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PURIFICATION OF RARE EARTHS FROM HANFORD WASTES BY SOLVENT EXTRACTION

L. A. BRAY and F. P. ROBERTS

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TABLE OF CONTENTS

I. INTRODUCTION

A process was recently developed$^{(1)}$ for separating cerium from the trivalent rare earths. This process consists of three steps:

A) coextraction of cerium and trivalent rare earths from an aqueous solution complexed with N-hydroxyethylethylenediaminetriacetic acid (HEDTA) or other suitable complexing agent (to prevent extraction of ions such as lead) at a pH above 1.5.

B) partition of cerium from the trivalent rare earths by stripping the latter into 2M HNO_3 containing persulfate and silver ions. The cerium is oxidized to cerium(IV) and remains in the organic phase.

C) re-extraction of the trivalent rare earths at a pH greater than 1.5 to remove the sulfate which is formed on decomposition of persulfate, as well as silver.

Several problems have become evident from actual experience using this process on a plant scale.

The first problem was the need to separate manganese from the rare earths in the co-extraction step. Manganese, which is present in Purex wastes from its use in the solvent clean-up, interferes seriously in the persulfate oxidation of cerium. The oxalate precipitation method used to recover rare earths from the waste did not provide for manganese removal. As a result, the crude cerium-rare earth feed contained large quantities of manganese which had to be removed prior to the persulfate step.

The second problem is that with repeated use of the solvent the partition step becomes marginal because radiolysis of the solvent generates reducing impurities which consume the persulfate and prevent oxidation of cerium to the quadrivalent state.

The third problem is the loss of trivalent rare earths during the sulfate-silver removal step. This has been found to be caused by precipitation of rare earth double sulfates when the pH is adjusted for the re-extraction step.

The results of studies designed to alleviate these problems are presented in this report.

II. SUMMARY

The co-extraction of cerium and rare earths into 0.4$\underline{M}$ di(2-ethylhexyl) phosphoric acid (D2EHPA) - 0.2$\underline{M}$ tri-n-butyl phosphate (TBP) is complicated if large quantities of manganese are present. (> 0.25 g Mn/l will interfere with the subsequent oxidation of cerium with persulfate-silver.) Although this situation may not occur in future rare earth processing, a separation scheme had to be found for processing a large batch of current feed material. Both laboratory and hot-cell experiments showed that a good separation of manganese and the rare earths is possible by controlled pH solvent extraction.

Because pH control is very difficult in the plant, unreliable results and high product losses occurred in the full-scale tests; the D2EHPA solvent extraction scheme for manganese removal proved impractical. An alternate scheme, based on sulfate precipitation was developed. This process, although complicated by the lack of a centrifuge in the plant, does not require pH control. The steps involved are:

a) Rare earth precipitation by the addition of $NaHSO_4$ to 2.5$\underline{M}$ $SO_4^=$, 15 minutes digestion at 80 C, and one hour for precipitate settling.

b) Decantation (drainage of the tank through a dip leg followed by a 1$\underline{M}$ Na_2SO_4 wash).

c) Metathesis with 3.5$\underline{M}$ NaOH (35 C).

d) Dissolution with HNO_3 - HEDTA.

e) Extraction of the rare earths into D2EHPA.

Preliminary Semiworks results indicate 85 - 95 per cent rare earth recovery through Step e) and an adequate manganese decontamination factor of 50 - 100.

The separation of cerium from trivalent rare earths with D2EHPA, is improved by the substitution of a straight chain hydrocarbon diluent for the branched chain diluent used previously. The effect of radiolysis is markedly reduced and high cerium distribution ratios are maintained.

The solubilities of both $K_2S_2O_8$ and $Na_2S_2O_8$ were measured as a function of HNO_3 concentration at 25 C. The sodium salt was found to be much more soluble than $K_2S_2O_8$ in all cases. Solubility of $K_2S_2O_8$ in 0, 1, 2 and 4$\underline{M}$ HNO_3 was 0.22, 0.26, 0.28 and 0.37$\underline{M}$; solubility of $Na_2S_2O_8$ was 2.4$\underline{M}$ in H_2O and 1.7$\underline{M}$ in 2$\underline{M}$ HNO_3. Performance of the two chemicals was identical. Use of the more soluble and less expensive $Na_2S_2O_8$ simplifies plant solution make-up and permits substantial savings.

Cerium distribution ratios of greater than 100 were obtained in 10 minutes when the aqueous phase was preoxidized 45 minutes before contact with the organic extractant. The aqueous phase was adjusted to contain 0.1$\underline{M}$ $K_2S_2O_8$, 0.02$\underline{M}$ silver, and 2$\underline{M}$ HNO_3. Lower concentrations of either silver or persulfate resulted in marginal distribution ratios.

Sodium nitrite (0.005 to 0.05$\underline{M}$ in 2$\underline{M}$ HNO_3) was shown to be effective for stripping cerium(IV) from D2EHPA. Ninety-five per cent of the cerium in the organic solvent can be stripped into 2$\underline{M}$ HNO_3 containing 0.05$\underline{M}$ $NaNO_2$ with a 5 minute contact. With 0.005$\underline{M}$ $NaNO_2$ a 25 minute contact was needed. With no added $NaNO_2$ a 220 minute contact was needed.

Addition of HEDTA to rare earth solutions containing sulfate prevents precipitation of rare earth double sulfates at pH values greater than about

2.8 while still permitting extraction and hence separation from sulfate. Distribution ratios for silver under these conditions are generally quite low.

A sugar denitration and concentration procedure was developed and successfully demonstrated to obtain a feed for further ion exchange processing.

III. RESULTS AND DISCUSSION

A. Co-extraction of Cerium and Rare Earths

The initial step in the process for separating cerium from rare earths consists of the co-extraction of cerium and rare earths. The aqueous feed is adjusted to contain HEDTA or other suitable complexing agents to prevent extraction of ions such as lead and iron into the organic solvent (0.4M D2EHPA, 0.2M TBP, NPH).

To provide aged promethium, a crude feed was obtained from stored alkaline Purex waste. This tank slurry was centrifuged in the Purex Plant. The solids were dissolved and the rare earths reprecipitated with oxalic acid. The oxalate precipitate was dissolved and served as the crude rare earth feed for subsequent processing. The analysis of this crude feed is shown in Table I.

TABLE I

CRUDE RARE EARTH FEED

Mn^{++}	15	g/l
Fe^{+++}	7.9	
Pb^{++}	10.3	
Al^{+++}	0.6	
R. E.	5.7	
Ce^{+++}	0.4	
H^{+}	5.7	

