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SEPARATIONS OF YTTRIUM AND SOME RARE EARTHS BY LIQUID-LIQUID EXTRACTION

By
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SEPARATION OF YTTRIUM AND SOME RARE EARTHS BY LIQUID-LIQUID EXTRACTION*

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Raymond A. Foos and H. A. Wilhelm

ABSTRACT

The use of liquid-liquid extraction for the separation of some inorganic compounds was demonstrated.

The yttrium-rare earth concentrates were obtained from Fergusonite ore, Gadolinite ore and a by-product from an ion-exchange resin separation process. In each case the mixture in terms of oxide was composed of from 50 to 60 per cent yttrium and 5 to 15 per cent heavy rare earths with the light rare earth fraction constituting the remaining material. Tributyl phosphate was generally employed for extracting nitric acid solutions of these concentrates.

Single stage extractions indicated that the relative extractability of certain rare earths from an aqueous system, 3.0 molar or greater in nitric acid, increases with atomic number. At lower nitric acid concentrations deviations from this trend were observed. The mass transfer values showed a minimum at a nitric acid concentration of about 6.0 molar. Yttrium extracts in the holmium region from a highly concentrated nitric acid system, in the dysprosium region from a 6 to 12 molar nitric acid system, in the gadolinium region from a 3.0 to 4.5 molar nitric acid system and with the lighter rare earths from very low nitric acid systems.

A number of 20 stage countercurrent extractions were carried out employing nitric acid solutions of yttrium and rare earths as the aqueous feed phase and tributyl phosphate as the organic phase. When extracting their concentrated nitric acid solutions, the organic product generally contained yttrium and heavy rare earths while the aqueous product contained the light rare earth fraction

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* This report is based on a Ph.D. thesis by Raymond A. Foos submitted July, 1954, to Iowa State College, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.

plus a small amount of yttrium and dysprosium. In one multistage extraction the organic product phase delivered 90 per cent of the total yttrium which gave an oxide that was 91 per cent pure. Extraction of a light rare earth fraction resulted in an enriched concentrate of praseodymium and samarium. Gadolinium and dysprosium were separated from yttrium to a considerable extent by extracting from a very low nitric acid solution. The extractions of these yttrium-rare earth concentrates showed the possibility of separating yttrium from any particular rare earth and of some individual rare earths.

The liquid-liquid system presented here indicated further the applicability of solvent extraction for separating inorganic compounds. Much of the information from this work is directly applicable to practical separation problems and therefore should be readily adaptable to specific laboratory and industrial scale operations.

INTRODUCTION*

Liquid-liquid extraction is becoming widely used for the separation of inorganic salts in industrial as well as in laboratory processes. Consequently, this technique was investigated as a method for the separation of some inorganic salts which are of current interest to the Atomic Energy Commission.

In general, a number of liquid-liquid systems containing yttrium and some rare earth salts were investigated. Various compositions of the aqueous phase were contacted with a variety of partially immiscible organic solvents in single stage extractions until equilibrium was obtained. Analyses of the equilibrium phases allowed calculation of the individual distribution coefficients, mass transfers from the aqueous phase to the organic phase and separation factors for each case. These equilibrium data afforded a method whereby the separation effectiveness of the various liquid-liquid systems was compared. From the single stage data the range of the optimum operating conditions was estimated for a separation by a multistage extraction. These conditions were tested in a multiple-contact countercurrent extractor employing as many as 20 equilibrium stages. A few multistage extraction experiments were usually required to obtain the most effective separation conditions.

The aqueous feed was usually a mineral acid solution containing the yttrium and some rare earth salts to be separated although basic media in some cases were also investigated. Such variables in the aqueous phase as pH, acid concentration, salt concentration, complexing agents and salting-out agents were investigated. For the organic phase, factors such as acidity, complexing agents, diluents and type of organic were found to be important in making separations. Relative volumes of the organic and aqueous phases were also varied to obtain separation data. Since separation of these salts on a commercial scale is desired, the economics of a process was an important factor in evaluating the practicability of a liquid-liquid system.

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*This introduction was written for a series of reports dealing with a number of liquid-liquid systems employed in separation studies. Only one of these systems is treated in this report. The other systems, including zirconium from hafnium and tantalum from niobium, are treated in Reports ISC-693 and ISC-694.

An enriched yttrium concentrate and concentrates of various rare earths resulted from extractions on the yttrium-rare earth mixtures. The use of liquid-liquid systems for separating these inorganic salts proved useful on a laboratory scale. In a few cases the operations were scaled up to pilot plant production where they proved equally satisfactory.

GENERAL HISTORY OF RARE EARTH SEPARATION

Yttrium, because of its favorable nuclear properties, offers materials of interest in connection with the development of atomic reactors. The preparation of yttrium concentrates was the objective of the present work. However, the association of yttrium in nature with rare earth elements requires that consideration be given to rare earth separations for yttrium purification studies.

The separation of rare earth salts into their pure components has puzzled chemists since 1839 when Mosander discovered that "ceria" in Cerite ore and "yttria" in Gadolinite ore were complex mixtures. Although there is still some disagreement, the term "rare earth" or "lanthanide" usually includes all the elements of atomic numbers 57 through 71 (lanthanum to lutetium). Although the position of yttrium in the periodic table is not within this range, it is chemically closely related to the lanthanides. Rare earth ores ordinarily contain yttrium which cannot be readily removed from the lanthanides by simple chemical procedures. Consequently, rare earth mixtures from ore treatments generally contain yttrium. The rare earths are generally classified into the heavy and light fractions. In the light fractions the elements with atomic numbers 57 to 64, inclusive, or lanthanum to gadolinium, are generally included while the remaining rare earths usually constitute the heavy fraction. Separation of the lanthanides into these fractions can be accomplished with some overlapping by chemical means. Yttrium is chemically near the border line of the two fractions but generally follows the heavy fraction. Further separation of each fraction into its individual elements is much more difficult.

Since the lanthanides are very similar chemically, progress on their separation has been slow. In 1855 von Welsbach introduced the double ammonium nitrate fractional crystallization of the light group while in 1900 Demarcay proposed the double magnesium nitrate method of fractionation (1). Moeller and Kremers (2) employed a double sodium sulfate precipitation to divide an yttrium-rare earth mixture into the following three fractions: (a) lanthanum, cerium, praseodymium, neodymium and samarium, (b) europium, gadolinium and terbium and (c) dysprosium, yttrium, holmium, erbium and thulium. Marsh (1) has reviewed the method of rare earth separation up to 1946. They primarily consisted of fractional crystallization of the sulfates or nitrates. Since 1946 purification by partial precipitation or fractional crystallization employing Versene complex formation (3,4), amino acid complexes (5), ferricyanide precipitation (6), oxalic acid precipitation (7), solubility of oxides in an ammonium acetate solution (8), precipitation with nitriloacetate (9), carbonate precipitation in a trichloroacetate solution (10) and solubility in potassium carbonate solution (11,12) have been reported. Separations of rare earths by these methods generally do not serve to readily isolate any individual pure rare earth salts. Some of the treatments show promise as a method for preparing concentrates which could be used in further processing by other techniques. Attempted separations of rare earth salts by employing paper chromatography (13-17), radiometric adsorption (18) and adsorption on aluminum oxide (19) have been reported. Distillation of rare earth chlorides as a possible means of separation was investigated by Vickery (20). Marsh (21) observed that some rare earth acetates have no amalgam forming power when treated with sodium amalgam. By this method he separated samarium from gadolinium and neodymium (22), and ytterbium from lutetium and thulium (23). As indicated for fractional crystallization none of these methods offer a means to effectively fractionate a complex rare earth salt mixture into its pure components.

In 1947 Spedding and co-workers (24-27) reported the use of ion-exchange resin columns for separating complex rare earth salts on a pilot plant scale. In the same year Ketelle and Boyd (28) and Tompkins, Khym and Cohn (29) employed ion-exchange resin columns for separation of selected mixtures of rare earth salts. Since then many other papers on rare earth separation by ion-exchange columns have been written (30-35). In general, this technique entails elutriating the rare earth chloride mixture through an ion-exchange resin, such as amberlite, with citric acid. The order of lanthanide elution was found to be that of decreasing atomic number while yttrium appeared in the gadolinium-dysprosium region. Since some rare earth concentrates contain considerable yttrium, the capacity of a resin column for the rare earth salts is reduced in these cases. The ion-exchange technique has aided rare earth salt separation greatly since it produces the salts in their pure form. However, the rate and cost of production of these salts by this process has to date limited its scale of operation to minor quantities. Consequently, a cheap method for large scale fractionation of yttrium and lanthanide mixtures is desired if relatively large quantities of the purified components are to become industrially important.

Since liquid-liquid extraction often permits low-cost, large-scale production, it was considered as a possible method for separating these yttrium and lanthanide salt mixtures. The reviews of Bock (36), Quill (37) and Wylie (38) stressed the importance of continuous liquid-liquid extraction for lanthanide fractionation.

The first use of solvent extraction for rare earth salt separation was reported in 1937 by Fischer, Dietz and Jubermann (39). They claimed a 50 per cent difference in the distribution coefficients of neighboring rare earths when extracting an aqueous lanthanide chloride solution with numerous organic compounds (ethers, alcohols and ketones). Unfortunately, none of these data were published at that time nor have they been substantiated by other investigators. An aqueous solution containing a mixture of lanthanum and neodymium thiocyanates was extracted with n-butyl alcohol by Appleton and Selwood (40). They reported low distribution values and a lanthanum-neodymium separation factor of only 1.06 with the latter element favoring the organic phase. Templeton and Peterson (41), when distributing a lanthanum-neodymium nitrate mixture between water and hexanol, obtained a separation factor of 1.5 with the latter element favoring the organic phase. A further investigation on a nitrate-alcohol system by Templeton (42) indicated a regular increase in extraction with atomic number for all the rare earths from lanthanum to samarium, inclusive. Studies on the extraction of an aqueous solution of neodymium and erbium chlorides with n-butanol indicated little transfer to the organic phase and no detectable separation (43). However, for a corresponding rare earth nitrate system, four times more material was transferred to this alcohol organic phase with increased separation factors. The presence of ammonium thiocyanate in the chloride or nitrate lanthanide system yielded slightly more transfer but with no appreciable change in their separation factors (43).

In 1952 Peppard, Faris, Gray and Mason (44) reported that the extractability of the lanthanides into tributyl phosphate from a hydrochloric acid solution or from an 8.0 to 15.6 molar nitric acid solution increased with increasing atomic number. The order was inverted for a 0.3 molar nitric acid aqueous phase. Yttrium was extracted between dysprosium and holmium, or the position predicted from consideration of atomic radii. Addition of sufficient aluminum nitrate or ammonium nitrate caused complete transfer of the lanthanides into the organic phase with no contamination from most other inorganic salts. Although these salting-out agents were useful in separating rare earths salts from accompanying impurities, a concentrated nitric acid system was superior to this mixed nitrate-nitric acid phase for separation of individual rare earths. For increasing nitric acid concentrations they showed that the logarithm of the distribution ratios for a given pair of lanthanides diverged; consequently, the theoretical maximum separation factors required concentrated acid. A constant separation factor of 1.9 was observed between nearest rare earth neighbors in a 15.6 molar aqueous nitric acid medium when extracting the rare earths whose atomic numbers were not greater than 67, the limit of their work. For a 12 molar nitric acid system the separation factors between nearest neighbors was 1.6. Since these separation factor relationships were obtained from single stage extractions of pure rare earths employing only radioactive tracers, their application to high concentrations of mixed rare earth salts might not be valid. It was concluded that any rare earth nitrate-nitric acid aqueous solution could be divided into two fractions by extracting with tributyl phosphate. The compositions of these fractions are a function of variables such as acidity, flow rates, rare earth concentration and the amount of diluent for the organic phase. Separations of complex lanthanide mixtures into two overlapping groups were reported using a simulated counter-current extraction.

Weaver, Topp and Kappelman (45) used a Varsol-tributyl phosphate organic phase and a nitric acid-rare earth nitrate aqueous system to prepare about a kilogram of 95 per cent gadolinium oxide. The remaining five per cent was essentially samarium with a small amount of dysprosium and terbium. However, the lanthanide starting material contained, in terms of oxides, about 66 per cent gadolinium, 15 to 20 per cent dysprosium, 3.0 to 5.0 per cent erbium and 1.0 to 3.0 per cent yttrium plus the other heavy rare earths. Two separate experiments employing an 11 stage York-Scheibel extraction column were required for this separation with 57 per cent of the total gadolinium recovered having a purity of 95 per cent. It was also reported that temperature increases resulted in a decrease in the total material transferred into the organic phase. The lanthanide distribution coefficients appeared to be nearly independent of rare earth concentration.

Investigation of the liquid-liquid extraction of a samarium and neodymium nitrate mixture dissolved in 12 molar nitric acid with various Varsol-tributyl phosphate compositions was reported by Topp (46). A nearly constant separation factor of 2.8 resulted between these two elements, although the temperatures and lanthanide concentrations were varied. The distribution values for these two elements were dependent upon temperature and independent of rare earth concentrations.

In a report by Bochinski, Smutz and Spedding (47) the partial separation of the lanthanide nitrates obtained from a monazite sand was discussed. They employed tributyl phosphate in various dilutions as the organic phase. Very little nitric acid was present in the aqueous phase. The starting mixture based on the oxides analyzed approximately 15 per cent praseodymium, 75 per cent neodymium, 6 per cent samarium and 4 per cent gadolinium plus minor amounts of others. The aqueous product was 25 per cent praseodymium, 75 per cent neodymium, while the organic phase product contained 48 per cent samarium and 34 per cent gadolinium plus others as oxides. Separation factors at these low acid conditions were reported to increase with increasing rare earth concentration but were independent of the particular rare earths in the mixture. It was also observed that the mass transfer to the organic phase was a function of lanthanide concentration and virtually independent of lanthanide composition. At high rare earth concentrations the per cent mass transfer of lanthanides to the organic phase was decreased by nitric acid, while an increase in per cent mass transfer was reported at low lanthanide concentrations. Aluminum nitrate increased the per cent mass transfer to the organic phase most at a low rare earth concentration. Diluents in the tributyl phosphate were found to decrease both mass transfer to the organic phase and the rare earth separation factors. They assumed that for a given nitric acid concentration the separation factors were a function of the total rare earth concentration and completely independent of the lanthanide components. Distillation calculations were then employed to determine equilibrium equations for predicting the product compositions when extracting this multicomponent rare earth mixture.

All of the reported liquid-liquid extraction studies on rare earth separations employing tributyl phosphate have been carried out on dilute lanthanide solutions (44) or on mixtures consisting essentially of only the light rare earths (47, 45, 46, 48). Separation of rare earth salts containing relatively large amounts of yttrium, dysprosium, gadolinium and the heavy rare earths by liquid-liquid extraction have not been reported. The report of Peppard and co-workers (44) on experiments employing dilute solutions indicated that separation of these heavier rare earths in high concentrations might be possible. In the extraction studies reported here the separations of rare earths that were obtained from Fergusonite ore, from Gadolinite and from the tailings of an ion-exchange column are discussed. The concentration and separation of yttrium from the rare earths was the primary objective of this work. However, the close association of yttrium with gadolinium and dysprosium required a detailed study involving the separation of these three elements from one another.

EXPERIMENTAL DETAILS

The techniques employed in this investigation for the separations of yttrium and rare earth salts dissolved in mineral acids involved liquid-liquid extractions. Various yttrium-lanthanide salt mixtures, salting-out agents, mineral acids and water immiscible organic liquids were tested. In some experiments the organic phase was first acidified with an equal volume of aqueous phase containing only the mineral acid to be used in the extraction. The acid concentration in the aqueous phase used for this treatment equaled the initial acid concentration of the feed solution containing the yttrium-rare earth salt mixture. The acid in the organic solution, however, was not, after this treatment, at the equilibrium concentration to be attained in the extractor.

The aqueous feed solutions consisting of yttrium and rare earth salts were usually prepared by dissolving the oxides directly in the mineral acid. However, for preparing low acidity feed solutions the hydroxides were first precipitated with ammonium hydroxide from a mineral acid solution. After this hydroxide precipitate was washed with water to remove the residual ammonium ions, it was dissolved in a minimum amount of the desired mineral acid. This technique was useful in obtaining stable concentrated yttrium-rare earth nitrate solutions having as little as 0.06 molar free nitric acid.

The acid concentration of the aqueous and organic phases containing no inorganic salt was determined by titration with sodium hydroxide using phenolphthalein as the indicator. However, before analyzing the organic phase for its acid concentration, acetone and water were added. The former compound insures a homogeneous phase while the latter compound allows sufficient dissociation of the indicator to observe the titration end point.

In the presence of the yttrium-rare earth salts and certain salting-out agents, phenolphthalein could not be used as the indicator for determination of the acid concentration. Because of their reaction with sodium hydroxide, these rare earth salts start to precipitate at about a pH of 4. Consequently, an alcoholic solution of bromphenol blue, which changes from yellow to blue in the pH range of 3.0 to 4.6, was employed as the indicator. The indicating effect of bromphenol blue was destroyed (probably by adsorption) at the end point when bromphenol blue was added to the aqueous solution at the beginning of the titration. Therefore, the indicator was not added until sufficient sodium hydroxide was present to form the first permanent precipitate. The blue solution was then back-titrated with standard acid until the yellow color persisted for about 60 seconds. This titration was reproducible to within 5 per cent of an average value. It is believed that this technique indicated the free acid concentration within 10 per cent of its actual value. With several mixtures of known composition, a pseudomolecular weight, based on the relative proportions of each component, was calculated. This molecular weight permitted the determination of the number of acid equivalents required to react with the mixed oxides. Several comparisons of these two methods for obtaining the acid concentration indicated that the values obtained from the bromphenol blue titrations were consistently 5 to 15 per cent lower than the values calculated from assuming an average molecular weight.

All single and multistage extractions were carried out at room temperature. In the single stage tests the organic and aqueous phases were placed in a separatory funnel and agitated vigorously by shaking for at least 60 seconds to insure equilibrium conditions. The equilibrium phases were allowed to separate and their volumes were then measured. Analytical data on the contents of each phase then permitted calculation of the yttrium and the rare earth distribution coefficients and their separation factors. The apparatus employed for the multistage extractions of the yttrium-rare earth mixtures appears in Figure 1.

After extraction of the aqueous solution with an organic phase, the yttrium plus rare earth content of each phase was determined. The yttrium and rare earth oxalates were quantitatively precipitated directly from the low acidic aqueous phase by addition of a water solution of oxalic acid. For the highly acid systems, ammonium hydroxide was first added to adjust the pH of the aqueous phase to about one. Addition of oxalic acid then insured quantitative and rapid precipitation. Asselin, Audrieth and Comings (43) concluded that either ammonium hydroxide or oxalic acid gives a quantitative precipitation of rare earths from aqueous acidic solutions. The oxalate precipitate is slightly granular and consequently can be filtered and washed much easier than the gelatinous yttrium and rare earth hydroxides.

For recovering the yttrium and rare earths from the organic phase it was found that two separate equal volume water scrubs of the organic phase was usually sufficient to back-extract all of the material. However, three separate equal volume water scrubs were usually employed. Addition of oxalic acid to the composite aqueous scrub solutions resulted in the quantitative recovery of the oxalates. A direct oxalic acid precipitation of the yttrium and rare earths from the organic phase is possible, although the addition of acetone is desirable to insure a homogeneous phase and ease of filtration. It is apparent that such a precipitation from the organic phase would probably make the recovery of the organic phase difficult. In preparation of analytical samples the oxalates were converted to oxides by calcining at 600 degrees Centigrade for at least two hours.

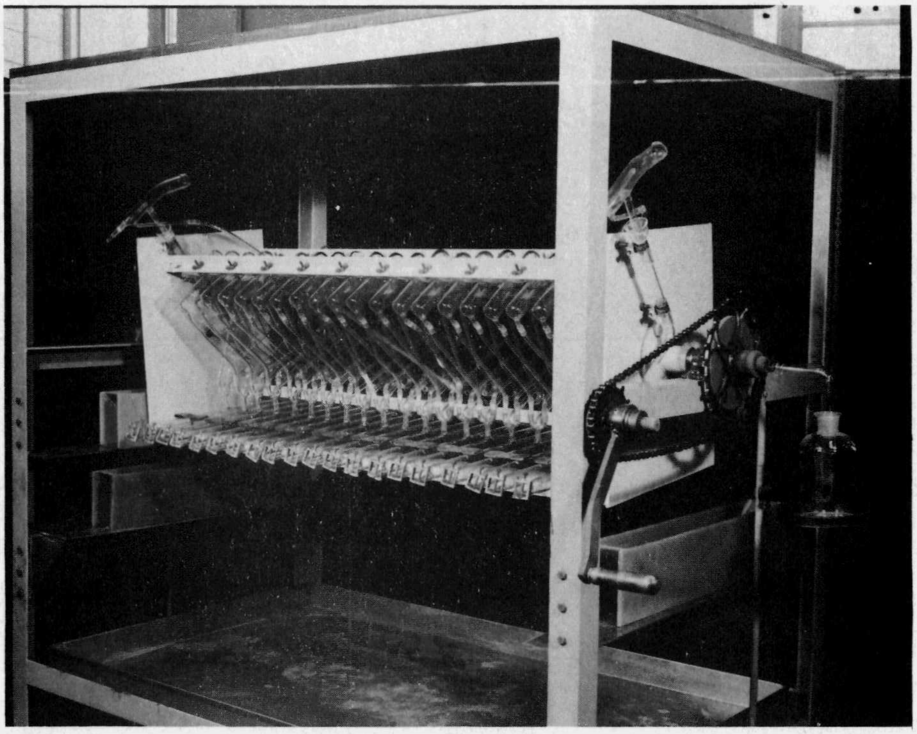

Figure 1 - Twenty Stage Countercurrent Liquid-Liquid Extractor.

Analyses of the complex oxide mixtures required both spectrographic and spectrophotometric methods. All percentages are expressed on the basis of an oxide weight referred to the total oxide weight of the sample. Some results were obtained from a series of analyses on similar samples and, consequently, represent an average value.

