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ANALYSIS OF THE
OPTIMUM EXTRACTION SYSTEM DESIGN
FOR THE SEPARATION AND PURIFICATION
OF RARE EARTHS

by
Kenneth Yeon-Kang Chan

A Dissertation
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

Department of Chemical Engineering,
Chemistry, and Environmental Science

January 1993

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APPROVED PAGE

Analysis of the
Optimum Extraction System Design
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of Rare Earths

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ABSTRACT

Analysis of the Optimum Extraction System Design for the Separation and Purification of Rare Earths

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A mathematical model for the liquid-liquid equilibrium of the lanthanide and yttrium oxides in the nitric acid - water - tributyl phosphate ($\text{HNO}_3\text{-H}_2\text{O-TBP}$) two-phase system has been developed. This model is based on the inter-relationships of chemical reactions, phase equilibrium, and material balance. The chemical reactions were modelled using experimentally derived empirical equations for components involved. The distribution coefficients of 16 rare earths which were experimentally determined by UK Harwell Laboratory were used to evaluate the parameters of this equilibrium model. Once model parameters are determined, material balance for all species in the $\text{HNO}_3\text{-H}_2\text{O-TBP}$ two-phase system can be accomplished simultaneously.

The developed equilibrium model was validated by a published experimental extraction system for the separation and purification of specific component from the mixture of lanthanide and yttrium elements.

This model was used for analyzing the minimum production cost of extraction systems for (1) separation and purification of europium from the lanthanide and yttrium mineral sample; and (2) purification of yttrium from the mixture of lutetium, ytterbium and yttrium.

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This thesis is dedicated to my parents
Shu-Chien and Chiming Chan

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CHAPTER 1

INTRODUCTION

1.1 Introduction

The rare earth elements of lanthanide and yttrium are important and essential raw materials for various industries. Currently, they are widely used in metallurgy, glass, ceramics, illumination, electronics, chemicals, magnets and nuclear areas. The largest use of rare earths is as catalysts in petroleum operations. However, specific rare earth elements are rapidly gaining importance as ingredients in many new applications. These include glass and ceramics, lasers, communication and computer systems, color television, and microwave. The demand for specific rare earths - yttrium, scandium, neodymium, samarium, lanthanum, cerium, and dysprosium - is expected to increase rapidly. This is due to their potential use in high technology applications such as high-intensity magnets, laser, and superconductor materials.

Due to their similar atomic structures and chemical properties, the separation of rare earths into individual elemental compounds is difficult. Because of technical and economic limitations, liquid-liquid extraction has emerged in recent years as a major separation process for rare earths. In a typical rare earths processing plant, over one hundred contact stages are being used in order to have them

separated and purified, and meet the purity specifications (sometimes up to 99.99%).

1.2 Development Of The Rare Earths Equilibrium Model

Tri-n-butyl Phosphate (TBP) has many desirable solvent characteristics in extracting rare earth nitrate from aqueous solution: its relatively high distribution coefficients and separation factors, low volatility, and immiscibility with water when pre-equilibrated with it. Therefore, many attempts and efforts have been done since the early fifties, in exploring the applicabilities of rare earths separation and purification, in developing a model for predicting the rare earths distribution in two immiscible phases, and in developing a method for foretelling the stage-wise process conditions in an liquid-liquid extraction operation (3).

This early research work was conducted by the Ames Laboratory of the Atomic Energy Commission, at Ames, Iowa. Bochinski and his colleagues (1) laid the groundwork by developing a method for stage-wise calculations from the equilibrium constants and separation factor data in an extraction operation. Knapp and co-workers (2) obtained equilibrium constants and separation factor data for various rare earth mixtures both in acidic and neutral organophosphorus extractant systems. Schoenherr (3) developed a method of predicting equilibria for certain rare earth nitrates in the $\text{HNO}_3\text{-H}_2\text{O-TBP}$ system. By observing

the distribution of neodymium nitrate - nitric acid mixtures, he found that the distribution of neodymium nitrate was approximately the same as that of nitric acid. This phenomenon was also observed for the distribution of mixtures of samarium nitrate and nitric acid. Thus the conclusion was drawn that the distribution of nitric acid alone could be used as a good approximation of the distributions of neodymium nitrate - nitric acid mixtures and samarium nitrate and nitric acid.

A Russian group made an extensive practical study of extraction of rare earths by TBP from nitrate solutions. Pebalk et al. (4) derived equations from equilibrium curves, so they could calculate the number of theoretical stages required for a specific degree of separation of rare earth elements by TBP extraction.

Some semiempirical models were also developed by Eills (5) and Ioannou et al. (6). Their theories are based on the similarity between gas adsorption or vapor-liquid equilibrium and extraction equilibrium. Models like this have greater applicability than others to hydrometallurgical systems.

Hoh and Bautista (7), presented a method for the prediction of distribution coefficients in the Pu(IV) and Np(IV) nitrate-HNO₃-TBP(dilute) systems, based on the thermodynamic equations for extraction of the species using chemically based models. The predictive model equation makes use of the aqueous actinide nitrate complex stoichiometric

stability constant expressed as degree of formation, the extraction mechanism derived by them, and the equilibrium constant for the extraction reaction. Good agreements were obtained between the reported experimental data and the predicted values. Later on, Hoh and Bautista (8) expanded their model from binary system to multicomponent systems. The theory for multicomponent was based on the assumption that the activity coefficient varies only slightly with its concentration. The experimental results show that the data fit the binary model very well and to a lesser degree the ternary model. The variance between the experimental data and the ternary models is attributed to the omission of the interaction terms between species.

Recently, Horng (9), Horng and Maa (10) developed a semiempirical model for the extraction of metals in acid media by neutral, acidic and basic solvent, based on reaction kinetics. After extensively studying the extraction kinetics for the metal using these three types of extractants, they assumed that the extraction rate of metallic species is pseudo first order with respect to its concentration and the concentration of organic extractant. The stripping rate of metallic species in the organic phase is also pseudo first order with respect to its concentration. Based on the assumptions they made, generalized expressions for the reaction kinetic were developed. The parameters of expressions were evaluated by fitting the expressions to the experimental equilibrium data

from 60 different systems. A non-linear optimization method was applied. The model has been tested in the $\text{UO}_2(\text{NO}_3)_2$ - HNO_3 -TBP system. The agreement between the experimental and predicted distribution data is very satisfactory except at low aqueous acidity.

1.3 The Scope Of This Research

The scope of this research has been in development of a mathematical model for predicting the distribution coefficients of rare earth in the HNO_3 - H_2O -TBP two-phase system, with large acidity range in the aqueous phase. Theoretically, this model is based on the inter-relationships of chemical reactions, phase equilibrium, material balance, activity coefficients, and empirical equations for the concentration of chemical species which are involved in the extraction mechanism. Because of the engineering point of view, this research is more focus on the fact than the theory. Multistage liquid-liquid extraction equipment is operated frequently in an adiabatic manner. When entering streams are at the same temperature and heat of mixing is negligible, the operation is also isothermal. Therefore, no relationship in heat or temperature is involved in this model, even though the temperature will affect the distribution coefficients (68). Practical process design of separation and purification of rare earths are also part of this research. Finally the analysis of the optimum extraction system design in terms of

capital costs and operating costs for the separation and purification of rare earths concludes this research.

Chapter 2 lays the theoretical foundation of this chemical based, semiempirical distribution coefficient model. Literatures, chemistry, theories, definitions, experimental data, and all necessary information involving the model construction are briefly discussed in this chapter.

Chapter 3 discusses the construction of the model. The expression of distribution model was derived in terms of activities, together with the development of other accessories relationships.

Chapter 4 discusses the evaluation of model parameters. A non-linear optimization technique is applied. The deviation of the model predicted data and the actual experimental data is treated as the object function in the optimization algorithm. The formulas or equations for the inter-relationships are used as equality constraints, and all specie concentrations and parameters as inequality constraints, because they all greater than zero and less than a positive finite number.

This model has been verified using published data with satisfactory results. The experiments of separating the promethium from mixed fission product rare earths by extraction were used to verify the accuracy of this model. By comparing the laboratory reported with model predicted operating conditions, we have concluded that this model

accurately predicts liquid-liquid equilibrium. All discussions of model verification are included in Chapter 5. A computer program was developed to simulate the liquid-liquid extraction operations.

Chapter 6 discuss the separation and purification of europium from a rare earths mineral sample taken from Jiangxi Province, China. The composition of the Jiangxi sample includes all 15 rare earth elements except promethium, because promethium does not exists in natural rocks. The effects of the number of stages on europium extraction were studied extensively in the $\text{HNO}_3\text{-H}_2\text{O-TBP}$ system. The conclusion drawn from the europium purification is that the recovery and purity of product are governed by the acidity of the aqueous solution, ratio of aqueous solution rate to the organic extractant rate, and the number of contact stages. Similar discussions for yttrium purification processes are included in Chapter 7.

All economic aspects are included in Chapter 8. The total production cost consists of capital investment and operating costs. The capital investment was estimated by directly relates the total capital cost to the expenses for purchased equipment by a multiplying factor. The operating costs include: costs for raw materials, replacing of loss solvent, labor and maintenance, loss incurred by unrecovered solute and interest charges. Cost analysis were made for three case studies: the separation and purification of europium oxide; the purification of yttrium oxide; and the

separation of gadolinium from the sub-group Ga-La. The optimum process parameters for all cases were also given, this includes operating conditions and number of stages required, in terms of minimum total production cost.

Finally, Chapter 9 concludes this research work and some suggestions were made for further development in the future.

CHAPTER 2

THEORETICAL BACKGROUND

2.1 Distribution Coefficient

Liquid-Liquid extraction is a separation technique which is widely used both in industries and laboratories. It involves two immiscible (or partial miscible) liquid phases: a second liquid, or solvent is introduced to the original mixture or solution, to provide a second phase.

This is in contrast to direct separation techniques. For example, distillation, where heat is used to provide a vapor phase. The second liquid is chosen such that the desired component in the original mixture is extracted or preferentially transfers into the second liquid. The two liquid phases are then physically separated and the extracted component is recovered from the solvent by other separation techniques, such as distillation, precipitation, etc.

Liquid-Liquid extraction is employed for separations when it is the only method available or the most economical technique. Because the foreign substance, or solvent, is added to the separation system, a second separation step is therefore needed to recover the extracted component from the solvent. This technique is obviously only used for separations which cannot easily be achieved in a single step. It is a method which exploits chemical or structural differences between the species of the mixture rather than

molecular size, and is therefore complementary to distillation (65).

When a solute is distributed between two liquid phases, the distribution coefficient (K_d) is defined as the ratio of the concentrations of the solute in each liquid phase at equilibrium:

$$K_d = \frac{Y_a}{X_a} \quad (2.1)$$

Where Y_a = mole fraction of solute a in the extract

X_a = mole fraction of solute a in the raffinate

The distribution coefficient K_d is one of the most important parameters used in the extraction operation.

The selectivity of a solvent for solute A as against B or separation factor (SF) can be described by the ratio of distribution coefficients for the two components:

$$SF = \frac{K_{da}}{K_{db}} = \frac{Y_a / X_a}{Y_b / X_b} \quad (2.2)$$

This is similar to relative volatility in distillation. When two components are to be separated by Liquid-Liquid extraction, the ratio of one component to another must be different in each of the two phases.

Most extractions of inorganic compounds involve very complex chemical reactions. For example, during the

extraction of rare earth species from nitric acid solution by tri-n-butyl phosphate (TBP), $(C_4H_9O)_3PO$, reactions take place not only between the TBP and the rare earth nitrate to be extracted, but also involved are: the ionization of nitric acid, the complexes formed between the rare earth ion and nitrate in the aqueous phase; and the complexes nitrate and TBP in the organic phase. In the following discussion, the brackets [] represent the activities, the parentheses () mean concentrations, and the subscripts A and O denote the aqueous phase and organic phase, respectively.

2.2 The Extraction System

Generally a liquid-liquid extraction system consists of an extraction section, scrubbing section, stripping section, and solvent washing section, if necessary (Figure 2.1). In all such operations, the solution which is to be extracted is called the feed, and the liquid with which the feed is contacted is the solvent. The solvent-rich product of the operation is called the extract, and the residual liquid from which solute has been removed is the raffinate.

If the concentration of impurities in the extract is greater than tolerance, it can be reduced by scrubbing in multistage countercurrent contact equipment. This involves contacting the extract with a second liquid phase, usually the same solvent as the original feed, which is immiscible with the extract. The composition of the scrub feed is chosen such that the desired solute is largely retained in

the extract phase while the impurities are washed out. Usually, some of the desired solute is passed into the scrub liquor. To recover this lost solute, the scrub raffinate is commonly combined with the main feed stream, with the solute then being extracted in the extraction section.

After the extract leaves the scrubbing section, it is passed to a further liquid-liquid contacting section where it is equilibrated. This involves a multistage countercurrent manner with a second immiscible liquid phase, in which the solute passes to the second phase. This operation is known as stripping (or backwashing). The stripped solvent is then recycled to the extraction section, via a solvent washing operation, if necessary.

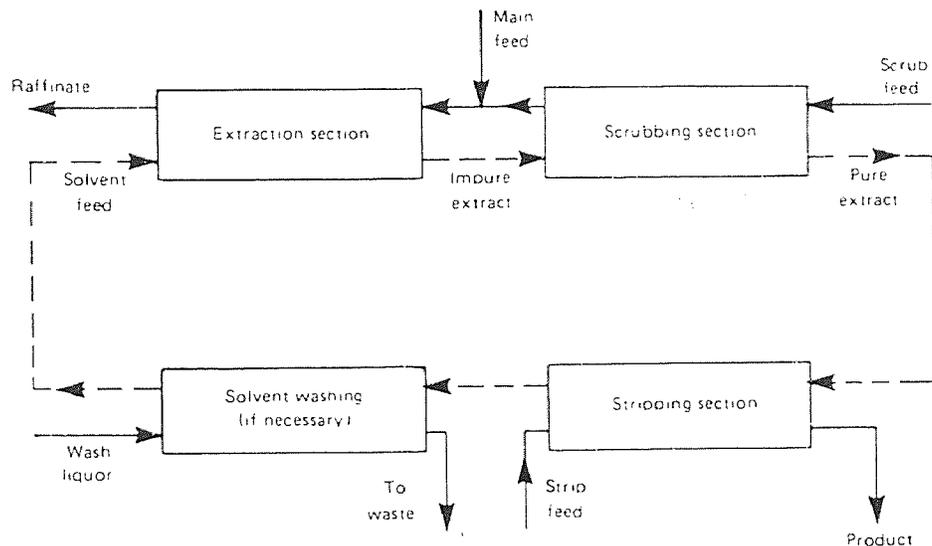


Figure 2.1 The Extraction System.

It is obvious that there is an interrelation between the stripping and extraction sections. It is not necessarily more economical to remove all the solute from the solvent in the stripping section. If we want to recover more solute from the feed, it may be less costly to use more stages or a higher solvent to feed ratio in the extraction section, than the additional stages in the stripping section to remove more solute.

2.3 Mixer Settler Extractor

Mixer-settlers have been used almost exclusively for rare earths separation (64). The mixer-settler is the simplest stagewise contactor. A mixer-settler consists of two chambers: in the first chamber, the mixer, aqueous and organic streams are continuously introduced, mixed and equilibrated; in the second chamber, the settler, the mixture overflowing from the mixer, is allowed to separate under quiescent conditions into organic and aqueous phases layers. After settling, the organic and aqueous phases are then pumped to the next stage of mixing chambers in a countercurrent manner. The basic mixer-settler is shown in Figure 2.2. Mixer-settlers are relatively easy to operate, reliable, flexible and fairly simple to design, are free of backmixing, and the stage efficiencies are usually greater than 90 per cent. With sufficient resident time and power in the mixer, and sufficient residence time in the settler, practically 100% stage efficiency can be reached (66).

A continuous multistage countercurrent mixer-settler extraction cascade is shown in Figure 2.3. Each stage will consist of a mixer and a settler. The liquids are generally pumped from one stage to the next, but gravity flow can be arranged if sufficient hydraulic head is available.

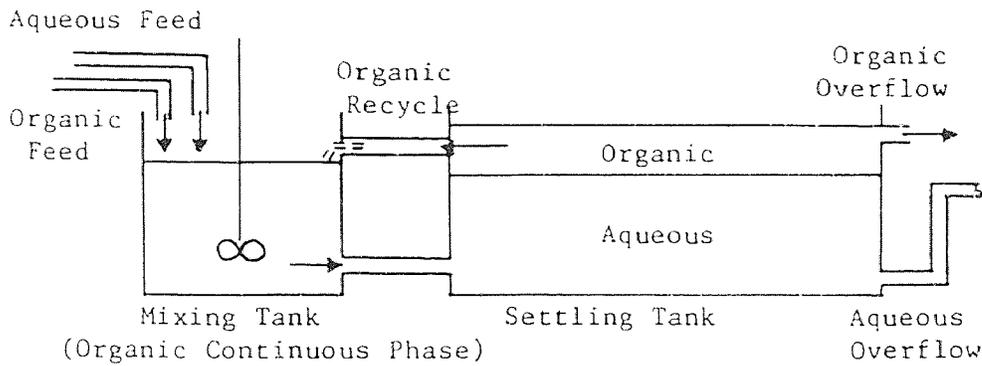


Figure 2.2 Mixer Settler Extractor.

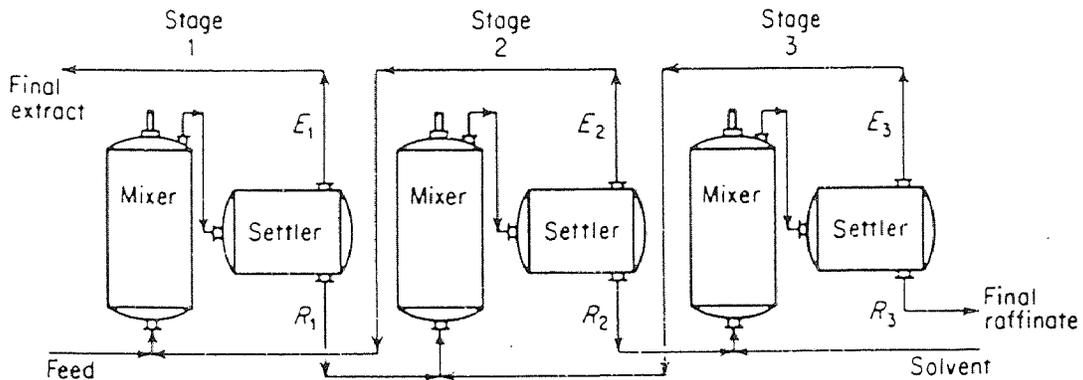
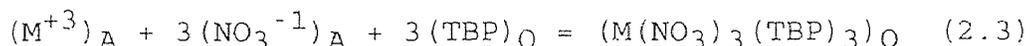


Figure 2.3 Countercurrent Mixer-settler Extraction Cascade.

2.4 Rare Earth Nitrate And TBP Complexes Formation

Most solvent extractions of inorganic compounds involve chemical reactions between the solvent and the inorganic species to be extracted. The generally accepted mechanism of rare earth oxides in nitric acid solution extracted by solvent TBP is:



The equilibrium constant is:

$$K_e = \frac{[M(NO_3)_3(TBP)_3]_O}{[M^{+3}]_A * [NO_3^{-1}]_A^3 * [TBP]_O^3} \quad (2.4)$$

McKay et al. (11) substantiated the existence of a grouping: a rare earth, three nitrate groups and three tributyl phosphate molecules. Hesford and co-workers (12) studied the TBP dependency of distribution ratio K_D for 9 different rare earths. They found by plotting that the log K_D vs. % TBP to be straight lines of slope 2.7-3.1. Thus, they concluded that the extracted species may be considered to be $M(NO_3)_3(TBP)_3$.

By using infra-red spectra, Bostian and Smutz (13) concluded that complexing takes place at the P=O bond on the solvent molecule; complex is formed by weak inter-molecular attractions depending on dipole effects; and therefore confirmed McKay's substantiation.

2.5 The Distribution Of Nitric Acid Between Water And TBP

Healy and McKay (14) and McKay (15) reported that nitric acid will dissolve in TBP and form the complex $\text{HNO}_3\text{-TBP}$. Alcock et al. (16) proposed that the reaction between nitric acid and TBP is given by the equation:



The equilibrium constant based on Alcock's experimental data is 0.16. Alcock et al. (16) postulated that all the nitric acid dissolves as $\text{HNO}_3\cdot\text{TBP}$ breaks down, thus such compounds as $(\text{HNO}_3)_2\cdot\text{TBP}$, $(\text{HNO}_3)_3\cdot\text{TBP}$, etc. may also formed.

Later, Fomin and Maiorova (17) investigated the distribution of nitric acid between the aqueous phase and 1 M TBP solution in benzene. They reported the equilibrium constant of the above reaction was 0.22 with the nitric acid concentration in the initial solution up to 4 M. They assumed that the reactions between nitric acid and TBP taking place may be expressed not only by equation (2.5), but also by the equation (2.6):



By assuming that the equilibrium constant for equation (2.5) 0.22 is correct, Fomin and Maiorova calculated the equilibrium constant 0.002 for equation (2.6).

Sheka and Kriss (18) studied the reaction between nitric acid and TBP by means of a physicochemical analytical method using the dielectric constant as the measured property. They found that the compound $\text{HNO}_3 \cdot \text{TBP}$ predominates at nitric acid concentrations up to 4 M and $\text{HNO}_3 \cdot (\text{TBP})_3$ is the major compound up to 9 M nitric acid concentration in the system of HNO_3 -TBP- CC_4 . By assuming that only the undissociated nitric acid molecules take part in the reaction, the equilibrium constants for compounds $\text{HNO}_3 \cdot \text{TBP}$ and $\text{HNO}_3 \cdot (\text{TBP})_3$ determined by them were 0.64 and 0.04, respectively.

Davis (19) made a series of studies on the thermodynamics of extraction of nitric acid by TBP. He postulated that compounds such as $\text{HNO}_3 \cdot \text{TBP}$, $(\text{HNO}_3)_2 \cdot \text{TBP}$, $(\text{HNO}_3)_3 \cdot \text{TBP}$ and $(\text{HNO}_3)_4 \cdot \text{TBP}$ may have formed successively, although evidence for complexes containing more than 2 moles of HNO_3 per mole of TBP is very skeptical. Nikolaeva and co-workers (20) reported that the composition of complexes, obtained by the mathematical modelling method, have been confirmed by the infrared spectra. These complexes consisted of $\text{HNO}_3 \cdot (\text{TBP})_3$, $\text{HNO}_3 \cdot (\text{TBP})_2 \cdot (\text{H}_2\text{O})_2$, $(\text{HNO}_3)_2 \cdot \text{TBP} \cdot (\text{H}_2\text{O})_3$, $\text{HNO}_3 \cdot \text{TBP}$, HNO_3 , TBP, and H_2O . Dong and his colleagues (21) conducted the dynamic simulation for a multistage countercurrent extraction process, and reported the equilibrium constants 0.19 and 0.004 for the complexes $\text{HNO}_3 \cdot \text{TBP}$ and $(\text{HNO}_3)_2 \cdot \text{TBP}$, respectively.

From the foregoing discussion of previous research results, it is clear that many forms of the $\text{HNO}_3 \cdot \text{TBP}$ complex exist in the TBP solution (or organic phase). It is very difficult to determine precisely the concentration for each form of $\text{HNO}_3 \cdot \text{TBP}$ complex. Complete forms of the $\text{HNO}_3 \cdot \text{TBP}$ complex are still undetermined, nor are the equilibrium constants for each form available. Thus, for mathematical modelling purposes, the concept of solubility of nitric acid in the TBP solution was used.

Many discussions of solubilities of nitric acid in TBP solution are in the published literature. Experimental data can be found in Schoenheer (3), Davis (19), Healy and Brown (22), Kinney and Smutz (23), Peppard and Ferraro (24), Shuler (25), and Davis et al. (26). Based on the summarized data made by Davis and co-workers (26), Figure 2.4 illustrates the solubility of nitric acid in the TBP phase as a function of nitric acid in the aqueous phase.

A correlation of the solubility of nitric acid in the TBP phase was made based on the smoothed data presented by Davis et al. (26), so the solubility data can be built into our model.

2.6 The Solubility Of Water In The TBP Solution

Similar to HNO_3 distribution in the TBP phase, water is also found in the TBP phase in many form of complexes. Alcock and his colleagues (16) described that since $\text{HNO}_3 \cdot \text{TBP}$ actually exists partially in hydrated form, the simplest assumption

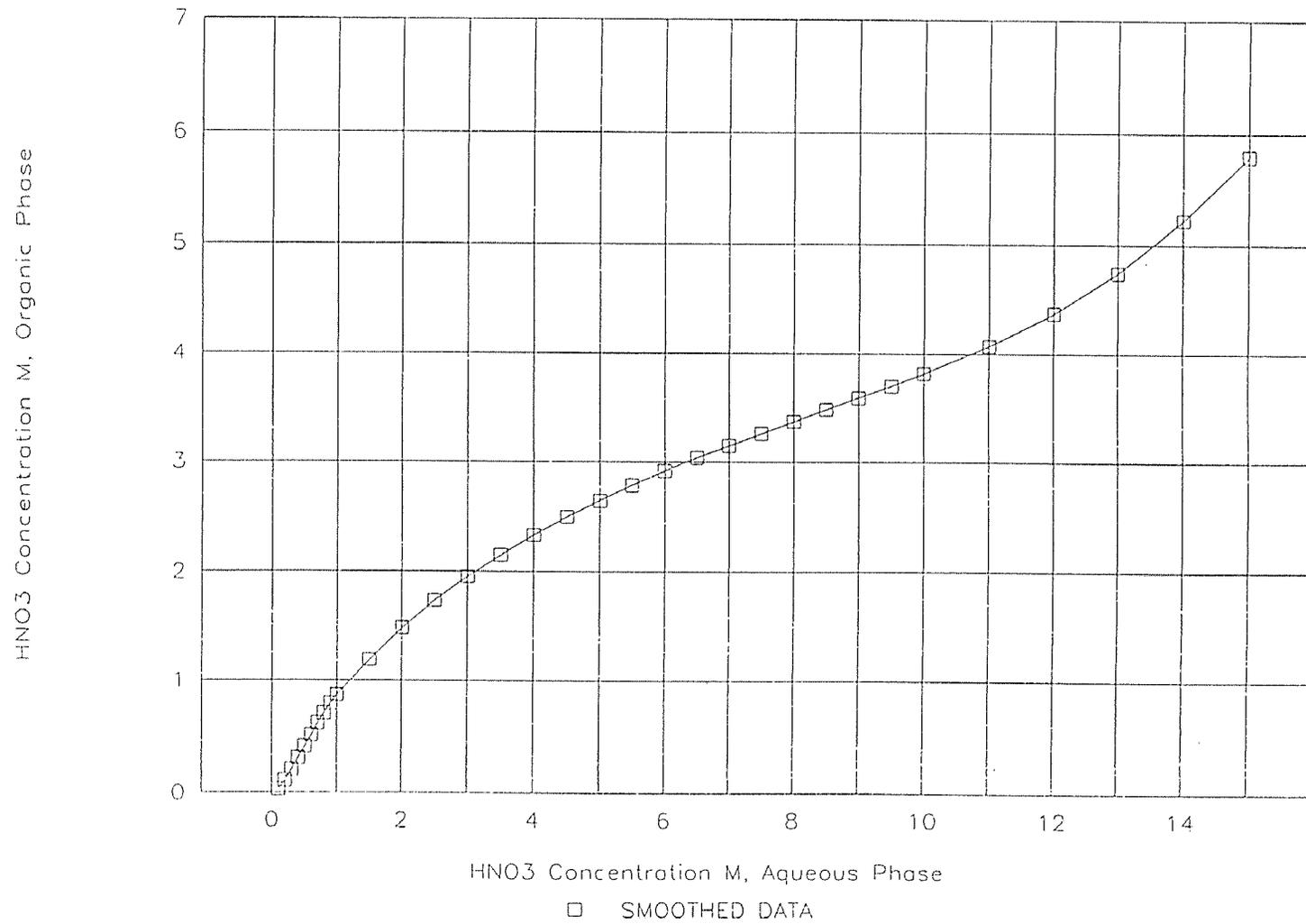


Figure 2.4 The Solubility of Nitric Acid in the TBP Phase.

is that $\text{HNO}_3 \cdot \text{H}_2\text{O} \cdot \text{TBP}$ is the chief product, through the conversion of $\text{HNO}_3 \cdot \text{TBP}$ to $\text{HNO}_3 \cdot \text{H}_2\text{O} \cdot \text{TBP}$, though other hydrates may be involved and may even be more important than the mono-hydrate.

Published data can be found in Schoenheer (3), Davis (19), Healy and Brown (22), Kinney and Smutz (23), Peppard and Ferraro (24), Shuler (25), and Davis et al. (26). Davis and his colleagues (26) smoothed all data from various sources, though the consistency of the analytical data for water is quite poor. Figure 2.5 demonstrates the solubility of water in the TBP phase as a function of nitric acid concentration in the aqueous phase.

A correlated equation was made based on the smoothed data presented by Davis and co-workers (26), so the solubility of water in the TBP phase can be built into our Liquid-liquid equilibrium model.

2.7 The Variation Of TBP Concentration In Organic Phase

As discussed in sections 2.5 and 2.6, nitrate and water molecules transfer to the organic phase through very complex chemical reactions in the HNO_3 - H_2O -TBP system. The quantity of nitrate and water molecules in the organic phase depends on the nitric acid concentration in the aqueous phase. After the equilibrium is reached, the density of organic phase change slightly. Davis and co-workers (26) summarized and smoothed TBP concentrations in the organic phase from various sources. Figure 2.6 was prepared based on the

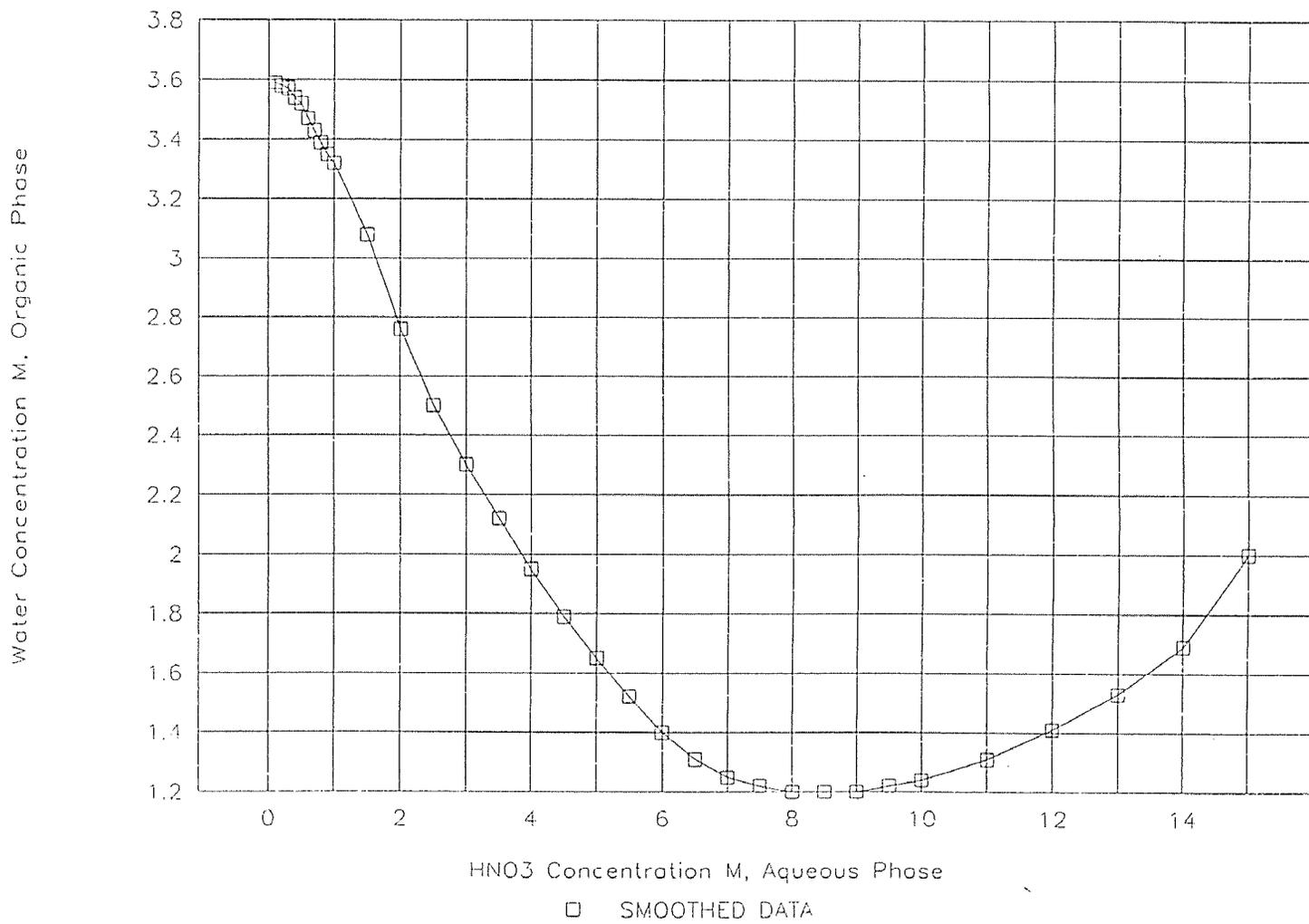


Figure 2.5 The Solubility of Water in the TBP Phase.

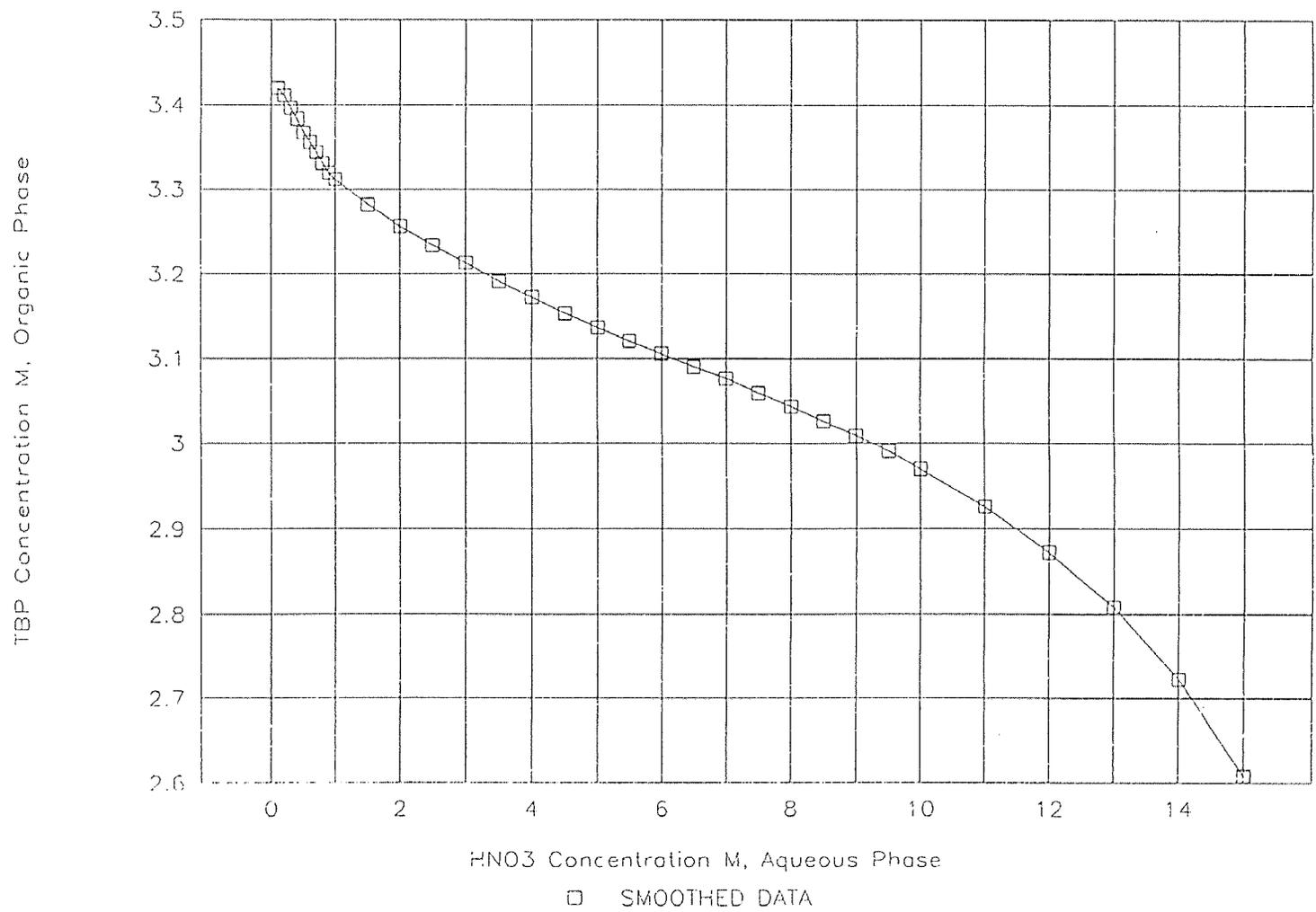


Figure 2.6 The Variation of TBP Concentration in the Organic Phase.

smoothed data presented by Davis et al. (26), which describes the variation of the TBP concentrations in the organic phase. A polynomial equation was also fitted to Davis's data and built into our equilibrium model.

2.8 The Solubility Of TBP In Aqueous Nitric Acid Solution

Baldwin and co-workers (27) and Burger and Forsman (28) reported the solubility of TBP in aqueous nitric acid to be $< 5.86 \times 10^{-3}$ mol/l over the range 0-15.6 M nitric acid. Alcock et al. (16) stated that TBP is generally less soluble in aqueous nitric acid than in pure water. Therefore, the TBP effect on most of the properties of the aqueous phase must be negligible.

2.9 The Degree Of Dissociation Of Nitric Acid

It is generally considered that nitric acid is only partially ionized and that in water the dissociation is:



The equilibrium constant is:

$$K_a = \frac{[\text{H}^+] * [\text{NO}_3^{-1}]}{[\text{HNO}_3]} \quad (2.8)$$

The literature contains a number of attempts to measure the dissociation constant of nitric acid (29), (30), (31),

(32), (33), (34). Davis and Bruin (35) obtained some new experimental data on liquid-vapor equilibrium in the system $\text{HNO}_3\text{-H}_2\text{O}$ by the transpiration technique. They combined new data and literature values on partial pressure of nitric acid with an activity coefficient derived from freezing point measurements to calculate the stoichiometric activity coefficients of nitric acid from the concentration range 0 to 100 per cent acid. This first requires evaluation of the ratio of the stoichiometric activity coefficients of nitric acid in the pure and infinitely dilute solutions. Water activities were then readily obtained by means of the Gibbs-Duhem equation. Finally, they combined the stoichiometric activity coefficients with published data for the degree of dissociation to obtain a consistent set of values of the degree of dissociation and of the mean ionic and molecular activity coefficients.

Figure 2.7 shows the nitric acid degree of dissociation of nitric acid in the aqueous phase. Figure 2.8 shows the ionization of aqueous nitric acid at 25°C . Because of the incomplete dissociation of nitric acid in the aqueous phase, NO_3^{-1} indeed rises to a maximum of 5.1 M at an acidity of 9.0 M at 25°C and then falls.

The consistent data developed by Davis and Bruin (35) were fitted into a polynomial equation, so the nitric acid dissociation constant can be build into our equilibrium model.

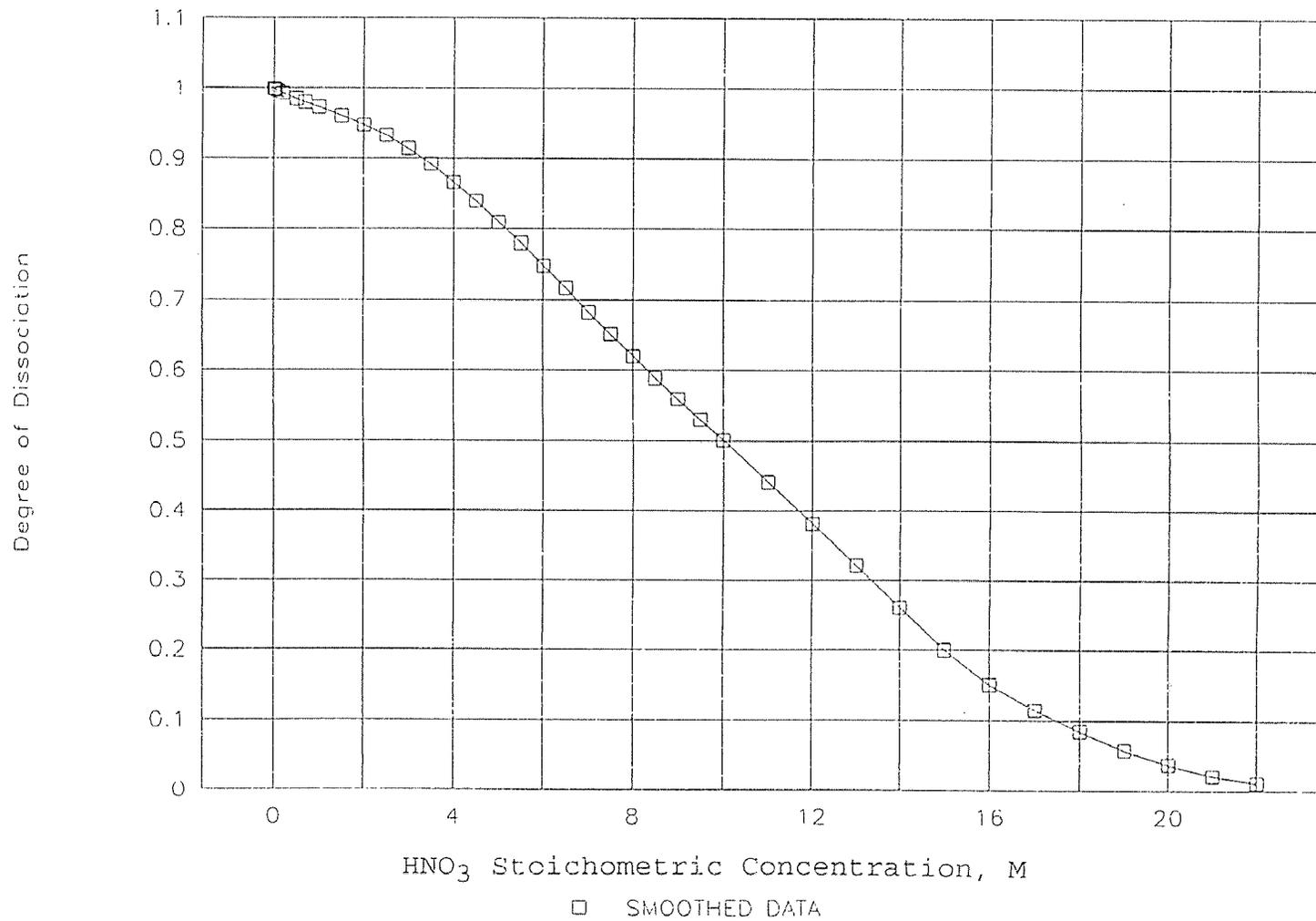


Figure 2.7 The Nitric Acid Degree of Dissociation.

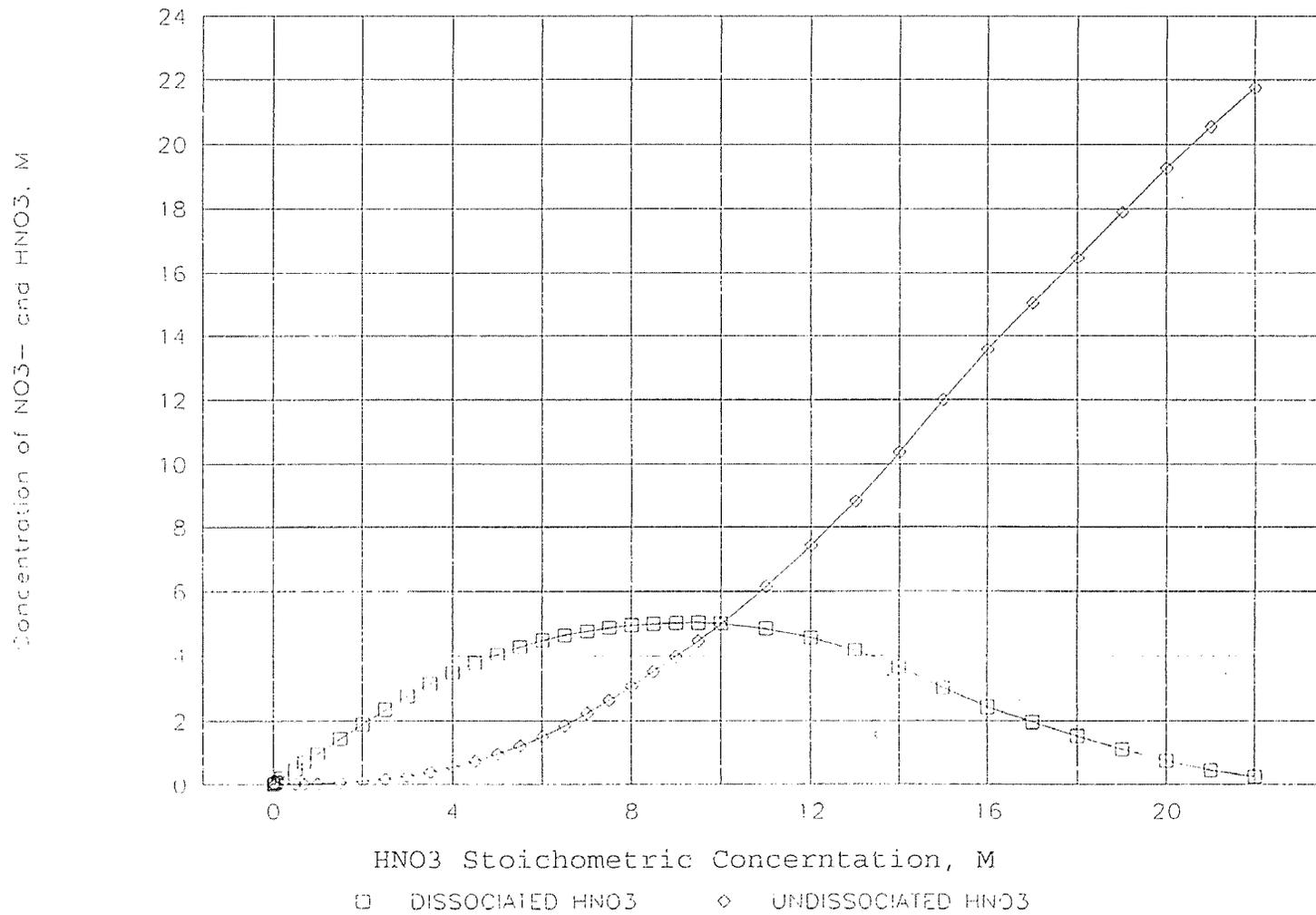
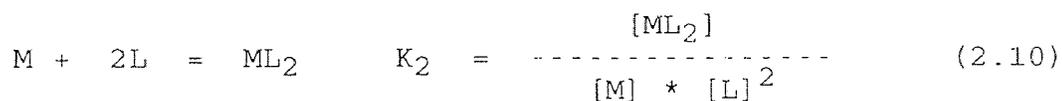
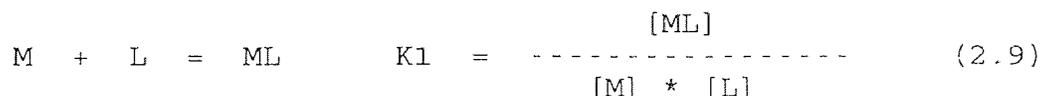


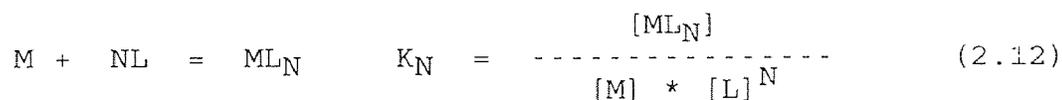
Figure 2.8 The Ionization of Aqueous Nitric Acid at 25°C.

2.10 The Stability Constants Of Rare Earth Complexes In Aqueous Solution

The thermodynamic stability of a complex can be indicated by an equilibrium constant relating its concentration to the concentration of other species when the system has reached equilibrium. If a solution contains aquated metal ions M and unidentate ligands L, and only soluble mononuclear complexes are formed, then the system at equilibrium may be described by the following equations and equilibrium constants:

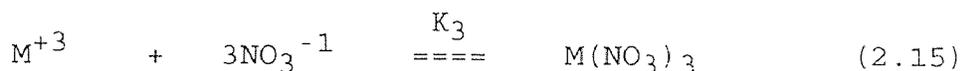
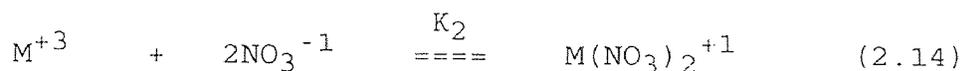
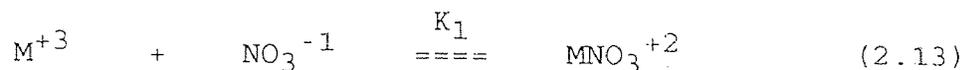


⋮
⋮
⋮
⋮



There will be N such equilibria, where N represents the maximum coordination number of the metal ion M for ligand L, and N may vary from one ligand to another. The K_i 's are called the overall stability constants.

Owing to its +3 charge the rare earth ion forms stable complexes with many anions such as chloride, nitrate, and sulfate. In general, the degree to which these complexes form is dependent only on the total ionic strength of the solution. The complexing reactions for rare earth nitrate are:



Choppin and Strazik (36) have determined that rare earth nitrate complexes are out-sphere in nature, a monolayer of water molecules separate the nitrate and rare earth. This layer of water acts as a dielectric and reduces the strength of the ionic bond that forms the complex. The neutral species $M(NO_3)_3$ is present only when the rare earth nitrate concentrations approaching the solubility limit. Since all solutions involved in this research were below the solubility limit, therefore, the neutral species $M(NO_3)_3$ is considered non-existent.

The stability constants for rare earth complexes in the aqueous phase are:

$$K_1 = \frac{[\text{MNO}_3^{+2}]_A}{[\text{M}^{+3}]_A * [\text{NO}_3^{-1}]_A} \quad (2.16)$$

$$K_2 = \frac{[\text{M}(\text{NO}_3)_2^{+1}]_A}{[\text{M}^{+3}]_A * [\text{NO}_3^{-1}]_A^2} \quad (2.17)$$

$$K_3 = 0 \quad (2.18)$$

Efforts have been made by Choppin and Strazik (36), Peppard et al. (37), Panova et al. (38), Fomin et al (39), Bansal et al (40) and Batyaev et al. (41) to determine the rare earth nitrate stability constants. These experimentally obtained stability constants will be used in Section 4.2 as initial value of model parameters.

2.11 The Experimental Data Of The Extraction Of Rare Earth Nitrate By 100% TBP

Many publications gave data in the distribution of rare earths in the tri-n-butyl phosphate (TBP) - nitric acid system (42), (43), (44), (45), (46), (47), (48), (49), (50), (51). The experimental results have shown the effective way to separate rare earths in the $\text{HNO}_3\text{-H}_2\text{O-TBP}$ two-phase system is with 12-18 M HNO_3 . With TBP, the extraction of rare earth nitrate into the organic phase increases in the order of increased atomic number, and with higher yttrium extractability (42). The most comprehensive set of distribution coefficients for extraction from HNO_3 are two

publications from the UK Harwell Laboratory (12), (52). Radioactive trace rare earth oxides were prepared from a solution of fission products in nitric acid by extraction first into 19% TBP in kerosene from 8 M HNO_3 . After a series of stripping and extracting purification procedures, the radioactive tracer ($< 1 \text{ g/l}$, or $< 0.01 \text{ M}$) was in the HNO_3 solution and ready for experiments. TBP is generally purified by boiling 100 ml crude or impure TBP with 500 ml of 0.4% caustic soda solution at atmospheric pressure until 200 ml of distillate has collected. Volatile impurities come over with the steam. The TBP remaining in the distillation flask is washed repeatedly with water and dried by warming under vacuum condition. The distribution coefficients were determined by stirring 5 ml of each phase together in a centrifuge tube for up to 60 minutes, centrifuging, and separating the phases for analysis. The distribution coefficients were measured with aqueous solution acidities 0.3-18 M, and with 100% TBP. All measurements were made at 25°C .

Distribution coefficients for a total of 16 rare earths, namely, lutetium, yttrium, ytterbium, thulium, erbium, holmium, dysprosium, terbium, gadolinium, europium, samarium, promethium, neodymium, praseodymium, cerium, and lanthanum, have been determined and tabulated with sufficiently small intervals, that almost any desired data can be interpolated or extrapolated. Graphics are also presented. Plotting of the data demonstrates these main

characteristics of behavior of the elements: the initial steep rise in the curves at low acidities; most form a maximum-minimum curve in the HNO_3 4-8 M region; then a further steep rise at a faster path at higher acidities ($\text{HNO}_3 > 10 \text{ M}$). Figure 2.9 shows a graphical presentation of all of the 16 rare earth elements distribution coefficient curves (63).

Scargill and co-workers (51) hypothesized that the characteristics of distribution coefficient curves are dominated by the following factors: salting-out from the aqueous phase by the nitrate ion at lower acidities; formation of nitrate complexes and nitric acid competition for the available TBP at moderate HNO_3 concentrations; and activity coefficient effects at high acidities.

Because Harwell Laboratory experimental results were obtained for micro-amounts of rare earth elements, Mikhlin and Korpusov (53) measured the distribution of macro-amounts of gadolinium, terbium, dysprosium, and yttrium between TBP and 8, 10, 12 and 14 N HNO_3 . For the same acidity, the distribution coefficient depends on the equilibrium rare earth concentration in the aqueous phase. With an increase in the rare earth equilibrium concentration there is a drop in the distribution coefficient owing to the decrease in the free solvent concentration. They also observed the order of increase in extractability with increase in atomic number of the element is the same for macro-amounts of rare earths as for micro-quantities (42). Their results indicate the

degree of separation of these elements and the position of yttrium in the rare earths series depends on both the nitric acid concentration and the rare earth concentration.

The Harwell Laboratory experimental data were used to determine the parameters of our rare earths liquid-liquid equilibrium model.

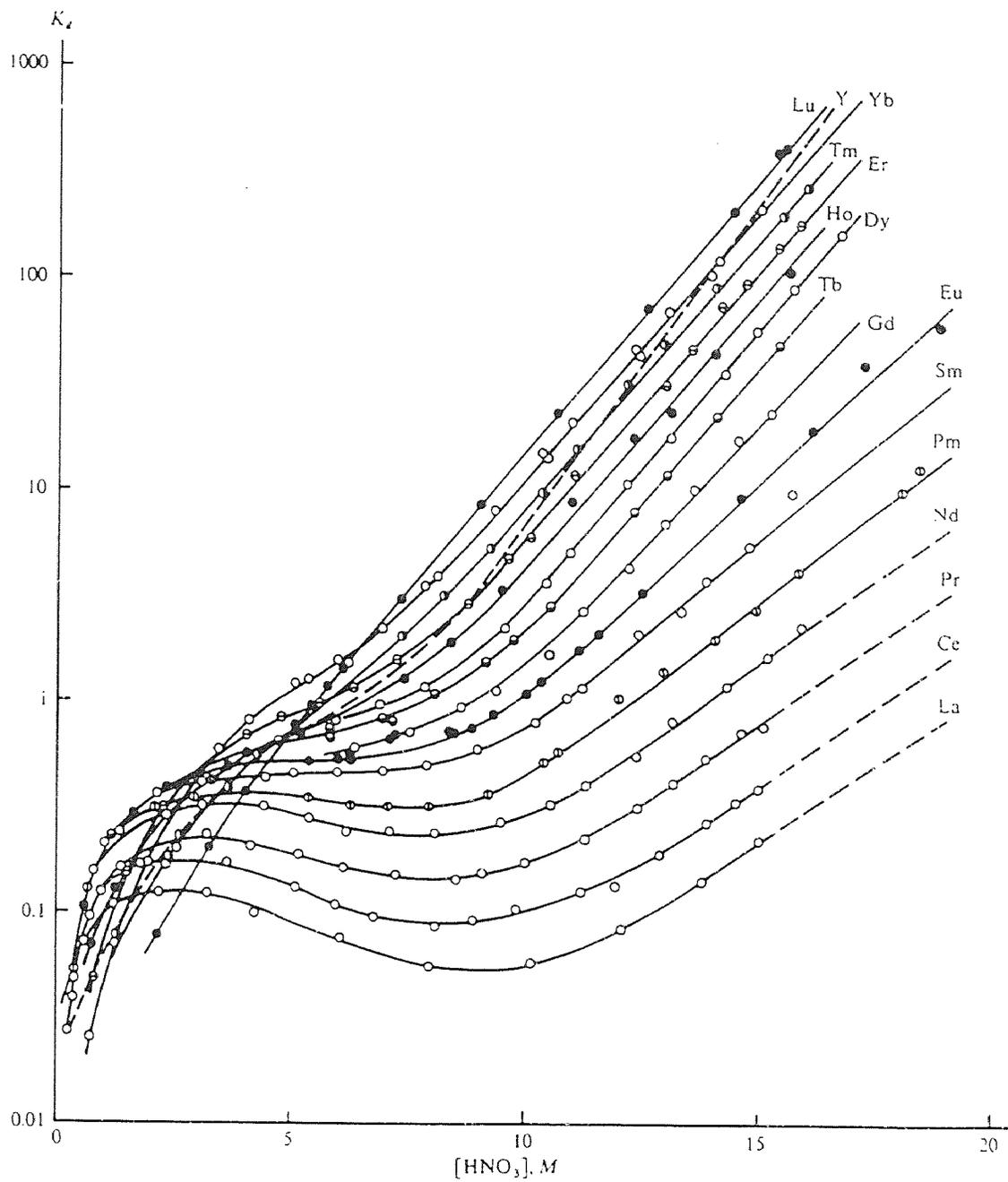


Figure 2.9 Distribution of Rare Earth Elements between 100% TBP and Aqueous Solution of HNO_3 as a Function of the Initial HNO_3 Concentration. Initial Concentration of Rare Earth Elements < 1 g/l; 25°C ; Contact Time up to 60 Minutes.

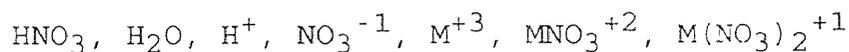
CHAPTER 3
DEVELOPMENT OF
LIQUID-LIQUID EQUILIBRIUM MODEL

3.1 Basic Assumptions

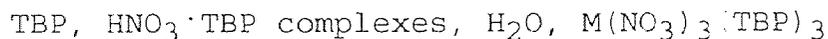
Having the theoretical background discussed in Chapter 2, let us assume that a nitric acid solution with an initial concentration $(\text{HNO}_3)_{\text{AI}}$ with a trace of rare earth oxides with an initial concentration $(\text{RRE})_{\text{AI}}$ dissolved in it, is equilibrated with an equal volume of TBP solvent with an initial concentration $(\text{TBP})_{\text{OI}}$ in a container at 25°C . After settling, two immiscible phases co-exist: aqueous phase and organic phase. The subscript I refers to initial.

Let us further assume that there is no volume change in either the aqueous phase or the organic phase after mixing and settling. Thus, the chemical species which can be found in the aqueous phase and the organic phase after settling are:

In the aqueous phase:



In the organic phase:



Where M^{+3} refers to rare earth ion with three charges.

Parameters involved in chemical reactions are:

$$K_d, SF, K_e, K_a, K_1, K_2$$

With the theoretical knowledge of rare earths compound (RRE) in the $\text{HNO}_3\text{-H}_2\text{O-TBP}$ two-phase system, coupled with the basic assumptions made in this section, the liquid-liquid extraction equilibrium model is now ready for development.

3.2 The Equilibrium Constant For The Complex Of Rare Earth Nitrate And TBP

Section 2.2 discussed the rare earth nitrate and the TBP complex formation in the $\text{HNO}_3\text{-H}_2\text{O-TBP}$ system. Equation (2.3) demonstrates the complex formation, and equation (2.4) expresses the equilibrium constant. Since the activity of a specific chemical compound is the product of the concentration and the activity coefficient of that compound at the same temperature, then, equation (2.4) can be expressed as:

$$K_e = \frac{(M(\text{NO}_3)_3(\text{TBP})_3)_O}{(M^{+3})_A * (\text{NO}_3^{-1})_A^3 * (\text{TBP})_O^3} * \frac{[[M(\text{NO}_3)_3(\text{TBP})_3]]_O}{[[M^{+3}]]_A * [[\text{NO}_3^{-1}]]_A^3 * [[\text{TBP}]]_O^3} \quad (3.1)$$

Let us define:

$$K_e' = \frac{(M(NO_3)_3(TBP)_3)_O}{(M^{+3})_A * (NO_3^{-1})_A^3 * (TBP)_O^3} \quad (3.2)$$

And again define:

$$K_{re} = \frac{[[M(NO_3)_3(TBP)_3]]_O}{[[M^{+3}]]_A * [[NO_3^{-1}]]_A^3 * [[TBP]]_O^3} \quad (3.3)$$

Thus

$$K_e = K_e' * K_{re} \quad (3.4)$$

The double brackets $[[\]]$ here refer to activity coefficients. All three equilibrium constants are functions of physical properties in the aqueous phase and the organic phase. Even though they are all equilibrium constants, they each have their own distinct physical definitions. K_e is the equilibrium constant of the complex formation for species M^{+3} , NO_3^{-1} and TBP, if the reaction is expressed in terms of chemical activities. K_e' is the equilibrium constant, if the reaction is expressed in terms of concentrations. K_{re} is the equilibrium constant, if the reaction is expressed in terms of activity coefficients. By definitions of chemical equilibrium and chemical activity, only the activity equilibrium constant is truly a constant.

3.3 The Stability Constants For The Complex Of Rare Earth Nitrate In Aqueous Phases

The stability constants for rare earth nitrate complex in the aqueous phase were discussed in Section 2.10. Because of their similarity in nature, the stability constants will be treated in the same manner in Section 3.2 for the rare earth nitrate and TBP complex equilibrium constants.

Express equation (2.16) and (2.17) by concentrations and activity coefficients:

$$K_1 = \frac{(MNO_3^{+2})_A}{(M^{+3})_A * (NO_3^{-1})_A} * \frac{[[MNO_3^{+2}]]_A}{[[M^{+3}]]_A * [[NO_3^{-1}]]_A} \quad (3.5)$$

$$K_2 = \frac{(M(NO_3)_2^{+1})_A}{(M^{+3})_A * (NO_3^{-1})_A^2} * \frac{[[M(NO_3)_2^{+1}]]_A}{[[M^{+3}]]_A * [[NO_3^{-1}]]_A^2} \quad (3.6)$$

Define:

$$K_{1'} = \frac{(MNO_3^{+2})_A}{(M^{+3})_A * (NO_3^{-1})_A} \quad (3.7)$$

$$K_{2'} = \frac{(M(NO_3)_2^{+1})_A}{(M^{+3})_A * (NO_3^{-1})_A^2} \quad (3.8)$$

$$K_{r1} = \frac{[[M^{+3}]]_A * [[NO_3^{-1}]]_A}{[[MNO_3^{+2}]]_A} \quad (3.9)$$

$$K_{R2} = \frac{[[M^{+3}]]_A * [[NO_3^{-1}]]_A^2}{[[M(NO_3)_2^{+1}]]_A} \quad (3.10)$$

Combining equations (3.5), (3.6), (3.7), (3.8), (3.9) and (3.10), we have:

$$K_1' = K_1 * K_{R1} \quad (3.11)$$

$$K_2' = K_2 * K_{R2} \quad (3.12)$$

Equilibrium constants K_{R1} in equation (3.9) and K_{R2} in equation (3.10) are the functions of the activity coefficients in the aqueous phase only. As we mentioned in Section 3.2, only the activity equilibrium constants K_1 and K_2 are true constants among all six equilibrium constants in this section.

Because traces of rare earth exists in the aqueous solution initially, and most of rare earth nitrate forms complex $M(NO_3)_3(TBP)_3$ with TBP and transfers to the organic phase, then the rare earth ions that remain in the aqueous phase and form complexes MNO_3^{+2} and $M(NO_3)_2^{+1}$ are in micro-quantity. Based on Henry's law activity coefficient (54), in infinite dilution, the solute activity coefficient approaches unity as the mole fraction goes to zero. In order words, activity coefficients $[[M^{+3}]]_A$, $[[MNO_3^{+2}]]_A$ and $[[M(NO_3)_2^{+1}]]_A$ all equal or approach to one. Thus,

$$K_1' = K_1 * [[\text{NO}_3^{-1}]]_A \quad (3.13)$$

$$K_2' = K_2 * [[\text{NO}_3^{-1}]]_A^2 \quad (3.14)$$

Assume that the nitrate activity coefficient $[[\text{NO}_3^{-1}]]_A$ varies only slightly at a specific acidity in the aqueous phase. Therefore, the equilibrium constants can be simply expressed only by the chemical specie concentrations.

3.4 The Correlation For Nitric Acid In The Organic Phase

We have discussed the distribution of nitric acid in aqueous and TBP organic phase in Section 2.5. Because numerous forms of $\text{HNO}_3 \cdot \text{TBP}$ complex exist in the organic phase, and the number of complex formulas are still not yet determined, it is not possible to calculate the equilibrium constant for each complex formation. Therefore, for mathematical modelling purposes, the concept of nitric acid solubility in the organic phase was introduced. The smooth data prepared by Davis and his colleagues (26) for the nitric acid solubility in the TBP organic phase was fitted to the following correlation formula:

$$\begin{aligned} ((\text{HNO}_3)_n \cdot \text{TBP})_O &= -0.07272 - 1.062423 * (\text{HNO}_3)_{AT} - \\ &0.173784 * ((\text{HNO}_3)_{AT})^{**2} + 0.0186665 * ((\text{HNO}_3)_{AT})^{**3} - \\ &0.001062 * ((\text{HNO}_3)_{AT})^{**4} + 0.0000261 * ((\text{HNO}_3)_{AT})^{**5} \end{aligned} \quad (3.15)$$

The formula $((\text{HNO}_3)_n \cdot \text{TBP})_O$ in equation (3.15) is defined as solubility of nitric acid in the organic phase, in mole per liter of solution. The symbol $(\text{HNO}_3)_n \cdot \text{TBP}$ is the hypothetical formula, which includes all forms of $\text{HNO}_3 \cdot \text{TBP}$ complexes in the organic phase for a specific nitric acid concentration in the aqueous phase. The subscript n here refers to the number of moles of HNO_3 in the complex associated with each molecule of TBP.

3.5 Material Balance For Nitrate NO_3^{-1}

The previous section defined the formula of $((\text{HNO}_3)_n \cdot \text{TBP})_O$. Since the nitrate NO_3^{-1} exists in both phases, then the material balance for nitrate NO_3^{-1} is:

$$\begin{aligned}
 (\text{HNO}_3)_{AI} &= (\text{HNO}_3)_{AT} + ((\text{HNO}_3)_n \cdot \text{TBP})_O + \\
 &3(\text{M}(\text{NO}_3)_3(\text{TBP})_3)_O + (\text{MNO}_3^{+2})_A + 2(\text{M}(\text{NO}_3)_2^{+1})_A
 \end{aligned}
 \tag{3.16}$$

The subscript **T** here means the **total free** nitric acid in aqueous phase after equilibrium is reached. In other words, $(\text{HNO}_3)_{AT}$ is the **total unreacted** nitric acid in the aqueous phase. The nitric acid will dissociate, as we discussed in Section 2.9, therefore, $(\text{HNO}_3)_{AT}$ should be considered to be the **sum of dissociated and undissociated** nitric acid in the aqueous phase after the chemical reaction equilibrium has been reached. The compounds $\text{M}(\text{NO}_3)_3(\text{TBP})_3$

and $M(NO_3)_{2+1}$ in equation (3.16) must be multiplied by the number of nitrates complex with rare earth ion.

3.6 Material Balance For Tri-n-Butyl Phosphate (TBP)

As discussed in Section 2.8, the solubility of TBP in the aqueous phase is small and its effect on the properties of the aqueous phase is negligible. Thus, TBP is considered to exist in the organic phase only. The material balance for TBP in entire system is :

$$(TBP)_{AI} = (TBP)_O + ((HNO_3)_n \cdot TBP)_O / NOH + 3(M(NO_3)_3(TBP)_3)_O \quad (3.17)$$

where the denominator NOH is defined as the **number of nitric acid moles** in conjunction with each TBP molecule in the complex. Thus, the subscript n and denominator NOH share the same definition. Because concentration of $((HNO_3)_n \cdot TBP)_O$ is specified in terms of molarity, which is expressed as the number of moles of HNO_3 per liter of solution, therefore, the number of moles of TBP in the complex $((HNO_3)_n \cdot TBP)_O$ is obtained by dividing $((HNO_3)_n \cdot TBP)_O$ concentration with NOH . NOH is not a constant, but varies when the acidity changes in the aqueous phase.

Three moles of TBP are attached in each mole of $M(NO_3)_3(TBP)_3$, thus the concentration of TBP is three times of $M(NO_3)_3(TBP)_3$ concentration.

3.7 Material Balance For Rare Earth Nitrate

The rare earth nitrate transfers from the aqueous phase to the organic phase by forming $M(NO_3)_3(TBP)_3$ complexes with TBP in the organic phase. Therefore, the rare earth species exist both in the aqueous and the organic phases. The following equation (3.18) describe the material balance for rare earth species (RRE):

$$(RRE)_{AI} = (M^{+3})_A + (M(NO_3)_3(TBP)_3)_O + (MNO_3^{+2})_A + (M(NO_3)_2^{+1})_A \quad (3.18)$$

Combining equations (3.2), (3.7), (3.8) and (3.18) and eliminating $(M(NO_3)_3(TBP)_3)_O$, $(MNO_3^{+2})_A$ and $(M(NO_3)_2^{+1})_A$ in equation (3.18):

$$(RRE)_{AI} = (M^{+3})_A + K_e' * (M^{+3})_A * (NO_3^{-1})_A^3 * (TBP)_O^3 + K_1' * (M^{+3})_A * (NO_3^{-1})_A + K_2' * (MNO_3^{+2})_A * (NO_3^{-1})_A \quad (3.19)$$

After rearranging:

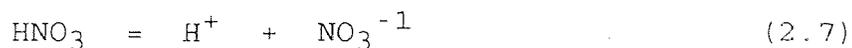
$$(RRE)_{AI} = (M^{+3})_A * (1 + K_e' * (NO_3^{-1})_A^3 * (TBP)_O^3 + K_1' * (NO_3^{-1})_A + K_2' * (NO_3^{-1})_A^2) \quad (3.20)$$

Consequently, the concentration of rare earth ion M^{+3}

in the aqueous phase can be expressed by initial rare earth concentration, nitrate concentration and chemical equilibrium constants.

