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*STAGewise SEPARATION OF URANIUM,
THORIUM AND THE RARE EARTHS
BY LIQUID-LIQUID EXTRACTION*

G. M. RITCEY AND B. H. LUCAS

EXTRACTION METALLURGY DIVISION

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STAGewise SEPARATION OF URANIUM, THORIUM AND
THE RARE EARTHS BY LIQUID-LIQUID EXTRACTION

by

G. M. Ritcey* and B. H. Lucas**

ABSTRACT

Rare earths and thorium are found associated with uranium at Elliot Lake, Ontario, one of the major uranium-producing areas of Canada. In addition to the recovery of uranium by ion exchange processing, minor quantities of thorium and rare earths are recovered as bulk concentrates. The work described shows the development of a stagewise separation of individual rare earths by liquid-liquid extraction from sulphuric acid barren liquors from the uranium recovery circuit. This is accomplished by the use of an alkylphosphoric acid dissolved in a kerosene diluent. Residual uranium and thorium are co-extracted with an amine, prior to rare-earth processing. The bench-scale results have indicated that extraction coefficients of individual rare earths, and separation factors between rare earths, are affected by the aqueous feed pH, solvent concentration, and the atomic number of the rare earth. The data presented show the possibility of selective separation of the rare earths singly or in small groups. A proposed flowsheet is given.

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LA SÉPARATION SÉLECTIVE DE L'URANIUM, DU THORIUM ET DES TERRES RARES PAR EXTRACTION LIQUIDE-LIQUIDE

par

G.M. Ritcey* et B.H. Lucas**

RÉSUMÉ

On retrouve des terres rares et du thorium en association avec de l'uranium à Elliot Lake (Ontario), qui est l'une des principales régions productrices d'uranium au Canada. En plus de récupérer de l'uranium par échange d'ions, on recouvre également de petites quantités de thorium et de terres rares sous forme de concentrés. La présente étude décrit la mise au point d'un procédé de séparation sélective des terres rares par extraction liquide-liquide à partir des solutions libres d'acide sulfurique provenant des circuits de récupération de l'uranium. Ceci s'accomplit par l'emploi d'acide alkylphosphorique dissous dans un diluant à base de kérosène. L'uranium résiduel et le thorium sont extraits avec une amine avant la récupération des terres rares. Les résultats des essais en laboratoire montrent que les coefficients d'extraction des diverses terres rares et les facteurs de séparation de ces dernières sont influencés par le pH de l'alimentation aqueuse, la concentration du solvant et le numéro atomique de la terre rare en question. Les résultats présentés indiquent la possibilité d'effectuer des séparations sélectives des terres rares individuellement ou par petits groupes. Un schéma de circulation est également proposé.

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CONTENTS

	<u>Page</u>
Abstract	i
Résumé	ii
Introduction	1
Procedure and Choice of Solvent	3
Results	4
1. Extraction of Uranium and Thorium	4
2. Extraction and Separation of Rare Earths	5
a) Effect of pH and solvent molarity with di-(2-ethylhexyl)phosphoric acid	5
b) Effect of pH and solvent molarity with Primene JM-T	6
c) Saturation loading tests for individual rare earths	7
d) Effect of sulphate concentration in feed..	7
e) Effect of iron	8
f) Effect of retention time	8
g) Effect of stagewise contact on the extract purity	9
Discussion	10
Conclusions	13
Acknowledgement	13
References	14-17
Figs. 1 to 12	18-29

<u>No.</u>	<u>Page</u>
1. Co-extraction of uranium and thorium with primary or secondary amine	18
2. Effect of pH on the extraction and separation of rare earths from sulphate solution, 0.1 M D2EHPA	19
3. Effect of solvent concentration on extraction and separation of rare earths at pH 2.0	20
4. Effect of pH on the extraction and separation of rare earths using 0.1 M Primene JM-T	21
5. Saturation loading for individual rare earths	22
6. Effect of successive contacts of some light and some heavy rare earths, along with uranium, thorium and iron, on purity of extract (0.1 M D2EHPA).....	23
7. Effect of contact time on co-extraction of iron	24
8. Effect of successive contacts of some light and some heavy rare earths on purity of extract (0.1 M D2EHPA)..	25
9. Effect of successive contacts of some heavy rare earths on purity of extract (0.1 M D2EHPA)	26
10. Effect of successive contacts of light rare earths on purity of extract (0.1 M D2EHPA)	27
11. Effect of successive contacts of some light and some heavy rare earths on purity of extract (0.1 M Primene JM-T).....	28
12. Proposed flowsheet for fractionation of rare earths ...	29

INTRODUCTION

At the Elliot Lake (Ontario) uranium mines, large volumes of barren liquor, relatively free from uranium but containing rare earth elements and thorium, are at present run to waste. This liquor results from sulphuric acid leaching of uranium ores, followed by removal of uranium from a filtered solution by ion exchange. The minerals brannerite, uraninite and uranothorite⁽¹⁾, from which the uranium is derived, contain lanthanum, yttrium, cerium, praesodymium, neodymium, samarium, ytterbium, thorium, and lesser quantities of dysprosium and erbium. During the present leaching process, while only about 20% of the total rare earths are leached, approximately 75% of the yttrium is leached along with uranium and thorium⁽¹⁾. The rare earths in the solid tailings are in the undissolved monazite. The thorium may be recovered from the barren liquor by extraction with primary or secondary amines⁽²⁾. Some of the mines currently recover a bulk rare-earth concentrate by liquid-liquid extraction with an alkylphosphoric acid⁽³⁾ from their barren solutions. This concentrate is further purified in the United States.

The present investigation, begun late in 1967, was aimed at finding suitable processes for the recovery of separate rare earths, of relatively high purity, directly from the waste liquors.

The possibility of solvent extraction for the recovery of the individual rare earths, or rare-earth groups, was considered.

Many workers have reported, in the literature, rare-earth separation schemes based on solvent extraction. From nitric acid systems, tributyl phosphate has generally been used^(5,6,7,8), although alkylphosphoric acids^(9,10,11,12), as well as tertiary amines⁽¹³⁾ and alcohols⁽¹⁴⁾, have also been used. In a hydrochloric acid medium, alkylphosphoric acids have been used^(15,16,17), as well as acetylacetone⁽¹⁸⁾. In a sulphuric acid system, alkylphosphoric acids have been most widely studied^(19 to 25), as well as primary amines^(26,27,28). The fractional extraction of the rare earths has also been improved by the use of chelating agents in the solvent extraction system^(21,23,29 to 35), which results in an increase in the separation factor of adjacent rare-earth pairs. In none of the literature pertaining to the sulphuric acid-alkylphosphoric acid system have sufficient data been found to show that fractionation of the individual rare earths might be possible if many are present in the leach solution.

Since the barren solutions from the Elliot Lake operations are of the sulphate type, alkylphosphoric acids and amines⁽¹⁹⁻²⁷⁾ were investigated as to their selectivity. The initial work was performed on synthetic sulphate solutions containing single rare-earth elements, to determine the relative extraction coefficients

at various pH ranges, as well as to determine the effect of other cations such as iron, uranium and thorium on the extraction and separation coefficients between various rare earths.

PROCEDURE AND CHOICE OF SOLVENT

The initial test work to determine the conditions needed for the successful separation of the individual rare earths was carried out on synthetic sulphate solutions, containing single rare earths, and, later, on various rare-earth mixtures. The concentrations of rare earths in these synthetic solutions, at about pH 2, approximated that of a typical barren solution from the Elliot Lake area. The compositions of these solutions ranged from 0.02 to 0.08 g/l for each individual rare earth, and contained about 17 g SO_4 /l, 3.3 g ferrous iron /l, and 0.3 g ferric iron /l.

The bench work, carried out in separatory funnels, determined the effect, on the extraction coefficients, of variables such as feed pH, solvent type and concentration, and retention time. Aliquots of usually 100 ml of feed solution were contacted at an A/O ratio of 5/1. The phases were allowed to separate and the aqueous raffinate was then analysed by X-ray fluorescence.

Early in the investigation, a survey was made of several organic reagents to determine the most suitable ones for the extraction of rare earths, uranium and thorium. The organics

tested at this time included amines, fatty acids, alkyl phosphates, and oximes. The survey indicated both Primene JM-T (Rohm & Haas primary amine) and di-(2-ethylhexyl)phosphoric acid (D2EHPA, Union Carbide) to be the most effective for rare earths extraction, and Primene JM-T and Adogen 283 (Ashland Chemicals ditridecyl amine) for co-extraction of uranium and thorium. Subsequent test work on the rare earths utilized Primene and D2EHPA at concentrations of 0.01, 0.10, and 0.25 M, in a kerosene diluent.