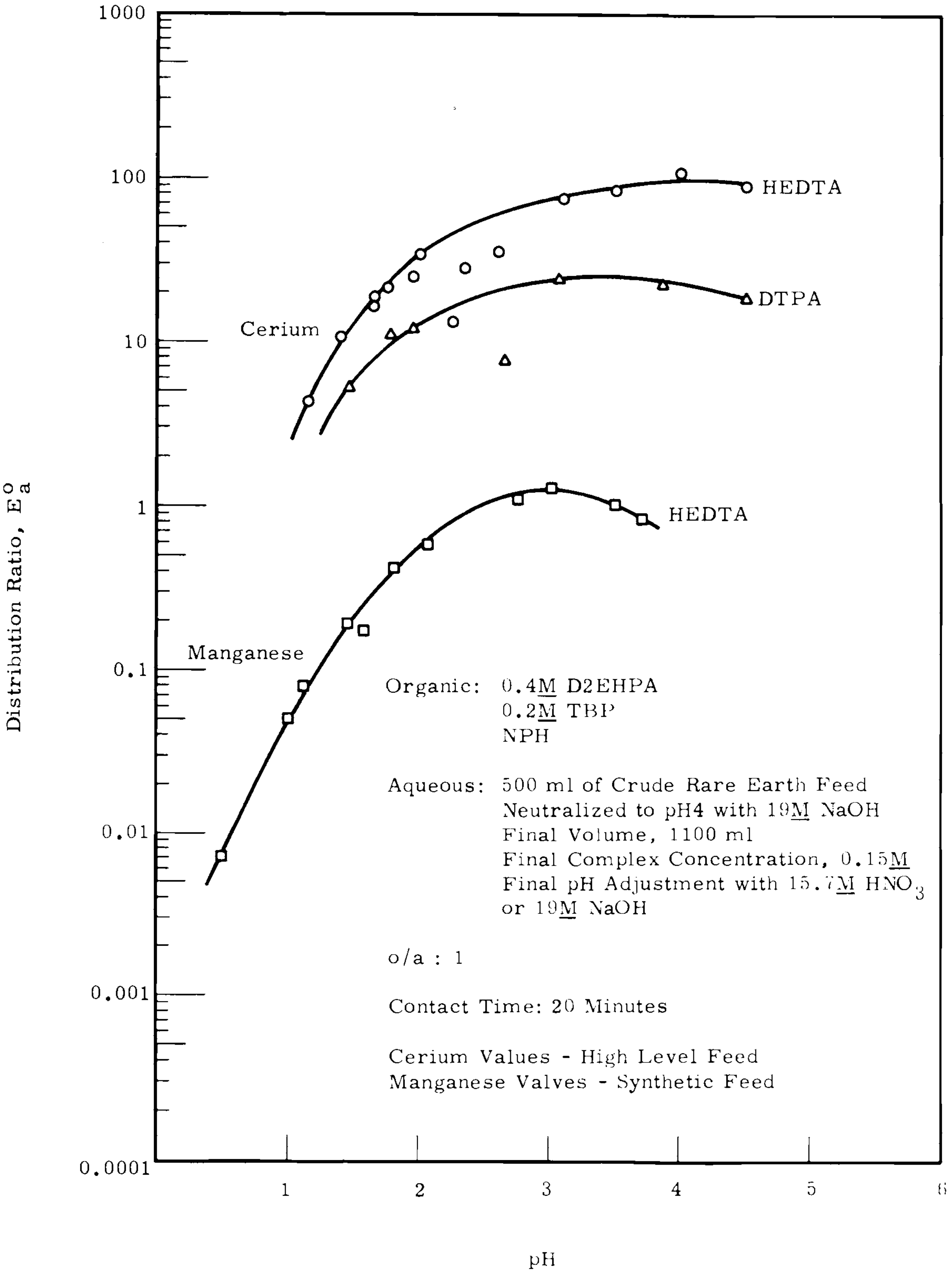
From these results, it was realized that manganese would also require separation from the rare earths to prevent interference in the persulfate step. Although manganese concentrations up to 1.2 g/l were tested through the persulfate step without affecting Ce(IV) distribution ratios, MnO_2 is precipitated out of solution and makes phase separation difficult. Manganese concentrations up to 0.25 g/l can be tolerated.

Destruction of $S_2O_8^{=}$ by reaction with Mn^{++} is not the severe problem it may seem since part of the Mn^{++} is converted to MnO_4^- which is also an effective cerium oxidant. Difficulties will be encountered only if the concentration of Mn^{++} is high enough to result in MnO_2 precipitation.

1) Separation of Manganese by Solvent Extraction

The plant has experienced difficulties in extracting the rare earths from the crude feed produced from the sludge leachings. Several initial laboratory experiments had indicated that it was possible to separate the rare earths from manganese without difficulty. A 5 gallon sample of the feed was therefore obtained for use in the High Level Radiochemical Facility. DTPA or HEDTA was added to portions of this feed, and cerium distribution ratios were determined as a function of pH. Manganese distributions under similar conditions were obtained (Figure I).

These results verified the feasibility of solvent extraction for the separation of manganese from rare earths. Other experiments indicated that the equilibrium for the cerium distribution was reached within 60 seconds. A third set of data indicated that the feed, adjusted with either DTPA or HEDTA at a pH of 3.7 - 4.0, was stable for at least 72 hours (> 90 per cent of the cerium remaining in solution). The plant



Organic: 0.4M D2EHPA
0.2M TBP
NPH

Aqueous: 500 ml of Crude Rare Earth Feed
Neutralized to pH4 with 19M NaOH
Final Volume, 1100 ml
Final Complex Concentration, 0.15M
Final pH Adjustment with 15.7M HNO_3
or 19M NaOH

o/a : 1

Contact Time: 20 Minutes

Cerium Values - High Level Feed
Manganese Valves - Synthetic Feed

FIGURE 1

CERIUM AND MANGANESE DISTRIBUTION RATIOS AS A FUNCTION OF pH AND COMPLEX ION however, experienced a gross precipitation of cerium and presumably promethium after several days' delay in processing a feed made up with DTPA, adjusted to a pH of 2.5 to 4.0. The precipitate was assumed to be a $(RE)_2(CO_3)_3$ and had to be redissolved in HNO_3 prior to further processing.

2) Separation of Manganese by Sulfate Precipitation

Because of the difficulty of pH control in the plant, the D2EHPA solvent extraction scheme for manganese removal proved impractical, and an alternate scheme was sought which could be performed in the limited plant equipment. A process, based on sulfate precipitation, was developed in the laboratory and then tested with actual feed in the High Level Radiochemical Facility. The application of a precipitation process was complicated by lack of a centrifuge in the plant, which necessitated use of multiple decantation for phase separation.

Rare earth sulfate precipitation methods are well known(2,3). Usually the solution containing cerium and rare earths is adjusted to contain ~ 1 molar sulfate and the pH is adjusted to ~ 0.5 - 1.0. It was therefore surprising to observe a precipitation when sodium bisulfate ($NaHSO_4$) was added to a synthetic waste containing ~ 6M H^+. As shown in Table II, complete cerium precipitation takes place when the final $SO_4^=$ concentration is 2.5M. In this experiment the H^+ was 5.4M. Under these conditions, manganese and iron remain in solution, thus providing an excellent separation from the rare earths without pH adjustment. The rare earth sulfate precipitate is then washed with 1M Na_2SO_4 to remove traces of manganese and converted to a hydroxide precipitate by adding 3.5M NaOH. (The sulfate associated with the precipitate converts to Na_2SO_4 and is soluble.) No digestion period at an

TABLE II

PRECIPITATION OF CERIUM - RARE EARTHS AS A FUNCTION OF SULFATE CONCENTRATION

Conditions: 50 ml of Synthetic Feed (Table I)
Add $NaHSO_4$ (5M)
Heat 80 - 90° C., 30 Minutes
Centrifuge and Sample

Cerium in Solution (%)	Manganese in Solution (%)	Sulfate Concentration (M)	Final Precipitate Volume (Ml)
23.6	90.9	0.8	3
4.2	92.8	1.4	5.5
1.6	93.8	1.9	5.5
0.7	93.5	2.2	4.5
0.3	100.0	2.5	3

elevated temperature is required for metathesis. HEDTA is then added and the slurry adjusted to a pH of 2 - 3 with HNO_3. The slurry will completely dissolve at ~ pH 7 and the rare earths will remain in solution as long as the complexant (HEDTA) is present to compete with the sulfate.

After defining the sulfate procedure in the laboratory a series of tests, using actual feed, were completed in the High Level Radiochemical Facility. The first test, using an equal volume of 5$\underline{M}$ $NaHSO_4$ to feed, precipitated 99 per cent of the cerium and carried 14 per cent of the manganese. A 1$\underline{M}$ Na_2SO_4 wash was used in subsequent tests to reduce the manganese contamination.