3.8 The Correlation For Nitrate NO_3^{-1} Concentration

As discussed in Section 2.9, nitric acid is only partially ionized:



The Davis and Burin's consistent data (35) for the nitric acid degree of dissociation (DOD) were fitted into a polynomial equation:

$$\begin{aligned} \text{DOD} = & 1.0006204 - 0.020407 * (\text{HNO}_3)_{\text{AT}} - \\ & 0.004496 * ((\text{HNO}_3)_{\text{AT}})^{**2} + 0.0001546 * ((\text{HNO}_3)_{\text{AT}})^{**3} \end{aligned} \quad (3.21)$$

The degree of dissociation (DOD) is the ratio of nitrate concentration $(\text{NO}_3^{-1})_{\text{A}}$ to total unreacted nitric acid $(\text{HNO}_3)_{\text{AT}}$ in the aqueous phase, thus the concentration of $(\text{NO}_3^{-1})_{\text{A}}$ is readily obtained:

$$(\text{NO}_3^{-1})_{\text{A}} = \text{DOD} * (\text{HNO}_3)_{\text{AT}} \quad (3.22)$$

Eliminating DOD in equation (3.22) by combining equations (3.21) and (3.22):

$$\begin{aligned}
 (\text{NO}_3^{-1})_A &= 1.0006204 * (\text{HNO}_3)_{AT} - 0.020407 * ((\text{HNO}_3)_{AT})^{**2} \\
 &- 0.004496 * ((\text{HNO}_3)_{AT})^{**3} + 0.0001546 * ((\text{HNO}_3)_{AT})^{**4}
 \end{aligned}
 \tag{3.23}$$

From equation (3.23), nitrate concentration can be easily calculated if $(\text{HNO}_3)_{AT}$ is given.

3.9 Material Balance For Hydrogen Atoms H

The rare earth ion M^{+3} has three charges, since the rare earth ions are extracted by a cation-exchange solvent, one mole of the rare earth extraction is accompanied by a discharge of three moles of hydrogen ion into the aqueous phase. Analogous to equation (2.3), we have:

$$\begin{aligned}
 (M^{+3})_A + (3/2) * (O^{-2})_A + 3(H^+)_A + 3(\text{NO}_3^{-1})_A + 3(\text{TBP})_O = \\
 (M(\text{NO}_3)_3(\text{TBP})_3)_O + 3(\text{H}_2\text{O})_A
 \end{aligned}
 \tag{3.24}$$

Trace of rare earth $(\text{RRE})_{AI}$ initially exists in this HNO_3 - H_2O - TBP two-phase system, and micro-quantities of $(M^{+3})_A$, $(M(\text{NO}_3)_2^{+1})_A$ and $(M\text{NO}_3^{+2})_A$ exist after equilibrium has been reached. For mathematical modeling purposes, it is assumed that almost all initial rare earths in the aqueous solution $(\text{RRE})_{AI}$ have formed the $(M(\text{NO}_3)_3(\text{TBP})_3)_O$ complex and have been extracted. Therefore, the initial rare earths $(\text{RRE})_{AI}$ and $(M(\text{NO}_3)_3(\text{TBP})_3)_O$ complexes have identical molarity, if volume does not change in both phases after

equilibrium has been established. It is convenient to set the hydrogen consumption during extraction process equal to one third of the $(RRE)_{AI}$.

$$(H^+)_{\text{consumed}} = (1/3) * (RRE)_{AI} \quad (3.25)$$

Or replace $(RRE)_{AI}$ by equation (3.20)

$$(H^+)_{\text{consumed}} = (1/3) * (M^{+3})_A * (1 + K_e' * (NO_3^{-1})_A^3 * (TBP)_O^3 + K_1' * (NO_3^{-1})_A + K_2' * (NO_3^{-1})_A^2) \quad (3.26)$$

The material balance for hydrogen atoms H around HNO_3 - H_2O -TBP two-phase system:

$$(HNO_3)_{AI} = (1-DOD) * (HNO_3)_{AT} + (H^+)_A + (H^+)_{\text{consumed}} + ((HNO_3)_n \cdot TBP)_O \quad (3.27)$$

Combining equation (3.25) and equation (3.27):

$$(HNO_3)_{AI} = (1-DOD) * (HNO_3)_{AT} + (H^+)_A + (1/3) * (RRE)_{AI} + ((HNO_3)_n \cdot TBP)_O \quad (3.28)$$

Or combine equation (3.26) and equation (3.27):

$$\begin{aligned}
 (\text{HNO}_3)_{\text{AI}} = & (1-\text{DOD}) * (\text{HNO}_3)_{\text{AT}} + (\text{H}^+)_{\text{A}} + ((\text{HNO}_3)_n \cdot \text{TBP})_{\text{O}} + \\
 & (1/3) * (\text{M}^{+3})_{\text{A}} * (1 + K_e' * (\text{NO}_3^{-1})_{\text{A}}^3 * (\text{TBP})_{\text{O}}^3 + \\
 & K_1' * (\text{NO}_3^{-1})_{\text{A}} + K_2' * (\text{NO}_3^{-1})_{\text{A}}^2) \quad (3.29)
 \end{aligned}$$

As we discussed in Section 3.5, $(\text{HNO}_3)_{\text{AT}}$ is the sum of dissociated and undissociated nitric acid in the aqueous phase. The term $(1-\text{DOD}) * (\text{HNO}_3)_{\text{AT}}$ in equation (3.29) represents the undissociated nitric acid after equilibrium has been reached.

3.10 The TBP Concentration In The Organic Phase

The variation of TBP concentration in the organic TBP solution was discussed in Section 2.7. Davis's smoothed data (26) was regressed to yield:

$$\begin{aligned}
 (\text{TBP})_{\text{O}} = & 3.428093 - 0.13173 * (\text{HNO}_3)_{\text{AT}} + \\
 & 0.028538 * ((\text{HNO}_3)_{\text{AT}})^2 - 0.003824 * ((\text{HNO}_3)_{\text{AT}})^3 + \\
 & 0.0002462 * ((\text{HNO}_3)_{\text{AT}})^4 - 0.000006359 * ((\text{HNO}_3)_{\text{AT}})^5 \quad (3.30)
 \end{aligned}$$

3.11 The Distribution Coefficients For Nitric Acid In The $\text{HNO}_3\text{-H}_2\text{O-TBP}$ System

All discussions of the distribution coefficients so far have been focused on the distribution of rare earths in the $\text{HNO}_3\text{-H}_2\text{O-TBP}$ two-phase system. We also mentioned that nitric

acid will form various complexes with TBP in the organic phase. Davis and co-workers (26) reported the distribution of nitric acid between the aqueous and the 100% TBP phase, after analyzing experimental data from different sources. Concentrations of nitric acid in both phases were given, so the distribution coefficients of nitric acid in the HNO_3 - H_2O -TBP system can be easily calculated and correlated into polynomial form:

$$\begin{aligned}
 (K_d)_{\text{nitric acid}} = & -25.4334 + 12.115960 * (\text{HNO}_3)_{\text{AT}} - \\
 & 10.24788 * ((\text{HNO}_3)_{\text{AT}})^{**2} + 26.14166 * ((\text{HNO}_3)_{\text{AT}})^{**3} - \\
 & 5.342299 * ((\text{HNO}_3)_{\text{AT}})^{**4} \qquad \qquad \qquad (3.31)
 \end{aligned}$$

Equation (3.31) will be used in the multicomponent multistage counter-current liquid-liquid extraction computer program.

3.12 The Distribution Coefficients For Water In The HNO_3 - H_2O -TBP System

Davis et al. (26) also reported the distribution of water between the aqueous and the 100% TBP phase. Concentrations of water in the organic phases were given, densities of aqueous solution along with different equilibrium nitric acid concentrations were also given, by the help of liquid densities, the concentrations of water in the aqueous

solution were calculated, and the distribution coefficients of water in the $\text{HNO}_3\text{-H}_2\text{O-TBP}$ system can be readily obtained and correlated into the following formula:

$$\begin{aligned} (K_d)_{\text{water}} = & 0.5196597 - 4.46808 * (\text{HNO}_3)_{\text{AT}} + \\ & 19.72675 * ((\text{HNO}_3)_{\text{AT}})^{**2} - 32.13729 * ((\text{HNO}_3)_{\text{AT}})^{**3} + \\ & 19.22704 * ((\text{HNO}_3)_{\text{AT}})^{**4} \end{aligned} \quad (3.32)$$

Equation (3.32) will also be used in the multicomponent multistage counter-current liquid-liquid extraction computer program.

3.13 Construction of Distribution Coefficients For Rare Earths

The distribution coefficient K_d of rare earths in the $\text{HNO}_3\text{-H}_2\text{O-TBP}$ system also can be expressed by:

$$K_d = \frac{\text{Concentration of } M^{+3} \text{ in organic phase}}{\text{Concentration of } M^{+3} \text{ in aqueous phase}} \quad (3.33)$$

From Section 3.1, the chemical species including M^{+3} the organic phase is $M(\text{NO}_3)_3(\text{TBP})_3$, and in the aqueous phase are: M^{+3} , $M\text{NO}_3^{+2}$, $M(\text{NO}_3)_2^{+1}$, thus we have:

$$K_d = \frac{(M(NO_3)_3(TBP)_3)_O}{(M^{+3})_A + (MNO_3^{+2})_A + (M(NO_3)_2^{+1})_A} \quad (3.34)$$

Combining equations (3.2), (3.7), (3.8) and (3.34) and eliminating (M^{+3}) in numerator and denominator, we obtained:

$$K_d = \frac{K_e' * (NO_3^{-1})_A^3 * (TBP)_O^3}{1 + K_1' * (NO_3^{-1})_A + K_2' * (NO_3^{-1})_A^2} \quad (3.35)$$

Eliminating K_e' , K_1' and K_2' in equation (3.35) by substituting equations (3.4), (3.13) and (3.14) into equation (3.35):

$$K_d = \frac{(K_e/K_{re}) * (NO_3^{-1})_A^3 * (TBP)_O^3}{(1 + K_1 * (NO_3^{-1})_A * [[NO_3^{-1}]]_A + K_2 * (NO_3^{-1})_A^2 * [[NO_3^{-1}]]_A^2)} \quad (3.36)$$

Expressing K_{re} in activity coefficients by combining equations (3.3) and (3.36):

$$K_d = \frac{K_e * (NO_3^{-1})_A^3 * (TBP)_O^3}{(1 + K_1 * (NO_3^{-1})_A * [[NO_3^{-1}]]_A + K_2 * (NO_3^{-1})_A^2 * [[NO_3^{-1}]]_A^2)} * \frac{[[M^{+3}]]_A * [[NO_3^{-1}]]_A^3 * [[TBP]]_O^3}{[[M(NO_3)_3(TBP)_3]]_O} \quad (3.37)$$

Equation (3.37) is a very complicated form. It consists of the nitrate concentration $(\text{NO}_3^{-1})_A$, the TBP concentration $(\text{TBP})_O$, the stability constants K_1 and K_2 , the activity equilibrium constant K_e , and the activity coefficients $[[M^{+3}]]_A$, $[[\text{NO}_3^{-1}]]_A$, $[[\text{TBP}]]_O$ and $[[M(\text{NO}_3)_3(\text{TBP})_3]]_O$ in both the aqueous phase and the organic phase. Without simplification, equation (3.37) has very little practical value.

Suppose there is a function, which is analogous to the Redlich-Kister expansion (55), that can accurately express the characteristics of the effects of all activity coefficients in the aqueous phase and the organic phase:

$$\left(\frac{[[\text{Activity Coefficients}]]_A}{[[\text{Activity Coefficients}]]_O} \right) =$$

$$A_0 + A_1 * (\text{HNO}_3)_{AT} ** A_2 + A_3 * (\text{HNO}_3)_{AT} ** A_4 \quad (3.38)$$

With the concept of overall effects of all activity coefficients in the aqueous phase and in the organic phase, eliminate all terms in the activity coefficient in the equation (3.37) by using equation (3.38):

$$K_d = \frac{K_e * (\text{NO}_3^{-1})_A^3 * (\text{TBP})_O^3}{1 + K_1 * (\text{NO}_3^{-1})_A + K_2 * (\text{NO}_3^{-1})_A^2} *$$

$$(A_0 + A_1 * (\text{HNO}_3)_{AT} ** A_2 + A_3 * (\text{HNO}_3)_{AT} ** A_4) \quad (3.39)$$

where A_0 , A_1 , A_2 , A_3 and A_4 are constants. As results of activity coefficient expression eliminations, the equation (3.37) is simplified considerably. Equation (3.39) is the final form of the rare earths distribution coefficient in the HNO_3 - H_2O -TBP System, and was used in our liquid-liquid equilibrium model.

CHAPTER 4

EVALUATION OF MODEL PARAMETERS

4.1 Evaluation Of Model Parameters

Many equations have been developed in Chapter 3. These equations express the chemical reactions taking place in the aqueous phase, and in the organic phase, so mass can transfer from one phase to another. The chemical reaction equilibrium constants, the phase equilibrium constants and the effects of activity coefficients, both in the aqueous phase and organic phase, were all incorporated into those relationships.

The development of equations is just part of model construction. The ultimate goal is to construct an equilibrium model that will predict accurately the rare earths distribution in the HNO₃-H₂O-TBP system by using the relationships developed in Chapter 3.

We have developed the distribution model:

$$K_d = \frac{K_e * (NO_3^{-1})_A^3 * (TBP)_O^3}{1 + K_1 * (NO_3^{-1})_A + K_2 * (NO_3^{-1})_A^2} * (A_0 + A_1 * (HNO_3)_{AT} * A_2 + A_3 * (HNO_3)_{AT} * A_4) \quad (3.39)$$

And the following nine simultaneous non-linear equations:

$$1. \quad (\text{NO}_3^{-1})_A = \text{DOD} * (\text{HNO}_3)_{AT} \quad (3.22)$$

$$2. \quad \text{DOD} = 1.0006204 - 0.020407 * (\text{HNO}_3)_{AT} - \\ 0.004496 * ((\text{HNO}_3)_{AT})^{**2} + 0.0001546 * ((\text{HNO}_3)_{AT})^{**3} \\ (3.21)$$

$$3. \quad ((\text{HNO}_3)_{n\text{-TBP}})_O = -0.07272 - 1.062423 * (\text{HNO}_3)_{AT} - \\ 0.173784 * ((\text{HNO}_3)_{AT})^{**2} + 0.0186665 * ((\text{HNO}_3)_{AT})^{**3} - \\ 0.001062 * ((\text{HNO}_3)_{AT})^{**4} + 0.0000261 * ((\text{HNO}_3)_{AT})^{**5} \\ (3.15)$$

$$4. \quad (\text{M}(\text{NO}_3)_3(\text{TBP})_3)_O = \\ K_e * (\text{M}^{+3})_A * (\text{NO}_3^{-1})_A^3 * (\text{TBP})_O^3 \\ (3.2)$$

$$5. \quad (\text{HNO}_3)_{AI} = (1 - \text{DOD}) * (\text{HNO}_3)_{AT} + (\text{H}^+)_A + \\ (1/3) * (\text{RRE})_{AI} + ((\text{HNO}_3)_{n\text{-TB}})_O \\ (3.28)$$

$$6. \quad (\text{RRE})_{AI} = (\text{M}^{+3})_A * (1 + K_e' * (\text{NO}_3^{-1})_A^3 * (\text{TBP})_O^3 + \\ K_1' * (\text{NO}_3^{-1})_A + K_2' * (\text{NO}_3^{-1})_A^2) \\ (3.20)$$

$$7. \quad (\text{HNO}_3)_{AI} = (\text{HNO}_3)_{AT} + ((\text{HNO}_3)_{n\text{-TBP}})_O + \\ 3(\text{M}(\text{NO}_3)_3(\text{TBP})_3)_O + (\text{MNO}_3^{+2})_A + 2(\text{M}(\text{NO}_3)_2^{+1})_A \\ (3.16)$$

$$8. \quad (\text{TBP})_{AI} = (\text{TBP})_O + ((\text{HNO}_3)_n\text{-TBP})_O/\text{NOH} + \\ 3(\text{M}(\text{NO}_3)_3(\text{TBP})_3)_O \quad (3.17)$$

$$9. \quad (\text{TBP})_O = 3.428093 - 0.13173 * (\text{HNO}_3)_{AT} + \\ 0.028538 * ((\text{HNO}_3)_{AT})^{**2} - 0.003824 * ((\text{HNO}_3)_{AT})^{**3} + \\ 0.0002462 * ((\text{HNO}_3)_{AT})^{**4} - 0.000006359 * ((\text{HNO}_3)_{AT})^{**5} \\ (3.30)$$

Eight model parameters:

$K_e, K_1, K_2, A_0, A_1, A_2, A_3$ and A_4

Nine unknowns in the simultaneous equations:

$(\text{NO}_3^{-1})_A, (\text{TBP})_O, (\text{HNO}_3)_{AT}, ((\text{HNO}_3)_n\text{-TBP})_O, (\text{H}^+)_A, \\ (\text{M}(\text{NO}_3)_3(\text{TBP})_3)_O, (\text{M}^{+3})_A, \text{DOD}$ and NOH

In addition, we have available experimental distribution coefficient data (K_d) for all 16 rare earth elements, over an acidity range of 0.3-16 M.

Based on the information we have summarized, it is now possible to evaluate the values of eight model parameters using a non-linear optimization technique. Mass balance for all chemical species involved in the $\text{HNO}_3\text{-H}_2\text{O-TBP}$ two-phase system can be achieved simultaneously.

4.2 Procedures For Evaluating The Model Parameters

A computer program was developed to determine the eight equilibrium model parameters. The strategy is to solve the nine simultaneous non-linear equations, obtaining the mass balance relationships in this two-phase system, and then to minimize the difference between the model predicting and experimental distribution coefficient data K_d by adjusting the value of model parameters until converging criteria has been reached. IMSL's subroutine program DBCLSF (56) was incorporated into the following evaluation procedure.

Step 1. Give the value for $(\text{HNO}_3)_{\text{AI}}$, $(\text{RRE})_{\text{AI}}$ and $(\text{TBP})_{\text{OI}}$.

Step 2. Assign the initial value for model parameters

K_e , K_1 , K_2 , A_0 , A_1 , A_2 , A_3 and A_4

Use published experimental data if available.

Step 3. Set the upper and lower bounds for 9 unknowns

$(\text{NO}_3^{-1})_{\text{A}}$, $(\text{TBP})_{\text{O}}$, $(\text{HNO}_3)_{\text{AT}}$, $((\text{HNO}_3)_{\text{n-TBP}})_{\text{O}}$, $(\text{H}^+)_{\text{A}}$,
 $(\text{M}(\text{NO}_3)_3(\text{TBP})_3)_{\text{O}}$, $(\text{M}^{+3})_{\text{A}}$, DOD and NOH

For arithmetic purposes, the initial guess values for the above nine unknowns are required by IMSL's DBCLSF subprogram.

Step 4. Solve the simultaneous non-linear equations using the DBCLS subroutine, and obtain the calculated values for above nine unknown terms.

Step 5. Calculate the distribution coefficient through distribution model.

Step 6. Minimize the difference between the model predicting and experimental distribution coefficient data K_d , by adjusting the value of eight model parameters.

IMSL subroutine program DBCLS F was called.

Step 7. Repeat Step 4 through Step 6 until the value of $(K_d)_{exp} - (K_d)_{calc}$ is less than tolerance.

4.3 Results

The value of the theoretical distribution model parameters for all 16 rare earth elements were listed in Table 4.1. Table 4.2 shows all 16 predicted distribution coefficients and their relative separation factors. The model predicts rare earths distribution coefficients accurately, with negligible deviations from the experimental data published by UK Harwell Laboratory. The verification of this theoretical model will be discussed in the next chapter. The source listing of the computer program for evaluating model parameters is attached in the Appendix C.

Table 4.1 The Parameters for the Distribution Model.

| Elements | Ke | K1 | K2 | A0 |
|--------------|------------|------------|------------|-------------|
| Lutetium | 3.7765E-03 | 6.0260E-01 | 1.5000E+01 | 9.8084E+00 |
| Yttrium | 1.6009E-04 | 6.0260E-01 | 1.5000E+01 | 4.2805E+02 |
| Ytterbium | 3.6319E-03 | 6.0260E-01 | 4.5017E+00 | 1.1246E+01 |
| Thulium | 4.4139E-03 | 7.0790E-01 | 1.2500E+01 | 8.2710E+00 |
| Erbium | 1.7464E-04 | 7.5000E-01 | 1.6105E+01 | 7.4199E+02 |
| Holmium | 4.8020E-02 | 7.5000E-01 | 1.0859E+01 | 1.7245E+00 |
| Dysprosium | 2.9289E-04 | 8.0000E-01 | 2.5000E+01 | 6.1135E+02 |
| Terbium | 7.3684E-03 | 1.1300E+00 | 3.5000E+01 | 3.0932E+01 |
| Gadolinium | 7.5454E-03 | 1.2500E+00 | 2.5000E+01 | 4.6249E+01 |
| Europium | 4.8544E-02 | 2.0400E+00 | 4.7091E+01 | 1.5713E+00 |
| Samarium | 9.1132E-04 | 3.2000E+00 | 3.5000E+01 | 3.0849E+02 |
| Promethium | 1.3855E-02 | 2.4800E+00 | 2.5000E+01 | -7.2923E+00 |
| Neodymium | 1.0000E-01 | 8.0000E-01 | 9.0243E+00 | -2.3811E-01 |
| Praseodymium | 1.0000E-01 | 1.6982E+00 | 3.2448E+01 | -2.9400E+00 |
| Cerium (III) | 3.2647E-01 | 1.6300E+00 | 1.9114E+01 | -2.2172E-01 |
| Lanthanum | 3.8348E-02 | 1.2882E+00 | 1.0765E+01 | -2.1943E-01 |

| Elements | A1 | A2 | A3 | A4 |
|--------------|-------------|-------------|------------|------------|
| Lutetium | 2.7193E-01 | 3.7806E+00 | 6.1514E-09 | 1.1706E+01 |
| Yttrium | 6.4441E+00 | 3.0916E+00 | 8.9564E-06 | 9.8854E+00 |
| Ytterbium | 6.7744E-02 | 3.5478E+00 | 1.7513E-06 | 8.7219E+00 |
| Thulium | 1.9270E+00 | 1.9068E+00 | 1.0011E-05 | 8.2586E+00 |
| Erbium | 2.8451E+00 | 3.4183E+00 | 8.0252E-06 | 9.6484E+00 |
| Holmium | 2.1721E-03 | 3.3385E+00 | 4.4457E-06 | 7.2040E+00 |
| Dysprosium | 3.3406E-01 | 4.0502E+00 | 6.0624E-07 | 1.0478E+01 |
| Terbium | 2.3170E-01 | 2.3466E+00 | 4.2961E-07 | 9.2689E+00 |
| Gadolinium | -2.2406E+01 | 1.2500E-01 | 3.5212E-06 | 7.9373E+00 |
| Europium | 6.9358E+00 | -4.5006E-01 | 9.6604E-07 | 7.7463E+00 |
| Samarium | -2.5754E+01 | 1.1617E+00 | 1.1257E-03 | 6.0768E+00 |
| Promethium | 2.3771E+01 | -4.1865E-01 | 1.0932E-05 | 6.4171E+00 |
| Neodymium | 1.0176E+00 | -5.4992E-01 | 3.3469E-07 | 6.3364E+00 |
| Praseodymium | 4.7418E+00 | -2.3403E-01 | 6.0574E-05 | 4.4400E+00 |
| Cerium (III) | 5.3016E-01 | -4.7404E-01 | 7.0708E-05 | 3.4566E+00 |
| Lanthanum | 1.3901E+00 | -8.6901E-01 | 1.0670E-05 | 4.5425E+00 |

Table 4.2 The Predicted Distribution Coefficients and Separation Factors.

| | 0.1 | 0.2 | 0.5 | 0.7 | 1 | 1.5 | 2 | 2.5 | 3 | 3.5 | 4 | 4.5 |
|-----------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| (HNO ₃) _{ai} | | | | | | | | | | | | |
| (HNO ₃) _{at} | 0.08383 | 0.13 | 0.2722 | 0.37 | 0.521 | 0.784 | 1.06 | 1.35 | 1.66 | 1.97 | 2.3 | 2.64 |
| (NO ₃ -1) _a | 0.08373 | 0.1298 | 0.2708 | 0.367 | 0.515 | 0.771 | 1.03 | 1.3 | 1.58 | 1.86 | 2.14 | 2.42 |
| (TBP) _o | 3.46 | 3.45 | 3.42 | 3.4 | 3.38 | 3.34 | 3.31 | 3.29 | 3.26 | 3.25 | 3.23 | 3.22 |
| Lutecium | 0.000782 | 0.0025 | 0.01302 | 0.02229 | 0.03695 | 0.06153 | 0.08701 | 0.1161 | 0.1532 | 0.2056 | 0.2841 | 0.4038 |
| SF Lu/Y | 0.540428 | 0.539956 | 0.540248 | 0.540494 | 0.540678 | 0.542592 | 0.549305 | 0.566065 | 0.598437 | 0.654985 | 0.742550 | 0.865038 |
| Yttrium | 0.001447 | 0.00463 | 0.0241 | 0.04124 | 0.06834 | 0.1134 | 0.1584 | 0.2051 | 0.256 | 0.3139 | 0.3826 | 0.4668 |
| SF Y/Yb | 1.571118 | 1.454602 | 1.107536 | 0.946088 | 0.795483 | 0.672597 | 0.618025 | 0.592090 | 0.580894 | 0.578297 | 0.581017 | 0.586505 |
| Ytterbium | 0.000921 | 0.003183 | 0.02176 | 0.04359 | 0.08591 | 0.1686 | 0.2563 | 0.3464 | 0.4407 | 0.5428 | 0.6585 | 0.7959 |
| SF Yb/Tm | 1.183804 | 1.258102 | 1.549857 | 1.741510 | 1.961415 | 2.120754 | 2.095666 | 1.976041 | 1.820322 | 1.661463 | 1.521487 | 1.410419 |
| Thulium | 0.000778 | 0.00253 | 0.01404 | 0.02503 | 0.0438 | 0.0795 | 0.1223 | 0.1753 | 0.2421 | 0.3267 | 0.4328 | 0.5643 |
| SF Tm/Er | 0.289326 | 0.296948 | 0.324699 | 0.341240 | 0.363184 | 0.400503 | 0.445050 | 0.499430 | 0.564598 | 0.639835 | 0.722778 | 0.809728 |
| Erbium | 0.002689 | 0.00852 | 0.04324 | 0.07335 | 0.1206 | 0.1985 | 0.2748 | 0.351 | 0.4288 | 0.5106 | 0.5988 | 0.6969 |
| SF Er/Ho | 1.515783 | 1.463917 | 1.312291 | 1.243641 | 1.180039 | 1.128482 | 1.106260 | 1.097560 | 1.096955 | 1.104238 | 1.119461 | 1.142833 |
| Holmium | 0.001774 | 0.00582 | 0.03295 | 0.05898 | 0.1022 | 0.1759 | 0.2484 | 0.3198 | 0.3909 | 0.4624 | 0.5349 | 0.6098 |
| SF Ho/Dy | 0.504407 | 0.551136 | 0.705416 | 0.787555 | 0.872013 | 0.948759 | 0.987281 | 1.009469 | 1.023834 | 1.033758 | 1.041269 | 1.047226 |
| Dysprosium | 0.003517 | 0.01056 | 0.04671 | 0.07489 | 0.1172 | 0.1854 | 0.2516 | 0.3168 | 0.3818 | 0.4473 | 0.5137 | 0.5823 |
| SF Dy/Tb | 0.847469 | 0.894157 | 0.997224 | 1.032395 | 1.059674 | 1.076655 | 1.080756 | 1.078651 | 1.073376 | 1.066777 | 1.058738 | 1.051652 |
| Terbium | 0.00415 | 0.01181 | 0.04684 | 0.07254 | 0.1106 | 0.1722 | 0.2328 | 0.2937 | 0.3557 | 0.4193 | 0.4852 | 0.5537 |
| SF Tb/Gd | 0.967591 | 0.953957 | 0.909691 | 0.899442 | 0.899918 | 0.9184 | 0.943273 | 0.971551 | 1.002536 | 1.036076 | 1.073213 | 1.114308 |
| Gadolinium | 0.004289 | 0.01238 | 0.05149 | 0.08065 | 0.1229 | 0.1875 | 0.2468 | 0.3023 | 0.3548 | 0.4047 | 0.4521 | 0.4969 |
| SF Gd/Eu | 0.238994 | 0.307960 | 0.475746 | 0.555249 | 0.643455 | 0.743457 | 0.814521 | 0.868927 | 0.913021 | 0.949554 | 0.980694 | 1.007706 |
| Europium | 0.017946 | 0.0402 | 0.10823 | 0.14525 | 0.191 | 0.2522 | 0.303 | 0.3479 | 0.3886 | 0.4262 | 0.461 | 0.4931 |
| SF Eu/Sm | 3.977393 | 3.210862 | 2.185581 | 1.875161 | 1.602348 | 1.362506 | 1.232208 | 1.154280 | 1.106177 | 1.078714 | 1.066389 | 1.066392 |
| Samarium | 0.004512 | 0.01252 | 0.04952 | 0.07746 | 0.1192 | 0.1851 | 0.2459 | 0.3014 | 0.3513 | 0.3951 | 0.4323 | 0.4624 |
| SF Sm/Pm | 0.308533 | 0.360599 | 0.467169 | 0.526580 | 0.608163 | 0.731620 | 0.843857 | 0.946013 | 1.039656 | 1.124359 | 1.200166 | 1.266849 |
| Promethium | 0.014624 | 0.03472 | 0.106 | 0.1471 | 0.196 | 0.253 | 0.2914 | 0.3186 | 0.3379 | 0.3514 | 0.3602 | 0.365 |
| SF Pm/Nd | 1.811245 | 1.679729 | 1.357929 | 1.245449 | 1.163204 | 1.119469 | 1.116903 | 1.128166 | 1.144260 | 1.162037 | 1.180596 | 1.199868 |
| N neodmium | 0.008074 | 0.02067 | 0.07806 | 0.11811 | 0.1685 | 0.226 | 0.2609 | 0.2824 | 0.2953 | 0.3024 | 0.3051 | 0.3042 |
| SF Nd/Pr | 0.819445 | 0.863048 | 1.079518 | 1.193150 | 1.299151 | 1.376370 | 1.403442 | 1.416959 | 1.428640 | 1.443436 | 1.463309 | 1.488986 |
| Praseodymium | 0.009853 | 0.02395 | 0.07231 | 0.09899 | 0.1297 | 0.1642 | 0.1859 | 0.1993 | 0.2067 | 0.2095 | 0.2085 | 0.2043 |
| SF Pr/Ce | 1.050874 | 1.066340 | 1.040581 | 1.034054 | 1.041767 | 1.076015 | 1.117859 | 1.161421 | 1.205247 | 1.250746 | 1.297448 | 1.344963 |
| Cerium (III) | 0.009376 | 0.02246 | 0.06949 | 0.09573 | 0.1245 | 0.1526 | 0.1663 | 0.1716 | 0.1715 | 0.1675 | 0.1607 | 0.1519 |
| SF Ce/La | 1.007630 | 1.102601 | 1.191733 | 1.215464 | 1.249749 | 1.307626 | 1.360883 | 1.403107 | 1.436348 | 1.460331 | 1.474311 | 1.481951 |
| Lanthanum | 0.009305 | 0.02037 | 0.05831 | 0.07876 | 0.09962 | 0.1167 | 0.1222 | 0.1223 | 0.1194 | 0.1147 | 0.109 | 0.1025 |

Table 4.2 The Predicted Distribution Coefficients and Separation Factors (Continued).

| | | | | | | | | | | | | |
|-----------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| (HNO ₃) _{ai} | 5 | 5.5 | 6 | 6.5 | 7 | 7.5 | 8 | 8.5 | 9 | 9.5 | 10 | 11 |
| (HNO ₃) _{at} | 2.99 | 3.34 | 3.71 | 4.08 | 4.49 | 4.85 | 5.24 | 5.64 | 6.04 | 6.44 | 6.85 | 7.66 |
| (NO ₃ -1) _a | 2.7 | 2.97 | 3.23 | 3.48 | 3.72 | 3.95 | 4.15 | 4.34 | 4.51 | 4.66 | 4.79 | 4.98 |
| (TBP) _o | 3.21 | 3.19 | 3.18 | 3.17 | 3.16 | 3.15 | 3.16 | 3.12 | 3.11 | 3.09 | 3.08 | 3.05 |
| Lutecium | 0.5852 | 0.8549 | 1.2454 | 1.796 | 2.5523 | 3.5667 | 4.9004 | 6.6269 | 8.8407 | 11.673 | 15.318 | 26.394 |
| SF Lu/Y | 1.022719 | 1.211936 | 1.423639 | 1.646799 | 1.867764 | 2.071013 | 2.239568 | 2.355561 | 2.404389 | 2.379767 | 2.288215 | 1.988398 |
| Yttrium | 0.5722 | 0.7054 | 0.8748 | 1.0906 | 1.3665 | 1.7222 | 2.1881 | 2.8133 | 3.6769 | 4.9051 | 6.6943 | 13.274 |
| SF Y/Yb | 0.592646 | 0.597189 | 0.598767 | 0.596543 | 0.590586 | 0.581843 | 0.572082 | 0.563663 | 0.559130 | 0.560896 | 0.570796 | 0.617596 |
| Ytterbium | 0.9655 | 1.1812 | 1.461 | 1.8282 | 2.3138 | 2.9599 | 3.8248 | 4.9911 | 6.5761 | 8.7451 | 11.728 | 21.493 |
| SF Yb/Tm | 1.331173 | 1.283355 | 1.264606 | 1.270907 | 1.297045 | 1.336539 | 1.381692 | 1.423994 | 1.455823 | 1.472214 | 1.472257 | 1.436986 |
| Thulium | 0.7253 | 0.9204 | 1.1553 | 1.4385 | 1.7839 | 2.2146 | 2.7682 | 3.505 | 4.5171 | 5.9401 | 7.966 | 14.957 |
| SF Tm/Er | 0.896095 | 0.977277 | 1.049318 | 1.110039 | 1.160109 | 1.202410 | 1.241289 | 1.281676 | 1.326880 | 1.377414 | 1.430392 | 1.520406 |
| Erbium | 0.8094 | 0.9418 | 1.101 | 1.2959 | 1.5377 | 1.8418 | 2.2301 | 2.7347 | 3.4043 | 4.3125 | 5.5691 | 9.8375 |
| SF Er/Ho | 1.175428 | 1.216010 | 1.261891 | 1.308197 | 1.346497 | 1.367944 | 1.365646 | 1.338112 | 1.291513 | 1.237091 | 1.186783 | 1.131696 |
| Holmium | 0.6886 | 0.7745 | 0.8725 | 0.9906 | 1.142 | 1.3464 | 1.633 | 2.0437 | 2.6359 | 3.486 | 4.6926 | 8.6927 |
| SF Ho/Dy | 1.052583 | 1.058783 | 1.067931 | 1.082978 | 1.109060 | 1.151359 | 1.214577 | 1.300973 | 1.407539 | 1.524001 | 1.633401 | 1.756881 |
| Dysprosium | 0.6542 | 0.7315 | 0.817 | 0.9147 | 1.0297 | 1.1694 | 1.3445 | 1.5709 | 1.8727 | 2.2874 | 2.8729 | 4.9478 |
| SF Dy/Tb | 1.046385 | 1.044701 | 1.048242 | 1.058803 | 1.077317 | 1.104457 | 1.139503 | 1.180329 | 1.222708 | 1.261596 | 1.292352 | 1.325208 |
| Terbium | 0.6252 | 0.7002 | 0.7794 | 0.8639 | 0.9558 | 1.0588 | 1.1799 | 1.3309 | 1.5316 | 1.8131 | 2.223 | 3.7336 |
| SF Tb/Gd | 1.160141 | 1.210790 | 1.266699 | 1.327035 | 1.390456 | 1.453996 | 1.513080 | 1.562272 | 1.596414 | 1.614227 | 1.620026 | 1.630393 |
| Gadolinium | 0.5389 | 0.5783 | 0.6153 | 0.651 | 0.6874 | 0.7282 | 0.7798 | 0.8519 | 0.9594 | 1.1232 | 1.3722 | 2.29 |
| SF Gd/Eu | 1.030992 | 1.051837 | 1.070459 | 1.088082 | 1.105322 | 1.123938 | 1.145922 | 1.173415 | 1.208921 | 1.253012 | 1.304496 | 1.414453 |
| Europium | 0.5227 | 0.5498 | 0.5748 | 0.5983 | 0.6219 | 0.6479 | 0.6805 | 0.726 | 0.7936 | 0.8964 | 1.0519 | 1.619 |
| SF Eu/Sm | 1.077731 | 1.098721 | 1.129494 | 1.168782 | 1.215598 | 1.267162 | 1.320077 | 1.369036 | 1.408340 | 1.436078 | 1.454306 | 1.488735 |
| Samarium | 0.485 | 0.5004 | 0.5089 | 0.5119 | 0.5116 | 0.5113 | 0.5155 | 0.5303 | 0.5635 | 0.6242 | 0.7233 | 1.0875 |
| SF Sm/Pm | 1.323328 | 1.370208 | 1.406967 | 1.434295 | 1.453822 | 1.467987 | 1.481321 | 1.499293 | 1.528342 | 1.571896 | 1.629788 | 1.765708 |
| Promethium | 0.3665 | 0.3652 | 0.3617 | 0.3569 | 0.3519 | 0.3483 | 0.348 | 0.3537 | 0.3687 | 0.3971 | 0.4438 | 0.6159 |
| SF Pm/Nd | 1.219633 | 1.240067 | 1.261157 | 1.284274 | 1.310614 | 1.341162 | 1.378217 | 1.423913 | 1.479534 | 1.544535 | 1.616168 | 1.757203 |
| Neodymium | 0.3005 | 0.2945 | 0.2868 | 0.2779 | 0.2685 | 0.2597 | 0.2525 | 0.2484 | 0.2492 | 0.2571 | 0.2746 | 0.3505 |
| SF Nd/Pr | 1.520748 | 1.558201 | 1.600446 | 1.644378 | 1.687617 | 1.723291 | 1.744989 | 1.745607 | 1.724567 | 1.684796 | 1.637447 | 1.575280 |
| Praseodymium | 0.1976 | 0.189 | 0.1792 | 0.169 | 0.1591 | 0.1507 | 0.1447 | 0.1423 | 0.1445 | 0.1526 | 0.1677 | 0.2225 |
| SF Pr/Ce | 1.393511 | 1.443850 | 1.493333 | 1.540565 | 1.581510 | 1.611420 | 1.626390 | 1.624243 | 1.605733 | 1.580364 | 1.557103 | 1.541926 |
| Cerium (III) | 0.1418 | 0.1309 | 0.12 | 0.1097 | 0.1006 | 0.09352 | 0.08897 | 0.08761 | 0.08999 | 0.09656 | 0.1077 | 0.1443 |
| SF Ce/La | 1.482333 | 1.478427 | 1.474201 | 1.473472 | 1.481154 | 1.506528 | 1.556780 | 1.639101 | 1.755559 | 1.898171 | 2.049866 | 2.289022 |
| Lanthanum | 0.09566 | 0.08854 | 0.0814 | 0.07445 | 0.06792 | 0.06206 | 0.05715 | 0.05345 | 0.05126 | 0.05087 | 0.05254 | 0.06304 |

Table 4.2 The Predicted Distribution Coefficients and Separation Factors (Continued).

| | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|-----------------------------------|----------|----------|----------|----------|----------|----------|----------|
| (HNO ₃) _{ai} | | | | | | | |
| (HNO ₃) _{at} | 8.48 | 9.29 | 10.1 | 10.89 | 11.68 | 12.45 | 13.22 |
| (NO ₃ -1) _a | 5.07 | 5.08 | 5 | 4.84 | 4.62 | 4.33 | 4 |
| (TBP) _o | 3.02 | 2.99 | 2.96 | 2.93 | 2.89 | 2.84 | 2.77 |
| Lutecium | 46.903 | 87.442 | 168.77 | 326.64 | 614.45 | 1098.4 | 1837.2 |
| SF Lu/Y | 1.695636 | 1.517221 | 1.458308 | 1.487431 | 1.574866 | 1.700388 | 1.852016 |
| Yttrium | 27.661 | 57.633 | 115.73 | 219.6 | 390.16 | 645.97 | 992 |
| SF Y/Yb | 0.696312 | 0.795607 | 0.904706 | 1.016807 | 1.128706 | 1.239603 | 1.350100 |
| Ytterbium | 39.725 | 72.439 | 127.92 | 215.97 | 345.67 | 521.11 | 734.76 |
| SF Yb/Tm | 1.386803 | 1.347276 | 1.325115 | 1.318015 | 1.321520 | 1.331842 | 1.346108 |
| Thulium | 28.645 | 53.767 | 96.535 | 163.86 | 261.57 | 391.27 | 545.84 |
| SF Tm/Er | 1.554934 | 1.525954 | 1.454015 | 1.363001 | 1.268341 | 1.177779 | 1.094108 |
| Erbium | 18.422 | 35.235 | 66.392 | 120.22 | 206.23 | 332.21 | 498.89 |
| SF Er/Ho | 1.156797 | 1.256866 | 1.418026 | 1.628114 | 1.878746 | 2.164939 | 2.484759 |
| Holmium | 15.925 | 28.034 | 46.82 | 73.84 | 109.77 | 153.45 | 200.78 |
| SF Ho/Dy | 1.694816 | 1.496982 | 1.257520 | 1.034622 | 0.847972 | 0.697848 | 0.578233 |
| Dysprosium | 9.3963 | 18.727 | 37.232 | 71.369 | 129.45 | 219.89 | 347.23 |
| SF Dy/Tb | 1.342597 | 1.375498 | 1.433411 | 1.512394 | 1.606041 | 1.709211 | 1.819291 |
| Terbium | 6.9986 | 13.6147 | 25.9744 | 47.1894 | 80.6019 | 128.65 | 190.86 |
| SF Tb/Gd | 1.684785 | 1.792658 | 1.938532 | 2.107610 | 2.290412 | 2.482105 | 2.680354 |
| Gadolinium | 4.154 | 7.5947 | 13.399 | 22.39 | 35.191 | 51.831 | 71.207 |
| SF Gd/Eu | 1.508406 | 1.576972 | 1.625894 | 1.662459 | 1.691712 | 1.716485 | 1.738197 |
| Europium | 2.7539 | 4.816 | 8.241 | 13.468 | 20.802 | 30.196 | 40.966 |
| SF Eu/Sm | 1.559399 | 1.676529 | 1.830845 | 2.011740 | 2.212155 | 2.427916 | 2.657541 |
| Samarium | 1.766 | 2.8726 | 4.5012 | 6.6947 | 9.4035 | 12.437 | 15.415 |
| SF Sm/Pm | 1.881926 | 1.953352 | 1.985881 | 1.992944 | 1.985200 | 1.969188 | 1.948700 |
| Promethium | 0.9384 | 1.4706 | 2.2666 | 3.3592 | 4.7368 | 6.3158 | 7.9104 |
| SF Pm/Nd | 1.862643 | 1.926634 | 1.962594 | 1.984170 | 1.998902 | 2.010568 | 2.020846 |
| Neodymium | 0.5038 | 0.7633 | 1.1549 | 1.693 | 2.3697 | 3.1413 | 3.9144 |
| SF Nd/Pr | 1.599365 | 1.704555 | 1.866655 | 2.065893 | 2.290893 | 2.535146 | 2.795600 |
| Praseodymium | 0.315 | 0.4478 | 0.6187 | 0.8195 | 1.0344 | 1.2391 | 1.4002 |
| SF Pr/Ce | 1.574212 | 1.639692 | 1.723878 | 1.817476 | 1.915910 | 2.016764 | 2.119588 |
| Cerium (III) | 0.2001 | 0.2731 | 0.3589 | 0.4509 | 0.5399 | 0.6144 | 0.6606 |
| SF Ce/La | 2.373665 | 2.336184 | 2.237531 | 2.122881 | 2.007809 | 1.900990 | 1.802947 |
| Lanthanum | 0.0843 | 0.1169 | 0.1604 | 0.2124 | 0.2689 | 0.3232 | 0.3664 |

Table 4.2 The Predicted Distribution Coefficients and Separation Factors (Continued).

CHAPTER 5

VERIFICATION OF THE THEORETICAL MODEL

5.1 Verification By Experimental Data

Verification is a necessary step to certify the correctness and accuracy for any kind of mathematical model. Only after certification, can the model be used with confidence. Comparing the experimental and model predicted data in different cases is one of the easiest methods to verify models. Tables 5.1 to 5.16 summarize the experimental and the predicted distribution coefficients, component concentrations in the aqueous phase and the organic phase for all 16 rare earth elements. The nitric acid degree of dissociation with different aqueous acidities was also shown in these tables. Figures 5.1 to 5.16 present the experimental and model predicted distribution coefficients graphically for all 16 elements. Figures 5.17 to 5.32 compare the published and model predicted data in a bar chart form versus the natural logarithm scale of K_D . The natural logarithm scale is a more distinct way to show the differences between the experimental data and the model predicted data. Table 5.1, Figure 5.1 and Figure 5.17, which are located in the following pages, shows the comparison of the experimental and model predicted distribution coefficients and the equilibrium concentrations for lutetium, a representative

Table 5.1 The Calculated Distribution Coefficients of Lutetium and Composition in Aqueous and Organic Phases.

| Test | (HNO ₃) _{ai} | Kd exp | Kd calc | (HNO ₃) _{at} | (MNO ₃ +2) _a | Deg Ioniz | (NO ₃ -1) _a |
|------|-----------------------------------|----------|----------|-----------------------------------|------------------------------------|-----------|-----------------------------------|
| 1 | 0.52 | 0.0133 | 0.0134 | 0.2785 | 1.660000E-05 | 0.9948 | 0.2769 |
| 2 | 1.03 | 0.0340 | 0.0399 | 0.5550 | 5.616000E-04 | 0.9879 | 0.5483 |
| 3 | 1.56 | 0.0600 | 0.0669 | 0.8417 | 3.977000E-04 | 0.9804 | 0.8251 |
| 4 | 2.17 | 0.0750 | 0.0998 | 1.1873 | 3.471000E-04 | 0.9703 | 1.1521 |
| 5 | 3.23 | 0.1980 | 0.1809 | 1.8283 | 2.091000E-04 | 0.9492 | 1.7355 |
| 6 | 4.36 | 0.4400 | 0.3764 | 2.5676 | 1.425000E-04 | 0.9212 | 2.3652 |
| 7 | 4.73 | 0.6300 | 0.4920 | 2.8215 | 1.548000E-04 | 0.9107 | 2.5696 |
| 8 | 5.38 | 0.9600 | 0.7985 | 3.2790 | 1.760000E-04 | 0.8907 | 2.9207 |
| 9 | 6.16 | 1.4800 | 1.4258 | 3.8479 | 2.003000E-04 | 0.8641 | 3.3248 |
| 10 | 7.35 | 3.1000 | 3.2655 | 4.7507 | 2.341000E-04 | 0.8181 | 3.8862 |
| 11 | 9.03 | 8.6000 | 9.0446 | 6.0760 | 2.722000E-04 | 0.7436 | 4.5177 |
| 12 | 10.80 | 24.0000 | 23.6909 | 7.5071 | 2.969000E-04 | 0.6565 | 4.9277 |
| 13 | 12.80 | 77.0000 | 76.8910 | 9.1360 | 3.043000E-04 | 0.5528 | 5.0500 |
| 14 | 14.40 | 220.0000 | 220.1889 | 10.4276 | 2.954000E-04 | 0.4701 | 4.9021 |
| 15 | 15.50 | 450.0000 | 449.9329 | 11.2980 | 2.827000E-04 | 0.4154 | 4.6923 |

| Test | (H+1) _a | (M+3) _a | (HNO ₃) _o | (M) _o | (M(NO ₃) ₂) _a | (TBP) _o | NOH |
|------|--------------------|--------------------|----------------------------------|------------------|--|--------------------|--------|
| 1 | 0.2993 | 0.0001 | 0.2159 | 0.0100 | 1.150100E-04 | 3.4038 | 1.0000 |
| 2 | 0.5536 | 0.0017 | 0.4665 | 0.0001 | 7.666130E-03 | 3.3631 | 1.5730 |
| 3 | 0.8311 | 0.0008 | 0.7090 | 0.0001 | 8.169480E-03 | 3.3353 | 2.1854 |
| 4 | 1.1585 | 0.0005 | 0.9729 | 0.0001 | 9.955000E-03 | 3.3060 | 2.7507 |
| 5 | 1.7423 | 0.0002 | 1.3916 | 0.0001 | 9.035880E-03 | 3.2619 | 3.4993 |
| 6 | 2.3722 | 0.0001 | 1.7822 | 0.0001 | 8.391250E-03 | 3.2233 | 4.0860 |
| 7 | 2.5766 | 0.0001 | 1.8981 | 0.0001 | 9.904260E-03 | 3.2122 | 4.2413 |
| 8 | 2.9306 | 0.0001 | 2.0877 | 0.0002 | 1.279573E-02 | 3.1942 | 4.4851 |
| 9 | 3.3386 | 0.0001 | 2.2950 | 0.0001 | 1.658144E-02 | 3.1745 | 4.7300 |
| 10 | 3.9062 | 0.0001 | 2.5761 | 0.0001 | 2.265382E-02 | 3.1464 | 5.0184 |
| 11 | 4.5459 | 0.0001 | 2.9228 | 0.0001 | 3.061441E-02 | 3.1064 | 5.2823 |
| 12 | 4.9618 | 0.0001 | 3.2558 | 0.0001 | 3.642334E-02 | 3.0600 | 5.4289 |
| 13 | 5.0859 | 0.0001 | 3.6252 | 0.0001 | 3.825375E-02 | 3.0010 | 5.5038 |
| 14 | 4.9357 | 0.0001 | 3.9358 | 0.0001 | 3.604587E-02 | 2.9486 | 5.5349 |
| 15 | 4.7229 | 0.0001 | 4.1685 | 0.0001 | 3.302651E-02 | 2.9086 | 5.5502 |

Initial Concentration:
 TBP 3.66 M
 Rare Earths 0.01 M

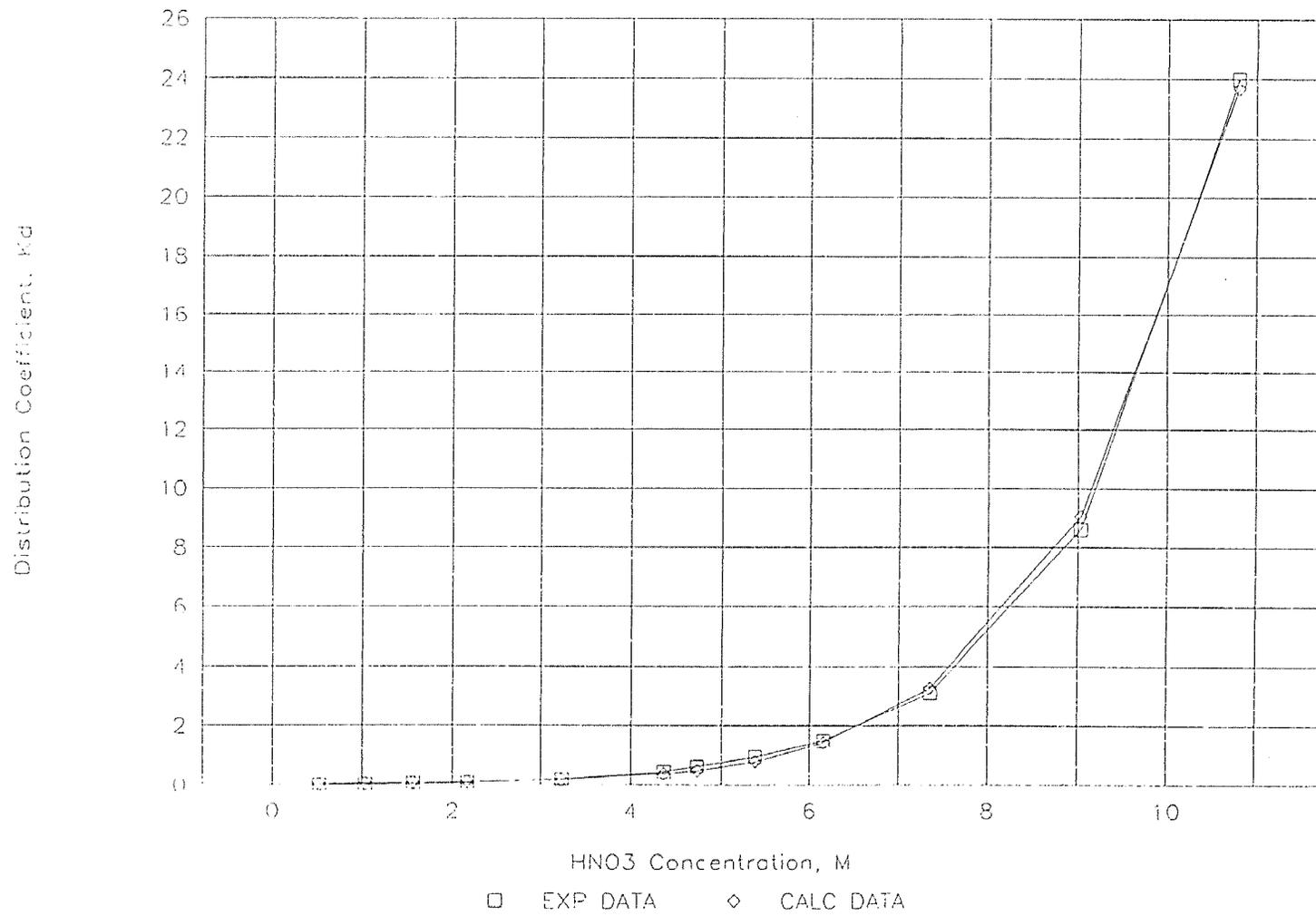


Figure 5.1 Comparison of the Experimental and Predicted Distribution Coefficients of Lutetium.

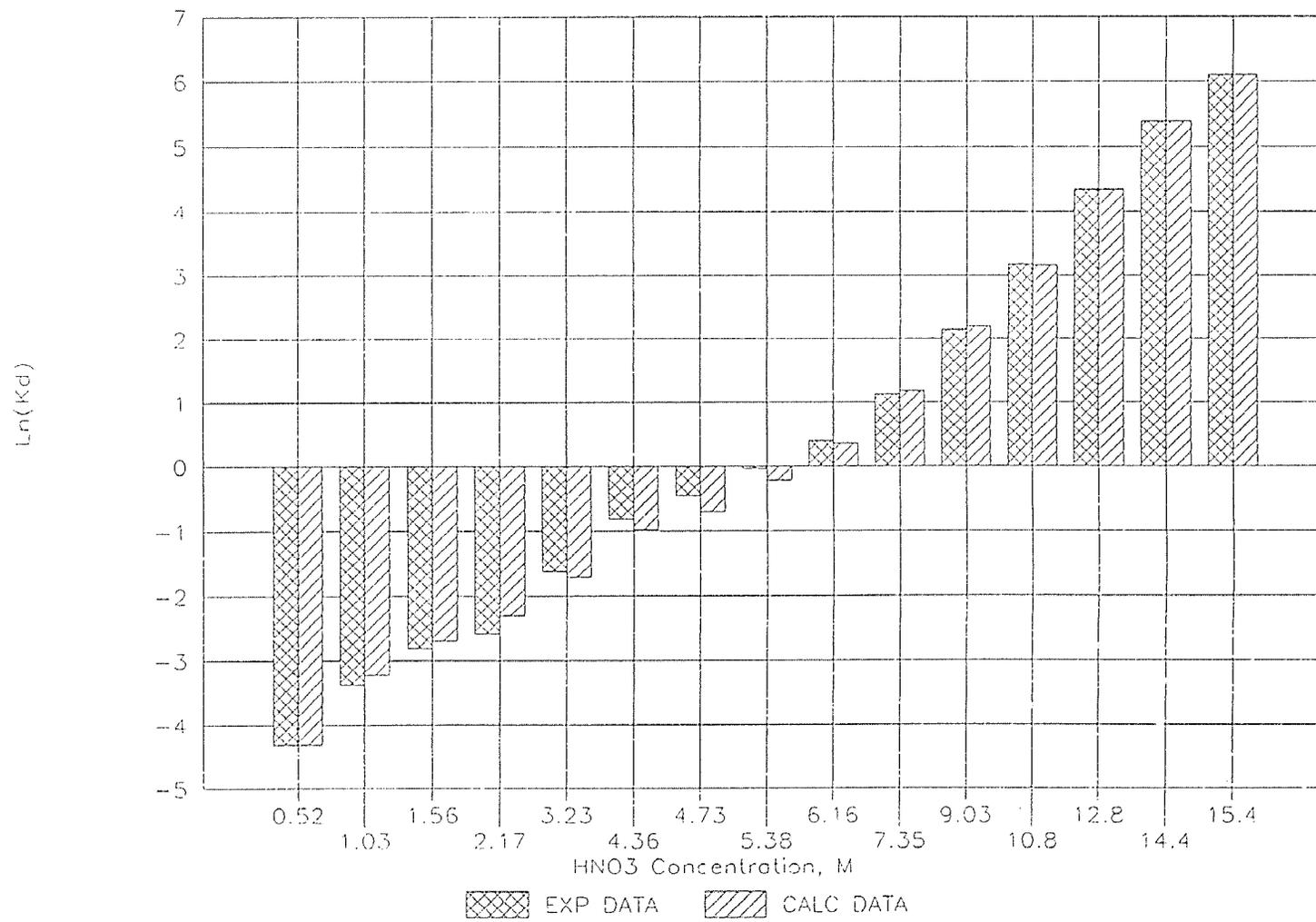


Figure 5.17 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Lutetium.

example for all 16 elements. The remaining cases are summarized in Appendices A and B.

5.2 Verification By Process Simulation

Verification of a model can be accomplished by practical model applications as well. Weaver and Kappelmann (57) of Oak Ridge National Laboratory developed a process for separating promethium from mixed fission product rare earths, by center-feed continuous multistage countercurrent extraction with 100% tri-n-butyl phosphate (TBP) from nitric acid of 12 N or higher concentration. A flowsheet for purification of promethium includes one cycle for separation of promethium from neodymium and lighter elements and a second cycle for removal of samarium and heavier elements. Each cycle consists of a series of countercurrent contact stages, followed by stripping stages and an evaporator. With 20 stages in the first cycle and 34 stages in the second, a 90% yield of promethium with a purity of 83% can be obtained, assuming a 100% stage efficiency. An increase to 25 stages in the first cycle would permit a 90% yield of 93% promethium. When the stages in the first cycle increased to 34, the promethium yield and purity increased to 93% and 99%, respectively.

The following are the important process parameters for Weaver and Kappelmann's flow sheet of the center-feed continuous multistage countercurrent extractor in the first cycle:

Number of Stages: 20 to 34 stages.

Feed: 0.5 l/h of 12.5 N HNO₃ solution, with 12.5 g of rare earths with composition (wt %):

| Component | Wt % | Component | Wt % |
|--------------------------------|--------|--------------------------------|--------|
| La ₂ O ₃ | 0.1421 | Pr ₂ O ₃ | 0.1421 |
| Nd ₂ O ₃ | 0.5372 | Pm ₂ O ₃ | 0.0630 |
| Sm ₂ O ₃ | 0.1080 | Eu ₂ O ₃ | 0.0036 |
| Gd ₂ O ₃ | 0.0007 | Y ₂ O ₃ | 0.0033 |

Extractant: 24.4 l/h of TBP, pre-equilibrated with 12 N HNO₃.

Scrub Solution: 14.5 l/h of 12 N HNO₃ solution.

We conducted several process simulations with stage numbers 20, 25 and 34 for the continuous multistage countercurrent extraction in the first cycle, with the Weaver and Kappelmann's process parameters. The theoretical equilibrium model developed by this research was used to predict the rare earths distribution in the HNO₃-H₂O-TBP system. The following is a comparison of promethium recovery from Weaver and Kappelmann's experiments with our simulations:

| | Promethium Recovery | | | |
|---------------------|---------------------|-----------|-----------|-----------|
| | 15 Stages | 20 Stages | 25 Stages | 34 Stages |
| Weaver & Kappelmann | n/a | 0.9000 | 0.9000 | 0.9524 |
| This Work | 0.9311 | 0.9989 | 0.9997 | 0.9999 |

The differences between the laboratory data obtained by Weaver and Kappelmann and our simulation results were caused by stage efficiencies. With limited data, the stage efficiency for Weaver and Kappelmann's extraction apparatus was estimated around 60-70%, while a 100% efficiency was used for all process simulations. Weaver and Kappelmann reported 90% recovery rate for both 20 stage and 25 stage cases. We doubt the accuracies of Weaver and Kappelmann's experiments, because their results are contrary to the principle of equilibrium stage operation. Generally, if same stage efficiency was used, and same acid strength was maintained, the recovery rate of a specific specie increases in accordance with the increasing of the number of contact stages.

Weaver and Kappelmann suggested that operation at higher acidity is possible with relative flow rates different with a smaller organic flow. We decided to verify this statement by extracting promethium from mixed fission product rare earths with center-feed extractor, stage numbers from 20 to 60, and with three acidities 11 N, 12 N, and 13 N. We have found that in lower acidity, relative higher organic flow rates were required, on the contrary, with higher acidities, relative lower organic flow rate would be enough. In general, a higher organic flow rate and a higher number of stages will have positive effects on promethium recovery. The results of investigation are shown in details in Tables 5.17 to 5.19 and Figures 5.33 to 5.35.

Table 5.17 and Figure 5.33 are located in the following pages, the remaining tables and figures are placed in Appendices A and B, respectively.

5.3 Computer Program For Liquid-Liquid Extraction Computation

A computer program was developed for the calculations of multicomponent, multistage, counter-current liquid-liquid extraction operations. The Isothermal Sum-Rates (ISR) algorithm which was presented by Tsuboka and Katayama (67) was chosen for its simplicity and numerical reliability, even though the ISR algorithm is slow in convergence compared to other algorithms such as the Newton-Raphson method proposed by Roche (58), (59), and Naphtali and Sandholm (60). Details on the ISR algorithm can be found from Henley and Seader (61). Some modifications were made on the ISR to adapt it to our needs. The program source listing and input file are attached in Appendix D.

5.4 Conclusion

Based on the above discussions, the theoretical model developed by this research accurately predicts the rare earths distribution coefficients in the $\text{HNO}_3\text{-H}_2\text{O-TBP}$ system. Therefore, we have confidence that this model can be used to predict the rare earth distribution in the $\text{HNO}_3\text{-H}_2\text{O-TBP}$ system under any circumstances.

Table 5.17 The Effect of Number of Stages on Promethium Extraction, HNO₃ 11.0 N.

| % OF PROMETHIUM EXTRACTED | | | |
|---------------------------|---------|---------|---------|
| STAGE | CASE A | CASE B | CASE C |
| 20 | 79,1367 | 84,5151 | 88,5961 |
| 25 | 82,1801 | 87,7845 | 91,6906 |
| 30 | 87,1867 | 92,1245 | 95,1901 |
| 35 | 89,4500 | 94,0271 | 96,6271 |
| 40 | 92,5172 | 96,2099 | 98,0773 |
| 45 | 93,9694 | 97,1814 | 98,6734 |
| 50 | 95,7633 | 98,2268 | 99,2488 |
| 55 | 96,6277 | 98,6939 | 99,4851 |
| 60 | 97,6449 | 99,1820 | 99,7093 |

Feed 11.0 N HNO₃ 0.5 l/h, center feed
 Rare Earth in feed 25.0 g/l
 Solvent TBP equilibrated with 11.0 N HNO₃
 case a: 25.40 l/h
 case b: 26.28 l/h
 case c: 27.15 l/h
 Scrub 11.0 N HNO₃, 14.5 l/h

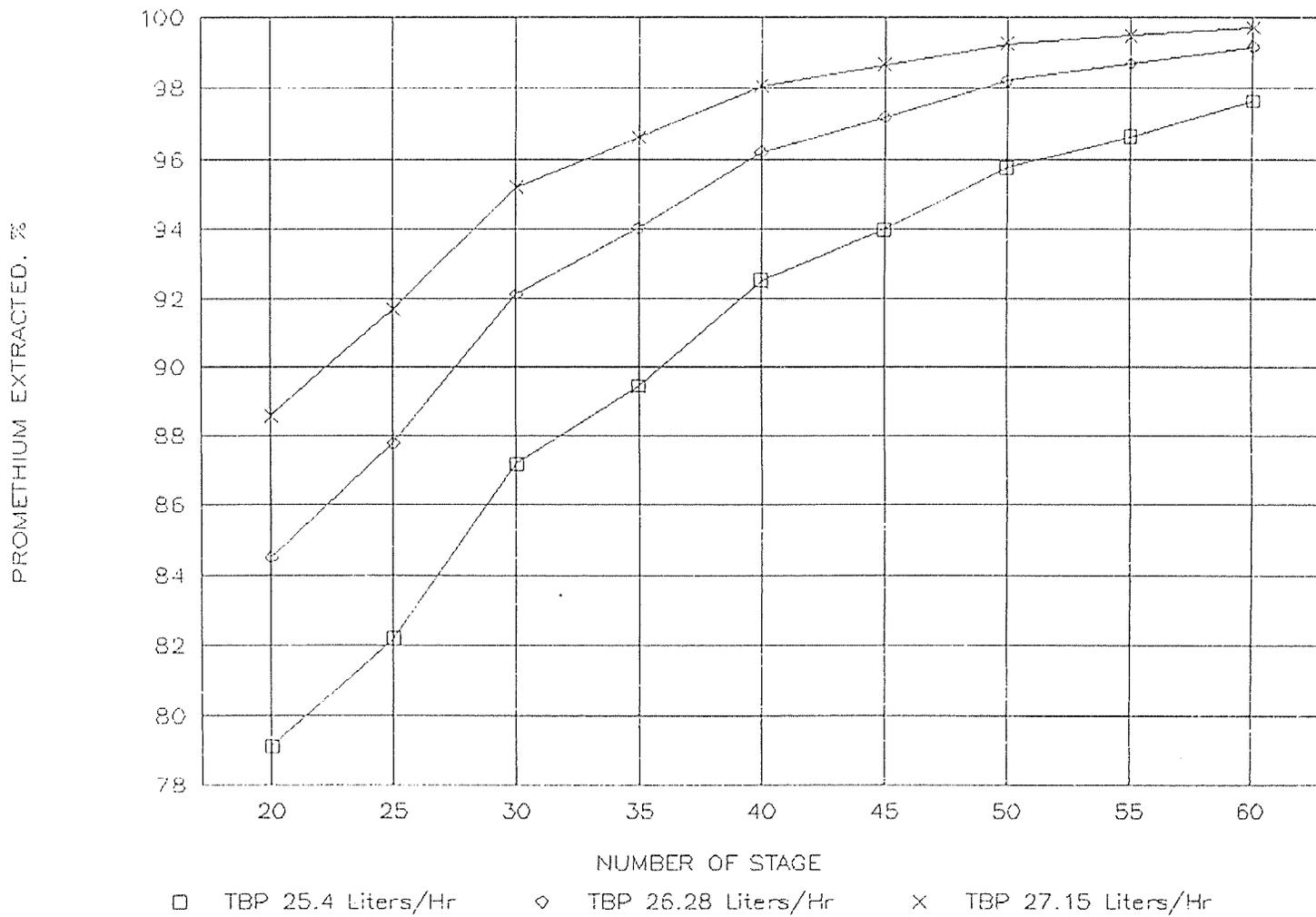


Figure 5.33 The Effect of Number of Stages on Promethium Extraction HNO₃ 11.0 N.

CHAPTER 6

SEPARATION OF EUROPIUM FROM JIANGXI MINERAL SAMPLE

6.1 The Design Basis For Separation And Purification

A lanthanide and yttrium mineral sample in the form of oxides was taken from Jiangxi Province, China (79) having the following composition (wt %):

| Component | Wt % | Component | Wt % |
|--------------------------------|---------|--------------------------------|---------|
| Lu ₂ O ₃ | 0.07675 | Y ₂ O ₃ | 7.6765 |
| Yb ₂ O ₃ | 0.5118 | Tm ₂ O ₃ | 0.07675 |
| Er ₂ O ₃ | 0.7677 | Ho ₂ O ₃ | 0.1024 |
| Dy ₂ O ₃ | 1.7912 | Tb ₂ O ₃ | 0.4094 |
| Gd ₂ O ₃ | 3.5824 | Eu ₂ O ₃ | 0.5630 |
| Sm ₂ O ₃ | 4.6060 | Nd ₂ O ₃ | 29.6827 |
| Pr ₂ O ₃ | 8.7001 | Ce ₂ O ₃ | 2.5588 |
| La ₂ O ₃ | 38.8945 | | |

It was decided to separate the contents of the Jiangxi mineral sample into two or three sub-groups and later on certain specific rare earths in the sub-group can be separated and purified to purity 99.9% or higher for market needs by the liquid-liquid extraction process in the HNO₃-H₂O-TBP system. The rare earth distributions in the aqueous phase and in the organic phase will be predicted by the theoretical model developed by this research.

6.2 Separation Of The Sub-Group Lu-Tb From Jiangxi Mineral Sample

The lanthanide and yttrium oxides mineral sample taken from Jiangxi, China was separated into two sub-groups Lu-Tb and Gd-La by a center-feed, multistage counter-current extractor. A 100% stage efficiency was used. The important process parameters we found are listed below. Those parameters are similar to Korpusov et al. (62) lanthanide and yttrium separation experience, but not identical.

