence of such an atmosphere and the vaporizing molecules reach the condensing surface without experiencing collisions with other gas molecules or with the walls of the system. In the following sections, consideration will be given to characteristics of these modes of distillation, to values of the mean free path under conditions of interest for MSBR processing, and to calculated values of maximum vaporization rates to be expected.

2.1 Equilibrium Distillation

Equilibrium distillation can be further divided into ebullient distillation and evaporative distillation. Ebullient distillation occurs when bubbles of vapor form within the bulk of the liquid which remains at a temperature such that the vapor pressure is equal to the total external pressure acting on the liquid (in the absence of other gases). Boiling promotes mixing in the liquid and the surface from which vaporization occurs is not depleted in the more volatile species.

Evaporative distillation occurs when the distillation is carried out at a temperature below the boiling point of the liquid. Under these conditions there is no formation of bubbles at points below the liquid surface and no visible movement of the liquid surface. Transfer of the more volatile species to the liquid surface occurs by a combination of molecular diffusion and convective mixing so that depletion of this species in the vicinity of the surface is possible. However, the rate of distillation is relatively low owing to the kinetic equilibrium which exists at the liquid-vapor interface and the liquid surface may have a composition near that of the bulk liquid.

2.2 Molecular Distillation

Molecular distillation is quite similar to evaporative distillation in that vaporization occurs only from a quiescent liquid surface and in that the vaporizing species is transferred to the surface by molecular diffusion and convective mixing. However, few of the vaporizing molecules are returned to the liquid surface by collisions in the vapor space above the liquid and vaporization proceeds at the greatest rate possible at the operating temperature. In order to achieve this condition, the distance between the vaporizing surface and the condensing surface should theoretically be less than the "mean free path" of the distilling molecules. This condition is seldom realized in practice, however the distance should

be no greater than a few mean free paths. These conditions favor a greater buildup of rare earth fluorides at the liquid surface than do those of evaporative distillation at the same temperature where vaporization is impeded by the vapor atmosphere above the liquid which serves to return most of the vaporized molecules to the liquid surface.

2.3 Mean Free Path

In a distillation system, the gases in the region between the vaporizing liquid and the condenser normally consist of a mixture of the distilling molecules and molecules of noncondensable gases. The calculation of the mean free path in this region is complicated by the fact that the vaporizing molecules, which have a net velocity component directed away from the liquid surface, pass into gas whose molecules are in random motion. The mean free path of a type 1 molecule in type 2 molecules may be obtained from a relation given by Loeb² as

$$\lambda_{1,2} = \frac{1}{\pi \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2 n \sqrt{1 + \frac{C_2^2}{C_1^2}}} \quad (1)$$

where

$\lambda_{1,2}$ = mean free path of a type 1 molecule moving among type 2 molecules

σ_1, σ_2 = collision diameters of type 1 and type 2 molecules

n = number of type 2 molecules per unit volume

C_1, C_2 = average velocity of type 1 and type 2 molecules.

By making appropriate substitutions into this relation, one can obtain the following relation for the mean free path of a type 1 molecule in type 2 molecules at a pressure P , both gases being at the temperature T .

$$\lambda_{1,2} = \frac{RT}{\pi \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2 P \left(1 + \frac{M_1}{M_2} \right)^{1/2}} \quad (2)$$

where

R = gas constant, (mm Hg) (cm³)/(°K)(gmole)

σ_1, σ_2 = collision diameters of type 1 and 2 molecules

M_1, M_2 = molecular weights of type 1 and 2 molecules.

Values for the mean free path of LiF in Ar and in LiF at 1000°C are given in Fig. 1. It should be noted that the mean free path of LiF at a pressure of 1 mm Hg is approximately 0.04 cm and that at a pressure of 0.01 mm Hg, the mean free path of LiF is approximately 4 cm. These distances are probably quite small in comparison with the distance between the condenser and the surface from which vaporization will occur in an MSBR distillation system. Hence, the rate of distillation in an MSBR system will be set by the pressure drop between the liquid surface and the condensing surface. The values for the mean free path are sufficiently large that slip-flow may be of importance in pressure drop considerations.

2.4 Langmuir Vaporization Rate

The maximum rate of evaporation of a pure substance was shown by Langmuir³ to be

$$W = 0.0583 \sqrt{\frac{M}{T}} P \quad (3)$$

where

W = evaporation rate, gms/cm².sec

M = molecular weight

T = absolute temperature, °K

P = vapor pressure, mm Hg.

A derivation of this relation will be given in order to show the region of its applicability. Consider a plane liquid surface at a temperature below its boiling point. At equilibrium, the rate of vaporization from the surface will equal the rate of condensation on the surface. Langmuir postulated that the rate of vaporization in a high vacuum is the same as the rate of vaporization in the presence of a saturated vapor and that the rate of condensation in

ORNL DWG 67-19

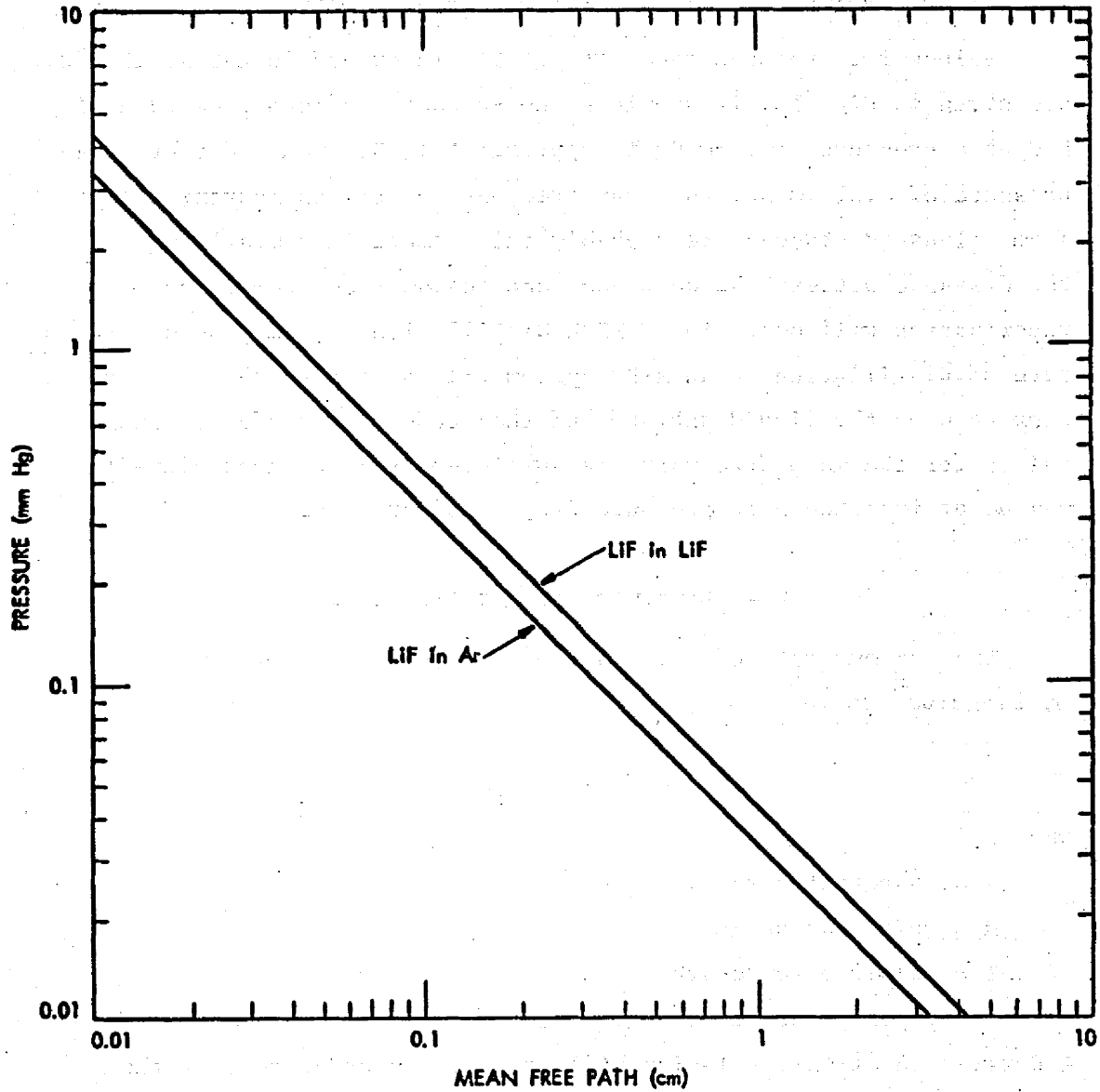


Fig. 1. Mean Free Path of LiF in Ar and in LiF at 1000°C.

a high vacuum is determined by the pressure of the vapor. At equilibrium the rates of vaporization and condensation are equal and the rate of vaporization can be calculated from the rate of condensation.

The vapor contained in a unit cube in contact with the liquid surface is in equilibrium when the number of molecules moving toward the surface equals the number moving away from the surface. For n molecules of mass m in the volume v , the quantity of vapor approaching the liquid surface will be

$$\frac{1}{2} \frac{mn}{v} = \frac{1}{2} \rho \quad (4)$$

where ρ is the vapor density. The average component of velocity of molecules moving toward the surface is $\frac{1}{2} U$, where U is the arithmetic mean velocity of the molecules. The mass of vapor striking a unit area of the liquid surface per unit time is then

$$W = \left(\frac{1}{2} \rho\right) \left(\frac{1}{2} U\right) = \frac{1}{4} \rho U. \quad (5)$$

If the vapor is an ideal gas,

$$\rho = \frac{PM}{RT} \quad (6)$$

and

$$PV = RT = \frac{1}{3} mn \bar{C}^2. \quad (7)$$

Solving for $(\bar{C}^2)^{1/2}$ yields

$$(\bar{C}^2)^{1/2} = \sqrt{\frac{3RT}{M}} \quad (8)$$

where $M = mn = \rho v$. The mean velocity U is related to the root mean square velocity, $(\bar{C}^2)^{1/2}$, as

$$\frac{U}{(\bar{C}^2)^{1/2}} = \sqrt{\frac{8}{3\pi}} \quad (9)$$

so that

$$U = \sqrt{\frac{8RT}{\pi M}}. \quad (10)$$

Thus

$$W = P \sqrt{\frac{M}{2\pi RT}} \quad (11)$$

or

$$W = 0.0583 \sqrt{\frac{M}{T}} P.$$

The assumptions implicit in the use of this relation for calculating the rate of vaporization from a liquid surface include the following:

- (1) The liquid surface is plane.
- (2) The liquid surface is of infinite extent, i.e. collisions of molecules with the vessel walls in the vapor space must exert a negligible influence on the rate of vaporization.
- (3) The vapor behaves as an ideal gas.
- (4) Every part of the liquid surface is within a fraction of the mean free path from every other part or from a condensing surface, i.e., the effect of collisions between evaporating molecules on the rate of vaporization is negligible.
- (5) The number of molecules leaving the liquid surface is not affected by the number striking the surface.
- (6) Vapor molecules striking the liquid surface are absorbed and revaporized in a direction given by a cosine relation which is independent of the direction of approach at the moment of absorption.