A second sulfate precipitation was also performed as follows:

Precipitation

1) Take 400 ml plant feed
2) Add 400 ml 5$\underline{M}$ $NaHSO_4$
3) Heat 80° C 30 minutes

Wash

1) Wash precipitate, 800 ml 1$\underline{M}$ Na_2SO_4

Metathesis and Dissolution

1) Add 600 ml 3.5$\underline{M}$ NaOH to the precipitate
2) Add 0.15 moles HEDTA
3) Adjust pH to 2.9 with 15.7$\underline{M}$ HNO_3

Solvent Extraction

1) Contact adjusted aqueous feed with 0.4$\underline{M}$ D2EHPA, 0.2$\underline{M}$ TBP, o/a = 1, final pH 2.6

Cerium - Rare Earth Partition

1) Contact loaded organic with 2M HNO_3, 0.2M $Na_2S_2O_8$, 0.02M $AgNO_3$, o/a = 1, 15 minutes.

Approximately 2 per cent of the cerium was lost in both the precipitation and washing steps with an over-all recovery of 95 per cent prior to solvent extraction. Twenty per cent of the manganese was associated with the initial sulfate precipitate, but after the sulfate wash step only 0.7 per cent remained to give a manganese decontamination factor of 140.

The extraction step gave a cerium distribution of > 100. The cerium-rare earth partition gave a cerium decontamination factor greater than 100.

Subsequent plant processing of the crude cerium-rare earth feed, using the sulfate precipitate method, has verified the laboratory results.

B. Partition of Cerium from Trivalent Rare Earths

The extraction of Ce(III) and trivalent rare earths into solvents such as D2EHPA in the pH range of 1 to 4 is well known(4). Trivalent rare earths and Ce(III) may then be removed from the organic phase by stripping with mineral acids (Figure 2). Ce(IV), however, extracts completely into D2EHPA with high extraction coefficients even in very acid solutions. This is the basis for a cerium-rare earth separation step.

For many years analytical chemists have relied on oxidizing cerium to Ce(IV) for the separation of cerium from rare earths. The application of this well-known technique to the separation of radio-cerium from the rare earths with solvents such as D2EHPA is hampered by the rapid destruction of the oxidizing agent in the extremely high radiation fields and the presence of easily oxidized materials carried over from prior process steps. This

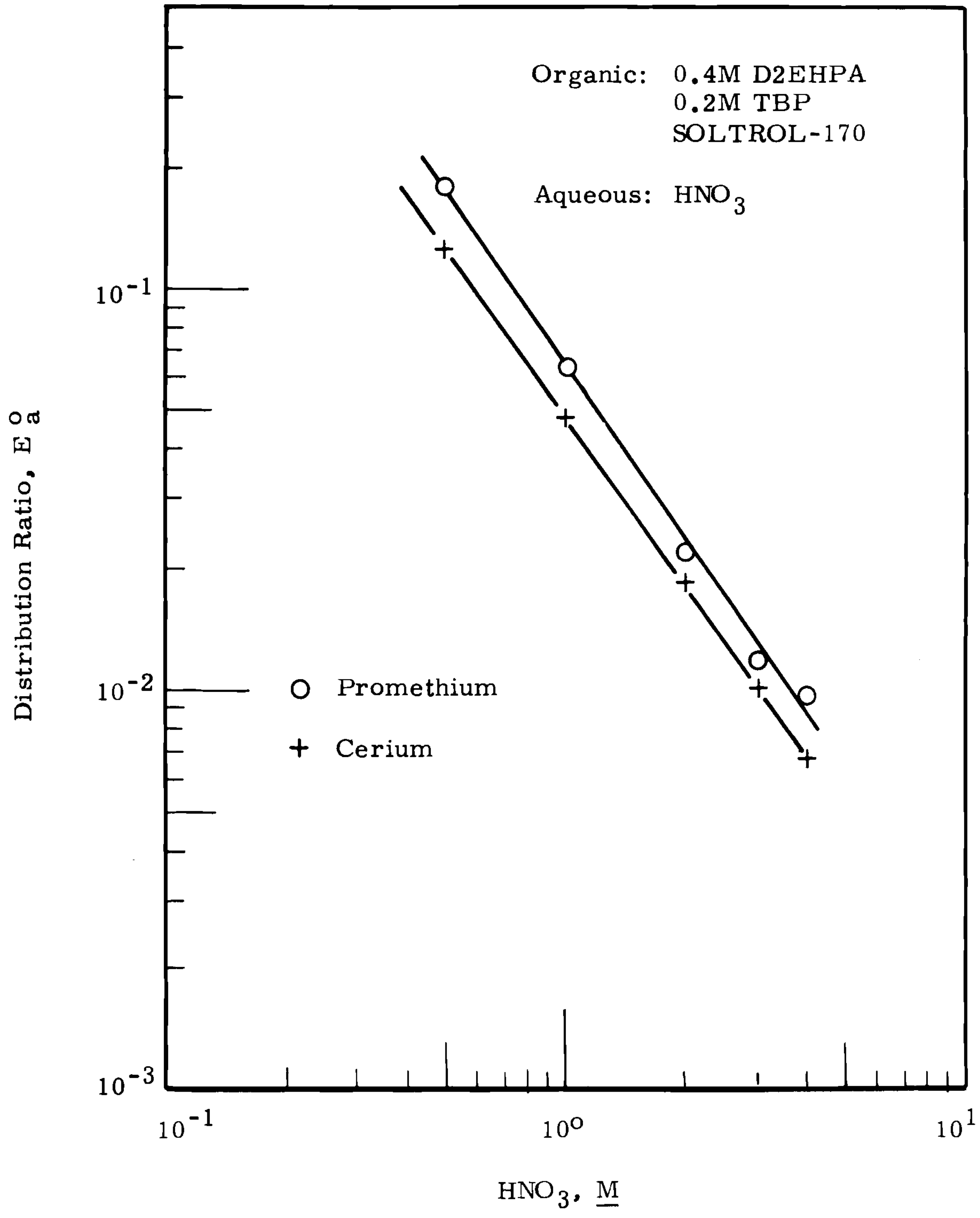


FIGURE 2

DISTRIBUTION OF Ce(III) AND PROMETHIUM AS A FUNCTION OF ACID CONCENTRATION (TRACER LEVEL) destruction cannot be duplicated in cold laboratory experiments but is assumed to be caused in part by the degradation products formed by radiolysis of the organic solvent and in part by the direct radiolysis of the oxidant itself.

Workers at ORNL have studied the use of anodic oxidation(5) and potassium permanganate(6) as methods for forming cerium(IV). They found that it was necessary in the latter process to continuously add permanganate during the batch contact to maintain the tetravalent state. A serious disadvantage of this oxidant is that solid manganese dioxide is formed and results in very difficult phase separations. Another approach to the separation of cerium from trivalent rare earths is the precipitation of cerium peroxyacetate(7, 8). This process also failed to routinely produce a satisfactory separation because of difficulties with pH control and radiolysis of the peroxide.

An oxidizing agent for use in extraction of fission product cerium must meet the following requirements:

- A sufficiently high potential to quantitatively oxidize cerium.
- Sufficiently slow kinetics so as not to react rapidly with the organic solvent.
- High radiation stability.

The persulfate ion has these properties. Unfortunately its reaction rate with cerium is so slow that at room temperature oxidation does not occur. However, addition of silver ion markedly increases the rate of cerium oxidation. Silver ion acts as a catalyst for persulfate in the oxidation of cerium. The following rate controlling step has been proposed(9)

$$S_2O_8^{=} + Ag^{+} = SO_4^{=} + \cdot SO_4^{-} + Ag^{++}$$

The sulfate radical ion $.SO_4^-$ and the Ag^{++} act as the active oxidants in this proposed mechanism. It was found in the initial investigation(1) that the reaction rate could be controlled by the concentration of silver and by the reaction temperature. As shown in Figure 3, it is essential to keep the temperature low for batch contacts to allow the cerium(IV) to be held in the organic phase long enough to permit the separation of the phases. However, when considering a solvent extraction column operation, in which residence times are in the order of 1-5 minutes, high reaction temperatures (50 - 60° C) would be advantageous.