Number of Stages: 34 to 65 stages

Feed: 8.2 N HNO₃, 1.0 l/h, with rare earths and yttrium 265.0 g/l of feed solution.

Extractant: TBP pre-equilibrated with 8.2 N HNO₃, 3.5 l/h.

Scrub Solution : 8.2 N HNO₃, 2.0 l/h.

The effect of the number of stages on the extraction of sub-group Lu-Tb was studied. Initially, 34 contact stages were used in the extraction device, resulting in 93.40% of terbium extracted by the TBP organic solution. However, when the number of stages increased to 65, 98.39% of terbium will be transferred to the organic phase from the aqueous phase by extraction. Higher extractabilities were reported for yttrium and elements heavier than terbium in both cases.

Calculation results were tabulated in Table 6.1 and plotted in Figure 6.1.

6.3 Separation Of The Sub-Group Lu-Sm From Jiangxi Mineral Sample

The separation of the sub-group Lu-Sm from Jiangxi lanthanide and yttrium oxides sample was also investigated. The reasons for samarium was chosen as a cut point in separation is because samarium has low economic value (70); higher percentage in composition; and large separation factor relative to neodymium. Here are the process parameters:

Number of Stages: 20 to 28 stages

Feed: 10.0 N HNO₃, 1.0 l/h, with rare earths and yttrium 160.0 g/l of feed solution.

Extractant: TBP pre-equilibrated with 10.0 N HNO₃, 6.0 l/h.

Scrub Solution: 10.0 N HNO₃, 2.0 l/h.

After process model simulation, we found that 98.76% of Samarium is extracted into the organic phase by a 20 contact stages extractor. When the contact stage increases to 28, the extraction rate for samarium increases to 99.70% accordingly. Results from this study were also summarized in Table 6.2 and plotted in Figure 6.2.

Table 6.1 The Effect of Number of Stages on the Separation
of Sub-group Lu-Tb from Jiangxi Mineral Sample.

RARE EARTH COMPONENTS EXTRACTED, %

| COMPONENT | NUMBER OF STAGE | | | | | | | |
|-----------|-----------------|----------|----------|----------|----------|----------|----------|----------|
| | 34 | 35 | 40 | 45 | 50 | 55 | 60 | 65 |
| Lu | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 |
| Y | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 |
| Yb | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 |
| Tm | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 |
| Er | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 |
| Ho | 99.9999 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 | 100.0000 |
| Dy | 99.9147 | 99.9149 | 99.9711 | 99.9860 | 99.9960 | 99.9981 | 99.9994 | 99.9997 |
| Tb | 93.3980 | 93.4077 | 94.9490 | 95.7482 | 97.0813 | 97.5467 | 98.0942 | 98.3876 |
| Gd | 6.4211 | 5.9011 | 5.0177 | 3.9768 | 3.8844 | 3.1820 | 2.7969 | 2.3145 |
| Eu | 0.0213 | 0.0135 | 0.0055 | 0.0014 | 0.0007 | 0.0002 | 0.0000 | 0.0000 |
| Sm | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Nd | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Pr | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Ce(III) | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| La | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Feed 8.2 N HNO₃ 1.0 l/h, center feed

Rare Earth in feed 265.0 g/l

Solvent TBP 3.5 l/h, equilibrated with 8.2 N HNO₃

Scrub 8.2 N HNO₃, 2.0 l/h

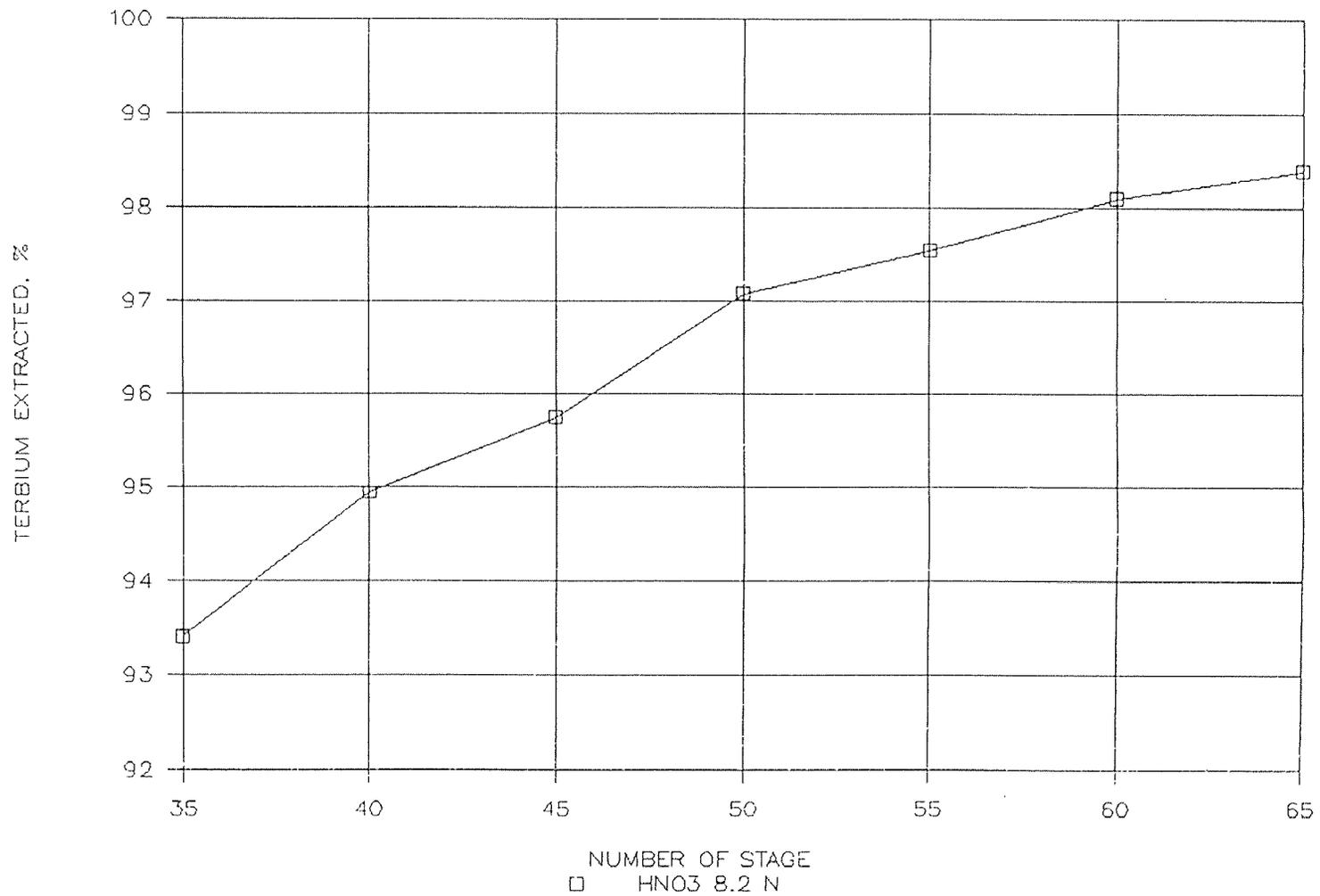


Figure 6.1 The Effect of Number of Stages on the Separation of Sub-group Lu-Tb from Jiangxi Mineral Sample.

Table 6.2 The Effect of Number of Stages on the Separation of Sub-group Lu-Sm from Jiangxi Mineral Sample.

| COMP | RARE EARTH COMPONENTS EXTRACTED, % | | | | |
|---------|------------------------------------|----------|----------|----------|----------|
| | NUMBER OF STAGE | | | | |
| | 20 | 22 | 24 | 26 | 28 |
| Lu | 100,0000 | 100,0000 | 100,0000 | 100,0000 | 100,0000 |
| Y | 100,0000 | 100,0000 | 100,0000 | 100,0000 | 100,0000 |
| Yb | 100,0000 | 100,0000 | 100,0000 | 100,0000 | 100,0000 |
| Tm | 100,0000 | 100,0000 | 100,0000 | 100,0000 | 100,0000 |
| Er | 100,0000 | 100,0000 | 100,0000 | 100,0000 | 100,0000 |
| Ho | 99,9999 | 100,0000 | 100,0000 | 100,0000 | 100,0000 |
| Dy | 100,0000 | 100,0000 | 100,0000 | 100,0000 | 100,0000 |
| Tb | 100,0000 | 100,0000 | 100,0000 | 100,0000 | 100,0000 |
| Gd | 99,9999 | 100,0000 | 100,0000 | 100,0000 | 100,0000 |
| Eu | 99,9968 | 99,9988 | 99,9995 | 99,9998 | 99,9999 |
| Sm | 98,7629 | 99,1301 | 99,3876 | 99,5686 | 99,6959 |
| Nd | 0,1699 | 0,0980 | 0,0566 | 0,0326 | 0,0188 |
| Pr | 0,0005 | 0,0002 | 0,0000 | 0,0000 | 0,0000 |
| Ce(III) | 0,0000 | 0,0000 | 0,0000 | 0,0000 | 0,0000 |
| La | 0,0000 | 0,0000 | 0,0000 | 0,0000 | 0,0000 |

Feed 10.0 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 160.0 g/l
 Solvent TBP 6.0 l/h, equilibrated with 10.0 N HNO₃
 Scrub 10.0 N HNO₃, 2.0 l/h

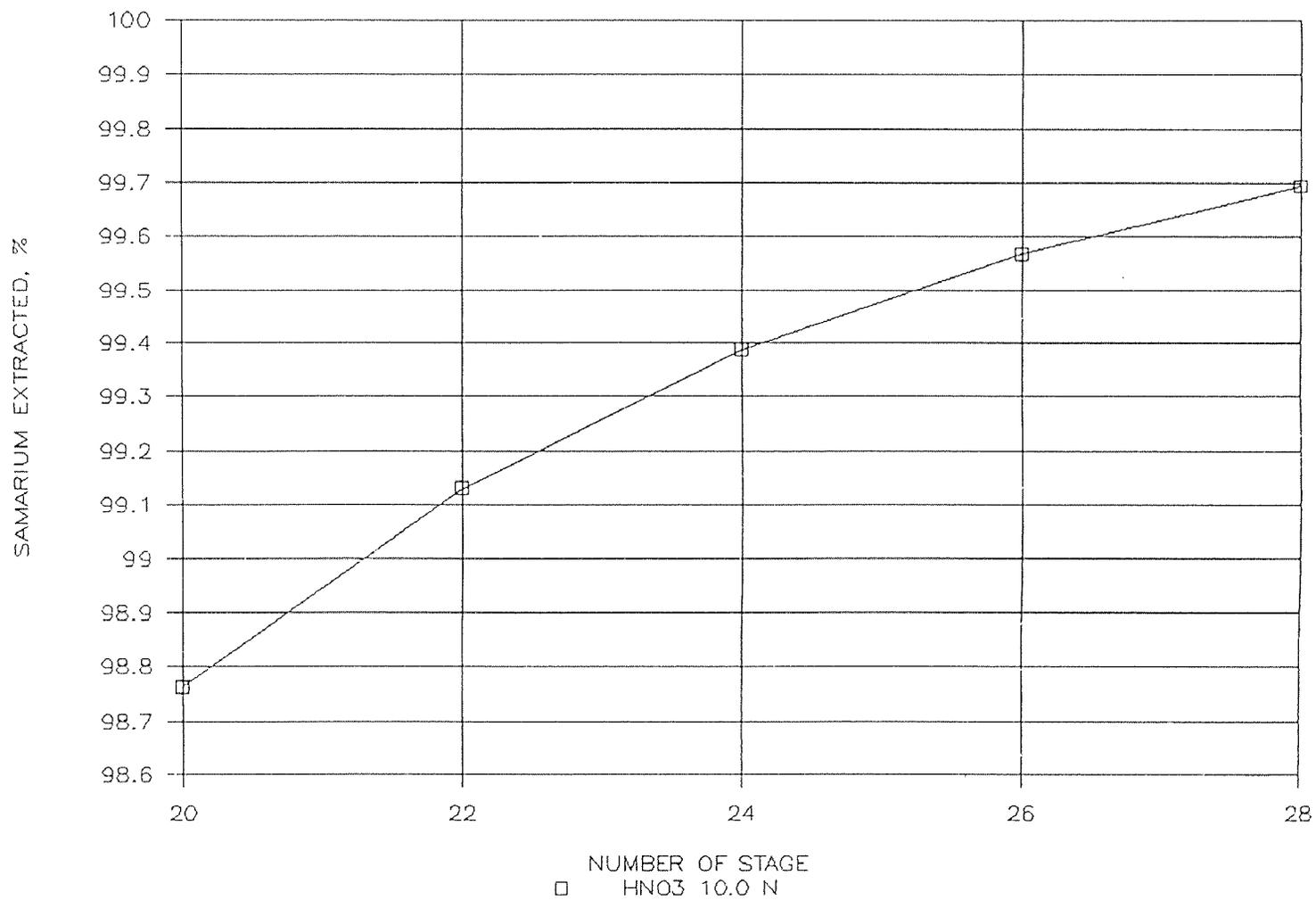


Figure 6.2 The Effect of Number of Stages on the Separation of Sub-group Lu-Sm from Jiangxi Mineral Sample.

Based on the experience gained by separating the sub-groups Lu-Sm and Lu-Tb from the Jiangxi rare earths mineral sample, the conclusion we draw is that the number of stages in an extraction operation has a positive impact on the cleanness of separation; i.e., the higher the number of stages used in the separation process, the cleaner the products are that can be obtained.

6.4 Separation Of Gadolinium From The Sub-Group Gd-La Of Jiangxi Mineral Sample

It was decided to separate gadolinium from the sub-group Gd-La of the lanthanide and yttrium oxides mineral sample which was taken from Jiangxi, China by extraction process, so europium can be sequentially separated from the remaining sub-group Eu-La exists in the aqueous phase and then be further processed to higher purity, or higher value commodity. The sub-group Gd-La which is the feed of this separation process, as a matter of fact, are the species remain unextracted and exist in the raffinate stream of the separation process which was discussed in Section 6.2, has the following composition (wt %):

| Component | Wt % | Component | Wt % |
|--------------------------------|---------|--------------------------------|---------|
| Gd ₂ O ₃ | 4.0439 | Eu ₂ O ₃ | 0.6355 |
| Sm ₂ O ₃ | 5.1994 | Nd ₂ O ₃ | 33.5066 |
| Pr ₂ O ₃ | 9.8209 | Ce ₂ O ₃ | 2.8884 |
| La ₂ O ₃ | 43.9052 | | |

A 100% stage efficiency was assumed. The optimum process parameters for separating gadolinium from the sub-group Gd-La are listed below:

Number of Stages: 66 to 120 stages.

Feed: 9.5 N HNO₃, 1.0 l/h, with rare earths 133 g/l
of feed solution.

Extractant: TBP pre-equilibrated with 9.5 N HNO₃,
1.9 l/h.

Scrub Solution : 9.5 N HNO₃, 2.0 l/h.

Because gadolinium has smaller separation factor (1.5 - 1.6) relative to europium, comparing to the separation factors of Sm/Nd (3.1 - 3.5) in Section 6.2 and Tb/Gd (1.8 - 1.9) in Section 6.3, the clean-cut separation of gadolinium from the sub-group Gd-La is rather difficulty, even with large stage numbers. For example, in above GD9519 case, initially 66 contact stages were used, 0.3678% of europium was extracted by the TBP extractant. As the stage number increased to 120, the europium extraction rate decreased to 0.0153%, i.e., 99.9847% of europium remained in the aqueous phase, therefore, 99.99% or higher purity of gadolinium was produced. However, the recovery rates for gadolinium were only 77.23 - 78.65 %. Simulation results were tabulated in Table 6.3 and plotted in Figure 6.3.

Table 6.3 The Effect of Number of Stages on the Separation of Gd from the Sub-group Gd-La, Gd Extracted %.

| STAGE | CASE NUMBERS | | | | | |
|-------|--------------|---------|---------|---------|---------|---------|
| | GD9029 | GD9031 | GD9035 | GD9519 | GD9520 | GD9522 |
| 66 | 84.7843 | 94.7356 | 99.7235 | 77.2364 | 87.6784 | 97.9363 |
| 72 | 85.2711 | 95.2944 | 99.8166 | 77.5584 | 88.2277 | 98.3146 |
| 80 | 85.8015 | 95.9126 | 99.8937 | 77.8878 | 88.8371 | 98.7048 |
| 88 | 86.2284 | 96.4196 | 99.9384 | 78.1333 | 89.3384 | 98.9985 |
| 86 | 86.5765 | 96.8415 | 99.9642 | 78.3179 | 89.7569 | 99.2219 |
| 104 | 86.8635 | 97.1968 | 99.9792 | 78.4577 | 90.1106 | 99.3931 |
| 112 | 87.1023 | 97.4993 | 99.9879 | 78.5641 | 90.4126 | 99.5252 |
| 120 | 87.3025 | 97.7589 | 99.9930 | 78.6456 | 90.6730 | 99.6276 |

Feed 9.0-9.5 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 132.88 g/l
 Solvent TBP 2.1 l/h, equilibrated with 9.0-9.5 N HNO₃
 Scrub 9.0-9.5 N HNO₃, 1.9-3.5 l/h

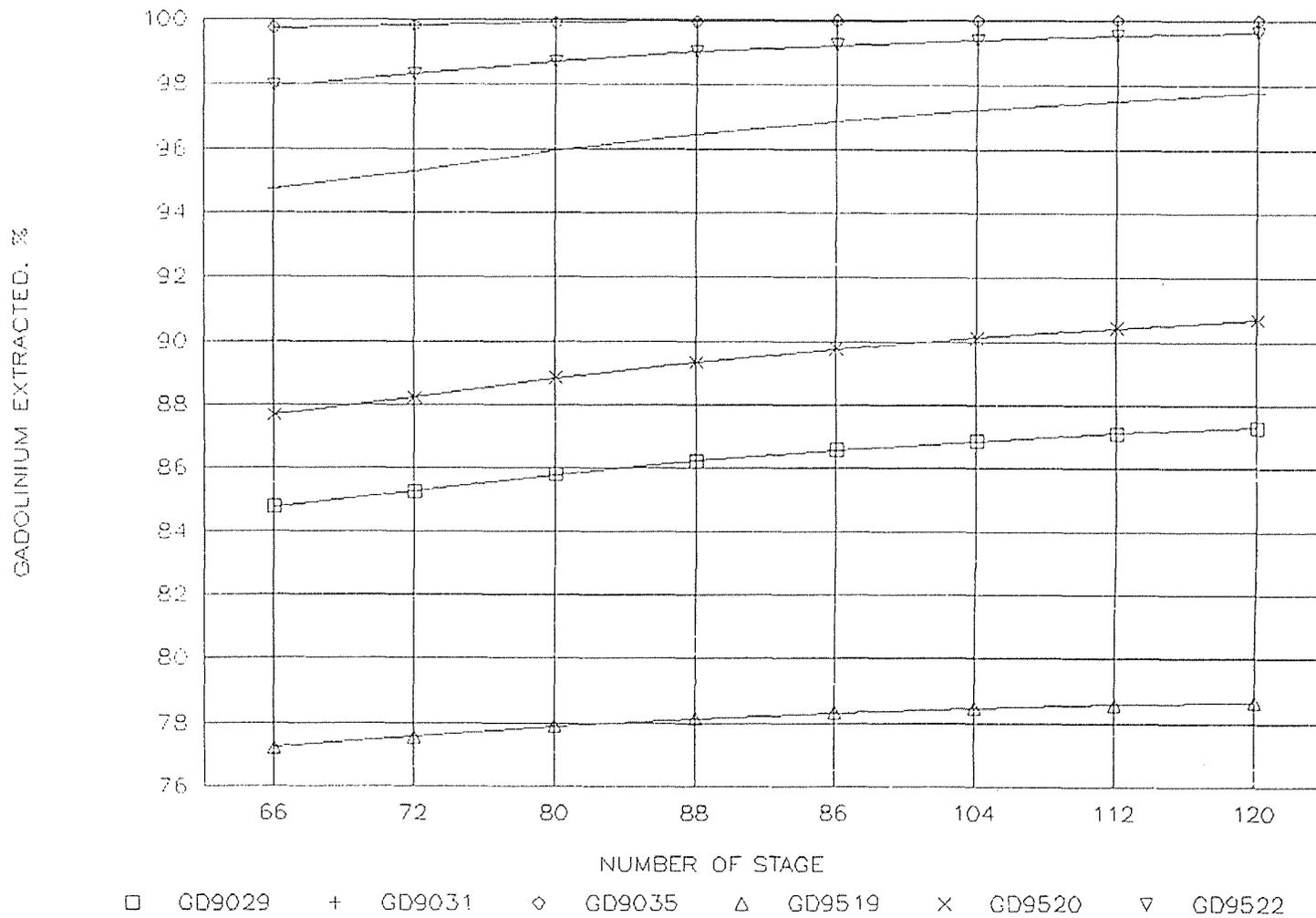


Figure 6.3 The Effect of Number of Stages on the Separation of Gd from the Sub-group Gd-La, Gd Extracted %.

The first two characters in the test code GD9519 tells which rare earth was tested, the next two digits represents the HNO_3 acid strength in the extraction system, and the last two digits means extractant flow rate in l/h. In the GD9519 case, gadolinium was tested in the 9.5 N HNO_3 acid strength aqueous solution with 1.9 l/h of extractant flow. The guideline for constructing test codes will be used throughout this research.

6.5 The Purification of Europium

Europium is an expensive and important raw material for the high technology area. Many high technology industries demand very high purity europium. Europium is being used as the additives material for colored cathode ray tubes. Obviously, it becomes more and more important for many rare earths producers to manufacture ultrahigh purity europium by more efficient methods. The retail price for 5 g of 99.9 % europium oxide is \$46.50 in 1992, it costs \$63.45 for 5 g of 99.99% europium oxide, however, when the purity increases to 99.999 %, the price goes up to \$96.65 for 5 g of europium oxide (70). Because so many factors dominate the europium purification process, we decided to institute a systematic investigation, with the objective of obtaining key process parameters.

We discussed the separation of gadolinium from the subgroup Gd-La in Section 6.4. Since the extractability of gadolinium is the highest among all species in the sub-

group Gd-La, gadolinium was extracted by TBP and others remained intact in the raffinate stream. After adjustment of rare earths concentration and acidity of raffinate, the unextracted lighter-weighted rare earth sub-group Eu-La was sent to the extraction circuit for europium separation and purification as feed. The composition (wt %) of feed stream is:

| Component | Wt % | Component | Wt % |
|--------------------------------|---------|--------------------------------|---------|
| Eu ₂ O ₃ | 0.6630 | Sm ₂ O ₃ | 5.4184 |
| Nd ₂ O ₃ | 34.9187 | Pr ₂ O ₃ | 10.2349 |
| Ce ₂ O ₃ | 3.0102 | La ₂ O ₃ | 45.7555 |

Because the europium oxide is the most extractable specie among all contents in the feed stream, the separation process is accomplished by extracting europium nitrate into the organic phase. The europium in the organic phase is then continue processed with more stages in the extraction system until 99.9% or higher purity was reached.

Since the commercial rare earth separation technologies are proprietary, specific operation details can not be easily found. Enormous efforts were necessary in finding acceptable process conditions. A 100% stage efficiency was used in all of the cases studied. The operating conditions we used in purifying europium oxide are:

Number of Stages: 42 to 132 stages.

Feed: 9.8-10.2 N HNO_3 , 1.0 l/h, with rare earths
100.0 g/l of feed solution.

Extractant: TBP pre-equilibrated with 9.8-10.2 N HNO_3 ,
1.9-2.6 l/h.

Scrub Solution: 9.8-10.2 N HNO_3 , 2.0 l/h.

Tables 6.4 to 6.19 give the recoveries and purities of the europium product with different stage numbers and operating conditions. The effect of the number of stages on europium recoveries and purities are shown in Figures 6.4 to 6.13. Table 6.20 and Figure 6.14 show the stage numbers effect on europium product impurities, mainly, samarium in europium product. Tables 6.4, 6.20 and Figures 6.4, 6.9, 6.14 are located in the following pages, all other tables and figures can be found in the Appendices A and B, respectively.

6.6 Discussions

Because the stability limitation of ISR algorithm was reached, cases with 10.3 N or higher acidity of HNO_3 were not obtained.

Figures 6.4 to 6.13 explicitly show, that the europium recovery and product purity are functions of aqueous acidity, feed to extractant flow ratio, aqueous to organic

Table 6.4 The Effect of Number of Stages on Europium Purification, HNO₃ 9.8 N, TBP 2.4 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 42 | 72.2573 | 97.9969 |
| 48 | 73.0191 | 99.0389 |
| 54 | 73.5814 | 99.5394 |
| 60 | 74.0000 | 99.7796 |
| 66 | 74.3139 | 99.8945 |
| 72 | 74.5507 | 99.9494 |
| 78 | 74.7303 | 99.9758 |
| 84 | 74.8670 | 99.9884 |
| 90 | 74.9713 | 99.9944 |
| 96 | 75.0512 | 99.9973 |
| 102 | 75.1124 | 99.9987 |
| 108 | 75.1594 | 99.9994 |
| 114 | 75.1955 | 99.9997 |
| 120 | 75.2233 | 99.9999 |
| 126 | 75.2446 | 99.9999 |
| 132 | 75.2610 | 99.9999 |

Feed 9.8 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 100.0 g/l
 Solvent TBP 2.4 l/h, equilibrated with 9.8 N HNO₃
 Scrub 9.8 N HNO₃, 2.0 l/h

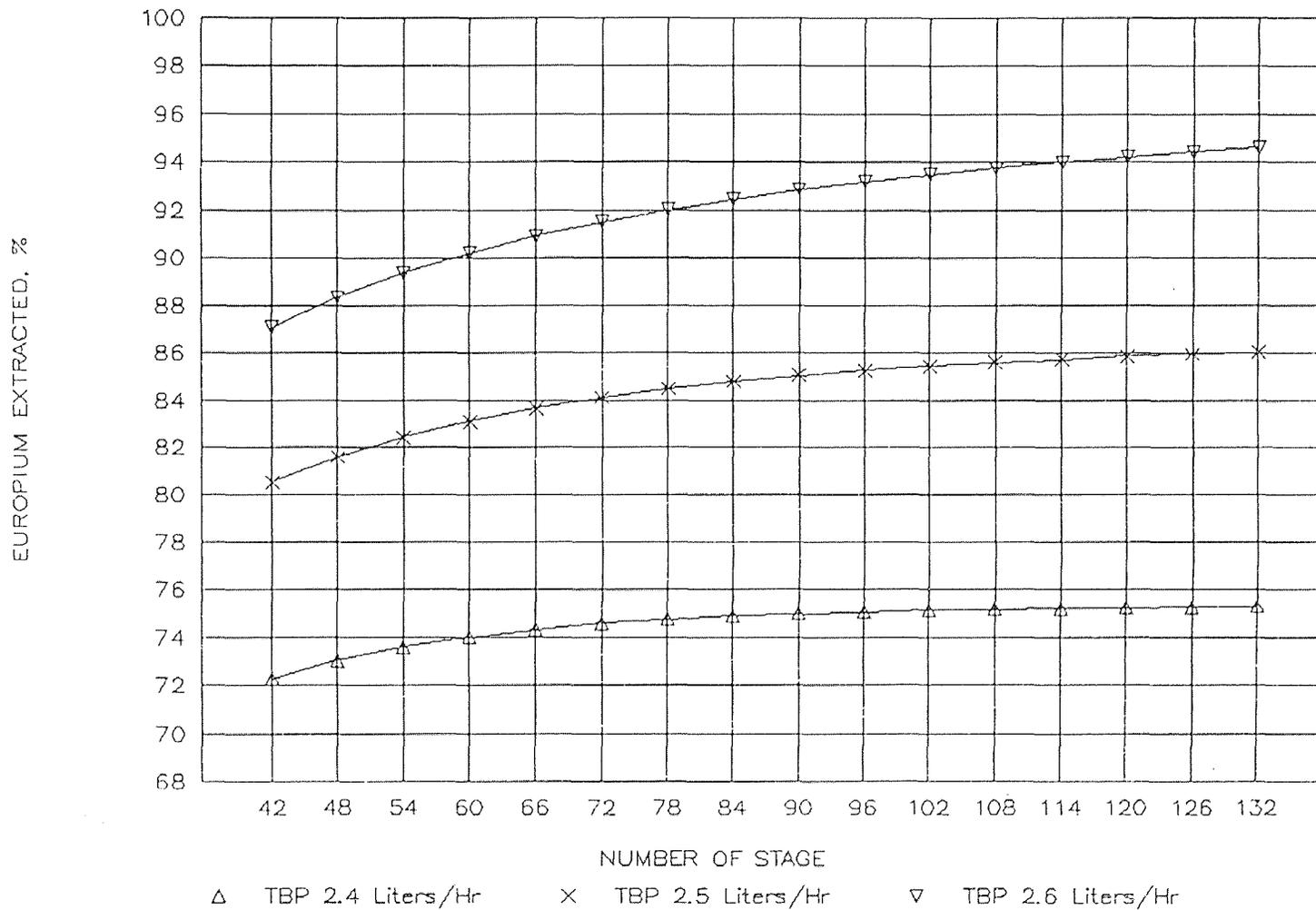


Figure 6.4 The Effect of Number of Stages on Europium Extraction, Europium Extracted %, HNO_3 9.8 N.

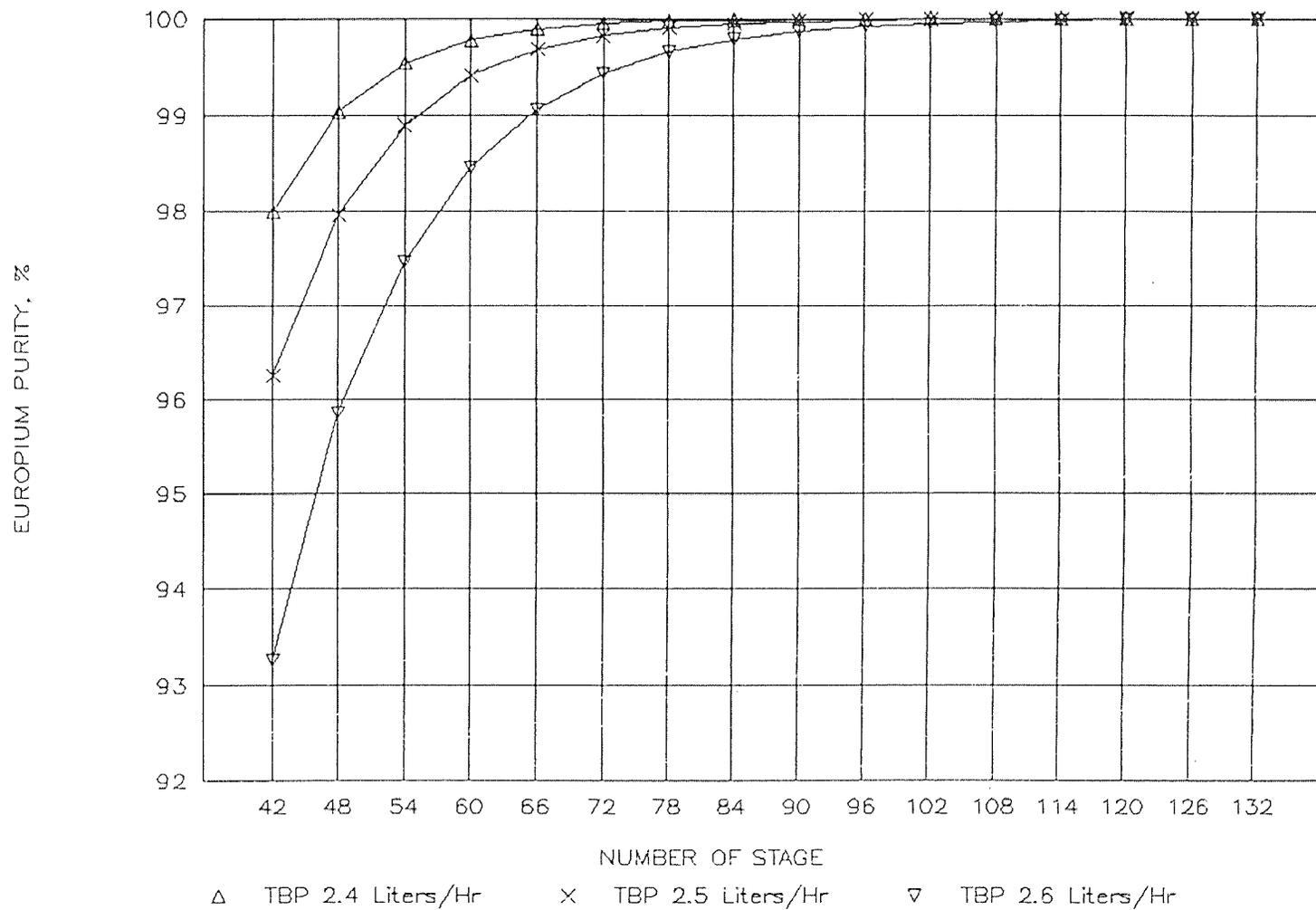


Figure 6.9 The Effect of Number of Stages on Europium Extraction, Europium Purity %, HNO_3 9.8 N.

Table 6.20 The Effect of Number of Stages on Europium Product Impurities, Samarium in Product %.

| STAGE | CASE NUMBERS | | |
|-------|--------------|---------|---------|
| | EU10219 | EU10220 | EU10221 |
| 42 | 1.6762 | 3.8164 | 8.1025 |
| 48 | 0.7907 | 2.1104 | 5.2355 |
| 54 | 0.3726 | 1.1633 | 3.3678 |
| 60 | 0.1756 | 0.6404 | 2.1603 |
| 66 | 0.0829 | 0.3525 | 1.3834 |
| 72 | 0.0391 | 0.1940 | 0.8850 |
| 78 | 0.0185 | 0.1068 | 0.5659 |
| 84 | 0.0087 | 0.0588 | 0.3618 |
| 90 | 0.0041 | 0.0322 | 0.2313 |
| 96 | 0.0020 | 0.0179 | 0.1478 |
| 102 | 0.0009 | 0.0099 | 0.0945 |
| 108 | 0.0004 | 0.0054 | 0.0604 |
| 114 | 0.0002 | 0.0030 | 0.0386 |
| 120 | 0.0001 | 0.0017 | 0.0247 |
| 126 | 0.0001 | 0.0009 | 0.0158 |
| 132 | 0.0001 | 0.0005 | 0.0101 |

Feed 10.2 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 100.0 g/l
 Solvent TBP 1.9-2.1 l/h, equilibrated with 10.2 N HNO₃
 Scrub 10.2 N HNO₃, 2.0 l/h

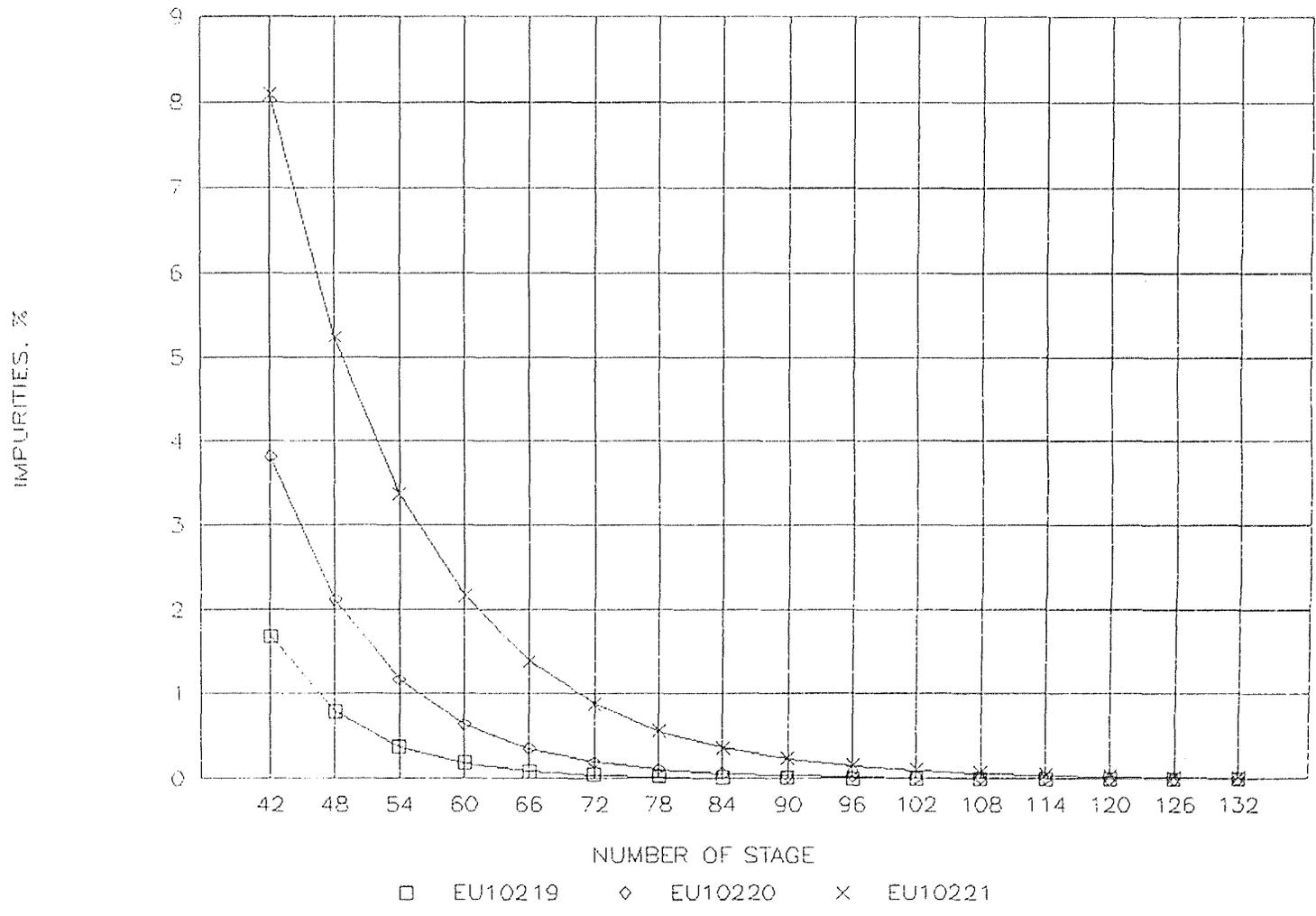


Figure 6.14 The Effect of Number of Stages on Europium Product Impurities, Samarium in Product %.

flow ratio, and the number of stages. Figures 6.4 to 6.13 also show that the europium extraction increases as the number of stages increases, but the rate of change gradually tapers off with large stage numbers, if the other operating conditions remain the same. If a larger ratio of solvent to the feed was used, the europium extraction rate increases, however, the product purity decreases. If the ratio of solvent to feed decreased, the europium purity decreased and the product recovery increases. Clearly, a balance lies between the recovery rate and product purity.

This observation leads to the conclusion that a cost analysis and optimization is necessary procedure to arrive at the rare earth separation and purification process design.

CHAPTER 7

PURIFICATION OF YTTRIUM

7.1 The Purification Of Yttrium

Yttrium is a very valuable commodity, it is also a very important material in certain industries, especially in the electronic industry. For example, high purity (99.9% or higher) of yttrium is one of the key raw materials for making color televisions and personal computer color monitors.

As discussed earlier, the rare earth nitrate extraction into TBP organic phase increases in the order of increasing atomic number. Because of their similar structures and chemical properties, the separation of rare earths into individual components is rather difficult, especially beyond Tb in the atomic number row. Therefore, high purity yttrium is very expensive. The retail price for 50 g of 99.99 % yttrium oxide is \$25.0 in 1992, however, when purity increases to 99.999 %, the price goes up more than three-fold to \$84.55 (70). Because so many variables are involved in purification process, a systematic approach seems necessary. The ultimate goal is to gain crucial process information.

The aim of yttrium purification is to improve the yttrium purity to 99.9% or higher. It is assumed that the sub-group of Lu_2O_3 , Y_2O_3 and Yb_2O_3 have been separated from the bulk of rare earth oxides in the Jiangxi mineral sample

by the manner of solvent extraction. The species Lu_2O_3 , Y_2O_3 and Yb_2O_3 were extracted into the TBP organic phase from the aqueous phase. After stripping with low acidity nitric acid solution (1 - 2 N), the components Lu_2O_3 , Y_2O_3 and Yb_2O_3 in the organic phase were concentrated in the aqueous phase.

The species Lu_2O_3 and Yb_2O_3 have higher distribution coefficients than that of Y_2O_3 in the HNO_3 - H_2O -TBP system for an acidity range of 6 to 15 N. Thus, we took advantage of the lower yttrium oxide distribution coefficients and larger separation factor of Yb/Y , to separate Y_2O_3 from the mixture of Lu_2O_3 , Yb_2O_3 and Y_2O_3 by extracting Lu_2O_3 and Yb_2O_3 into the organic phase, and leave Y_2O_3 in the aqueous solution.

The Lu_2O_3 , Yb_2O_3 and Y_2O_3 mixture composition (wt %) after stripping and distribution coefficient at acidity 9.0 N in the aqueous phase are tabulated below:

| Component | Wt % | K_d |
|-------------------------|---------|-------|
| Lu_2O_3 | 0.9288 | 8.84 |
| Yb_2O_3 | 6.1919 | 6.58 |
| Y_2O_3 | 92.8793 | 3.68 |

Since commercial rare earth processes are highly proprietary, specific details are not readily available. Therefore, tremendous efforts were made in searching the appropriate process conditions. The multicomponent, multistage, counter-current liquid-liquid extraction

computer program was used to simulate the extraction processes. Again, the stage efficiency was assumed to be 100%. After hundreds of cases were simulated and studied, the key process parameters such as: acidity in the aqueous phase, the rate ratio of the organic phase to feed, and rate ratio of the organic phase to the aqueous phase were found. We believe these process conditions are acceptable to the rare earths industries. The critical parameters are summarized below:

Number of Stages: 18 to 144 stages.

Feed: 6.1-6.4 N HNO₃, 1.0 l/h, with rare earths
10.0 g/l of feed solution.

Extractant: TBP pre-equilibrated with 6.1-6.4 N HNO₃,
2.5-3.4 l/h.

Scrub Solution: 6.1-6.4 N HNO₃, 2.0 l/h.

The recoveries and purities of yttrium product with different operating conditions were tabulated in Tables 7.1 to 7.20. The graphical representation of the effect of the number of stages on yttrium recovery and purity was made by plotting the recovery and purity data at the same aqueous acidity with different organic flow rates, and is shown in Figures 7.1 to 7.4 for yttrium recovery, and in Figures 7.5 to 7.8 for yttrium purity, respectively. Table 7.22 and

Figure 7.9 show the effect of stage numbers on yttrium product impurities, or more specifically, the lutetium and ytterbium in europium product. Tables 7.1 and 7.22, and Figures 7.1, 7.5 and 7.9 were placed in the following pages as representative of all cases that have been studied. The remaining tables and figures can be seen in Appendices A and B, respectively.

7.2 Discussions

Figures 7.1 and 7.5 have shown, that the yttrium recovery and product purity increases as the number of stages increases, but a gradual increase is obtained with large stage numbers. An effective way to increase recovery rate is by extracting the Lu_2O_3 and Yb_2O_3 by lowering the ratio of solvent to feed. However, at lower organic flow rate, the yttrium product purity decreases at lower stage numbers. On the contrary, if the ratio of solvent to feed increases, the yttrium purity increases accordingly, but low recovery will be achieved. Obviously, there is a balance between the recovery rate and product purity.

This observation enable us to draw the same conclusion as we did in the previous chapter and leads to the subject of the next chapter: the optimal design of europium and yttrium separation and purification systems. Factors involved in the optimization process are feed concentration, stage numbers, recovery rate, product purity, capitol costs, operating costs, interest rate, product sale price, etc.

Table 7.1 The Effect of Number of Stages on Yttrium Purification, HNO₃ 6.1 N, TBP 3.0 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 94.2405 | 98.3780 |
| 24 | 96.8635 | 98.7073 |
| 30 | 98.2502 | 98.9244 |
| 36 | 99.0124 | 99.0770 |
| 42 | 99.4398 | 99.1899 |
| 48 | 99.6815 | 99.2770 |
| 54 | 99.8188 | 99.3464 |
| 60 | 99.8969 | 99.4031 |
| 66 | 99.9414 | 99.4504 |
| 72 | 99.9666 | 99.4905 |
| 78 | 99.9810 | 99.5250 |
| 84 | 99.9892 | 99.5549 |
| 90 | 99.9939 | 99.5812 |
| 96 | 99.9965 | 99.6044 |
| 102 | 99.9980 | 99.6251 |
| 108 | 99.9989 | 99.6437 |
| 114 | 99.9994 | 99.6604 |
| 120 | 99.9996 | 99.6756 |
| 126 | 99.9998 | 99.6894 |
| 132 | 99.9999 | 99.7020 |
| 138 | 99.9999 | 99.7136 |
| 144 | 100.0000 | 99.7243 |

Feed 6.1 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 3.0 l/h, equilibrated with 6.1 N HNO₃
 Scrub 6.1 N HNO₃, 2.0 l/h

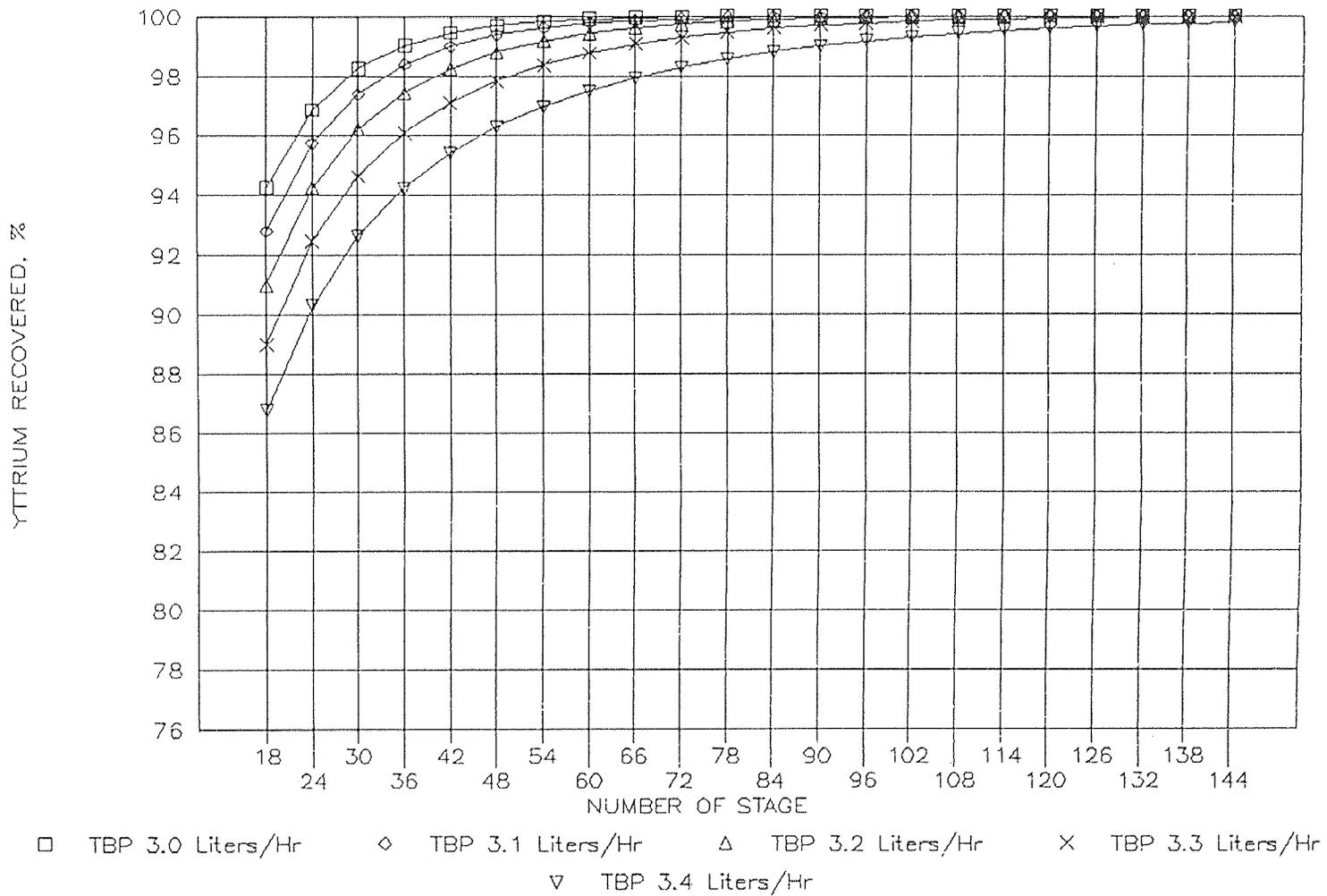


Figure 7.1 The Effect of Number of Stages on Yttrium Purification, Yttrium Recovered %, HNO₃ 6.1 N.

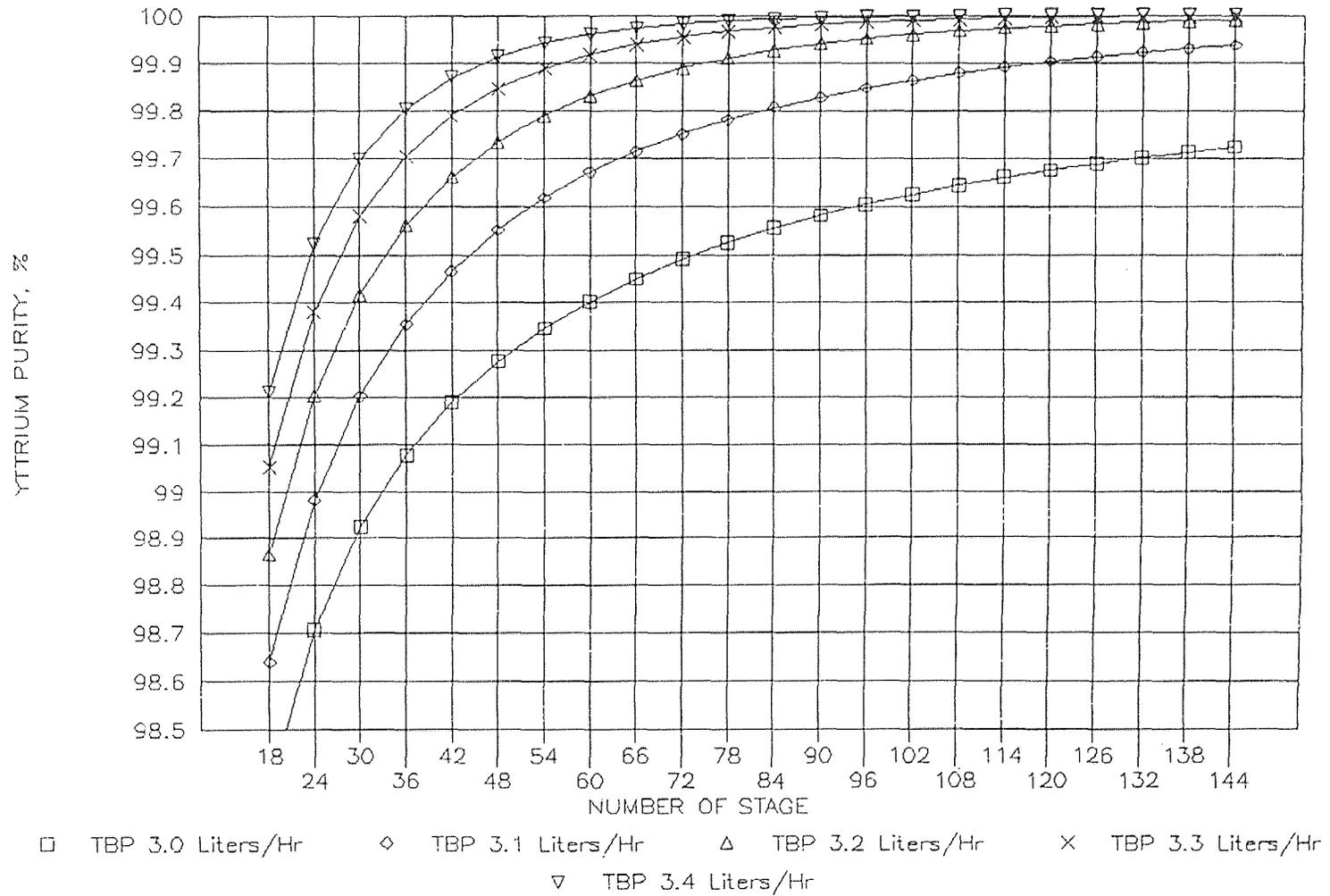


Figure 7.5 The Effect of Number of Stages on Yttrium Purification, Yttrium Purity %, HNO₃ 6.1 N.

Table 7.22 The Effect of Number of Stages on Yttrium Product Impurities, Lu and Yb in Product %.

| STAGE | CASE NUMBERS | | | | | |
|-------|--------------|--------|--------|--------|--------|--------|
| | Y6425 | Y6426 | Y6427 | Y6428 | Y6429 | Y6430 |
| 18 | 1.3693 | 1.0962 | 0.8757 | 0.7002 | 0.5620 | 0.4537 |
| 24 | 1.0256 | 0.7552 | 0.5522 | 0.4032 | 0.2955 | 0.2182 |
| 30 | 0.8035 | 0.5439 | 0.3630 | 0.2241 | 0.1607 | 0.1080 |
| 36 | 0.6499 | 0.4038 | 0.2451 | 0.1475 | 0.0891 | 0.0544 |
| 42 | 0.5378 | 0.3060 | 0.1685 | 0.0916 | 0.0500 | 0.0277 |
| 48 | 0.4526 | 0.2355 | 0.1172 | 0.0573 | 0.0282 | 0.0142 |
| 54 | 0.3857 | 0.1831 | 0.0821 | 0.0361 | 0.0160 | 0.0073 |
| 60 | 0.3321 | 0.1436 | 0.0579 | 0.0228 | 0.0091 | 0.0037 |
| 66 | 0.2881 | 0.1132 | 0.0410 | 0.0145 | 0.0052 | 0.0019 |
| 72 | 0.2516 | 0.0897 | 0.0291 | 0.0092 | 0.0030 | 0.0010 |
| 78 | 0.2221 | 0.0714 | 0.0207 | 0.0058 | 0.0017 | 0.0005 |
| 84 | 0.1948 | 0.0569 | 0.0148 | 0.0037 | 0.0010 | 0.0003 |
| 90 | 0.1724 | 0.0455 | 0.0105 | 0.0024 | 0.0006 | 0.0002 |
| 96 | 0.1531 | 0.0365 | 0.0075 | 0.0015 | 0.0003 | 0.0001 |
| 102 | 0.1363 | 0.0292 | 0.0054 | 0.0010 | 0.0002 | 0.0001 |
| 108 | 0.1217 | 0.0235 | 0.0038 | 0.0006 | 0.0001 | 0.0001 |
| 114 | 0.1088 | 0.0189 | 0.0027 | 0.0004 | 0.0001 | 0.0001 |
| 120 | 0.0975 | 0.0152 | 0.0020 | 0.0003 | 0.0001 | 0.0001 |
| 126 | 0.0875 | 0.0122 | 0.0014 | 0.0002 | 0.0001 | 0.0001 |
| 132 | 0.0787 | 0.0098 | 0.0010 | 0.0001 | 0.0001 | 0.0001 |
| 138 | 0.0708 | 0.0079 | 0.0007 | 0.0001 | 0.0001 | 0.0001 |
| 144 | 0.0638 | 0.0064 | 0.0005 | 0.0001 | 0.0001 | 0.0000 |

Feed 6.4 N HNO₃ 1.0 l/h, center feed

Rare Earth in feed 10.0 g/l

Solvent TBP 2.5-3.0 l/h, equilibrated with 6.4 N HNO₃

Scrub 6.4 N HNO₃, 2.0 l/h

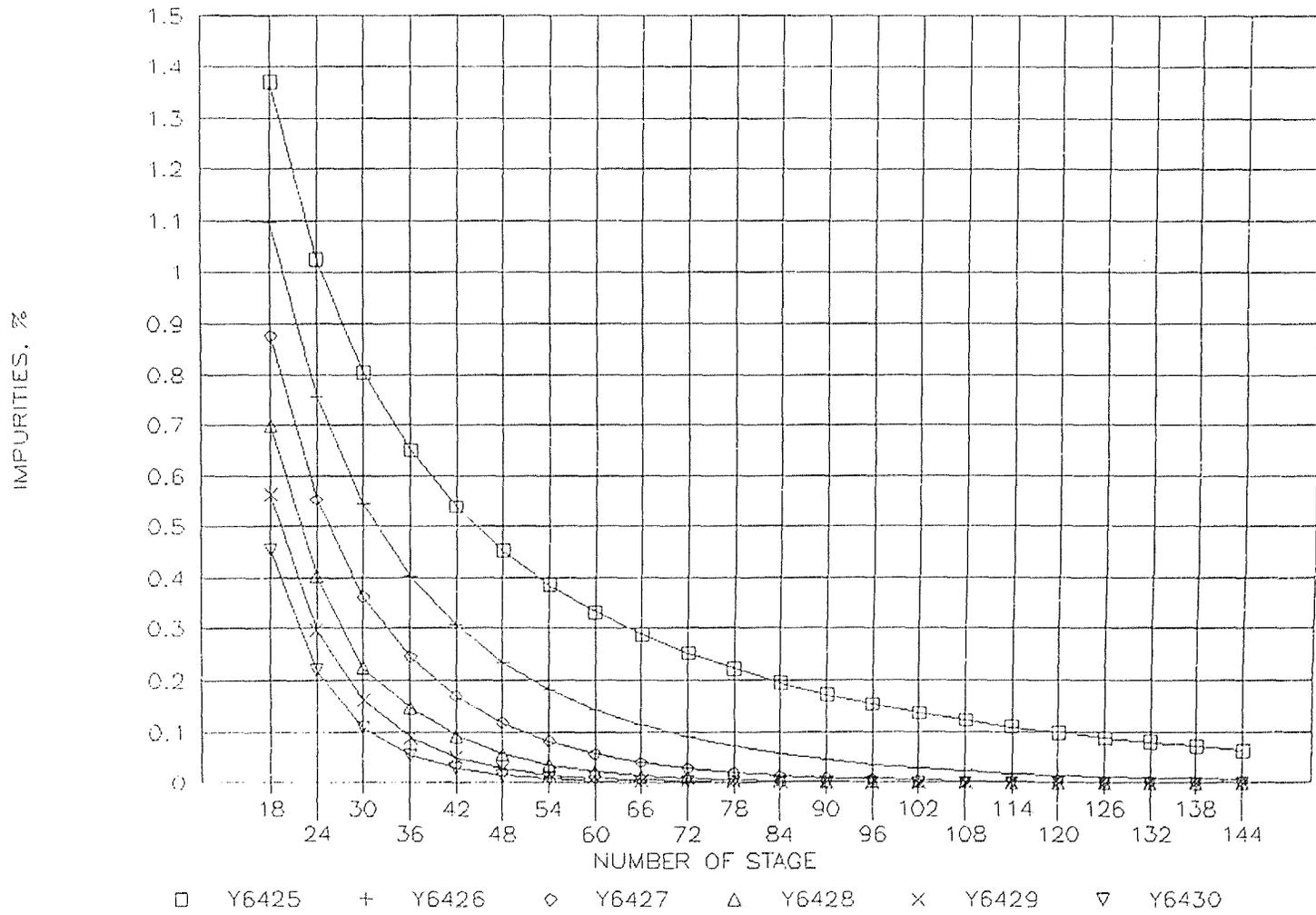


Figure 7.9 The Effect of Number of Stages on Yttrium Product Impurities, Lu and Yb in Product %.

CHAPTER 8

ECONOMIC ANALYSIS

8.1 General Principles

The economic analysis and optimization of processes involving solvent extraction are particularly important. The values of the solutes considered for recovery must be compared against the cost of extraction. Chemical processing industries generally consume large quantities of raw materials, as well as energy and capital. As mentioned earlier, the liquid-liquid extraction process is employed for separation when it is the only method available or the most economical technique when compared with alternative separation processes. Extraction processes may not be selected unless they have shown clear economic advantages.

Generally, economic analysis consists of the analysis of capital investment and operating costs (69).

8.2 Capital Investment

The capital investment is the amount of money spent to build the extraction plant. Before a chemical plant can be put into operation, a large sum of money must be supplied to purchase and install the necessary machinery and equipment. Land and service facilities must be obtained, and the plant must be erected complete with all piping, controls, and services. Besides, the money needed for the expenses of plant operation must also be available.

For a rare earths extraction system, the following factors may dominate the capital investment:

1. Number of stages, the number of mixer-settlers.
2. The size of the mixing and settling devices.
3. Flow rate and flow ratios.
4. Pumps, piping and instrumentation.
5. Land, site preparation, site preparation.
6. Utilities and buildings.
7. Raw materials and supplies carried in stocks.

There are many ways of estimating the total capital investment. Peters and Timmerhaus (71) proposed a method for estimating capital investment, their technique directly relates the total capital cost to the expenses for purchased equipment by a multiplying factor.

8.3 Operating Costs

Capital investment is the expense of obtaining a working plant, while the operating costs are the charges involved in running the plant after it has been constructed. Generally, the cost of an extraction operation is incurred for the following items:

1. Costs for feed, solvent and nitric acid.
2. Cost of preconditioning the feed stream. The feed may require acidity adjustment, or removal of unwanted materials.
3. Cost of pre-equilibration of the solvent may be required. For example, the solvent TBP is pre-equilibrated

with nitric acid in the cases of europium and yttrium separation and purification.

4. Cost of scrubbing and stripping. These are necessary operations for the rare earths extraction system. These steps involve extra operating costs for chemical agents, labor, power and maintenance.

5. Cost of solvent losses. The charges for replacing lost solvent are part of the regular operation cost. The factors which cause the solvent losses are: solubility of extractant in the raffinate solution; entrainment of extractant in the raffinate phase; degradation of extractant; crud formation; evaporation of extractant and physical losses due to leaks or spillages.

6. Labor and maintenance costs. The cost of operators together with the supervisors, usually account for a part of the operation costs.

7. Energy costs. Power will be required for mixers, instruments, pumps, lighting and heating of the plant.

8. Unrecovered desirable solute in the raffinate phase can also account for an increase in operating costs.

8.4 Total Production Cost Function

Based on the discussions of capital investments in section 8.2 and operating costs in section 8.3, the total production cost function for liquid-liquid extraction operations is then given by:

$$\text{Total Production Cost} = \text{Capitol Investment} + \text{Operating Costs} \quad (8.1)$$

8.5 Case Study 1: The Separation And Purification Of Europium

It was decided that europium is to be separated from 54.5 kg/hr of the sub-group Eu-La of rare earth oxides raw material from Jiangxi Province, China and further be purified to 99.9% or higher purity in the $\text{HNO}_3\text{-H}_2\text{O-TBP}$ system by the solvent extraction process.

Two processes are involved in above operation: separating the europium from the sub-group Eu-La of Jiangxi mineral raw material; and then purifying the separated europium to the desired purity. The operating conditions for separation and purification of europium were discussed in Section 6.5.

The process parameters for the europium separation and purification are listed below:

Number of Stages: 42 to 132 stages.

Feed: 9.8-10.2 N HNO_3 , 545 l/h, with rare earths 100.0 g/l of feed solution.

Extractant: TBP pre-equilibrated with 9.8-10.2 N HNO_3 , 1035-1420 l/h.

Scrub Solution: 9.8-10.2 N HNO_3 , 1090 l/h.

McCabe and Smith (74) suggested that 5 minutes resident time for mixing and 25 minutes for settling are typical. Their suggestion was used as minimum resident time criterion for mixer-settler extractor design. Denver Mineral Engineers, Inc. (73) recommended turbine pumping-mixing type mixer-settler be used, because this design allows entire system to be mounted on a single level without the need for interstage pumps. Turbine position may be varied to optimize pumping and mixing performance. Their design consists of 100 gallon mix tanks and 450 gallon settler tanks, and with 1/2 HP pump mix turbine impeller mixers. The budgetary prices for 80 stages system is \$650,000.00, and for 150 stages system is \$1,210,000.00.

The mixer-settlers system suggested by Denver Mineral Engineers, Inc. (73) was used for cost analysis. The total capital investment for this operation per stage of mixer-settler was estimated by the technique proposed by Peters and Timmerhaus (71). Their method is to relate the total capital cost to the expenses for purchased equipment by a multiplying factor. In the following page, Table 8.1 exhibits the estimated total capital investment per stage of mixer-settler.

Other important cost parameters are: the extraction units are operated 8 hours per shift, 3 shifts per day and 350 days per year. For a 40 stage system, one operator, one half maintenance man and one half supervisor (share with other process unit) are required per shift. Increment of one

Table 8.1 The Estimated Total Capital Investment per Stage of Mixer Settler.

| | Direct costs |
|---|----------------|
| Cost for mixer-settler per stage | \$8,100 |
| Purchased equipment-installation | \$3,807 |
| Instrumentation and controls | \$1,458 |
| Piping (installed) | \$5,346 |
| Electrical (installed) | \$891 |
| Buildings (including services) | \$1,458 |
| Yard improvements | \$810 |
| Service facilities (installed) | \$4,050 |
| Land | \$486 |
| Total direct plant cost | \$26,406 |
| | Indirect costs |
| Engineering and supervision | \$2,673 |
| Construction expenses | \$3,321 |
| Total direct and indirect plant costs | \$32,400 |
| Contractor's fee | \$1,620 |
| Contingency | \$3,240 |
| Fixed-capital investment | \$37,260 |
| Working Capital | \$5,589 |
| Total Capital investment | \$42,849 |

1. Cost for mixer-settler was estimated by Denver Mineral Engineers, inc. (73).
2. Turbine-Pump type of mixer-settler was proposed (73), including 100 gallon mixing tank, 450 gallon settler tank, and 1/2 HP mix turbine impeller mixer.
3. All cost factors are based on Peters and Timmerhaus (71).

operator for every 40 mixer-settlers increases. The annual cost for each labor is \$40,000.00. The cost for replacing the lost solvent is assumed to be \$10.00 per stage per day.

The 10 year straight line method was used in calculating the equipment and facilities depreciation. The capital investment of this extraction process plant is also compounded by an annual 8% interest rate.

Based on the retail prices suggested by Aldrich Catalog (70), allowing overhead expenses, discount for large quantities, federal and local taxes, and profits, the whole sale prices for europium oxide with different grades were assumed: \$1860.00/kg for 99.9% purity grade, \$2,538.00/kg for 99.99% purity grade, and \$3,866.00/kg for 99.999% purity grade.

The total production cost for the separation and purification of europium, which is based on the assumptions we made in this section and on the equation (8.1) is readily obtained. The results are expressed as dollars/kg of europium oxide produced.

$$\begin{aligned} \text{Total production cost} &= \text{Capitol cost} + \text{Cost of Labor} + \\ &\text{Cost of solvent loss} + \text{Loss from unrecovered} \\ &\text{desirable solute} + \text{Cost of interest} \quad (8.2) \end{aligned}$$

A few items which were discussed in Sections 8.2 and 8.3 are not included in equation (8.1), because neither they are influential nor easily estimate.

Table 8.2 shows the total production costs for all europium purification cases we have investigated. Each case which is shown in Table 8.2 also consists of three sub-cases, because final europium oxide product has three grades of purity. The parameters for the least purification costs are: 99.9% europium, case EU10221, 102 stages; 99.99% europium, case EU10220, 102 stages and 99.999% europium, case EU10220, 126 stages. As we have mentioned in Chapter 6, cases with 10.3 N HNO_3 are not available, due to the stability limitation of ISR algorithm was reached. Table 8.3 tabulates the break down for the minimum production costs in all three sub-cases with different purity grades.

8.6 Case Study 2: The Purification Of Yttrium

Similar to the cost analysis for the separation and purification of europium oxide in Case Study 1, this section deals with the purification of yttrium oxide from the mixtures of lutetium, ytterbium and yttrium. The objective is to improve the yttrium purity to 99.9% or higher. Details of purification processes were discussed in Chapter 7.

The process parameters for this operation are:

Number of Stages: 18 to 144 stages.

Feed: 6.1-6.4 N HNO_3 , 500 l/h, with rare earths
10.0 g/l of feed solution.

Table 8.2 Costs for Europium Oxide Purification.

| Cases | Eu Purity | | |
|---------|------------|------------|------------|
| | 99.9% | 99.99% | 99.999% |
| EU9824 | \$1,156.88 | \$1,509.39 | \$2,027.69 |
| EU9825 | \$828.56 | \$1,065.17 | \$1,411.72 |
| EU9826 | \$692.78 | \$860.32 | |
| EU9922 | \$1,275.11 | \$1,678.39 | \$2,261.55 |
| EU9923 | \$884.37 | \$1,147.74 | \$1,477.84 |
| EU9924 | \$707.73 | \$825.22 | |
| EU9925 | \$616.86 | | |
| EU10021 | \$1,012.53 | \$1,311.44 | \$1,741.02 |
| EU10022 | \$707.59 | \$893.06 | \$1,130.86 |
| EU10023 | \$607.15 | \$749.96 | |
| EU10120 | \$968.14 | \$1,248.97 | \$1,646.85 |
| EU10121 | \$667.44 | \$836.63 | \$1,045.71 |
| EU10122 | \$584.46 | \$724.16 | |
| EU10219 | \$806.19 | \$1,020.66 | \$1,301.06 |
| EU10220 | \$619.40 | \$697.11 | \$853.20 |
| EU10221 | \$564.03 | | |

1. Costs are in dollars/kg of Europium Oxide.
2. Costs data are based on 3.0 metric tons per year.

Table 8.3 Cost Analysis for the Separation and Purification of Europium Oxide.

| | | | |
|----------------|----------|----------|----------|
| Eu Purity | 99.9% | 99.99% | 99.999% |
| Equipment | \$147.06 | \$153.04 | \$187.20 |
| Capital Cost | \$147.06 | \$153.04 | \$187.20 |
| Labor | \$161.52 | \$168.12 | \$208.04 |
| Solvent Loss | \$120.13 | \$125.04 | \$152.91 |
| Unrecov. Eu | \$17.66 | \$128.48 | \$155.30 |
| Interest | \$117.66 | \$122.43 | \$149.75 |
| Operating Cost | \$416.97 | \$544.07 | \$666.00 |
| Total Cost | \$564.03 | \$697.11 | \$853.20 |

1. Design base: 3.0 metric tons of europium oxide per year.
2. Costs in Dollar/Kg of Europium Oxide.
3. 10 year straight line depreciation method used.
4. 8.0% interest rate.
5. Operator costs \$40,000 per year.
6. Mixer-settlers required for
 - Eu 99.9%: 102
 - Eu 99.99%: 102
 - Eu 99.999%: 126

Extractant: TBP pre-equilibrated with 6.1-6.4 N HNO_3 ,
1250-1700 l/h.