When applied to the vaporization of LiF-BeF₂ mixtures, the poorest of these assumptions is likely that of considering the vapor to behave as an ideal gas since it is known that gaseous LiF tends to associate. The vaporization rate given by Eq. 11 represents the maximum rate at which vaporization will occur and hence sets an upper limit on the vaporization rate. Values for the Langmuir vaporization rate of LiF are given in Fig. 2. The vaporization rates observed in practice may be considerably lower than the Langmuir rate since the fourth assumption is rarely met.

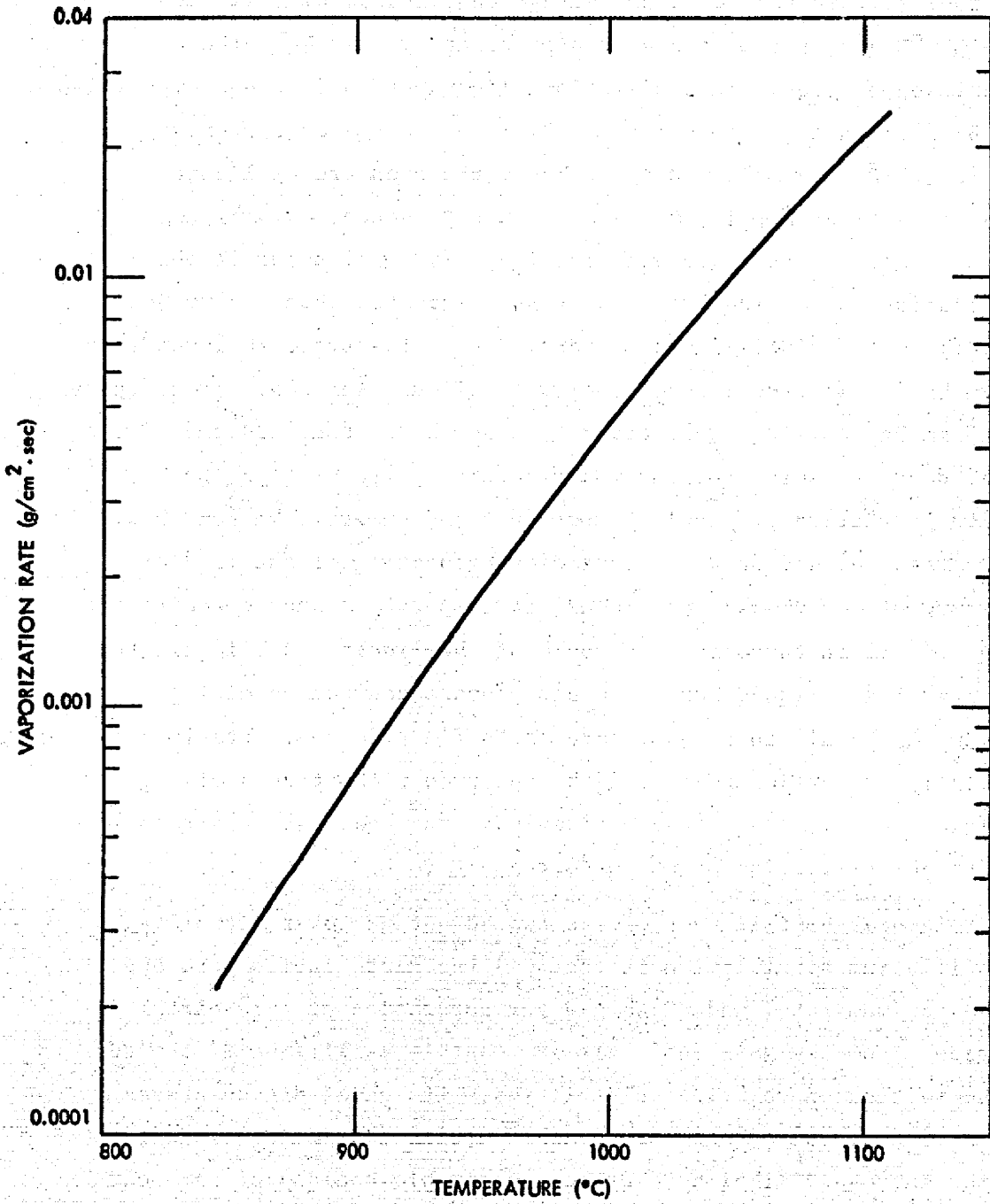


Fig. 2. Langmuir Vaporization Rate for LiF.

2.5 Probable Operating Mode for MSBR Processing

The mode of distillation currently envisioned for processing MSBR fuel salt is that of single stage equilibrium distillation at 950° - 1050° C and at a pressure of approximately 1 mm Hg. The composition of liquid in equilibrium with vapor having the composition of MSBR fuel salt (64 mole % LiF - 36 mole % BeF₂) is approximately 88 mole % LiF - 12 mole % BeF₂.⁴ The vapor pressure of liquid of this composition is \sim 1.5 mm Hg at 1000° C.⁵ Hence, evaporative distillation, with surface vaporization only, will occur if the distillation is carried out at a pressure greater than 1.5 mm Hg. However, if the distillation is carried out at a pressure lower than 1.5 mm Hg, boiling could occur below the liquid surface. At a pressure of 0.5 mm Hg, boiling could occur to a depth of about 0.7 cm. The actual depth to which boiling would occur is dependent on the vertical variation of liquid temperature and composition (and hence vapor pressure) and on the extent of superheating of the liquid; the value of 0.7 cm assumes a constant temperature and concentration and no superheat throughout the bulk of the liquid. Boiling in the vicinity of the liquid surface would promote convective mixing which would result in a lower rare earth fluoride concentration at the liquid surface than would be observed without such mixing. The lower surface concentrations would in turn decrease the relative rate of volatilization of REF with respect to LiF.

Molecular distillation offers two advantages over either type of equilibrium distillation in that (1) the distillation proceeds at the maximum rate, and (2) a greater separation of rare earth fluorides from the MSBR fuel salt is possible as will be discussed in the section on relative volatilities. Its chief disadvantages are the low pressure required to achieve this type of distillation and the increased likelihood of an undesirable buildup of rare earth fluoride at the liquid surface.

The MSBR distillation system will probably be operated at the vapor pressure of the liquid at the vaporization surface or possibly

at a pressure 0.5-1.0 mm Hg lower than the vapor pressure. A decrease in pressure could yield an increase in distillation rate and/or a decrease in operating temperature. Entrainment at the lower pressures should be considered. It is improbable that the advantages to be gained by molecular distillation justify the effort necessary to attain this mode of operation.

3. RELATIVE VOLATILITY

The relative volatility is a convenient form for presenting data relating the composition of liquid and vapor phases at equilibrium and is defined as

$$\alpha_{AB} = \frac{y_A/y_B}{x_A/x_B} \quad (12)$$

where

α_{AB} = relative volatility of component A referred to component B

y_A, y_B = mole fraction of component A, B in vapor

x_A, x_B = mole fraction of component A, B in liquid.

If the concentration of component A is low compared to that of the major component (B), the relative volatility can be expressed in a useful approximate form

$$\alpha_{AB} = \frac{C_v}{C_l} \quad (13)$$

where

C_v = moles A/unit volume of condensed vapor

C_l = moles A/unit volume of liquid.

and where the condensed vapor and liquid are at the temperature at which vaporization is carried out. In a binary system, the error introduced in relative volatility by this approximation depends on the concentration of component A, the relative volatility, and the relative molar volumes of components A and B. The error can be evaluated as follows.

Let α denote the actual relative volatility as defined by Eq. 12, and α^* denote the relative volatility in the approximate form defined by Eq. 13. From Eq. 13,

$$\alpha^* = \frac{Y_A}{X_A} \frac{X_A V_A + (1 - X_A)V_B}{Y_A V_A + (1 - Y_A)V_B}$$

The relation between Y_A and X_A is given by Eq. 12 and its use with the expression for α^* yields the fractional error in α^* as

$$\text{frac error} = \frac{\alpha^* - \alpha}{\alpha} = \frac{X_A(1 - \alpha)(V_A/V_B)}{1 - X_A[1 - \alpha(V_A/V_B)]}$$

The fractional error in α^* is given in Fig. 3 as a function of X_A for various values of α for the case where the molar volumes of A and B are equal. It should be noted that the error in α^* introduced by Eq. 13 is less than 18% for $X_A \leq 0.15$ mole fraction if $\alpha \leq 2.46$. For rare earth fluorides in LiF, the error in α^* will be approximately three times the values shown for $\alpha \leq 10^{-3}$ since the molar volume of rare earth fluorides is approximately three times that of LiF.

The definition of relative volatility given by Eq. 12 has been used throughout this report except in Section 5 where the definition given by Eq. 13 was used.

The appropriate forms of the relative volatility will be derived in the following sections for both equilibrium and molecular distillation, and a comparison of experimental and calculated values of relative volatility for several rare earth fluorides in LiF will be made.

3.1 Relative Volatility for Equilibrium Distillation

In equilibrium distillation, the relative volatility relates the composition of liquid and vapor which are in thermodynamic equilibrium. For the *i*th component of a system which obeys Raoult's Law, one can write

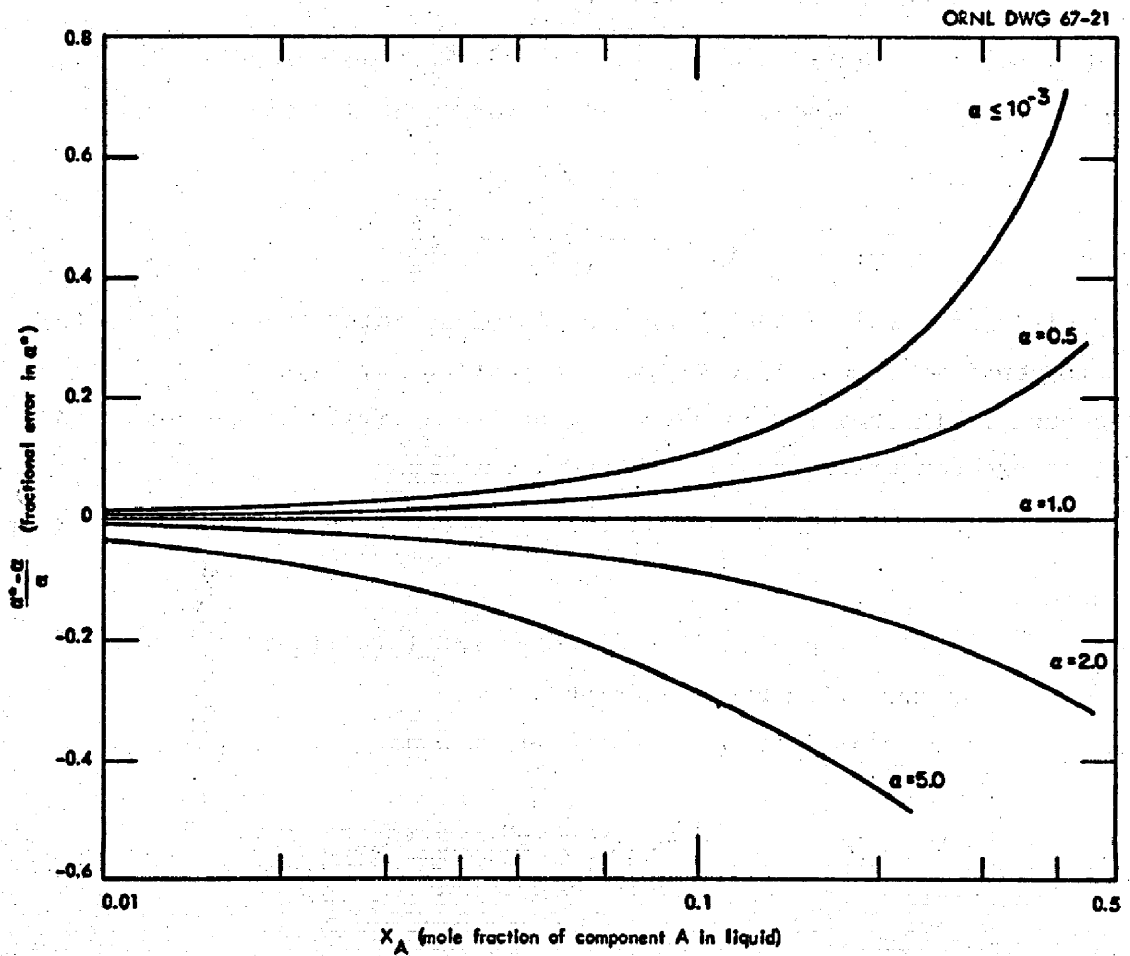


Fig. 3. Error Introduced in Relative Volatility by Use of Approximate Form of Relative Volatility.

$$\pi y_i = P_i x_i$$

where

π = total pressure

P_i = vapor pressure of component i

y_i = mole fraction of i in vapor

x_i = mole fraction of i in liquid.