1) Effect of Radiation on the Solvent - A series of experiments were performed in the High Level Radiochemical Facility to determine the effect of radiation on cerium extractions. These experiments were carried out by contacting an aqueous phase containing 300 curies/liter of Ce^{144}, 0.2M $K_2S_2O_8$, 0.02M $AgNO_3$, and 2M HNO_3 with an equal volume of plant solvent (0.4M D2EHPA, 0.2M TBP in SOLTROL-170) for up to 340 minutes. Samples of both phases were taken from time to time during the contact and the cerium distribution measured by the in-cell gamma spectrometer(10). The aqueous phase was then discarded and the cerium was stripped into 2M HNO_3 allowing 16 hours for the strip step. Sufficient $K_2S_2O_8$ and $AgNO_3$ were then added to the system to give concentrations of 0.2M $K_2S_2O_8$ and 0.02M $AgNO_3$ in the aqueous phase and the cerium re-extracted as before. This sequence was repeated six times to simulate repeated cycles of plant usage of the solvent. The SOLTROL-170 used in this experiment had been passed through a column of silica gel and then contacted with sulfuric acid prior to solvent make-up to insure the absence of any unsaturated hydrocarbons.

The results in Figure 4 are not entirely consistent but show a general decrease in the distribution ratio with re-use of the solvent. Also plotted

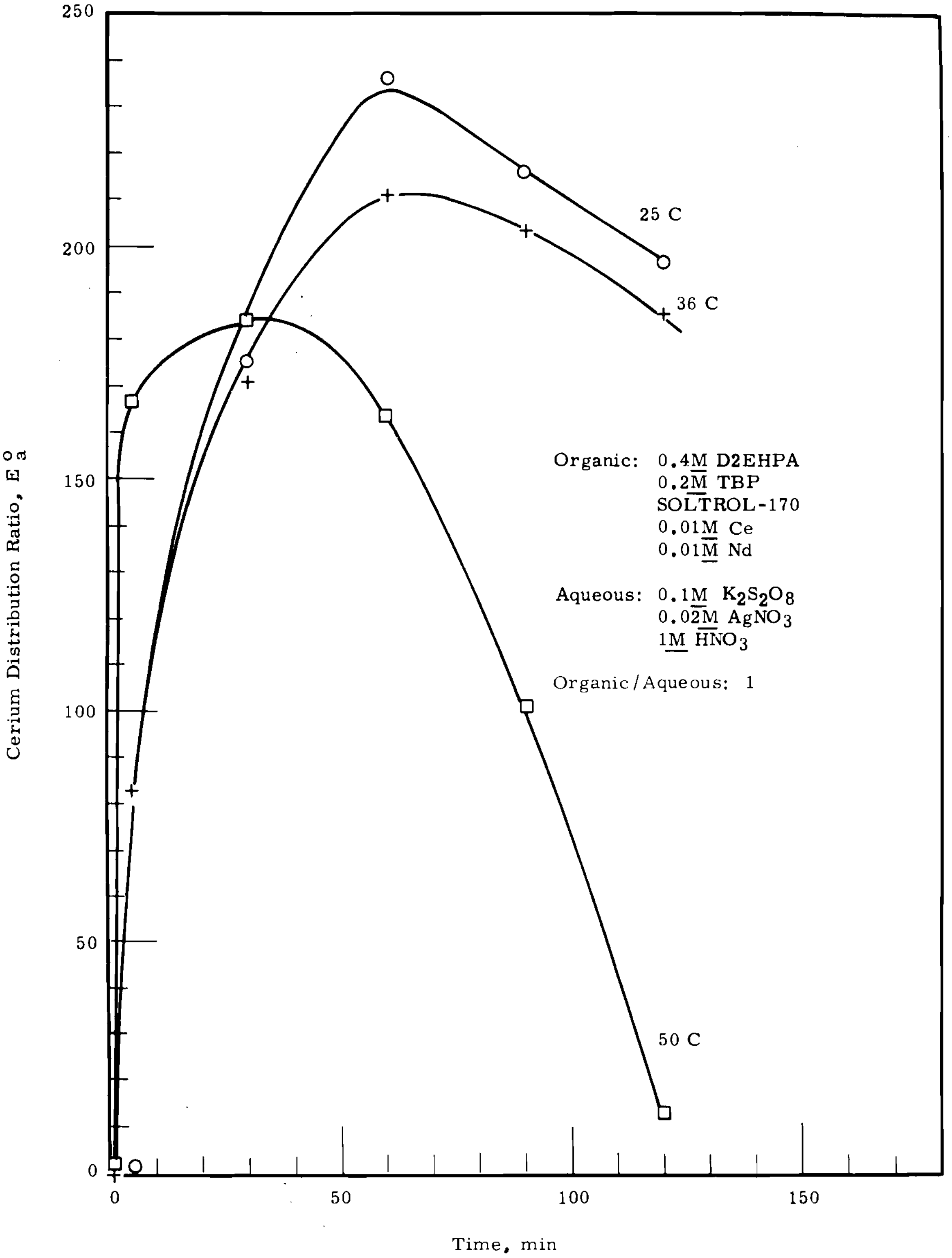


FIGURE 3

CERIUM DISTRIBUTION AS A FUNCTION OF TIME AND TEMPERATURE (TRACER LEVEL)