Scrub Solution: 6.1-6.4 N HNO_3 , 1000 l/h.

The mixer-settler system proposed by Denver Mineral Engineers, Inc (73) is still within the design criterion, and can be used for this operation. All other cost parameters remain the same as compared to Case Study 1. Based on the same rule we have used for the whole sale prices of europium oxide, the following yttrium oxide whole sale prices was thus assumed: for 99.9% purity product, the price is \$65.00/kg, for 99.99% purity product, the price is \$83.00/kg, and for 99.999% purity product, the price is \$282.00/kg.

The total production cost function which was described by equation (8.2) is also valid for yttrium purification.

Table 8.4 shows the total production costs for all yttrium oxide purification cases we have studied. Similar to europium purification in Case Study 1, each case shown in Table 8.4 consists of three sub-cases, because yttrium oxide product purity has three grades: 99.9%, 99.99% and 99.999%. The process parameters for the minimum costs for yttrium purification are: yttrium 99.9%, case Y6134, 48 stages, yttrium 99.99%, case Y6428, 72 stages and yttrium 99.999%, case Y6428, 102 stages. The break down for the minimum production costs in all three purity grades are shown in Table 8.5.

Table 8.4 Costs for Yttrium Oxide Purification.

| Cases | Y Purity | | |
|-------|----------|---------|---------|
| | 99.9% | 99.99% | 99.999% |
| Y6131 | \$45.33 | | |
| Y6132 | \$29.58 | \$52.73 | |
| Y6133 | \$25.72 | \$40.43 | |
| Y6134 | \$24.74 | \$35.28 | \$47.68 |
| Y6230 | \$35.30 | \$58.45 | |
| Y6231 | \$31.57 | \$44.63 | |
| Y6232 | \$30.95 | \$41.29 | \$49.58 |
| Y6233 | \$32.87 | \$37.57 | \$53.07 |
| Y6234 | \$32.89 | \$41.19 | \$65.28 |
| Y6328 | \$37.15 | \$65.14 | |
| Y6329 | \$33.92 | \$50.46 | \$68.31 |
| Y6330 | \$32.73 | \$43.21 | \$61.21 |
| Y6331 | \$31.78 | \$43.78 | \$68.99 |
| Y6332 | \$36.52 | \$48.36 | \$82.11 |
| Y6425 | \$46.33 | | |
| Y6426 | \$28.13 | \$49.54 | |
| Y6427 | \$25.05 | \$37.62 | \$49.92 |
| Y6428 | \$25.54 | \$31.37 | \$44.45 |
| Y6429 | \$25.49 | \$33.67 | \$55.15 |
| Y6430 | \$30.29 | \$39.25 | \$70.95 |

1. Costs are in dollars/kg of Yttrium Oxide.
2. Costs data are based on 4.2 metric tons per year.

Table 8.5 Cost Analysis for the Purification of Yttrium Oxide.

| | | | |
|----------------|---------|---------|---------|
| Y Purity | 99.9% | 99.99% | 99.999% |
| Equipment | \$5.09 | \$7.58 | \$10.59 |
| Capital Cost | \$5.09 | \$7.58 | \$10.59 |
| Labor | \$8.90 | \$8.85 | \$11.63 |
| Solvent Loss | \$4.16 | \$6.19 | \$8.65 |
| Unrecov. Y | \$2.52 | \$2.68 | \$5.09 |
| Interest | \$4.07 | \$6.07 | \$8.49 |
| Operating Cost | \$19.65 | \$23.79 | \$33.86 |
| Total Cost | \$24.74 | \$31.37 | \$44.45 |

1. Design base: 4.2 metric tons of yttrium oxide per year
2. Costs in Dollar/Kg of Yttrium Oxide.
3. 10 year straight line depreciation method used.
4. 8.0% interest rate.
5. Operator costs \$40,000 per year.
6. Solvent loss \$10.0 per stage per day.
7. Mixer-settlers required for
 - Y 99.9%: 48
 - Y 99.99%: 72
 - Y 99.999%: 102

8.7 Case Study 3: Separation Of Gadolinium From The Sub-Group Gd-La Of Jiangxi Mineral Sample

The separation of gadolinium from the sub-group Gd-La of Jiangxi mineral sample is a important operation too. Separation and purification of europium operation can not be proceed unless the gadolinium has been separated earlier. Separation of gadolinium was discussed in Section 6.4.

Due to the small separation factor of Gd/Eu, the separation of gadolinium from the sub-group Gd-La is rather difficulty. During separation process, gadolinium accompanied by some europium were extracted into the organic phase from the aqueous phase. Even with large stage numbers, clean-cut separations were still not easily obtained.

The optimum process parameters for this operation are:

Number of Stages: 66 to 120 stages.

Feed: 9.5 N HNO₃, 440.0 l/h, with rare earths
133 g/l of feed solution.

Extractant: TBP pre-equilibrated with 9.5 N HNO₃,
880.0 l/h.

Scrub Solution : 9.5 N HNO₃, 836.0 l/h.

The mixer-settler system suggested by Denver Mineral Engineers, Inc (73) is still available for this operation. All other cost parameters remain the same as Case Study 1. The whole sale prices for gadolinium oxide were estimated

based on the same rule we used before. The whole sale prices used in cost analysis are: \$250.00/kg for 99.9% purity gadolinium, \$1,444.00/kg for 99.99% purity gadolinium. The total production cost function which was described by equation (8.2) is also valid for gadolinium.

Only case GD9519 has successfully produced 99.99% purity gadolinium. Figure 8.1 shows the total production costs for case GD9519. The minimum point occurs between stages 80 to 88. Figure 8.1 also shows a step jump in the production cost at stage 120, this is attributed to the increase of one more operator per shift in operation.

8.8 Discussions

The feed concentration also plays a role in the process economics. Ritcey (72) reported the relationship between feed concentration and the processing costs for systems covering the acidic and basic extraction. Due to insufficient of experimental equilibrium data for higher concentration of rare earths in the feed, investigation was not conducted.

The optimum number of mixer-settlers for europium oxide separation and purification operation are 102 for 99.9% or 99.99% europium, and 126 for 99.999% europium product. The optimum process design for yttrium oxide purification includes an extraction system with 48 mixer-settlers for 99.9% purity yttrium, 72 mixer-settlers for

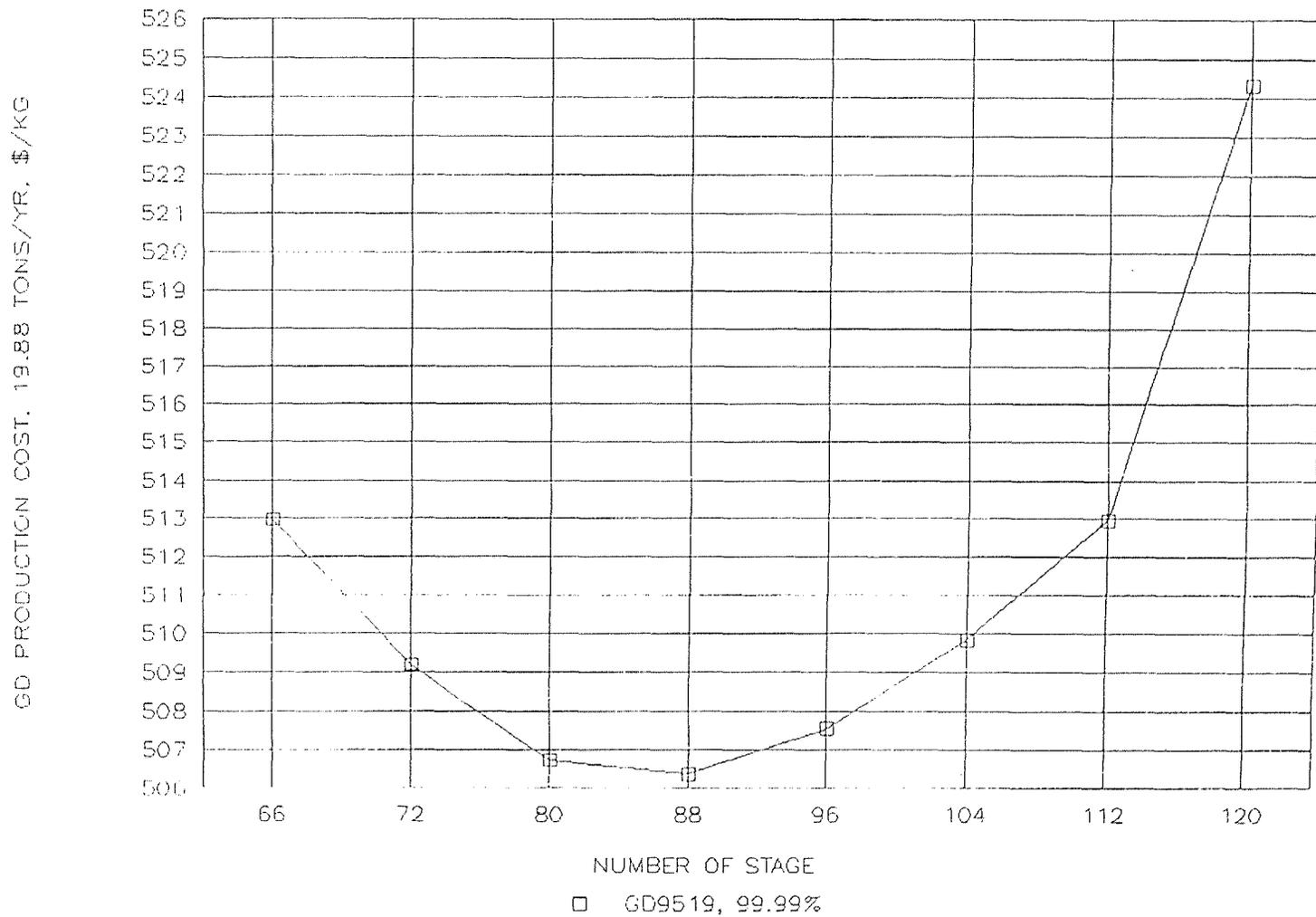


Figure 8.1 The Effect of Number of Stages on the Cost of Separation Gadolinium from the Sub-group Gd-La.

99.99% purity yttrium, or 102 mixer-settlers for 99.999% purity yttrium product.

As we examine Table 8.2, it clearly shows that as the ratio of extractant to feed increased, the costs for europium oxide purification decrease accordingly. However, Table 8.2 also shows, as the acidity in the aqueous phase increased, the costs decrease even more rapidly. Therefore, for the separation and purification of europium oxide in the $\text{HNO}_3\text{-H}_2\text{O-TBP}$ system, the acidity in the aqueous phase is more influential than the extractant to the feed ratio in determining the cost of operations.

The behaviors of the yttrium oxide purification costs are quite different. Table 8.4 shows at 99.9% yttrium purity, as the ratio of extractant to feed increased, the costs for yttrium oxide purification decrease. However, at 99.999% yttrium purity, as the ratio of extractant to feed increased, the costs for yttrium oxide purification increase as well. Perhaps it is because the yttrium oxide did not transfer to the organic phase by extraction and remained in the aqueous solution. As the extractant to the feed ratio increased, more Lu and Yb were extracted, thus 99.9% yttrium oxide purity can be easily reached by fewer number of stages. For the 99.999% yttrium purity case, a large number of stages are required. As the ratio of extractant to feed increased, more yttrium along with lutetium and ytterbium were extracted into the organic phase, as a result, less

yttrium oxide remained in the aqueous phase for recovery. Thus, the operation cost increases.

Since the acidity in the aqueous phase is more dominative than other factors in the total production costs for the europium separation and purification operations, one might think it is wise to optimize the operation conditions by adjusting the acidity alone. As we discussed in Chapter 5, when the acidity in the aqueous phase was changed, higher or lower extractant to feed ratio is required. However, an extremely large or small ratio of the extractant to the feed will cause troubles in the practical operation.

CHAPTER 9

CONCLUSIONS AND SUGGESTIONS

9.1 Conclusions

A mathematical model for the liquid-liquid equilibrium of the lanthanide and yttrium oxides in the nitric acid - water - tributyl phosphate ($\text{HNO}_3\text{-H}_2\text{O-TBP}$) two-phase system has been developed. All 16 rare earth distribution coefficients in this two-phase system which were experimentally determined by UK Harwell Laboratory were used to evaluate the parameters of this equilibrium model by a non-linear optimization technique. The uniquenesses of this model are:

1. This model is based on the inter-relationships of chemical reactions, phase equilibrium, and material balance. The chemical reactions were modelled using experimentally derived empirical equations for component involved. No heat of reaction or energy balance is considered in this model. Because model parameters were evaluated by solving non-linear simultaneous equations, therefore, once the numerical values of model parameters are determined, all concentration of species in the two-phase system are obtained simultaneously.

2. Most of the published liquid-liquid equilibrium models have a very narrow prediction range. Unlike other models, the model developed by this research has the capability of predicting the distribution coefficients for

all 16 rare earth oxides in the $\text{HNO}_3\text{-H}_2\text{O-TBP}$ two-phase system for a acidity range of 0.3 to 16 N.

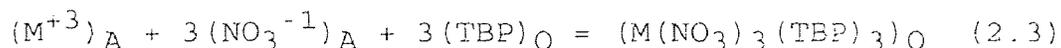
3. Because of the long range prediction capability, this model has practical value. This model can be used not only for predicting the liquid-liquid equilibrium in the laboratories, it also be used in actual process design for liquid-liquid extraction systems.

Based on the developed theoretical liquid-liquid equilibrium model, the optimum design of the liquid-liquid extraction systems in terms of capital investment and operating costs were analyzed for the following operations: (1) separation of gadolinium from the sub-group Gd-La of the lanthanide and yttrium oxides mineral sample; (2) separation and purification of europium from the sub-group Eu-La of the lanthanide and yttrium oxides mineral sample; and (3) purification of yttrium oxide from the mixture of lutetium, ytterbium and yttrium.

9.2 Suggestions

For further development of this mathematical liquid-liquid equilibrium model in the future, the following suggestions were made:

1. Incorporation of the macro-quantities of the initial rare earth concentrations into this model. Recall the extraction mechanism equation (2.3):



where $(M^{+3})_A$ and $(NO_3^{-1})_A$ represent the rare earth ion and nitrate in the aqueous phase, respectively. Consequently, the distributions of rare earth between the organic and aqueous phases are determined by two independent variables: the rare earth and acid concentrations in the aqueous phase, if the solvent concentration is fixed. The Harwell Laboratory experimental data in which our model were fitted into was determined in trace amounts of lanthanide and yttrium in the aqueous phase (<1 g/l). Therefore, if the initial rare earth concentrations are macro-quantities, the model may fail in predicting the distribution coefficients.

2. Conducting systematic investigations for the effect of feed stage location on the liquid-liquid extraction performance. Research efforts can also be focused on the effect of the feed concentration on the capital investment and operating costs.

3. Development of a liquid-liquid equilibrium model for predicting the simultaneous distribution of lanthanide and yttrium nitrates and nitric acid in the HNO_3 - H_2O -TBP two-phase system. A few publications have already addressed the issue of competitive extraction by TBP (75), (76), (77), (78).

APPENDIX A

Tables

Table 5.2 The Calculated Distribution Coefficients of Yttrium and Composition in Aqueous and Organic Phases.

| Test | (HNO ₃) _{ai} | Kd exp | Kd calc | (HNO ₃) _{at} | (MNO ₃ +2) _a | Deg Ionz | (NO ₃ -1) _a |
|------|-----------------------------------|----------|----------|-----------------------------------|------------------------------------|----------|-----------------------------------|
| 1 | 0.71 | 0.0440 | 0.0438 | 0.3881 | 6.728000E-04 | 0.9920 | 0.3850 |
| 2 | 1.52 | 0.1000 | 0.1194 | 0.8196 | 4.360000E-04 | 0.9810 | 0.8040 |
| 3 | 3.23 | 0.2700 | 0.2889 | 1.8284 | 2.091000E-04 | 0.9492 | 1.7356 |
| 4 | 4.84 | 0.6400 | 0.5441 | 2.8978 | 1.584000E-04 | 0.9075 | 2.6297 |
| 5 | 6.55 | 1.1000 | 1.1237 | 4.1396 | 2.119000E-04 | 0.8497 | 3.5174 |
| 6 | 7.14 | 1.3800 | 1.4665 | 4.5887 | 2.285000E-04 | 0.8267 | 3.7935 |
| 7 | 7.83 | 2.2000 | 2.0270 | 5.1244 | 2.464000E-04 | 0.7980 | 4.0891 |
| 8 | 9.10 | 3.6000 | 3.9115 | 6.1320 | 2.736000E-04 | 0.7407 | 4.5417 |
| 9 | 10.40 | 9.0000 | 8.7673 | 7.1818 | 2.931000E-04 | 0.6774 | 4.8645 |
| 10 | 13.10 | 62.0000 | 62.0520 | 9.3794 | 3.042000E-04 | 0.5383 | 5.0483 |
| 11 | 15.00 | 220.0000 | 219.9795 | 10.9046 | 2.898000E-04 | 0.4411 | 4.8098 |

| Test | (H+1) _a | (M+3) _a | (HNO ₃) _o | (M) _o | (M(NO ₃) ₂) _a | (TBP) _o | HOH |
|------|--------------------|--------------------|----------------------------------|------------------|--|--------------------|--------|
| 1 | 0.3890 | 0.0029 | 0.3145 | 0.0001 | 6.447780E-03 | 3.3810 | 1.1287 |
| 2 | 0.8100 | 0.0009 | 0.6911 | 0.0001 | 8.726610E-03 | 3.3373 | 2.1436 |
| 3 | 1.7422 | 0.0002 | 1.3916 | 0.0001 | 9.036920E-03 | 3.2619 | 3.4982 |
| 4 | 2.6372 | 0.0001 | 1.9313 | 0.0001 | 1.037298E-02 | 3.2090 | 4.2854 |
| 5 | 3.5333 | 0.0001 | 2.3913 | 0.0001 | 1.855815E-02 | 3.1651 | 4.4851 |
| 6 | 3.8125 | 0.0001 | 2.5291 | 0.0001 | 2.158598E-02 | 3.1513 | 4.9743 |
| 7 | 4.1117 | 0.0001 | 2.6799 | 0.0001 | 2.508110E-02 | 3.1352 | 5.1092 |
| 8 | 4.5703 | 0.0001 | 2.9364 | 0.0001 | 3.094055E-02 | 3.1046 | 5.2903 |
| 9 | 4.8978 | 0.0001 | 3.1820 | 0.0001 | 3.549504E-02 | 3.0709 | 5.4046 |
| 10 | 5.0843 | 0.0001 | 3.6817 | 0.0001 | 3.822799E-02 | 2.9916 | 5.5109 |
| 11 | 4.8421 | 0.0001 | 4.0601 | 0.0001 | 3.470126E-02 | 2.9273 | 5.5438 |

Initial Concentration:
 TBP 3.66 M
 Rare Earths 0.01 M

Table 5.3 The Calculated Distribution Coefficients of Ytterbium and Composition in Aqueous and Organic Phases.

| Test | (HNO ₃) _{ai} | Kd exp | Kd calc | (HNO ₃) _{at} | (MNO ₃ +2) _a | Deg Ioniz | (NO ₃ -1) _a |
|------|-----------------------------------|----------|----------|-----------------------------------|------------------------------------|-----------|-----------------------------------|
| 1 | 0.33 | 0.0087 | 0.0078 | 0.1809 | 1.080000E-05 | 0.9968 | 0.1803 |
| 2 | 0.69 | 0.0260 | 0.0451 | 0.3791 | 1.201100E-03 | 0.9923 | 0.3761 |
| 3 | 1.26 | 0.0730 | 0.1346 | 0.6787 | 1.168000E-03 | 0.9848 | 0.6684 |
| 4 | 1.95 | 0.1630 | 0.2576 | 1.0611 | 9.342000E-04 | 0.9741 | 1.0336 |
| 5 | 2.92 | 0.4200 | 0.4377 | 1.6356 | 6.594000E-04 | 0.9559 | 1.5634 |
| 6 | 3.90 | 0.7100 | 0.6470 | 2.2596 | 5.083000E-04 | 0.9333 | 2.1090 |
| 7 | 5.13 | 1.2000 | 1.0303 | 3.1020 | 3.359000E-04 | 0.8986 | 2.7876 |
| 8 | 5.96 | 1.5300 | 1.4528 | 3.7037 | 3.888000E-04 | 0.8712 | 3.2267 |
| 9 | 6.95 | 2.1000 | 2.2876 | 4.4506 | 2.237000E-04 | 0.8344 | 3.7135 |
| 10 | 8.10 | 4.0000 | 4.0957 | 5.3488 | 2.535000E-04 | 0.7865 | 4.2068 |
| 11 | 9.36 | 8.2000 | 8.2320 | 6.3580 | 2.792000E-04 | 0.7289 | 4.6343 |
| 12 | 10.40 | 15.4000 | 15.2504 | 7.2022 | 2.943000E-04 | 0.6782 | 4.8844 |
| 13 | 11.00 | 22.0000 | 21.9930 | 7.6909 | 3.003000E-04 | 0.6480 | 4.9839 |
| 14 | 13.00 | 74.0000 | 74.0502 | 9.3199 | 3.060000E-04 | 0.5450 | 5.0791 |
| 15 | 15.00 | 220.0000 | 219.9870 | 10.9236 | 2.914000E-04 | 0.4427 | 4.8362 |

| Test | (H+1) _a | (M+3) _a | (HNO ₃) _o | (M) _o | (M(NO ₃) ₂) _a | (TBP) _o | NOH |
|------|--------------------|--------------------|----------------------------------|------------------|--|--------------------|--------|
| 1 | 0.1879 | 0.0001 | 0.1382 | 0.0100 | 1.463000E-05 | 3.4485 | 1.0000 |
| 2 | 0.3777 | 0.0053 | 0.3060 | 0.0001 | 3.374880E-03 | 3.3821 | 1.1023 |
| 3 | 0.6724 | 0.0029 | 0.5739 | 0.0001 | 5.832400E-03 | 3.3507 | 1.8576 |
| 4 | 1.0392 | 0.0015 | 0.8800 | 0.0002 | 7.213940E-03 | 3.3162 | 2.5643 |
| 5 | 1.5701 | 0.0007 | 1.2744 | 0.0004 | 7.702200E-03 | 3.2739 | 3.3105 |
| 6 | 2.1162 | 0.0004 | 1.6298 | 0.0005 | 8.009210E-03 | 3.2381 | 3.8764 |
| 7 | 2.7953 | 0.0002 | 2.0170 | 0.0006 | 6.996280E-03 | 3.2009 | 4.4119 |
| 8 | 3.2346 | 0.0001 | 2.2450 | 0.0007 | 9.373970E-03 | 3.1793 | 4.6915 |
| 9 | 3.7216 | 0.0001 | 2.4879 | 0.0008 | 6.207880E-03 | 3.1555 | 4.9553 |
| 10 | 4.2152 | 0.0001 | 2.7395 | 0.0009 | 7.966730E-03 | 3.1285 | 5.1805 |
| 11 | 4.6424 | 0.0001 | 2.9905 | 0.0005 | 9.668180E-03 | 3.0976 | 5.3320 |
| 12 | 4.8924 | 0.0001 | 3.1865 | 0.0001 | 1.073986E-02 | 3.0703 | 5.4060 |
| 13 | 4.9924 | 0.0001 | 3.2973 | 0.0001 | 1.118188E-02 | 3.0537 | 5.4408 |
| 14 | 5.0880 | 0.0001 | 3.6678 | 0.0001 | 1.161315E-02 | 2.9939 | 5.5092 |
| 15 | 4.8440 | 0.0001 | 4.0652 | 0.0001 | 1.052894E-02 | 2.9266 | 5.5442 |

Initial Concentration:
 TBP 3.66 M
 Rare Earths 0.01 M

Table 5.4 The Calculated Distribution Coefficients of Thulium and Composition in Aqueous and Organic Phases.

| Test | (HNO ₃) _{ai} | Kd exp | Kd calc | (HNO ₃) _{at} | (MNO ₃ +2) _a | Deg Ioniz | (NO ₃ -1) _a |
|------|-----------------------------------|---------|---------|-----------------------------------|------------------------------------|-----------|-----------------------------------|
| 1 | 0.58 | 0.0270 | 0.0183 | 0.3148 | 2.878000E-04 | 0.9938 | 0.3128 |
| 2 | 1.28 | 0.0760 | 0.0660 | 0.6887 | 6.719000E-04 | 0.9845 | 0.6780 |
| 3 | 2.43 | 0.1700 | 0.1741 | 1.3398 | 3.663000E-04 | 0.9656 | 1.2937 |
| 4 | 2.72 | 0.2300 | 0.2109 | 1.5135 | 3.085000E-04 | 0.9600 | 1.4529 |
| 5 | 3.70 | 0.3900 | 0.3773 | 2.1289 | 2.828000E-04 | 0.9383 | 1.9975 |
| 6 | 4.74 | 0.6500 | 0.6502 | 2.8284 | 1.822000E-04 | 0.9104 | 2.5751 |
| 7 | 7.38 | 2.0000 | 2.1174 | 4.7768 | 2.762000E-04 | 0.8170 | 3.9024 |
| 8 | 8.30 | 3.2000 | 3.2085 | 5.4981 | 3.025000E-04 | 0.7774 | 4.2742 |
| 9 | 9.22 | 5.4000 | 5.1279 | 6.2326 | 3.242000E-04 | 0.7350 | 4.5809 |
| 10 | 10.40 | 10.0000 | 10.2845 | 7.1867 | 3.445000E-04 | 0.6774 | 4.8679 |
| 11 | 11.10 | 16.2000 | 16.0862 | 7.7562 | 3.524000E-04 | 0.6419 | 4.9787 |
| 12 | 14.00 | 97.0000 | 97.0071 | 10.1116 | 3.519000E-04 | 0.4917 | 4.9717 |

| Test | (H+1) _a | (M+3) _a | (HNO ₃) _o | (M) _o | (M(NO ₃) ₂) _a | (TBP) _o | NOH |
|------|--------------------|--------------------|----------------------------------|------------------|--|--------------------|--------|
| 1 | 0.3279 | 0.0013 | 0.2468 | 0.0059 | 1.589960E-03 | 3.3924 | 1.0000 |
| 2 | 0.6835 | 0.0014 | 0.5824 | 0.0001 | 8.044470E-03 | 3.3497 | 1.8789 |
| 3 | 1.3002 | 0.0004 | 1.0803 | 0.0001 | 8.368290E-03 | 3.2944 | 2.9585 |
| 4 | 1.4596 | 0.0003 | 1.1965 | 0.0002 | 7.915940E-03 | 3.2821 | 3.1702 |
| 5 | 2.0044 | 0.0002 | 1.5609 | 0.0002 | 9.975010E-03 | 3.2449 | 3.7661 |
| 6 | 2.5822 | 0.0001 | 1.9011 | 0.0003 | 8.288920E-03 | 3.2119 | 4.2506 |
| 7 | 3.9188 | 0.0001 | 2.5835 | 0.0001 | 1.903590E-02 | 3.1456 | 5.0252 |
| 8 | 4.2945 | 0.0001 | 2.7784 | 0.0001 | 2.283598E-02 | 3.1240 | 5.1863 |
| 9 | 4.6047 | 0.0001 | 2.9605 | 0.0001 | 2.623080E-02 | 3.1015 | 5.3039 |
| 10 | 4.8951 | 0.0001 | 3.1830 | 0.0001 | 2.962056E-02 | 3.0708 | 5.4048 |
| 11 | 5.0073 | 0.0001 | 3.3121 | 0.0001 | 3.098431E-02 | 3.0514 | 5.4448 |
| 12 | 5.0004 | 0.0001 | 3.8569 | 0.0001 | 3.089725E-02 | 2.9621 | 5.5284 |

Initial Concentration:
 TBP 3.66 M
 Rare Earths 0.01 M

Table 5.5 The Calculated Distribution Coefficients of Erbium and Composition in Aqueous and Organic Phases.

| Test | (HNO ₃) _{ai} | Kd exp | Kd calc | (HNO ₃) _{at} | (MNC ₃₊₂) _a | Deg Ioniz | (NO ₃ -1) _a |
|------|-----------------------------------|----------|----------|-----------------------------------|------------------------------------|-----------|-----------------------------------|
| 1 | 0.39 | 0.0280 | 0.0262 | 0.2115 | 1.570000E-05 | 0.9961 | 0.2106 |
| 2 | 0.79 | 0.0480 | 0.0908 | 0.4293 | 7.339000E-04 | 0.9910 | 0.4255 |
| 3 | 1.51 | 0.1490 | 0.2072 | 0.8140 | 4.792000E-04 | 0.9811 | 0.7987 |
| 4 | 2.05 | 0.2500 | 0.2916 | 1.1180 | 4.076000E-04 | 0.9724 | 1.0871 |
| 5 | 3.46 | 0.5800 | 0.5146 | 1.9743 | 2.795000E-04 | 0.9440 | 1.8637 |
| 6 | 4.10 | 0.7000 | 0.6276 | 2.3926 | 1.665000E-04 | 0.9282 | 2.2208 |
| 7 | 4.85 | 0.8800 | 0.7825 | 2.9042 | 1.975000E-04 | 0.9072 | 2.6346 |
| 8 | 4.89 | 0.8300 | 0.7917 | 2.9321 | 1.992000E-04 | 0.9060 | 2.6564 |
| 9 | 5.51 | 1.0000 | 0.9517 | 3.3716 | 2.241000E-04 | 0.8865 | 2.9888 |
| 10 | 6.33 | 1.1800 | 1.2308 | 3.9735 | 2.556000E-04 | 0.8579 | 3.4088 |
| 11 | 6.57 | 1.3100 | 1.3323 | 4.1535 | 2.644000E-04 | 0.8490 | 3.5262 |
| 12 | 7.30 | 1.5800 | 1.7175 | 4.7107 | 2.898000E-04 | 0.8203 | 3.8640 |
| 13 | 8.81 | 2.9000 | 3.1382 | 5.8981 | 3.337000E-04 | 0.7645 | 4.4499 |
| 14 | 9.67 | 4.8000 | 4.7111 | 6.5886 | 3.527000E-04 | 0.7138 | 4.7028 |
| 15 | 10.10 | 6.1000 | 5.8953 | 6.9362 | 3.603000E-04 | 0.6928 | 4.8053 |
| 16 | 12.90 | 33.0000 | 33.0530 | 9.2144 | 3.798000E-04 | 0.5497 | 5.0642 |
| 17 | 15.80 | 186.0000 | 186.0083 | 11.5292 | 3.483000E-04 | 0.4029 | 4.6449 |

| Test | (H+1) _a | (M+3) _a | (HNO ₃) _o | (M) _o | (M(NO ₃) ₂) _a | (TBP) _o | NOH |
|------|--------------------|--------------------|----------------------------------|------------------|--|--------------------|--------|
| 1 | 0.2230 | 0.0001 | 0.1628 | 0.0100 | 7.142000E-05 | 3.4343 | 1.0000 |
| 2 | 0.4300 | 0.0023 | 0.3528 | 0.0001 | 6.706370E-03 | 3.3765 | 1.2478 |
| 3 | 0.8047 | 0.0008 | 0.6866 | 0.0001 | 8.218980E-03 | 3.3378 | 2.1337 |
| 4 | 1.0935 | 0.0005 | 0.9223 | 0.0001 | 9.516330E-03 | 3.3115 | 2.6492 |
| 5 | 1.8704 | 0.0002 | 1.4757 | 0.0001 | 1.118774E-02 | 3.2534 | 3.6320 |
| 6 | 2.2275 | 0.0001 | 1.6973 | 0.0001 | 7.942900E-03 | 3.2315 | 3.9637 |
| 7 | 2.6430 | 0.0001 | 1.9341 | 0.0001 | 1.117866E-02 | 3.2088 | 4.2890 |
| 8 | 2.6650 | 0.0001 | 1.9461 | 0.0001 | 1.136443E-02 | 3.2076 | 4.3054 |
| 9 | 3.0005 | 0.0001 | 2.1234 | 0.0001 | 1.438647E-02 | 3.1908 | 4.5305 |
| 10 | 3.4249 | 0.0001 | 2.3372 | 0.0001 | 1.871387E-02 | 3.1704 | 4.7790 |
| 11 | 3.5436 | 0.0001 | 2.3958 | 0.0001 | 2.002509E-02 | 3.1647 | 4.8420 |
| 12 | 3.8856 | 0.0001 | 2.5646 | 0.0001 | 2.404556E-02 | 3.1476 | 5.0099 |
| 13 | 4.4795 | 0.0001 | 2.8793 | 0.0001 | 3.189049E-02 | 3.1119 | 5.2571 |
| 14 | 4.7363 | 0.0001 | 3.0450 | 0.0001 | 3.561834E-02 | 3.0903 | 5.3489 |
| 15 | 4.8404 | 0.0001 | 3.1257 | 0.0001 | 3.718790E-02 | 3.0791 | 5.3842 |
| 16 | 5.1035 | 0.0001 | 3.6434 | 0.0001 | 4.130307E-02 | 2.9980 | 5.5066 |
| 17 | 4.6774 | 0.0001 | 4.2354 | 0.0001 | 3.474669E-02 | 2.8971 | 5.5538 |

Initial Concentration:
 TBP 3.66 M
 Rare Earths 0.01 M

Table 5.6 The Calculated Distribution Coefficients of Holmium and Composition in Aqueous and Organic Phases.

| Test | (HNO ₃) _{ai} | Kd exp | Kd calc | (HNO ₃) _{at} | (MNO ₃ +2) _a | Deg Ioniz | (NO ₃ -1) _a |
|------|-----------------------------------|---------|---------|-----------------------------------|------------------------------------|-----------|-----------------------------------|
| 1 | 0.72 | 0.0710 | 0.0645 | 0.3932 | 9.654000E-04 | 0.9919 | 0.3901 |
| 2 | 1.23 | 0.1290 | 0.1417 | 0.6619 | 7.825000E-04 | 0.9852 | 0.6521 |
| 3 | 3.31 | 0.4200 | 0.4441 | 1.8764 | 2.667000E-04 | 0.9475 | 1.7780 |
| 4 | 4.10 | 0.6000 | 0.5571 | 2.3895 | 1.663000E-04 | 0.9283 | 2.2182 |
| 5 | 5.15 | 0.7300 | 0.7182 | 3.1128 | 2.096000E-04 | 0.8982 | 2.7958 |
| 6 | 7.47 | 1.3000 | 1.3388 | 4.8465 | 2.955000E-04 | 0.8131 | 3.9405 |
| 7 | 8.47 | 1.9900 | 2.0309 | 5.6341 | 3.251000E-04 | 0.7694 | 4.3350 |
| 8 | 9.45 | 3.5000 | 3.4208 | 6.4200 | 3.483000E-04 | 0.7235 | 4.6444 |
| 9 | 11.10 | 9.3000 | 9.3260 | 7.7596 | 3.730000E-04 | 0.6410 | 4.9737 |
| 10 | 14.00 | 47.0000 | 47.0004 | 10.1149 | 3.723000E-04 | 0.4909 | 4.9649 |

| Test | (H+1) _a | (M+3) _a | (HNO ₃) _o | (M) _o | (M(NO ₃) ₂) _a | (TBP) _o | NOH |
|------|--------------------|--------------------|----------------------------------|------------------|--|--------------------|--------|
| 1 | 0.3942 | 0.0033 | 0.3193 | 0.0004 | 5.453250E-03 | 3.3805 | 1.1468 |
| 2 | 0.6573 | 0.0016 | 0.5596 | 0.0001 | 7.388190E-03 | 3.3523 | 1.8206 |
| 3 | 1.7885 | 0.0002 | 1.4197 | 0.0020 | 6.865670E-03 | 3.2590 | 3.5954 |
| 4 | 2.2295 | 0.0001 | 1.6958 | 0.0024 | 5.343070E-03 | 3.2316 | 4.0262 |
| 5 | 2.8082 | 0.0001 | 2.0215 | 0.0023 | 8.487930E-03 | 3.2005 | 4.4670 |
| 6 | 3.9576 | 0.0001 | 2.6032 | 0.0010 | 1.686135E-02 | 3.1434 | 5.0693 |
| 7 | 4.3545 | 0.0001 | 2.8132 | 0.0006 | 2.040647E-02 | 3.1197 | 5.2253 |
| 8 | 4.6661 | 0.0001 | 3.0052 | 0.0003 | 2.342335E-02 | 3.0954 | 5.3318 |
| 9 | 4.9983 | 0.0001 | 3.3129 | 0.0001 | 2.686265E-02 | 3.0510 | 5.4426 |
| 10 | 4.9893 | 0.0001 | 3.8577 | 0.0001 | 2.676768E-02 | 2.9617 | 5.5266 |

Initial Concentration:
 TBP 3.66 M
 Rare Earths 0.01 M

Table 5.7 The Calculated Distribution Coefficients of Terbium and Composition in Aqueous and Organic Phases.

| Test | (HNO ₃) _{ai} | Kd exp | Kd calc | (HNO ₃) _{at} | (MNO ₃ +2) _a | Deg Ioniz | (NO ₃ -1) _a |
|------|-----------------------------------|---------|---------|-----------------------------------|------------------------------------|-----------|-----------------------------------|
| 1 | 1.36 | 0.2100 | 0.1601 | 0.7317 | 4.065000E-04 | 0.9834 | 0.7195 |
| 2 | 2.55 | 0.3900 | 0.3082 | 1.4111 | 1.538000E-04 | 0.9633 | 1.3594 |
| 3 | 4.29 | 0.5700 | 0.5300 | 2.5138 | 2.621000E-04 | 0.9231 | 2.3203 |
| 4 | 4.95 | 0.7000 | 0.6205 | 2.9642 | 3.027000E-04 | 0.9040 | 2.6794 |
| 5 | 5.80 | 0.7200 | 0.7457 | 3.5680 | 3.532000E-04 | 0.8762 | 3.1258 |
| 6 | 5.83 | 0.7300 | 0.7503 | 3.5898 | 3.549000E-04 | 0.8752 | 3.1411 |
| 7 | 7.05 | 0.8700 | 0.9572 | 4.4976 | 4.210000E-04 | 0.8287 | 3.7262 |
| 8 | 7.10 | 0.8500 | 0.9668 | 4.5357 | 4.235000E-04 | 0.8266 | 3.7484 |
| 9 | 8.10 | 1.1900 | 1.1911 | 5.3085 | 4.695000E-04 | 0.7831 | 4.1556 |
| 10 | 9.15 | 1.5500 | 1.5727 | 6.1389 | 5.083000E-04 | 0.7332 | 4.4990 |
| 11 | 9.77 | 2.0000 | 1.9607 | 6.6359 | 5.262000E-04 | 0.7021 | 4.6569 |
| 12 | 10.60 | 3.0000 | 2.8741 | 7.3065 | 5.439000E-04 | 0.6592 | 4.8141 |
| 13 | 12.30 | 8.2000 | 8.0892 | 8.6893 | 5.586000E-04 | 0.5692 | 4.9440 |
| 14 | 13.00 | 12.7000 | 12.8766 | 9.2598 | 5.566000E-04 | 0.5323 | 4.9264 |
| 15 | 16.30 | 53.0000 | 52.9787 | 11.1089 | 5.218000E-04 | 0.4159 | 4.6185 |

| Test | (H+1) _a | (M+3) _a | (HNO ₃) _o | (M) _o | (M(NO ₃) ₂) _a | (TBP) _o | NOH |
|------|--------------------|--------------------|----------------------------------|------------------|--|--------------------|--------|
| 1 | 0.7259 | 0.0005 | 0.6186 | 0.0001 | 9.059400E-03 | 3.3456 | 1.9692 |
| 2 | 1.3661 | 0.0001 | 1.1288 | 0.0001 | 6.467880E-03 | 3.2892 | 3.0470 |
| 3 | 2.3366 | 0.0001 | 1.7567 | 0.0001 | 1.884327E-02 | 3.2257 | 4.0479 |
| 4 | 2.7023 | 0.0001 | 1.9599 | 0.0001 | 2.512714E-02 | 3.2063 | 4.3229 |
| 5 | 3.1582 | 0.0001 | 2.1968 | 0.0001 | 3.419718E-02 | 3.1839 | 4.6172 |
| 6 | 3.1738 | 0.0001 | 2.2047 | 0.0001 | 3.453278E-02 | 3.1832 | 4.6265 |
| 7 | 3.7737 | 0.0001 | 2.5025 | 0.0001 | 4.859598E-02 | 3.1540 | 4.9490 |
| 8 | 3.7965 | 0.0001 | 2.5139 | 0.0001 | 4.917675E-02 | 3.1529 | 4.9600 |
| 9 | 4.2157 | 0.0001 | 2.7296 | 0.0001 | 6.044153E-02 | 3.1297 | 5.1499 |
| 10 | 4.5700 | 0.0001 | 2.9387 | 0.0001 | 7.084350E-02 | 3.1044 | 5.2923 |
| 11 | 4.7332 | 0.0001 | 3.0566 | 0.0001 | 7.590351E-02 | 3.0888 | 5.3539 |
| 12 | 4.8958 | 0.0001 | 3.2109 | 0.0001 | 8.111445E-02 | 3.0668 | 5.4153 |
| 13 | 5.0301 | 0.0001 | 3.5234 | 0.0001 | 8.555097E-02 | 3.0179 | 5.4896 |
| 14 | 5.0118 | 0.0001 | 3.6541 | 0.0001 | 8.494295E-02 | 2.9963 | 5.5079 |
| 15 | 4.6927 | 0.0001 | 4.1156 | 0.0001 | 7.465689E-02 | 2.9178 | 5.5472 |

Initial Concentration:

TBP 3.66 M

Rare Earths 0.01 M

Table 5.8 The Calculated Distribution Coefficients of
Dysprosium and Composition in Aqueous and Organic Phases.

| Test | (HNO ₃) _{ai} | Kd exp | Kd calc | (HNO ₃) _{at} | (MNO ₃ +2) _a | Deg Ioniz | (NO ₃ -1) _a |
|------|-----------------------------------|----------|----------|-----------------------------------|------------------------------------|-----------|-----------------------------------|
| 1 | 0.30 | 0.0310 | 0.0183 | 0.1656 | 1.320000E-05 | 0.9971 | 0.1651 |
| 2 | 0.78 | 0.0840 | 0.0890 | 0.4238 | 5.713000E-04 | 0.9912 | 0.4201 |
| 3 | 1.09 | 0.1230 | 0.1339 | 0.5865 | 4.632000E-04 | 0.9871 | 0.5790 |
| 4 | 2.05 | 0.2500 | 0.2661 | 1.1179 | 2.608000E-04 | 0.9724 | 1.0870 |
| 5 | 2.64 | 0.3500 | 0.3440 | 1.4652 | 2.254000E-04 | 0.9616 | 1.4088 |
| 6 | 3.67 | 0.5100 | 0.4780 | 2.1094 | 1.584000E-04 | 0.9390 | 1.9807 |
| 7 | 4.90 | 0.6700 | 0.6436 | 2.9346 | 2.126000E-04 | 0.9057 | 2.6576 |
| 8 | 5.90 | 0.8300 | 0.7997 | 3.6484 | 2.548000E-04 | 0.8731 | 3.1850 |
| 9 | 6.84 | 0.9900 | 0.9878 | 4.3489 | 2.915000E-04 | 0.8380 | 3.6439 |
| 10 | 7.78 | 1.1600 | 1.2557 | 5.0721 | 3.241000E-04 | 0.7989 | 4.0516 |
| 11 | 9.54 | 2.3000 | 2.3013 | 6.4684 | 3.708000E-04 | 0.7168 | 4.6357 |
| 12 | 10.50 | 3.7000 | 3.6550 | 7.2441 | 3.872000E-04 | 0.6685 | 4.8412 |
| 13 | 13.10 | 19.5000 | 19.5124 | 9.3600 | 3.985000E-04 | 0.5323 | 4.9813 |
| 14 | 16.60 | 174.0000 | 174.0049 | 12.1299 | 3.486000E-04 | 0.3593 | 4.3576 |

| Test | (H+1) _a | (M+3) _a | (HNO ₃) _o | (M) _o | (M(NO ₃) ₂) _a | (TBP) _o | NOH |
|------|--------------------|--------------------|----------------------------------|------------------|--|--------------------|--------|
| 1 | 0.1705 | 0.0001 | 0.1257 | 0.0100 | 6.814000E-05 | 3.4557 | 1.0000 |
| 2 | 0.4252 | 0.0017 | 0.3477 | 0.0001 | 7.500570E-03 | 3.3771 | 1.2304 |
| 3 | 0.5848 | 0.0010 | 0.4943 | 0.0001 | 8.381020E-03 | 3.3599 | 1.6487 |
| 4 | 1.0936 | 0.0003 | 0.9222 | 0.0001 | 8.861760E-03 | 3.3115 | 2.6486 |
| 5 | 1.4155 | 0.0002 | 1.1648 | 0.0001 | 9.923580E-03 | 3.2854 | 3.1121 |
| 6 | 1.9877 | 0.0001 | 1.5503 | 0.0001 | 9.807930E-03 | 3.2459 | 3.7468 |
| 7 | 2.6726 | 0.0001 | 1.9472 | 0.0001 | 1.765709E-02 | 3.2075 | 4.3062 |
| 8 | 3.2080 | 0.0001 | 2.2256 | 0.0001 | 2.536058E-02 | 3.1812 | 4.6507 |
| 9 | 3.6750 | 0.0001 | 2.4571 | 0.0001 | 3.319501E-02 | 3.1586 | 4.9035 |
| 10 | 4.0908 | 0.0001 | 2.6659 | 0.0001 | 4.103865E-02 | 3.1367 | 5.0978 |
| 11 | 4.6881 | 0.0001 | 3.0169 | 0.0001 | 5.372428E-02 | 3.0941 | 5.3341 |
| 12 | 4.8986 | 0.0001 | 3.1963 | 0.0001 | 5.859304E-02 | 3.0689 | 5.4099 |
| 13 | 5.0420 | 0.0001 | 3.6772 | 0.0001 | 6.203337E-02 | 2.9924 | 5.5104 |
| 14 | 4.4031 | 0.0001 | 4.4221 | 0.0001 | 4.747169E-02 | 2.8644 | 5.5602 |

Initial Concentration:
TBP 3.66 M
Rare Earths 0.01 M

Table 5.9 The Calculated Distribution Coefficients of Gadolinium and Composition in Aqueous and Organic Phases.

| Test | (HNO ₃) _{ai} | Kd exp | Kd calc | (HNO ₃) _{at} | (MNO ₃ +2) _a | Deg Ioniz | (NO ₃ -1) _a |
|------|-----------------------------------|---------|---------|-----------------------------------|------------------------------------|-----------|-----------------------------------|
| 1 | 0.72 | 0.1080 | 0.0859 | 0.3928 | 9.253000E-04 | 0.9920 | 0.3896 |
| 2 | 1.29 | 0.1930 | 0.1661 | 0.6938 | 5.978000E-04 | 0.9847 | 0.6832 |
| 3 | 2.31 | 0.3100 | 0.2891 | 1.2689 | 3.070000E-04 | 0.9680 | 1.2283 |
| 4 | 2.94 | 0.3700 | 0.3562 | 1.6478 | 3.936000E-04 | 0.9556 | 1.5746 |
| 5 | 3.56 | 0.4200 | 0.4172 | 2.0383 | 2.399000E-04 | 0.9417 | 1.9194 |
| 6 | 4.58 | 0.4900 | 0.5073 | 2.7139 | 3.104000E-04 | 0.9150 | 2.4832 |
| 7 | 5.47 | 0.5200 | 0.5764 | 3.3370 | 3.702000E-04 | 0.8876 | 2.9617 |
| 8 | 6.40 | 0.6300 | 0.6418 | 4.0177 | 4.292000E-04 | 0.8547 | 3.4336 |
| 9 | 7.54 | 0.7000 | 0.7275 | 4.8855 | 4.938000E-04 | 0.8088 | 3.9507 |
| 10 | 8.67 | 0.9500 | 0.8763 | 5.7727 | 5.467000E-04 | 0.7579 | 4.3741 |
| 11 | 9.40 | 1.1400 | 1.0725 | 6.3559 | 5.739000E-04 | 0.7226 | 4.5919 |
| 12 | 10.60 | 1.7000 | 1.8033 | 7.3254 | 6.058000E-04 | 0.6618 | 4.8468 |
| 13 | 12.20 | 4.6000 | 4.5619 | 8.6280 | 6.228000E-04 | 0.5777 | 4.9831 |
| 14 | 13.70 | 11.0000 | 11.0097 | 9.8466 | 6.138000E-04 | 0.4989 | 4.9110 |
| 15 | 15.30 | 25.0000 | 25.0022 | 11.1253 | 5.814000E-04 | 0.4182 | 4.6519 |

| Test | (H+1) _a | (M+3) _a | (HNO ₃) _o | (M) _o | (M(NO ₃) ₂) _a | (TBP) _o | NOH |
|------|--------------------|--------------------|----------------------------------|------------------|--|--------------------|--------|
| 1 | 0.3946 | 0.0019 | 0.3189 | 0.0100 | 7.209930E-03 | 3.3805 | 1.1422 |
| 2 | 0.6893 | 0.0007 | 0.5867 | 0.0001 | 8.168330E-03 | 3.3492 | 1.8897 |
| 3 | 1.2350 | 0.0002 | 1.0311 | 0.0001 | 7.543600E-03 | 3.2997 | 2.8647 |
| 4 | 1.5815 | 0.0002 | 1.2821 | 0.0002 | 1.239682E-02 | 3.2731 | 3.3182 |
| 5 | 1.9263 | 0.0001 | 1.5115 | 0.0002 | 9.210240E-03 | 3.2498 | 3.6897 |
| 6 | 2.4960 | 0.0001 | 1.8500 | 0.0001 | 1.541570E-02 | 3.2168 | 4.1767 |
| 7 | 2.9813 | 0.0001 | 2.1103 | 0.0001 | 2.192916E-02 | 3.1921 | 4.5129 |
| 8 | 3.4609 | 0.0001 | 2.3519 | 0.0001 | 2.947402E-02 | 3.1690 | 4.7929 |
| 9 | 3.9880 | 0.0001 | 2.6144 | 0.0001 | 3.902007E-02 | 3.1423 | 5.0532 |
| 10 | 4.4205 | 0.0001 | 2.8483 | 0.0001 | 4.783187E-02 | 3.1157 | 5.2355 |
| 11 | 4.6435 | 0.0001 | 2.9902 | 0.0001 | 5.271386E-02 | 3.0977 | 5.3203 |
| 12 | 4.9046 | 0.0001 | 3.2148 | 0.0001 | 5.872867E-02 | 3.0661 | 5.4160 |
| 13 | 5.0441 | 0.0001 | 3.5090 | 0.0001 | 6.207821E-02 | 3.0202 | 5.4867 |
| 14 | 4.9700 | 0.0001 | 3.7923 | 0.0001 | 6.029480E-02 | 2.9730 | 5.5224 |
| 15 | 4.7043 | 0.0001 | 4.1200 | 0.0001 | 5.410043E-02 | 2.9170 | 5.5472 |

Initial Concentration:
 TBP 3.66 M
 Rare Earths 0.01 M

Table 5.10 The Calculated Distribution Coefficients of Europium and Composition in Aqueous and Organic Phases.

| Test | (HNO ₃) _{ai} | Kd exp | Kd calc | (HNO ₃) _{at} | (MNO ₃ +2) _a | Deg Ioniz | (NO ₃ -1) _a |
|------|-----------------------------------|---------|---------|-----------------------------------|------------------------------------|-----------|-----------------------------------|
| 1 | 0.64 | 0.1050 | 0.1362 | 0.3513 | 9.250000E-04 | 0.9929 | 0.3488 |
| 2 | 1.67 | 0.3000 | 0.2759 | 0.9022 | 3.602000E-04 | 0.9786 | 0.8830 |
| 3 | 2.38 | 0.3900 | 0.3443 | 1.3097 | 2.582000E-04 | 0.9665 | 1.2658 |
| 4 | 3.76 | 0.4900 | 0.4491 | 2.1614 | 4.130000E-04 | 0.9369 | 2.0249 |
| 5 | 5.38 | 0.5300 | 0.5423 | 3.2587 | 5.919000E-04 | 0.0891 | 2.9017 |
| 6 | 6.11 | 0.5400 | 0.5767 | 3.7840 | 6.680000E-04 | 0.8658 | 3.2747 |
| 7 | 6.30 | 0.5400 | 0.5852 | 3.9234 | 6.871000E-04 | 0.8589 | 3.3682 |
| 8 | 7.22 | 0.5800 | 0.6269 | 4.6126 | 7.740000E-04 | 0.8231 | 3.7946 |
| 9 | 7.27 | 0.5900 | 0.6293 | 4.6507 | 7.785000E-04 | 0.8211 | 3.8163 |
| 10 | 8.46 | 0.7300 | 0.7110 | 5.5717 | 8.738000E-04 | 0.7694 | 4.2836 |
| 11 | 8.92 | 0.7600 | 0.7663 | 5.9343 | 9.048000E-04 | 0.7480 | 4.4356 |
| 12 | 9.35 | 0.8900 | 0.8409 | 6.2759 | 9.306000E-04 | 0.7275 | 4.5621 |
| 13 | 10.40 | 1.2600 | 1.1822 | 7.1184 | 9.800000E-04 | 0.6755 | 4.8042 |
| 14 | 12.50 | 3.4000 | 3.4332 | 8.8238 | 1.019400E-03 | 0.5669 | 4.9972 |
| 15 | 16.00 | 19.9000 | 19.8986 | 11.6338 | 9.257000E-04 | 0.3904 | 4.5381 |

| Test | (H+1) _a | (M+3) _a | (HNO ₃) _o | (M) _o | (M(NO ₃) ₂) _a | (TBP) _o | NOH |
|------|--------------------|--------------------|----------------------------------|------------------|--|--------------------|--------|
| 1 | 0.3543 | 0.0013 | 0.2798 | 0.0001 | 7.447900E-03 | 3.3852 | 1.0194 |
| 2 | 0.8900 | 0.0002 | 0.7574 | 0.0003 | 7.343260E-03 | 3.3298 | 2.3002 |
| 3 | 1.2732 | 0.0001 | 1.0596 | 0.0004 | 7.545150E-03 | 3.2966 | 2.9262 |
| 4 | 2.0419 | 0.0001 | 1.5784 | 0.0001 | 1.930834E-02 | 3.2431 | 3.7892 |
| 5 | 2.9403 | 0.0001 | 2.0802 | 0.0001 | 3.964997E-02 | 3.1950 | 4.4761 |
| 6 | 3.3249 | 0.0001 | 2.2738 | 0.0001 | 5.049878E-02 | 3.1766 | 4.7065 |
| 7 | 3.4216 | 0.0001 | 2.3213 | 0.0001 | 5.342366E-02 | 3.1720 | 4.7597 |
| 8 | 3.8635 | 0.0001 | 2.5373 | 0.0001 | 6.780627E-02 | 3.1505 | 4.9826 |
| 9 | 3.8861 | 0.0001 | 2.5484 | 0.0001 | 6.858401E-02 | 3.1493 | 4.9932 |
| 10 | 4.3727 | 0.0001 | 2.7990 | 0.0001 | 8.640835E-02 | 3.1216 | 5.2018 |
| 11 | 4.5316 | 0.0001 | 2.8899 | 0.0001 | 9.264941E-02 | 3.1106 | 5.2629 |
| 12 | 4.6638 | 0.0001 | 2.9729 | 0.0001 | 9.800935E-02 | 3.1000 | 5.3114 |
| 13 | 4.9175 | 0.0001 | 3.1695 | 0.0001 | 1.086876E-01 | 3.0728 | 5.4006 |
| 14 | 5.1198 | 0.0001 | 3.5554 | 0.0001 | 1.175957E-01 | 3.0126 | 5.4944 |
| 15 | 4.6375 | 0.0001 | 4.2672 | 0.0001 | 9.698086E-02 | 2.8915 | 5.5551 |

Initial Concentration:

TBP 3.66 M

Rare Earths 0.01 M

Table 5.11 The Calculated Distribution Coefficients of Samarium and Composition in Aqueous and Organic Phases.

| Test | (HNO ₃) _{ai} | Kd exp | Kd calc | (HNO ₃) _{at} | (MNO ₃ +2) _a | Deg Ioniz | (NO ₃ -1) _a |
|------|-----------------------------------|--------|---------|-----------------------------------|------------------------------------|-----------|-----------------------------------|
| 1 | 0.59 | 0.0770 | 0.0622 | 0.3208 | 8.158000E-04 | 0.9936 | 0.3187 |
| 2 | 1.04 | 0.2100 | 0.1285 | 0.5598 | 1.238700E-03 | 0.9878 | 0.5530 |
| 3 | 2.24 | 0.3800 | 0.2807 | 1.2279 | 7.616000E-04 | 0.9691 | 1.1900 |
| 4 | 3.25 | 0.4200 | 0.3805 | 1.8400 | 5.586000E-04 | 0.9489 | 1.7459 |
| 5 | 4.48 | 0.4400 | 0.4635 | 2.6414 | 7.757000E-04 | 0.9179 | 2.4243 |
| 6 | 5.06 | 0.4560 | 0.4874 | 3.0405 | 8.762000E-04 | 0.9007 | 2.7383 |
| 7 | 5.96 | 0.4500 | 0.5063 | 3.6839 | 1.026200E-03 | 0.8707 | 3.2069 |
| 8 | 7.01 | 0.4600 | 0.5080 | 4.4666 | 1.186700E-03 | 0.8305 | 3.7087 |
| 9 | 7.97 | 0.5000 | 0.5102 | 5.2061 | 1.314500E-03 | 0.7893 | 4.1079 |
| 10 | 9.04 | 0.6000 | 0.5584 | 6.0503 | 1.430200E-03 | 0.7391 | 4.4696 |
| 11 | 10.30 | 0.8300 | 0.7829 | 7.0625 | 1.525900E-03 | 0.6755 | 4.7686 |
| 12 | 11.00 | 1.0800 | 1.0479 | 7.6301 | 1.559400E-03 | 0.6390 | 4.8732 |
| 13 | 11.30 | 1.1600 | 1.2039 | 7.8740 | 1.569500E-03 | 0.6232 | 4.9047 |
| 14 | 13.90 | 4.1000 | 4.1170 | 9.9881 | 1.556700E-03 | 0.4873 | 4.8647 |
| 15 | 15.70 | 8.2000 | 8.1928 | 11.4216 | 1.457600E-03 | 0.3990 | 4.5552 |

| Test | (H+1) _a | (M+3) _a | (HNO ₃) _o | (M) _o | (M(NO ₃) ₂) _a | (TBP) _o | NOH |
|------|--------------------|--------------------|----------------------------------|------------------|--|--------------------|--------|
| 1 | 0.3325 | 0.0008 | 0.2521 | 0.0048 | 2.843950E-03 | 3.3910 | 1.0000 |
| 2 | 0.5591 | 0.0007 | 0.4707 | 0.0001 | 7.492320E-03 | 3.2626 | 1.5847 |
| 3 | 1.1967 | 0.0002 | 1.0020 | 0.0001 | 9.912700E-03 | 3.3028 | 2.8079 |
| 4 | 1.7541 | 0.0001 | 1.3985 | 0.0001 | 1.066858E-02 | 3.2612 | 3.5092 |
| 5 | 2.4430 | 0.0001 | 1.8168 | 0.0001 | 2.057030E-02 | 3.2199 | 4.1315 |
| 6 | 2.7629 | 0.0001 | 1.9919 | 0.0001 | 2.624400E-02 | 3.2033 | 4.3643 |
| 7 | 3.2418 | 0.0001 | 2.2384 | 0.0001 | 3.599472E-02 | 3.1800 | 4.6658 |
| 8 | 3.7565 | 0.0001 | 2.4932 | 0.0001 | 4.814059E-02 | 3.1550 | 4.9399 |
| 9 | 4.1674 | 0.0001 | 2.7025 | 0.0001 | 5.906194E-02 | 3.1327 | 5.1284 |
| 10 | 4.5406 | 0.0001 | 2.9172 | 0.0001 | 6.992063E-02 | 3.1072 | 5.2798 |
| 11 | 4.8498 | 0.0001 | 3.1553 | 0.0001 | 7.958841E-02 | 3.0749 | 5.3956 |
| 12 | 4.9581 | 0.0001 | 3.2843 | 0.0001 | 8.311827E-02 | 3.0558 | 5.4381 |
| 13 | 4.9907 | 0.0001 | 3.3393 | 0.0001 | 8.419628E-02 | 3.0473 | 5.4527 |
| 14 | 4.9488 | 0.0001 | 3.8269 | 0.0001 | 8.282857E-02 | 2.9672 | 5.5261 |
| 15 | 4.6284 | 0.0001 | 4.2040 | 0.0001 | 7.262446E-02 | 2.9025 | 5.5522 |

Initial Concentration:
 TBP 3.66 M
 Rare Earths 0.01 M

Table 5.12 The Calculated Distribution Coefficients of Promethium and Composition in Aqueous and Organic Phases.

| Test | (HNO ₃) _{ai} | Kd exp | Kd calc | (HNO ₃) _{at} | (MNO ₃ +2) _a | Deg Ionz | (NO ₃ -1) _a |
|------|-----------------------------------|--------|---------|-----------------------------------|------------------------------------|----------|-----------------------------------|
| 1 | 0.36 | 0.0530 | 0.0686 | 0.1961 | 4.840000E-05 | 0.9964 | 0.1954 |
| 2 | 0.70 | 0.1270 | 0.1493 | 0.3820 | 1.693600E-03 | 0.9922 | 0.3794 |
| 3 | 1.18 | 0.2200 | 0.2230 | 0.6340 | 1.241100E-03 | 0.9859 | 0.6256 |
| 4 | 2.16 | 0.3100 | 0.3061 | 1.1803 | 8.529000E-04 | 0.9705 | 1.1465 |
| 5 | 2.99 | 0.3600 | 0.3418 | 1.6773 | 3.972000E-04 | 0.9545 | 1.6020 |
| 6 | 4.04 | 0.3900 | 0.3630 | 2.3476 | 5.420000E-04 | 0.9297 | 2.1856 |
| 7 | 5.37 | 0.3600 | 0.3855 | 3.2591 | 7.213000E-04 | 0.8908 | 2.9087 |
| 8 | 6.27 | 0.3400 | 0.3581 | 3.9120 | 8.356000E-04 | 0.8595 | 3.3695 |
| 9 | 7.03 | 0.3300 | 0.3501 | 4.4822 | 9.247000E-04 | 0.8300 | 3.7287 |
| 10 | 7.94 | 0.3300 | 0.3457 | 5.1835 | 1.019500E-03 | 0.7912 | 4.1110 |
| 11 | 9.24 | 0.3700 | 0.3759 | 6.2114 | 1.127600E-03 | 0.7304 | 4.5470 |
| 12 | 10.40 | 0.5300 | 0.4875 | 7.1459 | 1.193300E-03 | 0.6720 | 4.8119 |
| 13 | 10.80 | 0.5700 | 0.5568 | 7.4705 | 1.208900E-03 | 0.6512 | 4.8748 |
| 14 | 13.00 | 1.4100 | 1.4150 | 9.2631 | 1.231200E-03 | 0.5352 | 4.9648 |
| 15 | 15.80 | 4.3000 | 4.2697 | 11.5043 | 1.125100E-03 | 0.3940 | 4.5367 |

| Test | (H+1) _a | (M+3) _a | (HNO ₃) _o | (M) _o | (M(NO ₃) ₂) _a | (TBP) _o | NOH |
|------|--------------------|--------------------|----------------------------------|------------------|--|--------------------|--------|
| 1 | 0.2055 | 0.0001 | 0.1505 | 0.0100 | 9.545000E-05 | 3.4414 | 1.0000 |
| 2 | 0.3845 | 0.0018 | 0.3092 | 0.0001 | 6.477490E-03 | 3.3817 | 1.1121 |
| 3 | 0.6317 | 0.0008 | 0.5361 | 0.0001 | 7.827500E-03 | 3.3551 | 1.7596 |
| 4 | 1.1533 | 0.0003 | 0.9686 | 0.0002 | 9.858460E-03 | 3.3065 | 2.7444 |
| 5 | 1.6091 | 0.0001 | 1.3011 | 0.0003 | 6.416010E-03 | 3.2712 | 3.3535 |
| 6 | 2.1951 | 0.0001 | 1.6764 | 0.0001 | 1.194211E-02 | 3.2335 | 3.9335 |
| 7 | 2.9278 | 0.0001 | 2.0824 | 0.0001 | 2.115133E-02 | 3.1947 | 4.4786 |
| 8 | 3.3962 | 0.0001 | 2.3197 | 0.0001 | 2.838382E-02 | 3.1721 | 4.7576 |
| 9 | 3.7620 | 0.0001 | 2.5008 | 0.0001 | 3.475800E-02 | 3.1542 | 4.9470 |
| 10 | 4.1523 | 0.0001 | 2.6995 | 0.0001 | 4.225080E-02 | 3.1330 | 5.1254 |
| 11 | 4.5981 | 0.0001 | 2.9595 | 0.0001 | 5.168802E-02 | 3.1017 | 5.3035 |
| 12 | 4.8694 | 0.0001 | 3.1777 | 0.0001 | 5.788595E-02 | 3.0716 | 5.4030 |
| 13 | 4.9339 | 0.0001 | 3.2515 | 0.0001 | 5.940918E-02 | 3.0606 | 5.4276 |
| 14 | 5.0259 | 0.0001 | 3.6582 | 0.0001 | 6.162309E-02 | 2.9955 | 5.5078 |
| 15 | 4.5870 | 0.0001 | 4.2313 | 0.0001 | 5.145411E-02 | 2.8977 | 5.5530 |

Initial Concentration:
 TBP 3.66 M
 Rare Earths 0.01 M

Table 5.13 The Calculated Distribution Coefficients of Neodymium and Composition in Aqueous and Organic Phases.

| Test | (HNO ₃) _{ai} | Kd exp | Kd calc | (HNO ₃) _{at} | (MNO ₃ +2) _a | Deg Ioniz | (NO ₃ -1) _a |
|------|-----------------------------------|--------|---------|-----------------------------------|------------------------------------|-----------|-----------------------------------|
| 1 | 0.53 | 0.0500 | 0.0817 | 0.2837 | 2.250000E-05 | 0.9945 | 0.2821 |
| 2 | 0.86 | 0.1580 | 0.1498 | 0.4651 | 9.946000E-04 | 0.9902 | 0.4605 |
| 3 | 1.40 | 0.2300 | 0.2203 | 0.7520 | 7.094000E-04 | 0.9828 | 0.7890 |
| 4 | 2.36 | 0.2900 | 0.2811 | 1.2950 | 4.007000E-04 | 0.9670 | 1.2523 |
| 5 | 3.12 | 0.3200 | 0.3003 | 1.7550 | 2.672000E-04 | 0.9518 | 1.6704 |
| 6 | 4.47 | 0.3300 | 0.3048 | 2.6364 | 1.936000E-04 | 0.9184 | 2.4212 |
| 7 | 5.31 | 0.2800 | 0.2964 | 3.2219 | 2.302000E-04 | 0.8932 | 2.8780 |
| 8 | 6.22 | 0.2400 | 0.2817 | 3.8846 | 2.679000E-04 | 0.8622 | 3.3490 |
| 9 | 7.16 | 0.2400 | 0.2642 | 4.5948 | 3.036000E-04 | 0.8260 | 3.7950 |
| 10 | 8.09 | 0.2400 | 0.2503 | 5.3175 | 3.345000E-04 | 0.7864 | 4.1815 |
| 11 | 9.53 | 0.2700 | 0.2565 | 6.4643 | 3.718000E-04 | 0.7191 | 4.6476 |
| 12 | 10.60 | 0.3300 | 0.3100 | 7.3319 | 3.901000E-04 | 0.6653 | 4.8772 |
| 13 | 11.40 | 0.4200 | 0.3968 | 7.9838 | 3.984000E-04 | 0.6240 | 4.9810 |
| 14 | 12.40 | 0.5800 | 0.5855 | 8.7990 | 4.024000E-04 | 0.5719 | 5.0311 |
| 15 | 13.20 | 0.8500 | 0.8187 | 9.4491 | 4.008000E-04 | 0.5303 | 5.0104 |
| 16 | 14.30 | 1.2500 | 1.2834 | 10.3383 | 3.919000E-04 | 0.4739 | 4.8988 |
| 17 | 15.10 | 1.7000 | 1.7330 | 10.9764 | 3.810000E-04 | 0.4340 | 4.7634 |
| 18 | 15.90 | 2.3000 | 2.2700 | 11.6032 | 3.670000E-04 | 0.3955 | 4.5887 |

| Test | (H+1) _a | (M+3) _a | (HNO ₃) _o | (M) _o | (M(NO ₃) ₂) _a | (TBP) _o | NOH |
|------|--------------------|--------------------|----------------------------------|------------------|--|--------------------|--------|
| 1 | 0.3052 | 0.0001 | 0.2199 | 0.0100 | 7.181000E-05 | 3.4015 | 1.0000 |
| 2 | 0.4665 | 0.0027 | 0.3856 | 0.0001 | 5.166970E-03 | 3.3726 | 1.3564 |
| 3 | 0.7482 | 0.0012 | 0.6355 | 0.0019 | 5.914030E-03 | 3.3436 | 2.0452 |
| 4 | 1.2646 | 0.0004 | 1.0493 | 0.0030 | 5.660980E-03 | 3.2977 | 2.9712 |
| 5 | 1.6842 | 0.0002 | 1.3478 | 0.0037 | 5.035980E-03 | 3.2664 | 3.5237 |
| 6 | 2.4371 | 0.0001 | 1.8144 | 0.0046 | 5.290230E-03 | 3.2202 | 4.2582 |
| 7 | 2.8974 | 0.0001 | 2.0653 | 0.0050 | 7.474720E-03 | 3.1963 | 4.6036 |
| 8 | 3.3737 | 0.0001 | 2.3075 | 0.0058 | 1.012147E-02 | 3.1732 | 4.9171 |
| 9 | 2.8262 | 0.0001 | 2.5309 | 0.0070 | 1.299681E-02 | 3.1509 | 5.1849 |
| 10 | 4.2196 | 0.0001 | 2.7314 | 0.0083 | 1.577893E-02 | 3.1291 | 5.3974 |
| 11 | 4.6949 | 0.0001 | 3.0157 | 0.0010 | 1.949265E-02 | 3.0937 | 5.6230 |
| 12 | 4.9265 | 0.0001 | 3.2161 | 0.0010 | 2.146617E-02 | 3.0652 | 5.6938 |
| 13 | 5.0313 | 0.0001 | 3.3634 | 0.0010 | 2.238961E-02 | 3.0426 | 5.7258 |
| 14 | 5.0818 | 0.0001 | 3.5478 | 0.0010 | 2.284227E-02 | 3.0129 | 5.7496 |
| 15 | 5.0607 | 0.0001 | 3.6980 | 0.0010 | 2.265470E-02 | 2.9881 | 5.7609 |
| 16 | 4.9446 | 0.0001 | 3.9132 | 0.0089 | 2.165673E-02 | 2.9518 | 5.7416 |
| 17 | 4.8048 | 0.0001 | 4.0793 | 0.0078 | 2.047611E-02 | 2.9235 | 5.7215 |
| 18 | 4.6253 | 0.0001 | 4.2672 | 0.0068 | 1.900171E-02 | 2.8929 | 5.7007 |