A spectrophotometric method similar to that proposed by Moeller and Brantley (49) was used to analyze the complex rare earth mixtures for the oxide percentages of samarium, praseodymium, neodymium and dysprosium. This method required about 0.2 gram of the rare earth oxide mixture dissolved in 10.0 milliliters of a 10 per cent aqueous solution of hydrochloric acid. When employing a one centimeter spectrophotometric cell in the rare earth analyses, the lower limits of detection were about 0.3 per cent for praseodymium, 0.5 per cent for neodymium and 1 per cent for samarium and dysprosium. This procedure is believed to be accurate to within ± 5 per cent of the total content of dysprosium, neodymium or praseodymium and ± 10 per cent of the samarium. The presence of minor amounts of other rare earths and common impurities should not alter these values (50) beyond these limits of error.

The spectrographic method of Fassel (51) was employed for analyzing the complex oxide mixtures for percentages of yttrium oxide and gadolinium oxide. This procedure required addition of ceric oxide as an internal standard to the complex yttrium-rare earth oxide mixture. A standard deviation of ± 2.5 per cent with a lower limit of detection of about 3.0 per cent for gadolinium oxide and for yttrium oxide was reported for this method. All qualitative analyses of the yttrium-rare earth mixtures were also done by spectrographic techniques.

RESULTS AND DISCUSSION

1. Separation of the yttrium and rare earths obtained from the ion-exchange column tailings

(a) Introduction. In the ion-exchange method employed by Spedding (30-32) for producing pure rare earth salts, an yttrium-lanthanide chloride mixture constitutes the charge for the resin columns. The rare earths and yttrium pass through the column as a series of separate bands which are collected individually with some overlapping. The heaviest of the rare earths emerge from the column first. After holmium and some of the dysprosium has been collected yttrium appears in the product. When the yttrium-lanthanide fraction from Gadolinite ore composed the initial mixture, yttrium oxide constituted more than 50 per cent of the total weight. In many cases only the production of heavy rare earth salts was desired in the work of Spedding and co-workers. Consequently, yttrium and the remaining light rare earth salts were stripped from the columns as a composite product. These column strippings, or tailings, were available and served as one rich source of yttrium for the present investigation. The partial composition of the column tailing yttrium-lanthanide mixture appears in Table 1 under the heading "initial percentage." The unaccounted for material in the mixture is probably lanthanum, cerium, and perhaps a small amount of heavy rare earths.

A method was desired in which most of the yttrium could be cheaply and rapidly removed from this light rare earth fraction. The recovered light rare earth fraction, low in yttrium, could then be employed as a charge for another ion-exchange column process to prepare the individual light rare earths. Such an increase in the per cent of light rare earths per charge would at least double the production rate for pure light rare earth salts from a given column.

According to the report of Peppard and co-workers (44), and from the analysis of this mixture, the separation of yttrium and dysprosium from gadolinium should result in a concentrated light rare earth fraction. Since maximum rare earth separation factors were reported at high nitric acid concentrations, an aqueous nitrate solution of the column tailings containing 13 molar nitric acid was employed for the first extraction. Highly acidified tributyl phosphate constituted the organic phase.

In order to quickly estimate the nitric acid concentration in the acidified organic phase a series of extractions was carried out in which pure tributyl phosphate was contacted with an equal volume of aqueous phases containing various nitric acid concentrations. The equilibrium phases were titrated for nitric acid concentration.

Figure 2 shows the equilibrium nitric acid concentration in the two phases. From Figure 2 it is apparent that a 13 molar nitric acid aqueous phase is in equilibrium with tributyl phosphate containing a nitric acid concentration of about 5.0 molar.

Table 1

Analysis of the Mixtures from the Column Tailings Before and after the Multistage Extraction

Component	Initial percentage	Product phase percentage Aq.	Org.
Pr_6O_{11}	2.0	3.4	N.D.
Nd_2O_3	7.6	22.	N.D.
Sm_2O_3	5.7	16.	N.D.
Gd_2O_3	8.4	22.	N.D.
Dy_2O_3	4.0	4.4	2.4
Y_2O_3	66.	24.	91.
Total	93.7	91.8	93.4

N.D. - Not detected

(b) Single stage extractions of the ion-exchange column tailings. Several single stage extractions were carried out to aid in selecting the proper flow rates to use in the 20 stage extractor. The aqueous phase which was 13 molar in nitric acid contained the equivalent of 52 grams of the oxides from the tailings per liter. Various relative volumes of the tributyl phosphate which was 5.0 molar in nitric acid was employed as the organic phase. Table 2 contains the results of these extractions.

It is apparent from Table 2 that the gadolinium-yttrium separation factors and the per cent mass transfers increased with the increased organic to aqueous phase volume ratio. According to Peppard and co-workers (44), who obtained

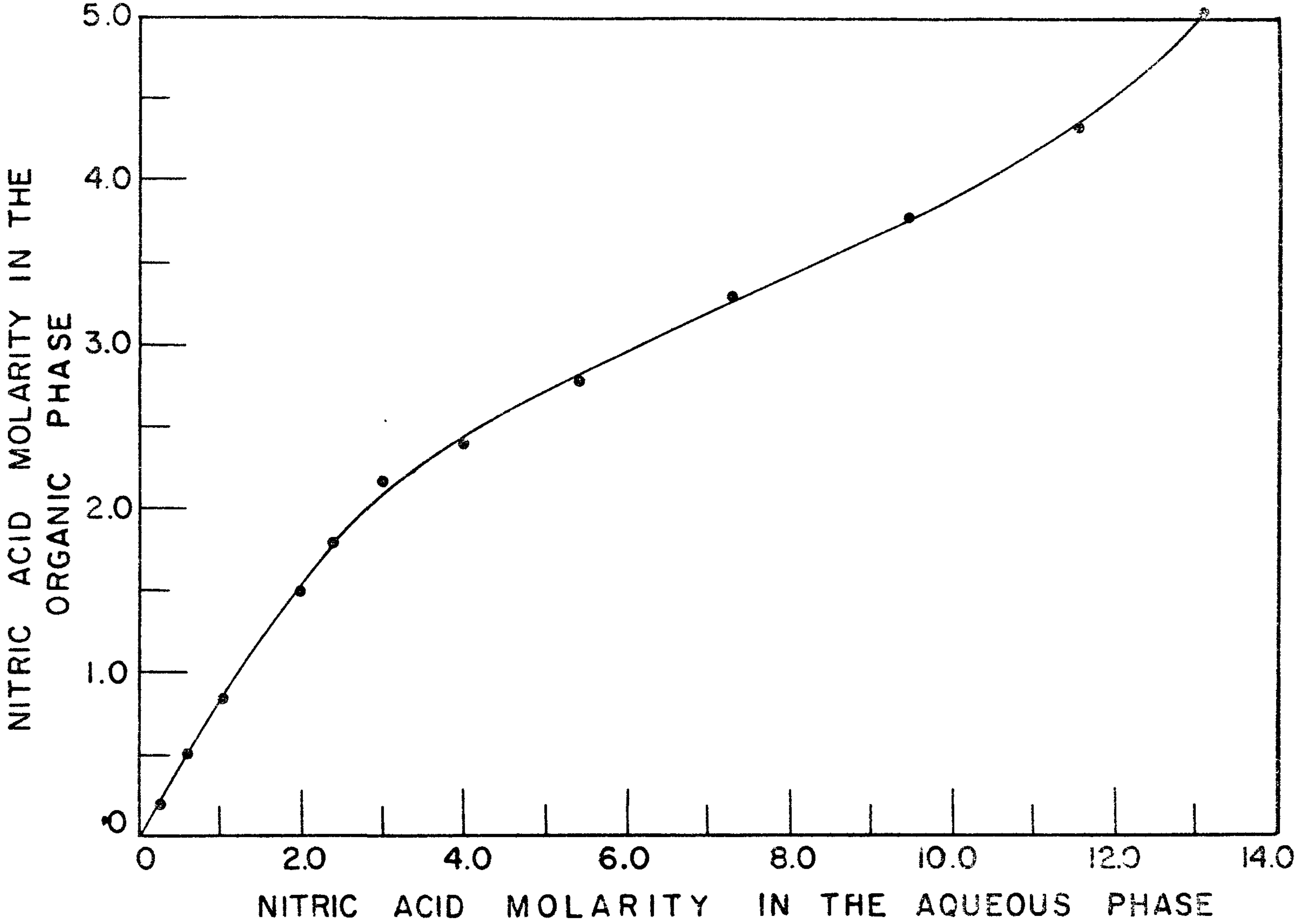

Figure 2 - Distribution of Nitric Acid between Water and Tributyl Phosphate.

distribution data on dilute solutions of the pure rare earth salts, the gadolinium-yttrium separation factor should be about 5.0 for a nitric acid concentration of 13 molar. This value is being approached as the concentrations of the rare earth salts in the equilibrium phases decrease.

Table 2

Single Stage Extraction Data for Separating the Yttrium-Rare Earth Nitrates Obtained from the Column Tailings

Org./ aq. vol.	% oxide weight in org.	Equil. anal. % Gd_2O_3 Aq.	Equil. anal. % Gd_2O_3 Org.	Equil. anal. % Y_2O_3 Aq.	Equil. anal. % Y_2O_3 Org.	Dist. coef. K_{Gd}	Dist. coef. K_Y	Gd-Y sepn. factor
1	72.1	10.6	6.2	33	67	1.51	4.97	3.29
3	89.5	5.9	8.3	15	67	3.92	13.6	3.47
9	97.4	3.6	8.6	5.9	64	9.87	44.7	4.53

(c) Multistage extraction of the ion-exchange column tailings. Since this original mixture contains 66 weight per cent yttrium oxide and 4 per cent dysprosium oxide, it is apparent from the mass transfer data in Table 2 that nearly equal volumes of the organic and aqueous phases are required for a desirable split of these two elements from the lighter rare earth portions. Consequently, a twenty stage counter-current extraction was carried out in which four volumes of organic, one volume of aqueous feed and four volumes of aqueous scrub were added for each cycle of operation. The aqueous feed contained the equivalent of 267 grams of the oxides per liter. It is apparent that when the one volume of aqueous feed mixed with the four volumes of aqueous scrub, a concentration equivalent to about 53 grams of oxides per liter resulted. Both the aqueous feed, introduced at stage 11, and the aqueous scrub, introduced at stage 20, were 13 molar in nitric acid. The organic phase was tributyl phosphate which had been pre-equilibrated with 13 molar nitric acid. It was added to the extractor at stage 1. The relative flow rates from stages 1 to 11, or the organic scrubbing section, were five volumes of aqueous to four volumes of organic, while from stages 12 to 20, or the aqueous scrubbing section, a one to one volume ratio existed.

This extraction was carried out for 176 cycles, although steady state based on the gadolinium and yttrium analyses and total oxide concentration was reached at about the 150th cycle. About 65 cycles and 100 cycles, respectively, of operation were necessary for gadolinium and yttrium to reach the aqueous outlet end of the extractor. Yttrium appeared in the organic product in the early stages of the extraction. Steady state analyses of the organic and aqueous product phases appear in Table 1.

The mass transfer of material to the organic product phase was about 60 per cent of the total weight as oxides. As indicated in Table 1, the organic product phase was primarily yttrium, although a small amount of dysprosium was also present. On the other hand, the aqueous product phase contained almost a quantitative recovery of the light rare earths. Consequently, this extraction based on oxides yielded a 90 per cent recovery of yttrium which was 91 per cent pure and about a threefold increase in the concentration of the light rare earths.

The results of this multistage extraction agree in general with the ideas presented by Peppard and co-workers (44). It is apparent that as the atomic number of the rare earths increase their preference to be extracted from a highly concentrated nitric acid solution by this organic phase also increase. For extracting a 13.0 molar nitric acid aqueous solution of rare earths and yttrium with a nearly equal volume of tributyl phosphate the rare earth phase preference should have reversed between element 61 and 62 according to Peppard and co-workers (44). However, the change in phase preference appeared just above the element with atomic numbers 66, or dysprosium. This deviation from the ideal predicted position was probably caused by the increased salt concentration. Peppard's distribution coefficients were obtained by extracting very dilute solutions of pure individual rare earth nitrates. The presence of the large amount of yttrium with the rare earth mixture might also cause a shift in individual distribution coefficients.

The results from the stagewise analyses of the aqueous and organic phases for total oxide, gadolinium and yttrium concentrations at steady state conditions appear in Figures 3, 4 and 5. From Figure 3 it is apparent that in many stages the concentration expressed as oxide

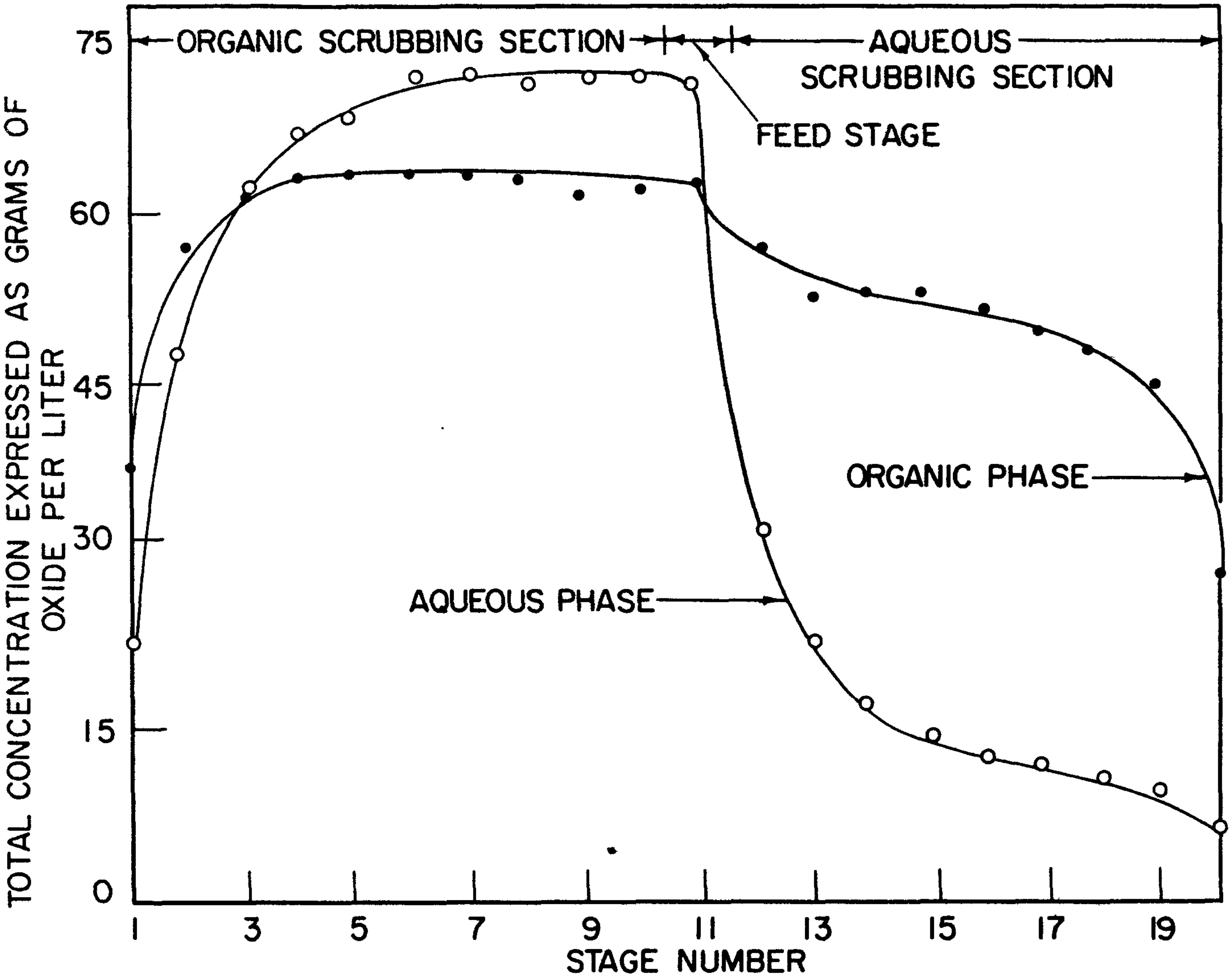

Figure 3 - Yttrium Plus Rare Earth Concentration in the Equilibrium Liquid Phases as a Function of Stage Number.

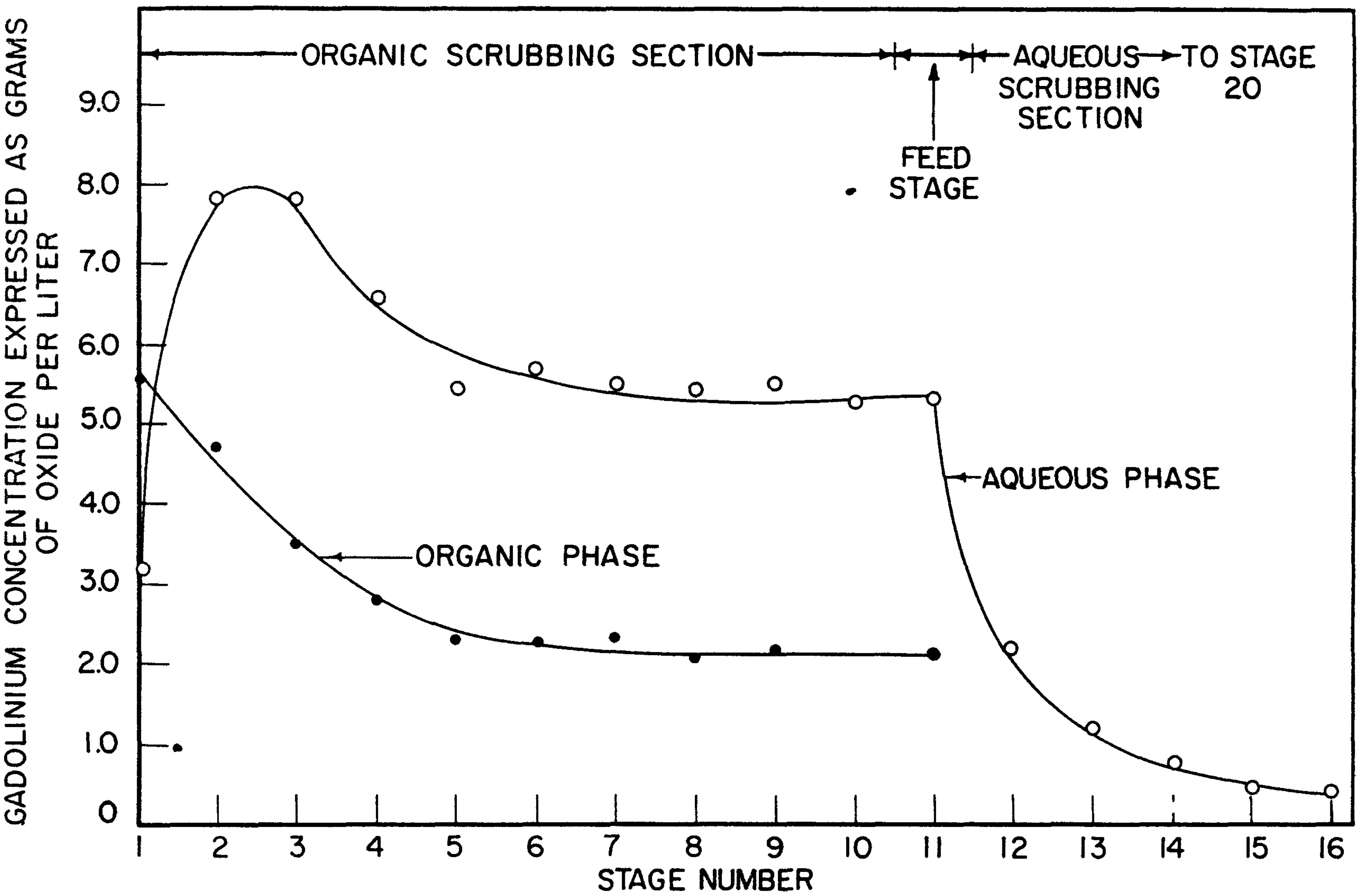

Figure 4 - Gadolinium Oxide Concentration in the Equilibrium Liquid Phases as a Function of Stage Number.