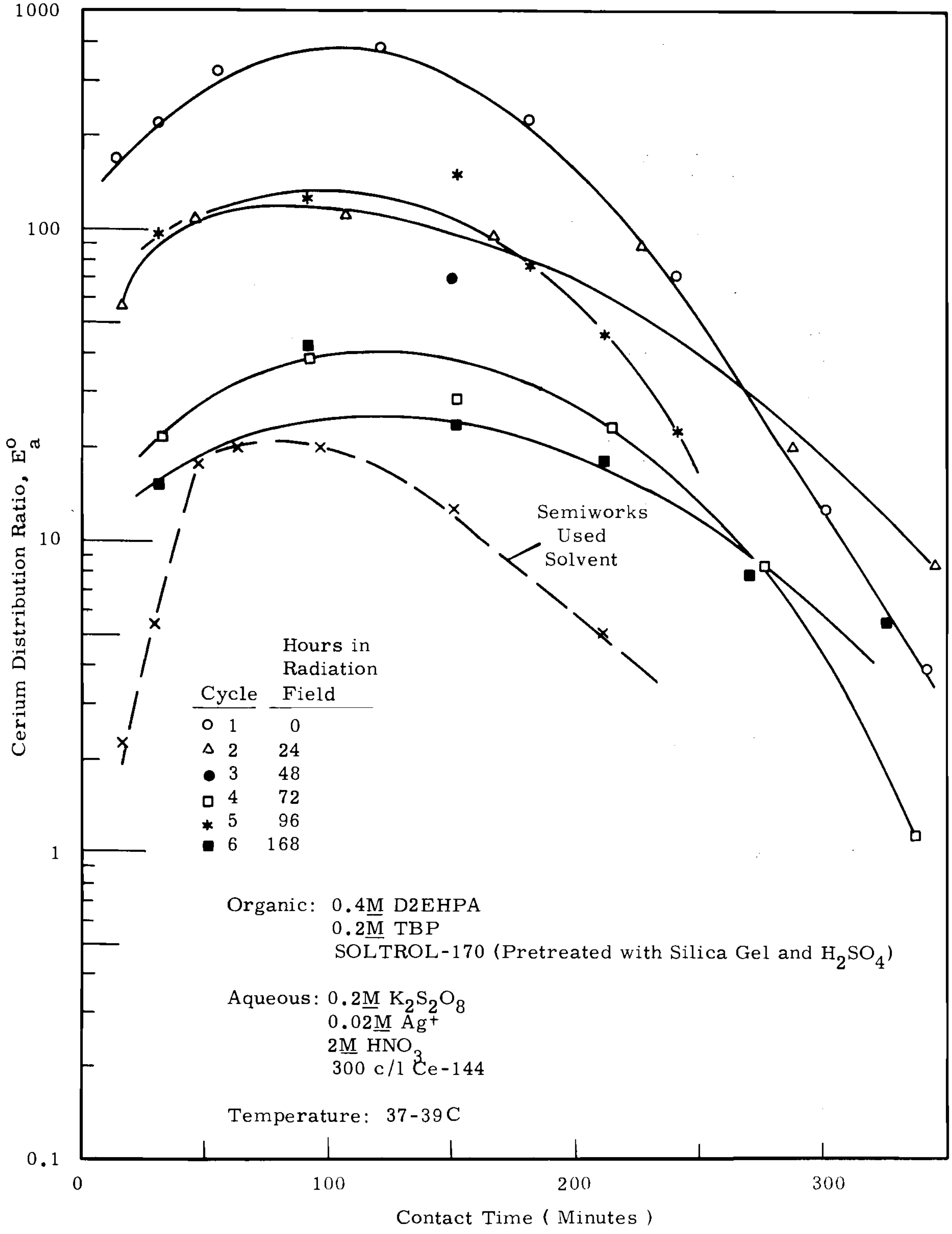


FIGURE 4

CERIUM DISTRIBUTION AS A FUNCTION OF CONTACT TIME AND SOLVENT RE-USE in this figure is a run similar to the above, but in which the solvent was "used" plant solvent. This solvent had been used for an undetermined number of strontium recovery runs and gave low distribution ratios for cerium, as was expected. Because of the pronounced decrease in cerium distribution with repeated use, it became imperative to find a more stable solvent.

E. C. Martin of this laboratory had investigated and recommended the use of a straight chain paraffin hydrocarbon in the Purex plant to reduce the fission product holdup in the organic solvent. Such a hydrocarbon is available in quantity at a reasonable cost from South Hampton Company, Houston, Texas. This diluent, referred to at Hanford as NPH (normal paraffin hydrocarbon), contains from 10 to 14 carbon atoms, and has been washed with sulfuric acid and silica gel treated prior to shipment.

Determination of cerium distribution ratios as a function of time of contact were performed using NPH as a diluent. Identical conditions were used as described above. Unfortunately sufficient cell time was not available to perform repeated cycles of extraction as before. However, to simulate these conditions the solvent was left in contact with the aqueous phase containing 300 curies/liter of cerium-144 for 150 hours and the distribution ratios measured again. The accumulated dose to the solvent would be roughly equivalent to that received by the SOLTROL-170 after six cycles. The data from these runs are plotted in Figure 5. Also shown are the runs using SOLTROL-170 for the first and sixth cycle of use for comparison. These data indicated NPH to be a superior diluent to SOLTROL-170, and its use has been adopted by the plant.

2) <u>Effect of Pre-oxidation of Cerium</u> - Several experiments were performed to determine if lower concentrations of potassium persulfate and/or silver nitrate could be used if the cerium were allowed to oxidize before

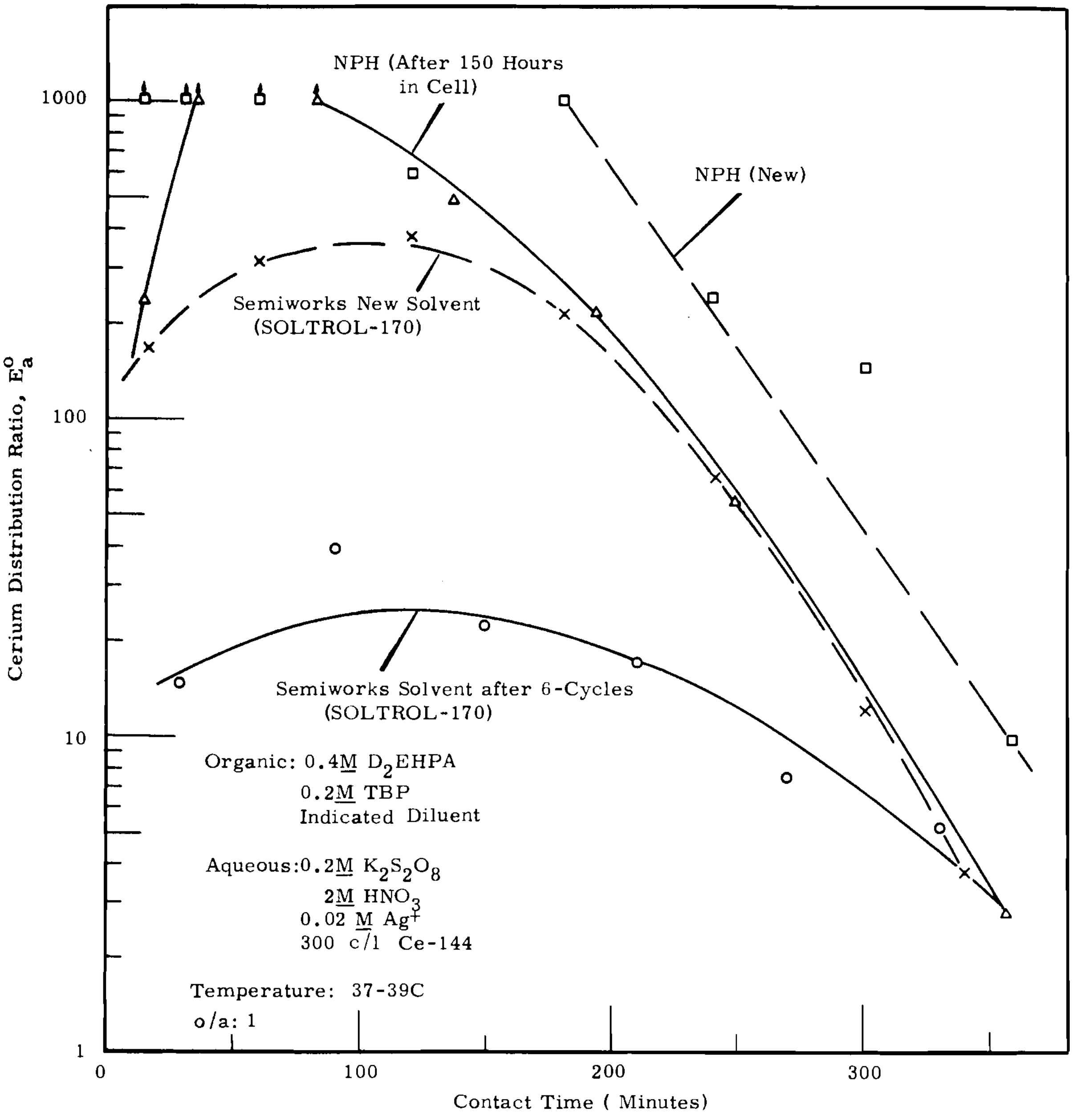


FIGURE 5

CERIUM DISTRIBUTION AS A FUNCTION OF CONTACT TIME (COMPARISON OF NPH AND SOLTROL-170 AS DILUENTS) contacting the organic phase.

In these experiments, solutions containing 300 curies/liter of Ce^{144}, 2M HNO_3, 0.1 or 0.05M $K_2S_2O_8$, and either 0.02 or 0.01M $AgNO_3$ were mixed for 45 minutes. The aqueous solution was then contacted with an equal volume of 0.4M D2EHPA, 0.2M TBP in SOLTROL-170 and sampled at intervals. The cerium distribution ratio was determined. The SOLTROL-170 was pretreated with silica gel and sulfuric acid as before. Used plant solvent was also tested.