Initial Concentration:

TBP 3.66 M

Rare Earths 0.01 M

Table 5.14 The Calculated Distribution Coefficients of Praseodymium and Composition in Aqueous and Organic Phases.

| Test | (HNO ₃) _{ai} | K _d exp | K _d calc | (HNO ₃) _{at} | (MNO ₃ +2) _a | Deg Ioniz | (NO ₃ -1) _a |
|------|-----------------------------------|--------------------|---------------------|-----------------------------------|------------------------------------|-----------|-----------------------------------|
| 1 | 0.34 | 0.0410 | 0.0438 | 0.1859 | 3.140000E-05 | 0.9967 | 0.1852 |
| 2 | 1.38 | 0.1640 | 0.1597 | 0.7419 | 6.193000E-04 | 0.9831 | 0.7294 |
| 3 | 2.58 | 0.2000 | 0.2033 | 1.4277 | 2.334000E-04 | 0.9629 | 1.3748 |
| 4 | 3.20 | 0.2200 | 0.2101 | 1.8079 | 2.917000E-04 | 0.9502 | 1.7178 |
| 5 | 4.13 | 0.2000 | 0.2082 | 2.4080 | 3.793000E-04 | 0.9278 | 2.2339 |
| 6 | 5.20 | 0.1910 | 0.1939 | 3.1404 | 4.782000E-04 | 0.8969 | 2.8164 |
| 7 | 6.16 | 0.1670 | 0.1762 | 3.8328 | 5.627000E-04 | 0.8647 | 3.3137 |
| 8 | 7.23 | 0.1520 | 0.1543 | 4.6372 | 6.483000E-04 | 0.8236 | 3.8179 |
| 9 | 8.54 | 0.1460 | 0.1414 | 5.6571 | 7.359000E-04 | 0.7664 | 4.3340 |
| 10 | 9.12 | 0.1590 | 0.1447 | 6.1177 | 7.675000E-04 | 0.7392 | 4.5199 |
| 11 | 10.00 | 0.1750 | 0.1654 | 6.8238 | 9.061000E-04 | 0.6961 | 4.7473 |
| 12 | 12.40 | 0.3300 | 0.3539 | 8.7731 | 8.526000E-04 | 0.5727 | 5.0209 |
| 13 | 15.10 | 0.8300 | 0.8225 | 10.9514 | 8.096000E-04 | 0.4356 | 4.7675 |

| Test | (H+1) _a | (M+3) _a | (HNO ₃) _o | (M) _o | (M(NO ₃) ₂) _a | (TBP) _o | NOH |
|------|--------------------|--------------------|----------------------------------|------------------|--|--------------------|--------|
| 1 | 0.1938 | 0.0001 | 0.1422 | 0.0100 | 1.112900E-04 | 3.4462 | 1.0000 |
| 2 | 0.7370 | 0.0005 | 0.6272 | 0.0007 | 8.631580E-03 | 3.3446 | 2.0016 |
| 3 | 1.3838 | 0.0001 | 1.1399 | 0.0013 | 6.132910E-03 | 3.2880 | 3.0961 |
| 4 | 1.7271 | 0.0001 | 1.3795 | 0.0009 | 9.574870E-03 | 3.2631 | 3.5001 |
| 5 | 2.2477 | 0.0001 | 1.7050 | 0.0001 | 1.619255E-02 | 3.2307 | 3.9746 |
| 6 | 2.8401 | 0.0001 | 2.0329 | 0.0001 | 2.573810E-02 | 3.1994 | 4.4161 |
| 7 | 3.3479 | 0.0001 | 2.2902 | 0.0001 | 3.562987E-02 | 3.1749 | 4.7238 |
| 8 | 3.8647 | 0.0001 | 2.5439 | 0.0001 | 4.729737E-02 | 3.1495 | 4.9862 |
| 9 | 4.3955 | 0.0001 | 2.8199 | 0.0001 | 6.094888E-02 | 3.1186 | 5.2114 |
| 10 | 4.5872 | 0.0001 | 2.9339 | 0.0001 | 6.628962E-02 | 3.1044 | 5.2830 |
| 11 | 4.8219 | 0.0001 | 3.1008 | 0.0001 | 7.312759E-02 | 3.0818 | 5.3653 |
| 12 | 5.1046 | 0.0001 | 3.5430 | 0.0001 | 8.179958E-02 | 3.0136 | 5.4835 |
| 13 | 4.8420 | 0.0001 | 4.0732 | 0.0001 | 7.375124E-02 | 2.9244 | 5.5397 |

Initial Concentration:
 TBP 3.66 M
 Rare Earths 0.01 M

Table 5.15 The Calculated Distribution Coefficients of Cerium and Composition in Aqueous and Organic Phases.

| Test | (HNO ₃) _{ai} | Kd exp | Kd calc | (HNO ₃) _{at} | (MNO ₃ +2) _a | Deg Ioniz | (NO ₃ -1) _a |
|------|-----------------------------------|--------|---------|-----------------------------------|------------------------------------|-----------|-----------------------------------|
| 1 | 0.27 | 0.0280 | 0.0295 | 0.1504 | 2.440000E-05 | 0.9974 | 0.1500 |
| 2 | 0.72 | 0.0990 | 0.0990 | 0.3915 | 1.202600E-03 | 0.9919 | 0.3883 |
| 3 | 0.98 | 0.1230 | 0.1241 | 0.5263 | 9.328000E-04 | 0.9886 | 0.5203 |
| 4 | 1.82 | 0.1680 | 0.1642 | 0.9830 | 4.692000E-04 | 0.9764 | 0.9597 |
| 5 | 2.38 | 0.1720 | 0.1725 | 1.3054 | 4.113000E-04 | 0.9667 | 1.2619 |
| 6 | 3.64 | 0.1690 | 0.1664 | 2.0812 | 3.188000E-04 | 0.9399 | 1.9561 |
| 7 | 5.20 | 0.1330 | 0.1371 | 3.1282 | 4.567000E-04 | 0.8959 | 2.8020 |
| 8 | 6.00 | 0.1100 | 0.1192 | 3.7037 | 5.234000E-04 | 0.8673 | 3.2113 |
| 9 | 6.85 | 0.0980 | 0.1018 | 4.3390 | 5.880000E-04 | 0.8319 | 3.6077 |
| 10 | 8.15 | 0.0900 | 0.0856 | 5.3459 | 6.687000E-04 | 0.7682 | 4.1030 |
| 11 | 8.95 | 0.0960 | 0.0856 | 5.9814 | 7.056000E-03 | 0.7245 | 4.3292 |
| 12 | 9.88 | 0.1080 | 0.0981 | 6.7304 | 7.360000E-04 | 0.6717 | 4.5155 |
| 13 | 11.30 | 0.1330 | 0.1455 | 7.8860 | 7.589000E-04 | 0.5912 | 4.6562 |
| 14 | 13.90 | 0.2800 | 0.3144 | 10.0012 | 7.439000E-04 | 0.4568 | 4.5640 |
| 15 | 15.00 | 0.4200 | 0.4067 | 10.8802 | 7.206000E-04 | 0.4067 | 4.4212 |

| Test | (H+1) _a | (M+3) _a | (HNO ₃) _o | (M) _o | (M(NO ₃) ₂) _a | (TBP) _o | NOH |
|------|--------------------|--------------------|----------------------------------|------------------|--|--------------------|--------|
| 1 | 0.1530 | 0.0001 | 0.1133 | 0.0100 | 4.300000E-05 | 3.4628 | 1.0000 |
| 2 | 0.3959 | 0.0019 | 0.3176 | 0.0140 | 5.475700E-03 | 3.3807 | 1.1546 |
| 3 | 0.5298 | 0.0011 | 0.4409 | 0.0020 | 5.691830E-03 | 3.3661 | 1.5316 |
| 4 | 0.9730 | 0.0003 | 0.8205 | 0.0034 | 5.281330E-03 | 3.3228 | 2.5098 |
| 5 | 1.2766 | 0.0002 | 1.0565 | 0.0041 | 6.087390E-03 | 3.2969 | 3.0129 |
| 6 | 1.9766 | 0.0001 | 1.5351 | 0.0054 | 7.313640E-03 | 3.2474 | 3.8718 |
| 7 | 2.8431 | 0.0001 | 2.0279 | 0.0094 | 1.500679E-02 | 3.1996 | 4.6915 |
| 8 | 3.2598 | 0.0001 | 2.2455 | 0.0100 | 1.971121E-02 | 3.1785 | 4.9733 |
| 9 | 3.6626 | 0.0001 | 2.4547 | 0.0100 | 2.487782E-02 | 3.1572 | 5.1913 |
| 10 | 4.1672 | 0.0001 | 2.7400 | 0.0100 | 3.217767E-02 | 3.1247 | 5.4221 |
| 11 | 4.3980 | 0.0001 | 2.9008 | 0.0100 | 3.582340E-02 | 3.1040 | 5.5148 |
| 12 | 4.5880 | 0.0001 | 3.0789 | 0.0100 | 3.897294E-02 | 3.0791 | 5.5888 |
| 13 | 4.7309 | 0.0001 | 3.3416 | 0.0100 | 4.143953E-02 | 3.0393 | 5.6575 |
| 14 | 4.6348 | 0.0001 | 3.8291 | 0.0100 | 3.981464E-02 | 2.9609 | 5.7225 |
| 15 | 4.4886 | 0.0001 | 4.0626 | 0.0100 | 3.736215E-02 | 2.9241 | 5.7409 |

Initial Concentration:

TBP 3.66 M

Rare Earths 0.01 M

Table 5.16 The Calculated Distribution Coefficients of Lanthanum and Composition in Aqueous and Organic Phases.

| Test | (HNO ₃) _{ai} | Kd exp | Kd calc | (HNO ₃) _{at} | (MNO ₃ +2) _a | Deg Ioniz | (NO ₃ -1) _a |
|------|-----------------------------------|--------|---------|-----------------------------------|------------------------------------|-----------|-----------------------------------|
| 1 | 0.63 | 0.0740 | 0.0731 | 0.3472 | 1.599000E-03 | 0.9930 | 0.3448 |
| 2 | 1.21 | 0.1080 | 0.1098 | 0.6505 | 1.238700E-03 | 0.9855 | 0.6411 |
| 3 | 2.15 | 0.1230 | 0.1235 | 1.1748 | 7.344000E-04 | 0.9708 | 1.1403 |
| 4 | 3.17 | 0.1240 | 0.1184 | 1.7889 | 4.381000E-04 | 0.9507 | 1.7007 |
| 5 | 4.27 | 0.1020 | 0.1054 | 2.5041 | 2.979000E-04 | 0.9238 | 2.3132 |
| 6 | 6.10 | 0.0760 | 0.0794 | 3.8044 | 4.245000E-04 | 0.8663 | 3.2957 |
| 7 | 8.05 | 0.0570 | 0.0563 | 5.3028 | 5.384000E-04 | 0.7883 | 4.1802 |
| 8 | 10.20 | 0.0600 | 0.0539 | 7.0274 | 6.219000E-04 | 0.6871 | 4.8280 |
| 9 | 13.80 | 0.1420 | 0.1511 | 9.9539 | 6.433000E-04 | 0.5018 | 4.9945 |
| 10 | 15.00 | 0.2200 | 0.2122 | 10.9121 | 6.199000E-04 | 0.4410 | 4.8122 |

| Test | (H+1) _a | (M+3) _a | (HNO ₃) _o | (M) _o | (M(NO ₃) ₂) _a | (TBP) _o | NOH |
|------|--------------------|--------------------|----------------------------------|------------------|--|--------------------|--------|
| 1 | 0.3483 | 0.0036 | 0.2760 | 0.0002 | 4.607340E-03 | 3.3856 | 1.0083 |
| 2 | 0.6474 | 0.0015 | 0.5498 | 0.0006 | 6.636770E-03 | 3.3535 | 1.8039 |
| 3 | 1.1486 | 0.0005 | 0.9637 | 0.0011 | 6.998770E-03 | 3.3070 | 2.7561 |
| 4 | 1.7103 | 0.0002 | 1.3682 | 0.0016 | 6.227290E-03 | 3.2643 | 3.5001 |
| 5 | 2.3238 | 0.0001 | 1.7519 | 0.0021 | 5.760230E-03 | 3.2262 | 4.0966 |
| 6 | 3.3079 | 0.0001 | 2.2801 | 0.0011 | 1.169255E-02 | 3.1759 | 4.7430 |
| 7 | 4.1967 | 0.0001 | 2.7275 | 0.0001 | 1.881083E-02 | 3.1298 | 5.1469 |
| 8 | 4.8510 | 0.0001 | 3.1466 | 0.0001 | 2.509276E-02 | 3.0759 | 5.3899 |
| 9 | 5.0193 | 0.0001 | 3.8184 | 0.0001 | 2.685332E-02 | 2.9684 | 5.5237 |
| 10 | 4.8349 | 0.0001 | 4.0621 | 0.0001 | 2.492879E-02 | 2.9269 | 5.5430 |

Initial Concentration:
 TBP 3.66 M
 Rare Earths 0.01 M

Table 5.18 The Effect of Number of Stages on Promethium Extraction HNO₃, 12.0 N.

| % OF PROMETHIUM EXTRACTED | | | |
|---------------------------|---------|---------|---------|
| STAGE | CASE A | CASE B | CASE C |
| 20 | 84,3153 | 94,3653 | 98,6706 |
| 25 | 87,5117 | 96,4835 | 99,3876 |
| 30 | 91,7250 | 98,3318 | 99,8110 |
| 35 | 93,6251 | 98,9834 | 99,9137 |
| 40 | 95,8179 | 99,5211 | 99,9734 |
| 45 | 96,8249 | 99,7099 | 99,9879 |
| 50 | 97,9270 | 99,8636 | 99,9963 |
| 55 | 98,4362 | 99,9175 | 99,9983 |
| 60 | 98,9811 | 99,9612 | 99,9995 |

Feed 12.0 N HNO₃ 0.5 l/h, center feed
 Rare Earth in feed 25.0 g/l
 Solvent TBP equilibrated with 12.0 N HNO₃
 case a: 15.73 l/h
 case b: 17.52 l/h
 case c: 20.14 l/h
 Scrub 12.0 N HNO₃, 14.5 l/h

Table 5.19 The Effect of Number of Stages on Promethium Extraction HNO₃, 13.0 N.

| % OF PROMETHIUM EXTRACTED | | | |
|---------------------------|---------|---------|---------|
| STAGE | CASE A | CASE B | CASE C |
| 20 | 78,6974 | 92,0872 | 98,8533 |
| 25 | 81,6161 | 94,6407 | 99,4827 |
| 30 | 86,3914 | 97,1537 | 99,8451 |
| 35 | 88,6171 | 98,1258 | 99,9307 |
| 40 | 91,6375 | 99,0132 | 99,9793 |
| 45 | 93,1176 | 99,3558 | 99,9908 |
| 50 | 94,9677 | 99,6617 | 99,9972 |
| 55 | 95,8932 | 99,7798 | 99,9988 |
| 60 | 97,0048 | 99,8844 | 99,9996 |

Feed 13.0 N HNO₃ 0.5 l/h, center feed
 Rare Earth in feed 25.0 g/l
 Solvent TBP equilibrated with 12.0 N HNO₃
 case a: 9.99 l/h
 case b: 11.14 l/h
 case c: 13.43 l/h
 Scrub 13.0 N HNO₃, 14.5 l/h

Table 6.5 The Effect of Number of Stages on Europium Purification, HNO_3 9.8 N, TBP 2.5 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 42 | 80.5147 | 96.2548 |
| 48 | 81.5966 | 97.9642 |
| 54 | 82.4452 | 98.8972 |
| 60 | 83.1223 | 99.4034 |
| 66 | 83.6700 | 99.6774 |
| 72 | 84.1183 | 99.8255 |
| 78 | 84.4887 | 99.9056 |
| 84 | 84.7973 | 99.9489 |
| 90 | 85.0560 | 99.9723 |
| 96 | 85.2742 | 99.9850 |
| 102 | 85.4591 | 99.9919 |
| 108 | 85.6163 | 99.9956 |
| 114 | 85.7505 | 99.9976 |
| 120 | 85.8654 | 99.9987 |
| 126 | 85.9640 | 99.9993 |
| 132 | 86.0489 | 99.9996 |

Feed 9.8 N HNO_3 1.0 l/h, center feed
 Rare Earth in feed 100.0 g/l
 Solvent TBP 2.5 l/h, equilibrated with 9.8 N HNO_3
 Scrub 9.8 N HNO_3 , 2.0 l/h

Table 6.6 The Effect of Number of Stages on Europium Purification, HNO₃ 9.8 N, TBP 2.6 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 42 | 87.1070 | 93.2620 |
| 48 | 88.3687 | 95.8596 |
| 54 | 89.3841 | 97.4679 |
| 60 | 90.2185 | 98.4556 |
| 66 | 90.9161 | 99.0593 |
| 72 | 91.5079 | 99.4274 |
| 78 | 92.0161 | 99.6515 |
| 84 | 92.4573 | 99.7879 |
| 90 | 92.8438 | 99.8709 |
| 96 | 93.1851 | 99.9214 |
| 102 | 93.4886 | 99.9521 |
| 108 | 93.7603 | 99.9708 |
| 114 | 94.0048 | 99.9822 |
| 120 | 94.2260 | 99.9892 |
| 126 | 94.4271 | 99.9934 |
| 132 | 94.6106 | 99.9960 |

Feed 9.8 N HNO₃ 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.6 l/h, equilibrated with 9.8 N HNO₃
Scrub 9.8 N HNO₃, 2.0 l/h

Table 6.7 The Effect of Number of Stages on Europium Purification, HNO₃ 9.9 N, TBP 2.2 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 42 | 69.3182 | 98.6852 |
| 48 | 69.9696 | 99.4156 |
| 54 | 70.4379 | 99.7405 |
| 60 | 70.7774 | 99.8847 |
| 66 | 71.0240 | 99.9488 |
| 72 | 71.2050 | 99.9772 |
| 78 | 71.3373 | 99.9899 |
| 84 | 71.4346 | 99.9955 |
| 90 | 71.5062 | 99.9980 |
| 96 | 71.5590 | 99.9991 |
| 102 | 71.5980 | 99.9996 |
| 108 | 71.6268 | 99.9998 |
| 114 | 71.6481 | 99.9999 |
| 120 | 71.6638 | 99.9999 |
| 126 | 71.6755 | 99.9999 |
| 132 | 71.6842 | 99.9999 |

Feed 9.9 N HNO₃ 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.2 l/h, equilibrated with 9.9 N HNO₃
Scrub 9.9 N HNO₃, 2.0 l/h

Table 6.8 The Effect of Number of Stages on Europium Purification, HNO_3 9.9 N, TBP 2.3 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 42 | 78.6484 | 97.3731 |
| 48 | 79.6610 | 98.6644 |
| 54 | 80.4461 | 99.3225 |
| 60 | 81.0641 | 99.6566 |
| 66 | 81.5567 | 99.8259 |
| 72 | 81.9536 | 99.9117 |
| 78 | 82.2760 | 99.9552 |
| 84 | 82.5397 | 99.9772 |
| 90 | 82.7567 | 99.9884 |
| 96 | 82.9361 | 99.9941 |
| 102 | 83.0850 | 99.9970 |
| 108 | 83.2089 | 99.9985 |
| 114 | 83.3125 | 99.9992 |
| 120 | 83.3992 | 99.9996 |
| 126 | 83.4720 | 99.9998 |
| 132 | 83.5330 | 99.9999 |

Feed 9.9 N HNO_3 1.0 l/h, center feed
 Rare Earth in feed 100.0 g/l
 Solvent TBP 2.3 l/h, equilibrated with 9.9 N HNO_3
 Scrub 9.9 N HNO_3 , 2.0 l/h

Table 6.9 The Effect of Number of Stages on Europium Purification, HNO_3 9.9 N, TBP 2.4 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 42 | 86.1331 | 94.9434 |
| 48 | 87.3786 | 97.0659 |
| 54 | 88.3796 | 98.3045 |
| 60 | 89.2008 | 99.0222 |
| 66 | 89.8861 | 99.4366 |
| 72 | 90.4661 | 99.6754 |
| 78 | 90.9631 | 99.8130 |
| 84 | 91.3933 | 99.8922 |
| 90 | 91.7692 | 99.9379 |
| 96 | 92.1001 | 99.9642 |
| 102 | 92.3935 | 99.9793 |
| 108 | 92.6551 | 99.9881 |
| 114 | 92.8898 | 99.9931 |
| 120 | 93.1013 | 99.9960 |
| 126 | 93.2927 | 99.9977 |
| 132 | 93.4667 | 99.9987 |

Feed 9.9 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.4 l/h, equilibrated with 9.9 N HNO_3
Scrub 9.9 N HNO_3 , 2.0 l/h

Table 6.10 The Effect of Number of Stages on Europium Purification, HNO₃ 9.9 N, TBP 2.5 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 42 | 91.5676 | 90.7664 |
| 48 | 92.8117 | 93.9040 |
| 54 | 93.8024 | 95.9945 |
| 60 | 94.6074 | 97.3761 |
| 66 | 95.2724 | 98.2843 |
| 72 | 95.8294 | 98.8795 |
| 78 | 96.3012 | 99.2686 |
| 84 | 96.7048 | 99.5228 |
| 90 | 97.0529 | 99.6886 |
| 96 | 97.3554 | 99.7968 |
| 102 | 97.6199 | 99.8674 |
| 108 | 97.8523 | 99.9135 |
| 114 | 98.0577 | 99.9435 |
| 120 | 98.2398 | 99.9631 |
| 126 | 98.4020 | 99.9759 |
| 132 | 98.5469 | 99.9843 |

Feed 9.9 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 100.0 g/l
 Solvent TBP 2.5 l/h, equilibrated with 9.9 N HNO₃
 Scrub 9.9 N HNO₃, 2.0 l/h

Table 6.11 The Effect of Number of Stages on Europium Purification, HNO₃ 10.0 N, TBP 2.1 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 42 | 75.0876 | 98.3907 |
| 48 | 75.9616 | 99.2526 |
| 54 | 76.6220 | 99.6532 |
| 60 | 77.1267 | 99.8391 |
| 66 | 77.5164 | 99.9253 |
| 72 | 77.8196 | 99.9653 |
| 78 | 78.0571 | 99.9839 |
| 84 | 78.2440 | 99.9925 |
| 90 | 78.3917 | 99.9965 |
| 96 | 78.5089 | 99.9984 |
| 102 | 78.6021 | 99.9992 |
| 108 | 78.6976 | 99.9995 |
| 114 | 78.7356 | 99.9998 |
| 120 | 78.7830 | 99.9999 |
| 126 | 78.8209 | 99.9999 |
| 132 | 78.8512 | 99.9999 |

Feed 10.0 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 100.0 g/l
 Solvent TBP 2.1 l/h, equilibrated with 10.0 N HNO₃
 Scrub 10.0 N HNO₃, 2.0 l/h

Table 6.12 The Effect of Number of Stages on Europium Purification, HNO₃ 10.0 N, TBP 2.2 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 42 | 83.9143 | 96.6536 |
| 48 | 85.1071 | 98.2080 |
| 54 | 86.0594 | 99.0432 |
| 60 | 86.8346 | 99.4897 |
| 66 | 87.4759 | 99.7278 |
| 72 | 88.0135 | 99.8548 |
| 78 | 88.4694 | 99.9225 |
| 84 | 88.8597 | 99.9586 |
| 90 | 89.1967 | 99.9779 |
| 96 | 89.4896 | 99.9882 |
| 102 | 89.7458 | 99.9937 |
| 108 | 90.0402 | 99.9958 |
| 114 | 90.1703 | 99.9982 |
| 120 | 90.3470 | 99.9990 |
| 126 | 90.5044 | 99.9995 |
| 132 | 90.6452 | 99.9997 |

Feed 10.0 N HNO₃ 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.2 l/h, equilibrated with 10.0 N HNO₃
Scrub 10.0 N HNO₃, 2.0 l/h

Table 6.13 The Effect of Number of Stages on Europium Purification, HNO₃ 10.0 N, TBP 2.3 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 42 | 90.3969 | 93.3760 |
| 48 | 91.6635 | 95.9195 |
| 54 | 92.6786 | 97.4977 |
| 60 | 93.5093 | 98.4693 |
| 66 | 94.2008 | 99.0649 |
| 72 | 94.7847 | 99.4291 |
| 78 | 95.2837 | 99.6515 |
| 84 | 95.7145 | 99.7873 |
| 90 | 96.0899 | 99.8701 |
| 96 | 96.4194 | 99.9207 |
| 102 | 96.7106 | 99.9516 |
| 108 | 97.0495 | 99.9652 |
| 114 | 97.2010 | 99.9819 |
| 120 | 97.4090 | 99.9889 |
| 126 | 97.5966 | 99.9932 |
| 132 | 97.7663 | 99.9959 |

Feed 10.0 N HNO₃ 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.3 l/h, equilibrated with 10.0 N HNO₃
Scrub 10.0 N HNO₃, 2.0 l/h

Table 6.14 The Effect of Number of Stages on Europium Purification, HNO₃ 10.1 N, TBP 2.0 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 42 | 76.1591 | 98.5175 |
| 48 | 77.0755 | 99.3197 |
| 54 | 77.7738 | 99.6881 |
| 60 | 78.3127 | 99.8569 |
| 66 | 78.7331 | 99.9343 |
| 72 | 79.0639 | 99.9698 |
| 78 | 79.3260 | 99.9861 |
| 84 | 79.5349 | 99.9936 |
| 90 | 79.7021 | 99.9971 |
| 96 | 79.8365 | 99.9986 |
| 102 | 79.9448 | 99.9994 |
| 108 | 80.0323 | 99.9997 |
| 114 | 80.1031 | 99.9999 |
| 120 | 80.1606 | 99.9999 |
| 126 | 80.2073 | 99.9999 |
| 132 | 80.2452 | 99.9999 |

Feed 10.1 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 100.0 g/l
 Solvent TBP 2.0 l/h, equilibrated with 10.1 N HNO₃
 Scrub 10.1 N HNO₃, 2.0 l/h

Table 6.15 The Effect of Number of Stages on Europium Purification, HNO₃ 10.1 N, TBP 2.1 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 42 | 85.1513 | 96.7813 |
| 48 | 86.3758 | 98.2850 |
| 54 | 87.3578 | 99.0887 |
| 60 | 88.1613 | 99.5163 |
| 66 | 88.8297 | 99.7432 |
| 72 | 89.3936 | 99.8636 |
| 78 | 89.8750 | 99.9276 |
| 84 | 90.2900 | 99.9615 |
| 90 | 90.6511 | 99.9795 |
| 96 | 90.9675 | 99.9891 |
| 102 | 91.2466 | 99.9942 |
| 108 | 91.4943 | 99.9969 |
| 114 | 91.7153 | 99.9984 |
| 120 | 91.9133 | 99.9991 |
| 126 | 92.0915 | 99.9995 |
| 132 | 92.2523 | 99.9998 |

Feed 10.1 N HNO₃ 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.1 l/h, equilibrated with 10.1 N HNO₃
Scrub 10.1 N HNO₃, 2.0 l/h

Table 6.16 The Effect of Number of Stages on Europium Purification, HNO_3 10.1 N, TBP 2.2 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 42 | 91.5144 | 93.3810 |
| 48 | 92.7591 | 95.9144 |
| 54 | 93.7508 | 97.4893 |
| 60 | 94.5570 | 98.4609 |
| 66 | 95.2234 | 99.0578 |
| 72 | 95.7819 | 99.4235 |
| 78 | 96.2553 | 99.6474 |
| 84 | 96.6605 | 99.7843 |
| 90 | 97.0103 | 99.8680 |
| 96 | 97.3144 | 99.9192 |
| 102 | 97.5805 | 99.9506 |
| 108 | 97.8145 | 99.9697 |
| 114 | 98.0214 | 99.9815 |
| 120 | 98.2050 | 99.9887 |
| 126 | 98.3686 | 99.9930 |
| 132 | 98.5149 | 99.9957 |

Feed 10.1 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.2 l/h, equilibrated with 10.1 N HNO_3
Scrub 10.1 N HNO_3 , 2.0 l/h

Table 6.17 The Effect of Number of Stages on Europium Purification, HNO₃ 10.2 N, TBP 1.9 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 42 | 80.3717 | 98.3238 |
| 48 | 81.4497 | 99.2093 |
| 54 | 82.2953 | 99.6274 |
| 60 | 82.9698 | 99.8244 |
| 66 | 83.5154 | 99.9171 |
| 72 | 83.9618 | 99.9609 |
| 78 | 84.3305 | 99.9815 |
| 84 | 84.6375 | 99.9913 |
| 90 | 84.8947 | 99.9959 |
| 96 | 85.1114 | 99.9980 |
| 102 | 85.2949 | 99.9991 |
| 108 | 85.4509 | 99.9996 |
| 114 | 85.5839 | 99.9998 |
| 120 | 85.6977 | 99.9999 |
| 126 | 85.7953 | 99.9999 |
| 132 | 85.8792 | 99.9999 |

Feed 10.2 N HNO₃ 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 1.9 l/h, equilibrated with 10.2 N HNO₃
Scrub 10.2 N HNO₃, 2.0 l/h

Table 6.18 The Effect of Number of Stages on Europium Purification, HNO₃ 10.2 N, TBP 2.0 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 42 | 88.7225 | 96.1836 |
| 48 | 89.9968 | 97.8896 |
| 54 | 91.0229 | 98.8367 |
| 60 | 91.8666 | 99.3596 |
| 66 | 92.5725 | 99.6475 |
| 72 | 93.1717 | 99.8060 |
| 78 | 93.6868 | 99.8932 |
| 84 | 94.1342 | 99.9412 |
| 90 | 94.5265 | 99.9678 |
| 96 | 94.8732 | 99.9821 |
| 102 | 95.1818 | 99.9901 |
| 108 | 95.4582 | 99.9946 |
| 114 | 95.7073 | 99.9970 |
| 120 | 95.9328 | 99.9983 |
| 126 | 96.1379 | 99.9991 |
| 132 | 96.3254 | 99.9995 |

Feed 10.2 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 100.0 g/l
 Solvent TBP 2.0 l/h, equilibrated with 10.2 N HNO₃
 Scrub 10.2 N HNO₃, 2.0 l/h

Table 6.19 The Effect of Number of Stages on Europium Purification, HNO₃ 10.2 N, TBP 2.1 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 42 | 94.0916 | 91.8975 |
| 48 | 95.2189 | 94.7645 |
| 54 | 96.0918 | 96.6322 |
| 60 | 96.7799 | 97.8397 |
| 66 | 97.3300 | 98.6166 |
| 72 | 97.7748 | 99.1150 |
| 78 | 98.1378 | 99.4341 |
| 84 | 98.4362 | 99.6382 |
| 90 | 98.6831 | 99.7687 |
| 96 | 98.8883 | 99.8522 |
| 102 | 99.0597 | 99.9055 |
| 108 | 99.2034 | 99.9396 |
| 114 | 99.3242 | 99.9614 |
| 120 | 99.4259 | 99.9753 |
| 126 | 99.5119 | 99.9842 |
| 132 | 99.5846 | 99.9899 |

Feed 10.2 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 100.0 g/l
 Solvent TBP 2.1 l/h, equilibrated with 10.2 N HNO₃
 Scrub 10.2 N HNO₃, 2.0 l/h

Table 7.2 The Effect of Number of Stages on Yttrium Purification, HNO₃ 6.1 N, TBP 3.1 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 92.7533 | 98.6399 |
| 24 | 95.7077 | 98.9812 |
| 30 | 97.3829 | 99.2020 |
| 36 | 98.3793 | 99.3547 |
| 42 | 98.9883 | 99.4662 |
| 48 | 99.3660 | 99.5510 |
| 54 | 99.6020 | 99.6175 |
| 60 | 99.7750 | 99.6710 |
| 66 | 99.8430 | 99.7147 |
| 72 | 99.9014 | 99.7510 |
| 78 | 99.9381 | 99.7816 |
| 84 | 99.9612 | 99.8075 |
| 90 | 99.9756 | 99.8298 |
| 96 | 99.9847 | 99.8490 |
| 102 | 99.9904 | 99.8656 |
| 108 | 99.9940 | 99.8802 |
| 114 | 99.9962 | 99.8929 |
| 120 | 99.9976 | 99.9041 |
| 126 | 99.9985 | 99.9140 |
| 132 | 99.9991 | 99.9228 |
| 138 | 99.9994 | 99.9305 |
| 144 | 99.9996 | 99.9375 |

Feed 6.1 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 3.1 l/h, equilibrated with 6.1 N HNO₃
 Scrub 6.1 N HNO₃, 2.0 l/h

Table 7.3 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.1 N, TBP 3.2 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 91.0069 | 98.8651 |
| 24 | 94.2481 | 99.2040 |
| 30 | 96.1913 | 99.4183 |
| 36 | 97.4288 | 99.5610 |
| 42 | 98.2439 | 99.6615 |
| 48 | 98.7926 | 99.7351 |
| 54 | 99.1669 | 99.7903 |
| 60 | 99.4242 | 99.8326 |
| 66 | 99.6018 | 99.8655 |
| 72 | 99.7246 | 99.8914 |
| 78 | 99.8096 | 99.9119 |
| 84 | 99.8685 | 99.9278 |
| 90 | 99.9091 | 99.9416 |
| 96 | 99.9372 | 99.9523 |
| 102 | 99.9567 | 99.9610 |
| 108 | 99.9701 | 99.9680 |
| 114 | 99.9794 | 99.9738 |
| 120 | 99.9858 | 99.9785 |
| 126 | 99.9902 | 99.9823 |
| 132 | 99.9932 | 99.9855 |
| 138 | 99.9953 | 99.9881 |
| 144 | 99.9968 | 99.9902 |

Feed 6.1 N HNO_3 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 3.2 l/h, equilibrated with 6.1 N HNO_3
 Scrub 6.1 N HNO_3 , 2.0 l/h

Table 7.4 The Effect of Number of Stages on Yttrium Purification, HNO₃ 6.1 N, TBP 3.3 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 89.0062 | 99.0524 |
| 24 | 92.4506 | 99.3813 |
| 30 | 94.6152 | 99.5796 |
| 36 | 96.0702 | 99.7046 |
| 42 | 97.0830 | 99.7899 |
| 48 | 97.8140 | 99.8481 |
| 54 | 98.3511 | 99.8892 |
| 60 | 98.7511 | 99.9187 |
| 66 | 99.0519 | 99.9400 |
| 72 | 99.2794 | 99.9556 |
| 78 | 99.4521 | 99.9670 |
| 84 | 99.5836 | 99.9753 |
| 90 | 99.6833 | 99.9817 |
| 96 | 99.7594 | 99.9864 |
| 102 | 99.8173 | 99.9898 |
| 108 | 99.8615 | 99.9923 |
| 114 | 99.8949 | 99.9943 |
| 120 | 99.9203 | 99.9958 |
| 126 | 99.9396 | 99.9968 |
| 132 | 99.9543 | 99.9976 |
| 138 | 99.9654 | 99.9982 |
| 144 | 99.9738 | 99.9987 |

Feed 6.1 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 3.3 l/h, equilibrated with 6.1 N HNO₃
 Scrub 6.1 N HNO₃, 2.0 l/h

Table 7.5 The Effect of Number of Stages on Yttrium Purification, HNO₃ 6.1 N, TBP 3.4 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 86.7247 | 99.2110 |
| 24 | 90.2918 | 99.5203 |
| 30 | 92.6018 | 99.6977 |
| 36 | 94.2084 | 99.8043 |
| 42 | 95.3774 | 99.8713 |
| 48 | 96.2587 | 99.9144 |
| 54 | 96.9412 | 99.9427 |
| 60 | 97.4808 | 99.9616 |
| 66 | 97.9140 | 99.9740 |
| 72 | 98.2660 | 99.9824 |
| 78 | 98.5548 | 99.9881 |
| 84 | 98.7940 | 99.9919 |
| 90 | 98.9913 | 99.9945 |
| 96 | 99.1563 | 99.9963 |
| 102 | 99.2942 | 99.9975 |
| 108 | 99.4097 | 99.9983 |
| 114 | 99.5064 | 99.9988 |
| 120 | 99.5876 | 99.9992 |
| 126 | 99.6556 | 99.9995 |
| 132 | 99.7126 | 99.9996 |
| 138 | 99.7604 | 99.9997 |
| 144 | 99.8003 | 99.9998 |

Feed 6.1 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 3.4 l/h, equilibrated with 6.1 N HNO₃
 Scrub 6.1 N HNO₃, 2.0 l/h

Table 7.6 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.2 N, TBP 3.0 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 90.9953 | 98.8655 |
| 24 | 94.2361 | 99.2060 |
| 30 | 96.1850 | 99.4191 |
| 36 | 97.4242 | 99.5617 |
| 42 | 98.2405 | 99.6622 |
| 48 | 98.7902 | 99.7357 |
| 54 | 99.1651 | 99.7909 |
| 60 | 99.4229 | 99.8331 |
| 66 | 99.6608 | 99.8660 |
| 72 | 99.7239 | 99.8918 |
| 78 | 99.8091 | 99.9123 |
| 84 | 99.8680 | 99.9287 |
| 90 | 99.9088 | 99.9419 |
| 96 | 99.9370 | 99.9526 |
| 102 | 99.9565 | 99.9612 |
| 108 | 99.9700 | 99.9683 |
| 114 | 99.9793 | 99.9740 |
| 120 | 99.9857 | 99.9787 |
| 126 | 99.9901 | 99.9825 |
| 132 | 99.9932 | 99.9856 |
| 138 | 99.9953 | 99.9882 |
| 144 | 99.9968 | 99.9903 |

Feed 6.2 N HNO_3 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 3.0 l/h, equilibrated with 6.2 N HNO_3
 Scrub 6.2 N HNO_3 , 2.0 l/h

Table 7.7 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.2 N, TBP 3.1 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 88.8417 | 99.0654 |
| 24 | 92.3015 | 99.3934 |
| 30 | 94.4857 | 99.5892 |
| 36 | 95.9528 | 99.7139 |
| 42 | 96.9817 | 99.7970 |
| 48 | 97.9255 | 99.8542 |
| 54 | 98.2743 | 99.8943 |
| 60 | 98.6852 | 99.9229 |
| 66 | 98.9957 | 99.9435 |
| 72 | 99.2318 | 99.9584 |
| 78 | 99.4121 | 99.9693 |
| 84 | 99.5501 | 99.9773 |
| 90 | 99.6558 | 99.9832 |
| 96 | 99.7368 | 99.9876 |
| 102 | 99.7989 | 99.9908 |
| 108 | 99.8464 | 99.9932 |
| 114 | 99.8827 | 99.9949 |
| 120 | 99.9105 | 99.9962 |
| 126 | 99.9318 | 99.9972 |
| 132 | 99.9480 | 99.9979 |
| 138 | 99.9604 | 99.9985 |
| 144 | 99.9698 | 99.9988 |

Feed 6.2 N HNO_3 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 3.1 l/h, equilibrated with 6.2 N HNO_3
 Scrub 6.2 N HNO_3 , 2.0 l/h

Table 7.8 The Effect of Number of Stages on Yttrium Purification, HNO₃ 6.2 N, TBP 3.2 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 86.3826 | 99.2300 |
| 24 | 89.9535 | 99.5376 |
| 30 | 92.2849 | 99.7117 |
| 36 | 93.9080 | 99.8151 |
| 42 | 95.0934 | 99.8797 |
| 48 | 95.9910 | 99.9210 |
| 54 | 96.6897 | 99.9478 |
| 60 | 97.2451 | 99.9653 |
| 66 | 97.6940 | 99.9769 |
| 72 | 98.0614 | 99.9846 |
| 78 | 98.3652 | 99.9897 |
| 84 | 98.6183 | 99.9931 |
| 90 | 98.8305 | 99.9954 |
| 96 | 99.0093 | 99.9969 |
| 102 | 99.1603 | 99.9979 |
| 108 | 99.2883 | 99.9986 |
| 114 | 99.3968 | 99.9991 |
| 120 | 99.4891 | 99.9994 |
| 126 | 99.5674 | 99.9996 |
| 132 | 99.6340 | 99.9997 |
| 138 | 99.6906 | 99.9998 |
| 144 | 99.7386 | 99.9999 |

Feed 6.2 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 3.2 l/h, equilibrated with 6.2 N HNO₃
 Scrub 6.2 N HNO₃, 2.0 l/h

Table 7.9 The Effect of Number of Stages on Yttrium Purification, HNO₃ 6.2 N, TBP 3.3 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 83.6241 | 99.3646 |
| 24 | 87.1825 | 99.6472 |
| 30 | 89.5498 | 99.7970 |
| 36 | 91.2243 | 99.8806 |
| 42 | 92.4663 | 99.9289 |
| 48 | 93.4222 | 99.9573 |
| 54 | 94.1800 | 99.9743 |
| 60 | 94.7951 | 99.9844 |
| 66 | 95.3041 | 99.9906 |
| 72 | 95.7322 | 99.9943 |
| 78 | 96.0971 | 99.9965 |
| 84 | 96.4117 | 99.9979 |
| 90 | 96.6856 | 99.9987 |
| 96 | 96.9262 | 99.9992 |
| 102 | 97.1391 | 99.9995 |
| 108 | 97.3288 | 99.9997 |
| 114 | 97.4988 | 99.9998 |
| 120 | 97.6519 | 99.9999 |
| 126 | 97.7905 | 99.9999 |
| 132 | 97.9165 | 99.9999 |
| 138 | 98.0315 | 99.9999 |
| 144 | 98.1368 | 99.9999 |

Feed 6.2 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 3.3 l/h, equilibrated with 6.2 N HNO₃
 Scrub 6.2 N HNO₃, 2.0 l/h

Table 7.10 The Effect of Number of Stages on Yttrium Purification, HNO₃ 6.2 N, TBP 3.4 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 80.5822 | 99.4739 |
| 24 | 83.9992 | 99.7298 |
| 30 | 86.2835 | 99.8567 |
| 36 | 87.8952 | 99.9226 |
| 42 | 89.0799 | 99.9577 |
| 48 | 89.9789 | 99.9767 |
| 54 | 90.6786 | 99.9872 |
| 60 | 91.2339 | 99.9929 |
| 66 | 91.6815 | 99.9961 |
| 72 | 92.0466 | 99.9978 |
| 78 | 92.3471 | 99.9988 |
| 84 | 92.5964 | 99.9993 |
| 90 | 92.8043 | 99.9996 |
| 96 | 92.9784 | 99.9998 |
| 102 | 93.1246 | 99.9999 |
| 108 | 93.2476 | 99.9999 |
| 114 | 93.3514 | 99.9999 |
| 120 | 93.4382 | 99.9999 |
| 126 | 93.5214 | 99.9999 |
| 132 | 93.6002 | 99.9999 |
| 138 | 93.6687 | 99.9999 |
| 144 | 93.7029 | 99.9999 |

Feed 6.2 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 3.4 l/h, equilibrated with 6.2 N HNO₃
 Scrub 6.2 N HNO₃, 2.0 l/h

Table 7.11 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.3 N, TBP 2.8 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 90.0098 | 98.9582 |
| 24 | 93.3693 | 99.2954 |
| 30 | 95.4408 | 99.5021 |
| 36 | 96.7954 | 99.6376 |
| 42 | 97.7168 | 99.7309 |
| 48 | 98.3597 | 99.7973 |
| 54 | 98.8158 | 99.8457 |
| 60 | 99.1428 | 99.8817 |
| 66 | 99.3787 | 99.9088 |
| 72 | 99.5495 | 99.9294 |
| 78 | 99.6733 | 99.9451 |
| 84 | 99.7632 | 99.9572 |
| 90 | 99.8285 | 99.9666 |
| 96 | 99.8758 | 99.9739 |
| 102 | 99.9101 | 99.9796 |
| 108 | 99.9350 | 99.9840 |
| 114 | 99.9530 | 99.9875 |
| 120 | 99.9660 | 99.9902 |
| 126 | 99.9754 | 99.9923 |
| 132 | 99.9822 | 99.9939 |
| 138 | 99.9872 | 99.9952 |
| 144 | 99.9907 | 99.9963 |

Feed 6.3 N HNO_3 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 2.8 l/h, equilibrated with 6.3 N HNO_3
 Scrub 6.3 N HNO_3 , 2.0 l/h

Table 7.12 The Effect of Number of Stages on Yttrium Purification, HNO₃ 6.3 N, TBP 2.9 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 87.4909 | 99.1561 |
| 24 | 91.0306 | 99.4750 |
| 30 | 93.3130 | 99.6597 |
| 36 | 94.8812 | 99.7735 |
| 42 | 96.0097 | 99.8467 |
| 48 | 96.8498 | 99.8951 |
| 54 | 97.4909 | 99.9276 |
| 60 | 97.9892 | 99.9498 |
| 66 | 98.3817 | 99.9651 |
| 72 | 98.6940 | 99.9756 |
| 78 | 98.9442 | 99.9830 |
| 84 | 99.1457 | 99.9881 |
| 90 | 99.3085 | 99.9916 |
| 96 | 99.4403 | 99.9941 |
| 102 | 99.5471 | 99.9959 |
| 108 | 99.6337 | 99.9971 |
| 114 | 99.7040 | 99.9980 |
| 120 | 99.7609 | 99.9986 |
| 126 | 99.8071 | 99.9990 |
| 132 | 99.8444 | 99.9993 |
| 138 | 99.8746 | 99.9995 |
| 144 | 99.8990 | 99.9996 |

Feed 6.3 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 2.9 l/h, equilibrated with 6.3 N HNO₃
 Scrub 6.3 N HNO₃, 2.0 l/h

Table 7.13 The Effect of Number of Stages on Yttrium Purification, HNO₃ 6.3 N, TBP 3.0 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 84.6121 | 99.3156 |
| 24 | 88.1918 | 99.6089 |
| 30 | 90.5631 | 99.7681 |
| 36 | 92.2353 | 99.8593 |
| 42 | 93.4727 | 99.9135 |
| 48 | 94.4232 | 99.9463 |
| 54 | 95.1751 | 99.9665 |
| 60 | 95.7841 | 99.9790 |
| 66 | 96.2868 | 99.9868 |
| 72 | 96.7084 | 99.9917 |
| 78 | 97.0666 | 99.9948 |
| 84 | 97.3744 | 99.9967 |
| 90 | 97.6413 | 99.9979 |
| 96 | 97.8747 | 99.9987 |
| 102 | 98.0801 | 99.9992 |
| 108 | 98.2621 | 99.9995 |
| 114 | 98.4242 | 99.9997 |
| 120 | 98.5692 | 99.9998 |
| 126 | 98.6994 | 99.9999 |
| 132 | 98.8188 | 99.9999 |
| 138 | 98.9229 | 99.9999 |
| 144 | 99.0190 | 99.9999 |

Feed 6.3 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 3.0 l/h, equilibrated with 6.3 N HNO₃
 Scrub 6.3 N HNO₃, 2.0 l/h

Table 7.14 The Effect of Number of Stages on Yttrium Purification, HNO₃ 6.3 N, TBP 3.1 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 81.3892 | 99.4430 |
| 24 | 84.8564 | 99.7078 |
| 30 | 87.1762 | 99.8414 |
| 36 | 88.8174 | 99.9123 |
| 42 | 90.0296 | 99.9509 |
| 48 | 90.9556 | 99.9724 |
| 54 | 91.6821 | 99.9844 |
| 60 | 92.2643 | 99.9911 |
| 66 | 92.7388 | 99.9950 |
| 72 | 93.1309 | 99.9971 |
| 78 | 93.4583 | 99.9984 |
| 84 | 93.7342 | 99.9991 |
| 90 | 93.9684 | 99.9995 |
| 96 | 94.1682 | 99.9997 |
| 102 | 94.3394 | 99.9998 |
| 108 | 94.4867 | 99.9999 |
| 114 | 94.6136 | 99.9999 |
| 120 | 94.7233 | 99.9999 |
| 126 | 94.8182 | 99.9999 |
| 132 | 94.9003 | 99.9999 |
| 138 | 94.9714 | 99.9999 |
| 144 | 95.0330 | 100.0000 |

Feed 6.3 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 3.1 l/h, equilibrated with 6.3 N HNO₃
 Scrub 6.3 N HNO₃, 2.0 l/h

Table 7.15 The Effect of Number of Stages on Yttrium Purification, HNO₃ 6.3 N, TBP 3.2 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 77.8520 | 99.5444 |
| 24 | 81.0563 | 99.7801 |
| 30 | 83.1893 | 99.8907 |
| 36 | 84.6740 | 99.9448 |
| 42 | 85.7414 | 99.9718 |
| 48 | 86.5276 | 99.9855 |
| 54 | 87.1172 | 99.9925 |
| 60 | 87.5652 | 99.9961 |
| 66 | 87.9090 | 99.9980 |
| 72 | 88.1745 | 99.9990 |
| 78 | 88.3804 | 99.9995 |
| 84 | 88.5406 | 99.9997 |
| 90 | 88.6654 | 99.9999 |
| 96 | 88.7627 | 99.9999 |
| 102 | 88.8386 | 99.9999 |
| 108 | 88.8977 | 99.9999 |
| 114 | 88.9438 | 99.9999 |
| 120 | 88.9797 | 99.9999 |
| 126 | 89.0076 | 99.9999 |
| 132 | 89.0292 | 99.9999 |
| 138 | 89.0461 | 99.9999 |
| 144 | 89.0592 | 100.0000 |

Feed 6.3 N HNO₃ 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 3.2 l/h, equilibrated with 6.3 N HNO₃
Scrub 6.3 N HNO₃, 2.0 l/h

Table 7.16 The Effect of Number of Stages on Yttrium Purification, HNO₃ 6.4 N, TBP 2.5 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 92.6828 | 98.6307 |
| 24 | 95.6561 | 98.9744 |
| 30 | 97.3459 | 99.1965 |
| 36 | 98.3531 | 99.3501 |
| 42 | 98.9698 | 99.4622 |
| 48 | 99.3531 | 99.5474 |
| 54 | 99.5931 | 99.6143 |
| 60 | 99.7744 | 99.6679 |
| 66 | 99.8389 | 99.7119 |
| 72 | 99.8986 | 99.7484 |
| 78 | 99.9362 | 99.7779 |
| 84 | 99.9599 | 99.8052 |
| 90 | 99.9748 | 99.8276 |
| 96 | 99.9842 | 99.8469 |
| 102 | 99.9900 | 99.8637 |
| 108 | 99.9937 | 99.8783 |
| 114 | 99.9961 | 99.8912 |
| 120 | 99.9975 | 99.9025 |
| 126 | 99.9984 | 99.9125 |
| 132 | 99.9990 | 99.9213 |
| 138 | 99.9994 | 99.9292 |
| 144 | 99.9996 | 99.9362 |

Feed 6.4 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 2.5 l/h, equilibrated with 6.4 N HNO₃
 Scrub 6.4 N HNO₃, 2.0 l/h

Table 7.17 The Effect of Number of Stages on Yttrium Purification, HNO₃ 6.4 N, TBP 2.6 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 90.4623 | 98.9038 |
| 24 | 93.7774 | 99.2448 |
| 30 | 95.7936 | 99.4561 |
| 36 | 97.0981 | 99.5962 |
| 42 | 97.9727 | 99.6940 |
| 48 | 98.5732 | 99.7645 |
| 54 | 98.9916 | 99.8169 |
| 60 | 99.2858 | 99.8564 |
| 66 | 99.4937 | 99.8868 |
| 72 | 99.6410 | 99.9103 |
| 78 | 99.7455 | 99.9286 |
| 84 | 99.8197 | 99.9431 |
| 90 | 99.8723 | 99.9545 |
| 96 | 99.9096 | 99.9635 |
| 102 | 99.9360 | 99.9708 |
| 108 | 99.9547 | 99.9765 |
| 114 | 99.9680 | 99.9811 |
| 120 | 99.9774 | 99.9848 |
| 126 | 99.9840 | 99.9878 |
| 132 | 99.9887 | 99.9902 |
| 138 | 99.9920 | 99.9921 |
| 144 | 99.9944 | 99.9936 |

Feed 6.4 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 2.6 l/h, equilibrated with 6.4 N HNO₃
 Scrub 6.4 N HNO₃, 2.0 l/h

Table 7.18 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.4 N, TBP 2.7 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 87.8294 | 99.1243 |
| 24 | 91.3557 | 99.4478 |
| 30 | 93.6192 | 99.6370 |
| 36 | 95.1667 | 99.7549 |
| 42 | 96.2740 | 99.8315 |
| 48 | 97.0927 | 99.8828 |
| 54 | 97.7127 | 99.9179 |
| 60 | 98.1904 | 99.9421 |
| 66 | 98.5631 | 99.9590 |
| 72 | 98.8563 | 99.9709 |
| 78 | 99.0885 | 99.9793 |
| 84 | 99.2731 | 99.9852 |
| 90 | 99.4203 | 99.9895 |
| 96 | 99.5378 | 99.9925 |
| 102 | 99.6317 | 99.9946 |
| 108 | 99.7066 | 99.9962 |
| 114 | 99.7665 | 99.9973 |
| 120 | 99.8143 | 99.9980 |
| 126 | 99.8524 | 99.9986 |
| 132 | 99.8828 | 99.9990 |
| 138 | 99.9070 | 99.9993 |
| 144 | 99.9262 | 99.9995 |

Feed 6.4 N HNO_3 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 2.7 l/h, equilibrated with 6.4 N HNO_3
 Scrub 6.4 N HNO_3 , 2.0 l/h

Table 7.19 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.4 N, TBP 2.8 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 84.7835 | 99.2998 |
| 24 | 88.3669 | 99.5968 |
| 30 | 90.7388 | 99.7759 |
| 36 | 92.4104 | 99.8525 |
| 42 | 93.6464 | 99.9084 |
| 48 | 94.5951 | 99.9427 |
| 54 | 95.3450 | 99.9639 |
| 60 | 95.9517 | 99.9772 |
| 66 | 96.4520 | 99.9855 |
| 72 | 96.8709 | 99.9908 |
| 78 | 97.2264 | 99.9942 |
| 84 | 97.5312 | 99.9963 |
| 90 | 97.7950 | 99.9976 |
| 96 | 98.0251 | 99.9985 |
| 102 | 98.2278 | 99.9990 |
| 108 | 98.4058 | 99.9994 |
| 114 | 98.5643 | 99.9996 |
| 120 | 98.7055 | 99.9997 |
| 126 | 98.8319 | 99.9998 |
| 132 | 98.9454 | 99.9999 |
| 138 | 99.0748 | 99.9999 |
| 144 | 99.1395 | 99.9999 |

Feed 6.4 N HNO_3 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 2.8 l/h, equilibrated with 6.4 N HNO_3
 Scrub 6.4 N HNO_3 , 2.0 l/h

Table 7.20 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.4 N, TBP 2.9 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 81.3420 | 99.4380 |
| 24 | 84.8080 | 99.7045 |
| 30 | 87.1281 | 99.8393 |
| 36 | 88.7698 | 99.9109 |
| 42 | 89.9822 | 99.9500 |
| 48 | 90.9083 | 99.9718 |
| 54 | 91.6346 | 99.9840 |
| 60 | 92.2164 | 99.9909 |
| 66 | 92.6904 | 99.9948 |
| 72 | 93.0818 | 99.9970 |
| 78 | 93.4084 | 99.9983 |
| 84 | 93.6835 | 99.9990 |
| 90 | 93.9166 | 99.9994 |
| 96 | 94.1154 | 99.9997 |
| 102 | 94.2855 | 99.9998 |
| 108 | 94.4317 | 99.9999 |
| 114 | 94.5575 | 99.9999 |
| 120 | 94.6661 | 99.9999 |
| 126 | 94.7599 | 99.9999 |
| 132 | 94.8409 | 99.9999 |
| 138 | 94.9109 | 99.9999 |
| 144 | 94.9715 | 99.9999 |

Feed 6.4 N HNO_3 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 2.9 l/h, equilibrated with 6.4 N HNO_3
 Scrub 6.4 N HNO_3 , 2.0 l/h

Table 7.21 The Effect of Number of Stages on Yttrium Purification, HNO₃ 6.4 N, TBP 3.0 l/h.

| STAGE | % RECOVERY | % PURITY |
|-------|------------|----------|
| 18 | 77.5412 | 99.5463 |
| 24 | 80.7175 | 99.7818 |
| 30 | 82.8308 | 99.8920 |
| 36 | 84.2991 | 99.9456 |
| 42 | 85.3516 | 99.9723 |
| 48 | 86.1238 | 99.9858 |
| 54 | 86.7000 | 99.9927 |
| 60 | 87.1355 | 99.9963 |
| 66 | 87.4674 | 99.9981 |
| 72 | 87.7722 | 99.9990 |
| 78 | 87.9180 | 99.9995 |
| 84 | 88.0692 | 99.9997 |
| 90 | 88.1861 | 99.9998 |
| 96 | 88.2765 | 99.9999 |
| 102 | 88.3463 | 99.9999 |
| 108 | 88.4002 | 99.9999 |
| 114 | 88.4419 | 99.9999 |
| 120 | 88.4740 | 99.9999 |
| 126 | 88.4988 | 99.9999 |
| 132 | 88.5179 | 99.9999 |
| 138 | 88.5326 | 99.9999 |
| 144 | 88.5439 | 100.0000 |

Feed 6.4 N HNO₃ 1.0 l/h, center feed
 Rare Earth in feed 10.0 g/l
 Solvent TBP 3.0 l/h, equilibrated with 6.4 N HNO₃
 Scrub 6.4 N HNO₃, 2.0 l/h

APPENDIX B

Figures

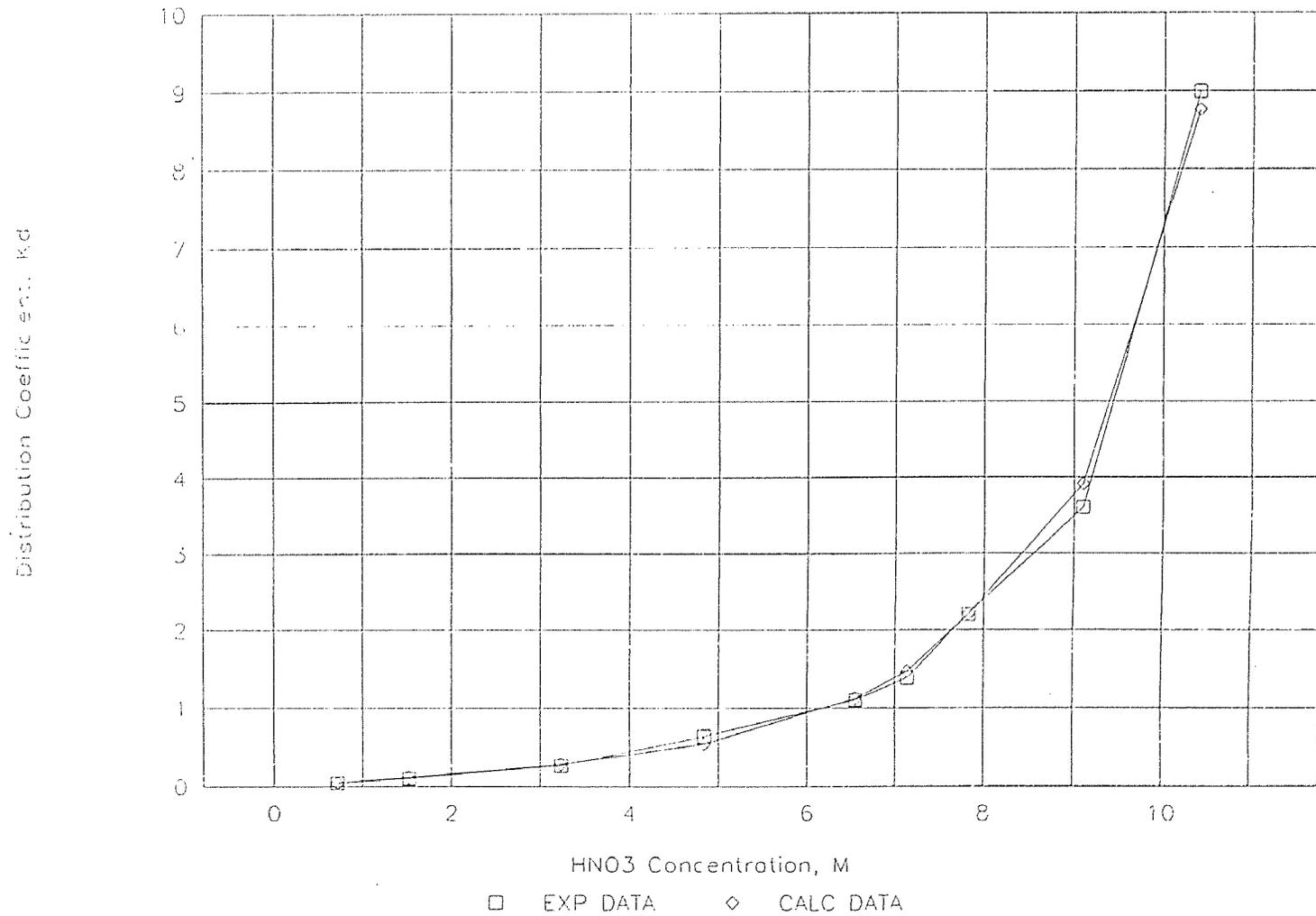


Figure 5.2 Comparison of the Experimental and Predicted Distribution Coefficients of Yttrium.

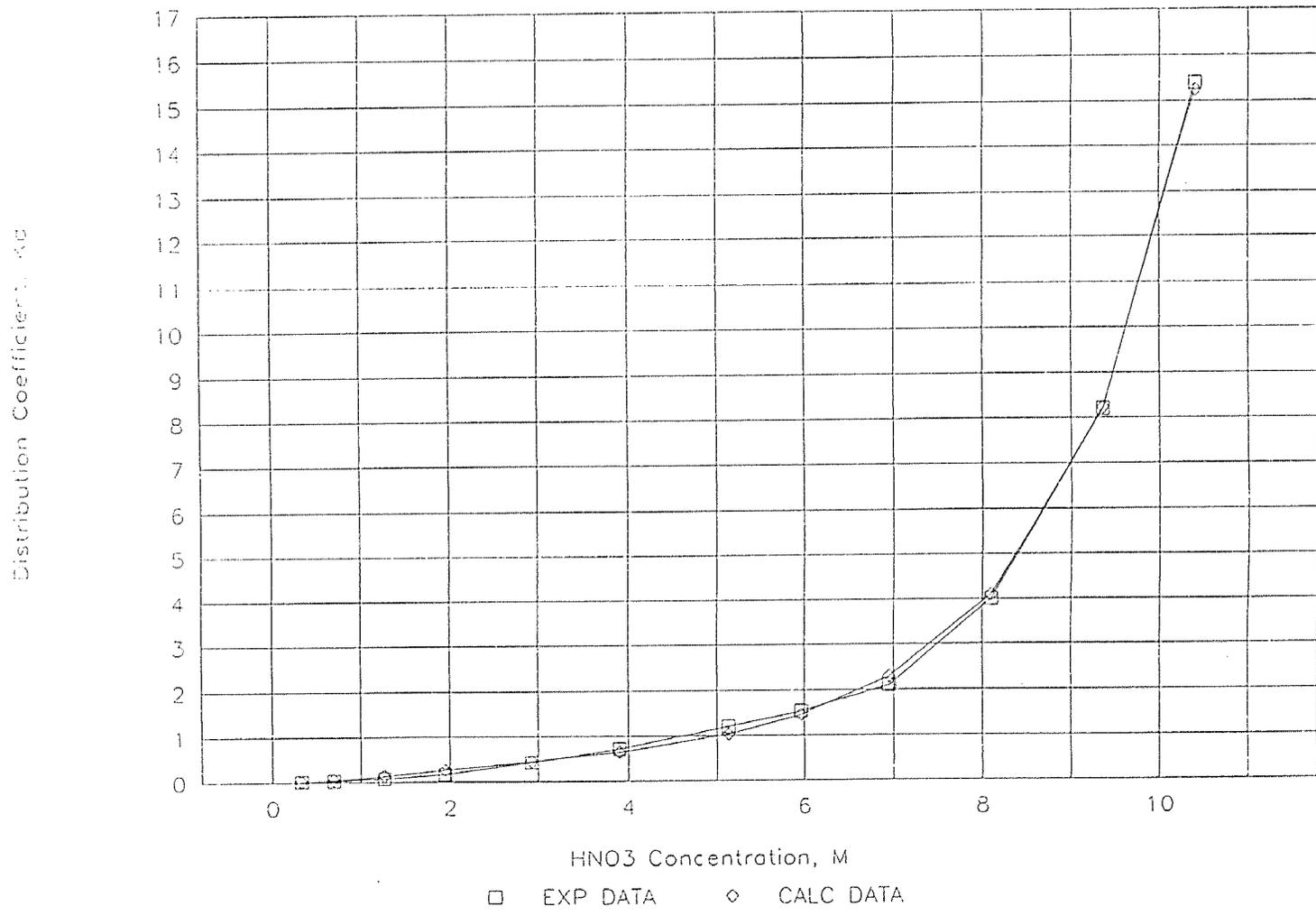


Figure 5.3 Comparison of the Experimental and Predicted Distribution Coefficients of Ytterbium.

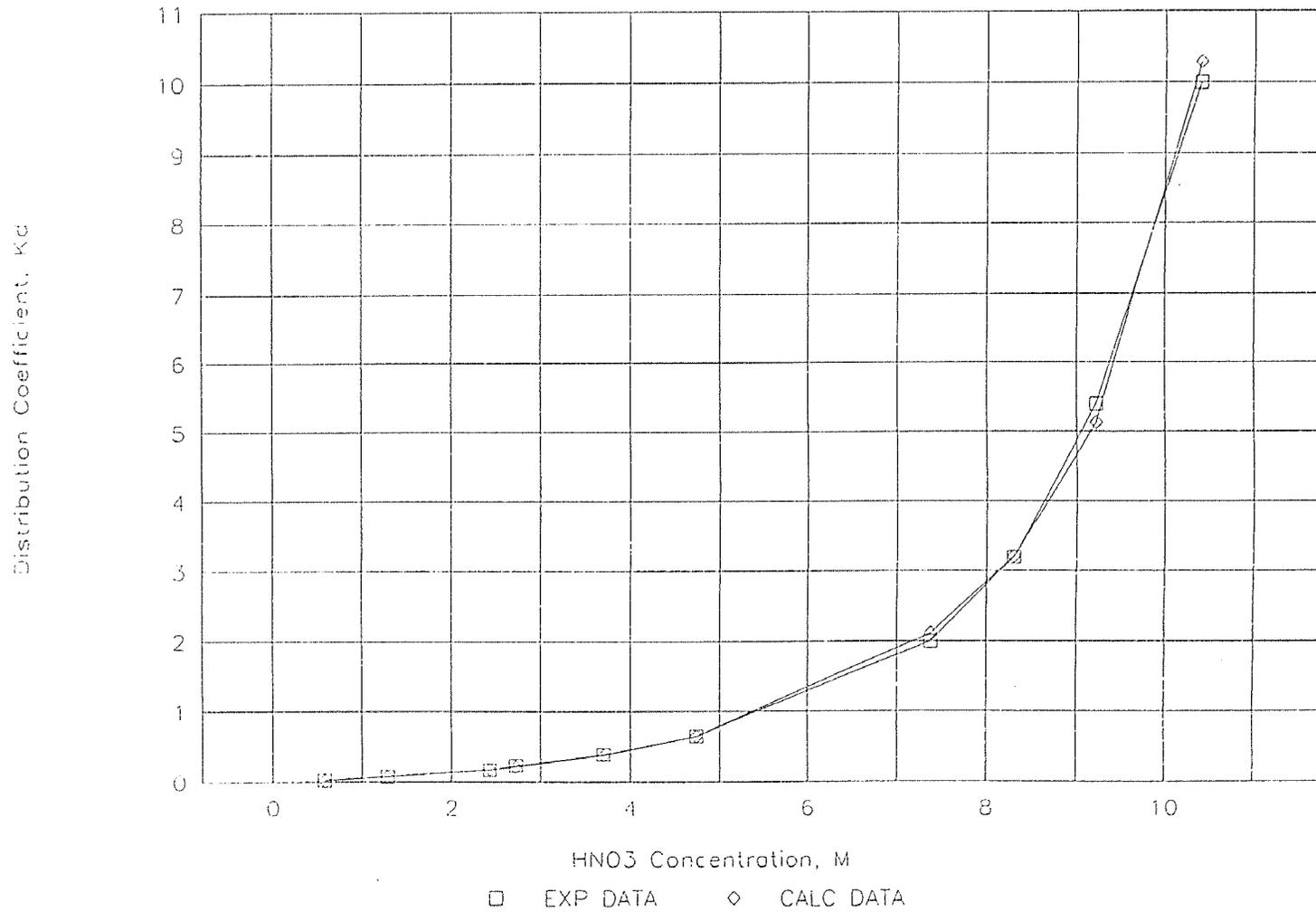


Figure 5.4 Comparison of the Experimental and Predicted Distribution Coefficients of Thulium.