Substitution of this relation into the definition for relative volatility of component A referred to component B yields

$$\alpha_{AB} = \frac{\frac{P_A x_A}{\pi} / \frac{P_B x_B}{\pi}}{x_A / x_B} = \frac{P_A}{P_B} \quad (14)$$

Raoult's Law implies the absence of chemical interaction between the components under consideration. Interaction may be taken into account if information is available on the activity of the components since one can write for the i th component

$$\pi y_i = \gamma_i P_i x_i \quad (15)$$

where

γ_i = activity coefficient of component i in liquid of the composition under consideration.

The relative volatility may then be written as

$$\alpha_{AB} = \frac{\gamma_A P_A}{\gamma_B P_B} \quad (16)$$

3.2 Relative Volatility for Molecular Distillation

With molecular distillation, the liquid and vapor phases are not in thermodynamic equilibrium; instead, the composition of the vaporizing material is related to that of the liquid by a dynamic equilibrium which is dependent on the relative rates for vaporization of the various components of the liquid. An expression for the rate of vaporization of a pure liquid was derived in Section 2.4.

Division of the rate equation (Eq. 11) by M , the molecular weight yields the molar rate of vaporization as

$$m = \frac{W}{M} = \frac{P}{\sqrt{2\pi RMT}} \quad (17)$$

Thus, the molar rate of vaporization for any substance, at a given temperature, is governed by the ratio of P/\sqrt{M} . In a binary system, if Raoult's Law is assumed,

$$P_i = x_i P_i \quad (18)$$

where

x_i = mole fraction of component i in the liquid

P_i = vapor pressure of pure component i

P_i = partial pressure of component i at liquid surface.

The mole ratio of components vaporizing from the liquid surface is then

$$\frac{m_A}{m_B} = \frac{P_A X_A}{\sqrt{M_A}} \frac{\sqrt{M_B}}{P_B X_B} = \frac{P_A}{P_B} \sqrt{\frac{M_B}{M_A}} \frac{X_A}{X_B} \quad (19)$$

Since the quantity m_A/m_B is related to the ratio of the mole fraction of components A and B in the vapor as

$$\frac{m_A}{m_B} = \frac{y_A}{y_B} \quad (20)$$

where

y_i = mole fraction of component i in vapor

one obtains α , the relative volatility as

$$\alpha = \frac{y_A/y_B}{x_A/x_B} = \frac{P_A}{P_B} \sqrt{\frac{M_B}{M_A}} \quad (21)$$

This should be compared with the relation for relative volatility for equilibrium distillation which was P_A/P_B .

3.3 Comparison of Experimental and Calculated Relative Volatilities for Rare Earth Fluorides

Relative volatilities for several rare earth fluorides in LiF have been measured at 1000°C by Hightower⁶ and the relative volatility of LaF₃ in 87.5 - 11.9 - 0.6 mole % LiF-BeF₂-LaF₃ has been measured at 1000° and 1028°C by Cantor.⁷ These experimental data and calculated relative volatilities for rare earth fluorides for which vapor pressure data^{8,9,10} are available are given in Table 1. Calculated values were obtained using Eq. 14 and Eq. 21.

4. SEPARATION POTENTIAL OF VARIOUS DISTILLATION METHODS

Several modes of operation are available for the distillation of MSBR fuel salt; the choice between these will involve consideration of their separation potential as well as factors such as degree of complexity, economics, etc. In the following sections, a comparison will be made of the separation potential of distillation systems employing continuous, batch, and semicontinuous methods. A semicontinuous system employing rectification will also be considered.

4.1 Continuous Distillation

Consider a continuous distillation system of the type shown in Fig. 4. Salt containing C_f moles REF/mole LiF is fed to the system at a rate of F moles LiF/unit time. A vapor stream containing αC moles REF/mole LiF is withdrawn at the rate of v moles LiF/unit time and salt containing C moles REF/mole LiF is discarded at the rate of $F-v$ moles LiF/unit time. A material balance on REF yields the relation

$$FC_f = (v\alpha + F-v)C.$$

The fraction of the REF removed by the distillation system is then given as

Table 1. Experimental and Calculated Relative Volatilities of Several Rare Earth Fluorides Referred to LiF at 1000°C

| Rare Earth Fluoride | Vapor Pressure mm Hg | Relative Volatility | | |
|---------------------|-------------------------|-----------------------------------|-----------------------------|---|
| | | Experimental | Equilibrium Distillation | Calculated Molecular Distillation |
| NdF ₃ | 1.6×10^{-4} | 6×10^{-4} | 3.1×10^{-4} | 1.1×10^{-4} |
| SmF ₃ | - | 5×10^{-4} | - | - |
| CeF ₃ | 1.3×10^{-4} | 3×10^{-3} | 2.4×10^{-4} | 8.7×10^{-5} |
| LaF ₃ | 2.8×10^{-5} | 3×10^{-4} ^a | 5.2×10^{-5} | 1.9×10^{-5} |
| | | 8.6×10^{-4} ^b | | |
| | | 1.09×10^{-3} | | |

^a Measured in 87.5-11.9-0.6 mole % LiF-BeF₂-LaF₃ at 1028°C.

^b Measured in 87.5-11.9-0.6 mole % LiF-BeF₂-LaF₃ at 1000°C.

ORNL DWG 67-22

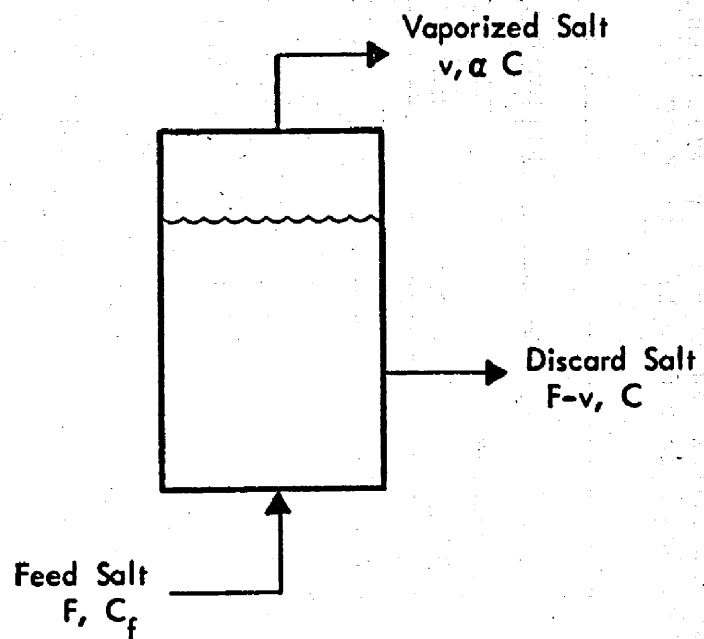


Fig. 4. Continuous Still Having a Uniform Concentration of Rare Earth Fluoride in Liquid.

$$\text{fraction of REF removed} = \frac{(F - v)C}{FC_f} = \frac{1}{1 + \frac{v\alpha}{F - v}} \quad (22)$$

If the fraction of the LiF fed to the system which is vaporized is denoted as f , where

$$f = \frac{v}{F}$$

then

$$\text{fraction of REF removed} = \frac{1}{1 + \frac{f\alpha}{1 - f}} \quad (23)$$

The fraction of REF removed was calculated using Eq. 23 for various values of f and α is shown in Fig. 5.

4.2 Semicontinuous Distillation with Continuous Feed

Consider a single-stage distillation system which contains V moles LiF at any time and a quantity of BeF_2 such that vapor in equilibrium with the liquid has the composition of the MSBR fuel salt. Assume that MSBR fuel salt containing X_0 moles REF/mole LiF is fed to the system at a rate of F moles LiF/unit time where it mixes with the liquid in the system. Let the initial REF concentration in the liquid be X_0 moles REF/mole LiF and let the concentration at any time t be X moles REF/mole LiF. From a mass balance on REF,

$$\frac{d}{dt} (VX) = FX_0 - F\alpha X \quad (24)$$

which has the solution

$$X = \frac{X_0}{\alpha} [1 - (1 - \alpha) \exp(-F\alpha t/V)] \quad (25)$$

for V constant.

The total quantity of REF fed to the system at time t is $(Ft + V)X_0$ and the quantity of REF remaining in the liquid at that