The data obtained, as shown in Figure 6, indicate that very satisfactory cerium distribution ratios are obtained under these conditions with 0.1M potassium persulfate - 0.02M silver nitrate. Lower concentrations of either constituent produced unsatisfactory results for batch contact operations. The "used" solvent was completely unsatisfactory.

3) Solubility of Persulfate - The solubilities of both the potassium and sodium persulfate were measured and $Na_2S_2O_8$ found to be much more soluble. Solubility (at 25° C) of $K_2S_2O_8$ in 0, 1, 2 and 4M HNO_3 was 0.22, 0.26, 0.28 and 0.37M. The solubility of $Na_2S_2O_8$ was 2.4M in water and 1.7M in 2M HNO_3. Hot-cell performance of the two chemicals was identical. Use of $Na_2S_2O_8$ was accordingly recommended. Besides much lower make-up volumes and improved operating flexibility, a savings in reagent cost was also realized (~ 12.5 ¢/mole $Na_2S_2O_8$ vs 23.2 ¢/mole $K_2S_2O_8$).

4) Stripping the Ce(IV)-Loaded Solvent - After cerium(IV) is extracted into 0.4M D2EHPA - 0.2M TBP - NPH, it must be stripped out of the organic extractant within a limited time to prevent degradation of the solvent. A series of experiments was performed in the High Level Radiochemical Facility to determine the conditions required for effective stripping. Figure 7 shows that a contact time > 200 minutes is required for stripping 95 per cent of