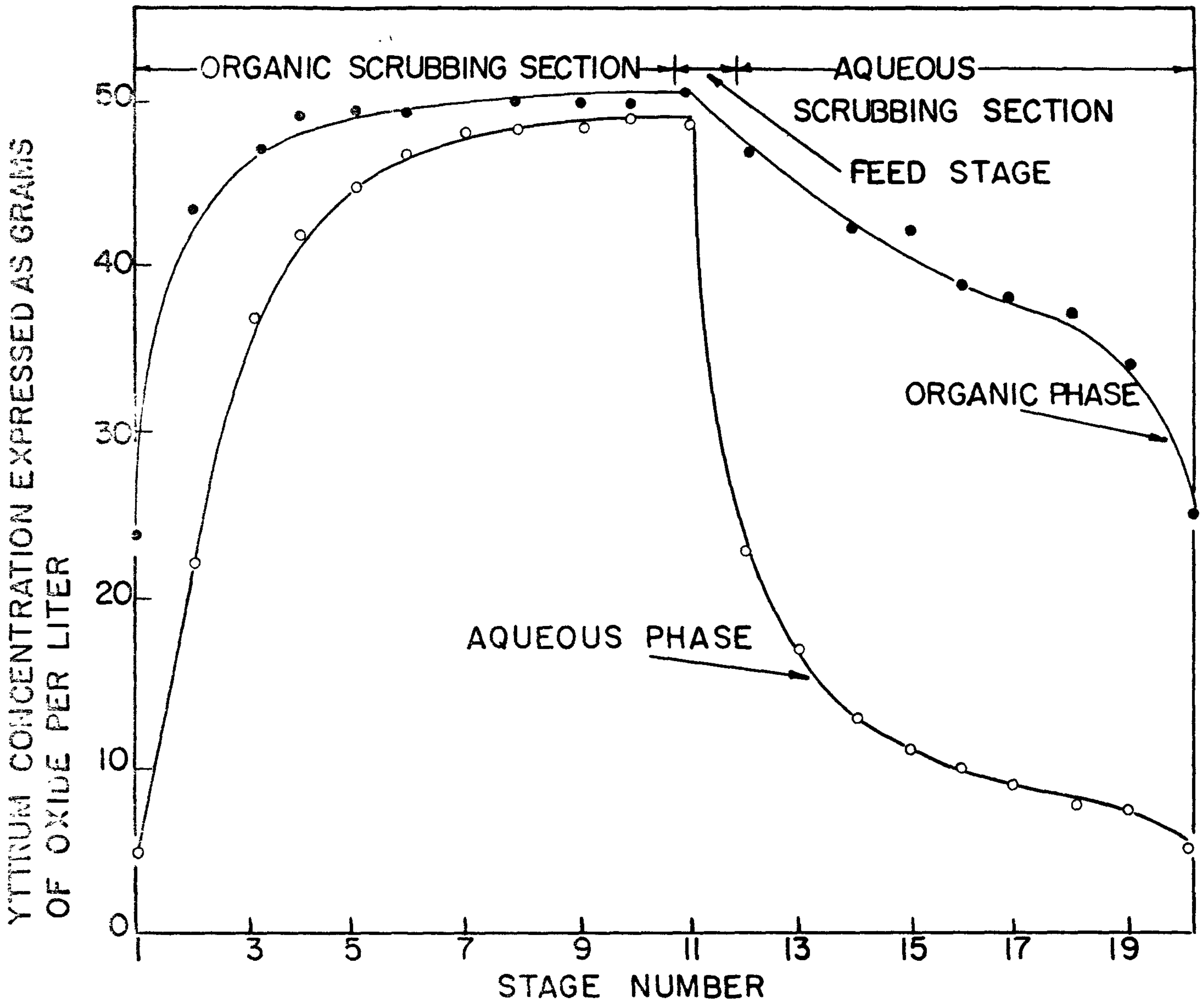

Figure 5 - Yttrium Oxide Concentration in the Equilibrium Liquid Phases as a Function of Stage Number.

was greatest in the organic phase. This was expected since yttrium, which prefers the organic phase, constituted more than half the starting mixture. Little variation in concentration in either phase took place in stages 6 to 11, inclusive, but at the ends of the extractor sharp decreases in concentrations appeared. This indicates that refluxing both the organic and aqueous product liquids would be useful in obtaining more highly concentrated products.

From Figure 4 it can be noted that gadolinium was not present in the organic phase beyond the feed stage, stage 11. Since this element was detected in the aqueous phase up to stage 16, there must have been gadolinium in the equilibrium organic phase to at least this stage. Evidently the amount of gadolinium in the organic phase from stages 12 to 16 was below the limit of detection (less than 3.0 per cent) by the analytical method employed. As is indicated by Figure 5, this condition did not exist for yttrium. It is also evident from Figures 4 and 5 that on a concentration basis yttrium favored the organic phase in every stage while gadolinium favored the aqueous phase in every stage except in stage one. The sharp decrease in the yttrium and gadolinium concentration at the ends of the extractor could probably have been prevented by refluxing.

The distribution coefficients and separation factor for gadolinium and yttrium as a function of stage number were calculated from the data in Figures 4 and 5 and plotted in Figure 6. Since gadolinium was not detected in the organic phase beyond stage 11, a distribution value could not be calculated past this stage. It is apparent from Figure 6 that only a small deviation resulted for the distribution values and for the gadolinium-yttrium separation factor from stages six to 11, inclusive. Since the concentration data for total oxides, gadolinium oxide and yttrium oxide appearing in Figures 3, 4 and 5 also indicated little change in these stages, it appears that the extractor might be shortened about six stages while obtaining the same results. Figure 6 also indicates that the gadolinium-yttrium separation factor reaches a maximum value of about 3.3 when the gadolinium oxide concentration has a maximum value in the aqueous phase.

This multistage extraction was successful in concentrating an yttrium oxide fraction analyzing 66 per cent to one analyzing 91 per cent and at the same time concentrating the light rare earths of the initial fraction by almost

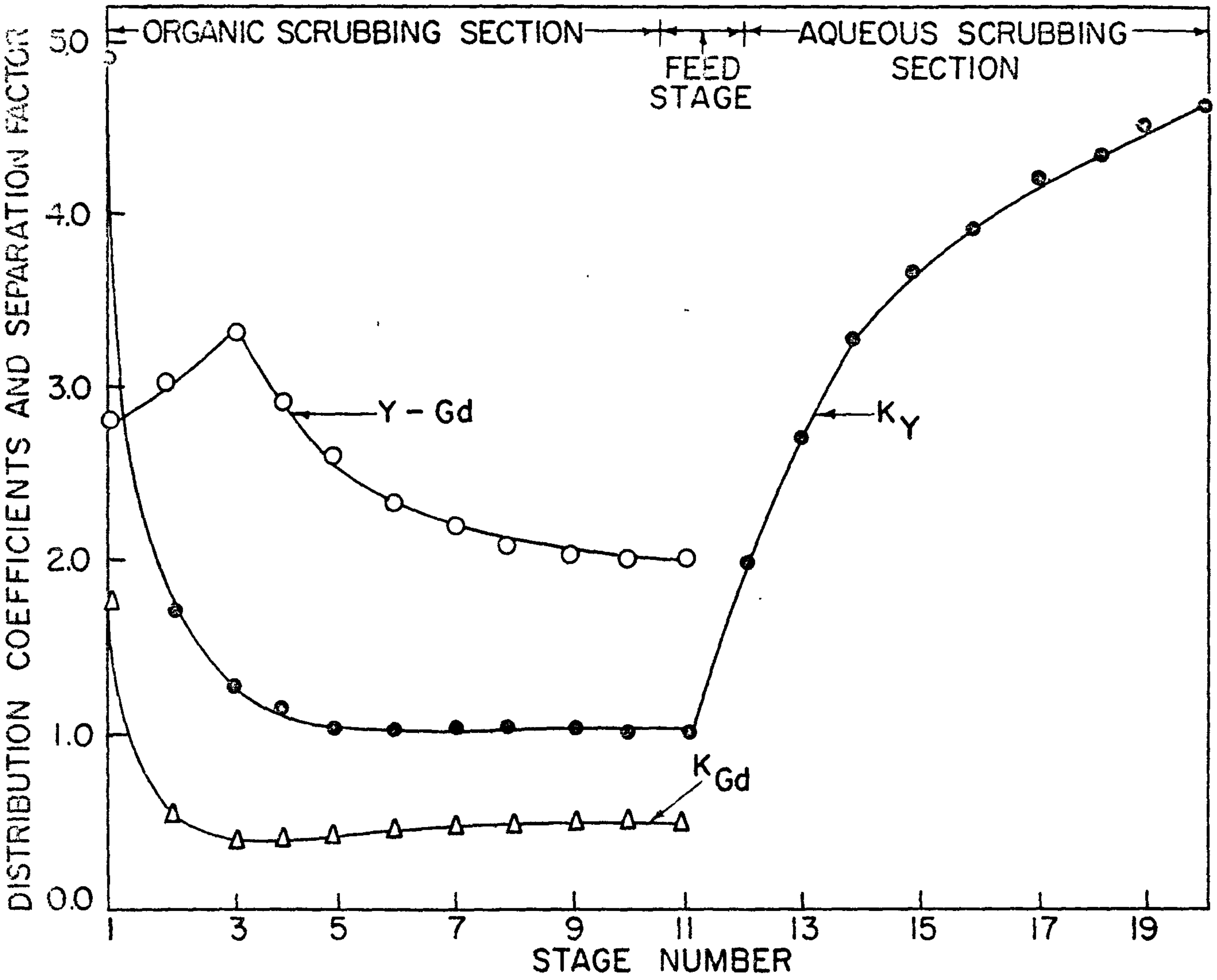

Figure 6 - Yttrium and Gadolinium Distribution Coefficients and their Separation Factor as a Function of Stage Number.

threefold. Since only 60 per cent of the total oxide weight was delivered by the organic product phase, better results would probably be obtained by increasing the organic phase volume by about 20 per cent per cycle. The conditions employed for this multistage extraction were approximately the same as those listed in the first single stage extraction reported in Table 2. However, the yttrium and gadolinium distribution coefficients as well as the over-all mass distribution were different while their separation factor was quite similar. This indicates that the single stage extraction data sometimes serve only as a means of estimating the conditions to be employed and results to be expected in a multistage extraction. Although the maximum separation of yttrium from these light rare earths was not expected in this first multistage extraction, these results indicate that liquid-liquid extraction would certainly be useful for concentrating both the yttrium and the light rare earths from their mixtures.

2. Concentration and separation of yttrium and rare earths obtained from Fergusonite ore

(a) Introduction. The results from extracting the yttrium-rare earth mixtures from the ion-exchange column tailings indicated that light and heavy rare earth fractions should easily be obtained by processing complex lanthanide mixtures. Further separation, assuming proper adjustment of such variables as acidity, concentration and flow rates, should also be possible by application of liquid-liquid extraction. Consequently, the yttrium-rare earth concentrate from Fergusonite ore, which is mined near Kingman, Arizona, was separated into several fractions by this method.

Fergusonite ore, which is slightly radioactive, is an oxide composed essentially of yttrium, rare earths, niobium and tantalum. The yttrium-rare earth oxide mixture constitutes about 25 per cent by weight of the ore while the niobium and tantalum oxides constitute approximately 40 per cent. The rare earth fraction from this ore is relatively high in gadolinium. The yttrium-rare earth oxide mixture is composed of about 50 per cent yttrium and contains only small quantities of the heavy rare earths. It is shown here that a preliminary separation of yttrium plus the few heavy rare earths from gadolinium and the other light rare earths could be accomplished by liquid-liquid extraction. The heavy and light lanthanide fractions which could also constitute charges for an ion-exchange column were separated further by other extractions.

(b) Processing of Fergusonite ore. The fusion of an alkali mixture in the presence of Fergusonite ore was used to render this mineral in a soluble form. A suitable charge consisted of 10.0 grams of finely ground ore, 8.0 grams of sodium hydroxide and 4.0 grams of sodium peroxide. Grinding the ore resulted in a smaller amount of unreacted material. This mixture was heated in a stainless steel crucible for about 30 minutes at approximately 650 degrees Centigrade. After allowing the fusion product to cool, a hot 1.0 molar sodium hydroxide leach was employed to remove much of the aluminum, tin and silicon. This basic liquid was filtered and the remaining solid mass leached with boiling 3.0 molar nitric acid for about ten minutes. When this acidic liquid was filtered, oxalic acid was added to the filtrate to precipitate the yttrium and rare earths as oxalates. The liquid obtained from filtering these yttrium and rare earth oxalates contained iron, aluminum, titanium, manganese, magnesium and calcium and a radioactive material. This radioactive substance is believed to be uranium. The material, which did not dissolve in either the sodium hydroxide or the nitric acid leaches, was treated with concentrated hydrofluoric acid to dissolve the niobium and tantalum fraction. The unreacted ore remained and was recovered as a residue since it is relatively inert to these three leaches. Table 3 gives the relative weights as oxides in each fraction from the leaching treatments while Table 4 shows the quantitative and Table 5 the qualitative analysis of the yttrium-rare earth concentrate. The total minor impurities probably do not constitute more than three per cent of the entire weight.

(c) Single stage extractions of the yttrium-rare earth concentrate from Fergusonite ore. The multistage extractions of the yttrium-rare earth mixture obtained from the ion-exchange column tailings showed that a concentrated nitric acid medium tended to concentrate the light rare earths and yttrium fractions in different phases. This was accomplished in a system having a gadolinium-yttrium separation factor of about three. Because of the excessive cost and corrosiveness of concentrated nitric acid, single

Table 3

Weights of Various Fractions from a Caustic Fusion Treatment of 10.0 Grams of Fergusonite Ore

	Operation	Oxide Weight
1.	Soluble in NaOH leach	0.89 g.
2.	Soluble in HNO_3 leach	
	(a) Oxalic acid precipitation	2.51 g.
	(b) NH_4OH precipitation of filtrate from (2a)	2.05 g.
3.	Soluble in HF leach	3.99 g.
4.	Insoluble (unreacted ore)	0.53 g.
	Total	9.97 g.

Table 4

Partial Analysis of the Yttrium-Rare Earth Oxide Concentrate from Fergusonite Ore

Component	Analysis (wt. %)
Pr_6O_{11}	2.0%
Nd_2O_3	10.0%
Sm_2O_3	10.0%
Gd_2O_3	11.0%
Dy_2O_3	7.0%
Ho_2O_3	$<$ 1.0%
Er_2O_3	$<$ 2.0%
Yb_2O_3	$<$ 2.0%
Y_2O_3	50.0%

Table 5

Qualitative Analysis for Common Impurities in the Yttrium-Rare Earth Concentrate from Fergusonite Ore

Element	Analysis	Element	Analysis
Ca	W	Nb	W
Cu	W	Si	VW
Cr	W	Sn	VW
Fe	W	Ti	--
Mg	VW	Ta	--
Mn	VW	Zr	W
Na	W		

W - Weak.
VW - Very weak.
-- - Not detected.

stage extractions employing less acidic conditions were carried out and the results compared with those for the highly acid systems. Various mineral acid systems, effects of hexone and tributyl phosphate and additions of ammonium thiocyanate were investigated. The yttrium-rare earth fraction from Fergusonite ore was dissolved in the proper aqueous phase and then extracted with an equal volume of the organic phase in each case. Only the gadolinium-yttrium separation factor was determined as this value was assumed to give a good indication of the trends for the other components in the system.

In Table 6 the equilibrium data appear for single stage extractions employing tributyl phosphate which had been pre-equilibrated with an equal volume of 6.0 molar nitric acid. The initial aqueous feed phase was 6.0 molar in nitric acid and contained the equivalent of 100 grams of total oxides per liter. Various amounts of hydrochloric, acetic or sulfuric acid were added to the aqueous feed phase before the extraction.

From the data in Table 6, it is apparent that the gadolinium-yttrium separation factor for the 6.0 molar nitric acid system was 1.37. This value is less than one half of that obtained from an extraction employing a concentrated nitric acid system and the yttrium-rare earth mixture from the column tailings. These data indicate that a decrease in the nitric acid concentration decreases the separation factor as reported by Peppard and co-workers (44). It is also apparent that for extracting this 6.0 molar nitric acid medium the mass transfer to the organic phase, as well as the yttrium and gadolinium distribution coefficients, were considerably lower than those for extracting the 13.0 molar nitric acid system. However, since these distribution coefficients and separation factors were obtained for slightly different mixtures and at a different total concentration, only a qualitative comparison is possible.

Addition of hydrochloric acid to the initial aqueous phase resulted in a definite increase in the gadolinium-yttrium separation factors while not essentially affecting the mass transfers to the organic phase. This increase in separation factor is probably due somewhat to the increased acidity of the aqueous phase, although the rapid increase up to about 1.0 molar hydrochloric acid indicates that the presence of small amounts of chloride ions may also be significant.

Table 6

Effect of Acid Addition on the Single Stage Extraction Data for Yttrium and Rare Earths from their 6.0 M HNO_3 Solution

(Yttrium-Rare Earth Fraction from Fergusonite Ore)

Init. aq. phase			Equil. anal.				Dist. coef.		Gd-Y sepn. factor
Acid added	Conc. of acid added (m.)	% oxide wt. in org.	% Gd_2O_3 Aq.	% Gd_2O_3 Org.	% Y_2O_3 Aq.	% Y_2O_3 Org.	K_{Gd}	K_Y	
----	0	35.1	13.3	9.9	51	51	0.38	0.52	1.37
HCl	0.50	34.9	15.4	10.5	52	58	0.34	0.55	1.62
HCl	1.0	33.3	13.7	9.4	50	61	0.32	0.57	1.78
HCl	2.0	37.3	13.6	8.8	48	57	0.34	0.64	1.88
HAc	0.50	37.1	13.6	9.7	48	58	0.39	0.67	1.72
HAc	1.0	35.8	13.4	9.1	49	58	0.36	0.61	1.70
HAc	2.0	39.1	13.6	9.3	49	55	0.40	0.66	1.65
HAc	4.0	44.7	13.8	10.0	48	59	0.52	0.74	1.42
H_2SO_4	0.25	33.3	15.3	9.5	50	57	0.29	0.55	1.90
H_2SO_4	0.50	32.0	15.3	9.4	49	58	0.27	0.53	1.97
H_2SO_4	1.0	32.0	16.4	8.0	53	61	0.21	0.50	2.38
H_2SO_4	2.0	22.0	12.8	7.6	49	61	0.15	0.33	2.20

The addition of acetic acid to the initial aqueous phase resulted in some unexplainable effects on this nitric acid system. In general, as the concentration of acetic acid increased, the mass transfer to the organic phase also increased. Addition of a small amount of acetic acid to the initial aqueous phase resulted in a large increase in the gadolinium-yttrium separation factor. On further addition of this organic acid, the value decreased until at 4.0 molar acetic acid the separation factor was nearly equal to that obtained for the pure 6.0 molar nitric acid system. No explanation can be given for these results although it is evident that the presence of excess acetic acid decreases the gadolinium-yttrium separation factor.

When sulfuric acid was added to the 6.0 molar nitric acid system, the mass transfers to the organic phase definitely decreased while the gadolinium-yttrium separation factors generally increased. The holdback effect of sulfuric acid did not become appreciable until a concentration of 2 molar was reached. Although this sulfate-nitrate system yielded a gadolinium-yttrium separation factor as high as 2.4, the decrease in mass transfer indicates that a high relative organic solvent rate would be required in a multistage liquid-liquid extraction of such a system.

Table 7 contains the single stage data from extracting an all chloride system. The yttrium-rare earth fraction from Fergusonite ore was dissolved in varying amounts of hydrochloric acid to give a solution containing the equivalent of 95 grams of oxides per liter. Since very little hydrochloric acid will dissolve in tributyl phosphate, the organic phase employed for these extractions was not pre-equilibrated with acid.

It is apparent from these data that as the concentration of hydrochloric acid increases, the per cent mass transfer to the organic phase also increases, while the gadolinium-yttrium separation factors remain essentially constant. Comparison of the data for the all nitrate and all chloride systems show that approximately six times more material was extracted by the organic phase from the corresponding nitrate system. The gadolinium-yttrium separation factor was also substantially higher for this nitrate system. It is apparent from these data that the nitrate system is much more effective than the chloride system for the separation of yttrium from gadolinium. This generality has been reported by other investigators (43, 40) while employing alcohols, esters, ketones, ethers and hydrocarbons as the organic phase and extracting mixtures of lanthanum and neodymium (40) and neodymium and erbium (43).

A single stage extraction of the 6.0 molar hydrochloric acid solution of yttrium and rare earth chlorides was carried out with pure methyl isobutyl ketone (hexone) constituting the organic phase. Only 1.34 per cent of the material was transferred to the organic phase with a gadolinium-yttrium separation factor of only 1.02. When 3.0 molar ammonium thiocyanate was added to the initial aqueous yttrium-rare earth chloride solution, a similar single stage extraction was carried out. At equilibrium, a mass transfer of 3.04 per cent of the total weight was detected in the organic phase with a gadolinium-yttrium separation factor of only 1.01. These extractions indicate that tributyl phosphate yields greater mass transfer to the organic phase with a higher gadolinium-yttrium separation factor than hexone under similar conditions.

Table 7

Effect of HCl Addition on the Single Stage Extraction Data for the Yttrium-Rare Earth Chlorides Employing Tributyl Phosphate
(Yttrium-Rare Earth Concentrate from Fergusonite Ore)

HCl conc. in aq. phase (m.)	% oxide wt. in org.	Equil. anal.				Dist. coef.		Gd-Y sepn. factor
		% Gd_2O_3		% Y_2O_3				
		Aq.	Org.	Aq.	Org.	K_{Gd}	K_Y	
2	2.60	12.0	*	51	*	----	----	----
4	2.78	12.5	11.5	54	42	.0268	.0224	1.20
6	5.47	13.0	11.5	53	44	.0465	.0433	1.07
8	7.70	12.5	11.3	54	43	.0703	.0620	1.14
10	7.40	13.0	10.5	52	40	.0618	.0590	1.05

*Insufficient sample for analysis.

They also indicate that ammonium thiocyanate, although increasing mass transfer to the organic, does not affect the gadolinium-yttrium separation factor. These generalities were reported by other investigators (43,40) employing alcohols as the organic phase.

(d) Multistage extractions of the yttrium-rare earth fraction from Fergusonite ore. The single stage extractions with tributyl phosphate employing a concentrated nitric acid aqueous solution containing the yttrium-rare earth nitrates gave the most effective separation of yttrium from gadolinium. It is implied here that this system is also effective in separating the heavy rare earth fraction from the light rare earth fraction. Consequently, some of the multistage liquid-liquid extractions of this mixture from Fergusonite ore were carried out under conditions derived from these single stage extractions.

The 20 stage extractor illustrated in Figure 1 was used for all multistage extractions. The initial conditions and results of each extraction appear in Table 8. Stage 1 was used in each extraction for introducing the organic phase and delivering the aqueous product phase. The aqueous scrub phase entered and the organic product phase left the extractor at stage 20. In all multistage extractions except the first one, the aqueous feed was added at stage 11. Stage 5 was used in this first extraction. Tributyl phosphate acidified with nitric acid was the organic phase in each case while a nitric acid solution of the yttrium-rare earth nitrates constituted the aqueous phase. The table gives for each extraction the analysis for yttrium and part of the rare earths, as well as the total equivalent oxide concentrations, the acidities and the flow rates for all the influents. For the product phases, or effluents, the steady state yttrium and partial rare earth analyses, the total equivalent oxide concentrations and the volumes delivered are given. In operating the extractor there is a five to ten volume per cent carry-over of the organic phase by the aqueous product phase. Since this carry-over was not included in the material balance, a quantitative recovery of all material was not indicated by these data.