RESULTS

1. Extraction of Uranium and Thorium

Because the ion-exchange barren solution contained thorium and trace quantities of uranium, it was necessary to remove these two metals prior to the rare-earth recovery. Although both the Primene and D2EHPA systems appeared suitable for the extraction of the rare earths, uranium and thorium were also co-extracted if present, as shown in Figs. 2, 3 and 4. In the amine system it became evident that a separation of uranium and thorium from the rare earths could be achieved, because of the relative differences in extraction coefficients (Fig. 4).

The co-extraction of uranium and thorium was initially applied to the ion-exchange barren solutions containing up to

0.02 g U/l. Later tests were performed on leach liquors containing about 0.5 g U/l and 0.12 g Th/l.

The separation of uranium and thorium from the rare earths does in fact occur, and is shown, for both the primary and secondary amines, in Fig. 1. The secondary amine appears the more favourable, due to a higher uranium loading and to a tendency for less co-extraction of iron. The rare earths were not extracted by either amine if the feed contained sufficient quantities of uranium or thorium which, because of their higher extraction coefficients in comparison to the rare earths, would preferentially extract.

The bench results for the co-extraction of uranium and thorium from a leach feed solution, using a primary amine, have been substantiated in a brief pilot-plant run.

Laboratory results have indicated that preferential separation of uranium from thorium was achieved by stripping the loaded extract with dilute nitric acid. The economics may, however, dictate a co-stripping, followed by separation of the two metals in an additional solvent extraction system.

2. Extraction and Separation of Rare Earths

a) Effect of pH and solvent molarity with di-(2-ethylhexyl)phosphoric acid

Preliminary tests were performed on solutions containing a single rare earth, and the extraction co-efficients were then

calculated. From these data, separation factors between rare-earth pairs were determined. These separation factors showed the possibility of the individual separation of the rare earths. Subsequent investigations were concerned with rare-earth mixtures. The solvent concentration was varied from 0.01M to 0.25M and the aqueous feed ranged from pH 1 to 4. In Figs. 2 and 3 are shown the effect of pH and solvent concentration of D2EHPA on the extraction coefficient (E_A) of the rare earths in various synthetic solution mixtures. In some cases a separation between adjacent rare earths can be effected by change in pH along with change in molarity of the solvent, whereas in other pairs no separation occurs. For example, Nd/Pr separation appears very difficult under all the conditions of pH and solvent concentration investigated, but the general bulk separation of yttrium plus the heavy rare earths (Tb to Lu) from the lighter rare earths appears quite feasible by varying the pH and the solvent concentration.

b) Effect of pH and solvent molarity with Primene JM-T

In tests similar to the D2EHPA series, the results showed that Primene JM-T was less effective than D2EHPA for the separation of individual rare earths from solution mixtures. The effect of pH on various rare-earth solution mixtures, as shown in Fig. 4, generally indicates an increase in the extraction coefficient of each rare earth with an increase in pH. There was very little

change in the extraction coefficient with a change in solvent concentration.

c) Saturation loading tests for individual rare earths

Tests were performed to determine the saturation levels for the individual rare earths in 0.1M D2EHPA at pH 2.0. Synthetic sulphate solutions, each containing approximately 1 g/l of a single rare earth, were contacted at A/O ratios ranging from 1/2 to 10/1. The saturation loadings for the various rare earths in the D2EHPA system are shown in Fig. 5 and indicate a trend towards higher loadings as the atomic number of the rare earth being loaded increases. Yttrium followed europium in the series. In similar tests using 0.1M Primene JMT, there was no apparent correlation between atomic number of the rare earth and the loading characteristic as was shown in the D2EHPA system. Also, the maximum loading obtained for any rare earth was 2 g/l, as against a saturation value of about 6 g/l in the D2EHPA system.

d) Effect of sulphate concentration in feed

To determine the effect of sulphate ion on the solvent extraction step, synthetic solutions at pH 2.0, containing the rare earths and various amounts of sodium sulphate ranging from 17 to 75 g SO_4 /l, were extracted at an A/O ratio of 5/1 for 5 minutes with 0.1 M solutions of Primene and D2EHPA. In the Primene system, sulphate concentrations of up to 75 g SO_4 /l had no

effect on the extraction of the rare earths. However, in the D2EHPA system, the extraction of the light rare earths is decreased when the SO_4 concentration is greater than 20 g SO_4/l , whereas heavy rare earths are unaffected up to a concentration of 75 g SO_4/l .

e) Effect of iron

Early in the investigation, tests indicated that up to 35% of the ferric iron is extracted in one stage at pH 2.0, using primary amines or alkylphosphoric acids. Ferrous iron, by contrast, has less affinity for D2EHPA than ferric iron, and therefore is more amenable to removal by scrubbing of the extract. Besides being a contaminant to the extract, iron occupies sites which ordinarily would be occupied by rare earths. The total loading of rare earths is therefore decreased because of co-extracted iron.

Fig. 6 shows what occurs when D2EHPA is contacted ten successive times with fresh feed solution containing several rare earths and iron. All tests were for 5 minutes duration at an A/O ratio of 5/1 and a feed pH of 2.0. The results show that the presence of iron resulted in a depression in the extraction of the higher atomic numbered rare earths. That the depression of the rare earth extraction is due to iron, is shown by the results in Fig. 8 from a solution containing no iron.

f) Effect of retention time

A series of batch shake-out tests was carried out to

determine whether extraction was time-dependent. The tests were carried out at a feed pH of 2.0 and an A/O ratio of 5/1, using both Primene and D2EHPA as 0.10 molar solvents. The results showed no difference in E_A^0 or in the separation factors of the rare earths, with shake-out time periods ranging from 0.5 to 5 minutes. However, an increase in the shake-out time resulted in an increase in the extraction of ferric iron in the D2EHPA system (Fig. 7). Obviously a short retention time will result in a minimum of iron contamination to the extract containing the rare earths. In the Primene system, the extraction of both ferric and ferrous iron was equal and similar to the extraction shown for ferrous iron in the D2EHPA system, over the time period investigated (Fig. 7).

g) Effect of stagewise contact on the extract purity

Since the previous tests have shown possible selectivity for the separation of rare earths, further investigations were carried out to simulate a continuous system of extraction. At phase ratios of 5/1 A/O, solvent was contacted with repeated fresh volumes of rare-earth synthetic feed solution at pH 2.0. Various feed compositions were used to determine the selectivity of extraction and whether scrubbing of certain metals occurred by repeated contact of organic solvent with fresh aqueous feed.

The results in Figs. 8,9 and 10 on the D2EHPA system indicate that, in fact, the higher atomic numbered metals in the particular series, having the highest extraction coefficients, remain on the loaded extract. For example, it would appear that yttrium and the heavy rare earths can be readily separated from the light rare earths (Fig. 8). Also, it may be possible to effect stagewise separation of both the heavy rare earths (Fig. 9) and the light rare earths (Fig. 10).

Fig. 11 shows essentially no selectivity of Primene for any of the light rare earths with repeated contacts.

DISCUSSION

Tests have shown that, generally, a decrease in extraction coefficient of the various rare earths occurs with an increase in the complexity of the feed solution. However, the relative separation factors of rare-earth pairs were not drastically altered by changing the feed solution composition, in either the amine or the alkylphosphate system.

In the Primene system, the results on solutions containing a single rare earth or rare-earth pairs agree with the separation factors obtained for pairs as described by Rice and Stone⁽²⁶⁾, and for single solutions as obtained by Crouse and Brown⁽²⁸⁾. The literature has no mention of fractionation in the Primene system,

and our data on complex solutions do not indicate either bulk or individual rare-earth separations.

In the D2EHPA system, the presence of ferric iron in the feed has a very serious effect on the extraction of the rare earths. This agrees with data as reported by several authors^(19,22).

Our data show an increase in the extraction coefficient with an increase in the atomic number of the rare earth. These data on the sulphate system correspond to similar data as found by Peppard et al.⁽¹⁵⁾ in a hydrochloric acid system.

The position of yttrium in the D2EHPA system, with respect to the rare earths, appears to change. In the saturation loading series it followed europium, as it also did in the molarity series when using 0.01 M D2EHPA. However, with variation of pH, at molarity concentrations of 0.1 and 0.25 M and stagewise extractions, yttrium closely resembled erbium. This similarity to erbium in the sulphate system agrees with the chloride system of Peppard⁽¹⁵⁾ and the nitrate system of Kolarik and Pankova⁽¹²⁾.

Our results from stagewise extraction show initial extraction of the heavier rare earths in the series, and the removal of the lighter metals during successive contacts (Figs. 8-10). This assumes that the relative concentrations of the rare earths to be separated are similar to one another. If concentrations

differ widely, the order of extraction will also depend on the metal with the highest concentration, rather than on extraction coefficients alone.

By proper choice of the extraction pH and the concentration of the D2EHPA in the solvent, a satisfactory split of the rare-earth series may be made (Figs. 2,3), thus improving the chances for fractionation of the desired rare earths.