ORNL DWG 67-23

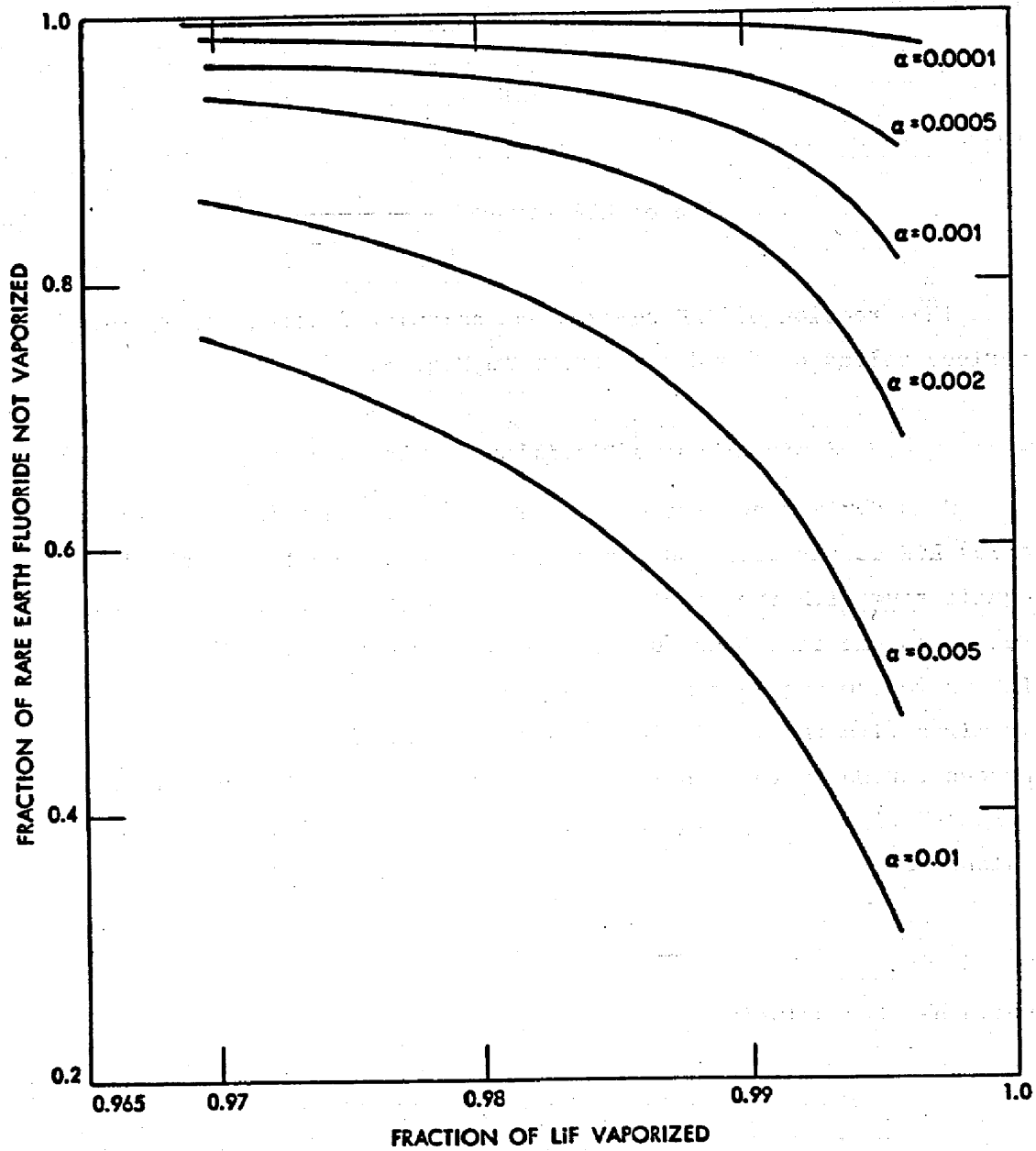


Fig. 5. Rare Earth Fluoride Removal in a Continuous Still as a Function of LiF Recovery and Rare Earth Fluoride Relative Volatility.

time is VX . Thus, the fraction of the REF not vaporized at time t is

$$f_{\text{REF}} = \frac{VX}{(Ft + V)X_0} = \frac{1 - (1 - \alpha) \exp(-F\alpha t/V)}{\alpha \left(\frac{Ft}{V} + 1 \right)} \quad (26)$$

where

f_{REF} = fraction of REF not vaporized at time t .

The fraction of the LiF vaporized at time t is given by the relation

$$f = \frac{Ft}{Ft + V}, \quad (27)$$

where

f = fraction of LiF vaporized at time t .

Substitution of Eq. 27 into Eq. 26 yields the desired relation:

$$f_{\text{REF}} = \frac{1 - f}{\alpha} [1 - (1 - \alpha) \exp(-\alpha f / (1 - f))]. \quad (28)$$

Values for the fraction of REF not volatilized as a function of the fraction of the LiF volatilized are shown in Fig. 6 for various values of REF relative volatility.

4.3 Semicontinuous Distillation with Rectification

Consider a distillation system as shown in Fig. 7, which consists of a reboiler and one theoretical plate to which reflux is returned. The feed stream to the reboiler consists of F moles LiF/unit time plus X_0 moles REF/mole LiF and Z_0 moles BeF_2 /mole LiF. The following assumptions will be made:

- (1) At any time the reboiler contains V moles LiF, where V is constant.
- (2) The initial REF concentration in the reboiler is X_0 moles REF/mole LiF.
- (3) The concentrations of BeF_2 (moles BeF_2 /mole LiF) throughout the system are the steady state values, i.e., the values which would be obtained at steady state with a feed stream containing Z_0 moles BeF_2 /mole LiF and no REF.

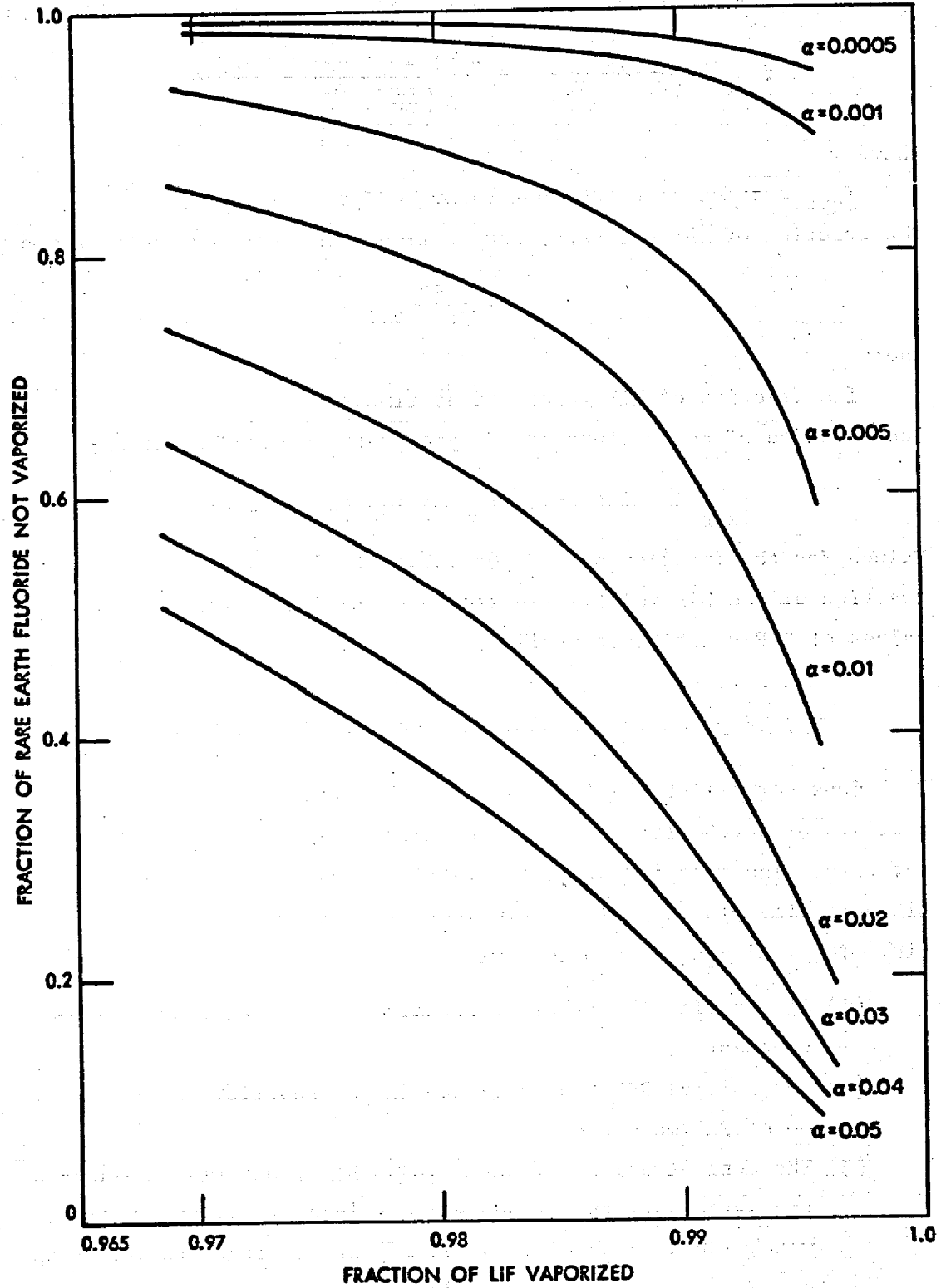


Fig. 6. Rare Earth Fluoride Removal in a Semicontinuous Still as a Function of LiF Recovery and Rare Earth Fluoride Relative Volatility.

ORNL DWG 67-25

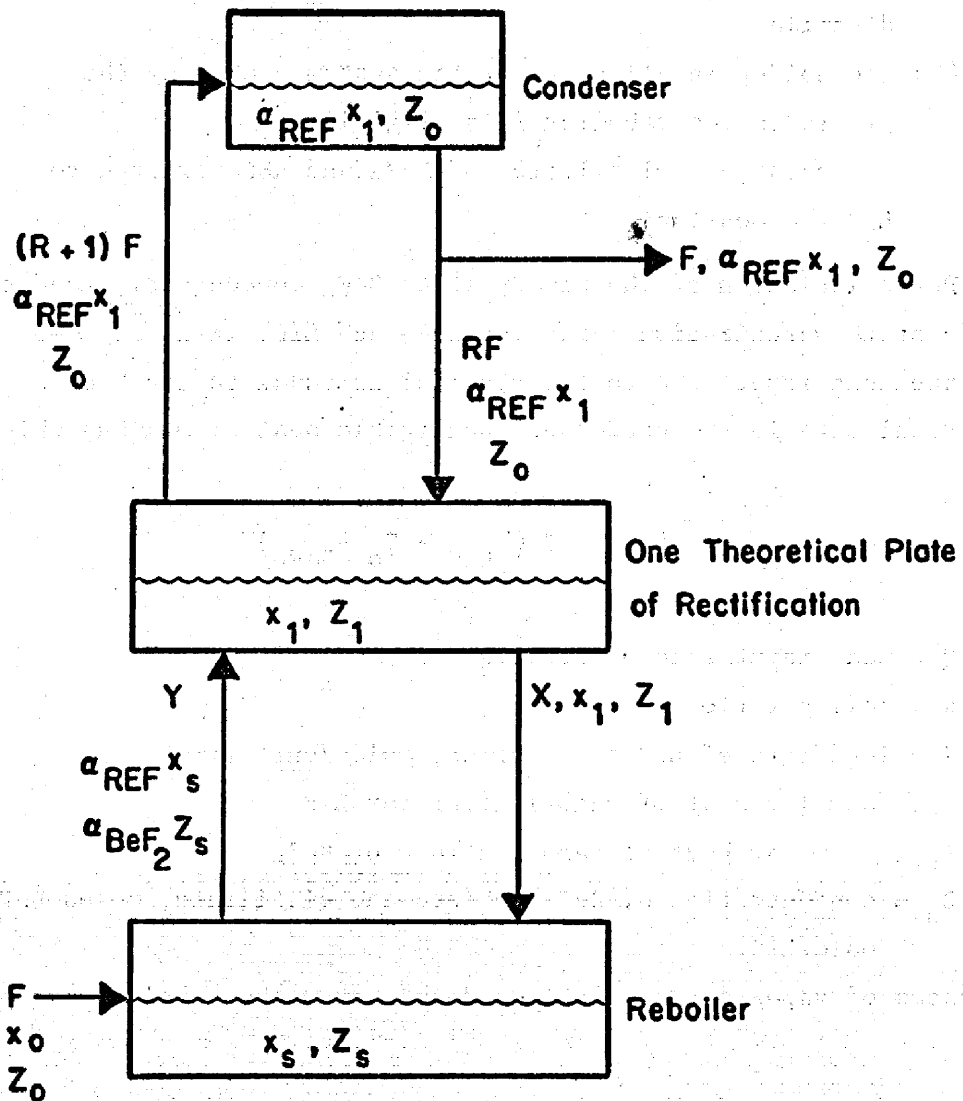


Fig. 7. Semicontinuous Distillation System with Rectification.