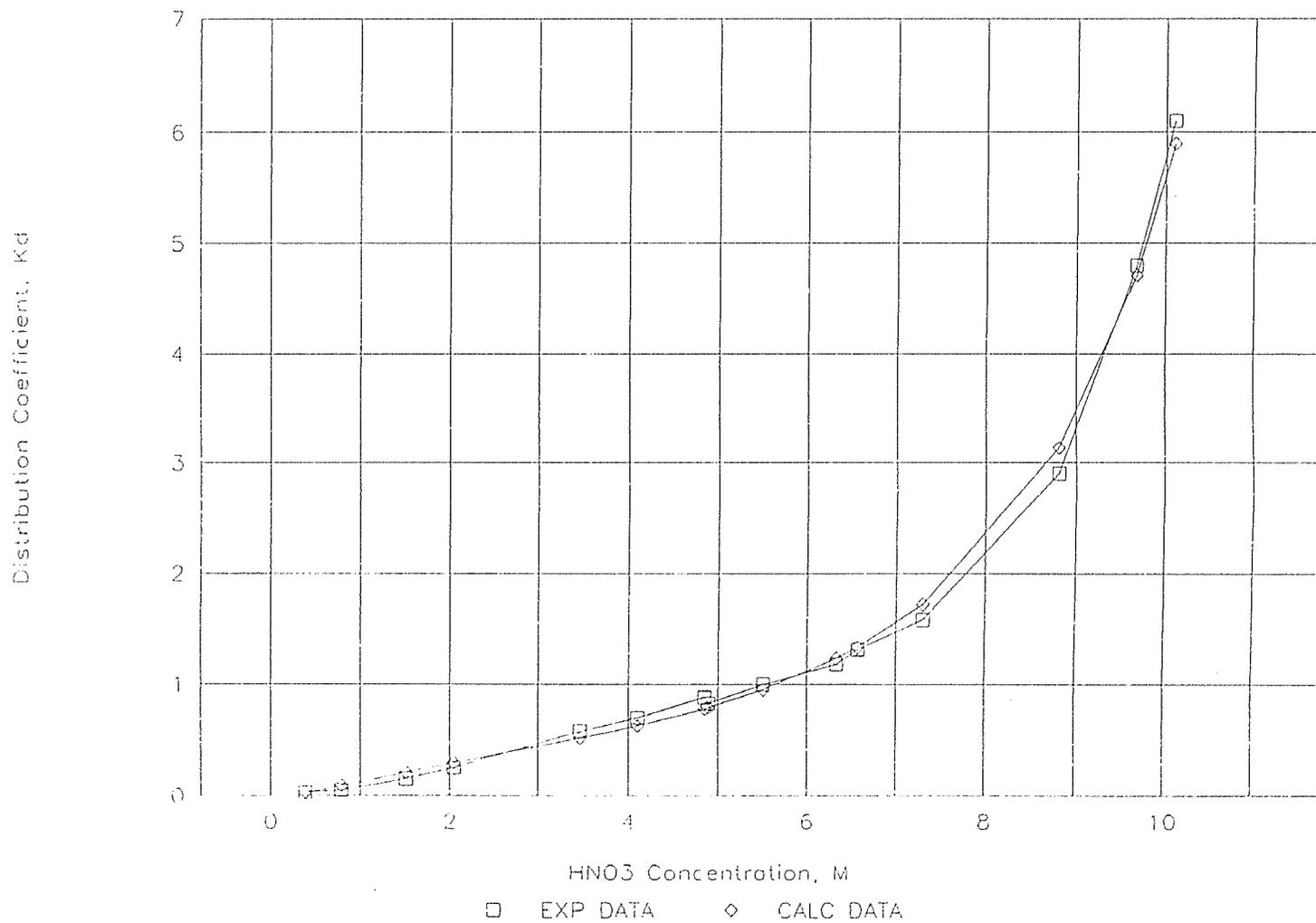


Figure 5.5 Comparison of the Experimental and Predicted Distribution Coefficients of Erbium.

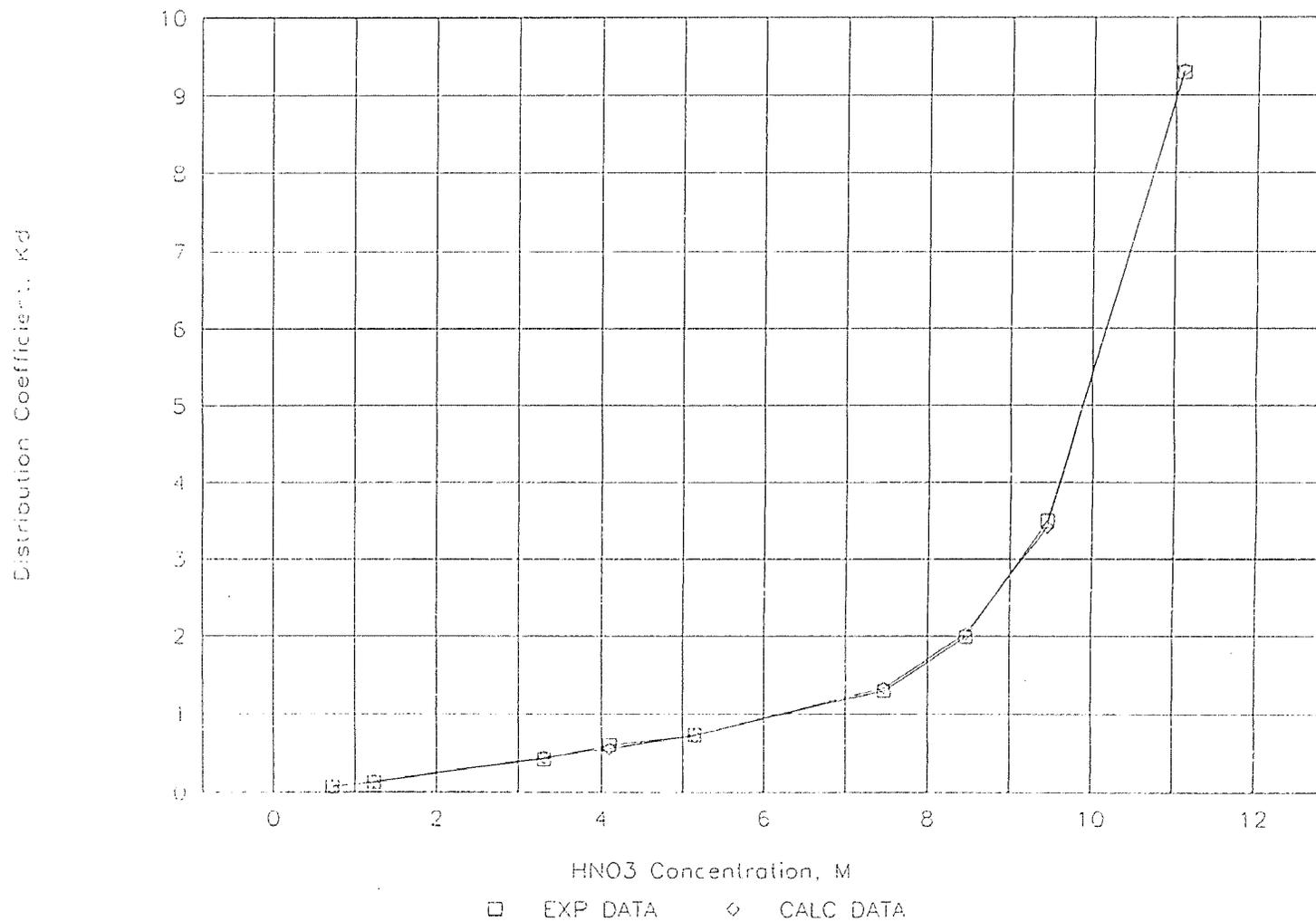


Figure 5.6 Comparison of the Experimental and Predicted Distribution Coefficients of Holmium.

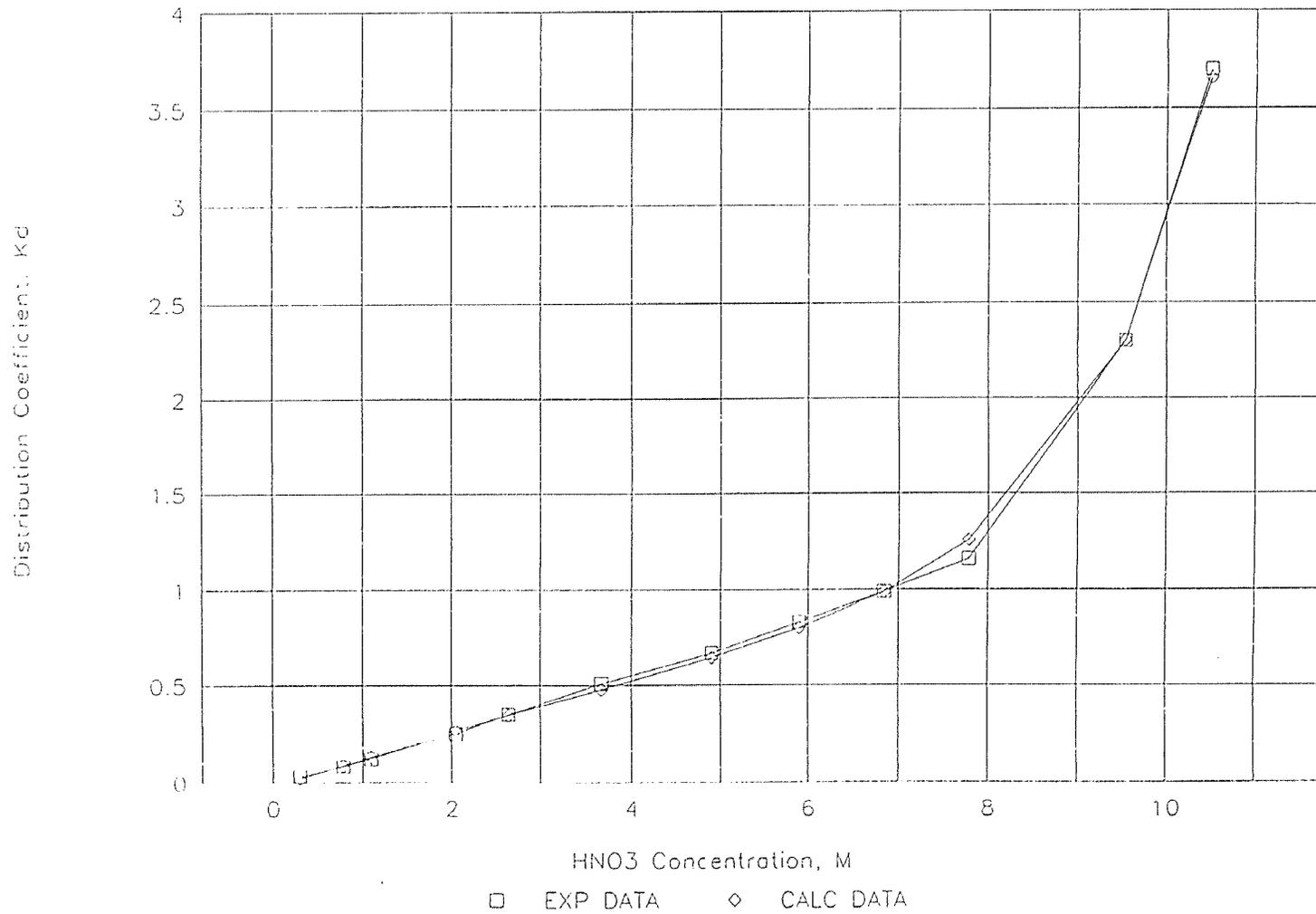


Figure 5.7 Comparison of the Experimental and Predicted Distribution Coefficients of Dysprosium.

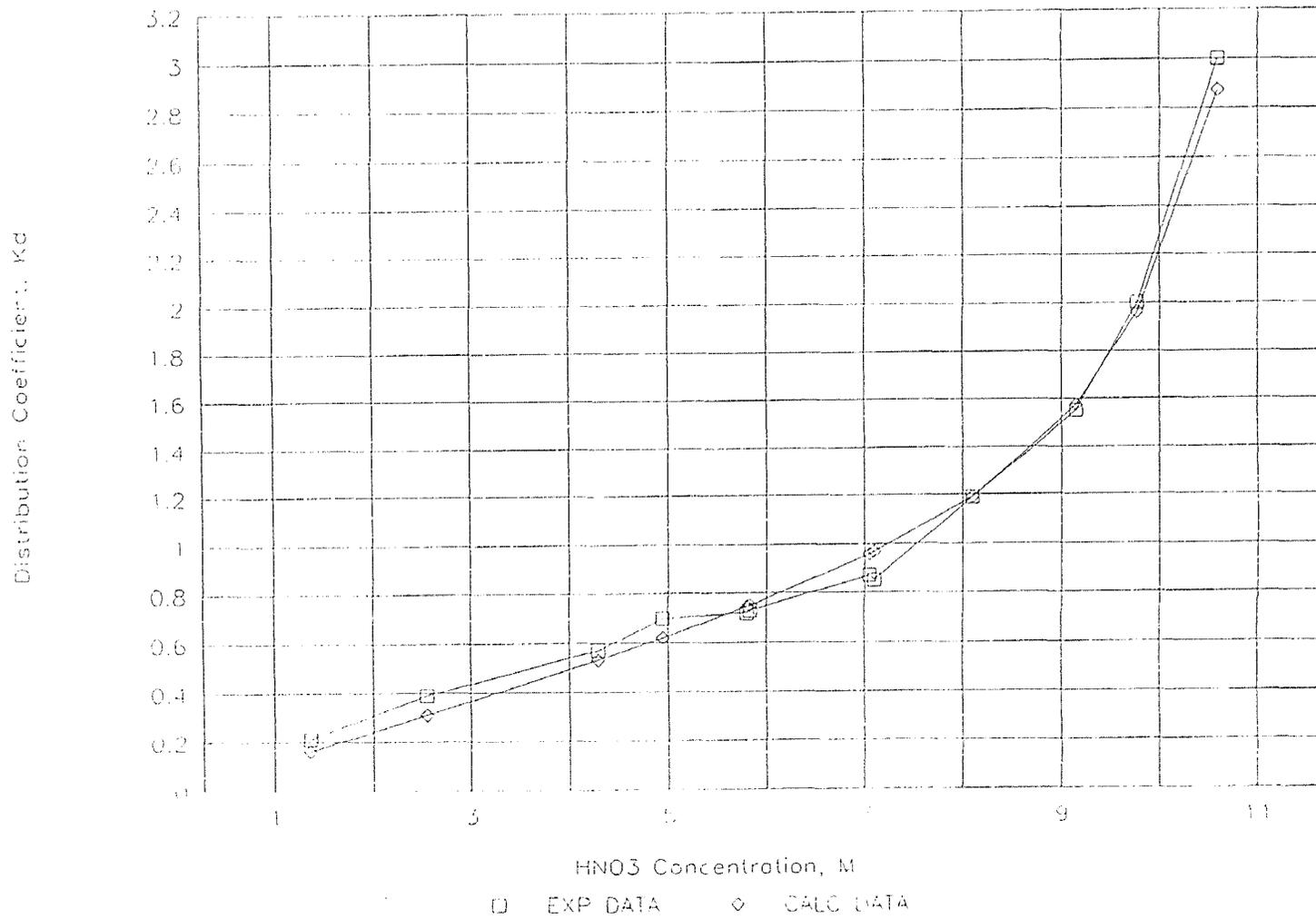


Figure 5.8 Comparison of the Experimental and Predicted Distribution Coefficients of Terbium.

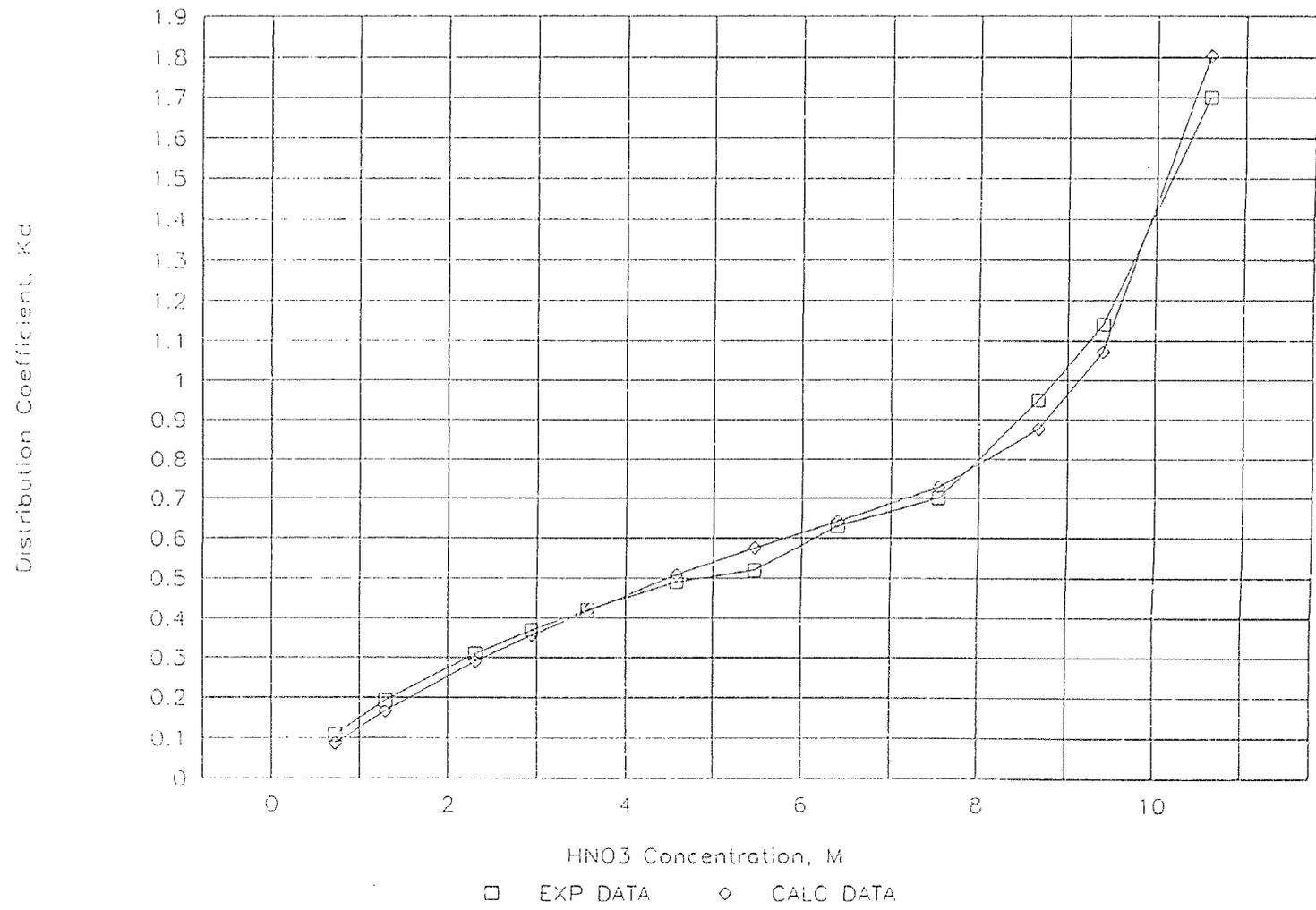


Figure 5.9 Comparison of the Experimental and Predicted Distribution Coefficients of Gadolinium.

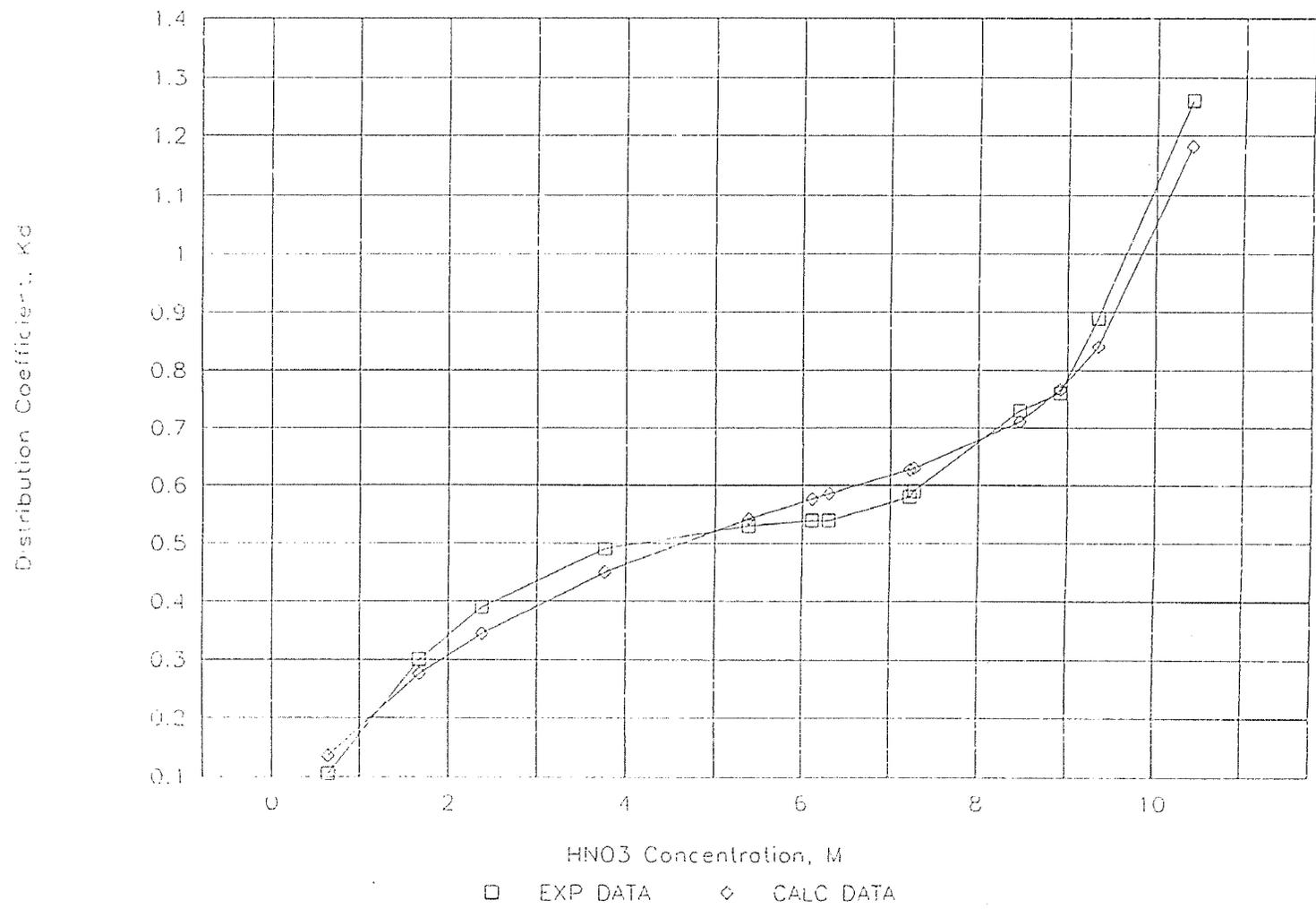


Figure 5.10 Comparison of the Experimental and Predicted Distribution Coefficients of Europium.

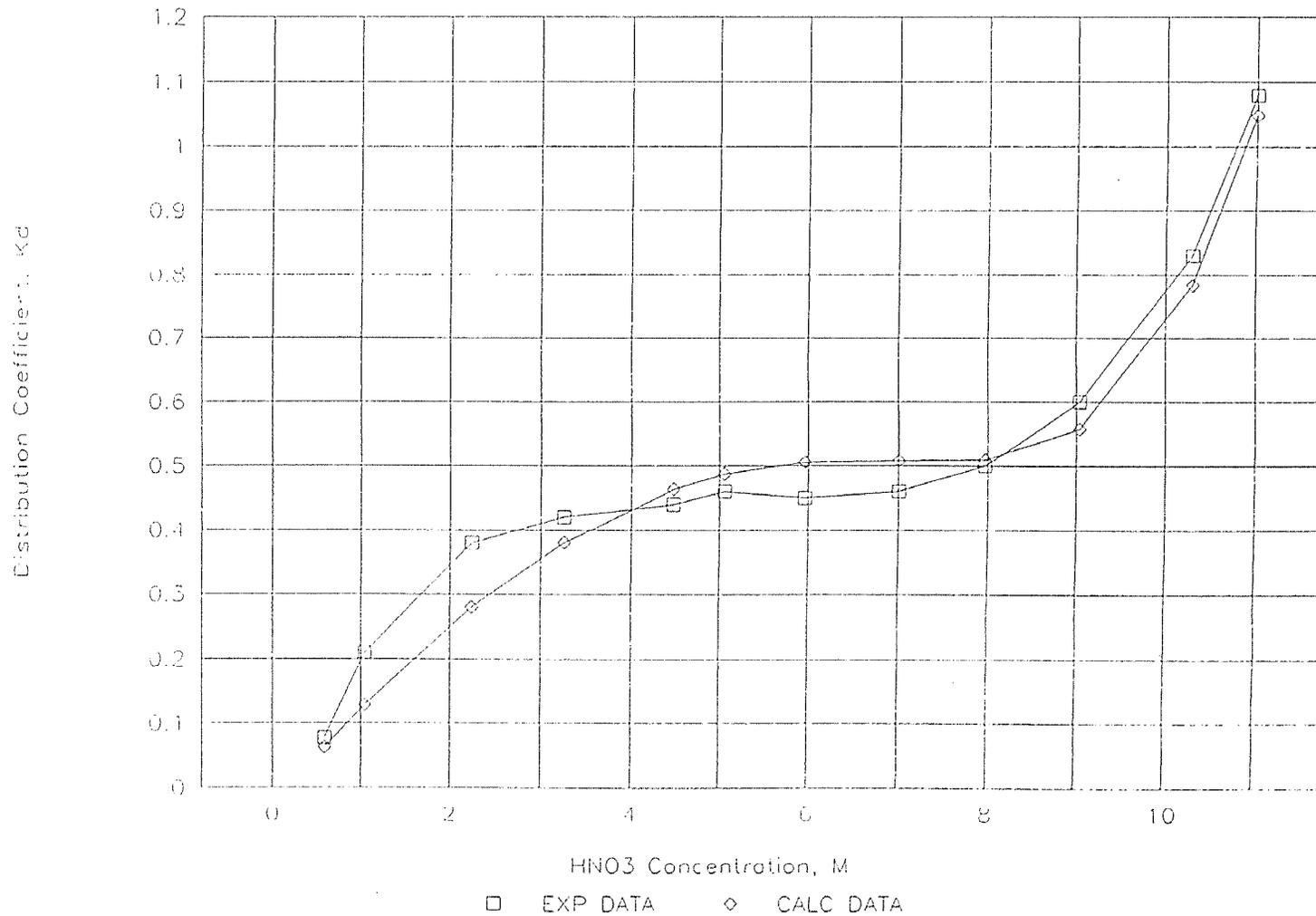


Figure 5.11 Comparison of the Experimental and Predicted Distribution Coefficients of Samarium.

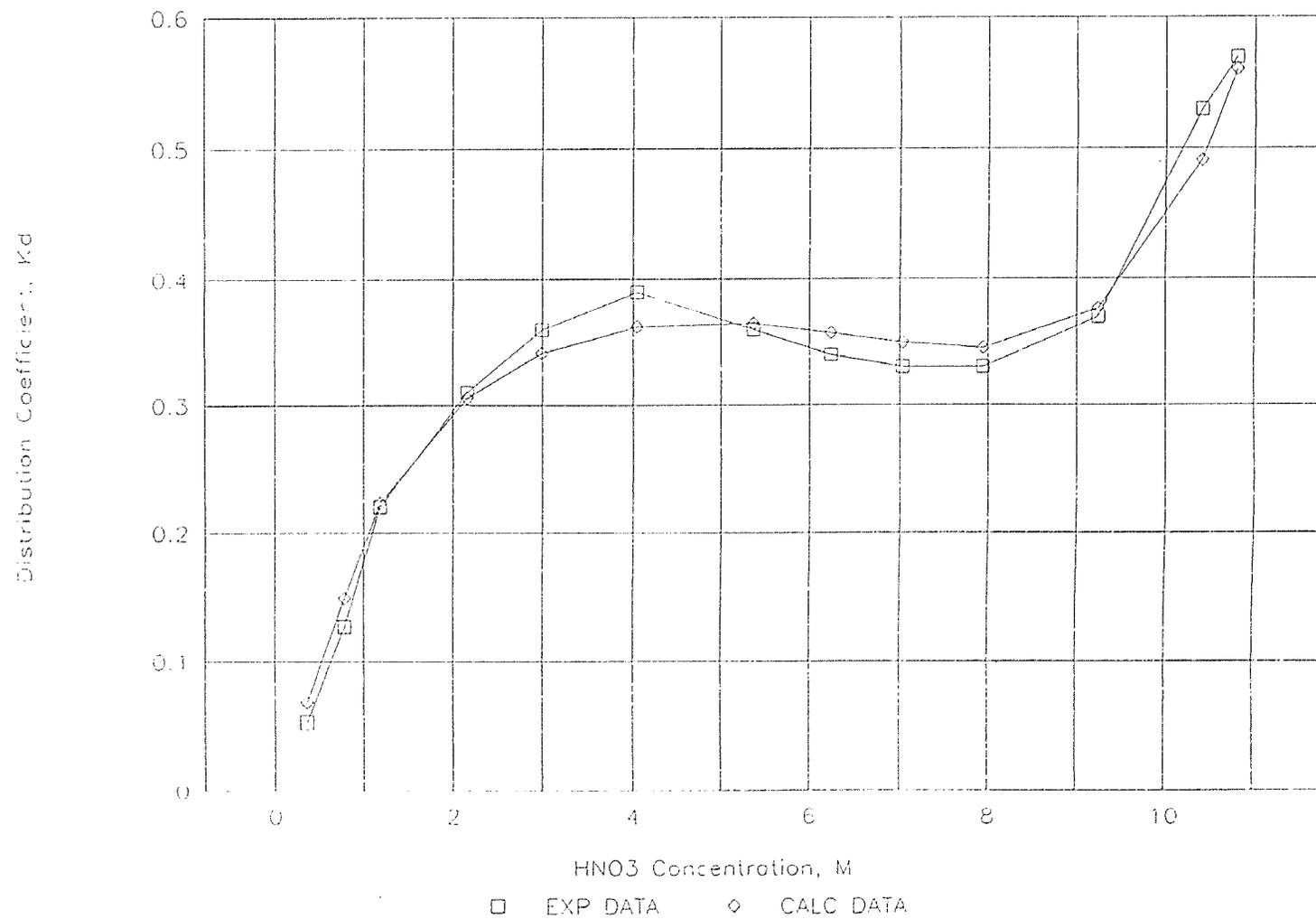


Figure 5.12 Comparison of the Experimental and Predicted Distribution Coefficients of Promethium.

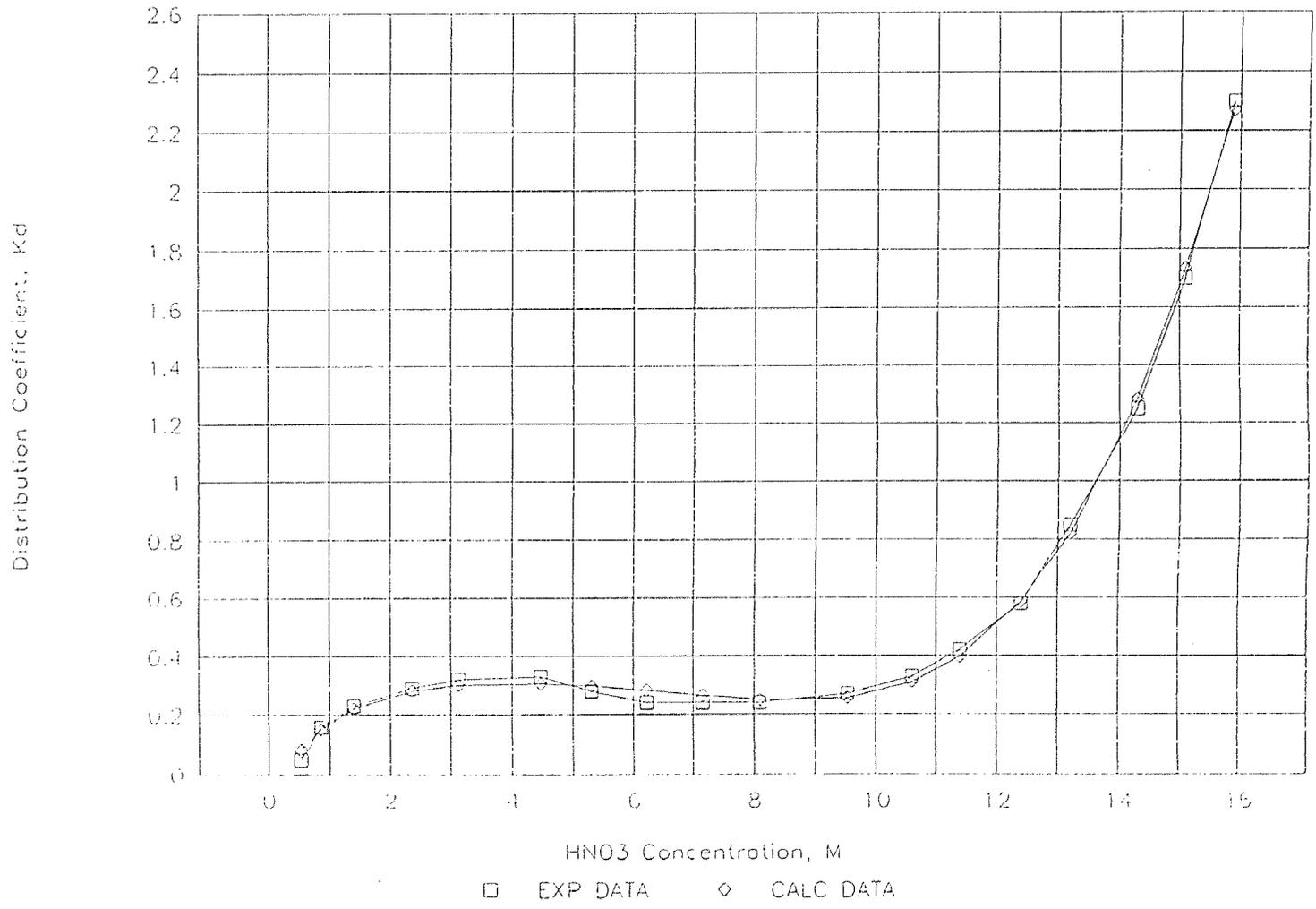


Figure 5.13 Comparison of the Experimental and Predicted Distribution Coefficients of Neodymium.

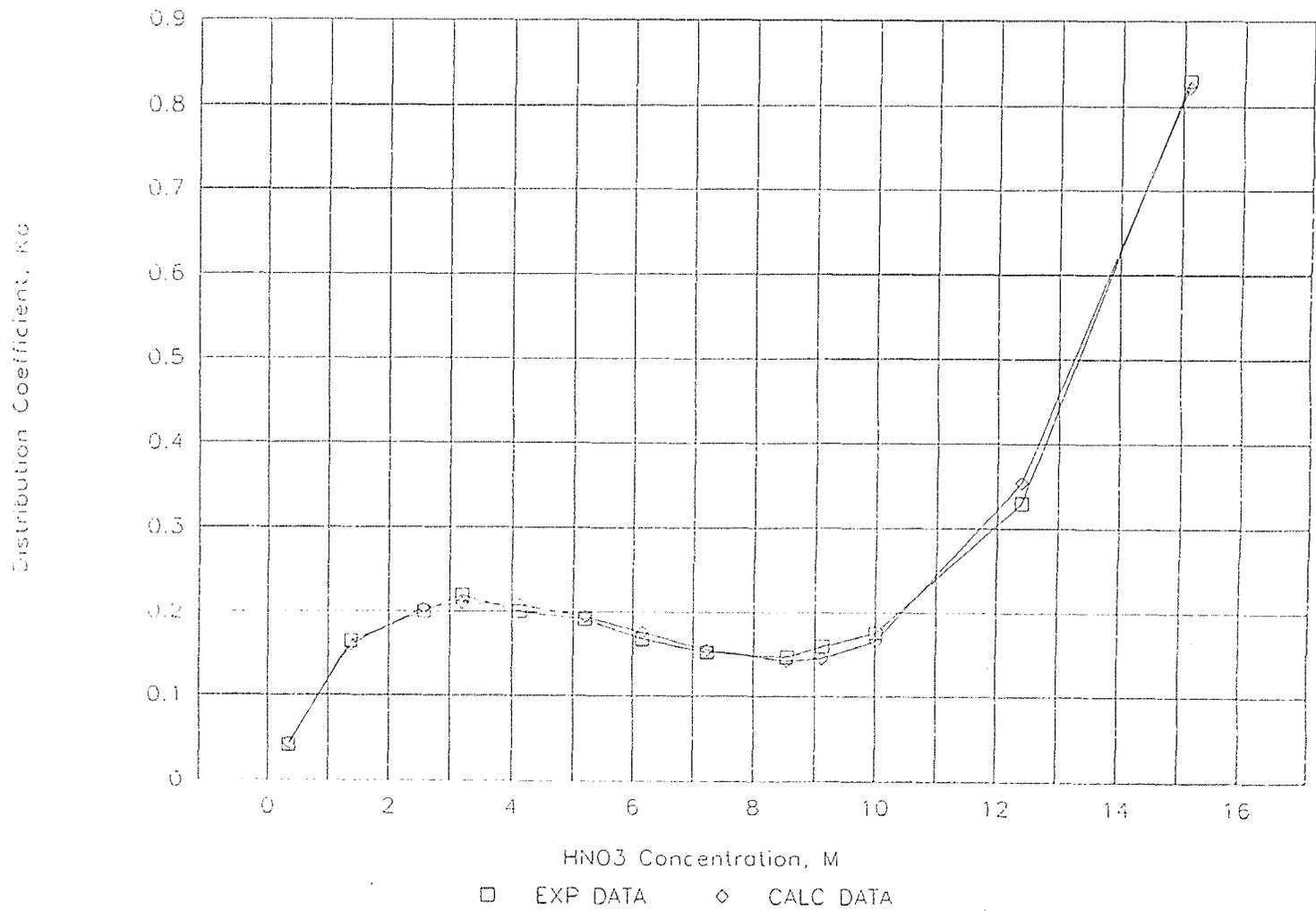


Figure 5.14 Comparison of the Experimental and Predicted Distribution Coefficients of Praseodymium.

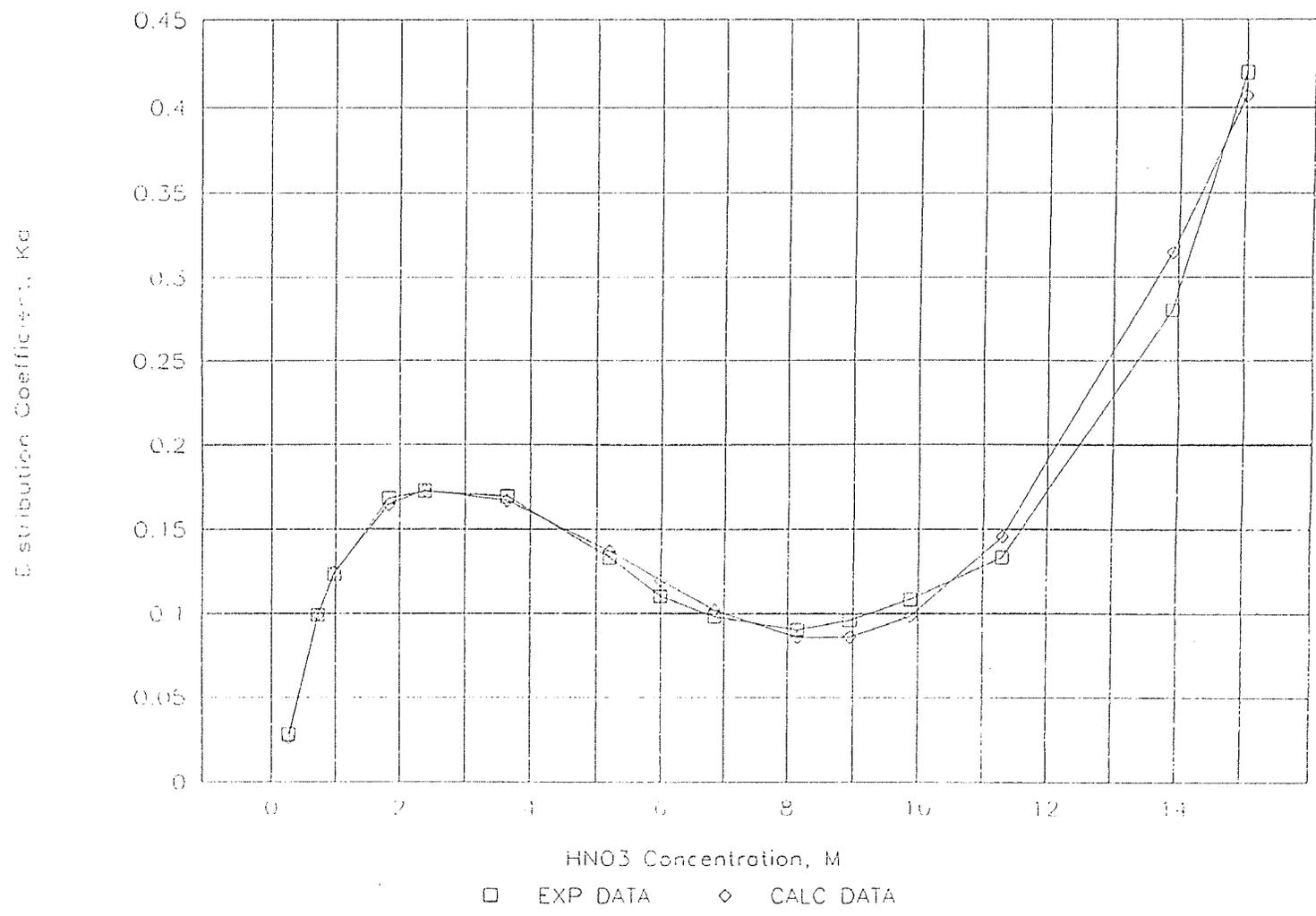


Figure 5.15 Comparison of the Experimental and Predicted Distribution Coefficients of Cerium.

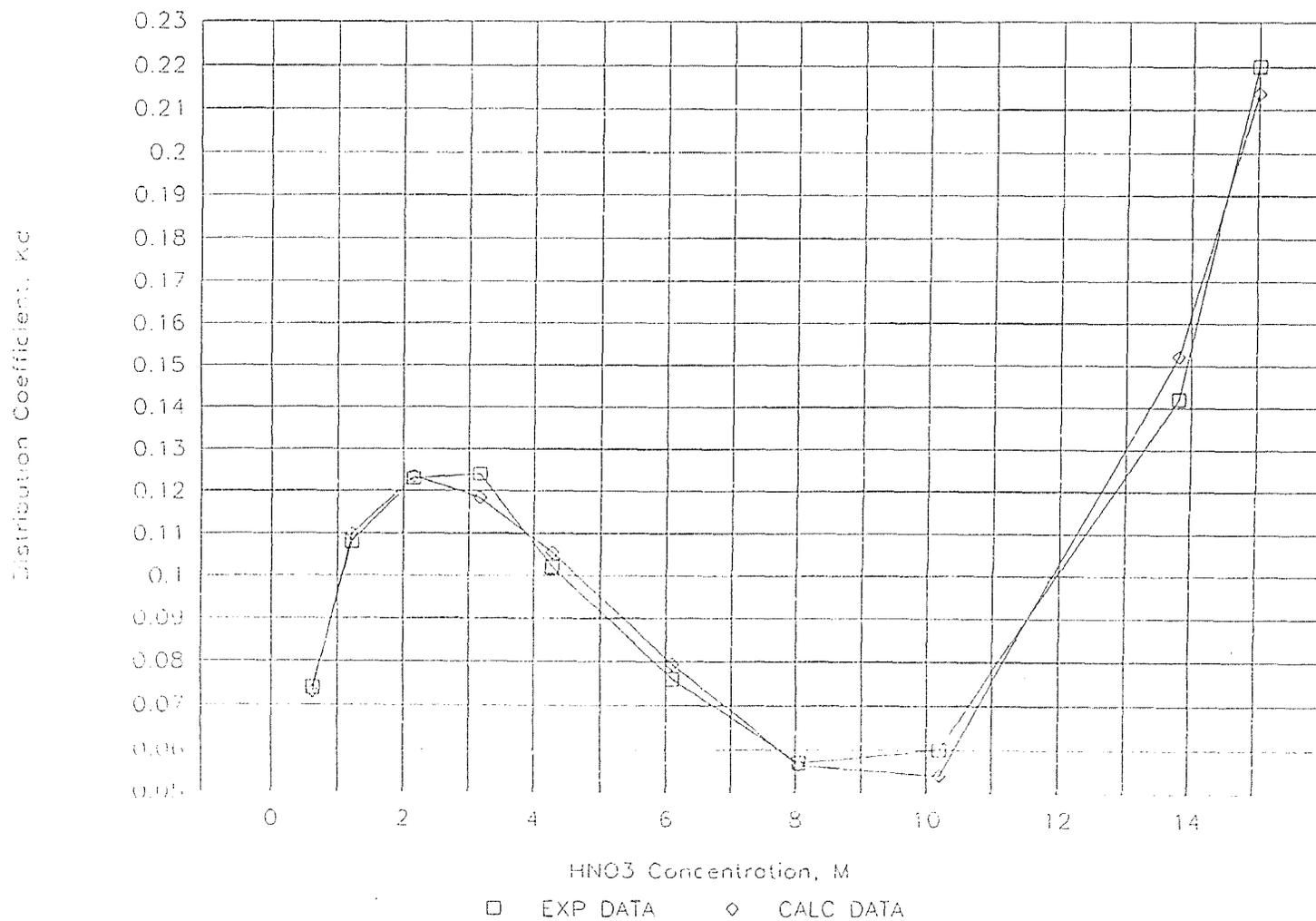


Figure 5.16 Comparison of the Experimental and Predicted Distribution Coefficients of Lanthanum.

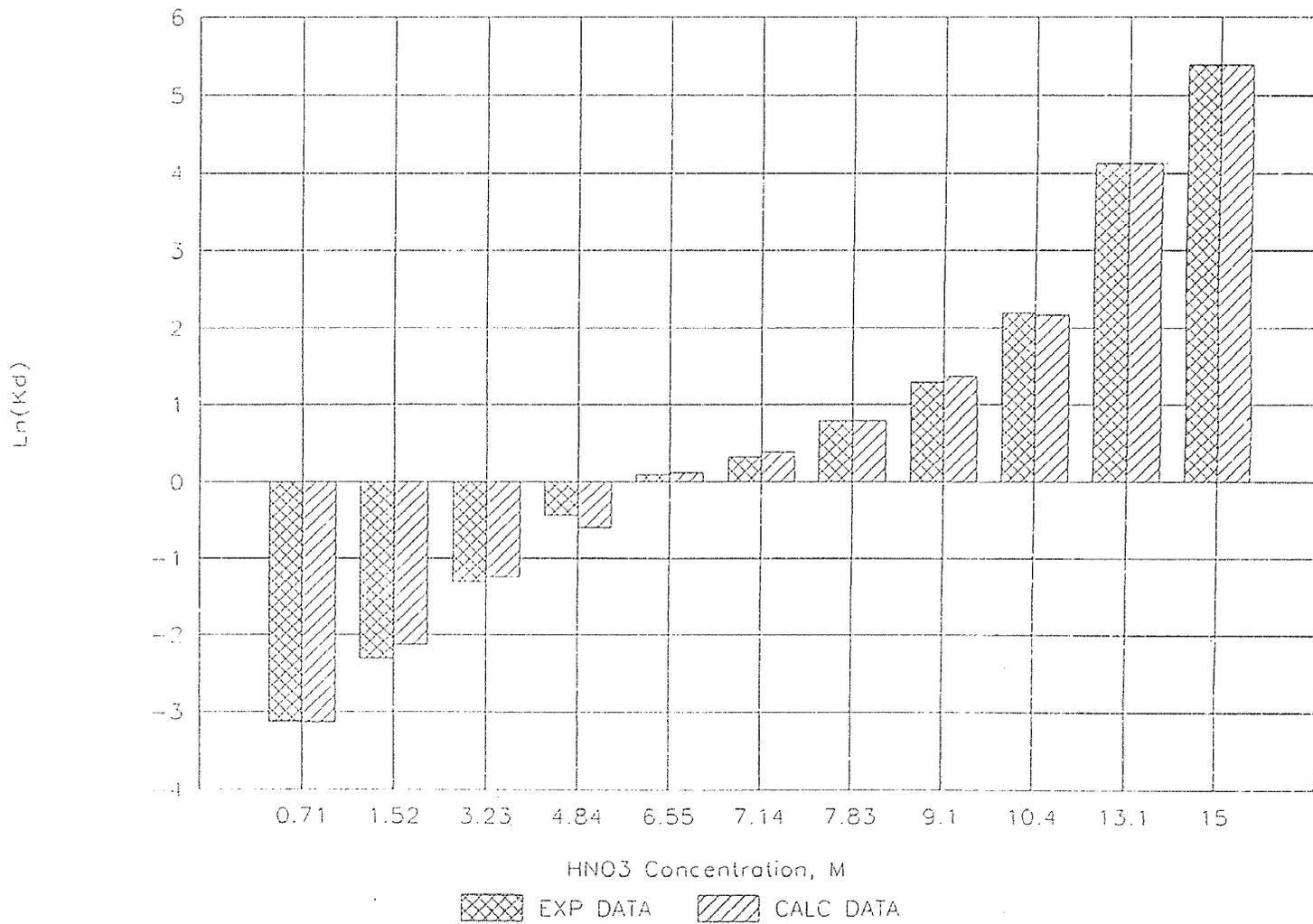


Figure 5.18 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Yttrium.

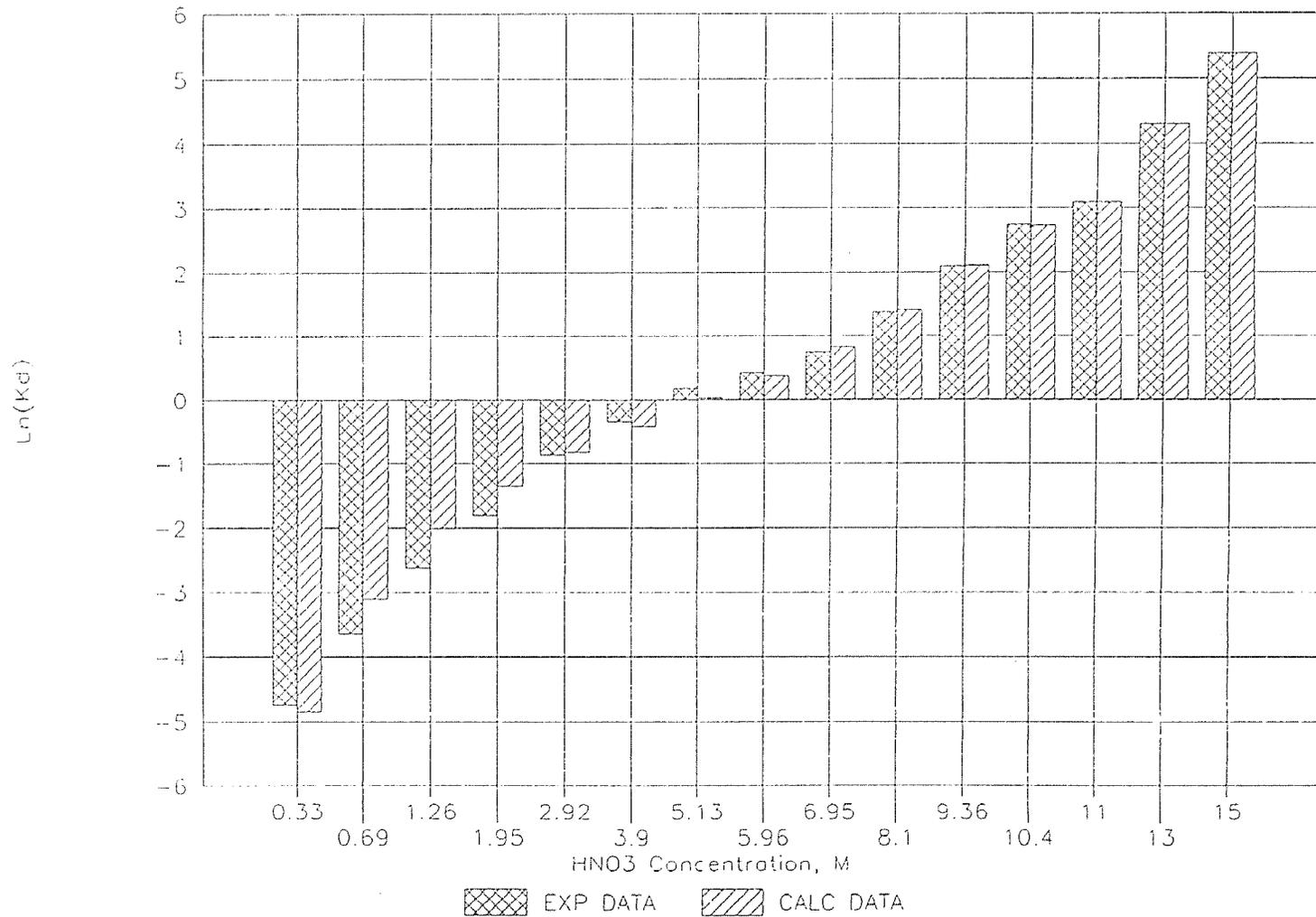


Figure 5.19 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Ytterbium.

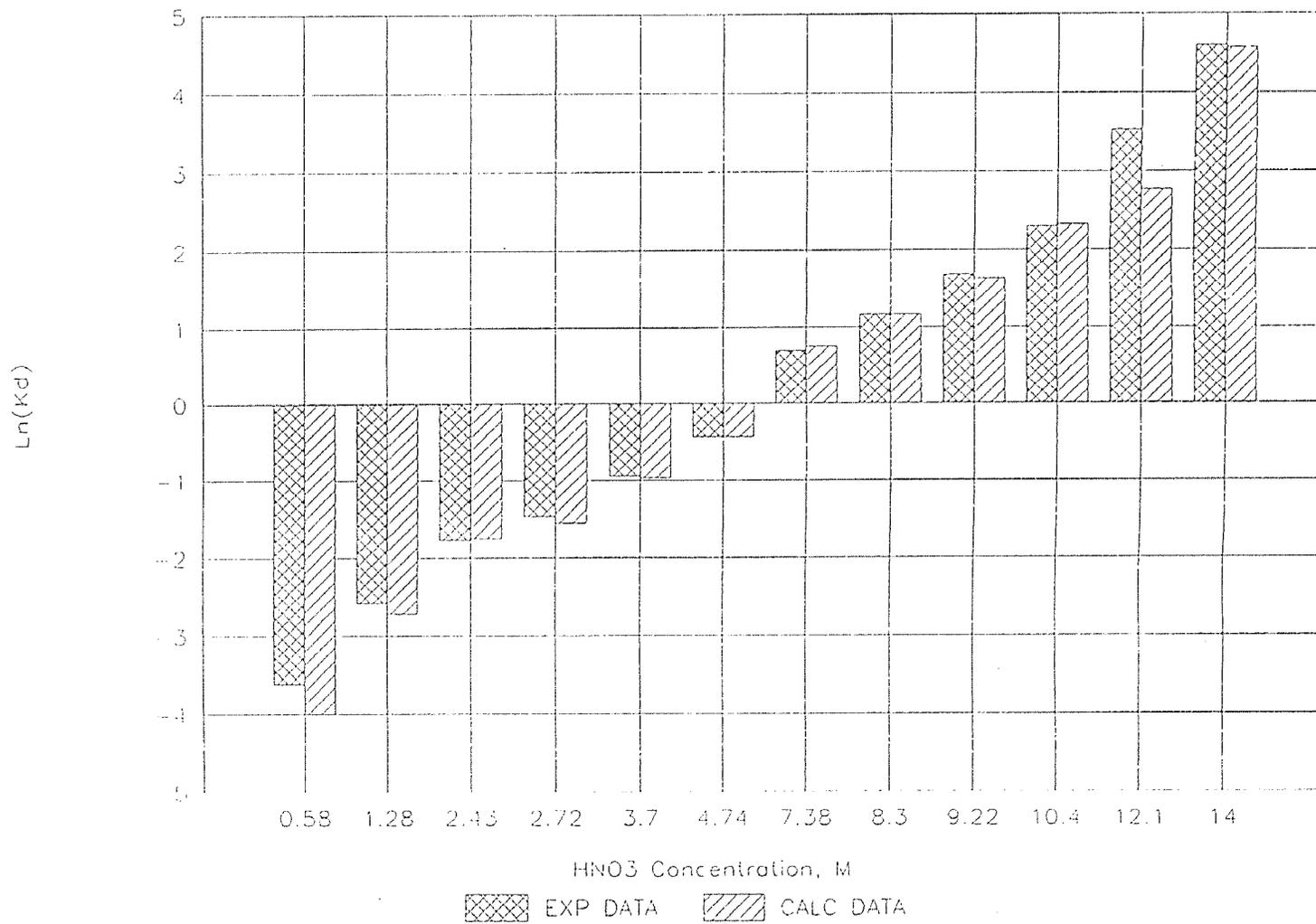


Figure 5.20 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Thulium.

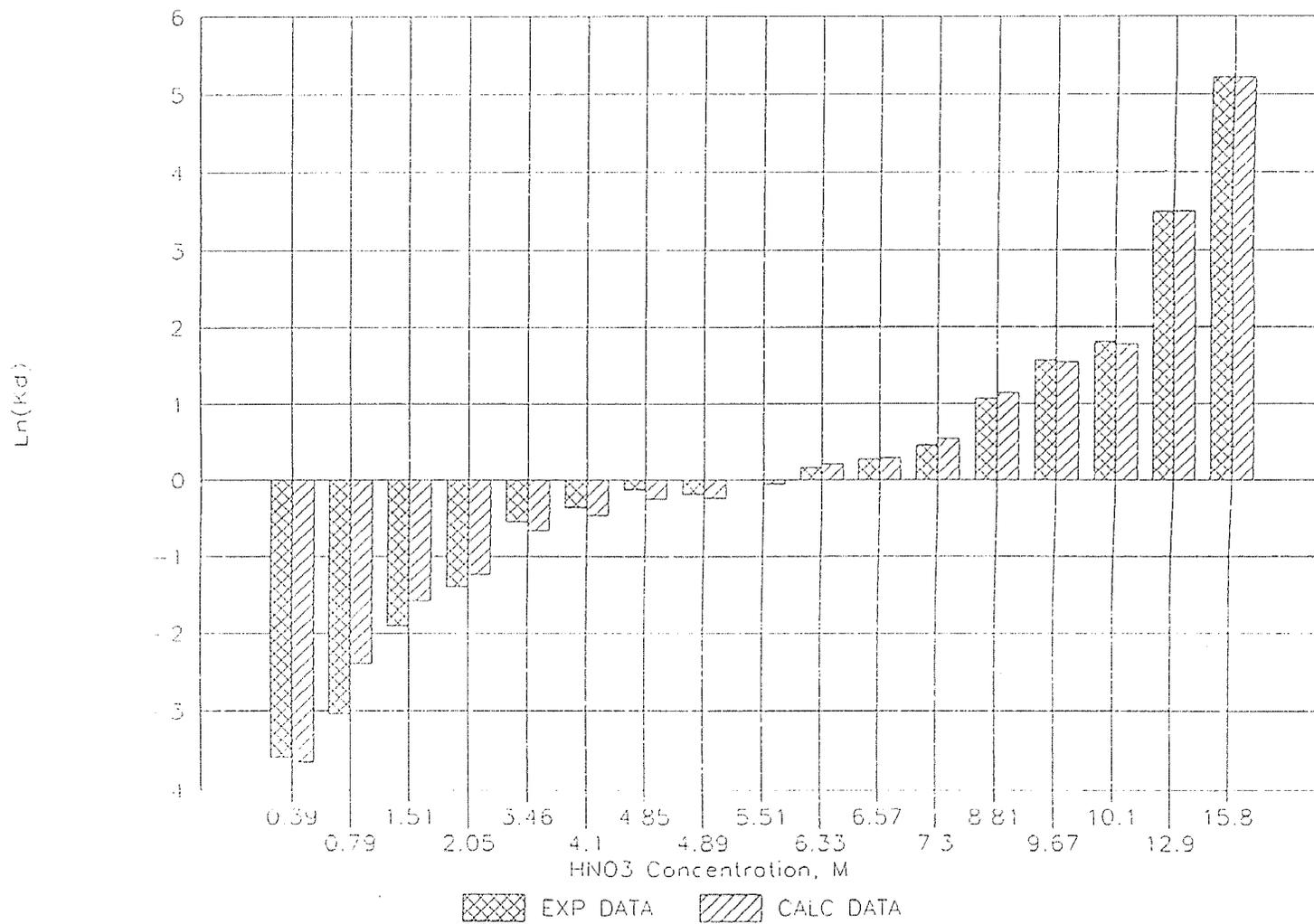


Figure 5.21 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Erbium.

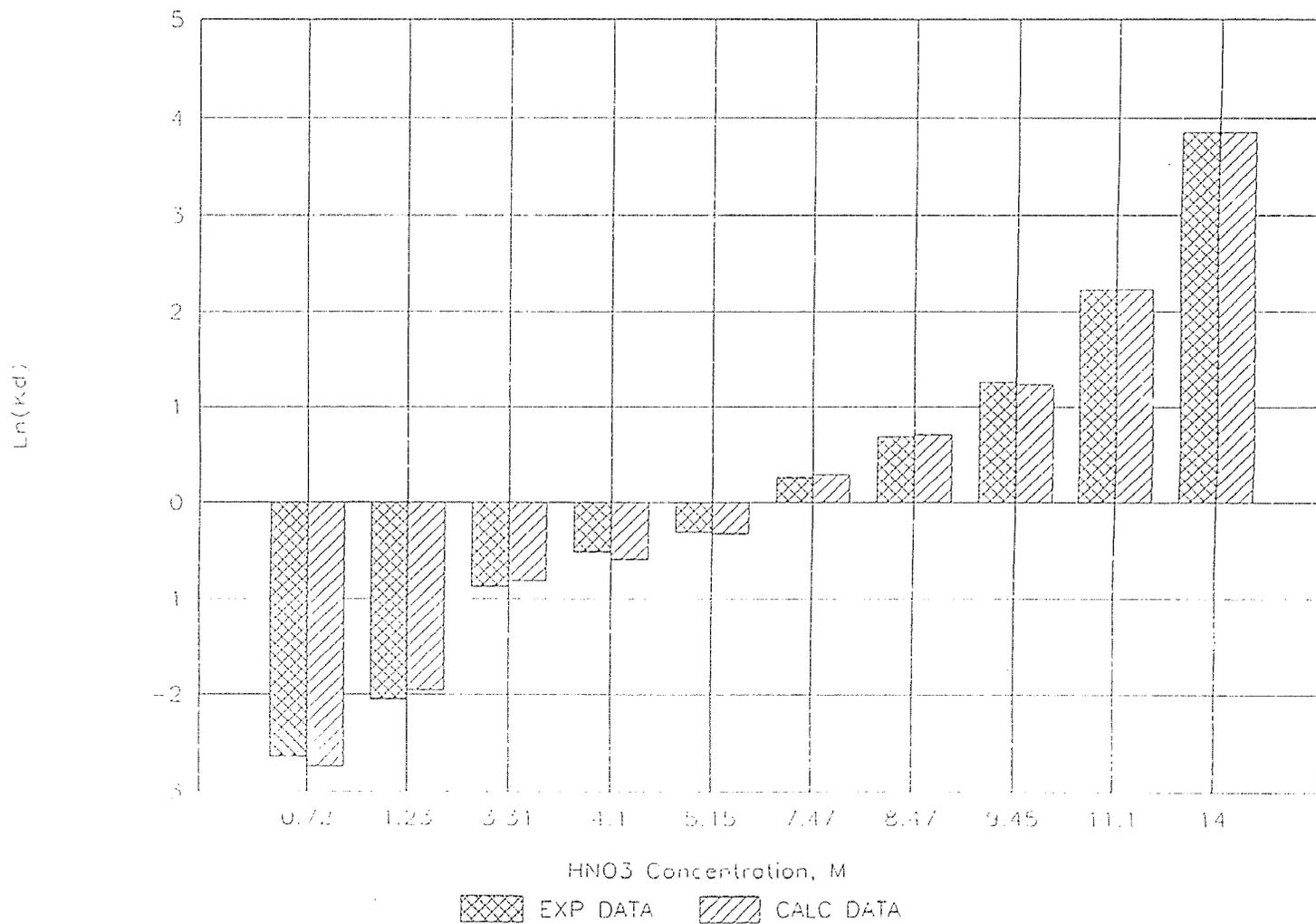


Figure 5.22 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Holmium.

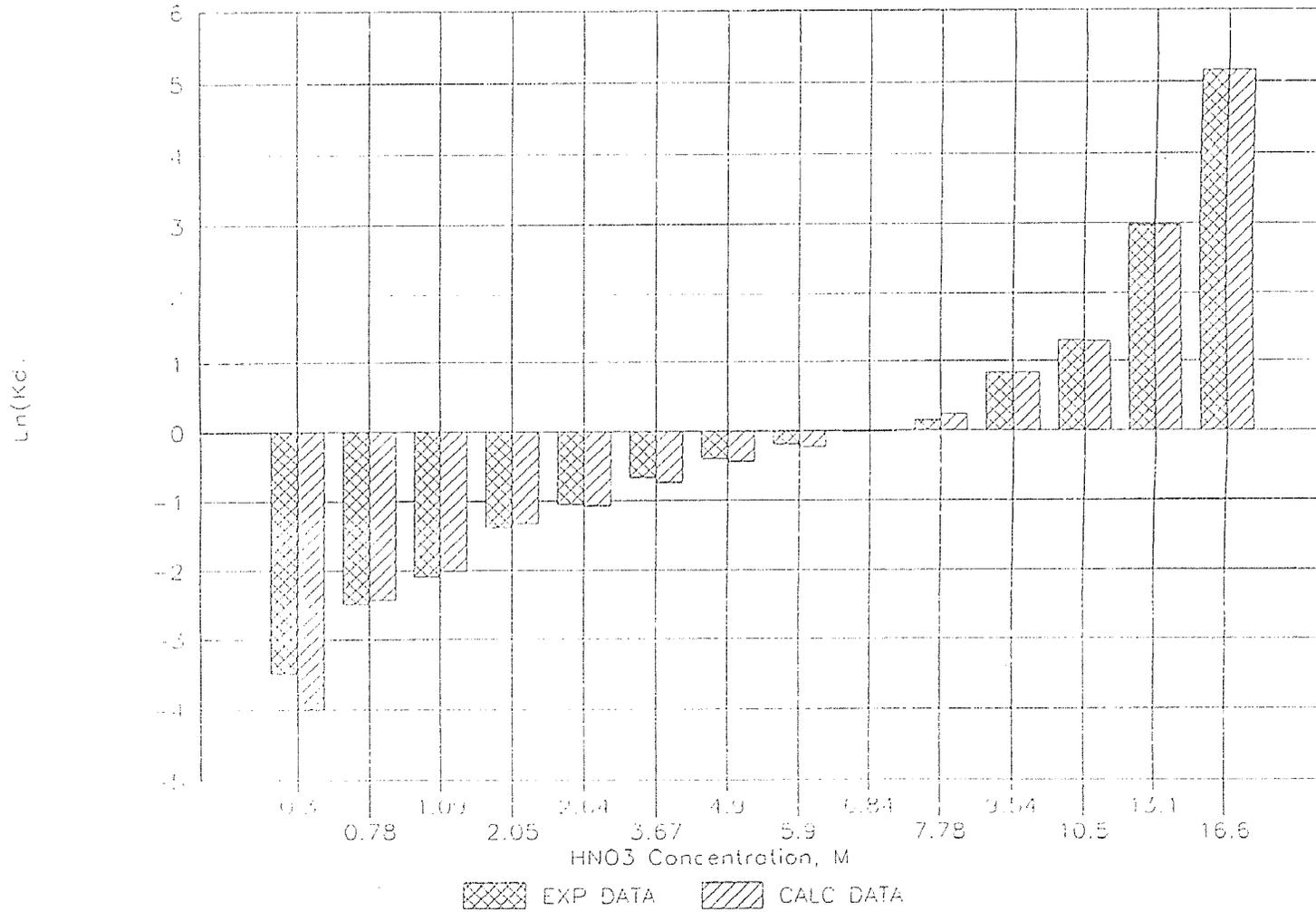


Figure 5.23 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Dysprosium.