As a result of our work, it is proposed to take advantage of the fact that scrubbing or replacement of a lighter with a heavier rare earth does occur with repeated stagewise contacts of D2EHPA with feed solution. Since many stages of extraction are anticipated for maximum separation of individual rare earths, a sieve-plate pulse column is being considered as the apparatus to provide sufficient stages for maximum rare-earth separation. The use of this type of equipment to obtain maximum separation of chemically similar metals, such as cobalt and nickel⁽³⁶⁾, and zirconium and hafnium⁽³⁷⁾, has been reported previously.

A proposed flowsheet for the treatment of Elliot Lake barren solutions is shown in Fig. 12. It is proposed to co-extract the trace uranium and thorium with a primary or secondary amine⁽³⁸⁾. Then a bulk separation of the heavy rare earths and yttrium will be made with D2EHPA. This should allow for the selective extraction, from a bulk strip solution, of the heavy rare earths.

Because of this concentration of the metals, smaller equipment could be used in subsequent fractionation. Similarly, for the light rare-earth fraction, a bulk extraction is performed, followed by stripping and separation as desired.

CONCLUSIONS

The results of the bench-scale test work indicate that recovery of certain individual rare earths, or bulk separations of several rare earths, are dependent on the relative atomic numbers and that these separations may be controlled by the following variables:

1. Solvent type and concentration
2. Feed pH
3. Number of stagewise extractions
4. Amount of co-extracted iron

The results of the work make it possible to propose a flowsheet for the fractionation of the rare earths with D2EHPA, after removal of uranium and thorium by co-extraction with a primary or secondary amine.

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GMR:BHL:(PES) MN

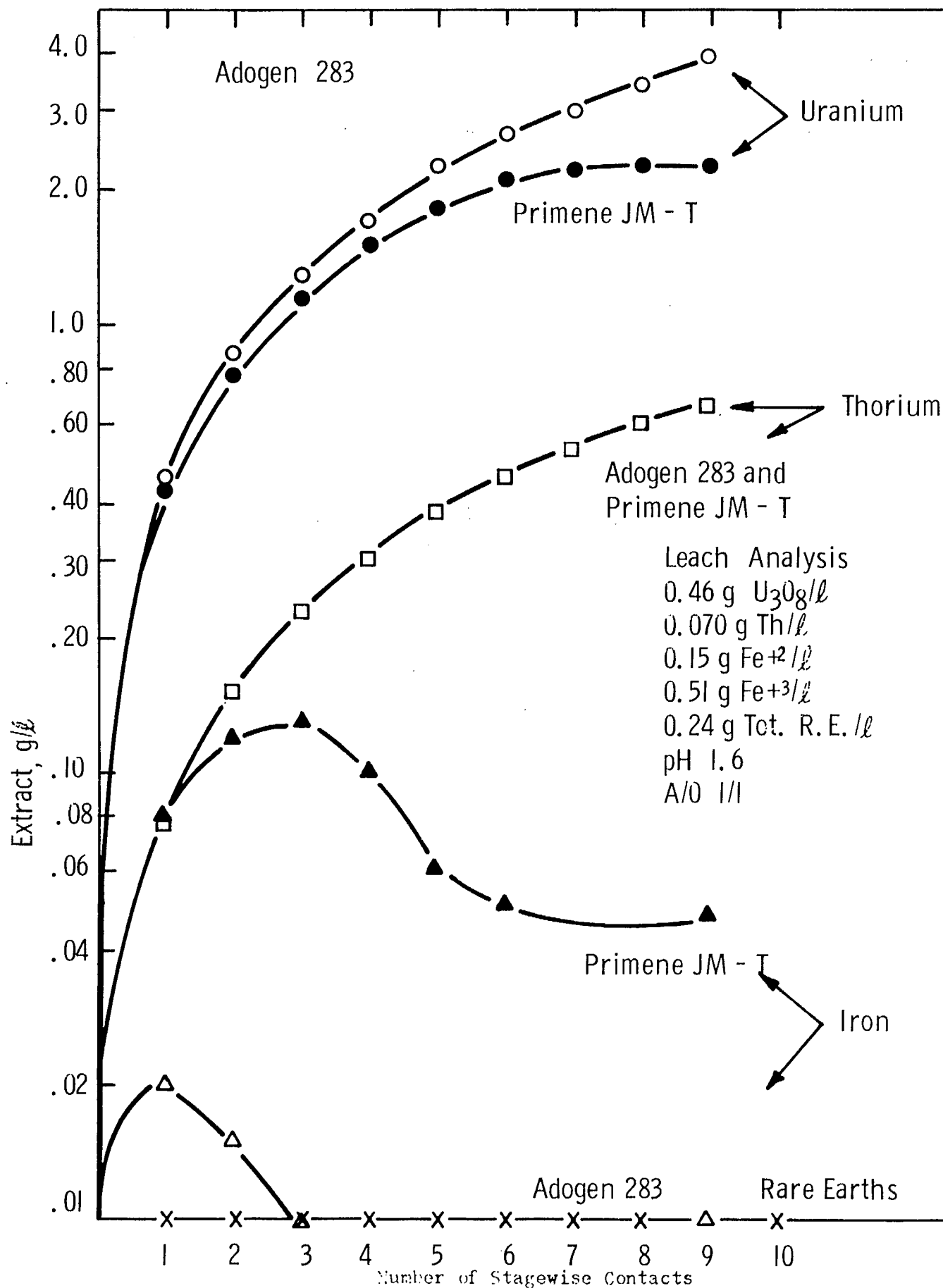


Fig. 1. Co-extraction of uranium and thorium with primary or secondary amine.

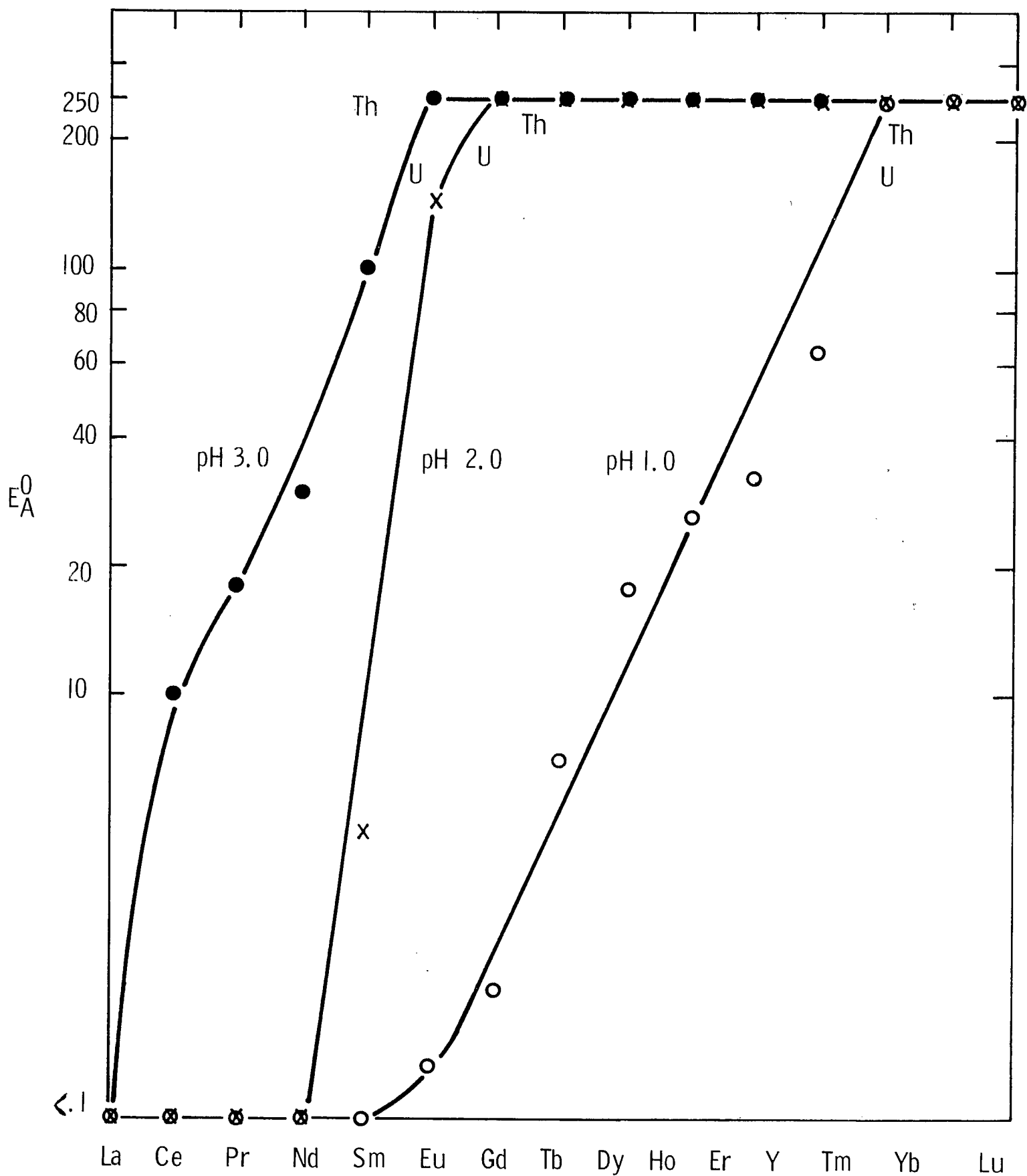


Fig. 2. Effect of pH on the extraction and separation of rare earths from sulphate solution, 0.1 M D2EHPA.