- (4) The vaporization rates for LiF and BeF₂ are unaffected by the presence of REF and hence are the steady state vaporization rates. This assumption is made in view of the low concentration of REF in the vapor from the reboiler and hence in the liquid on the plate and in the distillate.
- (5) The holdup in all parts of the system excluding the liquid in the reboiler is negligible.
- (6) The relative volatilities of BeF₂ and REF referred to LiF are constant.

For calculation of the steady state BeF₂ concentration and the steady state vaporization rates for BeF₂ and LiF, it is assumed that the heat input rate to the reboiler is equal to the heat withdrawal rate in the condenser (negligible heat of mixing) which is

$$Q = (R + 1)F (\lambda_{\text{LiF}} + Z_o \lambda_{\text{BeF}_2})$$

where

Q = heat input rate of reboiler

R = reflux ratio

F = feed rate of LiF to reboiler, moles/unit time

λ_{LiF} = molar heat of vaporization for LiF

λ_{BeF_2} = molar heat of vaporization for BeF₂

Z_o = concentration of BeF₂ in feed and distillate, moles BeF₂ mole/LiF.

The rates of vaporization of LiF and BeF₂ from the reboiler are then

$$\text{moles LiF vaporized/unit time} = \frac{Q}{\lambda_{\text{LiF}} + \alpha_{\text{BeF}_2} Z_s \lambda_{\text{BeF}_2}} \quad (29)$$

$$\text{moles BeF}_2 \text{ vaporized/unit time} = \frac{Q \alpha_{\text{BeF}_2} Z_s}{\lambda_{\text{LiF}} + \alpha_{\text{BeF}_2} Z_s \lambda_{\text{BeF}_2}} \quad (30)$$

where

α_{BeF_2} = relative volatility of BeF₂ referred to LiF

Z_s = concentration of BeF_2 in liquid in reboiler, moles $\text{BeF}_2/\text{mole LiF}$.

A material balance on LiF around plate 1 yields

$$\frac{Q}{\lambda_{\text{LiF}} + \alpha_{\text{BeF}_2} Z_s \lambda_{\text{BeF}_2}} + RF = (R + 1)F + X \quad (31)$$

from which

$$X = \frac{Q}{\lambda_{\text{LiF}} + \alpha_{\text{BeF}_2} Z_s \lambda_{\text{BeF}_2}} - F \quad (32)$$

where

X = moles LiF returned to reboiler/unit time from plate 1.

A material balance on BeF_2 around the reboiler gives

$$\frac{QZ_1}{\lambda_{\text{LiF}} + \alpha_{\text{BeF}_2} Z_s \lambda_{\text{BeF}_2}} - FZ_1 + FZ_0 = \frac{\alpha_{\text{BeF}_2} Z_s}{\lambda_{\text{LiF}} + \alpha_{\text{BeF}_2} Z_s \lambda_{\text{BeF}_2}} \quad (33)$$

Substitution of the definition of Q from Eq. 29 with the relation

$$Z_1 = \frac{Z_0}{\alpha_{\text{BeF}_2}}$$

into Eq. 33 yields

$$Z_s = \frac{Z_0}{\alpha_{\text{BeF}_2}} \frac{\frac{R + \alpha_{\text{BeF}_2}}{R + 1} \lambda_{\text{LiF}} + Z_0 \lambda_{\text{BeF}_2}}{\alpha_{\text{BeF}_2} \lambda_{\text{LiF}} + Z_0 \lambda_{\text{BeF}_2} \left[\frac{R \alpha_{\text{BeF}_2} + 1}{R + 1} \right]} \quad (34)$$

A material balance around plate 1 for REF yields

$$\begin{aligned} (R + 1)F\alpha_{\text{REF}}X_1 + \frac{QX_1}{\lambda_{\text{LiF}} + \alpha_{\text{BeF}_2} Z_s \lambda_{\text{BeF}_2}} - FX_1 &= \\ = \frac{Q\alpha_{\text{REF}}X_s}{\lambda_{\text{LiF}} + \alpha_{\text{BeF}_2} Z_s \lambda_{\text{BeF}_2}} + RF\alpha_{\text{REF}}X_1 & \quad (35) \end{aligned}$$

from which

$$X_1 = \frac{Q\alpha_{\text{REF}}X_s}{F(\alpha_{\text{REF}} - 1)(\lambda_{\text{LiF}} + \alpha_{\text{BeF}_2} Z_s \lambda_{\text{BeF}_2}) + Q} \quad (36)$$

A material balance around the reboiler on REF yields

$$V \frac{dX_s}{dt} = FX_0 - \frac{\alpha_{REF} X_s}{\lambda_{LiF} + \alpha_{BeF_2} Z_s \lambda_{BeF_2}} + X x_1 \quad (37)$$

which can be written as

$$\frac{dX_s}{dt} = \frac{F}{V} (X_0 - \beta X_s) \quad (38)$$

where

$$\beta = \frac{(\lambda_{LiF} + Z_0 \lambda_{BeF_2}) \alpha_{REF}^2}{\frac{R + \alpha_{REF}}{R + 1} \lambda_{LiF} + \lambda_{BeF_2} \left[Z_0 + \frac{\alpha_{REF}^{-1}}{R + 1} \alpha_{BeF_2} Z_s \right]}$$

The solution to Eq. 38, with the condition $X_s = X_0$ when $t = 0$ is

$$X_s = \frac{X_0}{\beta} [1 - (1 - \beta) \exp(-F\beta t/v)] \quad (39)$$

from which the fraction of the total REF not vaporized is given by

$$f_{REF} = \frac{1 - f}{\beta} [1 - (1 - \beta) \exp(-\beta f/1 - f)] \quad (40)$$

where

f_{REF} = fraction of total REF fed to system which is contained in liquid in reboiler

f = fraction of total LiF added to system which is vaporized

Values for the fraction of REF not vaporized as a function of the fraction of the LiF vaporized are shown in Fig. 8 for various values of the rare earth fluoride relative volatility. Data used in the calculation were as follows:

$$Z_0 = 0.45 \text{ moles BeF}_2/\text{mole LiF}$$

$$R = 1$$

$$\alpha_{BeF_2} = 5$$

$$\lambda_{LiF} = 53.8 \text{ kcal/mole}$$

$$\lambda_{BeF_2} = 50.1 \text{ kcal/mole}$$

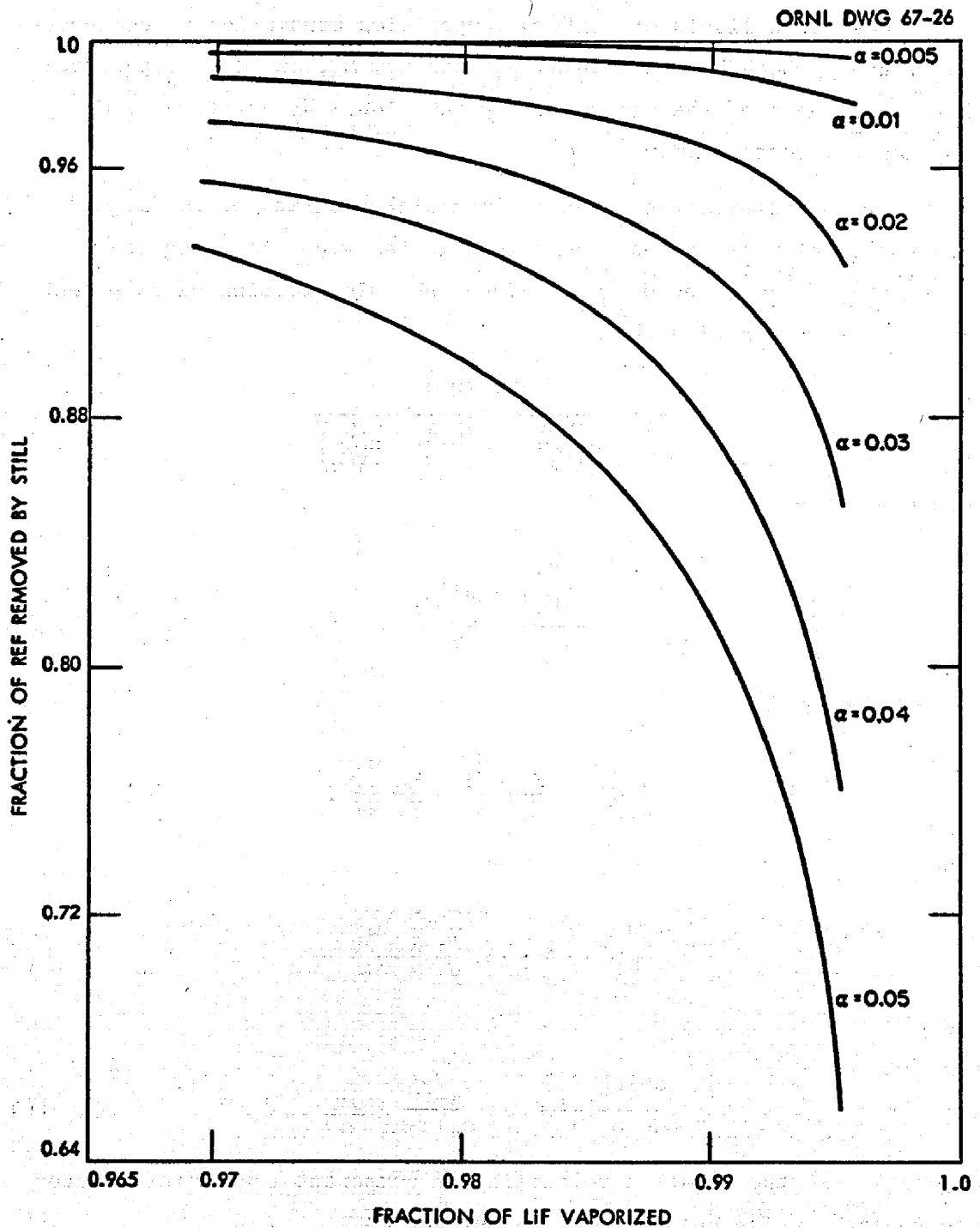


Fig. 8. Rare Earth Fluoride Removal in a Semicontinuous Still Having One Theoretical Stage with Rectification and a Reflux Ratio of Unity.

4.4 Batch Distillation

Consider a liquid of uniform composition consisting of components 1, 2, and 3 which have molecular weights M_1 , M_2 , and M_3 , respectively. Let the weights of the components in the liquid at any time be W_1 , W_2 , and W_3 , respectively.