Table 8

Steady State Analyses for the Multistage Extractions of the Yttrium-Rare Earth Concentrate from Fergusonite Ore by Tributyl Phosphate

Ext. no.		Oxide conc. (g./l.)	HNO_3 cond. (m.)	Flow rate (ml./cycle)	Equil. anal. (wt. %) Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Gd_2O_3	Dy_2O_3	Y_2O_3	% of product rep't.	% of oxide wt.
	Influents											
	Aq. feed	195	13	10.0	2.0	10.0	10.0	11.0	7.0	50	90.0	
	Aq. scrub	0	13	15.0								
1	Org. scrub	0	5.0	30.0								
	Effluents											
	Aq. prod.	35.5	---	24.0	4.3	19.7	17.2	19.0	6.8	21	88.0	44
	Org. prod.	40.7	---	27.0	N.D.	N.D.	N.D.	N.D.	7.2	80	87.2	56
	Influents											
	Aq. feed	205	13	10.0	2.0	10.0	10.0	11.0	7.0	50	90.0	
	Aq. scrub	0	13	15.0								
2	Org. scrub	0	5.0	25.0								
	Effluents											
	Aq. prod.	38.9	---	25.0	4.0	20.7	22.3	21.3	9.0	24	101.3	50
	Org. prod.	39.6	---	24.5	N.D.	N.D.	N.D.	N.D.	6.3	82	88.3	50

--- Not determined.

N.D. Not detected.

Table 8 (Continued)

Ext. no.		Oxide conc. (g./l.)	HNO_3 conc. (m.)	Flow rate (ml./cycle)	Equil. anal. (wt. %) Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Gd_2O_3	Dy_2O_3	Y_2O_3	% of product rep't.	% of oxide wt.
3	**Influents**											
	Aq. feed	100	8.0	10.0	2.0	10.0	10.0	11.0	7.0	50	90.0	
	Aq. scrub	0	8.0	15.0								
	Org. scrub	0	3.9	25.0								
	Effluents											
	Aq. prod.	29.9	---	25.0	2.3*	12.6	12.5*	12.5	8.9	46	94.8	81
	Org. prod.	9.8	---	24.5	N.D.	N.D.	N.D.	N.D.	5.3	71	76.3	19
4	**Influents**											
	Aq. feed	105	6.0	10.0	2.0	10.0	10.0	11.0	7.0	50	90.0	
	Aq. scrub	0	6.0	15.0								
	Org. scrub	0	3.0	20.0								
	Effluents											
	Aq. prod.	38.4	---	23.8	2.0*	9.3	9.1	12.6	7.5	53	93.5	94
	Org. prod.	3.2	---	17.0	N.D.	N.D.	N.D.	N.D.	N.D.	35	35.0	5.6
5	**Influents**											
	Aq. feed	100	2.0	10.0	N.D.	N.D.	N.D.	N.D.	7.2	80	87.2	
	Aq. scrub	0	2.0	15.0								
	Org. scrub	0	0.8	20.0								
	Effluents											
	Aq. prod.	37.5	---	24.8	N.D.	N.D.	N.D.	N.D.	7.2	83	90.2	98
	Org. prod.	1.3	---	18.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0	2.4

---

*Calculated value.

Table 8 (Continued)

Ext. no.		Oxide conc. (g./l.)	HNO_3 conc. (m.)	Flow rate (ml./cycle)	Equil. anal. (wt. %)						% of product rep't.	% of oxide wt.
					Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Gd_2O_3	Dy_2O_3	Y_2O_3		
6	**Influents**											
	Aq. feed	112	6.0	10.0	N.D.	N.D.	N.D.	N.D.	7.2	83	90.2	
	Aq. scrub	0	6.0	15.0								
	Org. scrub	0	3.0	20.0								
	Effluents											
	Aq. prod.	38.6	---	23.7	N.D.	N.D.	N.D.	N.D.	6.9	88	94.9	94
	Org. prod.	2.91	---	18.9	N.D.	N.D.	N.D.	N.D.	N.D.	53	53.0	5.7
7	**Influents**											
	Aq. feed	90.0	7.0	10.0	N.D.	N.D.	N.D.	N.D.	6.3	82	88.3	
	Aq. scrub	0	7.0	15.0								
	Org. scrub	0	3.2	20.0								
	Effluents											
	Aq. prod.	31.5	---	23.2	N.D.	N.D.	N.D.	N.D.	7.3	85	92.3	91
	Org. prod.	3.96	---	17.8	N.D.	N.D.	N.D.	N.D.	4.0	66	70.0	8.8
8	**Influents**											
	Aq. feed	50.0	15.0	10.0	2.3*	12.6	12.5*	12.5	8.9	46	94.8	
	Aq. scrub	0	15.0	15.0								
	Org. scrub	0	5.0	20.0								
	Effluents											
	Aq. prod.	4.37	---	24.3	10.4	67	1.6	N.D.	N.D.	N.D.	79.0	23
	Org. prod.	21.2	---	17.0	N.D.	1.0	11.8	17.9	9.3	55	95.0	77

Multistage extractions one to four employed the nitric acid solution of the yttrium-rare earth concentrate from Fergusonite ore as the aqueous feed while three of the remaining four multistage extractions used the products from the first four extractions as their feed mixtures. The first two extractions employed a nearly concentrated nitric acid system while for extractions three and four, 8.0 and 6.0 molar nitric acid was used, respectively. For extractions five to eight, nitric acid systems varying from 2 to 15.0 molar were used.

The multistage extraction of the yttrium-rare earth mixture obtained from the ion-exchange column tailings indicated that insufficient mass was transferred to the organic phase when employing a flow ratio of 5 volumes of the aqueous phase to 4 volumes of the organic phase with the feed introduced at stage 11. Since the Fergusonite ore concentrate and the column tailings had somewhat the same composition, similar separation relationships were presumed. Consequently, for the first multistage extraction of the yttrium-rare earth concentrate from Fergusonite ore, the over-all flow ratio selected was five volumes of the aqueous phase to six volumes of the organic phase. Stage five was used as the feed stage in order to obtain a longer aqueous scrubbing section for separation of the last traces of gadolinium from yttrium. This extraction was carried out for 170 cycles.

As is apparent from Table 8, the general trends for multistage extraction one were similar to those observed for the extraction of the ion-exchange column tailings. All the light rare earths favored the aqueous product phase; dysprosium was about equally divided between the two product phases and yttrium heavily favored the organic product phase. The light rare earth percentages in the product aqueous phase were approximately twice those in the original mixture. About 90 per cent of the total yttrium was delivered by the organic phase giving a product which analyzed 80 per cent yttrium oxide. The yttrium, then on a percentage oxide basis, was effectively concentrated from an initial mixture in which it constituted 50 per cent of the total weight. The analysis for holmium indicated that it composed about 1.2 per cent of the product from the organic phase while not being detected in the aqueous phase product. A qualitative analysis of the products showed very strong spectral lines for lanthanum in the aqueous phase while all the erbium (trace amounts) also appeared in the aqueous product phase. Ytterbium favored the organic phase while terbium was about equally distributed between the two product phases. Except for the trace amount of erbium, the heavy rare earths appeared to favor the organic phase while all the light rare earths definitely remained in the aqueous phase.

The results of stagewise analysis and calculations appear in Figures 7 to 10, inclusive. From Figure 7 it is apparent that on an equivalent oxide concentration basis a large salt build-up occurred in stages 3, 4 and 5 of the aqueous phase with stage 4 containing the highest salt concentration. A material build-up, although smaller, occurred for the organic phases in stages 3, 4 and 5. Figure 8 shows that a large gadolinium salt build-up occurred in both phases in stages 2 and 3 while from Figure 9 it is apparent that an yttrium salt concentration build-up occurred in stages 3, 4 and 5. This large increase in concentration of gadolinium in stage 2 was also noted for the multistage extraction of the yttrium-rare earth mixture obtained from the ion-exchange column tailings.

The high salt contents in the equilibrium aqueous phase are probably related to the large volumes of rather concentrated aqueous feed added per cycle of operation. Since reflux was not used, the total salt concentration of the aqueous phase decreased rapidly as it progressed toward stage one, the aqueous product outlet. As the organic scrubbing section was short, rapid changes in concentration, as shown in Figures 7 to 9, resulted in this section of the extractor. The difference in shape for the curves appearing in Figures 3 to 5 and 7 to 9 are perhaps explained by the fact that the organic scrubbing section for the extraction shown in the latter figures contained five less stages.

In the stagewise analyses, gadolinium was not detected in the organic phase past stage 10. Since it was detected in the aqueous phase of stage 19, a certain amount must also have been present in the organic phase. Extrapolation of the gadolinium concentration curve beyond stage 10, as shown in Figure 8, allows estimation of the gadolinium distribution coefficients for this region. The distribution coefficients for gadolinium and yttrium and their separation factor as a function of stage number appear in Figure 10.

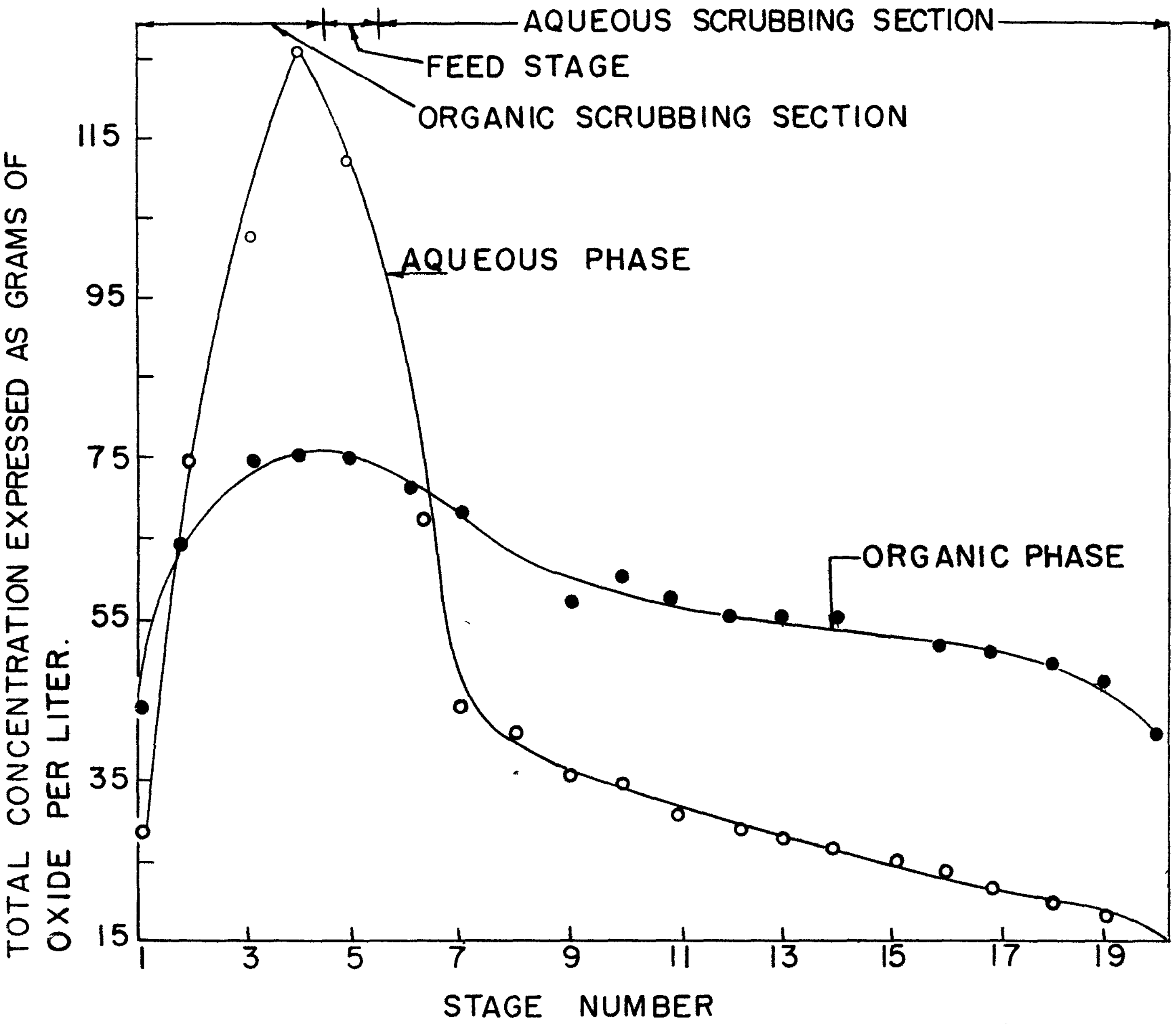

Figure 7 - Yttrium Plus Rare Earth Concentration in the Equilibrium Liquids as a Function of Stage Number.

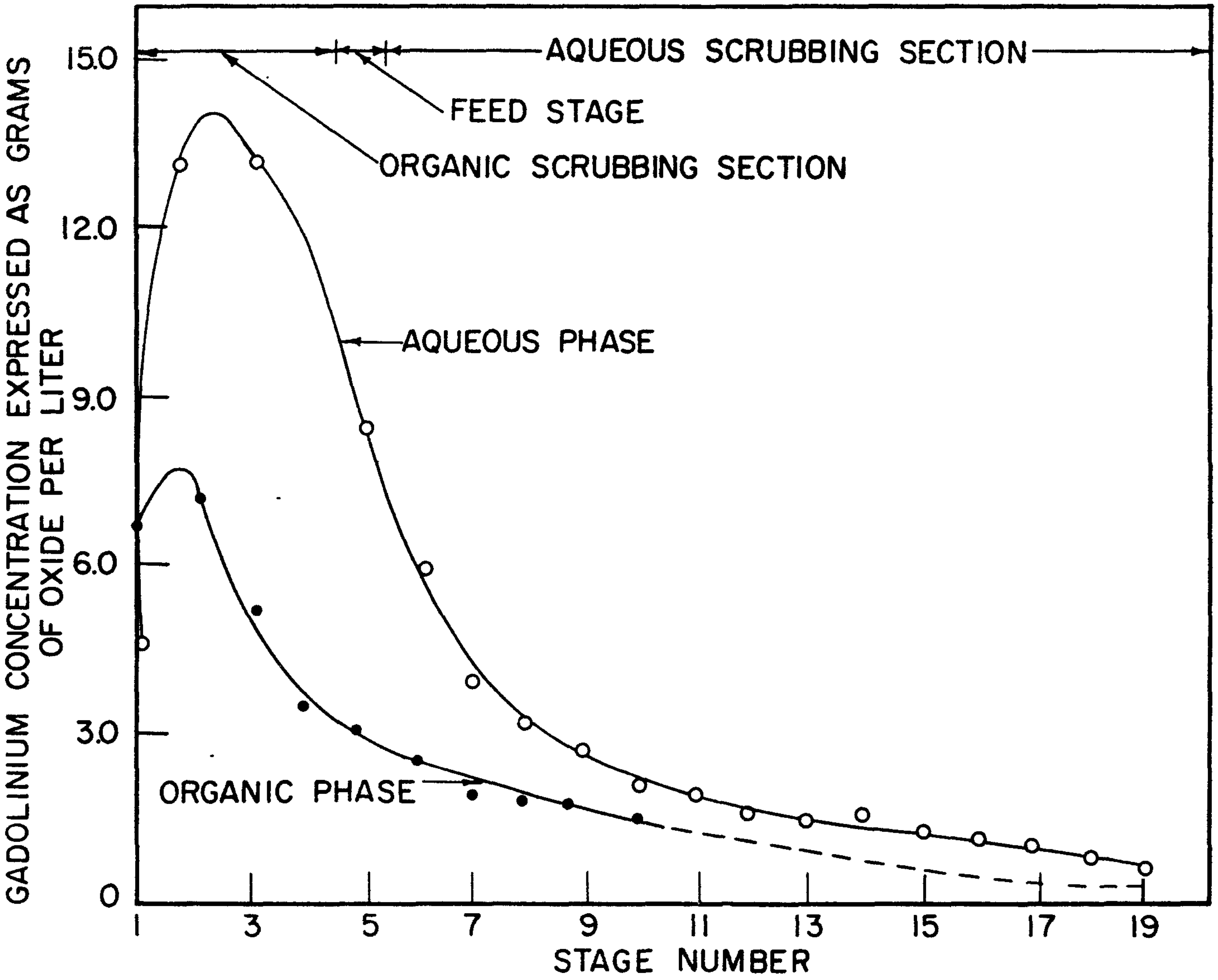

Figure 8 - Gadolinium Oxide Concentration in the Equilibrium Liquids as a Function of Stage Number.

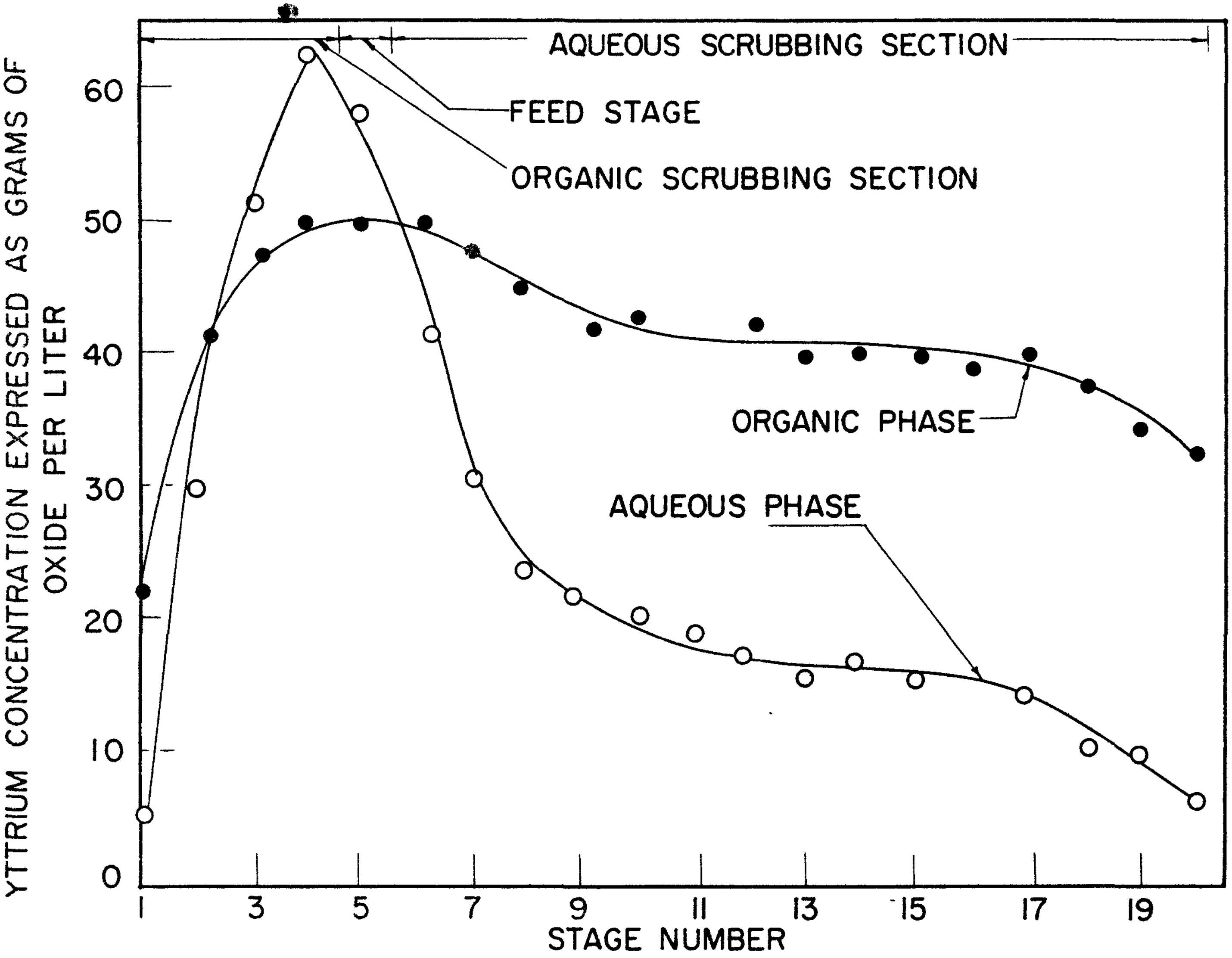

Figure 9 - Yttrium Oxide Concentration in the Equilibrium Liquids as a Function of Stage Number.