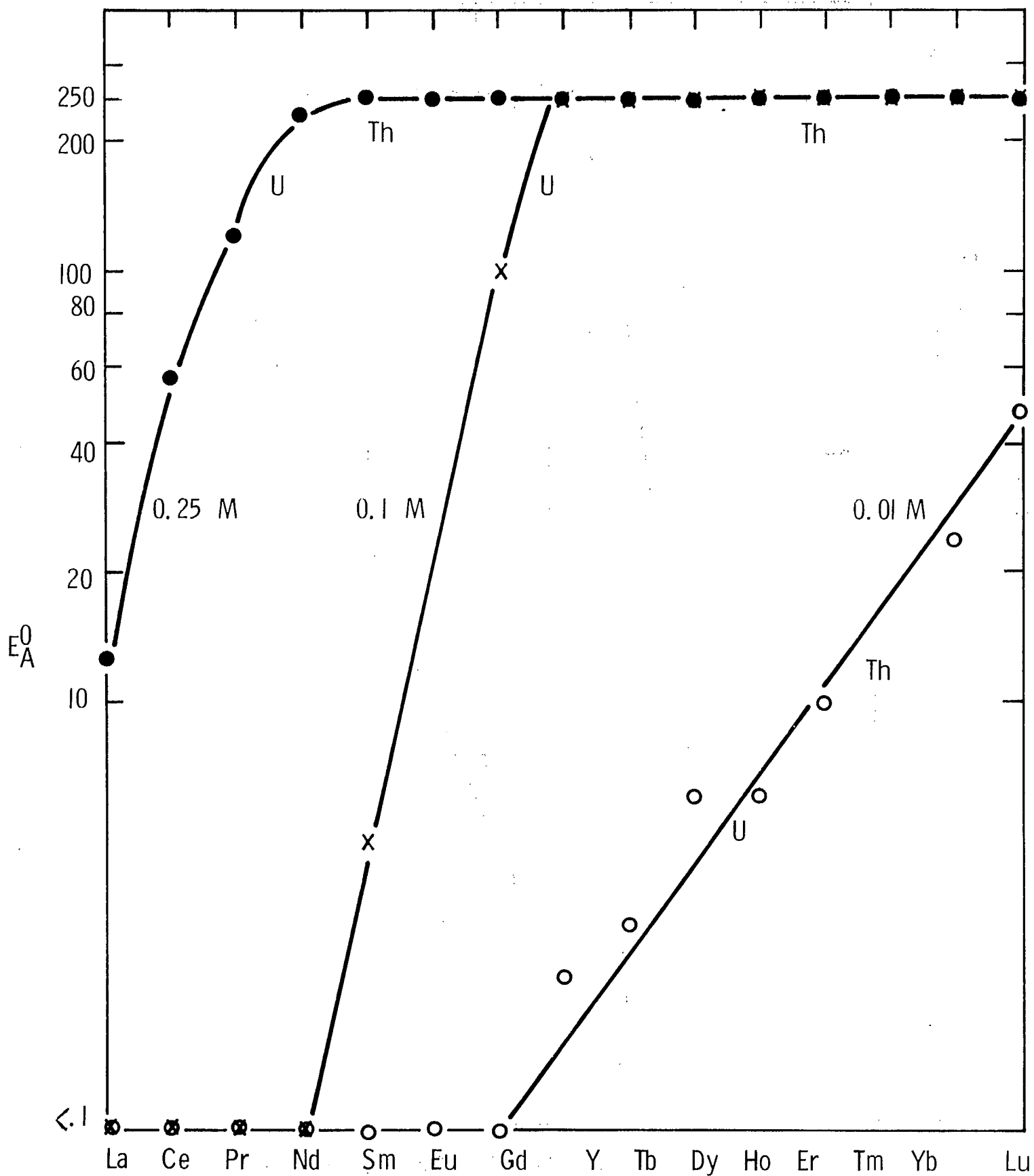


Fig. 3. Effect of solvent concentration on extraction and separation of rare earths at pH 2.0.

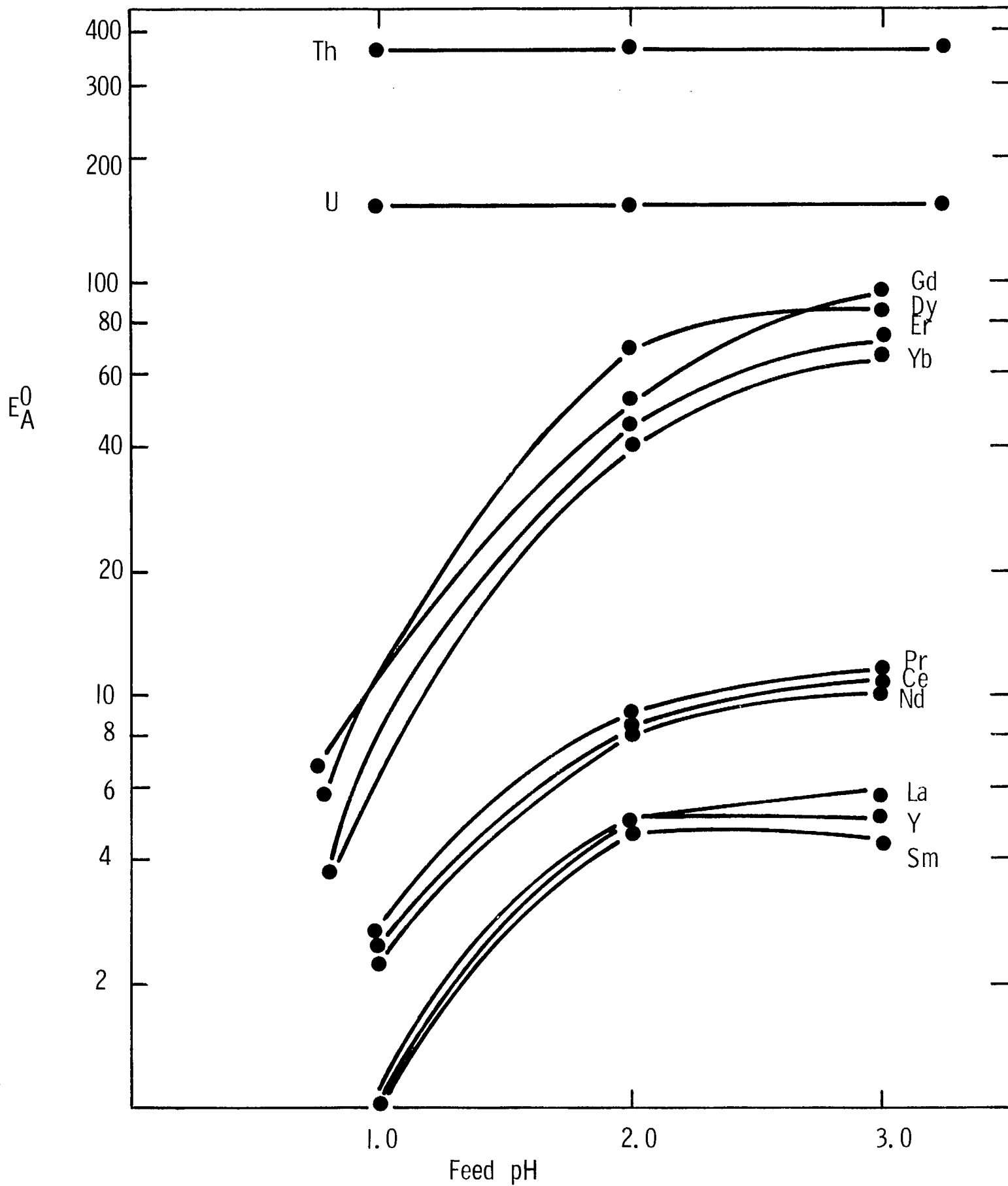


Fig. 4. Effect of pH on the extraction and separation of rare earths using 0.1 M Primene JM-T.