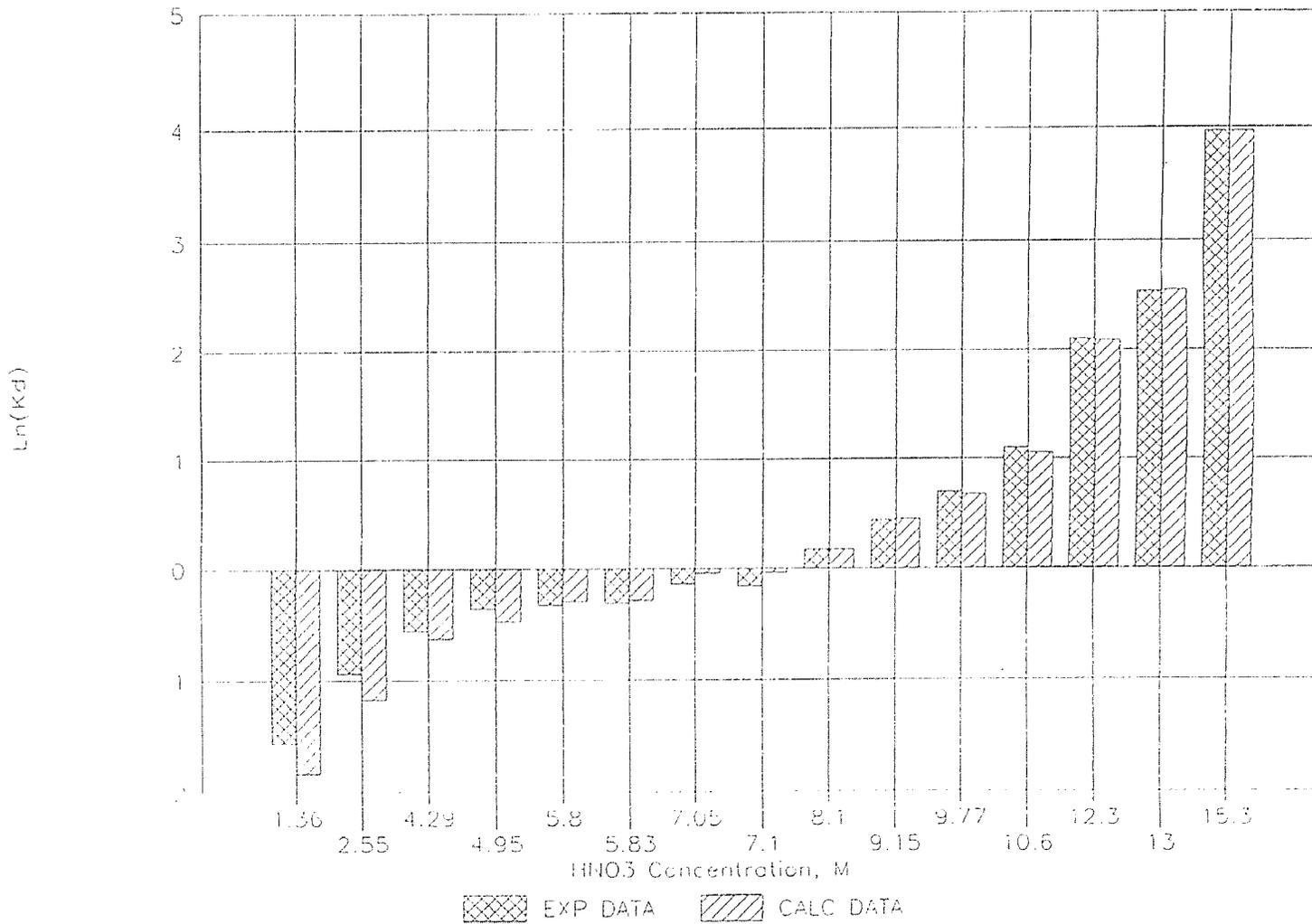


Figure 5.24 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Terbium.

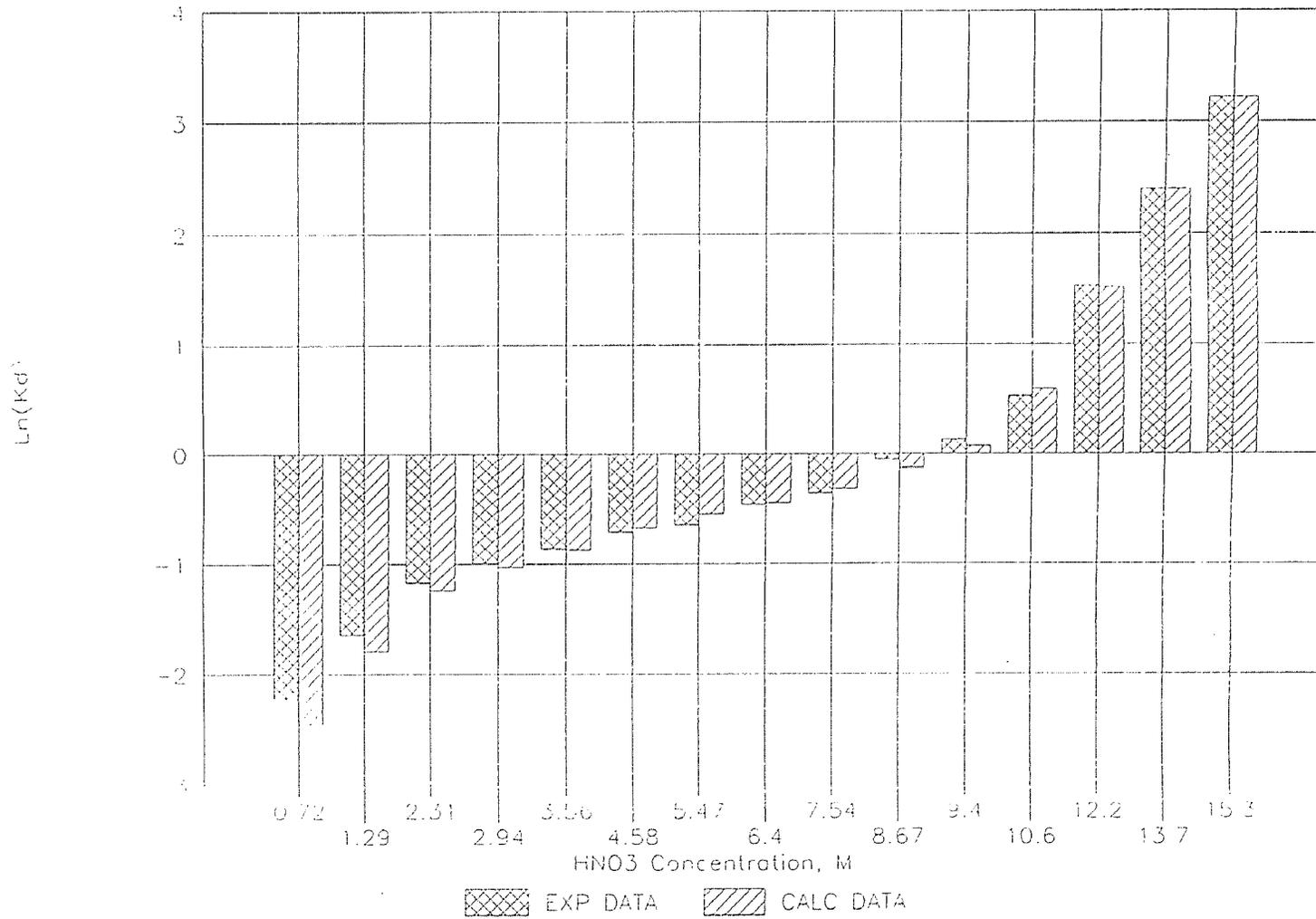


Figure 5.25 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Gadolinium.

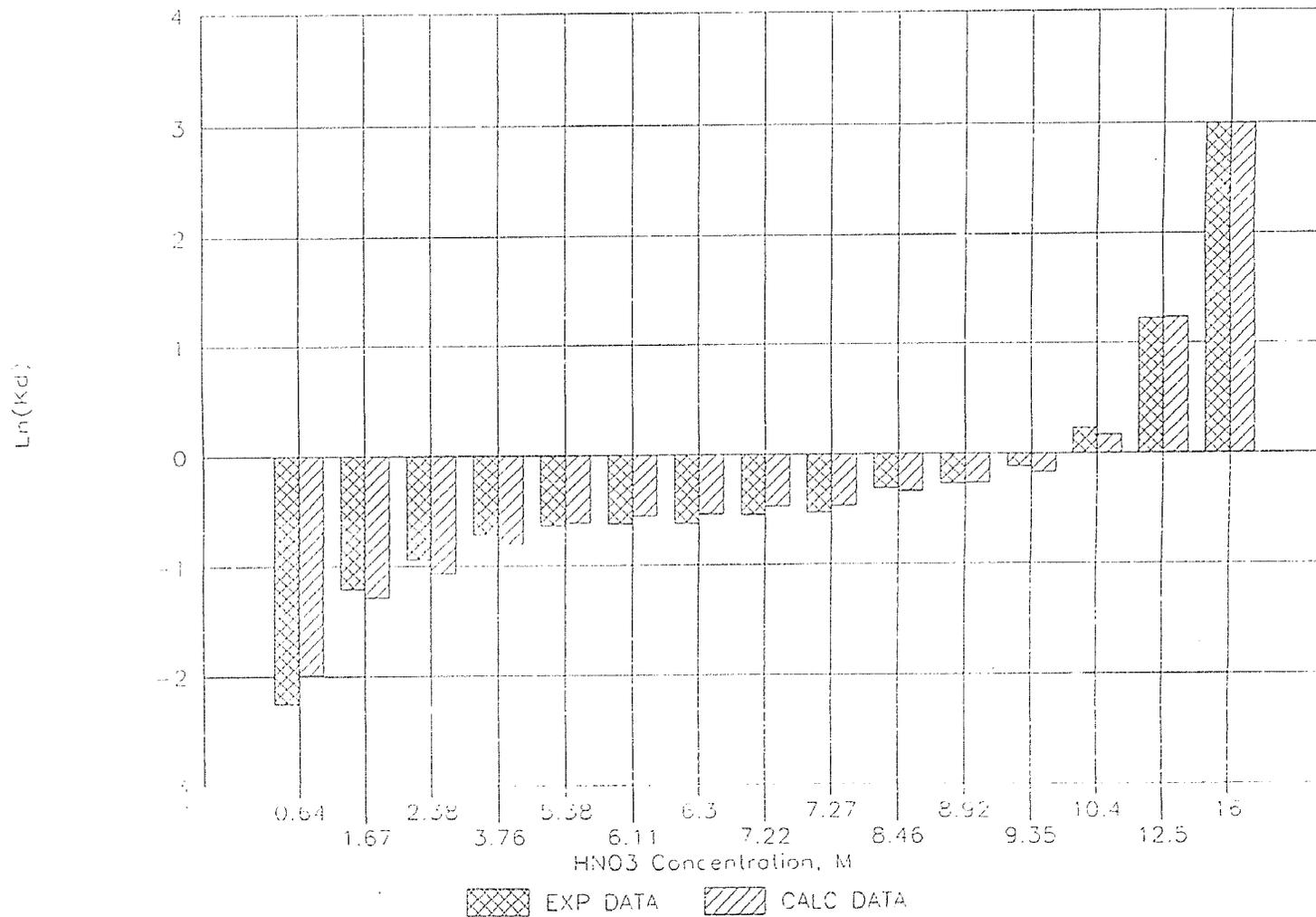


Figure 5.26 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Europium.

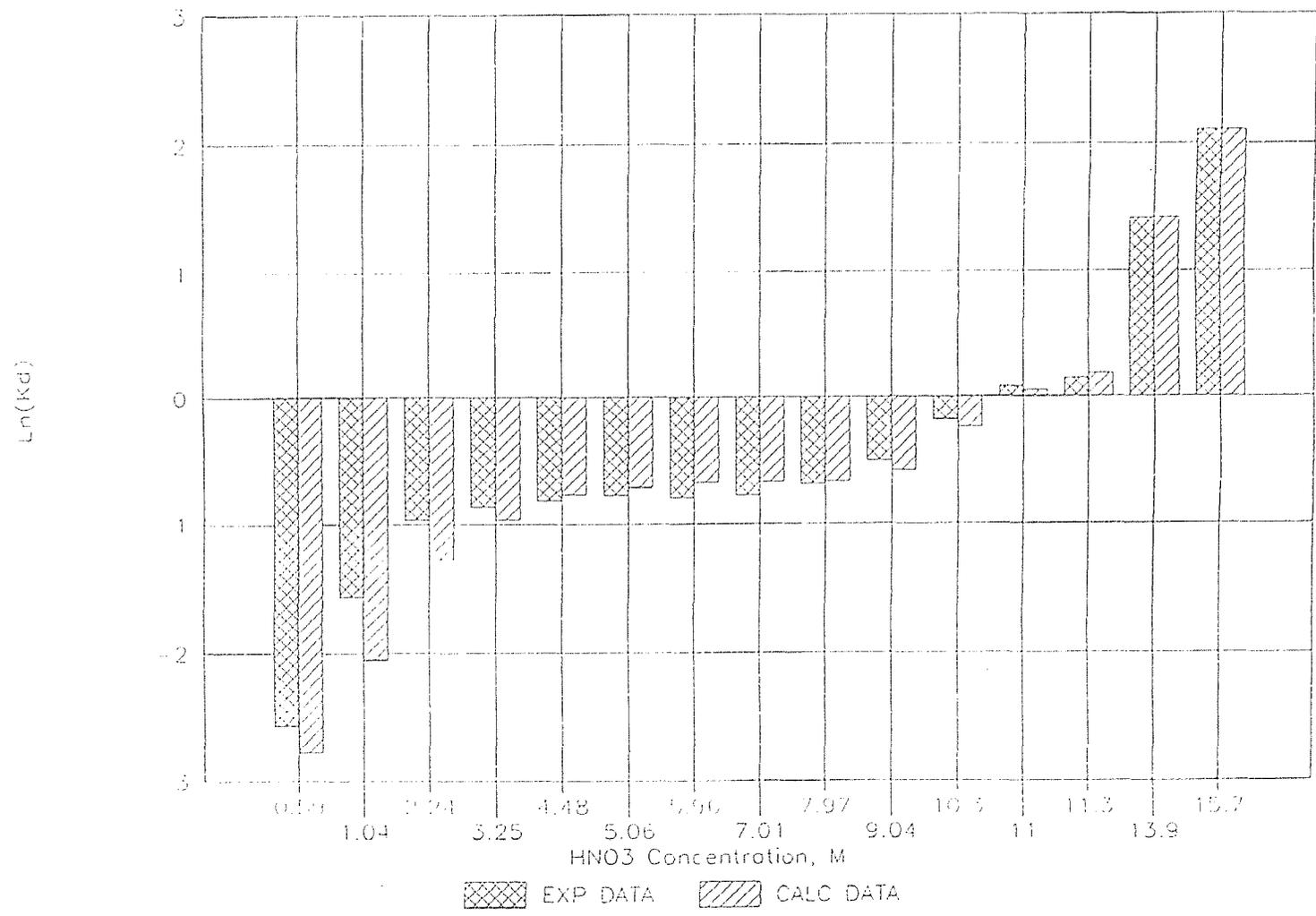


Figure 5.27 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Samarium.

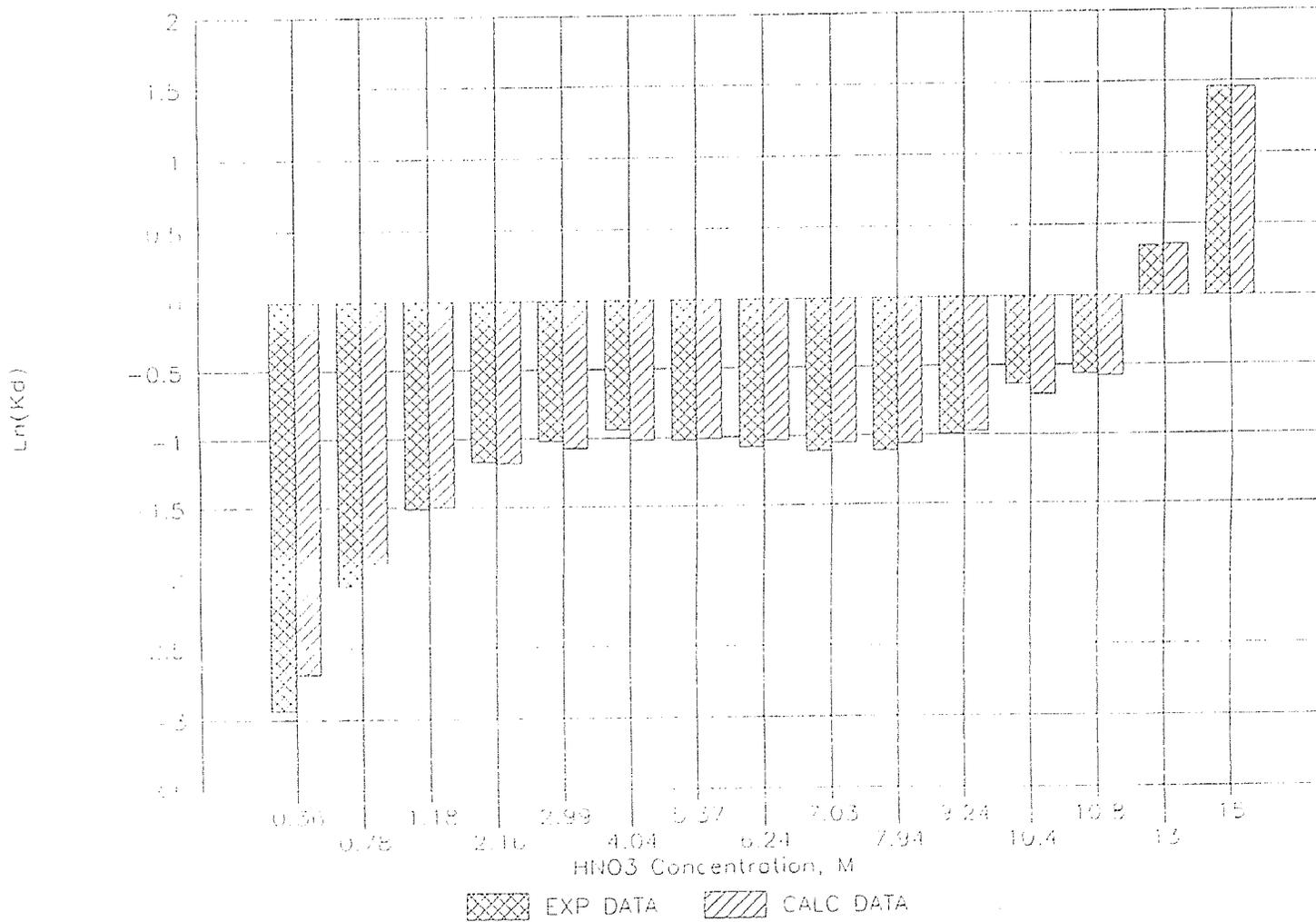


Figure 5.28 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Promethium.

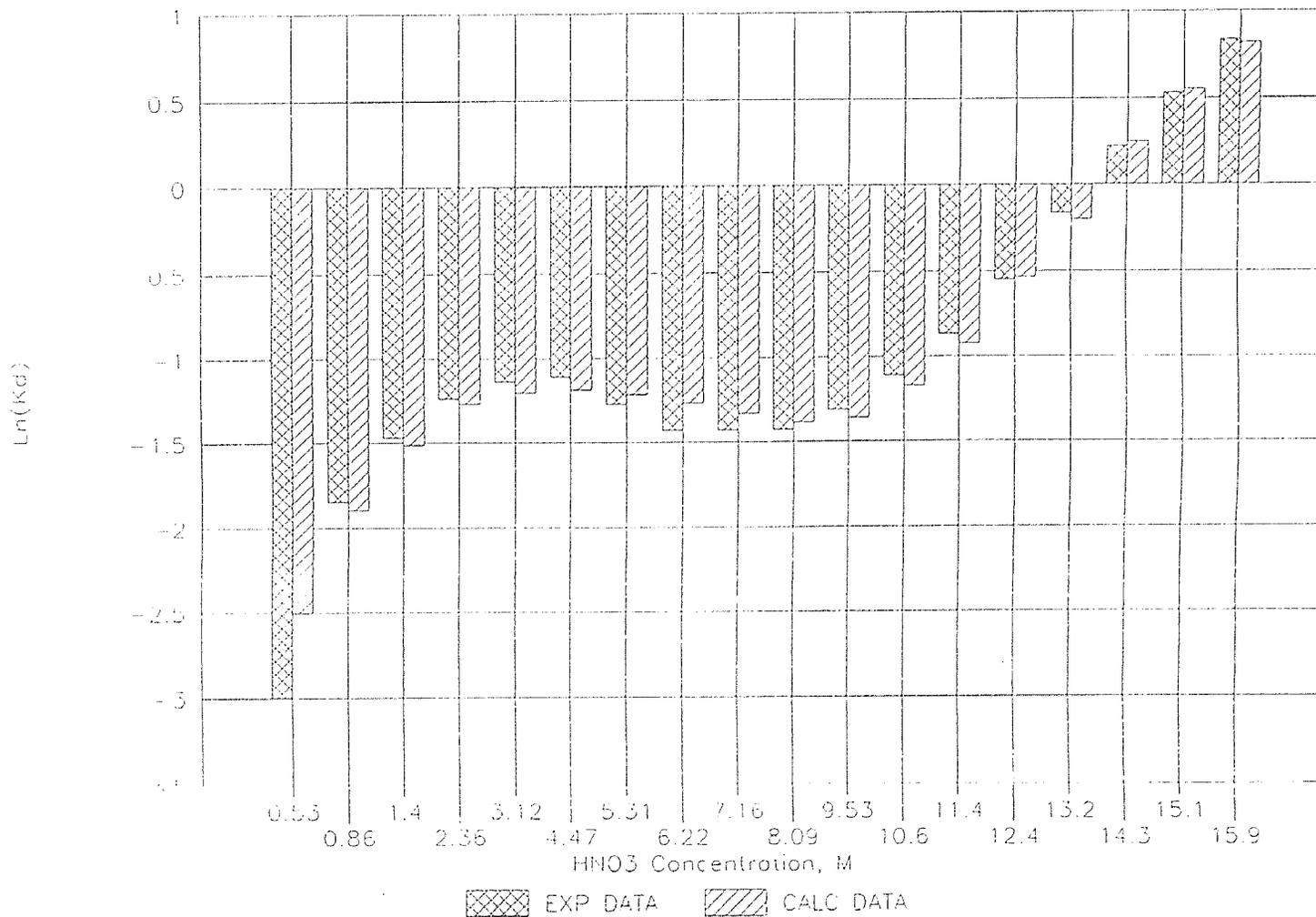


Figure 5.29 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Neodymium.

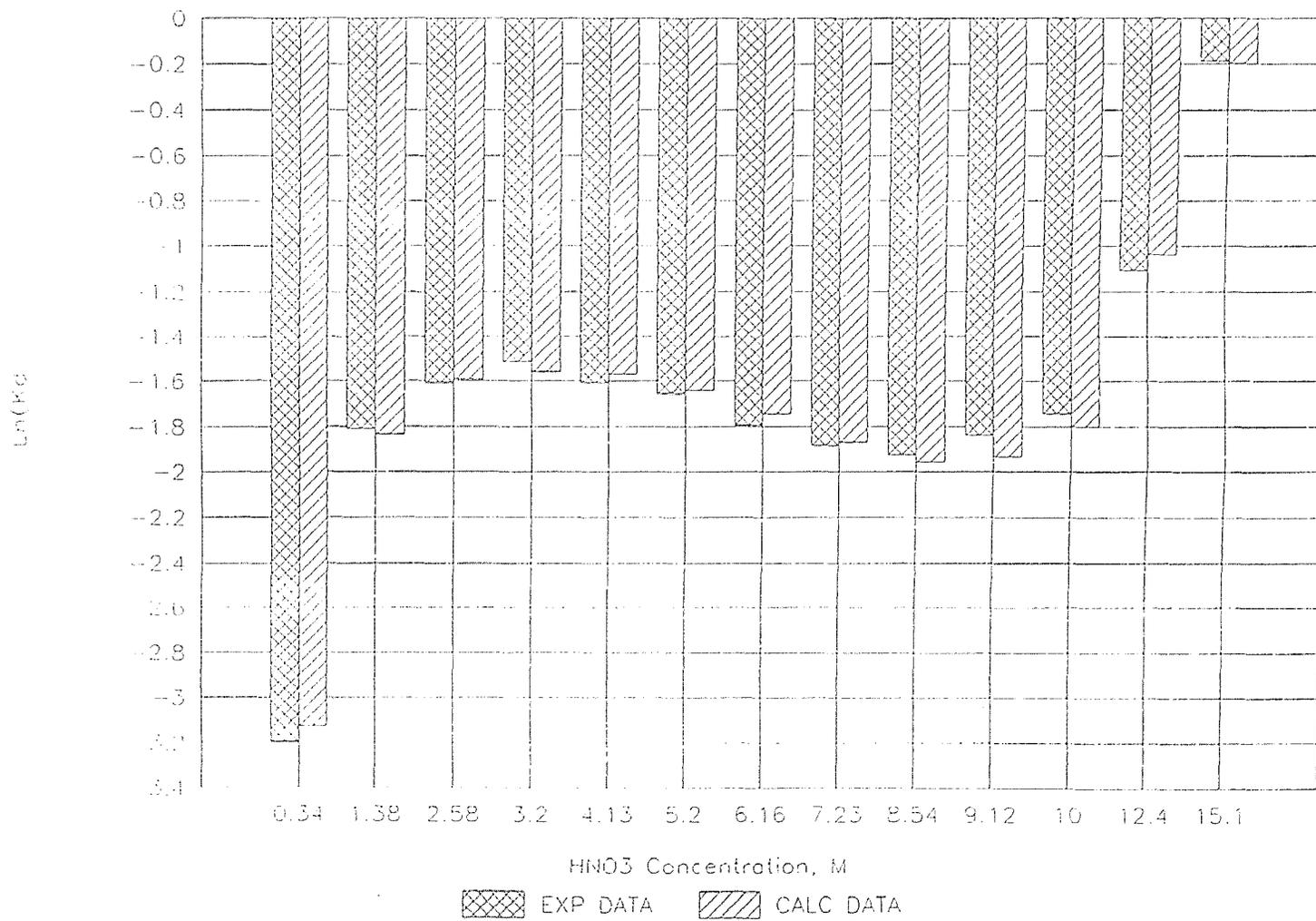


Figure 5.30 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Praseodymium.

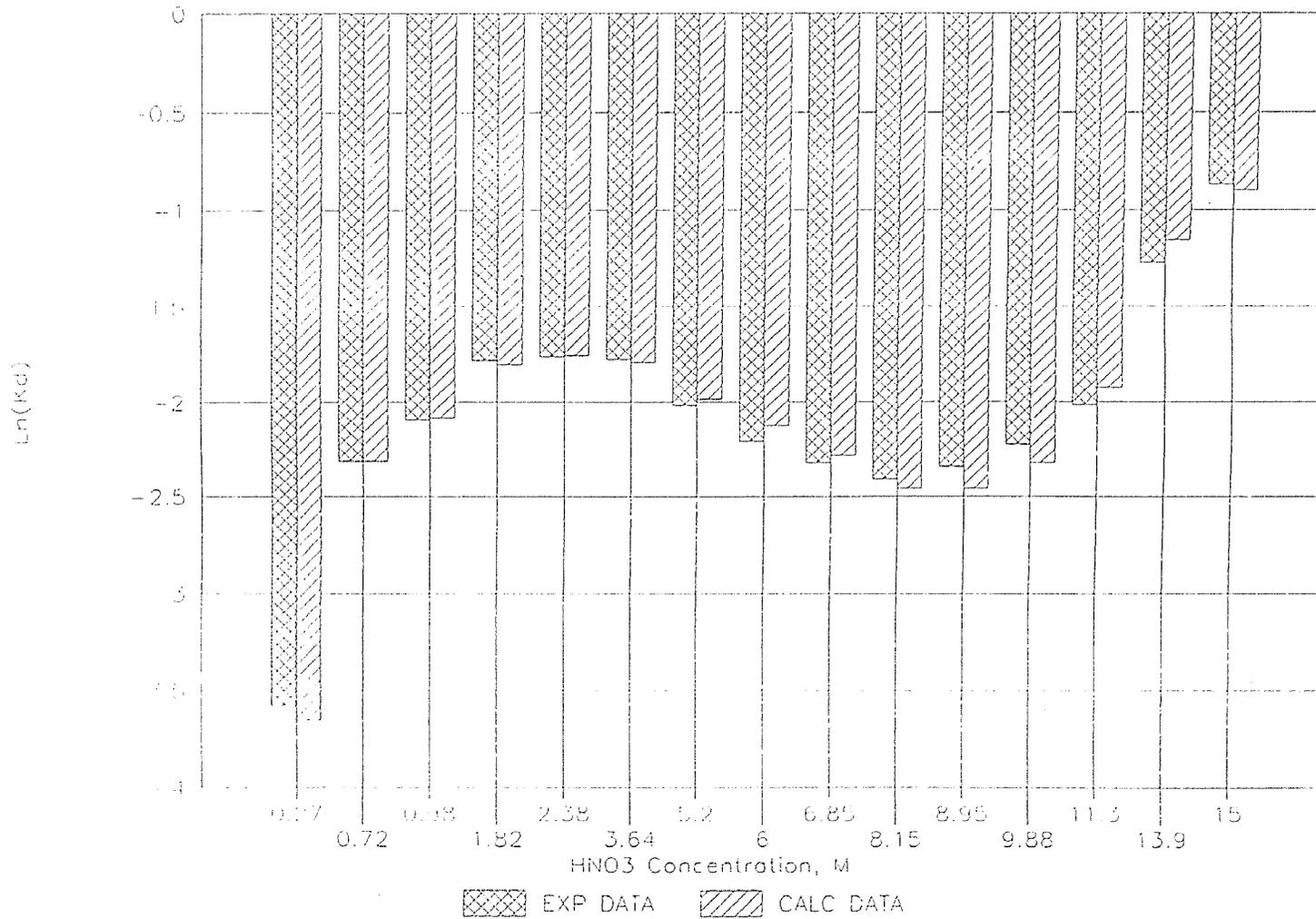


Figure 5.31 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Cerium.

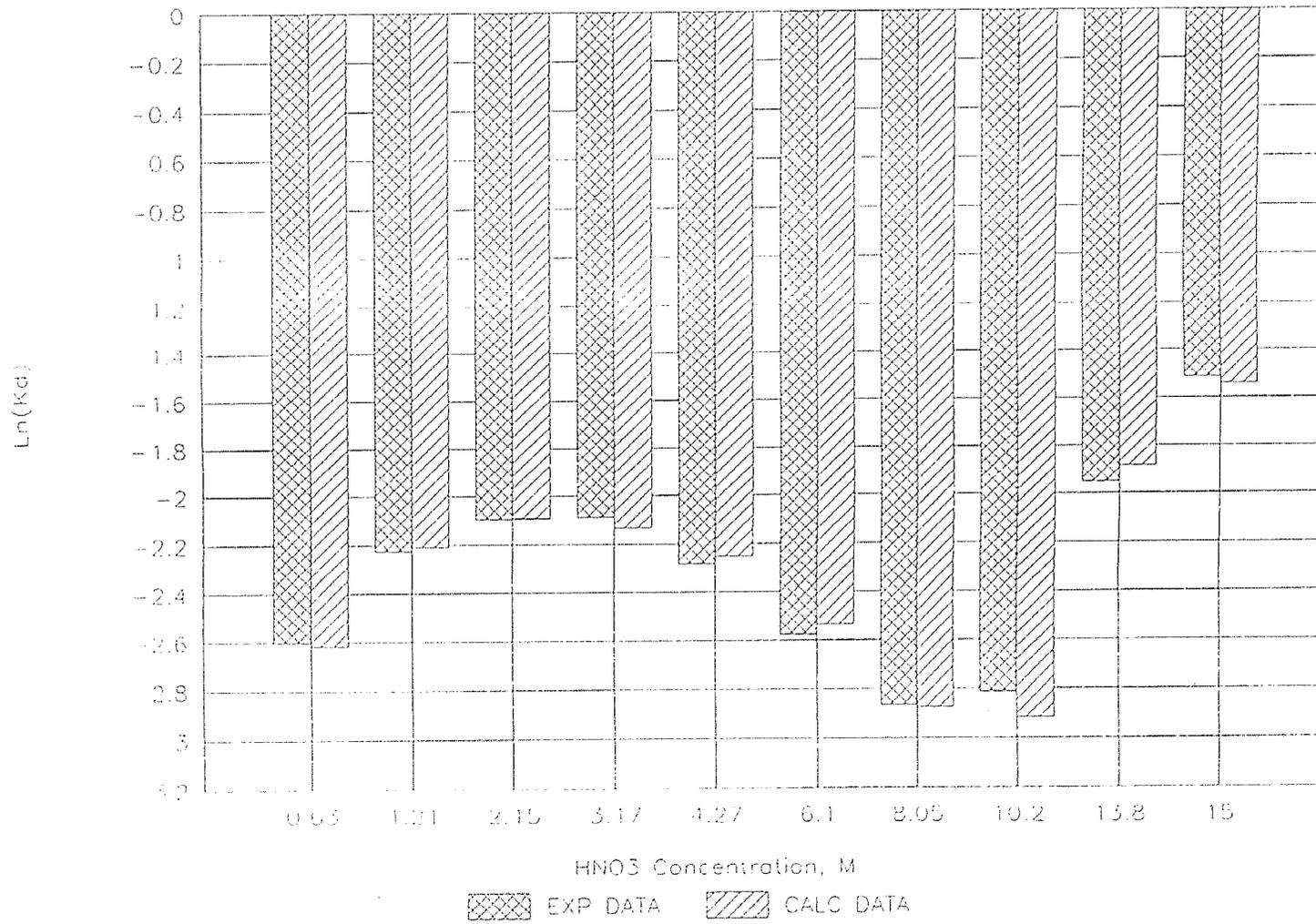


Figure 5.32 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Lanthanum.

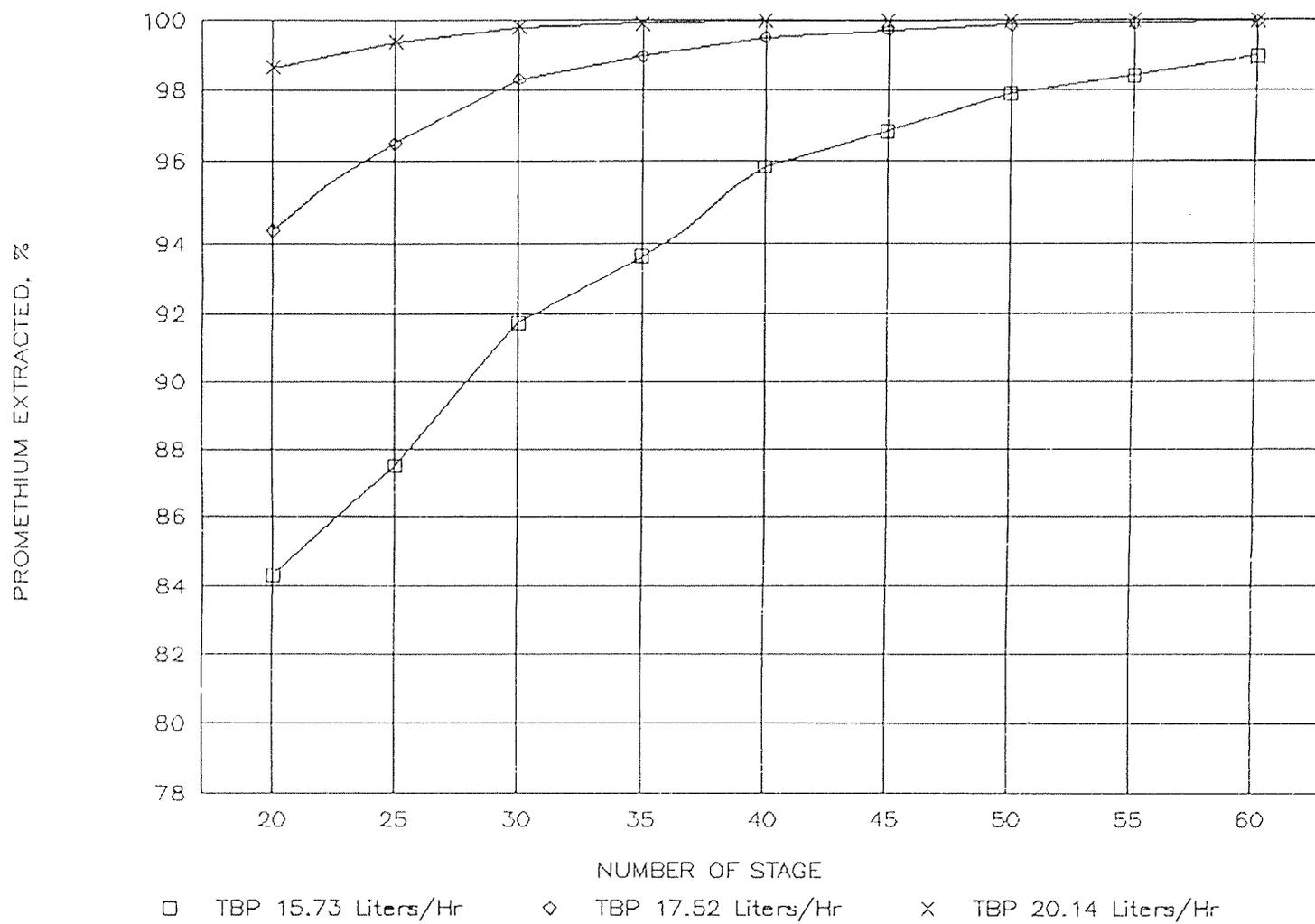


Figure 5.34 The Effect of Number of Stages on Promethium Extraction HNO₃ 12.0 N.

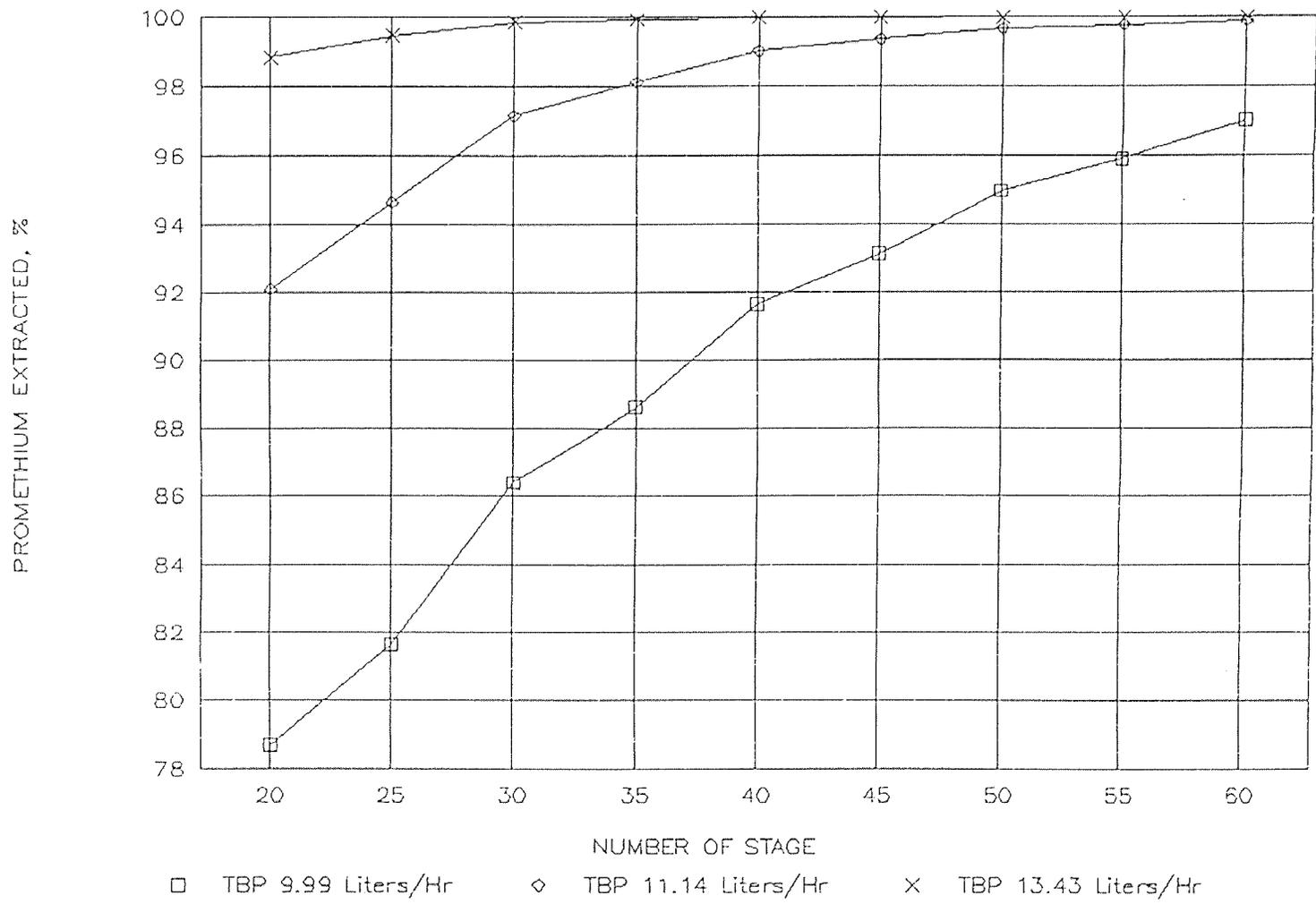


Figure 5.35 The Effect of Number of Stages on Promethium Extraction HNO_3 13.0 N.

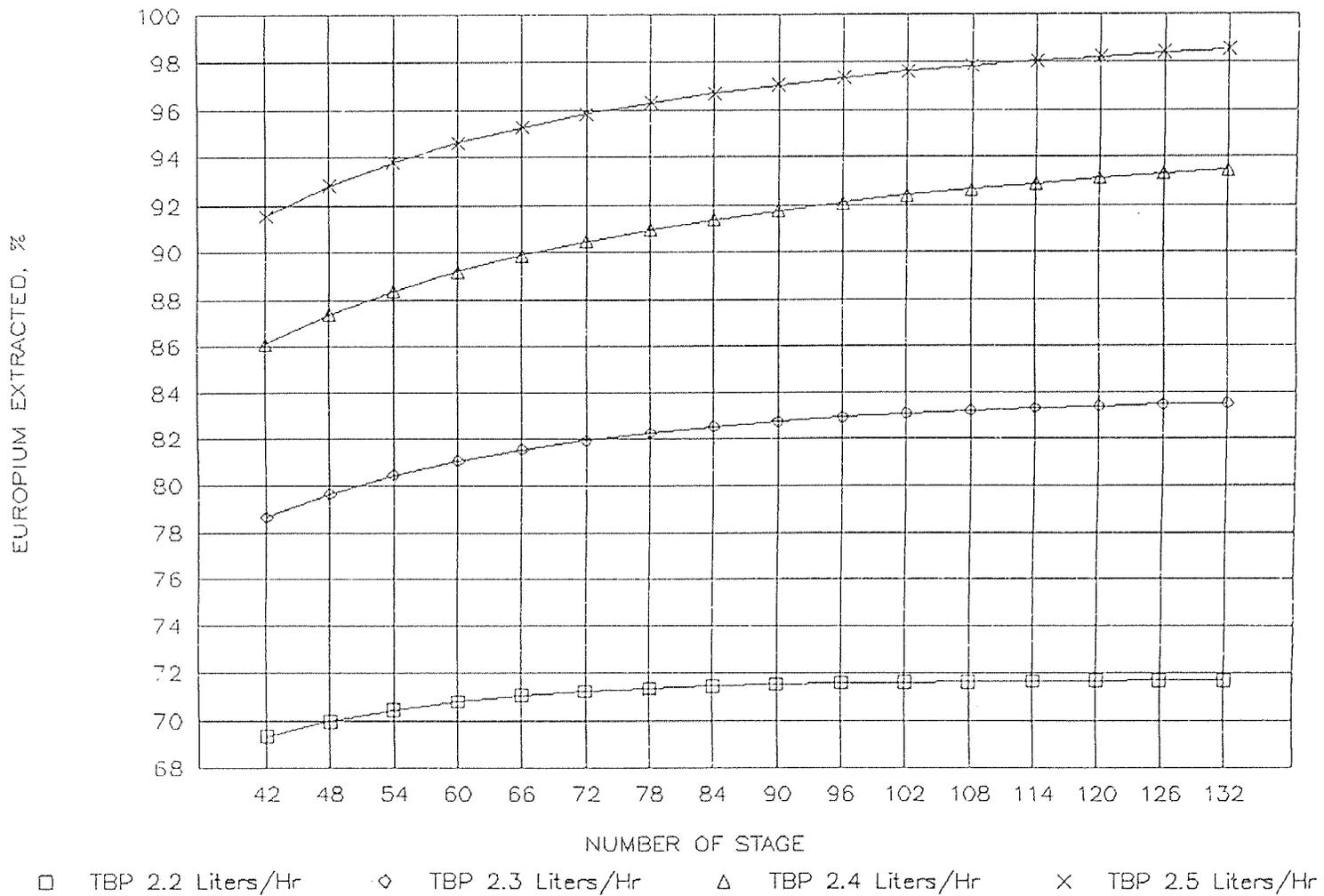


Figure 6.5 The Effect of Number of Stages on Europium Extraction, Europium Extracted %, HNO₃ 9.9 N.

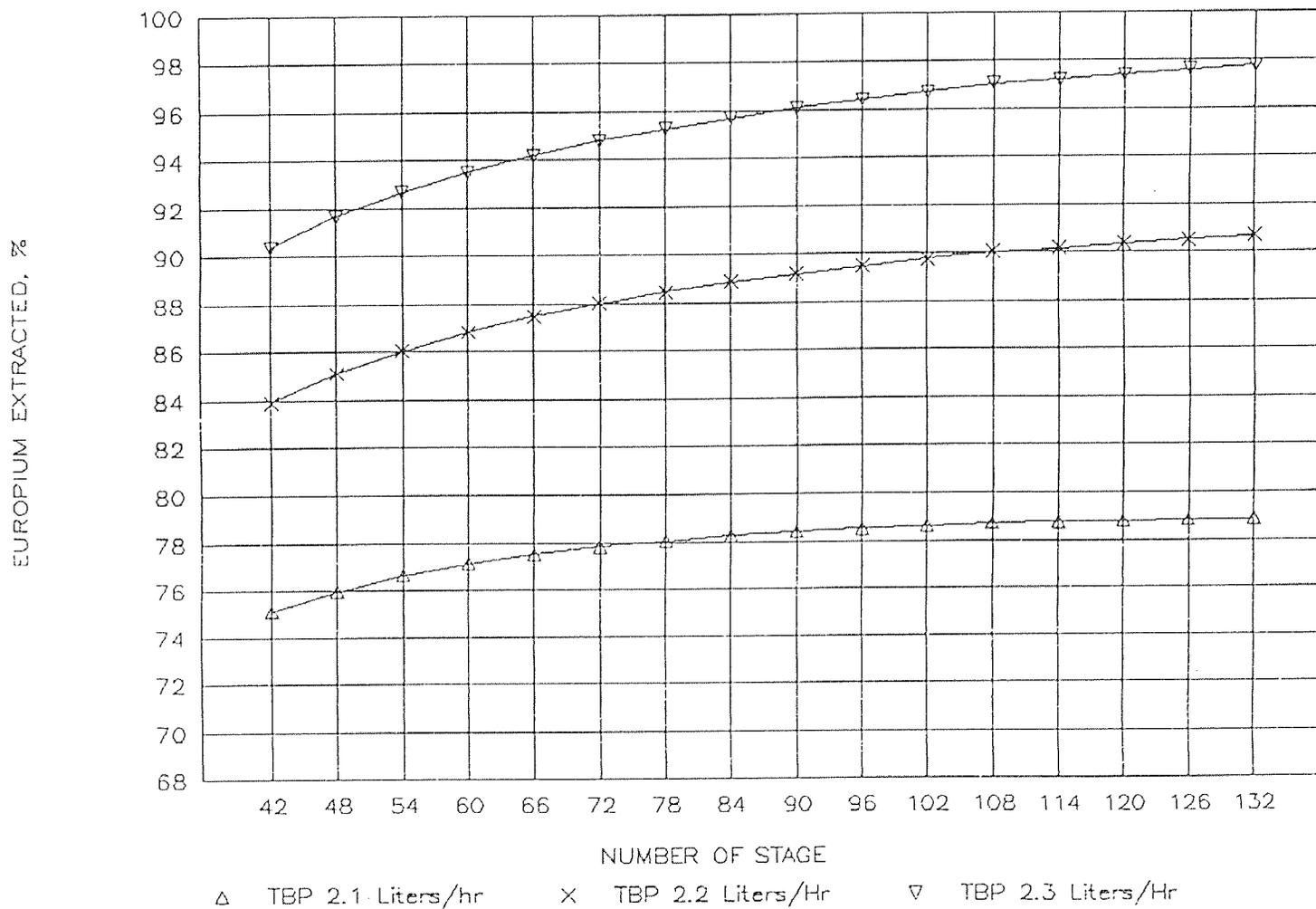


Figure 6.6 The Effect of Number of Stages on Europium Extraction, Europium Extracted %, HNO₃ 10.0 N.

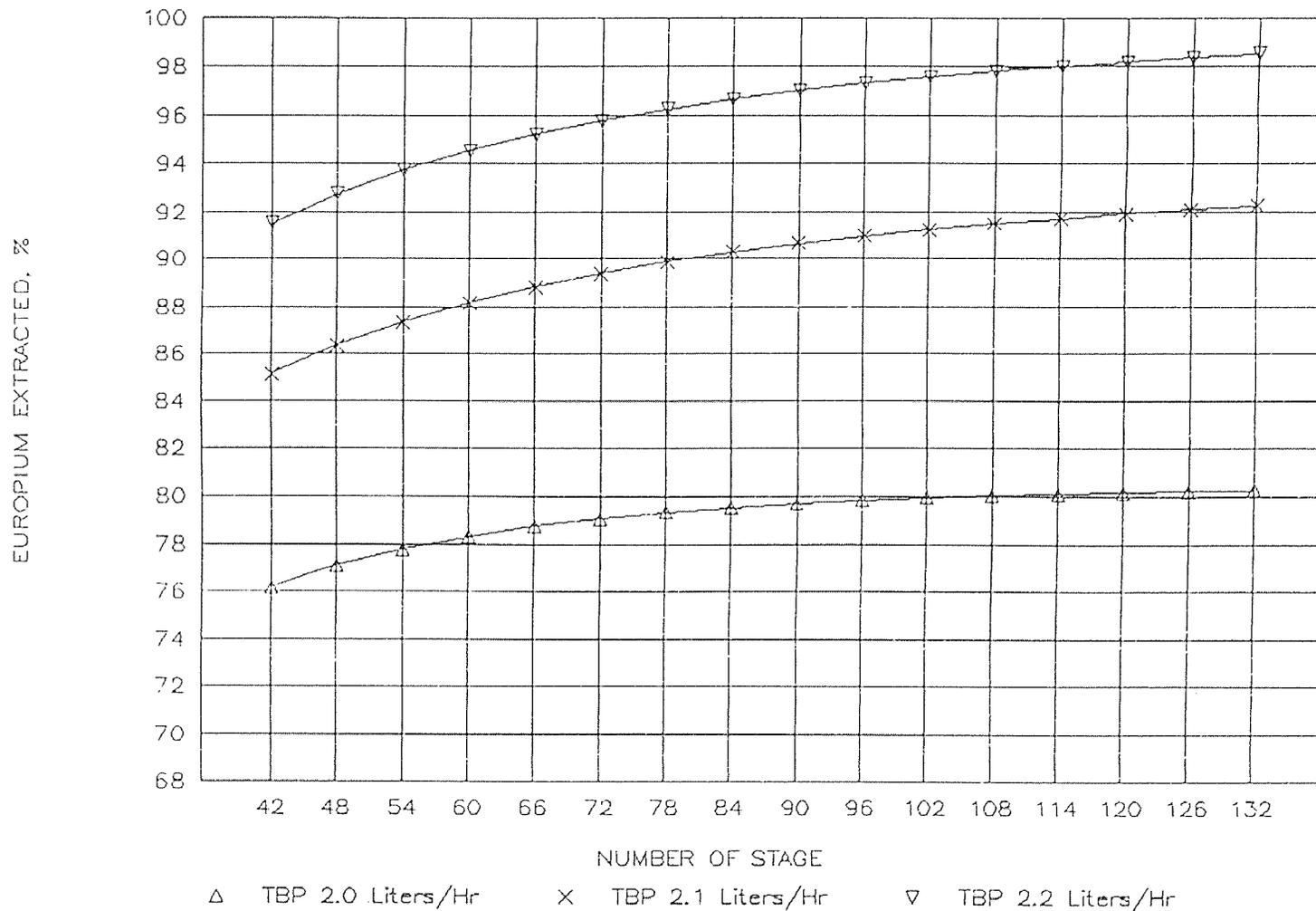


Figure 6.7 The Effect of Number of Stages on Europium Extraction, Europium Extracted %, HNO₃ 10.1 N.

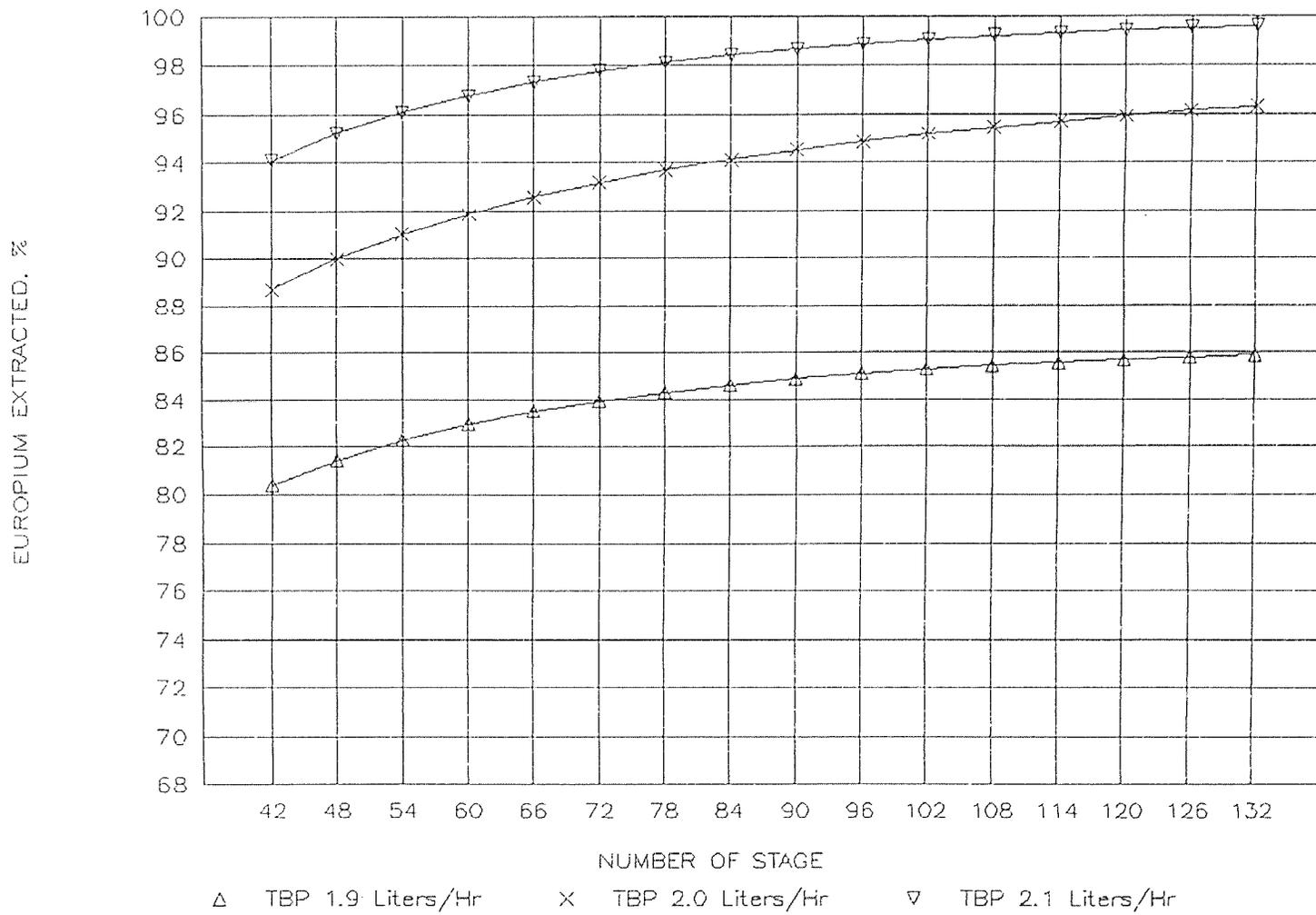


Figure 6.8 The Effect of Number of Stages on Europium Extraction, Europium Extracted %, HNO₃ 10.2 N.

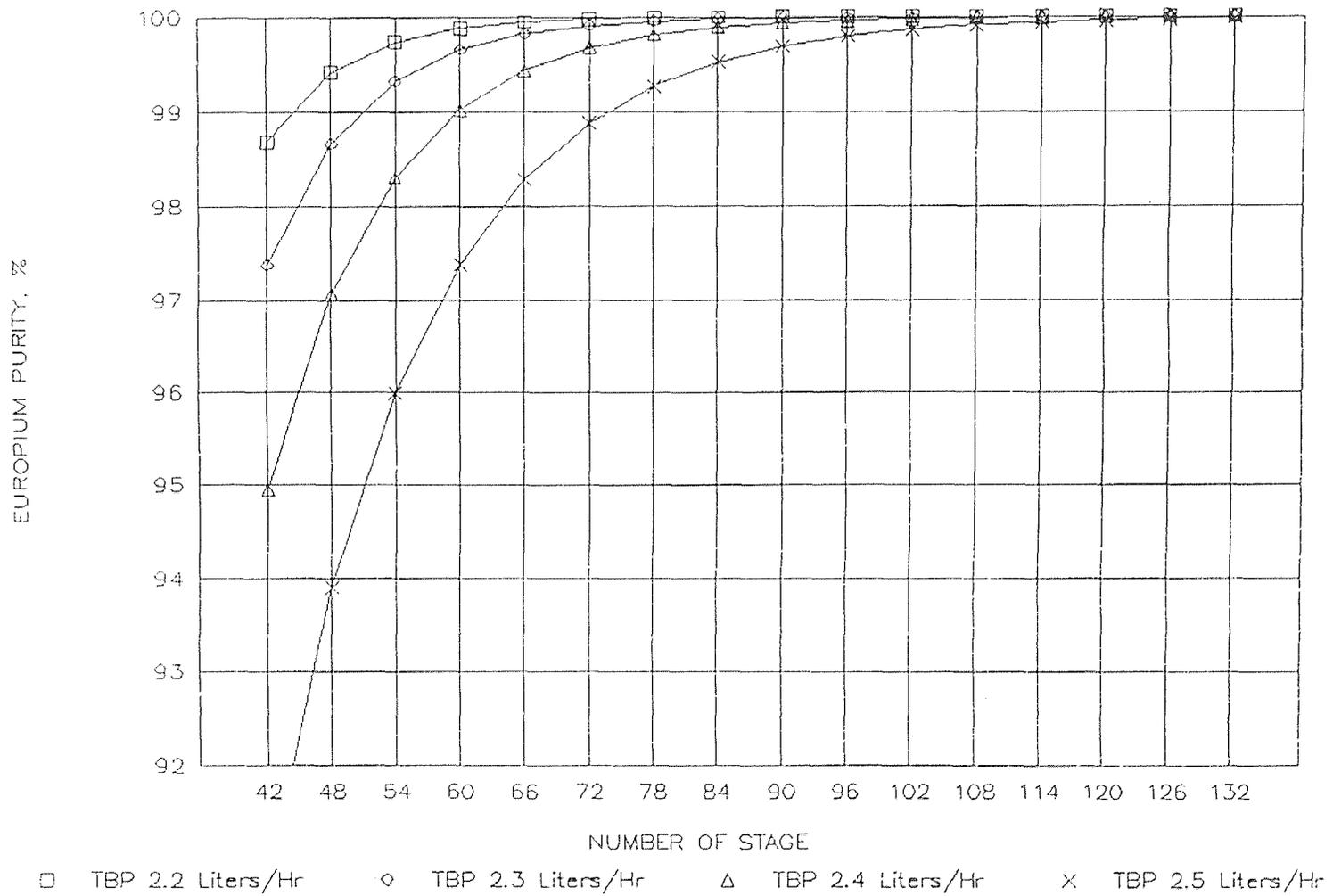


Figure 6.10 The Effect of Number of Stages on Europium Extraction, Europium Purity %, HNO_3 9.9 N.

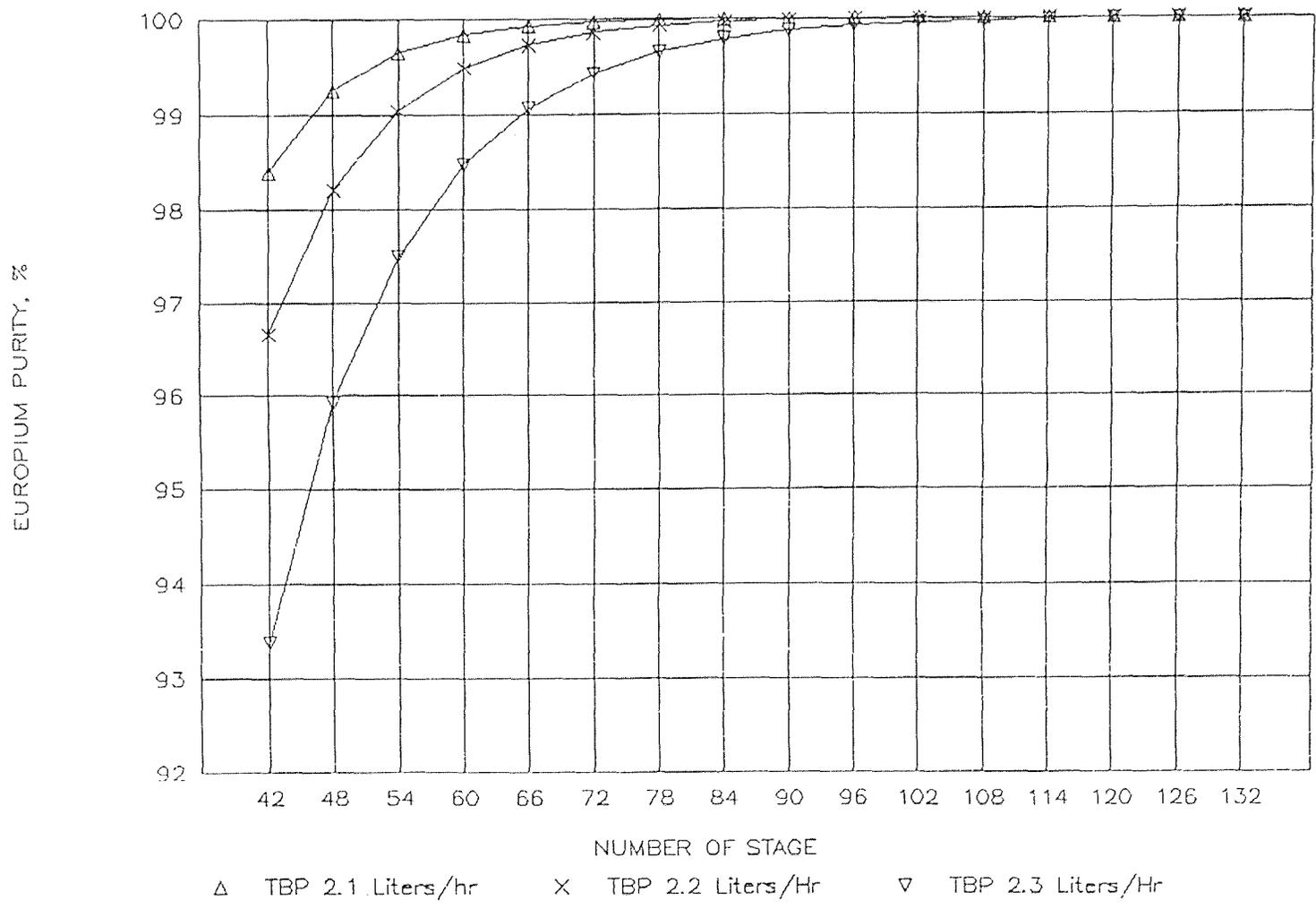


Figure 6.11 The Effect of Number of Stages on Europium Extraction, Europium Purity %, HNO₃ 10.0 N.

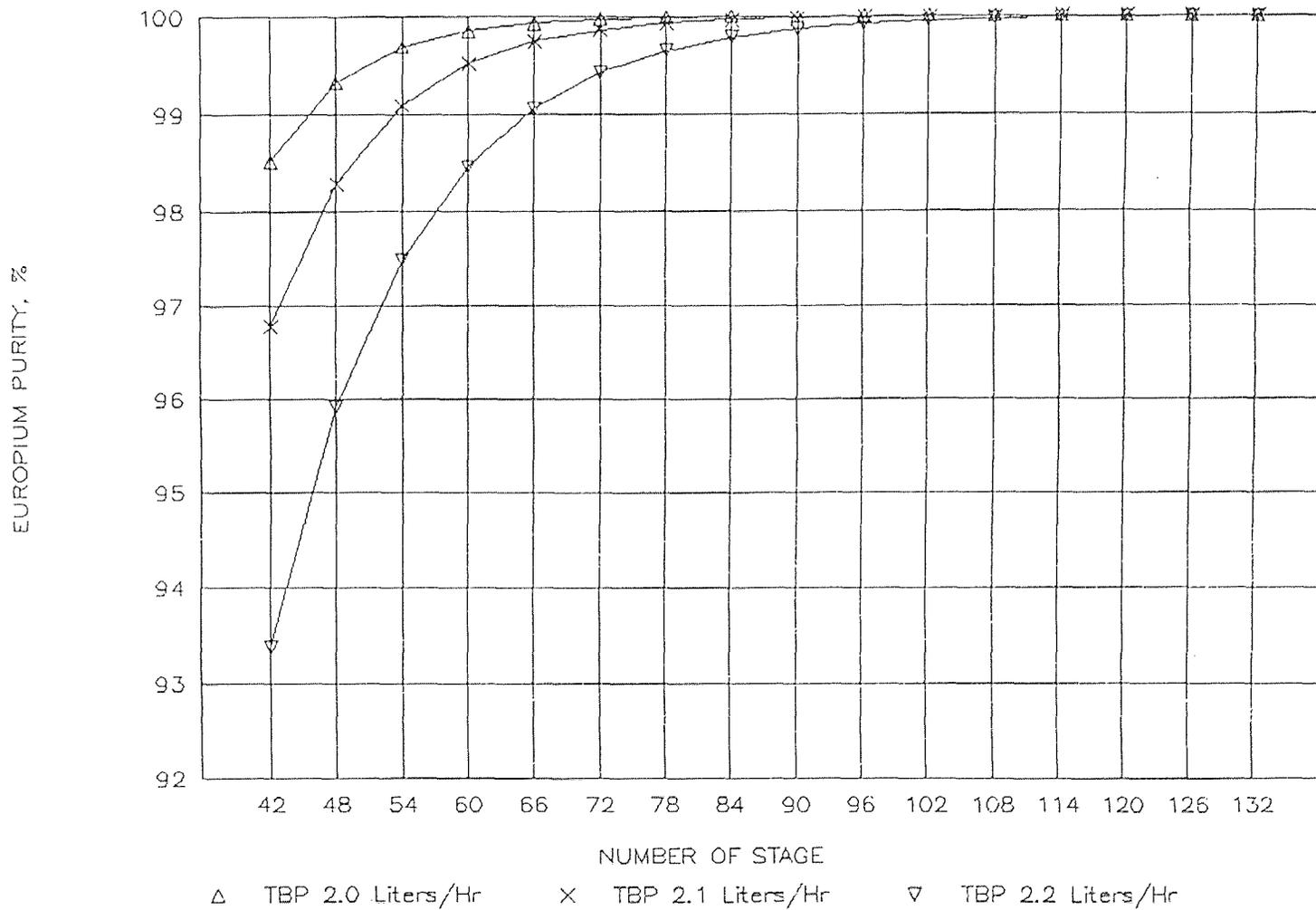


Figure 6.12 The Effect of Number of Stages on Europium Extraction, Europium Purity %, HNO_3 10.1 N.

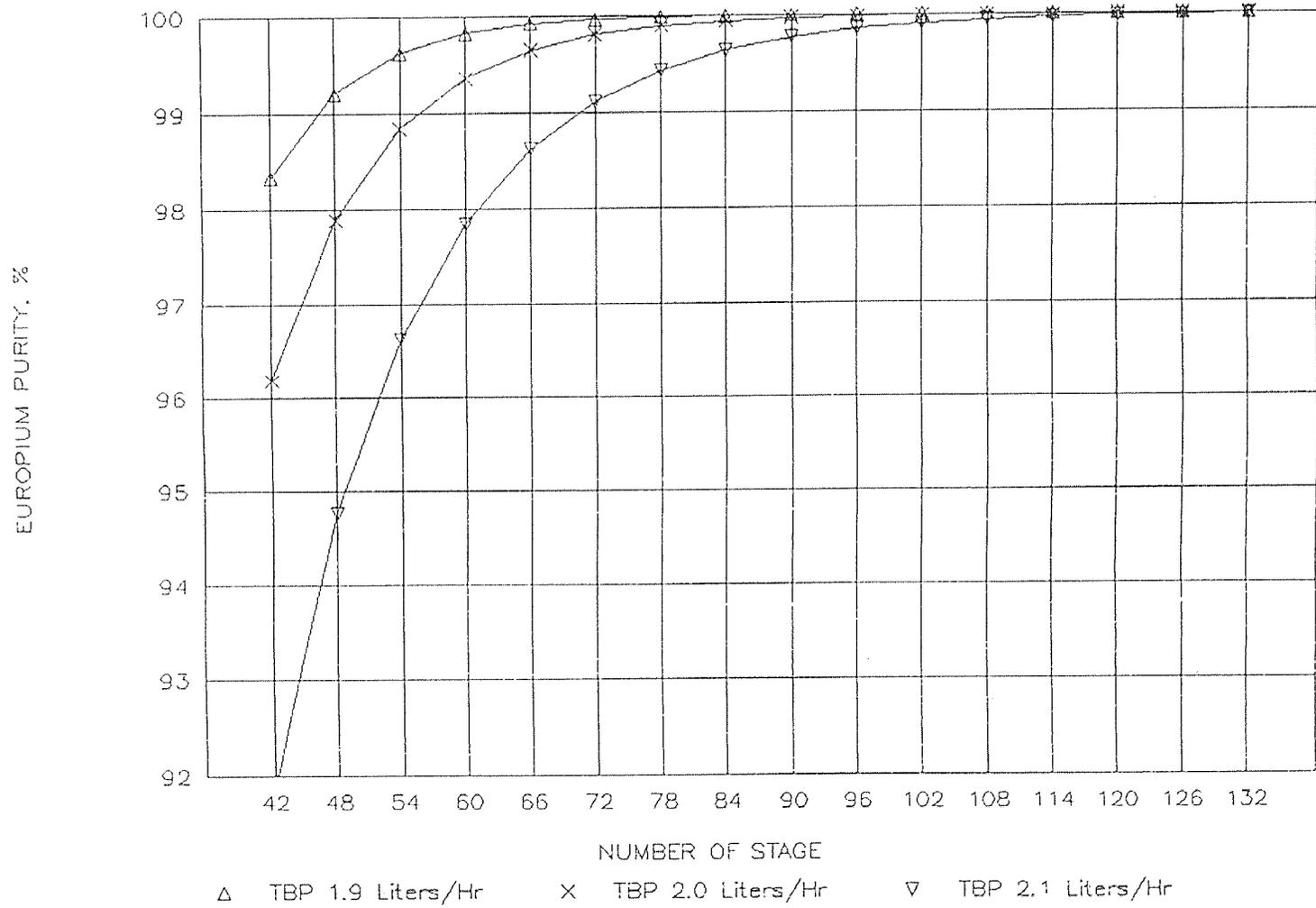


Figure 6.13 The Effect of Number of Stages on Europium Extraction, Europium Purity %, HNO₃ 10.2 N.