For the vaporization of a differential quantity of the liquid, the number of moles of each component in the vapor thus produced is $d\left(\frac{W_1}{M_1}\right)$, $d\left(\frac{W_2}{M_2}\right)$, and $d\left(\frac{W_3}{M_3}\right)$. Since the mole fraction of component i in the vapor is given by

$$y_i = \frac{d(W_i/M_i)}{d\left(\frac{W_1}{M_1}\right) + d\left(\frac{W_2}{M_2}\right) + d\left(\frac{W_3}{M_3}\right)} \quad (41)$$

one can write

$$\frac{d\left(\frac{W_i}{M_i}\right)}{y_i} = \frac{d\left(\frac{W_3}{M_3}\right)}{y_3} \quad (42)$$

In the liquid

$$\frac{W_3/M_3}{W_i/M_i} = \frac{X_3}{X_i}, \quad \frac{M_i}{M_3} = \frac{X_3}{X_i} \frac{W_i}{W_3}$$

Thus

$$\frac{dW_i}{dW_3} = \frac{y_i}{y_3} \frac{M_i}{M_3} = \frac{y_i}{y_3} \frac{X_3}{X_i} \frac{W_i}{W_3} \quad (43)$$

Then

$$\frac{d(\log W_i)}{d(\log W_3)} = \frac{y_i/y_3}{x_i/x_3} = \alpha_{i3} \quad (44)$$

where α_{i3} is the relative volatility of component i with respect to component 3. The quantity α_{i3} is defined as

$$\alpha_{i3} = \frac{(\text{moles } i/\text{mole } 3), \text{ vapor}}{(\text{moles } i/\text{mole } 3), \text{ liquid}} = \frac{(\text{mole frac } i/\text{mole frac } 3), \text{ vapor}}{(\text{mole frac } i/\text{mole frac } 3), \text{ liquid}} \quad (45)$$

If α_{13} is constant during the distillation, Eq. 44 can be integrated. Thus if Q_1 and Q_3 are the initial weights of components 1 and 3 in the liquid,

$$\int_{Q_1}^{W_1} d(\log W_1) = \alpha_{13} \int_{Q_3}^{W_3} d(\log W_3). \quad (46)$$

$$\frac{W_1}{Q_1} = \left(\frac{W_3}{Q_3} \right)^{\alpha_{13}} \quad (47)$$

where the quantity W_1/Q_1 represents the fraction of component 1 which remains in the liquid. If the components 1, 2, and 3 are now designated to be a rare earth fluoride (REF), BeF_2 and LiF respectively,

$$\frac{W_{\text{REF}}}{Q_{\text{REF}}} = \left(\frac{W_{\text{LiF}}}{Q_{\text{LiF}}} \right)^{\alpha_{\text{REF}}} \quad (48)$$

$$\frac{W_{\text{BeF}_2}}{Q_{\text{BeF}_2}} = \left(\frac{W_{\text{LiF}}}{Q_{\text{LiF}}} \right)^{\alpha_{\text{BeF}_2-\text{LiF}}} \quad (49)$$

The fraction of the rare earth fluoride not vaporized as a function of the fraction of the LiF vaporized for various values of α_{REF} was calculated from Eq. 48 and is shown in Fig. 9. The vaporization of BeF_2 can be regarded as complete for the probable range of LiF recoveries since for $\alpha_{\text{BeF}_2-\text{LiF}} = 3.0$, vaporization of 90% of the LiF results in vaporization of 99.9% of the BeF_2 .

4.5 Semicontinuous Distillation Followed by Batch Distillation

Consider a still containing V' moles LiF . If a feed stream consisting of F moles $\text{LiF}/\text{unit time}$ which contains X_0 moles $\text{REF}/\text{mole LiF}$ and which may also contain BeF_2 is fed to the still with the condition that the initial REF concentration in the still is X_0 , the concentration of REF in the liquid at time t is given by

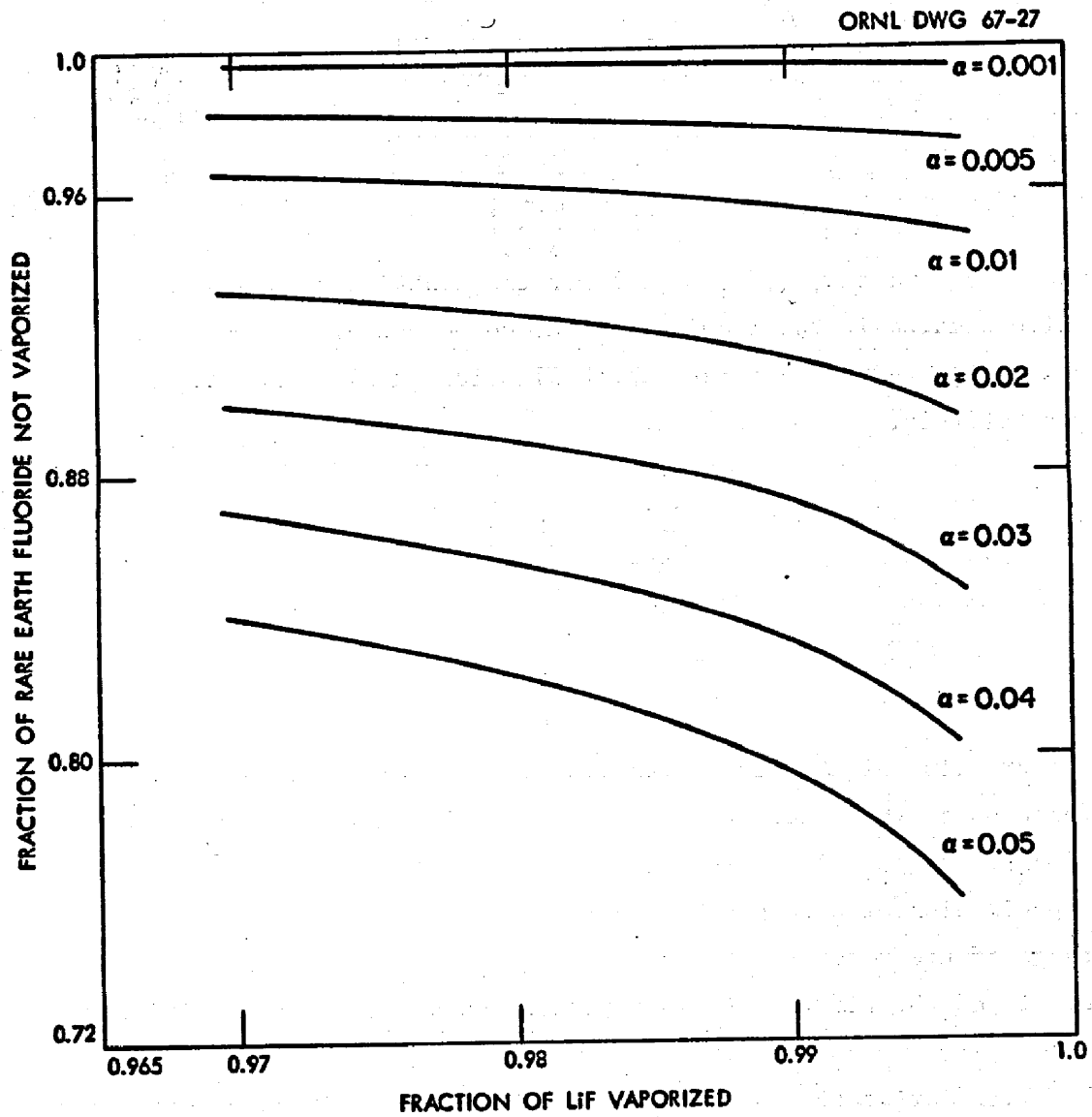


Fig. 9. Rare Earth Fluoride Removal in a Batch Still as a Function of LiF Recovery and Rare Earth Fluoride Volatility.

$$X = \frac{X_0}{\alpha} [1 - (1 - \alpha) \exp(-F\alpha t/V')] \quad (50)$$

where

X = REF concentration in still liquid, moles REF/mole LiF

X_0 = REF concentration in feed, moles REF/mole LiF

α = relative volatility of REF referred to LiF

F = feed rate, moles LiF/unit time

t = time

V' = moles LiF contained in liquid in still.

If at time t the feed is stopped and batch distillation is carried out on the liquid in the still to give a final liquid volume containing V moles LiF, the fraction of the REF which was present in the still at the beginning of batch distillation which remains in the still is then $(V/V')^\alpha$. The moles of REF at the beginning of batch operation is $V'X$ so that the moles of REF in the still at the end of batch operation is $V'X(V/V')^\alpha$. The total moles of REF fed to the system is $(Ft + V')X_0$. Hence the fraction of the total REF which remains in the still is

$$f_{\text{REF}} = \frac{V'X}{(Ft + V')X_0} \left(\frac{V}{V'}\right)^\alpha, \quad (51)$$

which can be written in the form

$$f_{\text{REF}} = \frac{1}{(n + 1)\alpha} [1 - (1 - \alpha) \exp(-n\alpha)] \xi^\alpha \quad (52)$$

where

f_{REF} = fraction of REF which remains in still

$\xi = V/V'$

V = final LiF content of still, moles

V' = initial LiF content of still, moles

$n = Ft/V'$, number of still volumes fed prior to batch operation

F = feed rate to still during semicontinuous operation,
moles/unit time

t = time

α = relative volatility of REF referred to LiF.

The fraction of the LiF which is vaporized by both methods of operation is given by

$$f_{\text{LiF}} = 1 - \frac{\xi}{n + 1} \quad (53)$$

where

f_{LiF} = fraction of LiF vaporized by both methods of distillation. The fraction of REF not volatilized as a function of the fraction of the LiF volatilized for $\xi = 0.1$ (final volume of 10% of still volume) is shown in Fig. 10 for various values of the REF relative volatility.

4.6 Comparison of Methods Considered

A comparison of the various distillation methods must take account of numerous factors such as separation potential, operability, economics, etc. Consideration of all of these factors is beyond the scope of this report, however, the two topics of separation potential and operational simplicity will be discussed.

For currently envisioned processing rates, the required removal efficiency for the rare earth fluorides is approximately 90% for the more important neutron poisons (Pm, Nd, Sm) and less for other members of this group. It should be recalled that the real requirement is the rate at which neutron poisons are removed from the reactor system, hence the "required removal efficiency" can be lowered at the expense of an increased throughput in the processing plant. With this in mind, a rare earth fluoride removal efficiency of 90% will be used as a basis for discussion of separation potential for the various distillation methods.

As shown in Table 1, recent measurements indicate the relative volatilities (referred to LiF) of some of the more important rare earth fluorides to be 6×10^{-4} for NdF_3 , 5×10^{-4} for SmF_3 , and 3×10^{-4} for LaF_3 at 1000°C in LiF. The relative volatility of CeF_3 was found to be 3×10^{-3} , however, the required removal efficiency for CeF_3 is only 8%.