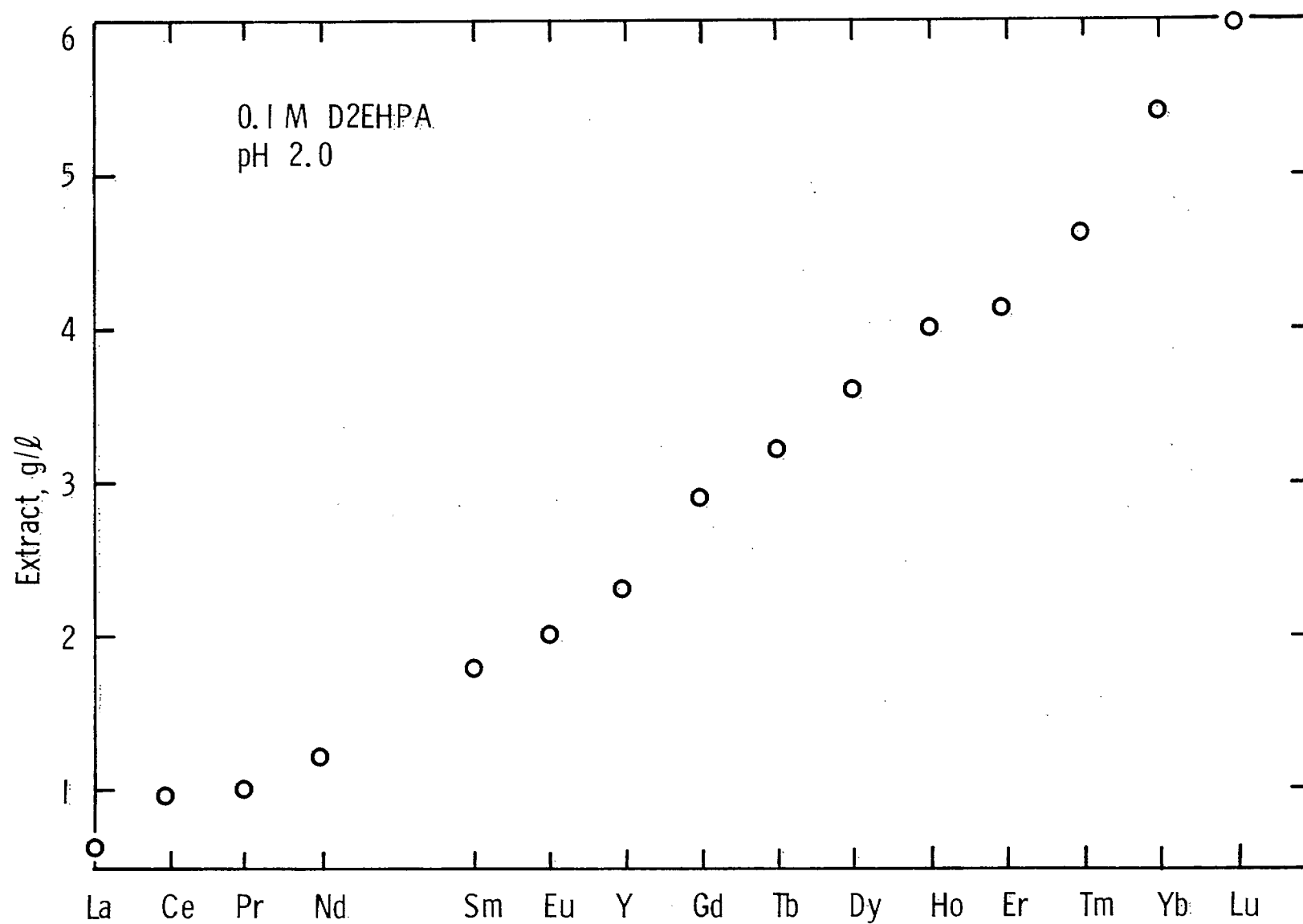


Fig. 5. Saturation loading for individual rare earths.

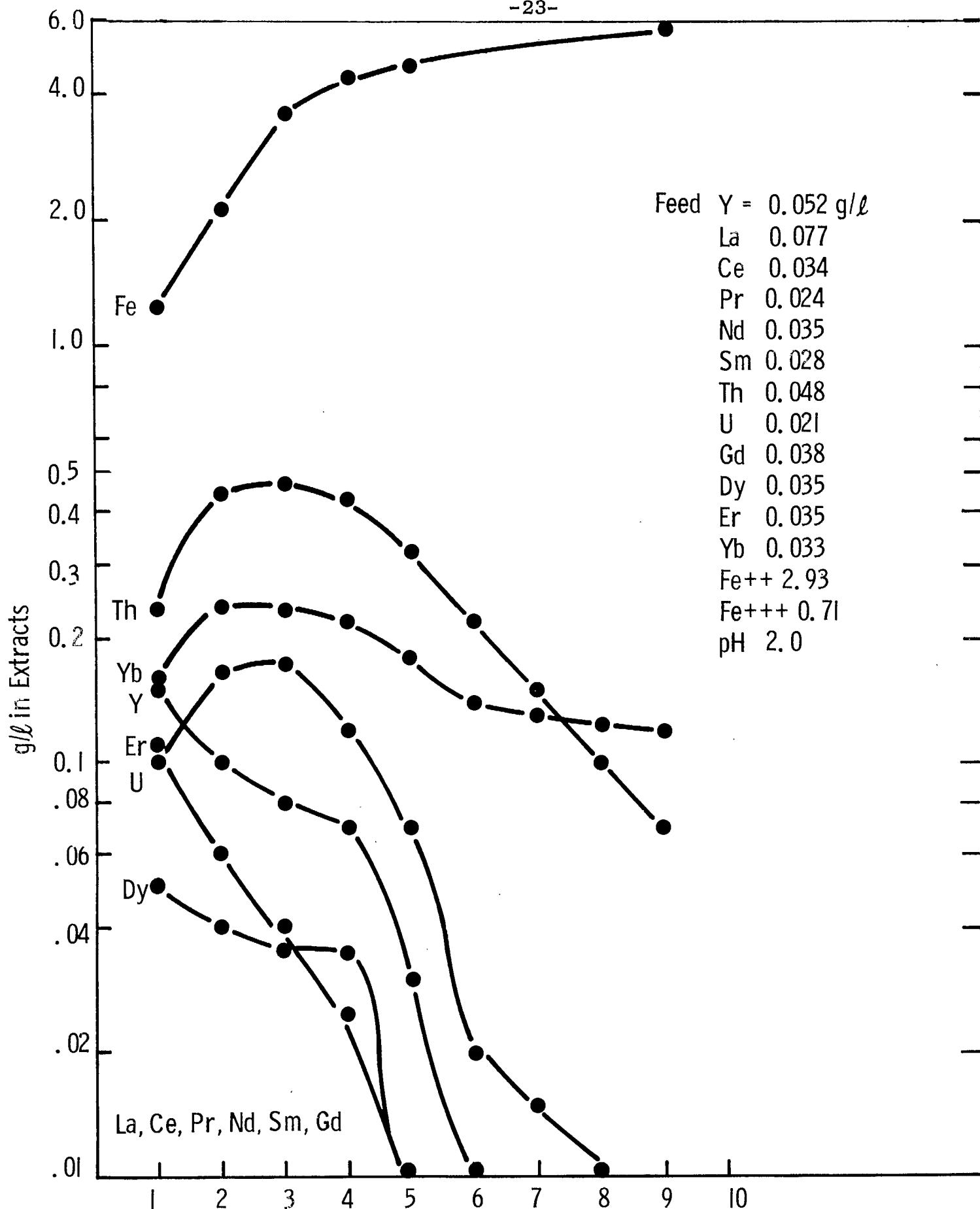


Fig. 6. Effect of successive contacts of some light and some heavy rare earths, along with uranium, thorium and iron, on purity of extract (0.1 M D2EHPA).