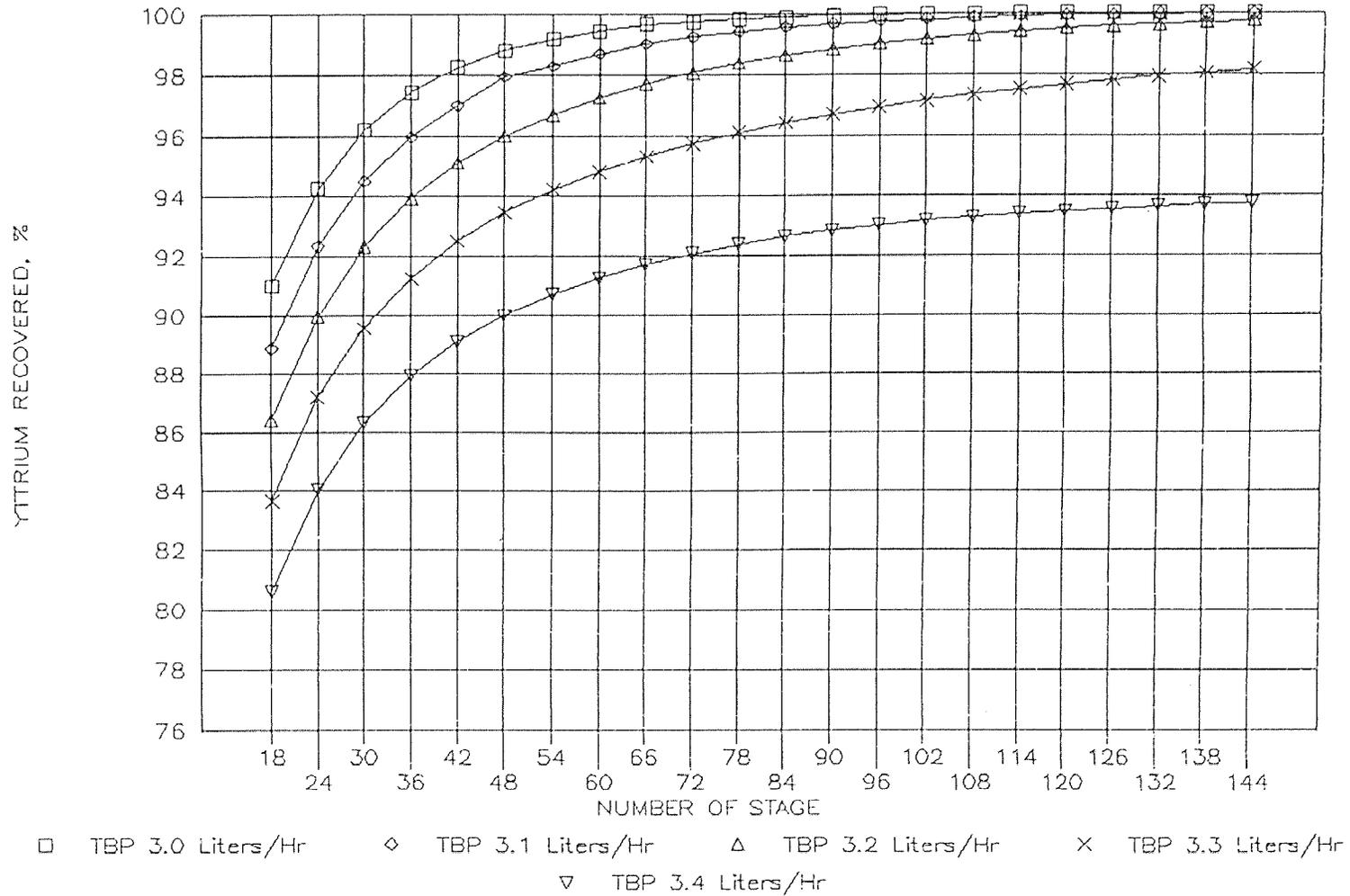


Figure 7.2 The Effect of Number of Stages on Yttrium Purification, Yttrium Recovered %, HNO_3 6.2 N.

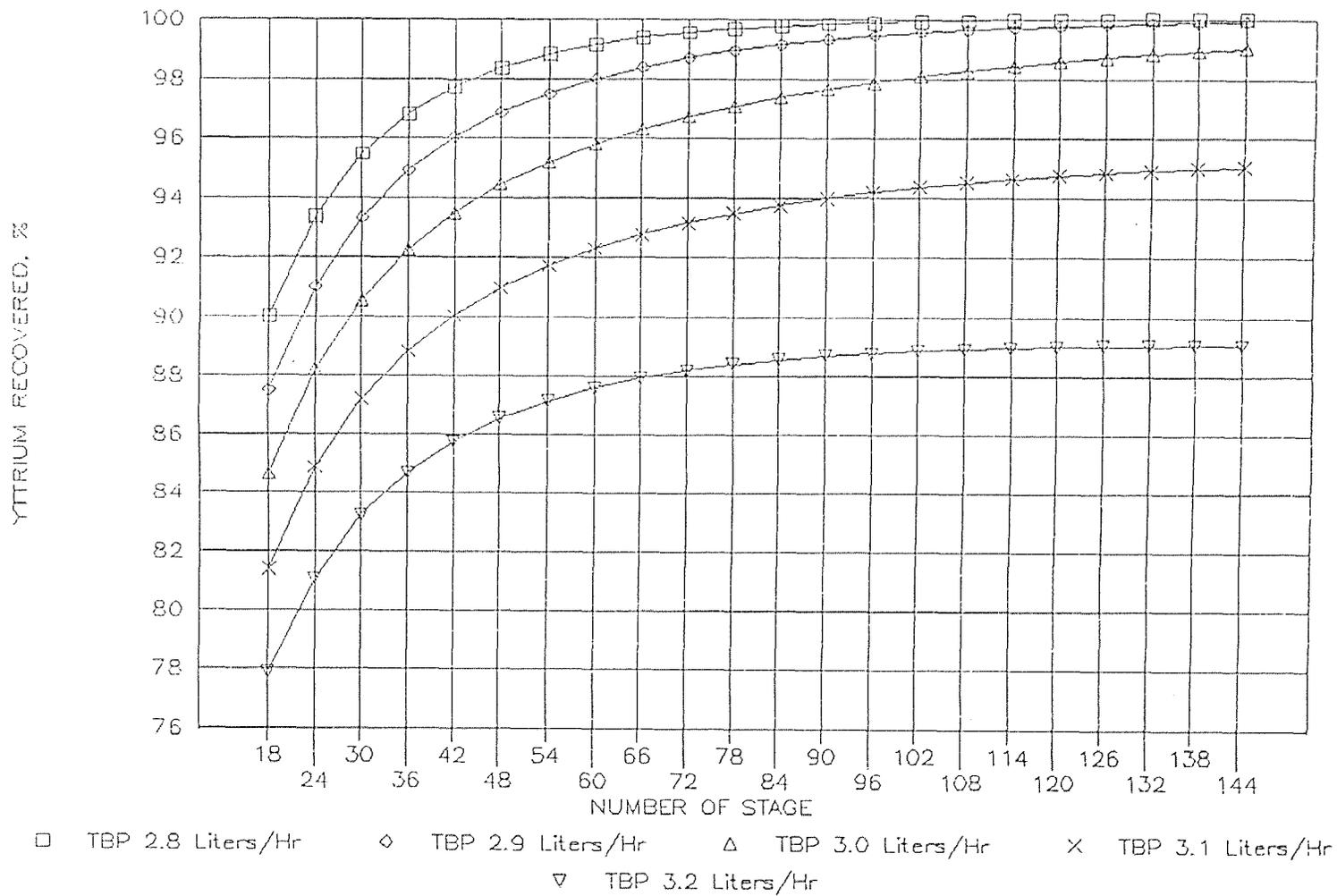


Figure 7.3 The Effect of Number of Stages on Yttrium Purification, Yttrium Recovered %, HNO₃ 6.3 N.

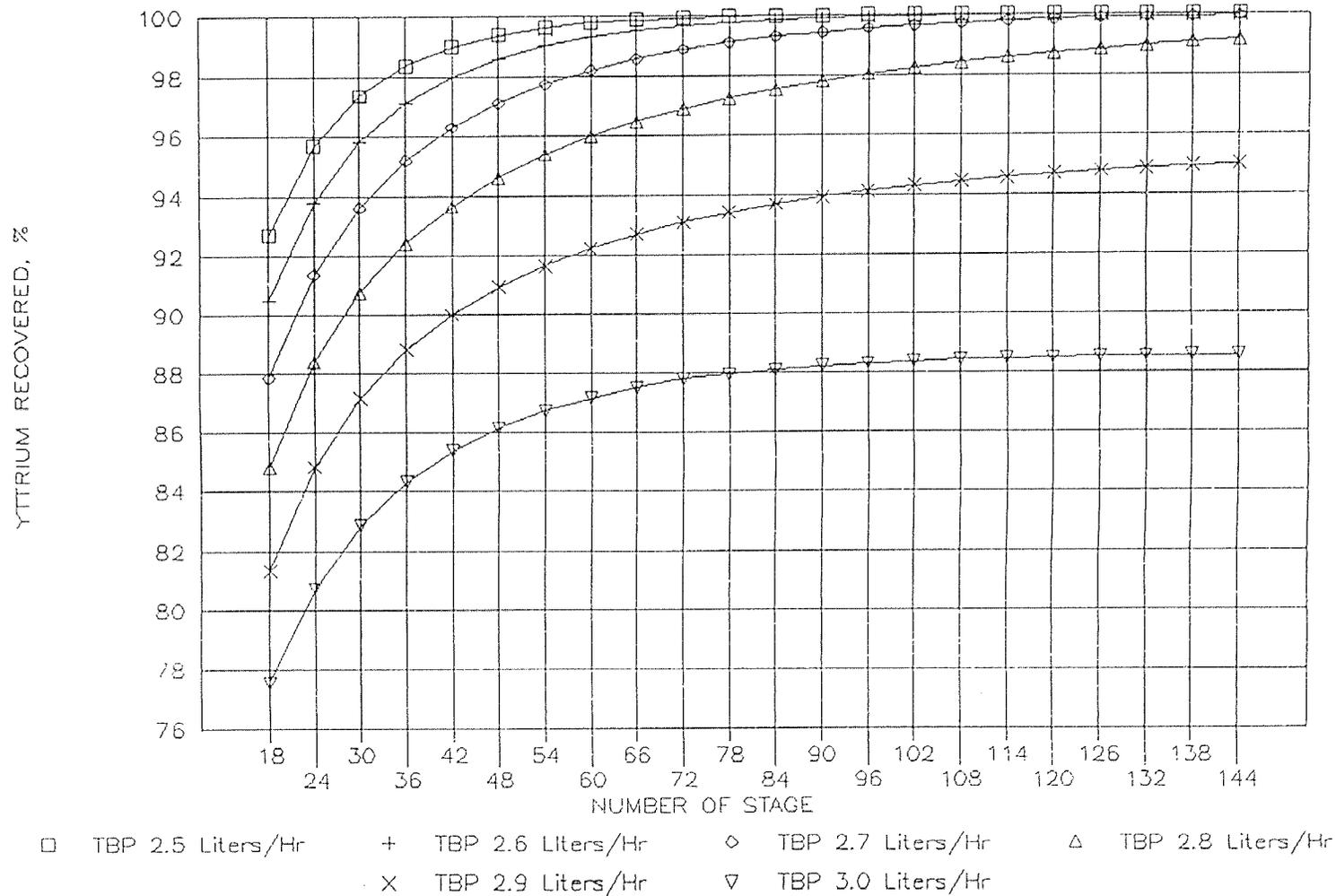


Figure 7.4 The Effect of Number of Stages on Yttrium Purification, Yttrium Recovered %, HNO₃ 6.4 N.

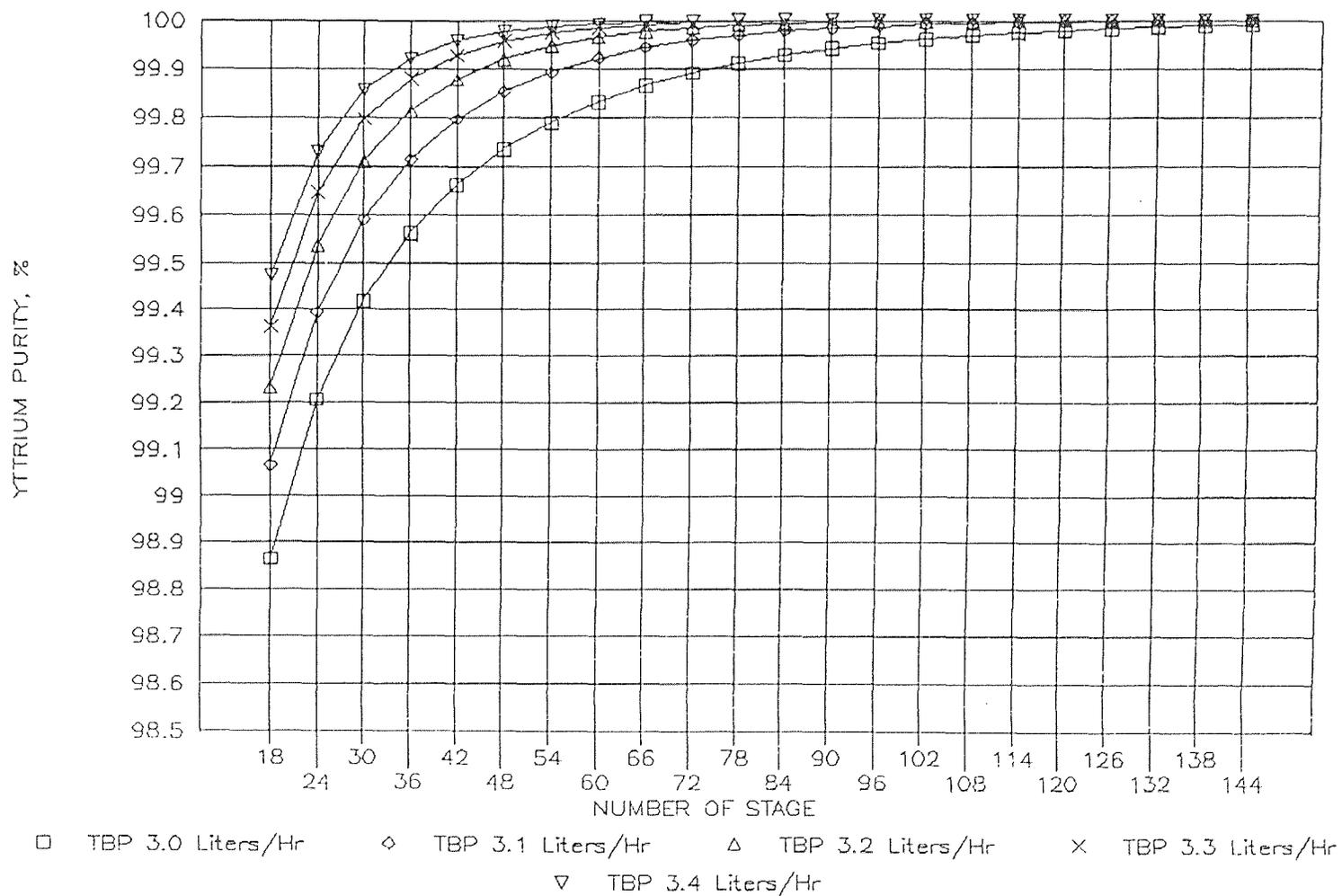


Figure 7.6 The Effect of Number of Stages on Yttrium Purification, Yttrium Purity %, HNO₃ 6.2 N.

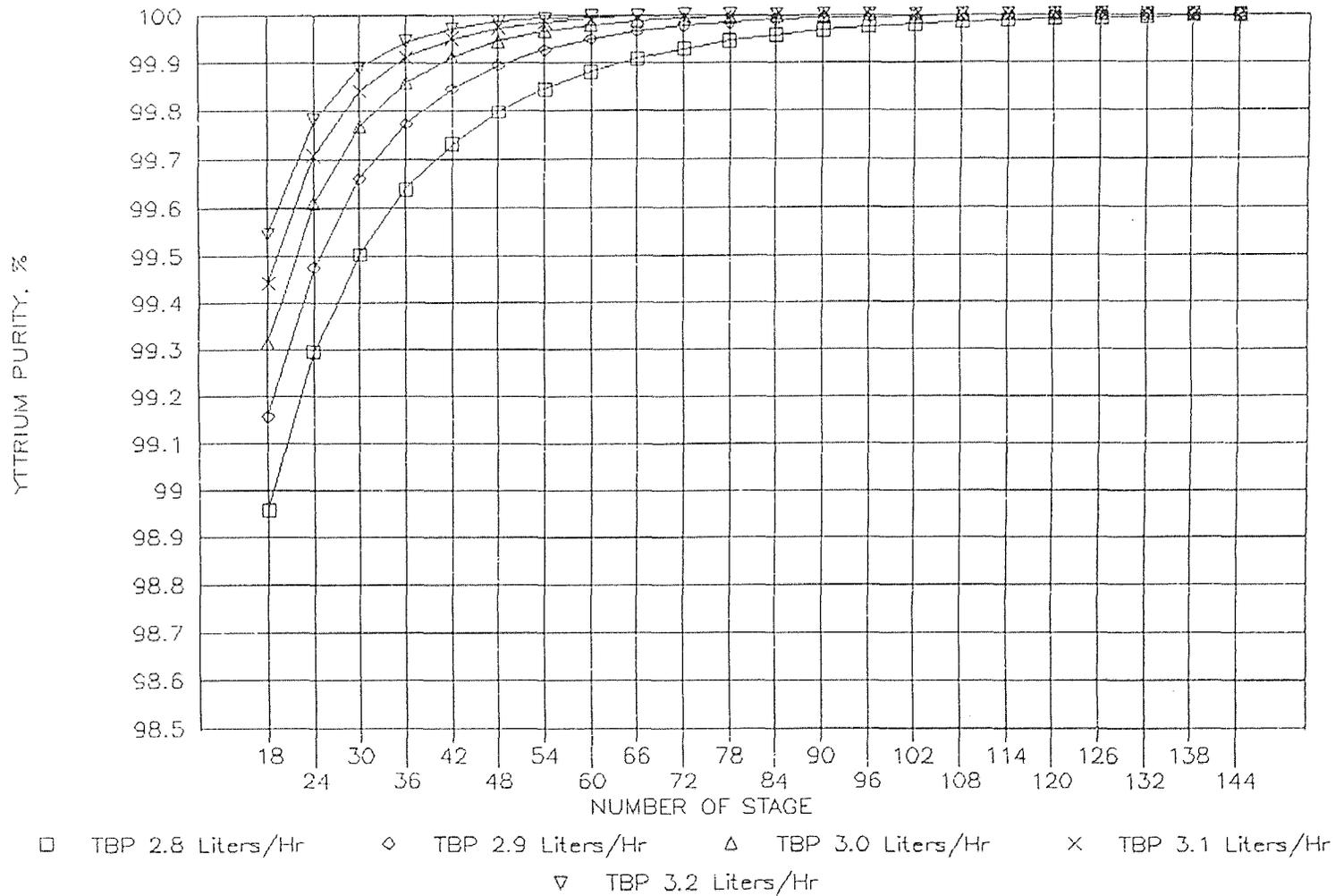


Figure 7.7 The Effect of Number of Stages on Yttrium Purification, Yttrium Purity %, HNO_3 6.3 N.

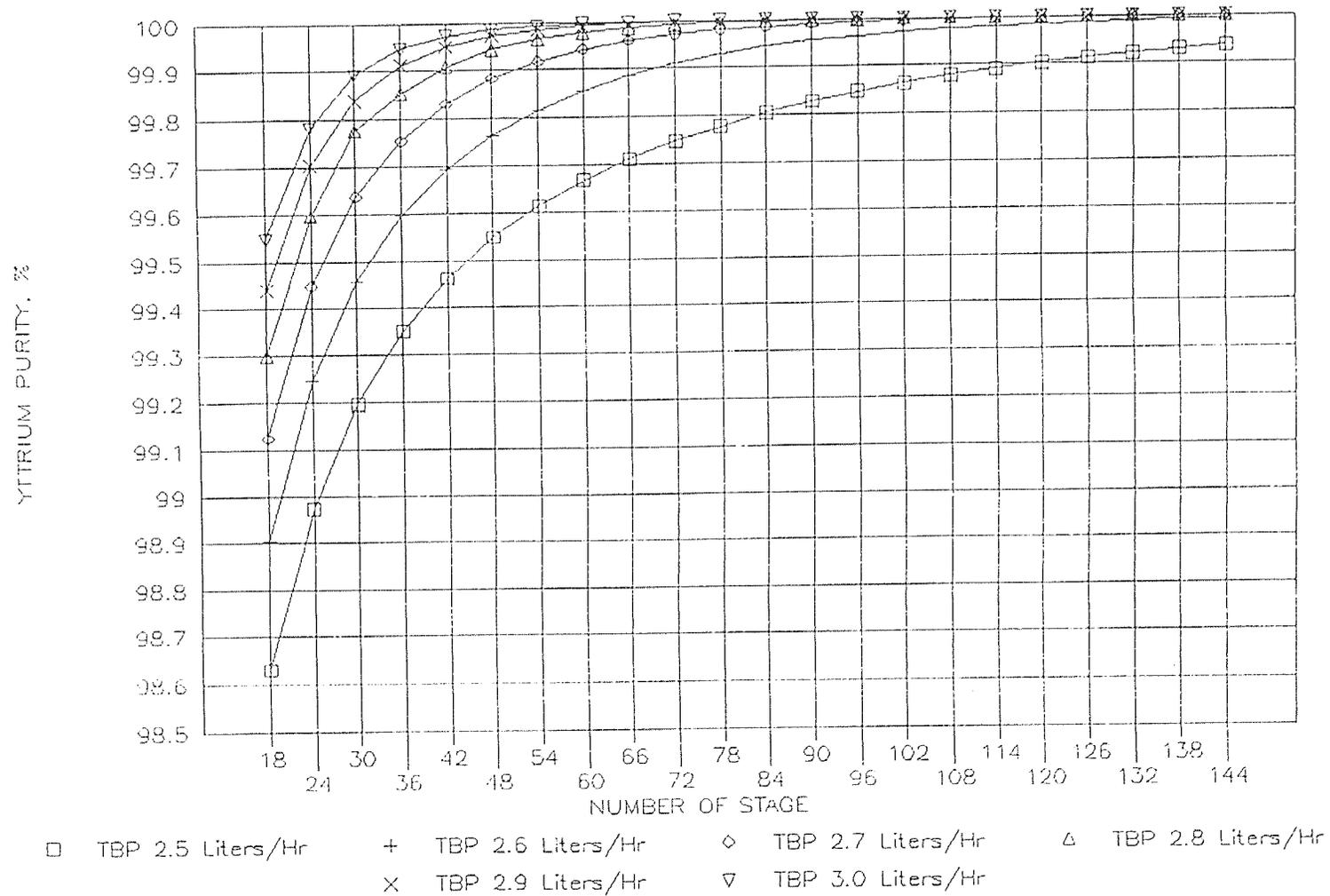


Figure 7.8 The Effect of Number of Stages on Yttrium Purification, Yttrium Purity %, HNO_3 6.4 N.

APPENDIX C

Computer Program for
Evaluation of Model Parameters

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C     MAIN PROGRAM
C
C     DECLARATION OF VARIABLES, DOUBLE PRECISION
C
C     INTEGER LDFJAC, M, N, NTEST, NPRAM, NOUT
C     PARAMETER (LDFJAC=9, M=9, N=9, NTEST=12, NPARM=8)
C     INTEGER IPARAM(7), ITP
C
C     DOUBLE PRECISION FJAC(LDFJAC,N), FSCALE(M), FVEC(M), HOUSTON,
C     & RPARAM(7), X(N), XGUESS(N), XLB(N), XS(N), XUB(N)
C     DOUBLE PRECISION THETA, TABLE, OTHETA, STHETA, AF
C     DOUBLE PRECISION XDATA, YDATA, GA, TBP, HNO3, RRE, EA
C
C     DIMENSION XDATA(NTEST), YDATA(NTEST), AF(0:3), EA(0:5)
C     DIMENSION TABLE(NTEST,14), GA(0:5), THETA(NPARM), OTHETA(NPARM)
C
C     COMMON/PARAM1/ TBP, HNO3, RRE, GA
C     COMMON/PARAM2/ THETA
C     COMMON/PARAM3/ TABLE
C     COMMON/PARAM4/ AF, EA
C
C     EXTERNAL DBCLSF, UMACH, HOUSTON, DOVER, DU4LSF
C
C     FOLLOWING ARE INITIAL DATA AND DATA ESTIMATION
C
C     INITIAL TBP, HNO3 AND RARE EARTH CONCENTRATIONS
C     TBP = 3.66
C     HNO3 = 0.5
C     RRE = 0.01
C
C     INITIAL ESTIMATED BETA1, BETA2, BETA3 AND KE
C     THETA(1) = 0.0000
C     THETA(2) = 12.500
C     THETA(3) = 0.0000
C     THETA(4) = 0.003800
C     THETA(5) = 16.775
C     THETA(6) = 0.7250000
C     THETA(7) = 0.000002616
C     THETA(8) = 3.0000
C
C     HNO3 DEGREE OF IONIZATION CURVE FIT PARAMETERS
C     AF(0) = 1.0006204
C     AF(1) = -0.020407
C     AF(2) = -0.004496
C     AF(3) = 0.0001546
C
C     HNO3 IN ORGANIC PHASE EQUALIBRIUM CURVE FIT PARAMETERS
C     GA(0) = -0.07272
C     GA(1) = 1.062423
C     GA(2) = -0.173784
C     GA(3) = 0.0186665
C     GA(4) = -0.001062
C     GA(5) = 0.0000261
C
C     TBP IN ORGANIC PHASE EQUILIBRIUM CURVE FIT PARAMETERS
C     EA(0) = 3.428093
C     EA(1) = -0.13173
C     EA(2) = 0.028538
C     EA(3) = -0.003824
C     EA(4) = 0.0002462

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EA(5) = -0.000006359
C
C   EXPERIMENTAL KD DATA TO BE FITTED INTO MODEL
C
C   THULIUM
DATA XDATA/0.58, 1.28, 2.43, 2.72, 3.70, 4.74, 7.38, 8.30, 9.22,
& 10.4, 11.1, 14.0/
DATA YDATA/0.027, 0.076, 0.17, 0.23, 0.39, 0.65, 2.0, 3.2, 5.4,
& 10.0, 16.2, 97.00/
C
C
C   THE GUESS RESULTS OF ALL X FOR THE FIRST OBSERVATION
DATA XGUESS/0.15, 3.50, 0.15, 0.15, 0.15, 0.003, 0.003, 0.98, 1.0/
C
C   ALL THE BOUNDS ARE PROVIDED
DATA XLB/0.0, 0.0001, 0.0, 0.0001, 0.0, 0.0001, 0.0001, 0., 1.0/
DATA XUB/1.00, 3.60, 1.00, 6.66, 1.00, 0.010, 0.010, 1.00, 8.0/
C
C   MISCELLANEOUS DATA
DATA XS/N*1.0E0/, FSCALE/M*1.0E0/, NOUT/6/
C
C   COMPUTE THE LEAST SQUARES FOR ROSENBROCK FUNCTION
ITP=0
C
DO 35 J=1, N
    TABLE(1,J+3)=XGUESS(J)
35 CONTINUE
C
CALL UMACH (2, NOUT)
C
DO 500 JK=1, 30
C
    STHETA=0.0
    DO 45 JB=1, NPARAM
        STHETA=STHETA+(OTHETA(JB)-THETA(JB))**2
45 CONTINUE
C
    IF (STHETA.LT.1.0E-6) THEN
        GOTO 600
    ENDIF
C
DO 55 IJ=1, N
    XGUESS(IJ)=TABLE(1,IJ+3)
55 CONTINUE
C
DO 400 I=1, NTEST
C
C   DEFAULT PARAMETER ARE NOT USED
ITP=0
CALL DU4LSF (IPARAM, RPARAM)
IPARAM(3)=500
IPARAM(4)=500
IPARAM(5)=500
C
C   INITIALIZE THE HNO3 CONCENTRATION AND SOLUTION BOUNDS
HNO3=XDATA(I)
XLB(8)=TABLE(I,11)
XUB(1)=XDATA(I)
XUB(3)=XDATA(I)
XUB(5)=XDATA(I)

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      CALL DBCLSF (HOUSTON, M, N, XGUESS, ITP, XLB, XUB, XS, FSCALE,
&                IPARAM, RPARAM, X, FVEC, FJAC, LDFJAC)
C
      WRITE (NOUT, 2000) IPARAM(3), IPARAM(4), FVEC
2000  FORMAT(/, ' THE NUMBER OF ITERATION FOR THETA IS ', 5X, I6, /,
&          ' THE NUMBER OF FUNCTION EVALUATION IS ', 5X, I6, /,
&          ' THE FUNCTION EVALUATED FOR THETA AT THE SOLUTION IS ',
&          /, 2X, 10F9.4)
C
C   FILLING TABLE
C
      TABLE(I, 1)=XDATA(I)
      TABLE(I, 2)=YDATA(I)
      TABLE(I, 3)=(THETA(4)*(X(1)*X(2))**3)*(THETA(5)+
&                THETA(6)*X(3)**(1.9068)+THETA(7)*X(3)**THETA(8))/
&                (1.0+THETA(1)*X(1)+THETA(2)*X(1)**2+THETA(3)*X(1)**3)

      DO 200 J=1, N
      XGUESS(J)=X(J)
      TABLE(I, J+3)=X(J)
200   CONTINUE
      TABLE(I, 13)=(THETA(4)*(X(1)*X(2))**3)/(1.0+THETA(1)*X(1)+THETA(2)*
&                X(1)**2+THETA(3)*X(1)**3)
      TABLE(I, 14)=(THETA(5)+
&                THETA(6)*X(3)**(1.9068)+THETA(7)*X(3)**THETA(8))
400   CONTINUE
C
      DO 75 JB=1, NPARM
      OTHETA(JB)=THETA(JB)
75   CONTINUE
C
      CALL OUTPUT (NPARM, TABLE, N, NTEST, NOUT, THETA, JK)
C
      CALL R2D2 (ITP, IPARAM, RPARAM, THETA)
C
500   CONTINUE
600   END
C
      SUBROUTINE HOUSTON (M, N, X, F)
C
      INTEGER M, N
      PARAMETER(NPARM=8)
      DOUBLE PRECISION X(N), F(M)
      DOUBLE PRECISION TBP, HNO3, RRE, GA, AF, THETA, EA
C
      DIMENSION AF(0:3), THETA(NPARM), GA(0:5), EA(0:5)
C
      COMMON/PARAM1/ TBP, HNO3, RRE, GA
      COMMON/PARAM2/ THETA
      COMMON/PARAM4/ AF, EA
C
      TEN EQUATIONS
C
      F(1) = X(8)-AF(0)-AF(1)*X(3)-AF(2)*X(3)**2-AF(3)*X(3)**3
      F(2) = X(1)-X(3)*X(8)
      F(3) = X(4)-GA(0)-GA(1)*X(3)-GA(2)*X(3)**2-GA(3)*X(3)**3-
&          GA(4)*X(3)**4-GA(5)*X(3)**5
      F(4) = X(6)-THETA(4)*X(7)*(X(1)*X(2))**3
      F(5) = HNO3-X(5)-X(3)+X(3)*X(8)-X(4)-RRE/3.0
      F(6) = RRE-X(7)-THETA(1)*X(1)*X(7)-THETA(2)*X(7)*X(1)**2-

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&      THETA(3)*X(7)*X(1)**3-X(6)
F(7) = HNO3-X(3)-X(4)-3.0*X(6)-THETA(1)*X(1)*X(7)-THETA(2)*
&      X(7)*X(1)**2-THETA(3)*X(7)*X(1)**3
F(8) = TBP-3.0*X(6)-X(2)-X(4)/X(9)
F(9) = X(2)-EA(0)-EA(1)*X(3)-EA(2)*X(3)**2-EA(3)*X(3)**3-
&      EA(4)*X(3)**4-EA(5)*X(3)**5
C
RETURN
END
C
C
SUBROUTINE R2D2 (ITP, IPARAM, RPARAM, THETA)
C
INTEGER LDFJAC, M, N, ITP, IPARAM(7), NTEST, NPARM, NOUT
PARAMETER (LDFJAC=12, M=12, N=8)
DOUBLE PRECISION FJAC(LDFJAC,N), FSCALE(M), FVEC(M), DOVER,
&      RPARAM(7), X(N), XGUESS(N), XLB(N), XS(N), XUB(N)
DOUBLE PRECISION THETA, TABLE
C
DIMENSION THETA(N), TABLE(M,14)
COMMON/PARAM3/ TABLE
C
EXTERNAL DBCLSF, DOVER, DU4LSF
C
FOLLOWING ARE INITIAL DATA AND DATA ESTIMATION
C
THE ESTIMATED THETA AND BOUNDS
DO 100 I=1, N
  XGUESS(I)=THETA(I)
100 CONTINUE
WRITE (NOUT, 1010) (XGUESS(I), I=1,N)
1010 FORMAT (/, ' THE GUESSED THETA ARE = ', 8E12.5)
DATA XS/N*1.0E0/, FSCALE/M*1.0E0/, NOUT/6/
DATA XLB/0.7079, 12.5, 0.00, 0.00, -999., -999., -999./
DATA XUB/999., 99.00, 0.0, 2.50, 999., 999., 999., 999./
C
ITP=0
CALL DU4LSF (IPARAM, RPARAM)
IPARAM(3)=500
IPARAM(4)=500
IPARAM(5)=500
C
C
CALL DBCLSF (DOVER, M, N, XGUESS, ITP, XLB, XUB, XS, FSCALE,
&      IPARAM, RPARAM, X, FVEC, FJAC, LDFJAC)
C
WRITE (NOUT, 1111) (X(J), J=1,N)
1111 FORMAT (' THE CALC THETA AFTER R2D2 = ', 8E12.5)
DO 300 J=1, N
  THETA(J)=X(J)
300 CONTINUE
C
WRITE (NOUT, 3000) IPARAM(3), IPARAM(4), FVEC
3000 FORMAT(/, ' THE NUMBER OF ITERATION FOR THETA IS ', 5X, I6, /,
&      ' THE NUMBER OF FUNCTION EVALUATION IS ', 5X, I6, /,
&      ' THE FUNCTION EVALUATED FOR THETA AT THE SOLUTION IS',
&      /, 2X, 14F9.4, /, 2X, 14F9.4)
RETURN
END
C

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```

C
C
C   SUBROUTINE DOVER (M, N, X, F)
C
C   INTEGER M, N
C   PARAMETER (NTEST=12, NPARM=8)
C   DOUBLE PRECISION F(M), X(N)
C   DOUBLE PRECISION TABLE
C
C   DIMENSION TABLE(NTEST,14)
C   COMMON/PARAM3/ TABLE
C
C   DO 300 J=1, M
C   F(J)=TABLE(J,2)-
C   & (X(4)*(TABLE(J,4)*TABLE(J,5))**3)*
C   & (X(5)+X(6)*TABLE(J,6)**(1.9068)+X(7)*TABLE(J,6)**X(8))/
C   & (1.0+X(1)*TABLE(J,4)+X(2)*TABLE(J,4)**2+
C   & X(3)*TABLE(J,4)**3)
300 CONTINUE
C
C   RETURN
C   END
C
C
C   SUBROUTINE OUTPUT (NPARM, TABLE, N, NTEST, NOUT, THETA, JK)
C
C   INTEGER N, NTEST, NOUT, JK, NPARM
C   DIMENSION TABLE(NTEST,14), THETA(NPARM)
C   DOUBLE PRECISION TABLE, THETA
C
C           PRINT RESULTS
C
C   WRITE (NOUT, 4000) JK
C
C   WRITE (NOUT, 5000) THETA
C
C   WRITE (NOUT, 6000)
C
C   DO 103 I=1, NTEST
C   WRITE (NOUT, 7000) I, (TABLE(I,J), J=1, 14)
103 CONTINUE
C
4000 FORMAT (/, ' NUMBER OF ITERATIONS FOR THETA = ', I5)
5000 FORMAT (/, ' THE THETAE ', 2X, E12.5, 2X, E12.5, 2X, E12.5,
& 2X, E12.5, 2X, E12.5, 2X, E12.5, 2X, E12.5, 2X, E12.5)
6000 FORMAT (/, 2X, 'RUN', 2X, '(HNO3)AI', 3X, 'KD EXP', 2X, 'KD CALC',
& 2X, '(NO3-1)A', 2X, '(TBP)O',
& 2X, '(HNO3)AT', 2X, '(HNO3)O', 2X, '(H+1)A',
& 3X, '( M )O', 3X, '(M+3)A', 2X, 'DEG ION',
& 1X, 'NO (HNO3)O', 2X, 'KD1', 3X, 'KD2')
C
7000 FORMAT (2X, I3, 2X, F6.2, 2X, 13F9.4)
C
C   RETURN
C   END

```

APPENDIX D

Computer Program for
Liquid-Liquid Extraction Computation

```

C
C-----MAIN PROGRAM
C-----MULTICOMPONENT MULSTAGE COUNTER-CURRENT LIQUID-LIQUID EXTRACTION
C-----KENNETH Y. CHAN   JULY 12, 1992
C
      INTEGER PHASE
      CHARACTER*1 PAGEJC,SNGLSP,DUBLSP
      CHARACTER*16 COMP(20)
      DOUBLE PRECISION XFEED(20),VOLD(20),F(100),L(100),B(6,20)
      DOUBLE PRECISION W(100),U(100),V(100),A(100,101),XFLOW
      DOUBLE PRECISION X(20,100),Y(20,100),XSUM(100),YSUM(100)
      DOUBLE PRECISION XF(20,100),AK(20,100),KCONST(8,20)
      DOUBLE PRECISION STD,TAL,TOL,DIFF,VRATE,RATE,SUM,SUMMF
      DOUBLE PRECISION HNO3(100),MW(20),TXFLOW,TFHNO3
      DOUBLE PRECISION C(2,20),REFTOT,ETOTAL,RTOTAL
      DIMENSION JP(20),PH(2)
      COMMON/BK1/JS,F,W,U,V
      COMMON/BK2/X,Y,XSUM,YSUM
      COMMON/BK3/XF,L,AK
      COMMON/BK4/KCONST,HNO3
      COMMON/BK5/A
      OPEN(UNIT=5,FILE='GENLLE.INP',STATUS='OLD')
      OPEN(UNIT=6,FILE='GENLLE.OUT',STATUS='NEW')
C
      DATA PAGEJC,SNGLSP,BUBLSP/'1',' ','0'/
      DATA PH(1),PH(2)/'ORG','AQU'/
C
C      ASSIGN BASIC COMPONENT NAMES, MOLECULAR WEIGHTS AND
C      PARAMETERS FOR EQUILIBRIUM CONSTANT CORRELATIONS
C
      DATA (COMP(I),I=1,3)/'TBP ','HNO3','H2O '/
      DATA (MW(I),I=1,3)/266.32,63.0,18.0/
      DATA (KCONST(I,1),I=1,8)/.999999999E26,.0,.0,.0,.0,.0,.0/
      DATA (KCONST(I,2),I=1,8)/-25.54334,12.11596,-10.24788,26.14166,
1      -5.342299,.0,.0,.0/
      DATA (KCONST(I,3),I=1,8)/.5196597,-4.468081,19.72675,-32.13729,
1      19.22704,.0,.0,.0/
C
C      INPUT NUMBER OF RARE EARTH COMPONENTS FOR SEPARATION AND
C      MAXIMUM NUMBER OF COLUMN ITERATIONS AND COLUMN ITERATION
C      CONVERGENCE CRITERION CONSTANT
C
      READ (5,*) NRE, NCI, TAL
      IC = NRE + 3
      IF (IC .LT. 3 .OR. IC .GT. 20) THEN
          WRITE (6,*) 'NUMBER OF COMPONENTS ARE OUT OF PROGRAM LIMITS'
          GO TO 190
      END IF
C
C      INPUT NAME OF RARE EARTH COMPONENTS
C
      READ (5,*) (COMP(I),I=4,IC)
C
C      INPUT MOLECULAR WEIGHT OF RARE EARTH COMPONENTS
C
      READ (5,*) (MW(I),I=4,IC)
C
C      INPUT PARAMETERS FOR RARE EARTH DISTRIBUTION COEFFICIENT MODELS
C
      DO 13 J = 4, IC
          READ (5,*) (KCONST(I,J),I=1,8)
13 CONTINUE
C

```

```

C      INPUT CASE NUMBER, NUMBER OF STAGES, NUMBER OF FEEDS,
C      NUMBER OF ORGANIC SIDEDRAWS, NUMBER OF AQUEOUS SIDEDRAWS,
C      AND FREQUENCY OF PRINTOUT FOR RESULTS OF COLUMN ITERATION
C
15  READ (5,*) NC, JS, NOF, NOVS, NOLS, KP
    IF (KP .EQ. 0) THEN
        KP=15
    END IF
    IF (JS .LE. 2 .OR. JS .GT. 100) THEN
        WRITE (6,*) 'NUMBER OF STAGES ARE OUT OF PROGRAM LIMITS'
        GO TO 190
    END IF
C
C      ZERO OUT CERTAIN ARRAYS BEFORE STARTING A CASE
DO 22 J = 1, 100
    DO 20 I = 1, 20
        AK(I,J)=0.0
        XF(I,J)=0.0
        X(I,J)=0.0
        Y(I,J)=0.0
20  CONTINUE
    HNO3(J)=0.0
    F(J)=0.0
    V(J)=0.0
    L(J)=0.0
    W(J)=0.0
    U(J)=0.0
22  CONTINUE
    TOL = TAL* JS
    WRITE (6,219) PAGEJC
219  FORMAT (A)
    WRITE (6,219) DUBLSP
    WRITE (6,*) 'CASE NUMBER', NC
    WRITE (6,219) SNGLSP
    WRITE (6,*) 'NO. OF CHEMICAL COMPONENTS = ', IC
    WRITE (6,219) SNGLSP
    WRITE (6,*) 'NO. OF THEORETICAL STAGES = ', JS
    WRITE (6,219) SNGLSP
    WRITE (6,*) 'NO. OF FEED STREAMS = ', NOF
    WRITE (6,219) SNGLSP
    WRITE (6,*) 'NO. OF ORGANIC SIDEDRAWS = ', NOVS
    WRITE (6,219) SNGLSP
    WRITE (6,*) 'NO. OF AQUEOUS SIDEDRAWS = ', NOLS
    WRITE (6,219) DUBLSP
    WRITE (6,240) (JK, COMP(JK),MW(JK), JK=1,IC)
240  FORMAT (/T10,'COMPONENT NUMBER',T30,'COMPONENT NAMES',T50,
1      'MOLECULAR WEIGHTS'//(T15,I5,T35,A15,T55,F12.6)/)
    WRITE (6,245) 'FEED AND SIDEDRAWS SPECIFICATIONS'
245  FORMAT (A34)
    WRITE (6,219) DUBLSP
    WRITE (6,270) 'FLOW RATE', 'PHASE'
270  FORMAT (///T23,A9,T38,A5)
    WRITE (6,271) 'STAGE', '(KGMOL/HR)', 'CONDITION',
1      'COMPONENT MOLE FRACTIONS FOR COMPONENTS 1 TO ', IC, ' FEEDS'
271  FORMAT (/T15,A5,T22,A12,T36,A9,T63,A45,I3//T5,A5/)
    TXFLOW = 0.0
    TFHNO3 = 0.0
    DO 35 L1 = 1, NOF
        READ (5,*) JF, PHASE,XFLOW
        READ (5,*) (XFEED(I), I = 1, IC)
        IF (PHASE .EQ. 1) THEN
            WPHASE = PH(1)
        ELSE

```

```

        WPHASE = PH(2)
    END IF
    SUMMF = 0.0
    DO 25 M = 1, IC
        SUMMF = SUMMF + XFEED(M)
25    CONTINUE
    IF (SUMMF .LT. 0.9999 .OR. SUMMF .GT. 1.0001) THEN
        DO 26 M = 1, IC
            XFEED(M) = XFEED(M) / SUMMF
26    CONTINUE
        WRITE (6,219) DUBLSP
        WRITE (6,*) 'FEED MOLE FRACTIONS FOR STAGE', JF
        WRITE (6,*) 'DO NOT SUM TO 1.000. PROBLEM FIXED'
    END IF
    WRITE (6,285) JF, XFLOW, WPHASE, (XFEED(L2), L2 = 1, IC)
285    FORMAT (/14X,I5,F15.8,4X,A4,8X,5F14.10/3((50X,5F14.10)/))
    F(JF) = XFLOW
    JP(JF) = PHASE
    IF (PHASE .EQ. 2) THEN
        TXFLOW = TXFLOW + XFLOW
        TFHNO3 = TFHNO3 + XFLOW * XFEED(2)
    END IF
    DO 30 L2 = 1, IC
        XF(L2,JF) = XFEED(L2)
30    CONTINUE
35    CONTINUE
C
C    COMPUTE INITIAL HNO3 MOLE FRACTIONS IN AQUEOUS PHASE
C
    DO 36 J = 1, JS
        X(2,J) = TFHNO3 / TXFLOW
36    CONTINUE
    KKK = 0
    IF (NOVS .EQ. 0) THEN
        GO TO 45
    ELSE
        WPHASE = PH(1)
        WRITE (6,*) ' SIDEDRAWS'
        KKK = 1
        DO 40 L3 = 1, NOVS
            READ (5,*) JSV, VRATE
            WRITE (6,295) JSV, VRATE, WPHASE
295        FORMAT (/14X,I5,F15.8,4X,A4)
            IF (JSV .LT. 2 .OR. JSV .GT. (JS-1)) THEN
                GO TO 190
            ELSE
                W(JSV) = VRATE
            END IF
40        CONTINUE
    END IF
45    IF (NOLS .EQ. 0) THEN
        GO TO 55
    ELSE
        WPHASE = PH(2)
        IF (KKK .EQ. 0) THEN
            WRITE (6,*) ' SIDEDRAWS'
        END IF
        DO 50 L4 = 1, NOLS
            READ (5,*) JSL, RATE
            WRITE (6,295) JSL, RATE, WPHASE
            IF (JSL .LT. 2 .OR. JSL .GT. (JS-1)) THEN
                GO TO 190
            ELSE

```

```

          U(JSL) = RATE
          END IF
50    CONTINUE
      END IF
C
C    COMPUTE INITIAL ORGANIC RATE PROFILES - INITIALIZE TEAR VARIABLES
C
55    JK = JS - 1
      V(JS) = F(JS) - W(JS)
      DO 60 J = JK, 1, -1
          IF (JP(J) .EQ. 2) THEN
              V(J) = V(J+1) - W(J)
          ELSE
              V(J) = V(J+1) + F(J) - W(J)
          END IF
60    CONTINUE
      WRITE (6,325) 'INTERMEDIATE RESULTS WILL BE PRINTED OUT EVERY',
1      KP, 'COLUMN ITERATIONS'
325  FORMAT (//A48,I5,2X,A17/)
C
C    COMPUTE INITIAL AQUEOUS RATE PROFILES
C
      JL1 = JS - 1
      SUM = 0.0
      DO 70 I = 1, JL1
          SUM = SUM + F(I) - W(I) - U(I)
          L(I) = V(I+1) + SUM - V(1)
70    CONTINUE
      L(JS) = SUM + F(JS) - W(JS) - U(JS) - V(1)
      K1 = 0
      K2 = 0
75    K1 = K1 + 1
      K2 = K2 + 1
      DO 78 J = 1, JS
          DO 77 I = 1, IC
              IF (I .LE. 3) THEN
                  CALL BASEKV(J)
              ELSE
                  CALL EQUILK(I,J)
              END IF
77    CONTINUE
          VOLD(J) = V(J)
78    CONTINUE
C
C    COMPUTE MATRIX COEFFICIENTS FOR AQUEOUS MOLE FRACTION
C
      DO 80 I = 1, IC
          CALL SETUPA (I)
C
C    SOLVE MATRIX FOR AQUEOUS MOLE FRACTIONS
C
          CALL THOMAS(I)
80    CONTINUE
C
C    COMPUTE ORGANIC MOLE FRACTIONS, AND NEW ORGANIC RATE PROFILES
C
      DO 95 JA = 1, JS
          XSUM(JA) = 0.0
          YSUM(JA) = 0.0
          DO 85 I = 1, IC
              IF (X(I,JA) .GT. 1.0) THEN
                  X(I,JA) = (X(I,JA) + 1.0) / 2.0
              END IF
          END IF
      END IF

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```

      IF (X(I,JA) .LT. 0.0) THEN
        X(I,JA) = X(I,JA) / 2.0
      END IF
      XSUM(JA) = XSUM(JA) + X(I,JA)
85  CONTINUE
      DO 90 I = 1, IC
        X(I,JA) = X(I,JA) / XSUM(JA)
        Y(I,JA) = X(I,JA) * AK(I,JA)
        YSUM(JA) = YSUM(JA) + Y(I,JA)
90  CONTINUE
      V(JA) = V(JA) * YSUM(JA)
95  CONTINUE
C
C  COMPUTE NEW AQUEOUS RATE PROFILE
C
      JL2 = JS - 1
      SUM = 0.0
      DO 100 I = 1, JL2
        SUM = SUM + F(I) - W(I) - U(I)
        L(I) = V(I+1) + SUM - V(1)
100 CONTINUE
      L(JS) = SUM + F(JS) - W(JS) - U(JS) - V(1)
      DO 110 J = 1, JS
        IF (V(J) .LT. 0.0) THEN
          WRITE (6,445) 'COMPUTED ORGANIC RATE OF', V(J), 'FOR STAGE',
1          J, 'OF COLUMN ITERATION', K1, 'IS NEGATIVE'
445  FORMAT (//T20,A24,F15.8,T58,A9,I4,T73,A19,I4,T98,A8/)
          WRITE (6,*)
          WRITE (6,*) 'THE FEED OR SIDESTREAM SPECIFICATIONS'
          WRITE (6,*) 'MAY BE IMPROPER. CASE TERMINATED'
          WRITE (6,*) 'SHOULD REPEAT RUN WITH REVISED SPECIFICATIONS'
          GO TO 15
        END IF
        IF (L(J) .LT. 0.0) THEN
          WRITE (6,455) 'COMPUTED AQUEOUS RATE OF', L(J), 'FOR STAGE',
1          J, 'OF COLUMN ITERATION', K1, 'IS NEGATIVE'
455  FORMAT (//T20,A24,F15.8,T58,A9,I4,T73,A19,I4,T98,A8/)
          WRITE (6,*)
          WRITE (6,*) 'THE FEED OR SIDESTREAM SPECIFICATIONS'
          WRITE (6,*) 'MAY BE IMPROPER. CASE TERMINATED'
          WRITE (6,*) 'SHOULD REPEAT RUN WITH REVISED SPECIFICATIONS'
          GO TO 15
        END IF
110 CONTINUE
      IF (K2 .NE. KP .AND. K1 .NE. NCI) THEN
        GO TO 130
      ELSE
        WRITE (6,*)
        WRITE (6,*) 'INTERMEDIATE RESULTS FOR ITERATION ', K1
        WRITE (6,330) 'ORGANIC RATE', 'AQUEOUS RATE',
1          'AQUEOUS, FOLLOWED BY ORGANIC MOLE FRACTION',
1          'ORGANIC MOLE'
330  FORMAT (///T13,A12,T29,A12,T64,A43,T119,A12)
        WRITE (6,331) 'STAGE', '(KGMOL/HR)', '(KGMOL/HR)',
1          'FOR COMPONENTS 1 TO ', IC, 'FRACTION SUM'
331  FORMAT (/T5,A5,T13,A12,T29,A12,T74,A20,I3,T119,A12/)
        K2 = 0
        DO 125 J = 1, JS
          WRITE (6,335) J, L(J), (X(I,J), I = 1, IC)
335  FORMAT (/4X,I4,15X,F15.8,12X,5F14.10/3((50X,5F14.10)/))
          WRITE (6,345) V(J), (Y(I,J), I = 1, IC)
345  FORMAT (/8X,F15.8,27X,5F14.10/3((50X,5F14.10)/))
          WRITE (6,340) YSUM(J)

```

```

340     FORMAT (/116X,F14.10/)
125     CONTINUE
      END IF
C
C     CONVERGENCE TEST
C
130     STD = 0.0
      DO 135 J = 1, JS
          DIFF = V(J) - VOLD(J)
          STD = STD + (DIFF / V(J))**2
135     CONTINUE
      IF (STD .GT. TOL .AND. K1 .LE. NCI) THEN
          WRITE (6,355) 'AFTER ITERATION',K1,
1              'CALCULATIONS ARE NOT CONVERGED'
355     FORMAT (/A16,I5,2X,A31/)
          WRITE (6,*) 'COLUMN ITERATION CONVERGENCE FACTOR IS', STD
          WRITE (6,*) 'WHICH IS GREATER THAN TOLERANCE OF ', TOL
          GO TO 75
      ELSE IF (STD .LE. TOL .AND. K1 .LE. NCI) THEN
          GO TO 140
      ELSE
          WRITE (6,365) 'CALCULATION ARE NOT CONVERGED AFTER THE ',
1              'ITERATIONS EXCEED THE MAXIMUM NUMBER', NCI
365     FORMAT (/A40,A36,I5)
          WRITE (6,*) 'THE UNCONVERGED RESULTS ARE PRINTED AS FOLLOW'
          WRITE (6,*) 'REPEAT CASE WITH A LARGER VALUE OF NCI'
          GO TO 145
      END IF
140     WRITE (6,360) 'AFTER ITERATION', K1,
1              'CALCULATIONS ARE CONVERGED'
360     FORMAT (/A16,I5,2X,A26/)
          WRITE (6,*) 'COLUMN ITERATION CONVERGENCE FACTOR IS', STD
          WRITE (6,*) 'WHICH IS LESS THAN TOLERANCE OF ', TOL
          WRITE (6,*)
          WRITE (6,*) 'FINAL DETAILED RESULTS ARE AS FOLLOW'
          WRITE (6,219) PAGEJC
145     WRITE (6,361) DUBLSP,'FINAL RESULTS OF PRODUCT STREAMS'
361     FORMAT (A,A33)
          WRITE (6,370) 'FROM', 'PHASE', 'FLOW RATE',
1              'COMPONENT MOLE FRACTIONS'
370     FORMAT (/T16,A4,T24,A5,T38,A9,T70,A25)
          WRITE (6,371) 'STREAM', 'STAGE', 'CONDITION', '(KMOLES/HR)',
1              'FOR COMPONENTS 1 TO ', IC
371     FORMAT (/T5,A6,T15,A5,T23,A9,T36,A12,T71,A20,I4)
          WRITE (6,375) PH(1), V(1), (Y(K,1), K=1, IC)
375     FORMAT (/5X,'EXTRACT',5X,2H 1,5X,A4,3X,F15.8,4X,5F14.10/
1              3((50X,5F14.10)/))
          JSS = JS - 1
          IF (NOVS .EQ. 0) THEN
              GO TO 155
          ELSE
              DO 150 I = 2, JSS
                  IF (W(I) .LT. .00001) THEN
                      GO TO 150
                  ELSE
                      WRITE (6,380) I, PH(1), W(I), (Y(K,I), K=1, IC)
                  END IF
150             CONTINUE
          END IF
155     IF (NOLS .EQ. 0) THEN
              GO TO 165
          ELSE
              DO 160 I = 2, JSS

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        IF (U(I) .LT. .00001) THEN
            GO TO 160
        ELSE
            WRITE (6,380) I, PH(2), U(I), (X(K,I), K=1, IC)
380      FORMAT (/5X,'SIDEDRAW',T17,I3,5X,A4,3X,F15.8,4X,
1          5F14.10/3((50X,5F14.10)/))
            END IF
160      CONTINUE
        END IF
165      WRITE (6,385) JS, PH(2), L(JS), (X(K,JS), K=1, IC)
385      FORMAT (/5X,'RAFFINATE',2X,I3,5X,A4,3X,F15.8,4X,5F14.10/
1          3((50X,5F14.10)/))
            WRITE (6,219) PAGEJC
            WRITE (6,219) DUBLSP
175      WRITE (6,390) 'CONCENTRATION PROFILES AND',
1          'DISTRIBUTION COEFFICIENTS'
390      FORMAT (A27,1X,A25)
            WRITE (6,395) 'PHASE','ORGANIC RATE','AQUEOUS RATE',
1          'COMPONENT MOLE FRACTIONS'
395      FORMAT (//T11,A5,T22,A12,T38,A12,T70,A25)
            WRITE (6,396) 'STAGE','CONDITION','(KGMOL/HR)','(KGMOL/HR)',
1          'FOR COMPONENTS 1 TO ', IC
396      FORMAT (/T2,A5,T9,A9,T22,A12,T38,A12,T71,A20,I4)
            DO 185 I = 1, JS
                WRITE (6,400) I, PH(1), V(I), (Y(K,I), K=1, IC)
400          FORMAT (//2X,I4,5X,A4,2X,F15.8,18X,5F14.10/3((50X,5F14.10)/))
180          WRITE (6,405) I, PH(2), L(I), (X(K,I), K=1, IC)
405          FORMAT (/2X,I4,5X,A4,16X,F15.8,4X,5F14.10/3((50X,5F14.10)/))
                WRITE (6,401) 'HNO3 IN STAGE',I, HNO3(I),'M','KD =',
1          (AK(K,I), K=1, IC)
401          FORMAT (//T10,A13,I5,T30,F8.4,1X,A1,5X,A4,2X,5E14.6/
1          3((50X,5E14.6)/))
185      CONTINUE
C
C      PRINT SUMMARY TABLES
C
            WRITE (6,219) PAGEJC
            WRITE (6,490) DUBLSP,' SUMMARY TABLE 1'
490      FORMAT (A,A16)
            WRITE (6,470) 'COMPONENT','COMPONENT','TOTAL FEED','TOTAL FEED',
1          'EXTRACT','RAFFINATE','% RECOVERY',
1          '% RECOVERY'
470      FORMAT (////T2,A10,T15,A9,T35,A10,T51,A10,T69,A7,T84,A9,
1          T101,A10,T117,A10)
            WRITE (6,475) 'NUMBER','NAME','(KGMOL/HR)','(KG/HR)',
1          '(KG/HR)','(KG/HR)','FROM EXTRACT',
1          'FROM RAFFINATE'
475      FORMAT (/T3,A7,T17,A4,T35,A11,T53,A7,T69,A7,T85,A7,
1          T100,A12,T115,A14)
            DO 215 J=1, 20
                DO 210 I=1, 6
                    B(I,J)=0.0
210          CONTINUE
                DO 211 I=1, 2
                    C(I,J)=0.0
211          CONTINUE
215      CONTINUE
            DO 205 I=1, IC
                DO 200 J=1, JS
                    B(1,I) = B(1,I) + F(J)*XF(I,J)
200          CONTINUE
                    B(2,I) = B(1,I)*MW(I)
                    B(3,I) = V(1)*Y(I,1)*MW(I)

```

```

      B(4,I) = L(JS)*X(I,JS)*MW(I)
      B(5,I) = B(3,I)*100.0/B(2,I)
      B(6,I) = B(4,I)*100.0/B(2,I)
      WRITE (6,480) I, COMP(I), (B(J,I), J=1,6)
205 CONTINUE
480 FORMAT (/I5,T15,A15,5X,4(E12.6,4X),2(F12.6,4X))
      WRITE (6,219) PAGEJC
      WRITE (6,490) DUBLSP, ' SUMMARY TABLE 2'
      WRITE (6,219) DUBLSP
      REFTOT = 0.0
      ETOTAL = 0.0
      RTOTAL = 0.0
      DO 206 I=4,IC
          REFTOT = REFTOT + B(2,I)
          ETOTAL = ETOTAL + B(3,I)
          RTOTAL = RTOTAL + B(4,I)
206 CONTINUE
      WRITE (6,484) 'TOTAL RARE EARTH IN FEEDS      =',REFTOT,' KG/HR'
      WRITE (6,484) 'TOTAL RARE EARTH IN EXTRACT    =',ETOTAL,' KG/HR'
      WRITE (6,484) 'TOTAL RARE EARTH IN RAFFINATE =',RTOTAL,' KG/HR'
484 FORMAT (//3X,A31,E14.6,1X,A6)
      WRITE (6,481) 'COMPONENT', 'COMPONENT', 'EXTRACT', 'RAFFINATE'
481 FORMAT (////T2,A10,T15,A9,T35,A7,T51,A9)
      WRITE (6,482) 'NUMBER', 'NAME', 'WT. %', 'WT. %'
482 FORMAT (/T3,A7,T17,A4,T36,A5,T53,A5)
      DO 207 I=4,IC
          C(1,I) = B(3,I)*100.0/ETOTAL
          C(2,I) = B(4,I)*100.0/RTOTAL
          WRITE (6,483) I, COMP(I), (C(J,I), J=1,2)
207 CONTINUE
483 FORMAT (/I5,T15,A15,2X,2(F12.6,4X))
      GO TO 15
190 WRITE (6,*) 'DATA INPUT MAY CONTAIN ERROR, CASE TERMINATED'
      STOP
      END

```

C
C
C

```

SUBROUTINE BASEKV(J)
DOUBLE PRECISION XF(20,100),L(100),AK(20,100),X(20,100)
DOUBLE PRECISION KCONST(8,20),HNO3(100),NO3,TBP
COMMON/BK2/X,Y,XSUM,YSUM
COMMON/BK3/XF,L,AK
COMMON/BK4/KCONST,HNO3
AK(1,J)=KCONST(1,1)
AK(2,J)=KCONST(1,2)+KCONST(2,2)*X(2,J)+KCONST(3,2)*X(2,J)**2+
1      KCONST(4,2)*X(2,J)**(-.2)+KCONST(5,2)*X(2,J)**(-.4)
AK(3,J)=KCONST(1,3)+KCONST(2,3)*X(2,J)+KCONST(3,3)*X(2,J)**2+
1      KCONST(4,3)*X(2,J)**3+KCONST(5,3)*X(2,J)**4
RETURN
END

```

C
C
C

```

SUBROUTINE EQUILK(I,J)
DOUBLE PRECISION XF(20,100),L(100),AK(20,100),X(20,100)
DOUBLE PRECISION KCONST(8,20),HNO3(100),AT,NO3,TBP
COMMON/BK2/X,Y,XSUM,YSUM
COMMON/BK3/XF,L,AK
COMMON/BK4/KCONST,HNO3
HNO3(J)=55.62736*X(2,J)-44.62263*X(2,J)**2+72.36273*X(2,J)**3--
1      358.0529*X(2,J)**4+498.3536*X(2,J)**5
AT=HNO3(J)

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```

      NO3 = 1.0006204*AT - 0.020407*AT**2 - 0.004496*AT**3 +
1      0.0001546*AT**4
      TBP = 3.428093 - 0.13173*AT + 0.028538*AT**2 - 0.003824*AT**3 +
1      0.0002462*AT**4 - 0.000006359*AT**5
      AK(I,J) = (KCONST(3,I)*(NO3*TBP)**3) * (KCONST(4,I) +
1      KCONST(5,I)*AT**KCONST(6,I)+KCONST(7,I)*AT**KCONST(8,I))/
1      (1.0 + KCONST(1,I)*NO3 + KCONST(2,I)*NO3**2)
      RETURN
      END
C
C
C
      SUBROUTINE SETUPA(I)
      DOUBLE PRECISION F(100),W(100),U(100),V(100),L(100),SUMB
      DOUBLE PRECISION XF(20,100),AK(20,100),A(100,101),SUM
      COMMON/BK1/JS,F,W,U,V
      COMMON/BK3/XF,L,AK
      COMMON/BK5/A
      M1 = JS +1
      DO 10 I1 = 1, 100
         DO 5 JJ = 1, 101
            A(I1,JJ) = 0.0
5      CONTINUE
10 CONTINUE
C
C
      FIRST ROW ELEMENTS
      A(1,1) = -V(2) - F(1) + V(1) + W(1) - (V(1) + W(1)) * AK(I,1)
      A(1,2) = V(2) * AK(I,2)
      A(1,M1) = -F(1) * XF(I,1)
C
C
      LAST ROW ELEMENTS
      A(JS,JS-1) = W(JS) + V(JS) + L(JS) + U(JS) - F(JS)
      A(JS,JS) = -L(JS) - U(JS) - (W(JS) + V(JS)) * AK(I,JS)
      A(JS,M1) = -F(JS) * XF(I,JS)
C
C
      MIDDLE ROW ELEMENTS
      JMINS = JS - 1
      NSTEP = 0
      SUM = 0.0
      DO 15 J1 = 2, JMINS
         SUM = SUM + F(J1-1) - W(J1-1) - U(J1-1)
         SUMB = SUM + F(J1) - W(J1) -U(J1)
         A(J1,NSTEP+1) = V(J1) + SUM - V(1)
         A(J1,NSTEP+2) = -(V(J1)+W(J1))*AK(I,J1)-U(J1)-V(J1+1)-SUMB+V(1)
         A(J1,NSTEP+3) = V(J1+1) * AK(I,J1+1)
         A(J1,M1) = -F(J1) * XF(I,J1)
         NSTEP = NSTEP + 1
15 CONTINUE
      RETURN
      END
C
C
C
      SUBROUTINE THOMAS(I)
      DOUBLE PRECISION A(100,101),P(100),QA(100),X(20,100)
      COMMON/BK1/JS,F,W,U,V
      COMMON/BK2/X,Y,XSUM,YSUM
      COMMON/BK5/A
      M1 = JS + 1
      P(1) = A(1,2)/A(1,1)
      QA(1) = A(1,M1)/A(1,1)
      NM1N = JS - 1
      DO 5 J1 = 2, JS

```

```
      P(J1) = A(J1,J1+1) / (A(J1,J1) - A(J1,J1-1) * P(J1-1))
      QA(J1) = (A(J1,M1) - A(J1,J1-1) * QA(J1-1)) /
1         (A(J1,J1) - A(J1,J1-1) * P(J1-1))
5 CONTINUE
  X(I,JS) = QA(JS)
  DO 10 J1 = 1, NMIN
    JSUB = NMIN - J1 + 1
    X(I,JSUB) = QA(JSUB) - P(JSUB) * X(I,JSUB+1)
10 CONTINUE
  RETURN
  END
```

15,400,1.0E-14

'LU2O3','Y2O3','YB2O3','TM2O3','ER2O3','HO2O3','DY2O3','TB2O3',
'GD2O3','EU2O3','SM2O3','ND2O3','PR2O3','CE2O3','LA2O3'

397.94,225.81,394.08,385.868,382.52,377.86,373.0,365.848,
362.50,351.92,348.70,336.48,329.814,328.24,325.82

0.6026,15.0,0.37765E-2,9.8084,0.27193,3.7806,0.61514E-8,11.706,

0.6026,15.0,0.16009E-3,428.05,6.4441,3.0916,0.89564E-5,9.8854,

0.6026,4.5017,0.36319E-2,11.246,0.67744E-1,3.5478,0.17513E-5,8.7219,

0.7079,12.5,0.44139E-2,8.2710,1.927,1.9068,0.10011E-4,8.2586,

0.75,16.105,0.17464E-3,741.99,2.8451,3.4183,0.80252E-5,9.6484,

0.75,10.859,0.4802E-1,1.7245,0.21721E-2,3.3385,0.44457E-5,7.2040,

0.8,25.0,0.29289E-3,611.35,0.33406,4.0502,0.60524E-6,10.478,

1.13,35.0,0.73684E-2,30.932,0.2317,2.3466,0.42961E-6,9.2689,

1.25,25.0,0.75454E-2,46.249,-22.406,0.125,0.35212E-5,7.9373,

2.04,47.091,0.48544E-1,1.5713,6.9358,-0.45006,0.96604E-6,7.7463,

3.2,35.0,0.91132E-3,308.49,-25.754,1.1617,0.11257E-2,6.0768,

0.8,9.0243,0.1,-0.23811,1.0176,-0.54992,0.33469E-6,6.3364,

1.6982,32.448,0.1,-2.94,4.7418,-0.23403,0.60547E-4,4.44,

1.63,19.114,0.32647,-0.22172,0.53016,-0.47404,0.70708E-4,3.4566,

1.2882,10.765,0.38348E-1,-0.21943,1.3901,-0.86901,0.1067E-4,
4.5425

1,24,3,0,0,500

1,2,0.09618242

.0,9.007960,39.08325,.0,.0,.0,.0,.0,.0,.0,.0,.0,.0,.0,.0

12,2,0.048456294

.0,9.007960,39.08325,2.269472E-4,0.039992,1.527702E-3,2.340474E-4,

2.360959E-3,3.186559E-4,5.649296E-3,1.316474E-3,0.011626,1.881959E-3,

0.015539,0.103776,0.031032,9.170678E-3,0.140432

24,1,0.046797258

3.009,3.59,1.2,.0,.0,.0,.0,.0,.0,.0,.0,.0,.0,.0,.0

1,30,3,0,0,500

1,2,0.09618242

.0,9.007960,39.08325,.0,.0,.0,.0,.0,.0,.0,.0,.0,.0,.0,.0

15,2,0.048456294

.0,9.007960,39.08325,2.269472E-4,0.039992,1.527702E-3,2.340474E-4,

2.360959E-3,3.186559E-4,5.649296E-3,1.316474E-3,0.011626,1.881959E-3,

0.015539,0.103776,0.031032,9.170678E-3,0.140432

30,1,0.046797258

3.009,3.59,1.2,.0,.0,.0,.0,.0,.0,.0,.0,.0,.0,.0,.0

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