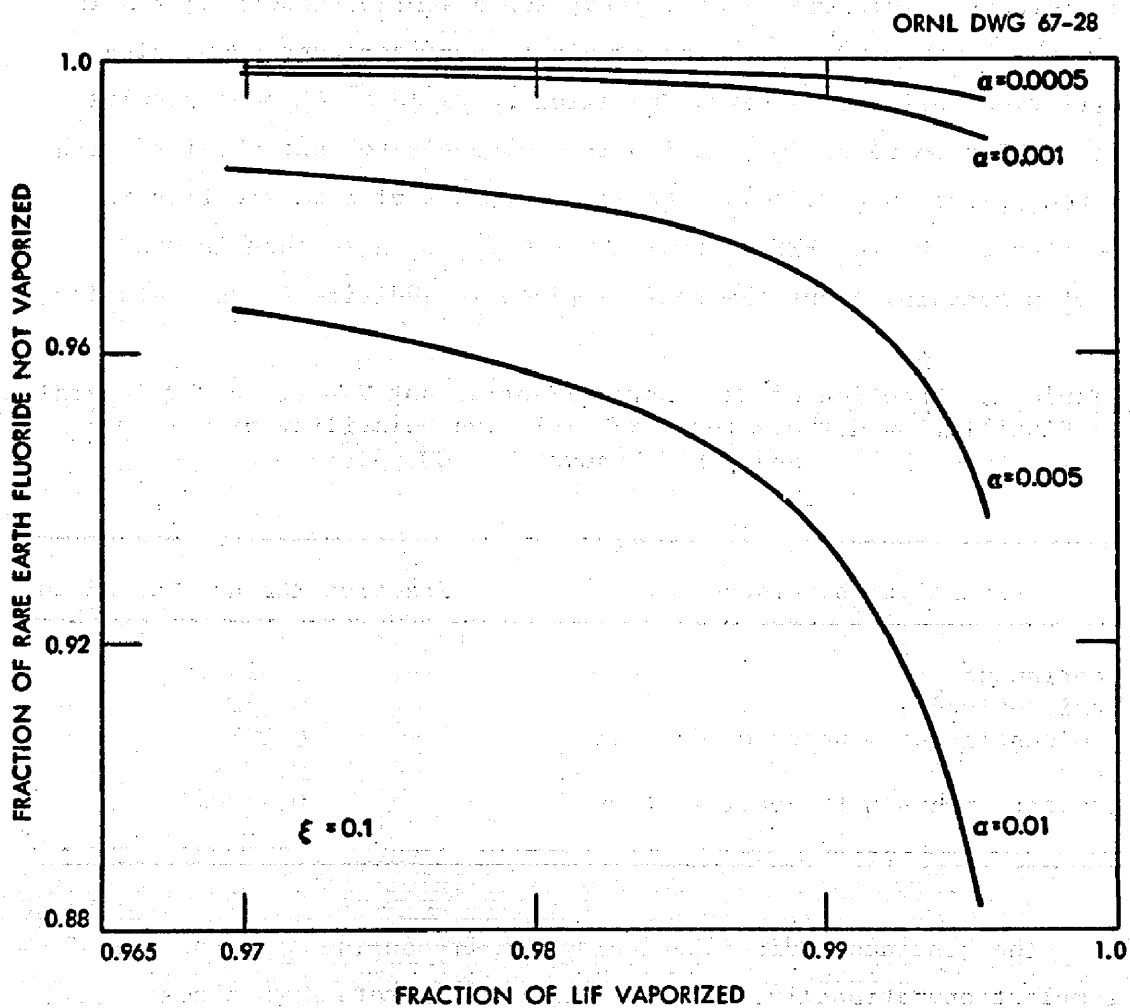


Fig. 10. Variation of Rare Earth Fluoride Removal in a Semi-continuous Still Using a Final Batch Volume Reduction to 10% of the Still Volume.

The fraction of REF not vaporized for the various distillation methods considered is given in Table 2. The values were calculated for a REF relative volatility of 5×10^{-4} and a LiF recovery of 99.5%. As would be expected, the continuous system yields the poorest REF removal (91%) although this is an adequate removal efficiency. The removal efficiency for a semicontinuous system is somewhat higher (95.2%). The combination of semicontinuous distillation followed by batch operation to yield a 10% heel results in a REF removal of 99.5% which is comparable to that obtained with batch operation (99.74%). The effectiveness of rectification is pointed out by the REF removal (99.9967%) for a semicontinuous system containing one theoretical plate in addition to the reboiler.

Table 2. Fraction of Rare Earth Fluoride not Vaporized for Several Distillation Methods for a REF Relative Volatility of 5×10^{-4} and a LiF Recovery of 99.5%.

| Distillation Method | Fraction REF not Vaporized |
|-----------------------------------|----------------------------|
| Continuous | 0.91 |
| Semicontinuous | 0.952 |
| Semicontinuous + batch (10%) heel | 0.995 |
| Batch | 0.9974 |
| Semicontinuous with Rectification | 0.999967 |

The continuous distillation system is considered to be the simplest operationally. This system will operate with a near constant heat load (due to fission product decay) and liquid level which will allow prediction and control of concentration and temperature gradients in the liquid phase and will simplify instrumenting the system. Waste salt could be removed from the system at frequent intervals rather than continuously.

The semicontinuous system is considered to be slightly more complex operationally than the continuous system; this complexity

arises primarily from the transient nature of this mode of operation and the associated variation of the fission product heat load with time. Reduction of the liquid volume in the system near the end of a cycle by batch operation will not complicate instrumenting the system if the heel volume is not less than approximately 10% of the initial still volume.

Operation of a batch system will be significantly more complicated than either of the above systems for a number of reasons. The cycle time for this system should be relatively short in order to maintain an acceptably low salt inventory, hence the system must be charged and discharged frequently. Control of temperature and concentration gradients in the liquid will be complicated by the continual variation of both liquid level and heat generation per unit volume. Near the end of a cycle, the liquid volume in the system will be approximately 0.5% of the initial volume; accurate measurement of liquid level at this point may be difficult.

Conceivably, a continuous distillation system employing rectification would be as simple operationally as a continuous system without rectification. However, a system using rectification probably requires a greater extension of present technology than any of the systems considered. Problems such as vapor-liquid contact are aggravated by the necessity for low pressure, high temperature operation. The very high rare earth removal efficiency achievable with rectification is not required for MSBR processing.

Based on the factors considered, the distillation methods can be listed in order of decreasing desirability as follows:

1. continuous
2. semicontinuous with batch reduction to yield a 10% heel
3. semicontinuous
4. batch
5. continuous with rectification

5. PREVENTION OF BUILDUP OF NONVOLATILES AT A VAPORIZING SURFACE BY LIQUID PHASE MIXING

During vaporization of a multicomponent mixture, materials less volatile than the bulk of the mixture tend to remain in the liquid phase and are removed from the liquid surface by the processes of convection and molecular diffusion. As noted in Section II, low pressure distillation will result in little if any convective mixing in the liquid and an appreciable variation in the concentration of materials of low volatility is possible if these materials are removed by diffusion only. The extent of surface buildup and the effectiveness of liquid phase mixing will be examined for a continuous still, although the phenomena is common to all types of stills.

Consider a continuous still of the type shown in Fig. 11. Fuel carrier salt (LiF-BeF_2) containing fission product fluorides is fed to the bottom of the system continuously. Most of the LiF-BeF_2 fed to the system is vaporized and a salt stream containing most of the nonvolatile materials is withdrawn continuously. The positive x direction will be taken as vertically upward and the liquid withdrawal point and the liquid surface will be located at $x = 0$ and $x = l$, respectively. Assume that above the liquid withdrawal point, molten LiF containing rare earth fluorides (REF) flows upward at a constant velocity V . At the surface, a fraction v/V of the LiF vaporizes and the remaining LiF is returned to the bottom of the still.

Above the withdrawal point, the concentration of REF satisfies the relation

$$D \frac{d^2C}{dx^2} - V \frac{dC}{dx} = 0 \quad (54)$$

and the boundary conditions are:

at $x = l$

$$-D \left. \frac{dC}{dx} \right|_{x=l} + VC_s = v\alpha C_s + (V - v)C_s \quad (55)$$

ORNL DWG 67-29

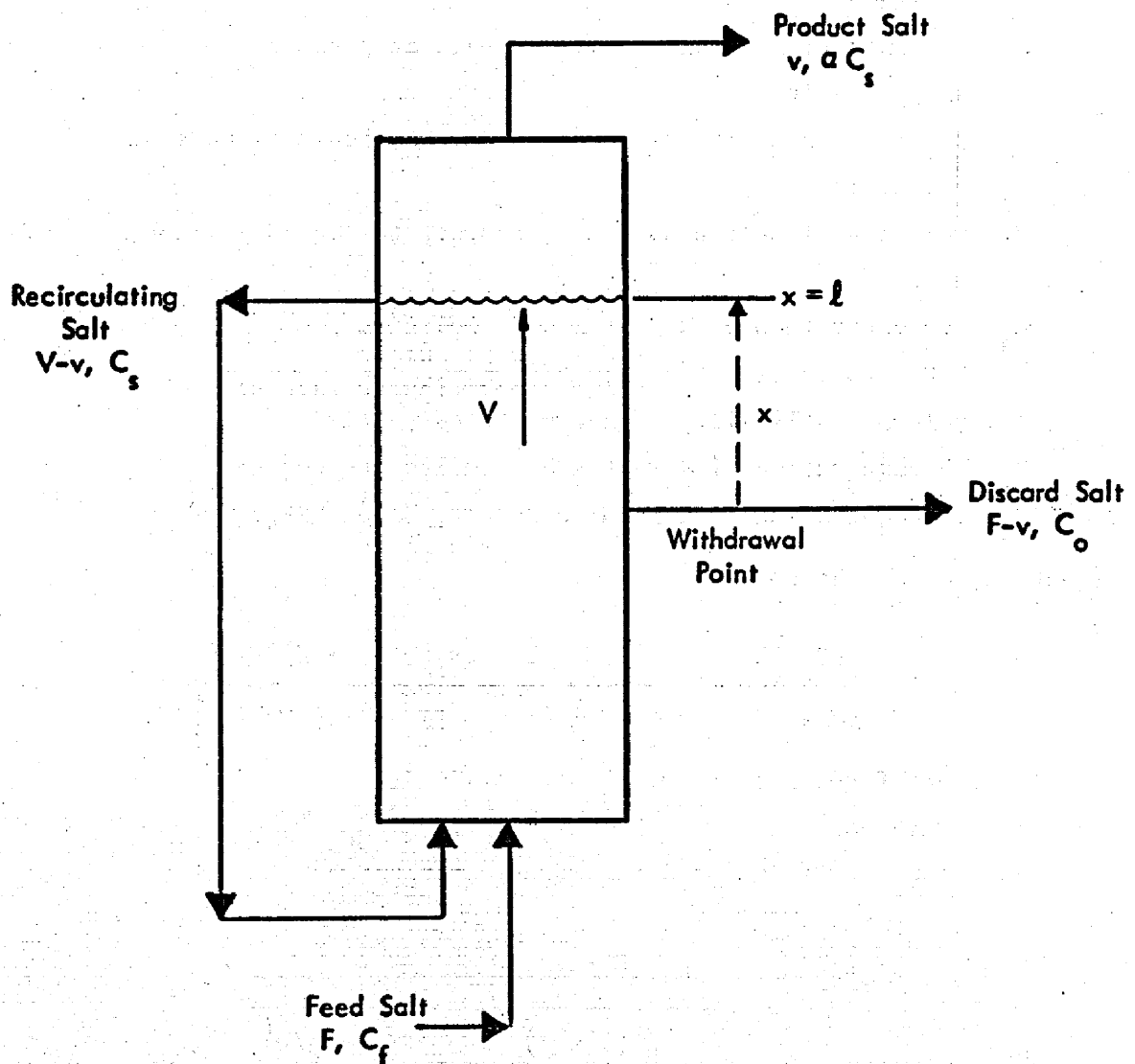


Fig. 11. Continuous Still Having External Circulation and a Nonuniform Liquid Phase Rare Earth Fluoride Concentration Gradient.

and at $x = 0$

$$-D \frac{dC}{dx} \Big|_{x=l} + VC_0 = (V - v)C_s + FC_f - (F - v)C_0 \quad (56)$$

where

D = diffusivity of REF in molten salt of still pot concentration, cm^2/sec

C = concentration of REF in molten salt at position x , moles REF/ cm^3 salt

x = position in molten salt measured from liquid withdrawal point, cm

V = velocity of molten salt with respect to liquid surface, cm/sec

C_s = concentration of REF at $x = l$, moles REF/ cm^3 salt

v = LiF vaporization rate, $\frac{\text{cm}^3 \text{ LiF (liquid)}}{\text{cm}^2 \text{ vaporizing surface} \cdot \text{sec}}$