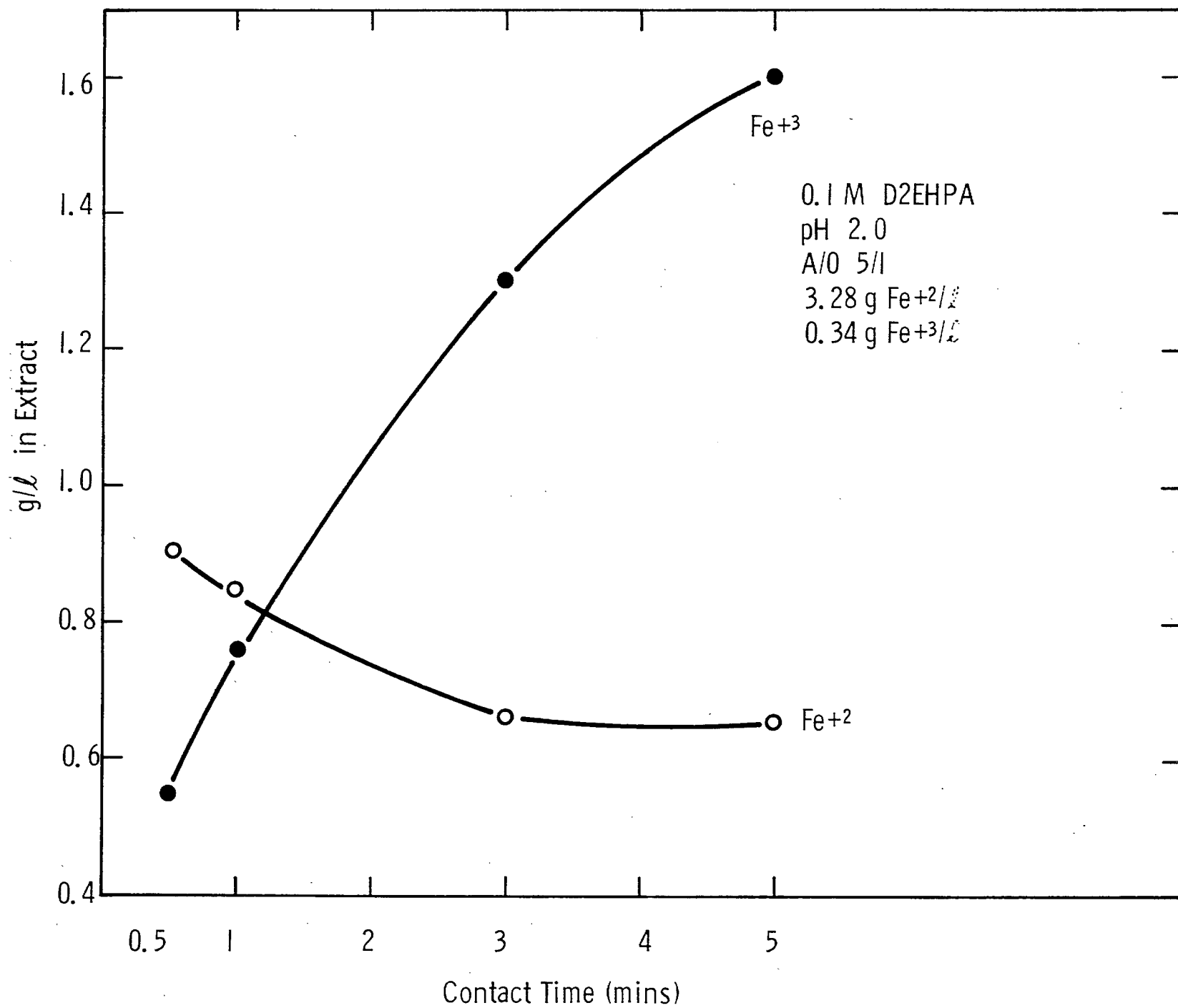


Fig. 7. Effect of contact time on co-extraction of iron.

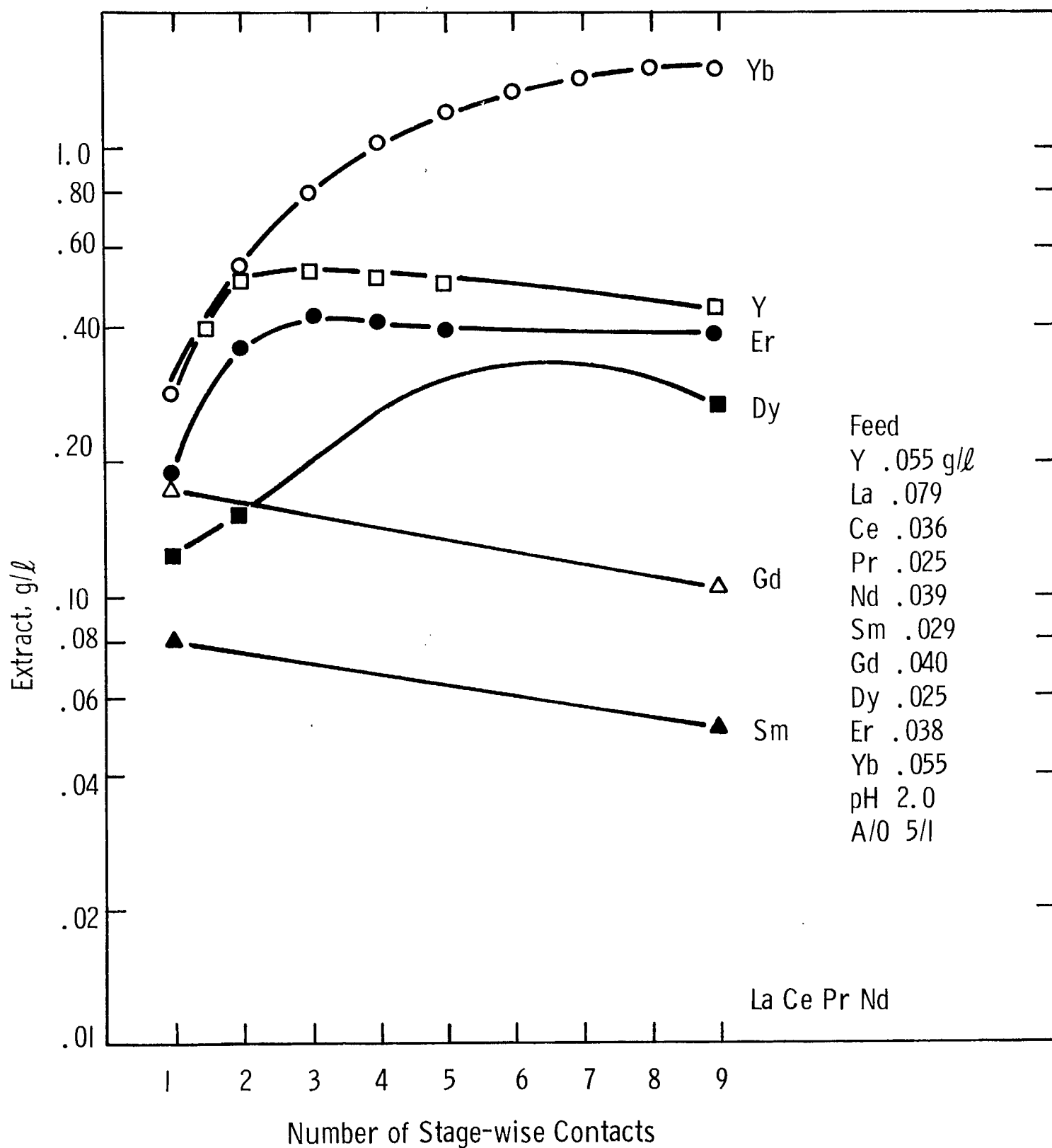


Fig. 8. Effect of successive contacts of some light and some heavy rare earths on purity of extract (0.1 M D2EHPA).