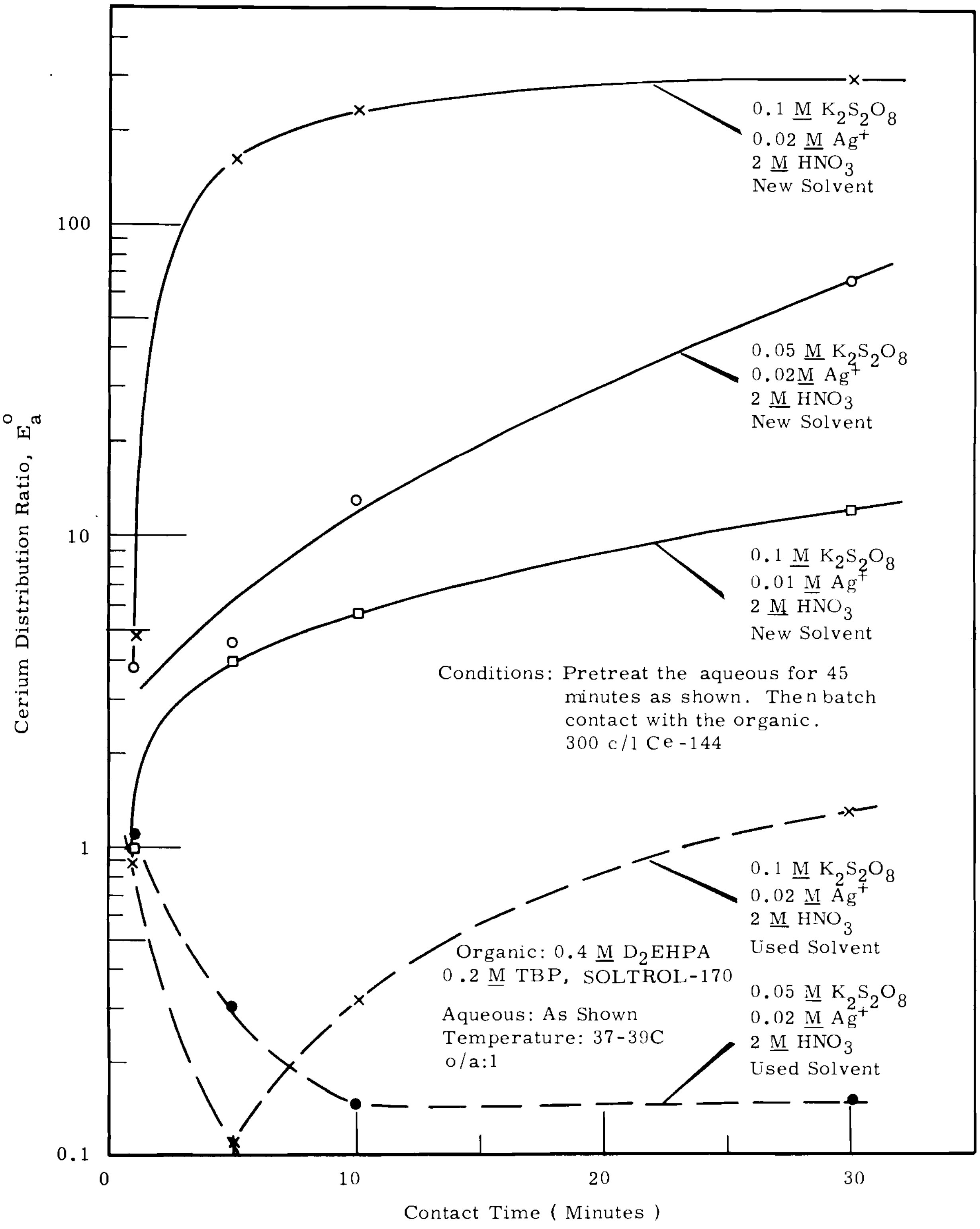


FIGURE 6

CERIUM DISTRIBUTION AS A FUNCTION OF TIME FOR DIFFERENT CONCENTRATIONS OF SILVER AND PERSULFATE

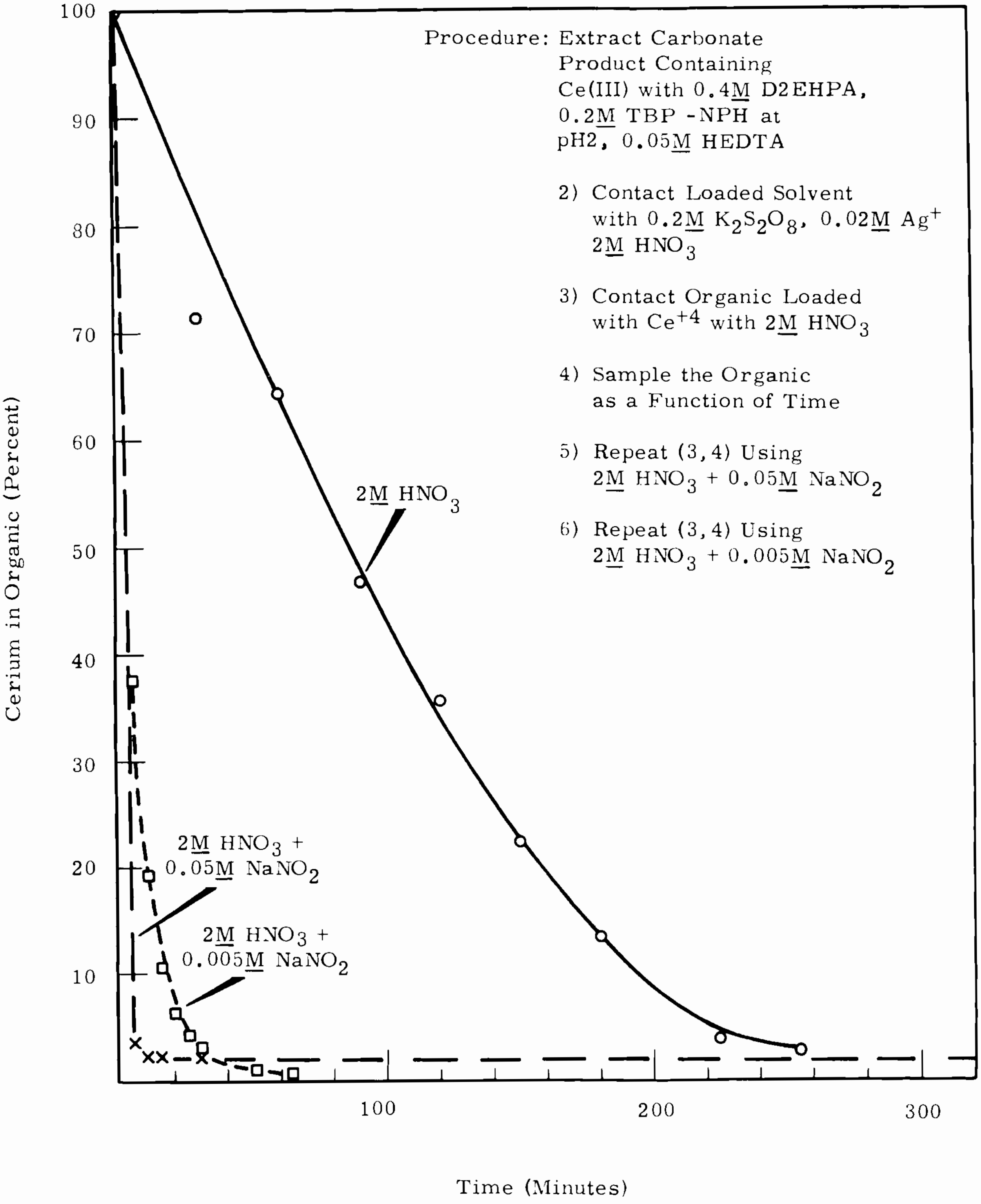


FIGURE 7

STRIPPING STUDIES FOR Ce^{+4}
(HOT CELL)

the cerium into $2\underline{M}$ HNO_3. The addition of $0.005\underline{M}$ $NaNO_2$ reduces the time to 25 minutes and $0.05\underline{M}$ $NaNO_2$ to 5 minutes. Therefore, a $2\underline{M}$ HNO_3 strip containing $0.005\underline{M}$ $NaNO_2$ was recommended for batch contacts.

The cerium free extractant should then be washed with $2\underline{M}$ HNO_3, $0.2\underline{M}$ $Na_2S_2O_8$ and $0.02\underline{M}$ $AgNO_3$ to destroy entrained NO_2^- before being reused for cerium partition steps.

C. Re-Extraction of Trivalent Rare Earths

1) Trivalent Rare Earth Losses During the Sulfate-Silver Removal Step

The undesired precipitation of rare earth double sulfates under conditions encountered in plant operation was also studied. A solution containing either $0.2\underline{M}$ or $0.4\underline{M}$ $K_2S_2O_8$, $0.02\underline{M}$ $AgNO_3$, $0.001\underline{M}$ $Ce(NO_3)_3$, $0.01\underline{M}$ $Nd(NO_3)_3$, trace amounts of Ce-144 and $2\underline{M}$ HNO_3 was heated 60 minutes at 80 C to destroy the persulfate. Ce-144 was used to trace the path of the rare earths in these experiments because of the ease of its measurement. Hydrogen peroxide was added to insure that only Ce(III) was present and that all the persulfate was converted to sulfate. The pH was then adjusted to a desired value with NaOH and the solution was digested at 40-50 C for 60 minutes and centrifuged. The fraction of rare earths remaining in the supernate was determined. The experiment was repeated with additions of citric acid or HEDTA prior to pH adjustment. The results (Figure 8) show rare earth losses by precipitation to be greater than 90 per cent at $pH \geq 1$ in the absence of complexing agents. However at a $pH > 2.8$ in the presence of $0.05\underline{M}$ citric acid or HEDTA the rare earths remain in solution with $0.4\underline{M}$ sulfate. Conditions were not found which would prevent rare earth precipitation when the solution contained $> 0.4\underline{M}$ sulfate.

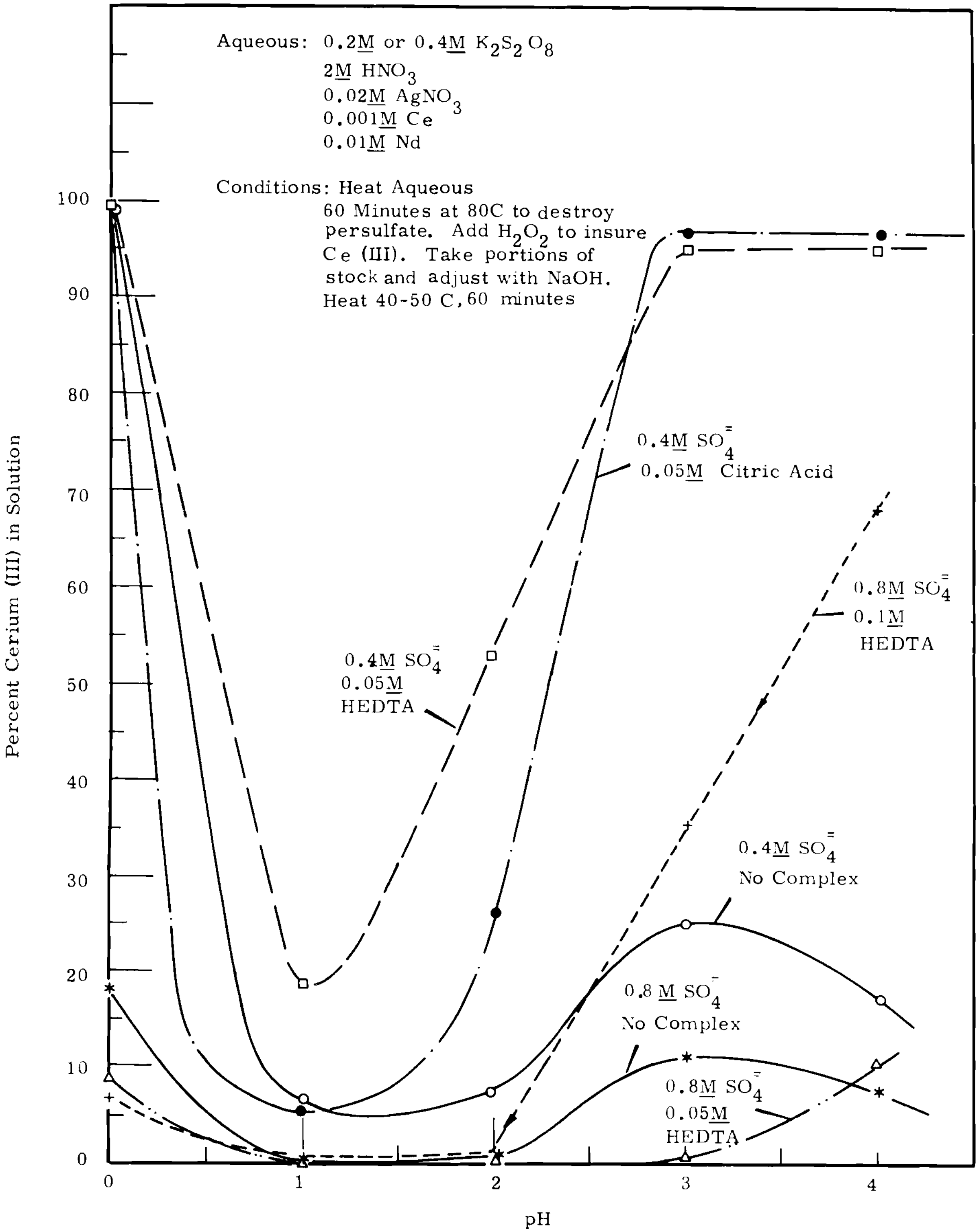


FIGURE 8

RARE EARTH SOLUBILITY IN THE PRESENCE OF VARYING CONCENTRATIONS OF SULFATE AND COMPLEXANT AS A FUNCTION OF pH

To ascertain the solvent extraction behavior of rare earths complexed with HEDTA in the presence of sulfate, solutions prepared as described above were contacted with equal volumes of 0.4M D2EHPA, 0.2M TBP, in NPH diluent and the cerium and promethium distribution ratios measured. HEDTA at 0.05M was chosen for these experiments. The initial persulfate concentration was 0.2M in every case. The total rare earth concentration was varied from 0.01 to 0.03M. The distribution ratios of silver were also measured. The results are shown in Figure 9. The data from Figures 8 and 9 indicate that a pH of 3 is nearly optimum. Part of the silver is also extracted but should not interfere in subsequent ion exchange separation of the individual rare earths.