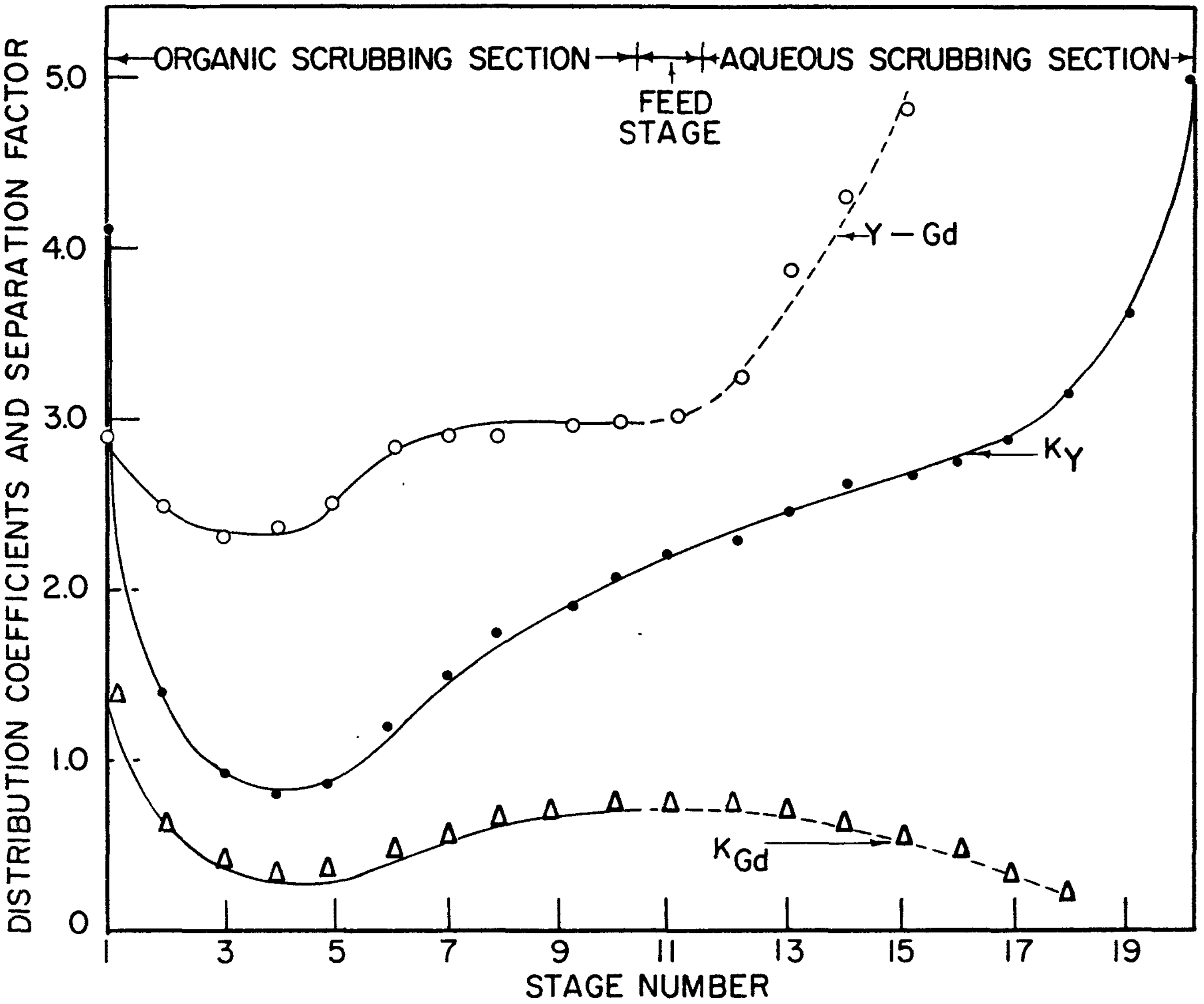

Figure 10 - Distribution Coefficients and Their Separation Factor as a Function of Stage Number.

From this figure it can be noted that the lowest gadolinium-yttrium separation factor which was about 2.4 occurred in the vicinity of the feed stage of the extractor. This relationship was also noted in the multistage extraction of the ion-exchange column tailing mixture. As the salt concentration decreased throughout the extractor, the gadolinium-yttrium separation factors increased. Since the distribution coefficient curves for gadolinium and yttrium diverge rapidly in the extrapolated region beyond stage 12, their separation factors increase considerably in this region.

The material expressed as oxide delivered by the organic product phase of this multistage extraction was about 56 per cent of the initial weight. Based on the analysis of the original mixture this should be about the optimum weight fraction for separating the heavy rare earths plus yttrium from dysprosium and the light rare earths. However, it is apparent from Table 8 that dysprosium, although slightly favoring the organic phase, failed to concentrate appreciably in either product phase. Peppard and co-workers (44) predicted that the separation of yttrium from dysprosium would be more difficult than the separation of yttrium from gadolinium or of dysprosium from gadolinium. In light of these data, this prediction appears to be correct.

In the second multistage extraction of the Fergusonite ore concentrate the feed stage was changed to stage 11 and the organic scrub was decreased to 25 milliliters per cycle. Since the other variables were similar to the first multistage extraction of this Fergusonite ore concentrate, similar results were generally expected. Even though the aqueous scrubbing section consisted of 11 stages instead of five, a smaller transfer to the organic phase was expected because of the decrease in the relative organic flow rate.

The steady state data in Table 8, which were obtained after 115 complete cycles of operation, indicate that this second multistage extraction resulted in delivery of 50 per cent of the total weight as oxide by the organic product phase. The light rare earth fraction concentrated in the aqueous product phase while the fraction delivered by the organic product phase consisted of 82 per cent yttrium oxide. This also represented an 82 per cent recovery of the total yttrium oxide in the organic phase. Dysprosium favored the aqueous phase appreciably, although a good separation of it from yttrium was not obtained. It appears that when extracting a concentrated nitric acid solution of the Fergusonite ore yttrium-rare earth mixture with tributyl phosphate, a complete separation of yttrium from dysprosium cannot be accomplished in 20 stages. However, proper adjustment of flow rates and over-all concentrations would probably improve their separation in the high nitric acid system.

In the third and fourth multistage extractions of the Fergusonite ore concentrate, the nitric acid concentrations of the influent aqueous scrub and feed phases were 8.0 and 6.0 molar, respectively. The flow rate of the organic phase was decreased to 20 milliliters per cycle while the flow rates of the aqueous scrub and feed solutions were the same as employed in the two multistage extractions given just above. Multistage extractions three and four were carried out for 205 and 145 complete cycles of operation, respectively. A separation of yttrium plus the light rare earths from the heavy rare earths was desired in extractions with these lower nitric acid systems.

The decrease of nitric acid concentration from 8.0 to 6.0 molar resulted in a decrease of mass transfer to the organic phase of from 19.3 per cent to 5.6 per cent. In multistage extraction three, yttrium percentagewise favored the organic phase while dysprosium remained in the aqueous phase. However, in extraction four both yttrium and dysprosium preferred the aqueous phase. All the light rare earths which were detected appeared in the equilibrium aqueous product phase in each extraction. In both extraction three and extraction four about 3.7 per cent of the total oxide processed and which occurred in the organic product was not accounted for by the individual element analyses. This unreported fraction probably constitutes the heavy rare earth components of the lanthanide mixture.

Multistage extractions three and four substantiate qualitatively the predictions of Peppard and co-workers (44) that variations in the nitric acid concentration would change the position of dividing the yttrium-rare earth mixture into two fractions. A direct comparison of the nitric acid concentration effects from the first four multistage extractions cannot be made because of varying flow ratios and feed concentrations. However, it appears from these data that the lower nitric acid conditions resulted in an enriched yttrium-light rare earth fraction.

On this basis, a nitric acid concentration of about four to five molar might result in a more complete separation of the heavy rare earth salts from yttrium and the light rare earth fraction in about 20 stages.

Since further separations were desired, the products from the above multistage extractions of the Fergusonite concentrate were employed as the feed mixtures for other extraction studies. The yttrium-rare earth mixture in the organic phase products from multistage extraction one and two were used for multistage extractions five and seven, respectively. Extraction six used the yttrium-rare earth mixture in the aqueous phase product from multistage extraction five, while extraction eight employed the yttrium-rare earth mixture in the aqueous phase product from extraction three.

Further separation of the organic phase products required essentially the separation of the heavy rare earths from yttrium. Consequently, a series of single stage extractions at varying nitric acid concentrations was carried out to determine favorable conditions. The yttrium-heavy rare earth mixture in the organic product phase of multiple extraction one was employed in preparing the initial aqueous feed. In each single stage extraction, equal volumes of the aqueous feed and acidified tributyl phosphate were used. The initial aqueous phase contained the equivalent of 96 grams of the oxides per liter. Figure 11 shows the dependence of the yttrium distribution coefficient and the ratio of total oxide weight in the two equilibrium phases on the nitric acid concentration in the aqueous feed.

It is apparent from Figure 11 that the mass transfer to the organic phase was a minimum between 3.0 and 4.0 molar nitric acid. The yttrium distribution factor decreases with decreasing nitric acid concentration, although its variation becomes less pronounced for the low acid systems. The divergence of the two curves below three molar nitric acid indicates that a reverse in the trend for phase preference must have occurred for some of the components of the mixture. Inversion in extractability of rare earth nitrates at low nitric acid concentrations was observed by Peppard and co-workers (44).

Multistage extractions five, six and seven were carried out to observe the effects of lower nitric acid media on the separation of yttrium from the heavy rare

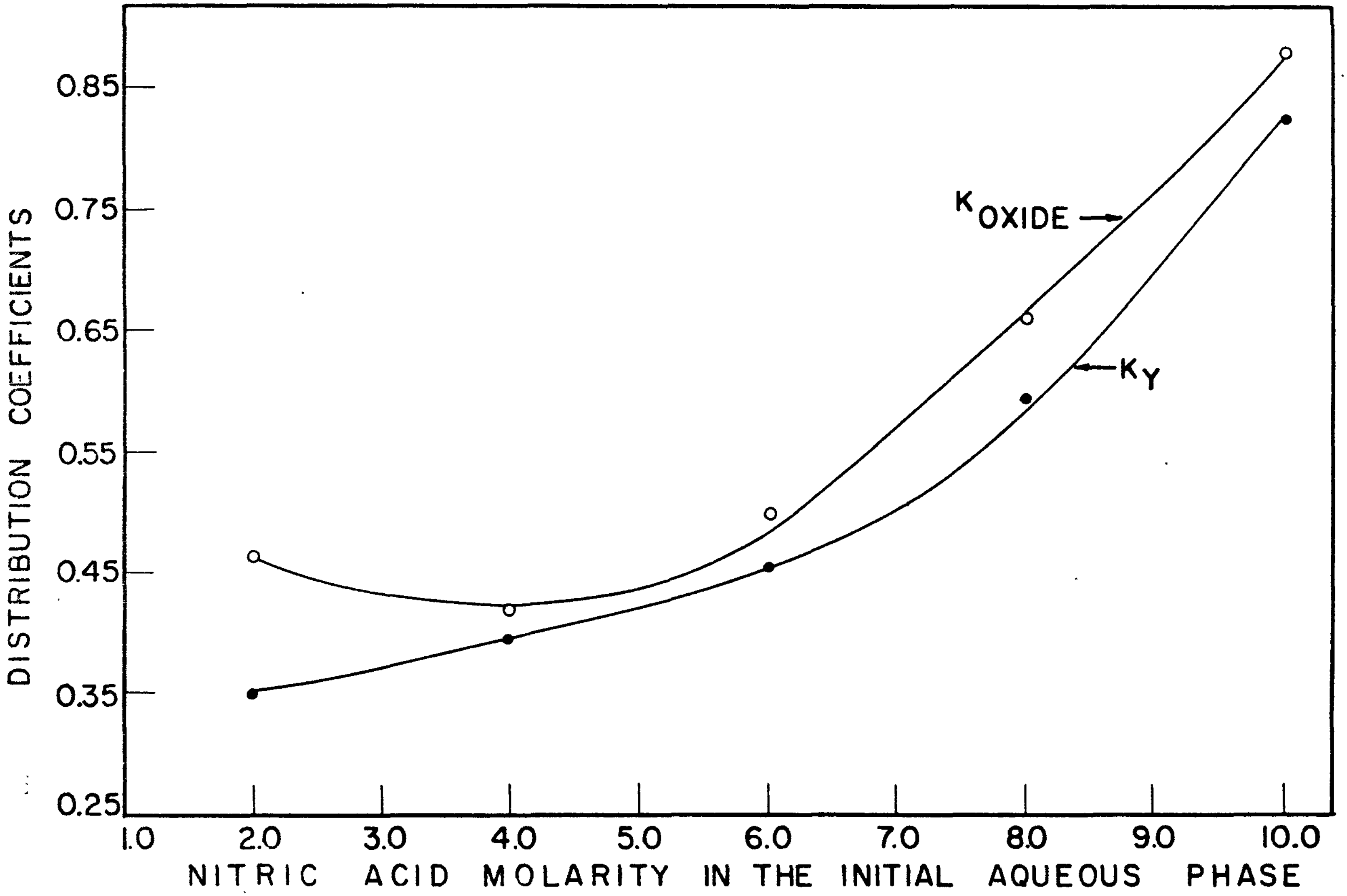

Figure 11 - Yttrium and Total Oxide Distribution Coefficients at Various Nitric Acid Concentrations.

earths. Multistage extraction five, which consisted of 90 cycles, employed a feed solution which was 2.0 molar in nitric acid and contained a mixture which consisted primarily of yttrium and heavy lanthanides. As the data in Table 8 indicate, only 2.4 per cent of the total material as oxide, which contained no yttrium or dysprosium, was transferred to the organic phase. A qualitative spectrographic analysis of this organic phase product showed it was strong in cerium and contained no heavy rare earths. The resulting aqueous phase product, which was initially 80 per cent yttrium oxide, was concentrated to 83 per cent yttrium oxide. The data indicated that an inversion of the light and heavy rare earth fractions had resulted when extracting the 2.0 molar nitric acid solution of these nitrates.

Since the transfer of the heavy rare earth fraction to the organic phase was desired for separating them from yttrium, multistage extraction six employed a 6.0 molar nitric acid aqueous feed. The aqueous feed solution contained the yttrium-rare earth fraction obtained from the aqueous phase product of multistage extraction five (see Table 8). After 47 complete cycles, 5.7 per cent, of the material as oxide had been delivered by the organic product phase. The product from this phase was about half yttrium oxide and contained no light rare earths. Spectrophotometric analyses indicated this product was concentrated in the heavy rare earth components. The aqueous phase product which analyzed 88 per cent yttrium oxide contained about 97 per cent of the total yttrium. Since only 47 cycles were used for this extraction, essentially steady state was probably not reached, although the general separation trends should still apply.

Since multistage extraction six showed a favorable concentration of yttrium, similar conditions were used in multistage extraction seven. However, in this multistage extraction the influent aqueous solutions were 7.0 molar in nitric acid. The extraction was carried out for 165 complete cycles. As was expected, the mass transfer to the organic product phase increased, reaching a value of 8.7 per cent expressed as oxide of the total material processed. The yttrium oxide percentage, which initially was 82 per cent, was increased to 85 per cent in the aqueous phase product. This percentage change was small because the organic phase product contained substantial amounts of yttrium. Spectrophotometric analyses indicated that the heavy lanthanide components considerably favored the organic product phase, although some were also detected in the aqueous phase product. It appears from these multistage extractions that the heavy rare earth fraction cannot be separated from yttrium as easily as yttrium can be separated from the light rare earth fraction. However, these data show that with a larger number of stages the separation of yttrium from the heavy rare earth fraction should be possible.

In multistage extraction eight an attempt was made to separate the light rare earths obtained from the aqueous phase product of multistage extraction three. A concentrated (15 molar) nitric acid medium and a fairly dilute yttrium-rare earth concentration was employed in this 140 cycle extraction. From the data in Table 8, it is apparent that the mixture was divided between neodymium and samarium with most of the samarium and essentially all of the gadolinium, dysprosium and yttrium delivered by the organic product phase. If a 13 molar nitric acid aqueous feed had been employed, the mixture would probably have been separated between gadolinium and dysprosium. This again substantiates the predictions of Peppard and co-workers.

These eight 20 stage countercurrent extractions of yttrium-rare earth concentrates obtained from Fergusonite ore indicated that a series of such extractions should result in a number of highly enriched fractions. These fractions could be further purified by either additional extractions or by employing them as a feed for ion-exchange resin columns. Flow ratios, salt concentrations, acidities, numbers of stages and variation in yttrium-rare earth composition appear to be the important variables connected with the aqueous phase which must be controlled in order to obtain any particular separation. The data presented here indicate quite conclusively the potentiality of solvent extraction for separating the yttrium and rare earth fraction from Fergusonite ore. However, a great deal of work still remains to be done before a specific plan for the complete separation of such a mixture can be drawn.

3. Concentration and separation of yttrium and rare earths obtained from Gadolinite ore

(a) Introduction. The data for extracting the Fergusonite ore yttrium-rare earth mixture indicated that a series of extractions yielded a number of enriched fractions. Gadolinite ore is one of the sources of rare earth mixtures employed in this Laboratory for charging the ion-exchange columns. Various enriched fractions prepared by liquid-liquid extraction of the yttrium-rare earth concentrate from Gadolinite ore should be useful for increasing the production capacity for certain pure rare earth salts by the resin columns. Because of the similarities in the yttrium and rare earth compositions of the concentrates from Gadolinite ore and from Fergusonite ore, it can be assumed that the solvent extraction data should apply about equally to both concentrates.

Gadolinite ore, which is mined in the Scandanavian countries, is essentially a silicate of iron, beryllium, yttrium and rare earths. Usually between 40 and 50 per cent of the total weight composes the yttrium-rare earth fraction. The chief advantage of this ore as a source of rare earth salts is its relatively high content of the heavy rare earth fraction. Analyses have indicated that about 15 to 20 per cent of the yttrium-rare earth mixture is composed of lanthanides having an atomic number of 66 or higher. The yttrium-rare earth fraction can be recovered from the ore either by several leaches with concentrated nitric acid or by carrying out a caustic treatment of the ore with a subsequent acid leach. Generally, the caustic treatment appears to recover from the ore slightly more yttrium plus rare earth salts.

(b) Processing of Gadolinite ore. The fusion of an alkali mixture in the presence of Gadolinite ore was used to render its yttrium-rare earth fraction in an easily soluble form. A suitable charge consisted of 10.0 grams of Gadolinite ore, 8.0 grams of sodium hydroxide and 4.0 grams of sodium peroxide. The mixture was heated in a stainless steel crucible at 650°C for 30 minutes. When the melt cooled, it was transferred to a beaker and washed with water to dissolve sodium, beryllium, silicon, aluminum and tin. The residue was then treated with concentrated nitric acid. After boiling for about ten minutes, the resulting mother liquor was filtered. Oxalic acid was added to the filtrate to precipitate the rare earth oxalates. After the rare earth oxalate slurry was filtered, ammonium hydroxide was added to this filtrate to precipitate iron, titanium, manganese, and other soluble oxalates. A qualitative spectrographic analysis of the yttrium-rare earth fraction indicated weak amounts of iron and manganese, a very weak amount of calcium and trace amounts of chromium, magnesium and silicon. The material, insoluble in the concentrated nitric acid leach, was mainly silicic acid with a little unreacted ore. It usually contained a few per cent yttrium. Table 9 gives the approximate weights of the various fractions after they were converted to oxides by calcining for at least two hours at 800 degrees Centigrade. Table 10 shows an average analysis of the yttrium-rare earth concentrate from Gadolinite ore.

Table 9

Weights of the Various Fractions from Processing 10.0 Grams of Gadolinite Ore

Operation	Weight
1. Soluble in HNO_3 leach	
a. Oxalic acid precipitation	4.55 g.
b. NH_4OH precipitation of filtrate from 1(a)	2.00 g.
2. Acid insoluble fraction	2.86 g.

(c) <u>Single stage extraction of the yttrium-rare earth concentrate from Gadolinite ore</u>.

(1) <u>Extractions employing tributyl phosphate</u>. The extraction data for the Fergusonite ore concentrate showed that in a concentrated nitric acid system yttrium and the heavy rare earths could be separated from gadolinium and the other light rare earths by liquid-liquid extraction. However, yttrium and dysprosium were not easily separated from each other. At low nitric acid concentrations an inversion was noted for the extractability of a number of the elements. It has been reported by Peppard and co-workers (4) that inorganic salting-out agents such as the nitrates of aluminum, magnesium, calcium and ammonium tended to increase the mass transfer of rare earths to the organic phase. These salting-out agents were extracted by the organic phase in only trace amounts. The fractionations of the rare earths were reported to be little affected by the presence of these salting-out agents.

Table 10

Analyses of the Yttrium-Rare Earth Concentrate from Gadolinite Ore

Component	Analysis (wt. %)
Pr_6O_{11}	2.0
Nd_2O_3	5.0
Sm_2O_3	5.0
Eu_2O_3	4.7
Gd_2O_3	5.2
Dy_2O_3	7.6
Ho_2O_3	1.1
Yb_2O_3	4.6
Lu_2O_3	2.7
Y_2O_3	61.0

In light of these observations a series of single stage extractions employing low nitric acid conditions were carried out on the Gadolinite ore yttrium-rare earth concentrate. Various concentrations of aluminum nitrate, aluminum chloride, magnesium nitrate, magnesium chloride and sodium chloride were added to the initial aqueous phase. Equal volumes of the aqueous and organic phases were used for each extraction while unacidified tributyl phosphate constituted the organic phase. Some of the equilibrium data obtained from these extractions are represented graphically in Figures 12 to 21, inclusive.

The variations of the gadolinium, yttrium and dysprosium distribution coefficients with the nitric acid concentration of the initial aqueous phase appear in Figure 12. No salting-out agent was added to these systems. It is apparent that gadolinium prefers the organic phase to a greater degree than dysprosium up to nitric acid concentration of about 1.0 molar. However, the relative preference of these two elements for the organic phase is reversed at all higher nitric acid concentrations. Gadolinium prefers the organic phase to a greater degree than yttrium below about 4.7 molar nitric acid, although this relative preference is also reversed at higher nitric acid concentrations. Up to at least 6.0 molar nitric acid, dysprosium prefers the organic phase more than yttrium. The data from extraction of the Fergusonite ore concentrate indicated that at higher nitric acid concentrations, yttrium favored the organic phase slightly more than did dysprosium, while gadolinium preferred the aqueous phase to a much greater extent than either dysprosium or yttrium. Evidently, the distribution coefficient curves for yttrium and dysprosium cross at an acid concentration somewhere slightly above 6.0 molar nitric acid.

The data shown in Figure 12 indicate that separation of gadolinium and dysprosium from yttrium could be accomplished most efficiently at a very low nitric acid concentration. This is most effectively indicated in Figure 13 where the various separation factors are plotted as a function of the nitric acid concentration in the initial aqueous phase. The highest yttrium-dysprosium and yttrium-gadolinium separation factors occur in the very low nitric acid media. It was reported above that extracting the more concentrated nitric acid solutions yielded high gadolinium-yttrium and gadolinium-dysprosium separation factors. In the 3.0 to 6.0 molar nitric acid region all three separation factors were between 1.0 to 1.5. This shows why only little separation of these three elements was obtained in this range of acid concentration. The change in sign of the slope in the gadolinium-dysprosium and gadolinium-yttrium separation factor curves in Figure 13 occur where the distribution coefficient curves of Figure 12 cross each other. This reverse in relative phase preference causes a change in slope. These observations are directly related to the arbitrary definition employed here for the separation factor. These data together with other considerations definitely show that yttrium, gadolinium and dysprosium pass through an inversion in relative phase preferences within the range of 1.0 to 8.0 molar nitric acid.