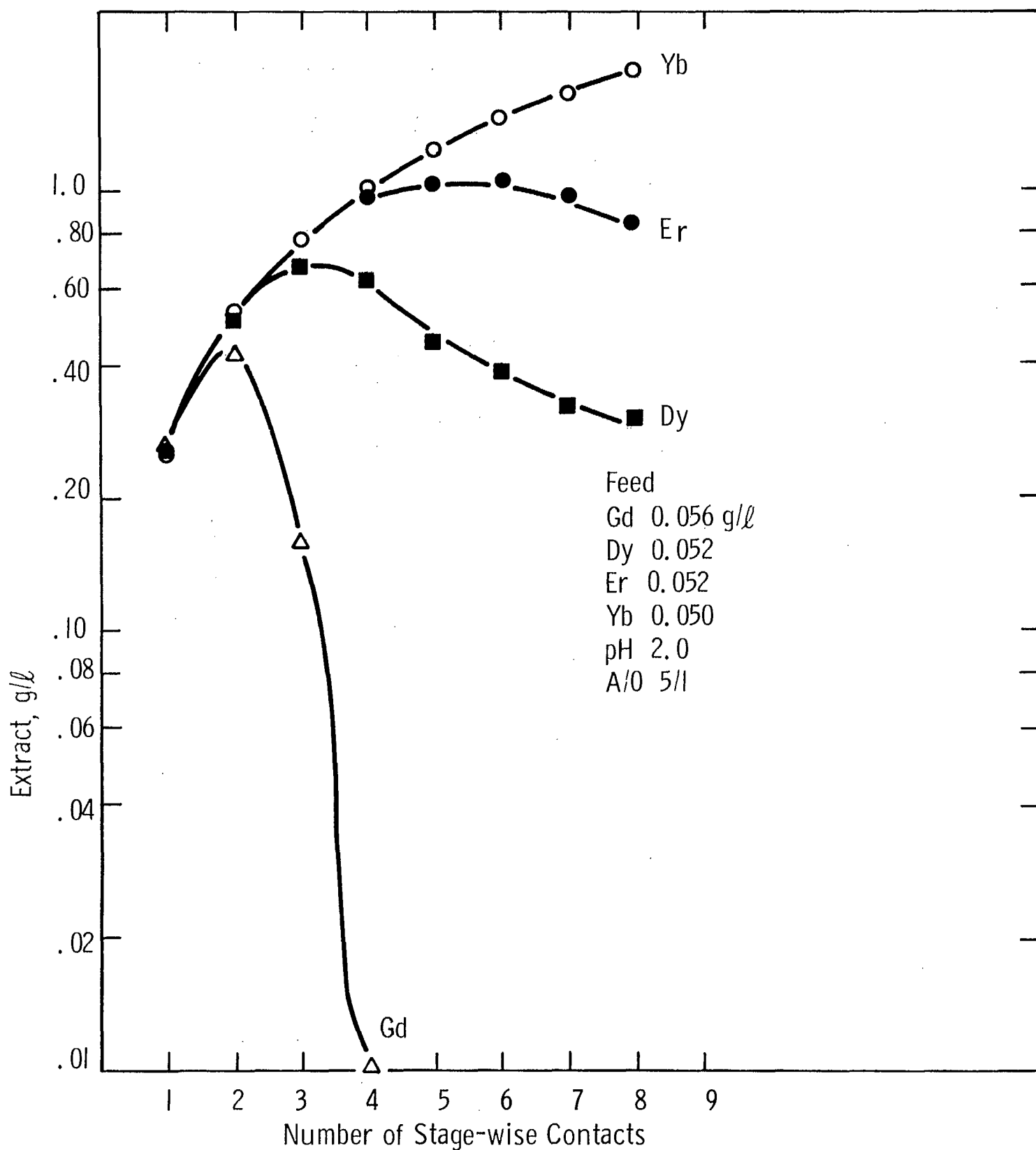


Fig. 9. Effect of successive contacts of some heavy rare earths on purity of extract (0.1 M D2EHPA).

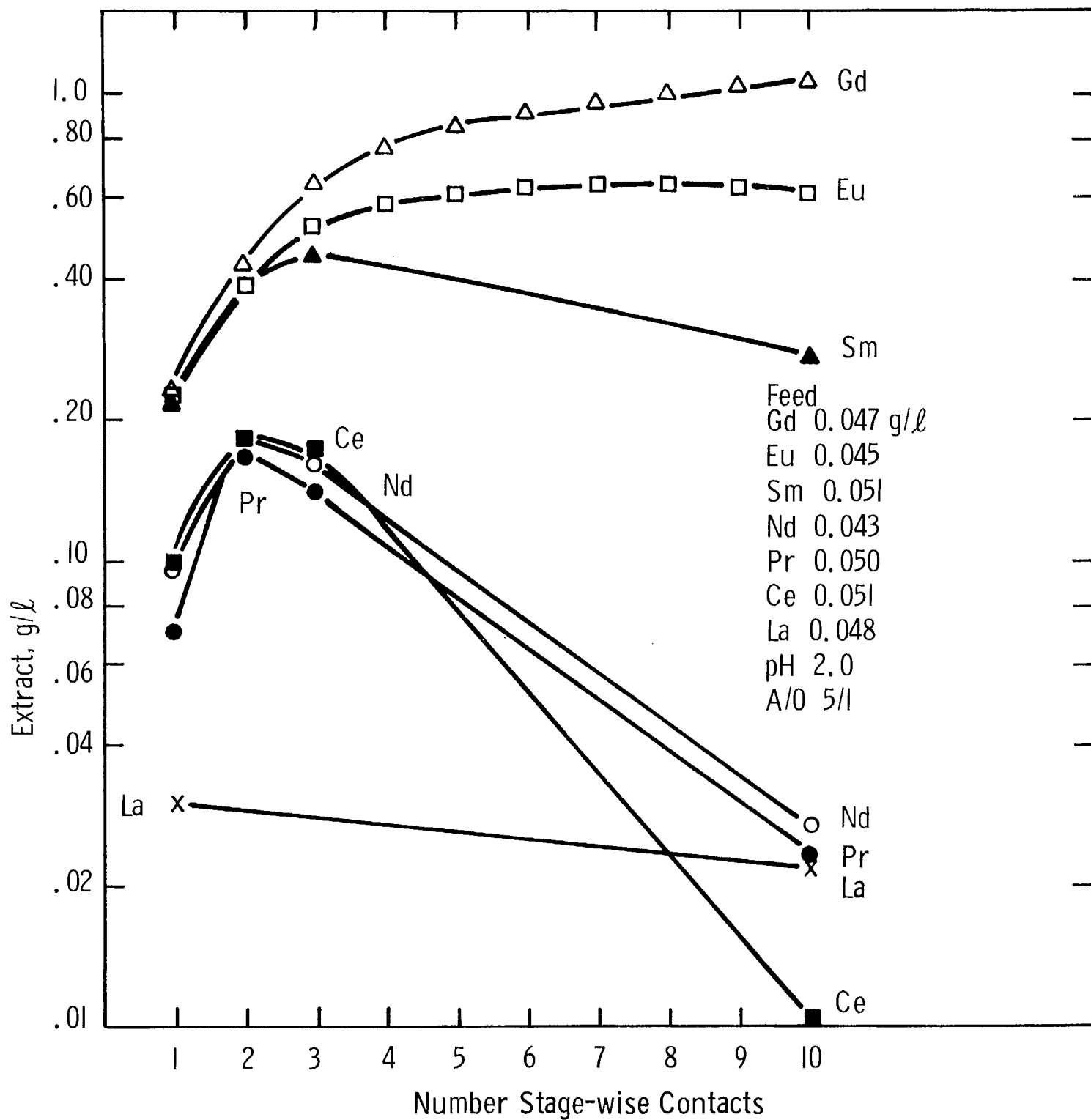


Fig. 10. Effect of successive contacts of light rare earths on purity of extract (0.1 M D2EHPA).

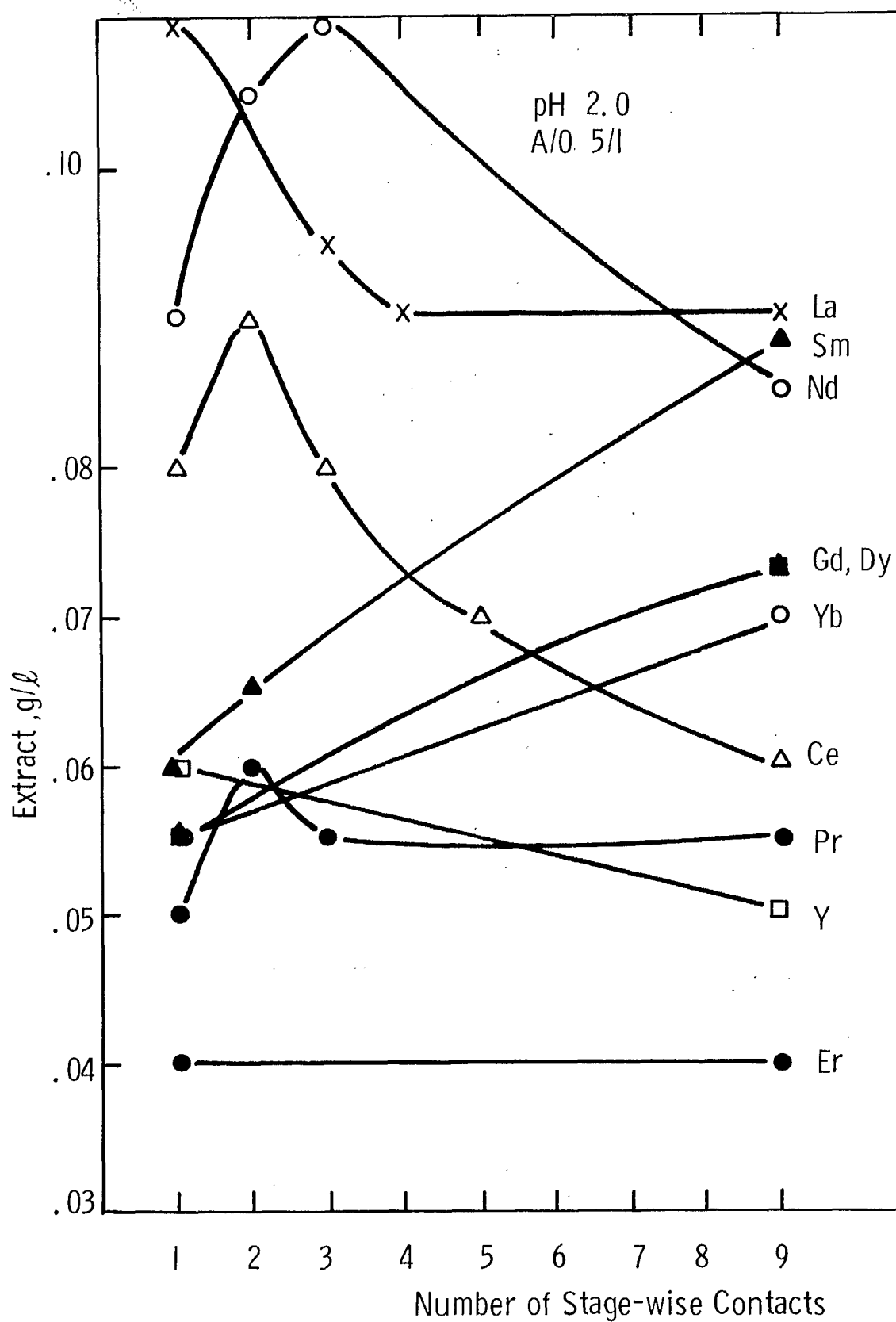


Fig. 11. Effect of successive contacts of some light and some heavy rare earths on purity of extract (0.1 M Primene JM-T).