2) Concentration and Denitration of the Rare Earth Product

After the rare earths have been re-extracted into the organic, leaving the sulfate and silver in the aqueous phase, they are stripped with 2M HNO_3. This solution is the feed for further purification by ion exchange. Because of the high acidity and large volume of this solution a concentration step is desired. Wheelwright has suggested a ratio of 0.2 mole of rare earths per mole of hydrogen ion as a desired feed condition for chromatographic purification of promethium(11). To meet this requirement, sucrose denitration(12, 13) was investigated.

A 1000 ml solution containing 2M HNO_3, 0.05M $Nd(NO_3)_3$ and 0.001M $Fe(NO_3)_3$ was concentrated and denitrated using sucrose to a final volume of 126 ml and 2.2M H^+. The conditions were as follows:

1) Take 300 ml of solution and concentrate to 100 ml (6M HNO_3).
2) Add ~ 15 ml of 2M sucrose to 700 ml of the remaining solution. Slowly concentrate this by adding it to the 100 ml in 1), keeping

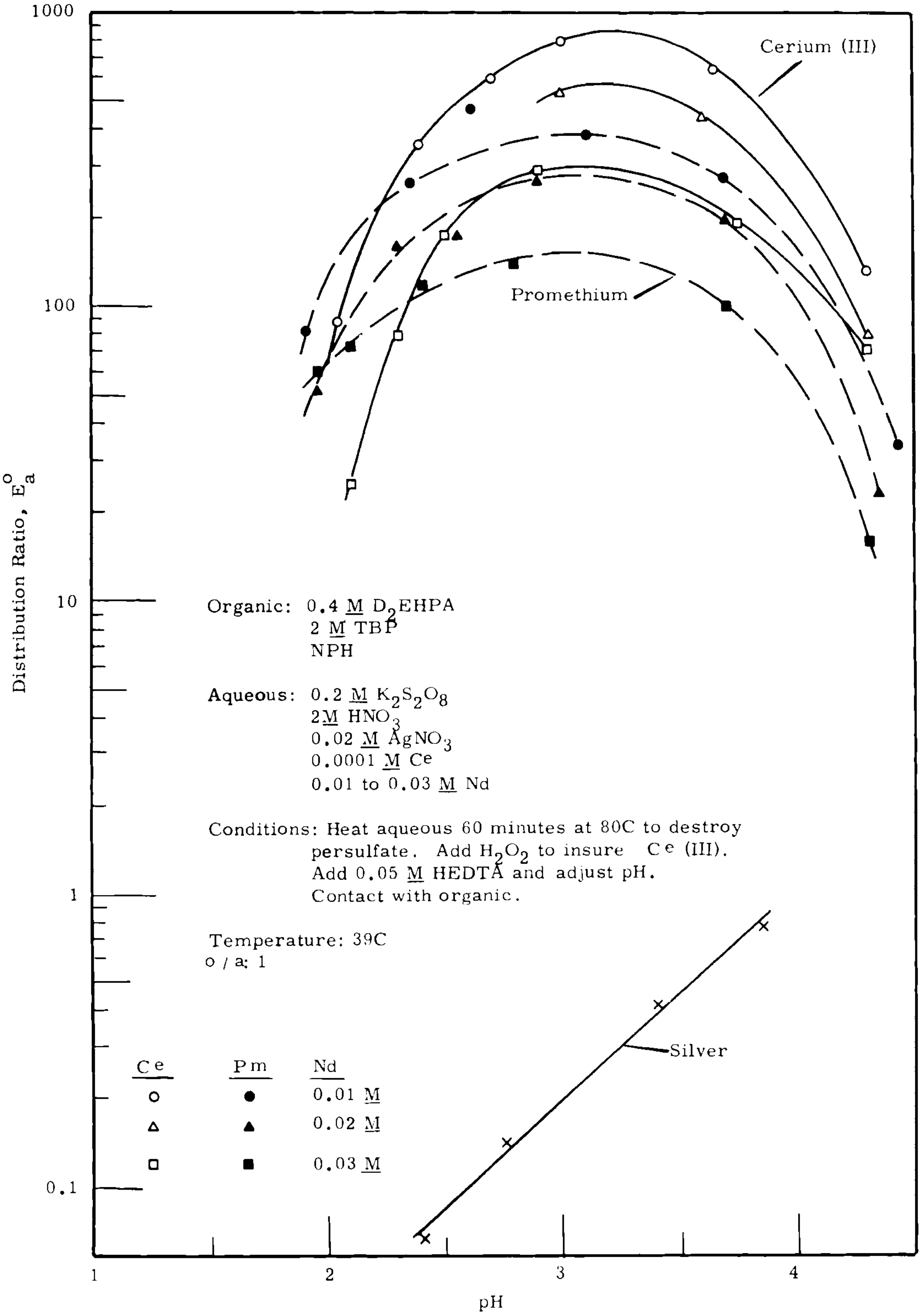


FIGURE 9

EXTRACTION OF RARE EARTHS AND SILVER FROM SULFATE SOLUTIONS CONTAINING HEDTA AS A FUNCTION OF pH the volume constant.

3) Digest the concentrated solution for 48 hours.

The volume was reduced by a factor of 8. The residual carbon, H^+, NO_3^- and Nd final concentrations were 0.3M, 2.2M, 3.2M and 0.4M respectively. The Nd to H^+ ratio was 0.18. This process was subsequently applied to an actual plant rare earth concentration-denitration with complete success.

IV. Future Rare Earth Processing

The development of a fission product cerium-rare earth separation process has been arduous. Early workers were only partially successful, mainly because of the intensive radiation fields encountered which destroyed the oxidizing agents or produced degradation products by radiolysis of the organic reagents. Varying rare earth feed sources containing high concentrations of iron, lead, manganese, sodium or other interferences have also added to the difficulties. Future source materials should be thoroughly analyzed for contaminants which might reduce the effectiveness of the oxidizing agent.

The current process consists of a batch sodium persulfate oxidation - D2EHPA extraction to separate cerium(IV) from the trivalent rare earths. A straight chain paraffin hydrocarbon (NPH) is used as the diluent for the extractant. Even with these improvements, the difficult phase separation and long process time cycles can result in high product losses and inefficient operation. A continuous process is essential for future rare earth processing.

A solvent extraction column process has been proposed. "Cold" pilot plant studies have been completed by G. L. Richardson(14), of this laboratory, to test the feasibility of such a process. The preliminary results are very favorable with cerium decontamination factors of > 135. Most of the runs have been made with the feed heated to 60 C; with the aqueous phase continuous; with a strip solution containing 2M HNO_3, 0.2M $Na_2S_2O_8$, and 0.02M $AgNO_3$; and with a feed to organic flow ratio of 5/1. The organic Ce(IV)-loaded solvent is then stripped with 0.005 - 0.05M $NaNO_2$ and 2M HNO_3. A more detailed study has been proposed for future applications and this, combined with the technology gained from the investigations now completed, should form the basis for the optimum rare earth flow sheet.

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