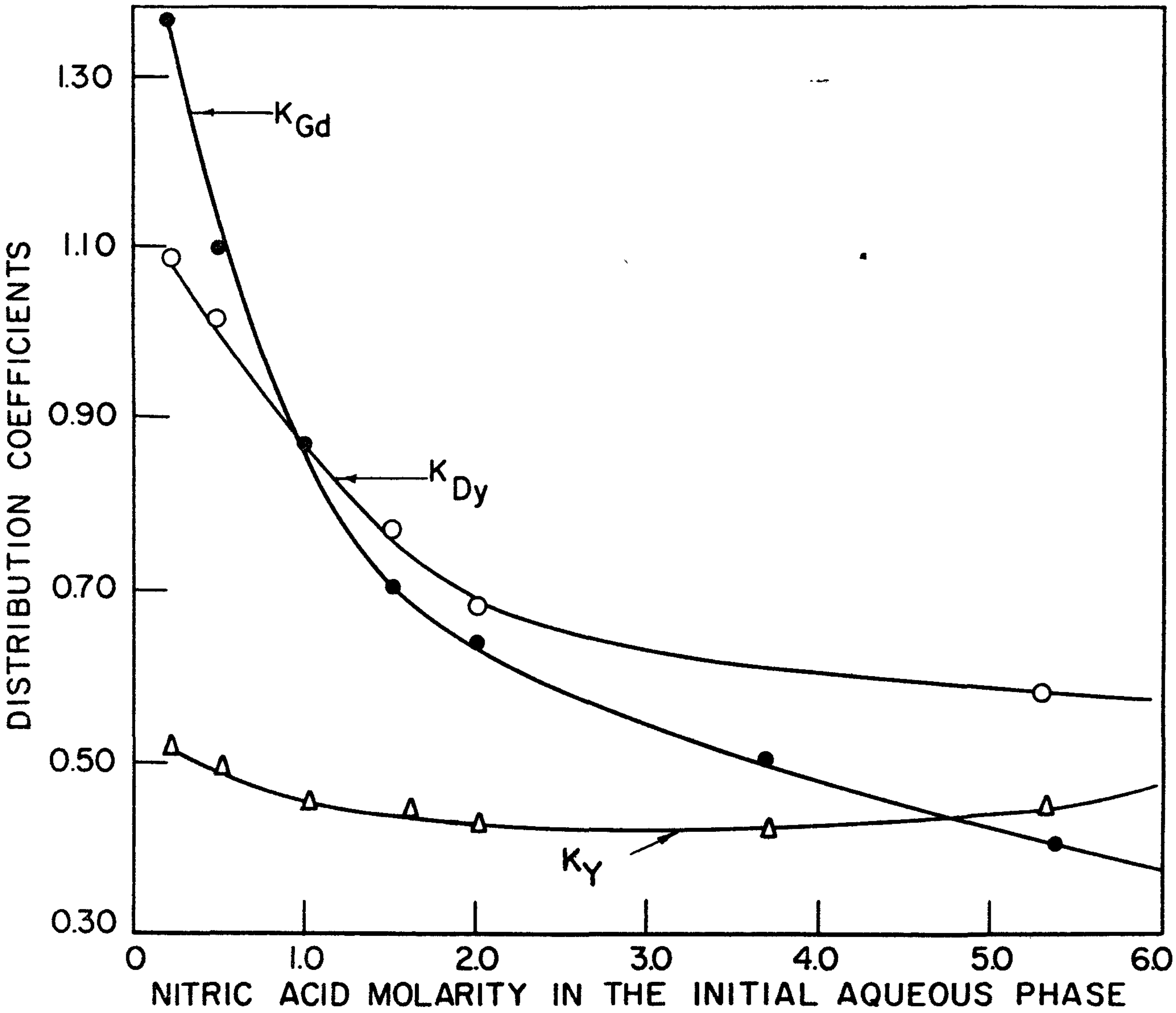

Figure 12 - Distribution Coefficients at Various Nitric Acid Concentrations.

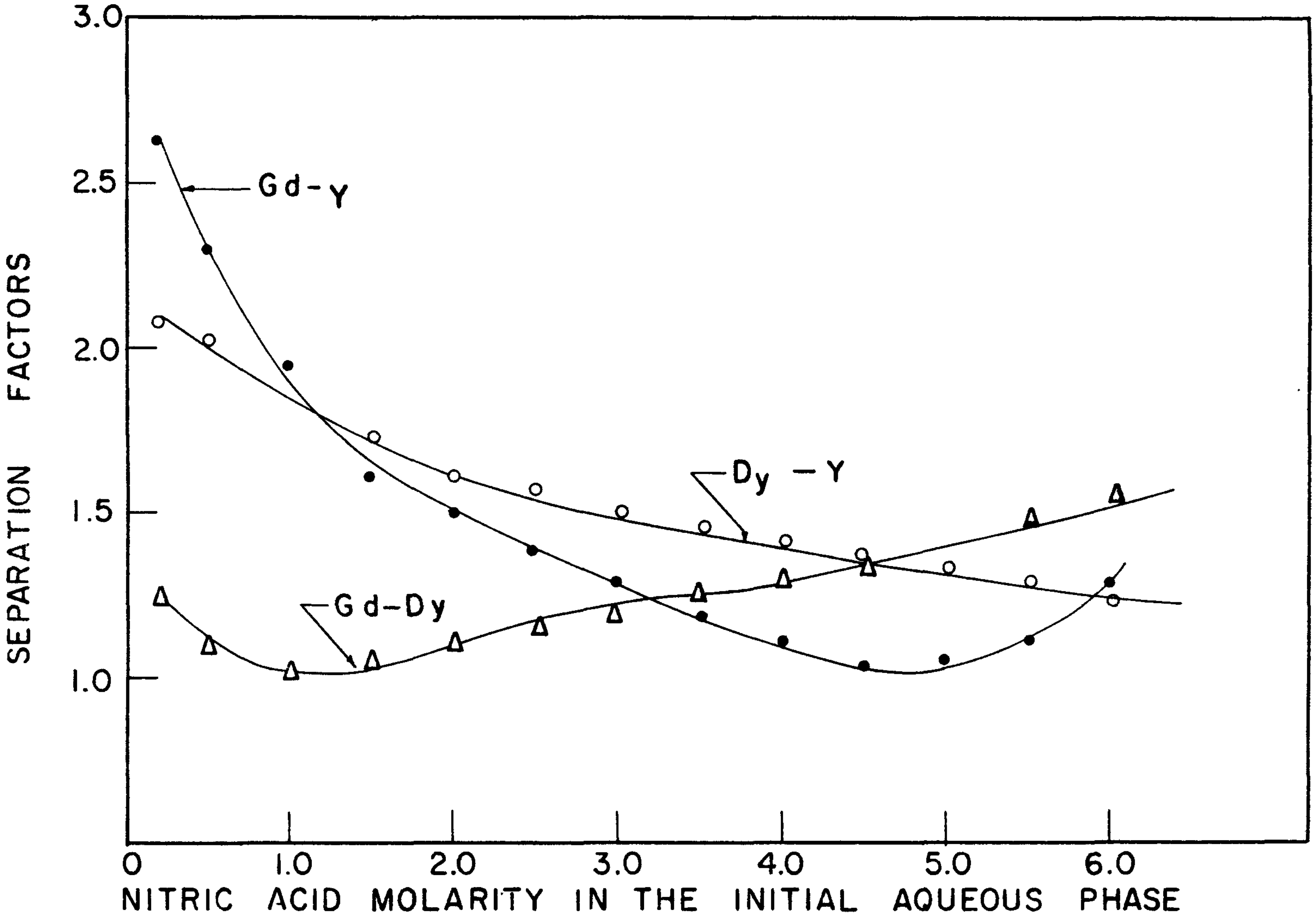

Figure 13 - Separation Factors at Various Nitric Acid Concentrations.

Figure 14 shows the per cent mass transfer as oxide to the organic phase as a function of nitric acid concentration when various 1.0 molar salting-out agents were present in the initial aqueous phase. In general, up to at least 5.3 molar nitric acid, the amount of material transferred to the organic phase decreases with increasing acidity. The single stage extractions of the Fergusonite ore concentrate indicated the opposite trends at higher nitric acid concentrations. The presence of a salting-out agent definitely increased the mass transfer to the organic phase in the range up to 5.3 molar nitric acid. As is indicated by Figure 14, aluminum nitrate increased mass transfer more than a corresponding amount of aluminum chloride while magnesium nitrate was more effective than magnesium chloride. In general, at constant cation concentration, the nitrates appear to effect transfer of the yttrium-rare earth salts to the organic phase more than the corresponding chlorides. The results also indicate that for similar anions and at a constant salting-out agent concentration the higher valence cations are most effective for increasing mass transfer to the organic phase.

Figure 15 shows the relationship between mass transfer in terms of oxide, and the aluminum chloride concentration in the aqueous phase at various nitric acid concentrations. It is apparent that the mass transfer increases as the concentration of this salting-out agent increases. However, the relative effect of the salting-out agent decreases as the nitric acid concentration increases. At very high nitric acid concentrations, the effect of the salting-out agent on mass transfer would probably be negligible. Since, in a highly concentrated nitric acid system the concentration of salting-out agent is negligible relative to the concentration of hydrogen and nitrate ions, the behavior of the system would probably be controlled by these two ions.

The effects of the presence of 1.0 molar aluminum salts on the gadolinium, yttrium and dysprosium distribution coefficients at various nitric acid concentrations are illustrated in Figure 16 and 17. A comparison of these data with those in Figure 12 where no salting-out agent was employed indicates the same general trends. The distribution coefficients were considerably higher for the systems containing the salting-out agents.

From the distribution data appearing in Figure 16 and 17 the separation factors as a function of nitric acid

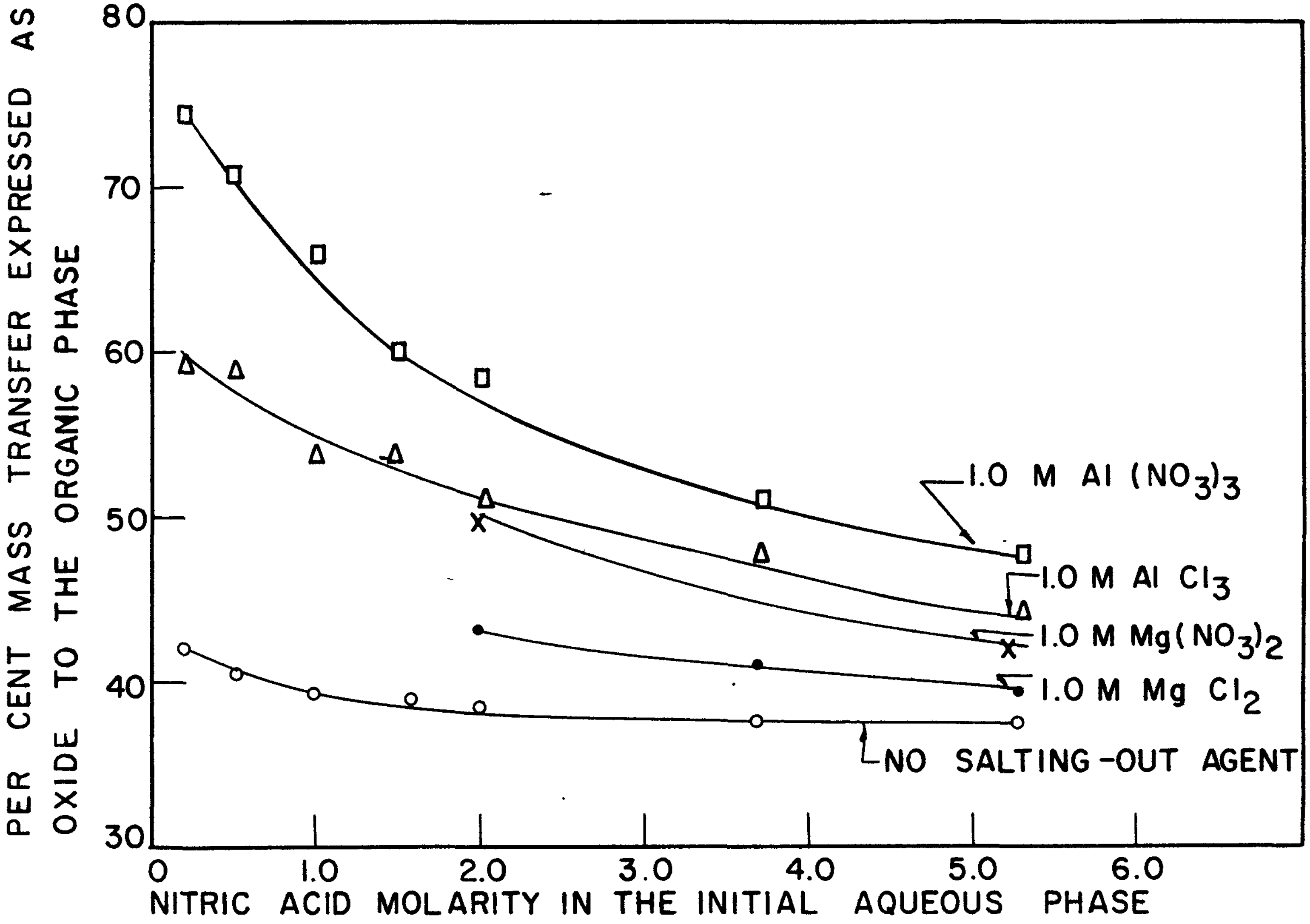

Figure 14 - Mass Distribution as a Function of Salting-Out Agents and Nitric Acid Concentrations.

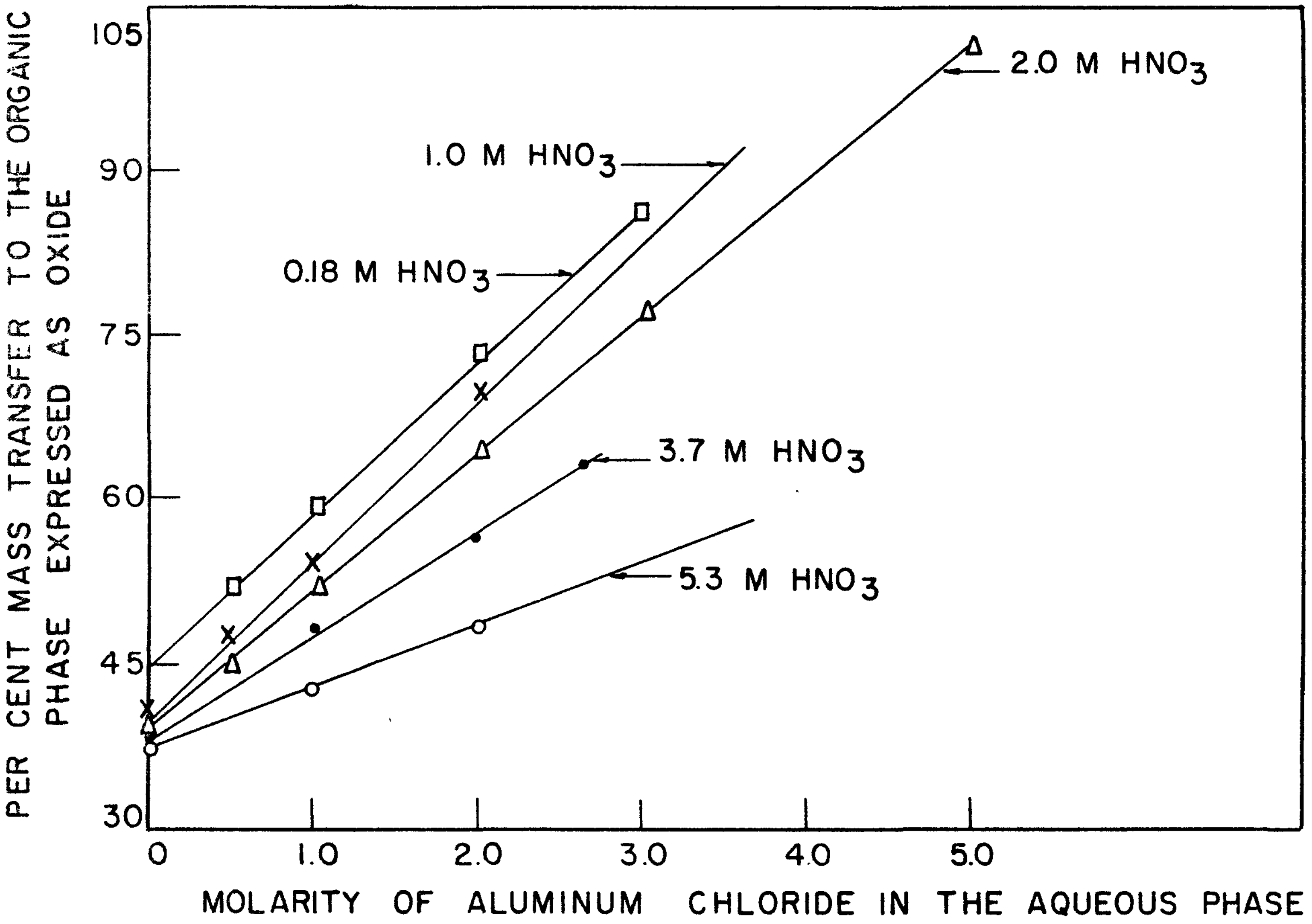

Figure 15 - Mass Distribution at Various Nitric Acid and Aluminum Chloride Concentrations.

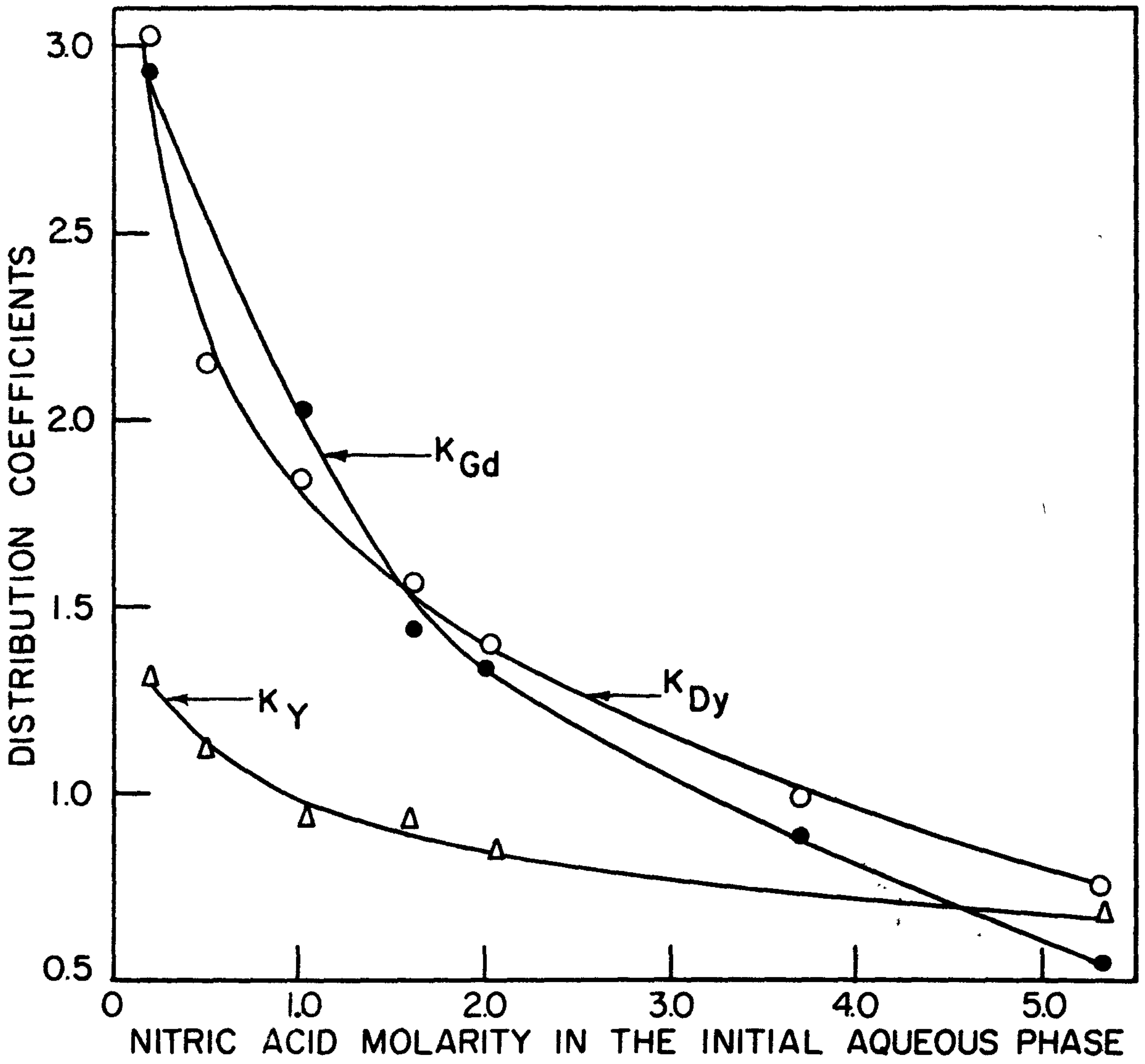

Figure 16 - Distribution Coefficients at Various Nitric Acid Concentrations in the Presence of 1.0 Molar Aluminum Chloride.