α = relative volatility of REF referred to LiF

C_0 = concentration of REF at $x = 0$, moles REF/ cm^3 salt

C_f = concentration of REF in feed salt, moles REF/ cm^3 salt

Equation 54 has the solution

$$C(x) = \frac{FC_f \left\{ 1 - \frac{v}{V} (1 - \alpha) [1 - \exp(-V(l - x)/D)] \right\}}{v\alpha + (F - v) \left\{ 1 - \frac{v}{V} (1 - \alpha) [1 - \exp(-Vl/D)] \right\}} \quad (57)$$

The fraction of the REF removed by the still is

$$\begin{aligned} \text{fraction REF removed} &= \frac{(F - v)C_0}{FC_f} = \\ &= \frac{F - v}{F - v + \frac{v\alpha}{1 - \frac{v}{V} (1 - \alpha) [1 - \exp(-Vl/D)]}} \end{aligned} \quad (58)$$

The fractional removal of REF for a continuous system having a perfectly mixed liquid phase was derived earlier and is given by Eq. 23. The ratio of the fractional removal of REF in a system

having a nonuniform concentration to that in a still having a uniform concentration will be denoted as ϕ and can be obtained by dividing Eq. 58 by Eq. 23. Thus

$$\phi = \frac{1 + \frac{v\alpha}{F - v}}{1 + \frac{\frac{v\alpha}{F - v}}{1 - \frac{v}{V}(1 - \alpha)[1 - \exp(-Vl/D)]}} \quad (59)$$

Values of ϕ calculated for a still in which 99.5% of the LiF fed to the still is vaporized ($v/F - v = 199$) and in which the relative volatility of REF is 5×10^{-4} are given in Fig. 12. The following two effects should be noted:

1. The value of ϕ is essentially unity for $Vl/D < 0.1$ for any value of v/V (fraction of LiF vaporized per circulation through still). Within this region, a near uniform REF concentration is maintained by diffusion of REF within the liquid and mixing by liquid circulation is not required.
2. The value of ϕ is strongly dependent on v/V for $Vl/D > 1$. Within this region, a near uniform REF concentration can be maintained only if liquid circulation is provided. For $Vl/D = 100$, ϕ has a value of 0.0055 with no liquid circulation and a value of 0.99 if 90% of the LiF is returned to the bottom of the still.

An actual still would probably operate in the region $Vl/D > 1$ so that the importance of liquid circulation can not be over emphasized. Liquid phase mixing by circulation is believed to be an essential feature of an effective distillation system. In the case considered, circulation was provided by an external loop for mathematical convenience. In an actual still internal circulation could be provided by a toroidal liquid flow path which, for a liquid having a strong volume heat source (provided in the present case by fission product decay), would result if more cooling were provided to the still in an outer annular region than in the center.

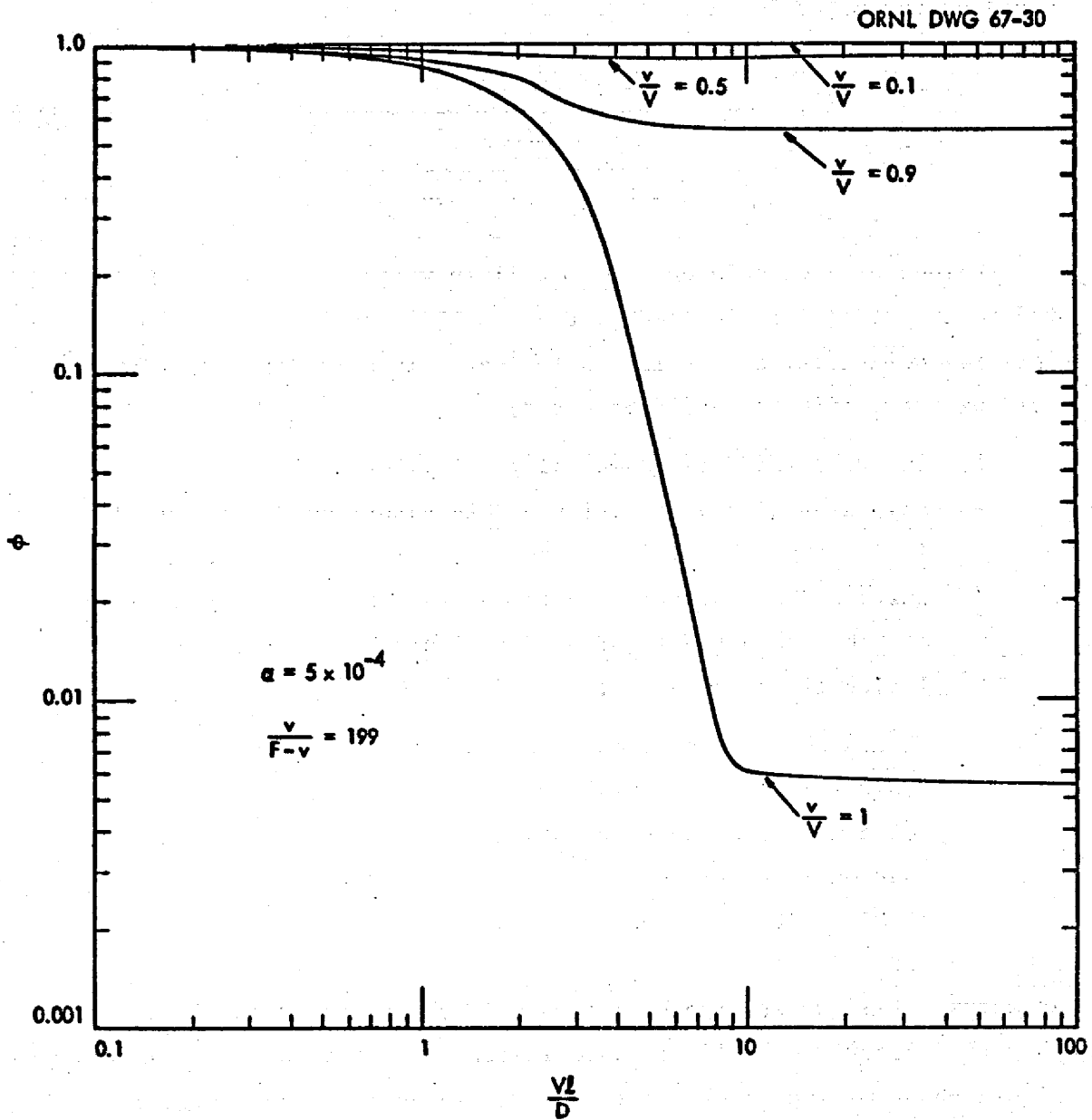


Fig. 12. Ratio of Fraction of Rare Earth Fluoride Removed in Still Having Nonuniform Concentration to That Still Having Uniform Concentration.

6. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions have been drawn from the information considered in this report:

1. Distillation at low pressure allows the adequate removal of rare earth fluorides from MSBR fuel salt and the simultaneous recovery of more than 99.5% of the fuel salt.
2. Recently reported relative volatilities of several rare earth fluorides allow a great deal of latitude in still design and operational mode. A single contact stage such as a liquid pool is adequate and rectification is not necessary.
3. The effectiveness of a distillation system can be seriously decreased by the buildup of rare earth fluorides at the surface of the vaporizing liquid.
4. Liquid circulation can provide adequate liquid phase mixing and is an essential feature of an effective distillation system.

The following recommendations are made:

1. Further consideration should be given to the use of single-stage, continuous distillation for removal of rare earth fluorides from the fuel stream of an MSBR.
2. The study of liquid phase temperature and concentration profiles should be extended to stills having configurations of interest for MSBR processing. Methods should be devised for the calculation of velocity, temperature and concentration in the liquid phase of a three dimensional still having a distributed heat source. The effect of variations in heat generation rate should be considered.

3. Removal of fission product decay heat from a distillation system should be studied. Heat removal systems which maintain the temperature within acceptable limits in the event of failure of the primary cooling system should be devised.
4. Factors which limit distillation rate such as operating pressure, the presence of noncondensables, and entrainment should be examined.

REFERENCES

1. P. R. Kasten et al., Design Studies of 1000-Mw(e) Molten Salt Breeder Reactors, USAEC Report ORNL-3996, Oak Ridge National Laboratory, August 1966.
2. L. B. Loeb, The Kinetic Theory of Gases, McGraw-Hill Book Co., New York, 1934, p. 98.
3. G. Burrows, Molecular Distillation, Clarendon Press, Oxford, 1960, p. 20.
4. Oak Ridge National Laboratory, Molten-Salt Reactor Program Semiannual Progress Report for Period Ending February 1966, USAEC Report ORNL-3936, p. 130.
5. Oak Ridge National Laboratory, Reactor Chemistry Division Annual Progress Report for Period Ending December 31, 1965, USAEC Report ORNL-3913.
6. Oak Ridge National Laboratory, Unit Operations Section Quarterly Progress Report for Period Ending September 1966, USAEC Report ORNL-4075.
7. Oak Ridge National Laboratory, Molten-Salt Reactor Program Semiannual Progress Report for Period Ending August 1966, USAEC Report ORNL-4037.
8. Lim, M. J., Vapor Pressure and Heat of Sublimation of Cerium (III) Fluoride, UCRL-16150, University of California, 1965.
9. Mar, R. W., Vaporization Studies of Lanthanum Fluoride, UCRL-16649, University of California, 1966.
10. Zmbov, K. F., and J. L. Margrave, Mass-Spectrometric Studies at High Temperatures. XI. The Sublimation Pressure of NdF_3 and the Stabilities of Gaseous NdF_2 and NdF , Journal of Chemical Physics, 45, 3167 (1966).



DISTRIBUTION

1. MSRP Directors Office, 9204-1
2. G. M. Adamson
3. C. F. Baes
4. S. E. Beall
5. E. S. Bettis
6. R. E. Blanco
7. F. F. Blankenship
8. E. G. Bohlman
9. R. B. Briggs
10. R. E. Brooksbank
11. S. Cantor
12. W. L. Carter
13. G. I. Cathers
14. W. H. Cook
15. F. L. Culler, Jr.
16. D. E. Ferguson
17. L. M. Ferris
18. H. A. Friedman
19. H. E. Goeller
20. W. R. Grimes
21. C. E. Guthrie
22. P. N. Habenreich
23. J. R. Hightower, Jr.
24. R. W. Horton
25. P. R. Kasten
26. R. J. Kedl
27. M. J. Kelly
28. C. R. Kennedy
29. H. T. Kerr
30. S. S. Kirslis
31. R. B. Lindauer
32. H. G. McPherson
33. H. F. McDuffie
34. L. E. McNeese
35. R. L. Moore
36. E. L. Nicholson
37. A. M. Perry
38. D. Scott
39. J. H. Schaffer
40. C. E. Schilling
41. M. J. Skinner
42. J. R. Tallackson
43. R. E. Thoma
44. J. S. Watson
45. A. M. Weinberg
46. M. E. Whatley

DISTRIBUTION (contd)

- 47-48. Central Research Library
- 49-50. Document Reference Section
- 51-53. Laboratory Records
- 54. Laboratory Records-RC
- 55. Research and Development Div (ORO)
- 56-70. DTIE