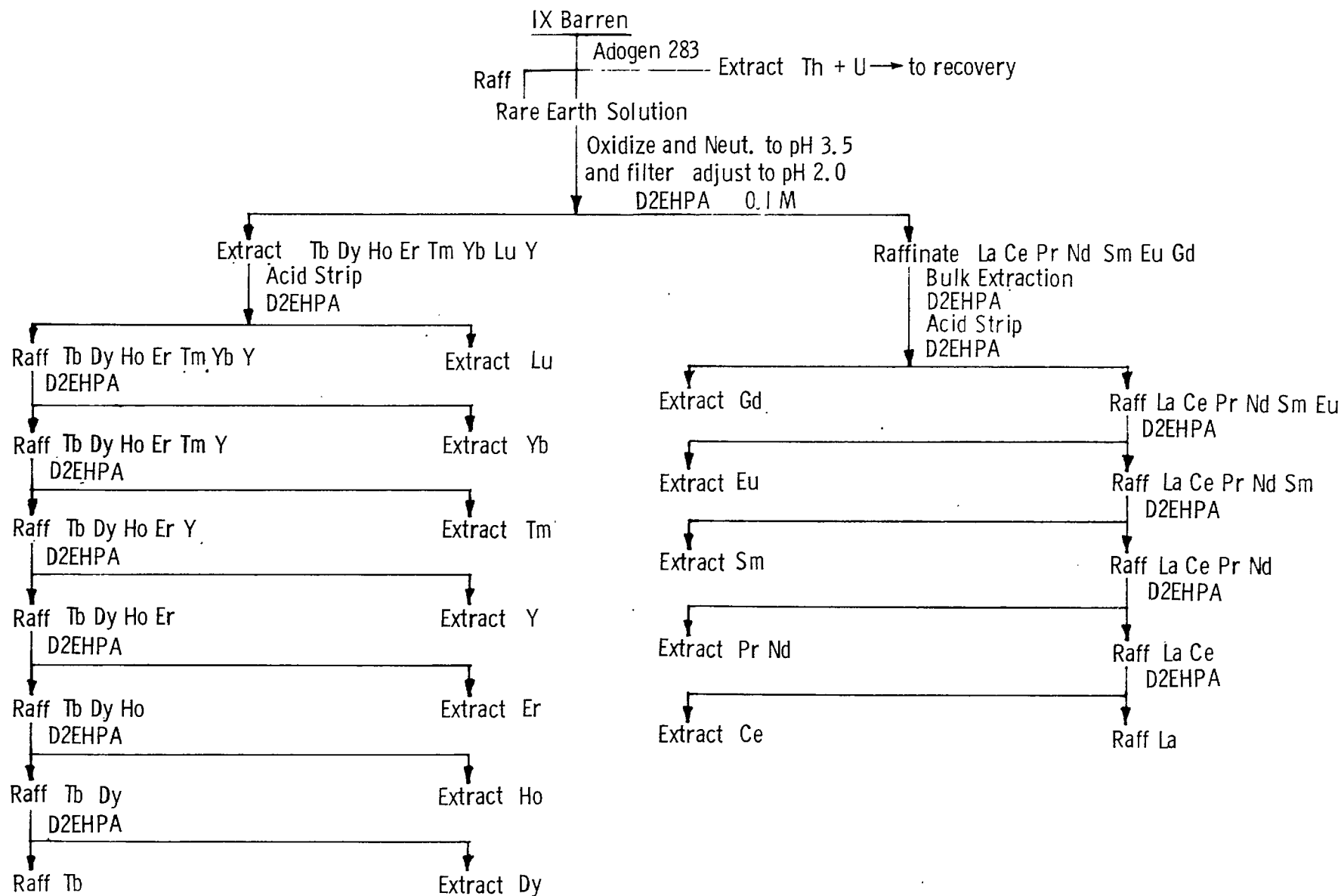


Fig. 12. Proposed flowsheet for fractionation of rare earths.

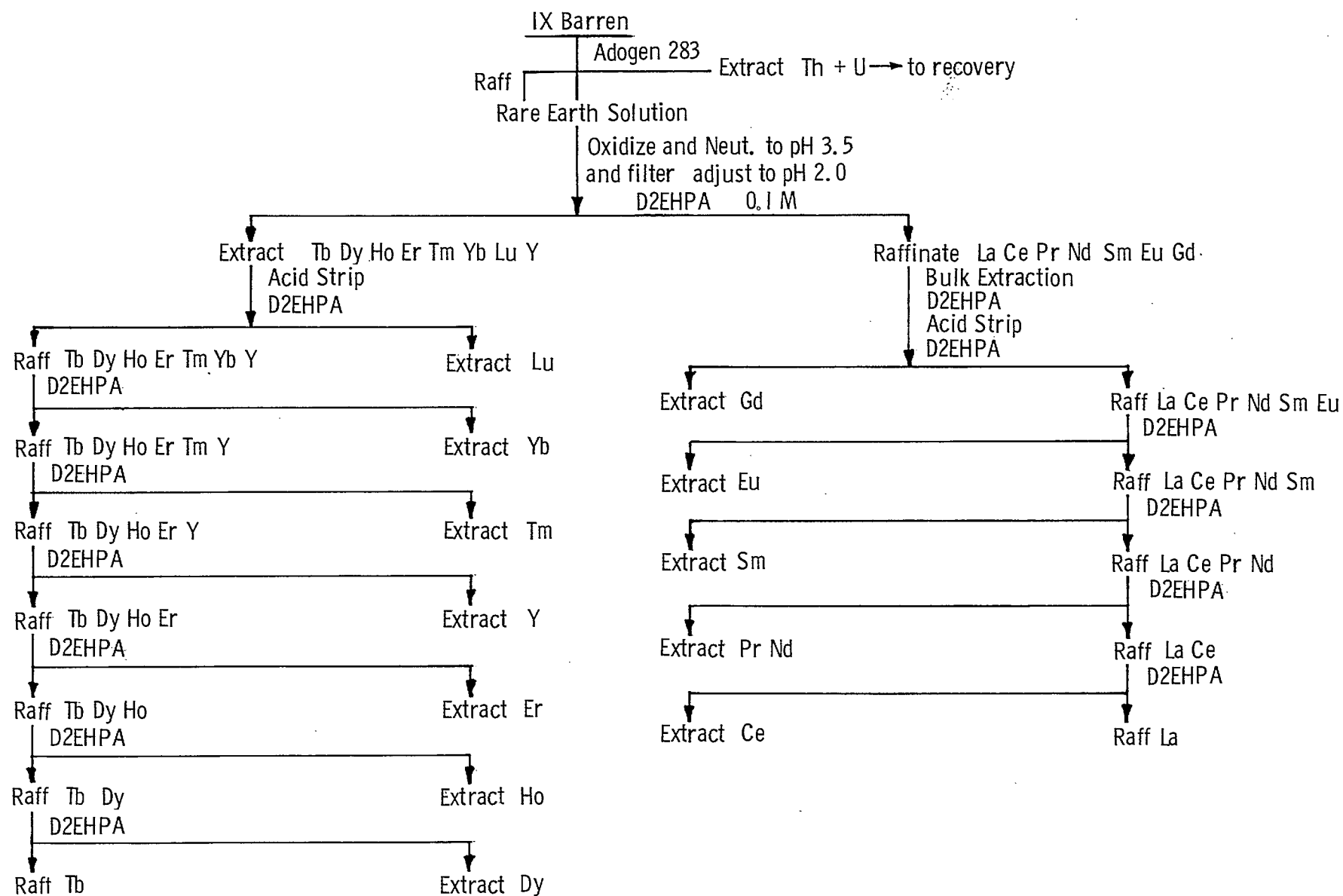


Figure 12 Proposed Flowsheet for Fractionation of Rare Earths