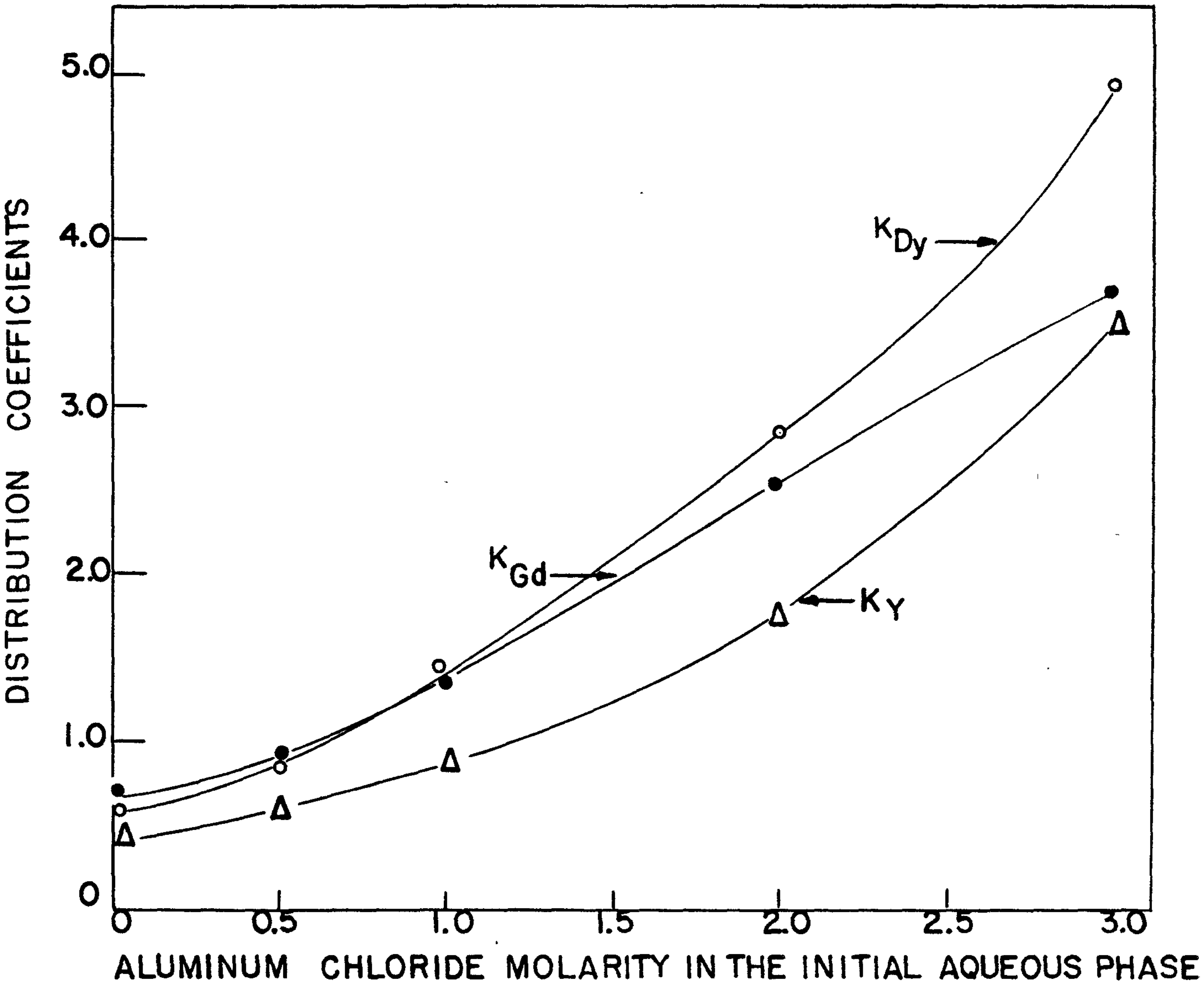

Figure 17 - Distribution Coefficients at Various Nitric Acid Concentrations in the Presence of 1.0 Molar Aluminum Nitrate.

concentration at constant salting-out agent concentration were calculated and then plotted in Figures 18 and 19. A comparison of the extraction data for the aluminum chloride system with the system containing no salting-out agent (see Figure 13) indicates similar relationships, although the presence of this aluminum salt generally decreased the separation factors slightly. The gadolinium-yttrium separation factor in the aluminum nitrate system, as shown in Figure 19, has the same general variation with acidity as indicated for the other two systems discussed above. However, the gadolinium-dysprosium and yttrium-dysprosium separation factors which were obtained in the presence of aluminum nitrate were considerably different. No reason is known for these behaviors. Partial data for the magnesium nitrate system indicates a behavior similar to that of the aluminum nitrate system while the magnesium chloride system appears to give results similar to the aluminum chloride system. However, both the chloride and nitrate salting-out agents maintained high separation factors for dysprosium and gadolinium relative to yttrium in the very low nitric acid concentration range. It is obvious from Figure 19 that a mixture of yttrium, dysprosium and gadolinium could be separated into three enriched fractions by two consecutive multistage extractions employing nitric acid concentrations of about 0.5 molar and about 3.0 molar.

The variations of the gadolinium, dysprosium, and yttrium distribution coefficients with aluminum chloride concentration in a 2.02 molar nitric acid aqueous solution appear in Figure 20. As the data plotted in Figure 15 indicated, these distribution values increased with increasing concentration of the salting-out agent. From the data appearing in Figure 20, the separation factors were calculated and plotted in Figure 21 as a function of the aluminum chloride concentration. The data for the 4.0 molar salting-out agent were employed here to determine the direction of the curves above the 3.0 molar concentrations. It is apparent from Figure 21 that the separation factor trends were similar to those obtained when the nitric acid concentration was varied at a constant concentration of aluminum chloride (see Figure 18). Evidently, the addition of excess salting-out agent has the same effect as increasing the nitric acid concentration. This indicates that the ionic strength of the system might also be an important factor in controlling preferred extractibility of yttrium, dysprosium and gadolinium salts.

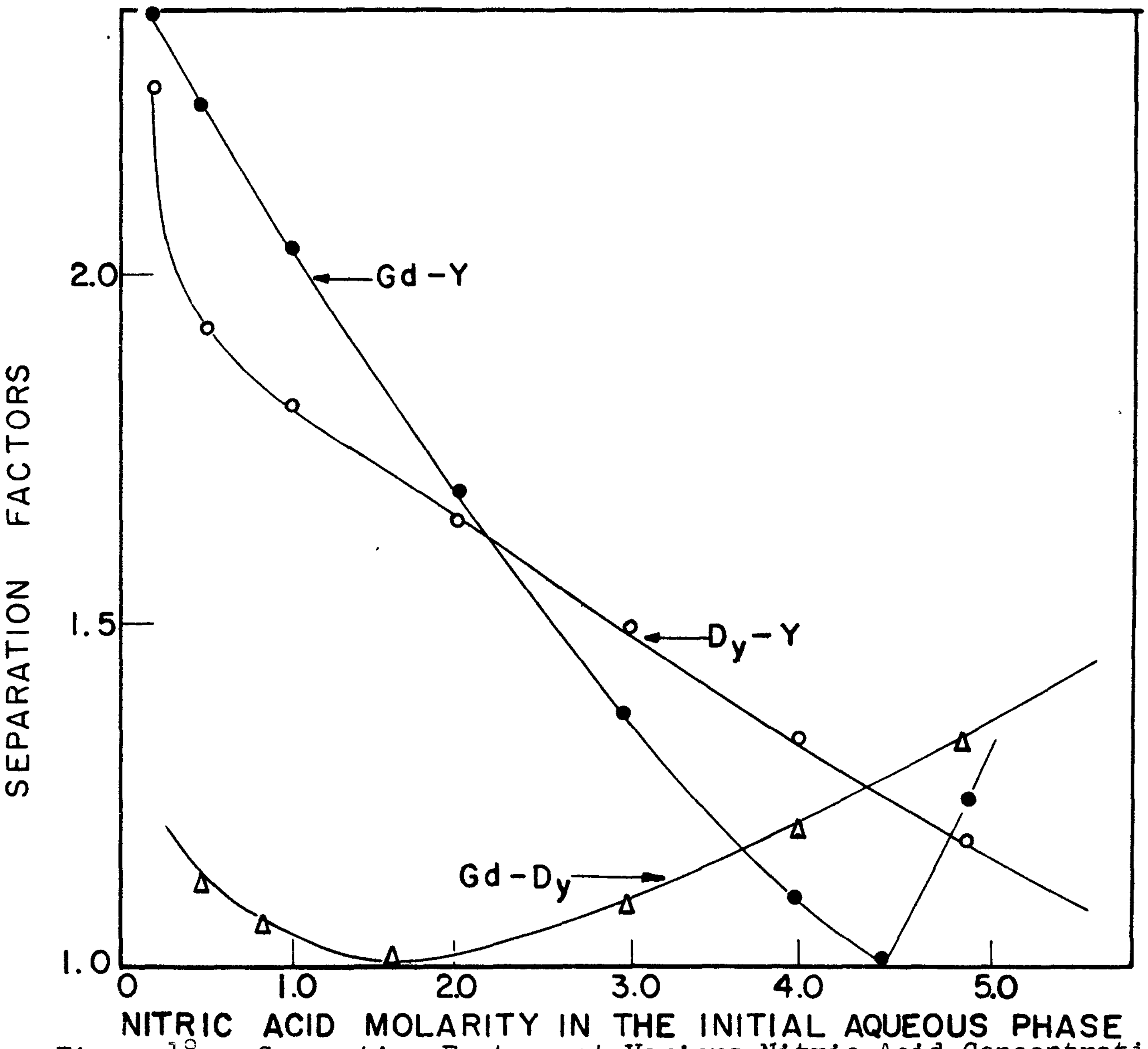

Figure 18 - Separation Factors at Various Nitric Acid Concentrations in the Presence of 1.0 Molar Aluminum Chloride.

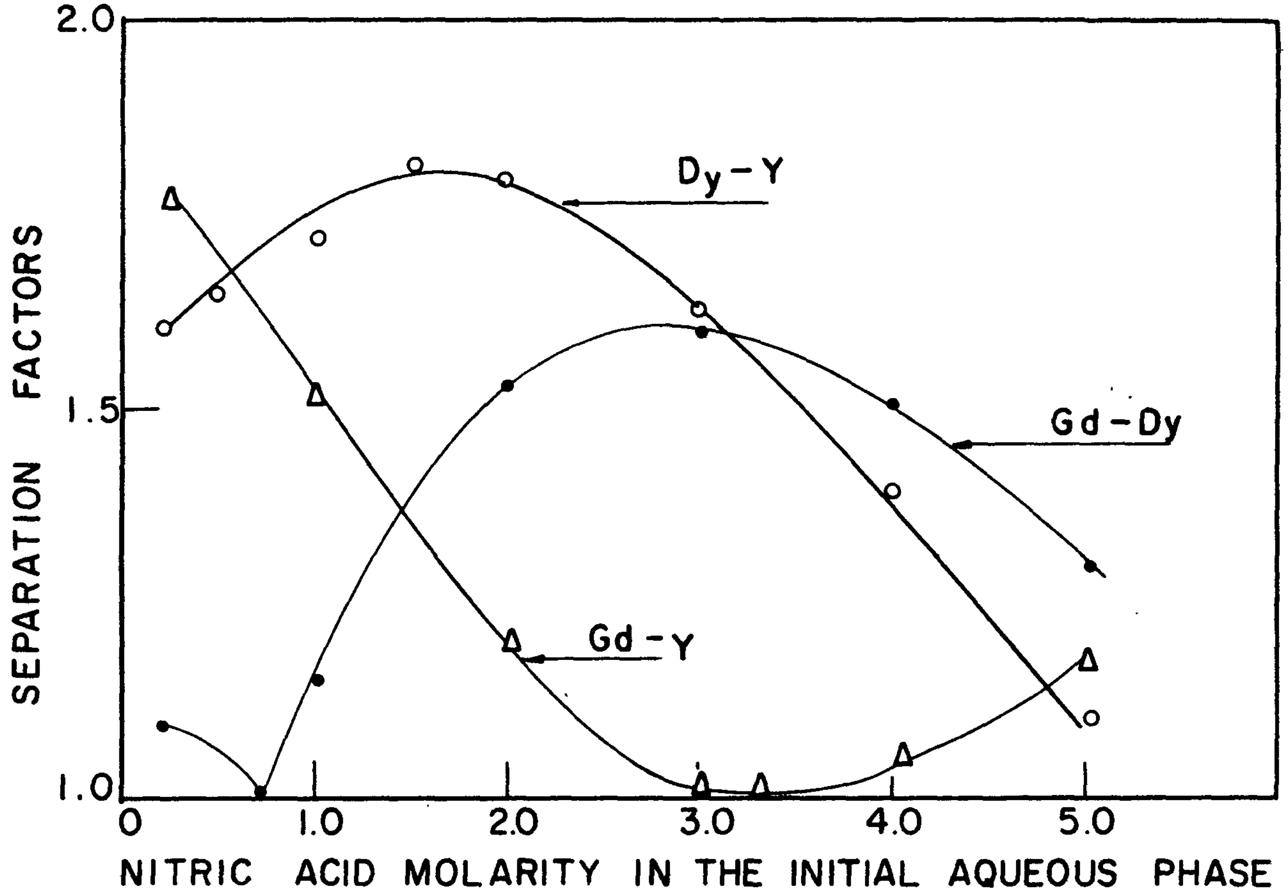

Figure 19 - Separation Factors at Various Nitric Acid Concentrations in the Presence of 1.0 Molar Aluminum Nitrate.

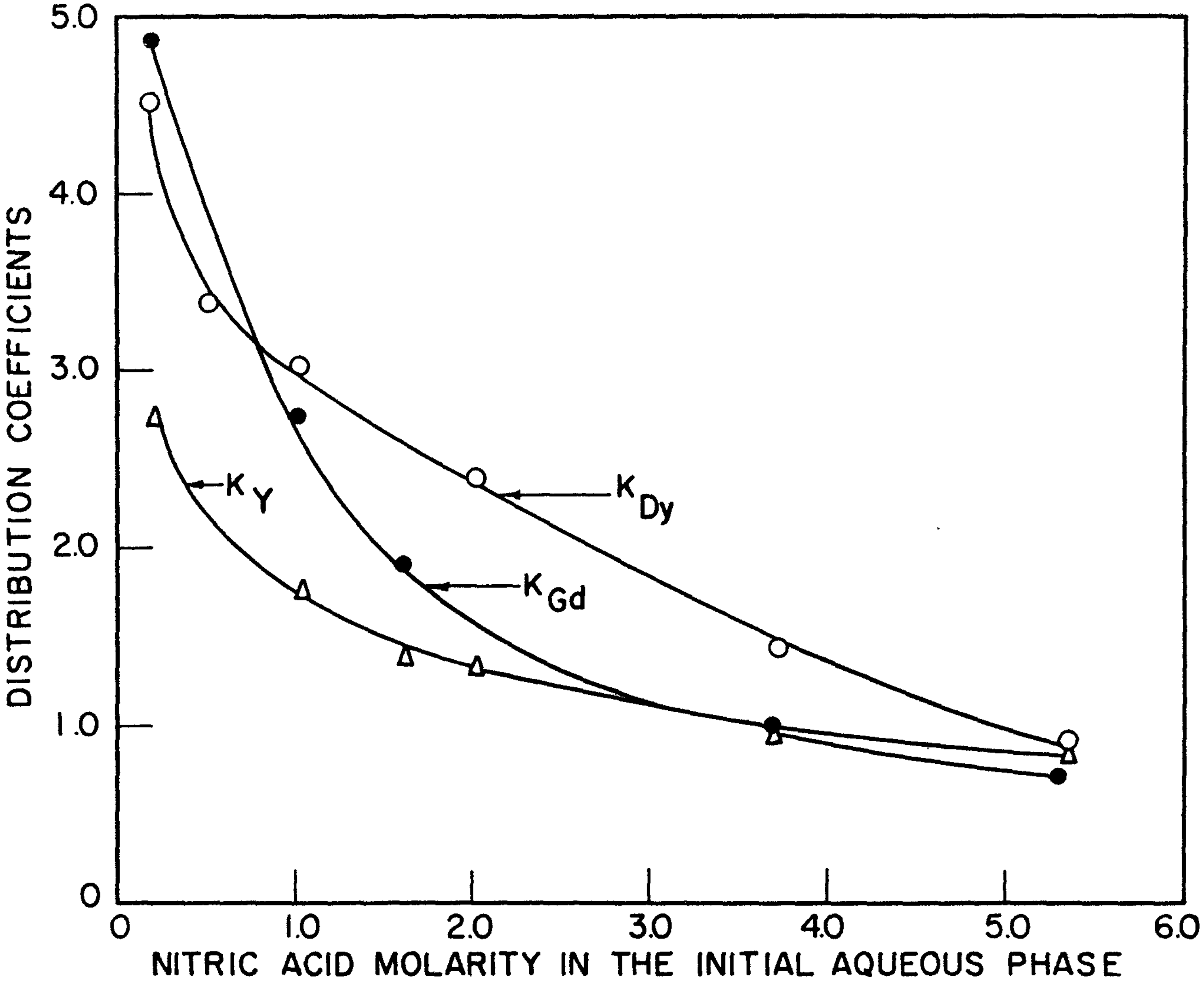

Figure 20 - Distribution Coefficients at Various Aluminum Chloride Concentrations in the Presence of 2.02 Molar Nitric Acid.

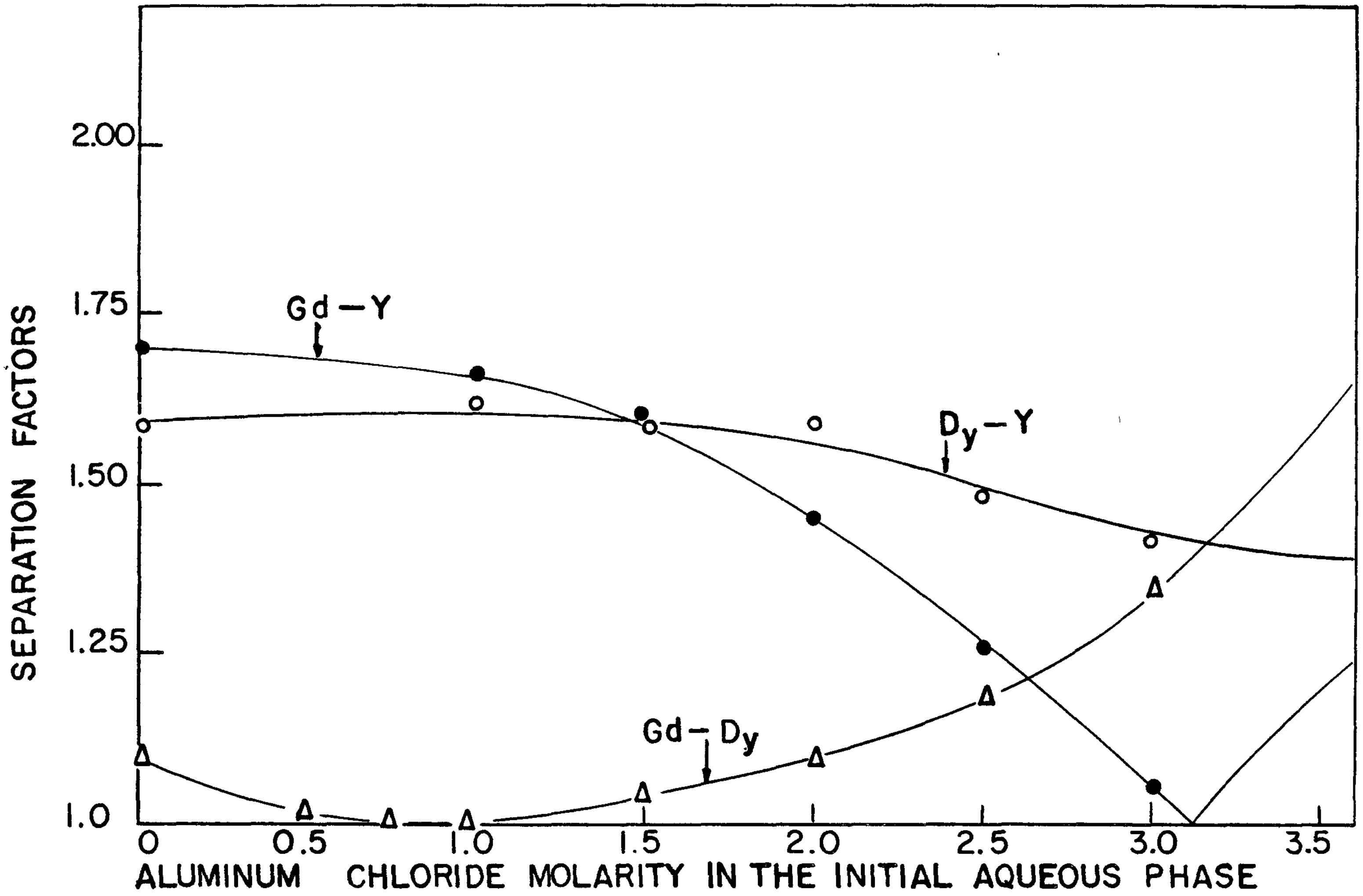

Figure 21 - Separation Factor at Various Aluminum Chloride Concentrations in the Presence of 2.02 Molar Nitric Acid.

In the operation of a multistage extraction process the time required for separation of the equilibrated phases is an important variable from the practical viewpoint. For extracting these yttrium-rare earth nitrate systems the phase separation time decreased as the acidity increased. In the 0.18 molar nitric acid system containing 2.0 molar aluminum chloride the phase separation time was about 20 minutes while for a similar system containing 5.3 molar nitric acid only about one minute was required. As the concentration of the salting-out agent increased, the phase separation time also increased. In the 1.02 molar nitric acid medium, free of any salting-out agent, 50 seconds was needed for phase separation. When 2.0 molar aluminum chloride was added to this 1.02 molar nitric acid system, the separation time was 9.0 minutes. Although factors other than the salting-out agent and nitric acid concentration are important in controlling phase separation times, these variables must be carefully considered in selecting a system for the multistage extractions.

In general, extraction of the very low nitric acid yttrium-rare earth systems with tributyl phosphate gave a separation of gadolinium and dysprosium from yttrium. Although salting-out agents decrease these separation factors slightly, they increase the mass transfer of rare earth salts to the organic phase. Consequently, the required volume of organic solvent is decreased.

(2) Extractions employing various organic phosphates and phosphites. A number of single stage extractions were carried out employing various pure organic phosphates and phosphites as the organic phase. The nitric acid aqueous phase in each case contained the yttrium-rare earth concentrate from Gadolinite ore. The aqueous feed solution contained the equivalent of 280 grams of the combined oxides per liter. Equal volumes of the organic and aqueous phases were employed in each extraction.

Some generalities were evident from the observations made when employing organic phosphites. As their molecular weight increased, less material was extracted by the organic phase with a decrease in the yttrium and gadolinium distribution coefficients. The gadolinium-yttrium separation factor increased almost linearly with per cent mass transfer to the organic phase. The values for di-2-ethylhexyl hydrogen phosphite did not follow these trends because of its low stability in the acid system. Partial hydrolysis of this organic phosphite resulted in the formation of complex phosphites and in subsequent inaccurate oxide weights. Diethyl hydrogen phosphite, because of its rapid hydrolysis, gave a completely miscible system. The distribution coefficient for the yttrium was larger than for the gadolinium in a corresponding system involving a phosphite extraction.

Upon comparison of similar organic phosphites and phosphates as solvents, higher gadolinium-yttrium separation factor and distribution values were obtained in the phosphite systems. More material was extracted by the organic phosphite than by the corresponding organic phosphate. The assumptions were made in this work that the organic phosphite did not oxidize to the corresponding organic phosphate in this nitric acid system. Consequently, these extractions show that the doubly bonded oxygen of the phosphate radical is not an important factor in the yttrium-gadolinium separation. Fewer stages would probably be required for separation of yttrium from gadolinium when extracting with an organic phosphite rather than with the corresponding organic. The low stability of the organic phosphites, however, would probably decrease their utility for a continuous operation.

(d) *Multistage extraction of the yttrium-rare earth concentrate from Gadolinite ore.* Single stage extractions of the yttrium-rare earth nitrate mixture from Gadolinite ore showed that a low nitric acid system permitted separation of gadolinium and dysprosium from yttrium quite efficiently. Consequently, a 20 stage extraction employing this low acid condition was carried out in the countercurrent extractor shown in Figure 1. The aqueous feed solution was 0.12 molar in nitric acid and contained the equivalent of 230 grams of yttrium-rare earth oxides per liter. Five milliliters per cycle of this feed solution were introduced at stage 14. Tributyl phosphate which was 0.05 molar in nitric acid constituted the organic phase. It was added at stage one at a rate of 17.5 milliliters per cycle. Twenty-five milliliters per cycle of 0.12 molar nitric acid solution which was 0.50 molar aluminum chloride were added at stage 20. The nitric acid concentrations in the initial aqueous and organic phases constituted equilibrium values. In the aqueous phase the concentration of aluminum chloride was approximately 0.5 molar throughout the entire column. In addition to increasing the mass transfer to the organic phase, this aluminum chloride gave a nearly constant ionic strength throughout the extractor.

After 100 cycles of operation, no rare earth or yttrium was detected in the organic product phase. However, stagewise analyses of aliquots indicated that the organic phase of stage 19 contained the equivalent of 4.0 grams of oxide per liter. Since a complete separation of gadolinium and dysprosium from yttrium requires that approximately 25 per cent of the total material be transferred to the organic phase, a tap-off device was added at stage 16 to deliver 7.0 milliliters of the organic phase for each cycle of operation. The remaining portion of the organic phase which was delivered at stage 20 was added to the product phase delivered from the tap-off stream. The extraction was then continued for 100 more complete cycles.

Analyses of the product phase from the last 20 cycles indicated that 0.90 of a gram of oxide was delivered by the aqueous product phase while 0.28 of a gram was delivered by the organic product phase per cycle. This represented a 76-24 per cent split of the mixture by weight. Analyses of most of the major constituents of the initial feed mixture and product phases appear in Table 11.

It is apparent from these data that gadolinium and dysprosium preferred the organic phase and were separated from most of the yttrium which remained in the aqueous phase. It can also be noted that on an enrichment basis samarium and holmium to a great degree and neodymium to a lesser degree favored the organic phase. According to the analyses in Table 11, only yttrium on this same basis preferred the aqueous phase. However, a spectrographic qualitative analysis indicated that thulium and ytterbium also favored the aqueous phase.

From a material balance it was calculated that 89 per cent of the yttrium was delivered by the aqueous product phase. Approximately 80 per cent of the dysprosium and greater than 85 per cent of the gadolinium was delivered by the organic product phase. It is apparent, therefore, that about 90 per cent of the yttrium was separated from about 80 to 85 per cent of the gadolinium and dysprosium in a continuous extractor. Further work on the improvement of this system and an increase in the number of stages should improve this separation of gadolinium and dysprosium from yttrium.

Table 11

Analyses of the Oxide Mixtures from the Multistage Extraction of the Yttrium-Rare Earth Concentrate from Gadolinite Ore

	Feed	Aqueous phase product	Organic phase product
Nd_2O_3	5.0%	4.1%	6.6%
Sm_2O_3	5.0%	1.0%	11.0%
Gd_2O_3	5.2%	$<3.0\%$	20.2%
Dy_2O_3	7.6%	2.0%	24.8%
Ho_2O_3	1.1%	1.0%	4.0%
Y_2O_3	61.0%	70.0%	26.4%

Figure 22 shows the total oxide concentration in the organic and aqueous phases as a function of stage number for this multistage extraction. It is apparent from this figure that no appreciable amount of material was detected in either phase past stage 17. Evidently all the rare earths, which were not delivered through the tap-off device in stage 16, were easily back-extracted by the aqueous phase. In almost all stages the rare earth salts preferred the organic phase on a concentration basis. The decrease in yttrium-rare earth concentration at the organic inlet end of the extractor as shown in Figures 3, 4, 6, 8, 9 and 10 was not as pronounced for this system. This was probably caused by the presence of the salting-out agent in the aqueous phase.

The results of this multistage extraction of the yttrium-rare earth concentrate from Gadolinite ore substantiate the single stage extraction data. This multistage extraction showed that dysprosium and gadolinium can be separated from yttrium quite readily on a continuous basis by extracting a low nitric acid feed solution of yttrium plus the rare earths with tributyl phosphate. The

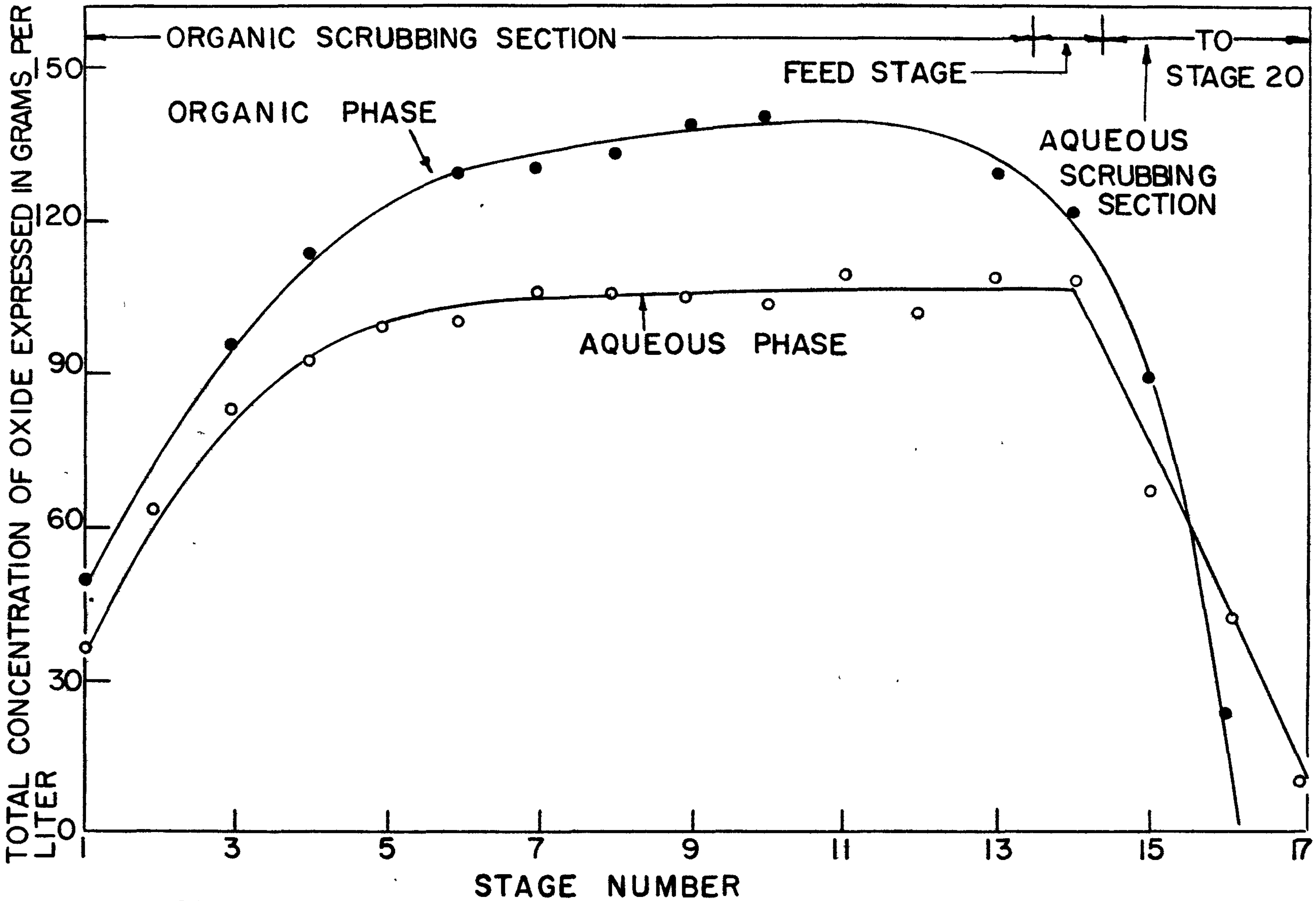

Figure 22 - Yttrium Plus Rare Earth Concentration in the Liquid Phases as a Function of Stage Number.

inversion of certain rare earth extractability as was also observed by Peppard and co-workers (44) was found useful in effecting separations. It is believed that for many separations the extraction of this dilute nitric acid solution of yttrium and rare earths would prove more economical than extractions employing the highly concentrated nitric acid.

CONCLUSIONS

1. Ore processing

a. A Gadolinite ore was leached several times with hot concentrated nitric acid to obtain its yttrium-rare earth content. An ion-exchange resin treatment was employed to remove a certain fraction of the heavy rare earths. The remaining mixture, referred to as tailings, analyzed in terms of oxide about 65 per cent yttrium, about five per cent heavy rare earths and about 30 per cent light rare earths.

b. The yttrium-rare earth fraction of a Fergusonite ore was rendered soluble by treatment of the ore with fused alkali followed by an acid leach. This yttrium-rare earth concentrate in terms of oxides consisted of about 50 per cent yttrium, 10 per cent heavy rare earths and 40 per cent light rare earths.

c. The yttrium-rare earth fraction of a Gadolinite ore was recovered also by an alkali fusion followed by an acid leach. The resulting yttrium-rare earth concentrate in terms of oxide was about 60 per cent yttrium, 15 per cent heavy rare earths and 25 per cent light rare earths.

2. Single stage extractions

a. Tributyl phosphate, in general, preferentially extracts the rare earths from a concentrated nitric acid solution according to their increasing atomic number. For low nitric acid systems some inversions in their relative extractability occurs. The mass transfers from the aqueous phase to the organic phase were a minimum for about a 6.0 molar nitric acid aqueous phase. Yttrium, which has an anomalous behavior since it resembles the low atomic numbered rare earths in a low nitric acid system, is similar to gadolinium in a 4.5 molar nitric acid system, resembles dysprosium in about the 6.0 to 8.0 molar nitric acid medium and acts like holmium in the concentrated nitric acid systems. Consequently, the control of nitric acid concentration permits the separation of yttrium from the rare earth salts.

b. The yttrium-rare earth mixture obtained from the ion-exchange column tailings was dissolved in 13 molar aqueous nitric acid and extracted with various volumes of tributyl phosphate. The mass transfers from the aqueous to the organic phase and the gadolinium-yttrium separation factors increased as the volume ratio of the organic to the aqueous phase increased. A mass transfer of 72.1 per cent in terms of oxides and a gadolinium-yttrium separation factor of about 3.3 were obtained from an extraction employing equal volumes of the organic and aqueous phases.

Extraction of a 6.0 molar nitric acid solution of the yttrium-rare earth concentrate obtained from Fergusonite ore with an equal volume of tributyl phosphate resulted in a mass transfer to the organic phase of 35.1 per cent on an oxide basis and a gadolinium-yttrium separation factor of 1.37.

Addition of hydrochloric acid to this 6.0 molar nitric acid system before extraction resulted in a somewhat higher gadolinium-yttrium separation factor with little change in mass transfer.

The addition of acetic acid to the 6.0 molar nitric acid system increased the mass transfer from the aqueous to the organic phase. Small amounts of acetic acid increased the gadolinium-yttrium separation factor while large amounts decreased it.

Sulfuric acid, when added to this nitric acid medium before extraction, increased the gadolinium-yttrium separation factor while decreasing the mass transfer to the organic phase.

c. Extractions of the Fergusonite ore yttrium-rare earth concentrate dissolved in from 2 to 10 molar hydrochloric acid with equal volumes of tributyl phosphate indicated that an increase in acidity resulted in an increase in mass transfer to the organic phase. However, in no case was more than 7.7 per cent of the total yttrium-rare earth content expressed as oxide extracted by this organic phase. The gadolinium-yttrium separation factor remained approximately 1.1 over the entire hydrochloric acid range. Consequently, the nitric acid system appeared to be superior to the hydrochloric acid system for separating yttrium-rare earth salts by liquid-liquid extraction.

d. The extraction of the Fergusonite ore yttrium-rare earth concentrate dissolved in 6.0 molar hydrochloric acid with an equal volume of hexone gave a mass transfer to the organic phase of only about one per cent and a gadolinium-yttrium separation factor of only 1.02. The addition of 3.0 molar ammonium thiocyanate to this aqueous phase before extraction caused slightly more extraction but no change in the gadolinium-yttrium separation factor. Tributyl phosphate appeared to be superior to hexone in a hydrochloric acid medium for yttrium-rare earth separations by liquid-liquid extraction.

e. Extractions of a nitric acid solution of the Gadolinite ore yttrium-rare earth concentrate with tributyl phosphate indicated that the presence of aluminum nitrate, aluminum chloride, magnesium nitrate, magnesium chloride or sodium chloride in the initial aqueous phase increased the mass transfer of rare earths to the organic phase. The higher the concentration of the salting-out agent in the initial aqueous phase the greater was the mass transfer to the organic phase. Likewise, there was a corresponding increase in the yttrium, dysprosium, and gadolinium distribution coefficients. The effect of these salting-out agents was most pronounced in the low nitric acid systems. For a given anion the higher valence cations effected the greatest mass transfer. The nitrate ion was more effective in increasing yttrium-rare earth transfer than the chloride ion for a given cation at equal concentrations.

The use of the chloride salts as a salting-out agent, in general, slightly decreased the gadolinium-yttrium, yttrium-dysprosium and gadolinium-dysprosium separation factors. The same general variation in the values of the separation factors with nitric acid concentration resulted with or without the presence of any salting-out agent. In the presence of the nitrate salting-out agents this gadolinium-yttrium separation factor trend was unchanged. However, in this case, a large variation in the yttrium-dysprosium and gadolinium-dysprosium separation factors resulted. In the presence of both the nitrate and chloride salting-out agents the dysprosium and the gadolinium separation factors, with respect to yttrium, were relatively high at low nitric acid concentrations.

The extraction of an aqueous phase containing increasing amounts of aluminum chloride at constant nitric acid concentration yielded the same general trends as increasing the nitric acid concentration at constant aluminum chloride concentration. The ionic strength of the solution might be an important factor in controlling preferred yttrium-rare earth extractability.

f. The Gadolinite ore yttrium-rare earth mixture, dissolved in nitric acid concentrations ranging from 0.17 to about 6.0 molar, was extracted with tributyl phosphate. Gadolinium and dysprosium could best be separated from yttrium at low nitric acid concentration while yttrium and dysprosium can be separated most efficiently from gadolinium at high nitric acid concentrations. Dysprosium and gadolinium had similar distribution coefficients at about 1.0 molar nitric acid while the gadolinium and yttrium distribution coefficients were the same at about 4.5 molar nitric acid.

g. Extractions of a nitric acid solution of the Gadolinite ore yttrium-rare earth concentrate with a series of organic phosphites indicated an increase in mass transfer to the organic phase as the molecular weight of the organic phosphite decreased. The gadolinium-yttrium separation factor was inversely proportional to the per cent transfer to the organic phase.

Comparison of extractions with corresponding organic phosphites and phosphates indicated that the phosphites yielded the highest gadolinium-yttrium separation factors and mass transfers to the organic phase. This indicated that the doubly bonded oxygen in organic phosphate is not required for yttrium-rare earth extraction and separation.

3. Multistage extractions

a. The more promising conditions obtained from the single stage extractions were employed in a series of 20 stage countercurrent liquid-liquid extraction processes. The same general trends observed in the single stage extractions were observed in the multistage experiments although the separations were more pronounced.

b. The yttrium-rare earth nitrate mixture from the ion-exchange column tailings was divided into a fraction analyzing, on an oxide basis, greater than 90 per cent yttrium with about a 90 per cent recovery of the total yttrium present. The other fraction, or the aqueous phase product, contained the light rare earths and the remaining 10 per cent of the yttrium. A 13 molar nitric acid medium constituted the aqueous phase.

c. The Fergusonite ore yttrium-rare earth concentrate was separated into a fraction containing 85 per cent yttrium on the oxide basis by two separate countercurrent extractions. The nitric acid concentrations in the aqueous phases for the extraction processes were 13 molar and 7.0 molar, respectively. Tributyl phosphate was the organic phase in both cases. The yttrium depleted fraction, or the aqueous phase product from the first extraction process, was further separated into two fractions. One contained essentially only praseodymium and neodymium while the other was composed chiefly of samarium, gadolinium, dysprosium and yttrium.

d. Extraction of a 0.12 molar nitric acid solution of the yttrium-rare earth mixture from Gadolinite ore with tributyl phosphate gave an aqueous product which was enriched in yttrium and an organic product containing relatively large amounts of samarium, gadolinium and dysprosium. Consequently, this extraction indicated a method of separating yttrium from gadolinium and dysprosium.

SUMMARY

The yttrium-rare earth mixtures, which were investigated, were obtained from Fergusonite ore, Gadolinite ore and tailings from a process employing an ion-exchange resin column. In each case the mixture in terms of oxide was composed of from 50 to 60 per cent yttrium and 5 to 15 per cent heavy rare earths with the light rare earth fraction constituting the remaining material. In general, tributyl phosphate was employed for extracting the nitric acid solutions of these rare earth mixtures although the use of other organic liquids was briefly investigated.

Single stage extraction data indicated that the preferential extractability of the rare earths from an aqueous system greater than 3.0 molar in nitric acid increases with increasing atomic number. At lower nitric acid concentrations some deviations from this trend appeared. The mass transfers of yttrium and rare earths increased with nitric acid concentrations above about 6.0 molar. The reverse mass transfer trend resulted for the range below about 6.0 molar nitric acid. Yttrium extracts in combination with holmium in a highly concentrated nitric acid system. However, in the 6 to 12 molar nitric acid system it extract essentially with dysprosium while in a 3.0 to 4.5 molar nitric acid system it resembles gadolinium. In lower nitric acid systems yttrium extracts with the lower atomic number rare earths.

The use of salting-out agents such as aluminum nitrate and chloride, magnesium nitrate and chloride and sodium chloride was investigated. These salting-out agents caused an increase in the mass transfer to the organic phase, although in most cases not affecting the yttrium-rare earth separation factors to any appreciable extent. As the nitric acid concentration in the system increased, the effect of these salting-out agents on mass transfer became less pronounced. The nitrate salting-out agents were more effective in increasing mass transfer than corresponding chloride salts. The high valence cations also caused the greatest mass transfer of yttrium and rare earths from the aqueous to the organic phase.

The extractions of the nitric acid solutions of yttrium and the rare earths containing various amounts of hydrochloric, acetic and sulfuric acids were carried out. In general, the presence of these acids increased the gadolinium-yttrium separation factor slightly. Tributyl phosphate extracted a very small amount of yttrium and the rare earths from their hydrochloric acid solutions. The gadolinium-yttrium separation factors were close to unity for this system. The use of hexone as the organic phase and addition of ammonium thiocyanate to this chloride solution resulted in no appreciable yttrium or rare earth transfer or separation of gadolinium from yttrium. Since the gadolinium-yttrium, yttrium-dysprosium and the gadolinium-dysprosium separation factors seldom exceeded a value of 3.0, many stages were required for their separation.

A number of 20 stage countercurrent extractions employing a nitric acid yttrium-rare earth solution as the aqueous phase and tributyl phosphate as the organic phase was carried out. For a concentrated nitric acid system the organic product phase generally contained yttrium and the heavy rare earths, while the aqueous product phase contained the light rare earth fraction plus a small amount of yttrium and dysprosium. In one multistage extraction the organic product phase delivered 90 per cent of the total yttrium which analyzed to be 91 per cent pure on an oxide basis. The heavy and light fractions of the yttrium-rare earth concentrate from Fergusonite ore was easily separated by liquid-liquid extraction. An additional extraction of the light fraction resulted in a fraction enriched in praseodymium and neodymium. Gadolinium and dysprosium were separated from yttrium to a great extent on a continuous basis by a multistage extraction employing a 0.12

molar nitric acid aqueous solution of the yttrium-rare earth mixture. The extractions of these yttrium-rare earth concentrates showed the possibility of separating yttrium from any particular rare earth and the rare earths themselves on a continuous basis by combinations of liquid-liquid extractions.

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