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**CONTINUOUS SEPARATION OF CERIUM
FROM TRIVALENT RARE EARTHS
BY PERSULFATE OXIDATION
AND D2EHPA SOLVENT EXTRACTION:
PILOT PLANT STUDIES**

G. L. RICHARDSON

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BY PERSULFATE OXIDATION AND D2EHPA SOLVENT EXTRACTION:
PILOT PLANT STUDIES

By

G. L. Richardson

Chemistry Department
Chemical Development Section

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PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON

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INTRODUCTION

Bray and Roberts recently developed a process for separating cerium from the other rare earths.^(1,2)

The process consists of:

- Coextraction of the rare earths from an aqueous fission product solution [complexed with N-hydroxyethylethylenediaminetriacetic acid (HEDTA) or other suitable complexing agent to prevent extraction of unwanted ions such as lead] into a di(2-ethylhexyl) phosphoric acid (D2EHPA) solvent solution.
- Partition of the highly radioactive cerium from the other rare earths by stripping the latter into 2M HNO_3 containing persulfate and silver ions. The cerium is oxidized to Ce(IV) and remains in the solvent phase.
- Stripping the cerium from the solvent with 2M HNO_3 containing 0.05M NaNO_2 to reduce the cerium to Ce(III).

The cerium-free rare earths are subsequently purified from sulfate and silver ions by a second D2EHPA extraction cycle.

The process was designed primarily for the production of a low-activity rare earth product from which Pm^{147} can be conveniently recovered and purified by a chromatographic ion exchange technique.⁽³⁾ The process will be conducted on an interim basis in the Strontium Semiworks⁽⁴⁾ and later on a routine basis in the Han-

ford Waste Management Program B-Plant facility.⁽⁵⁻⁷⁾

As originally developed, the process used batch contacts to transfer the rare earths to and from the solvent phase; however, it was recognized that a substantial improvement in efficiency and control could be obtained by continuous countercurrent solvent extraction. The following report describes "cold" pilot-plant pulse column studies of some of the major variables involved. The work was divided into three parts. The first studied the feasibility of accomplishing the desired cerium-rare earth separation in a pulse column simulating the geometry of the Strontiums Semiworks IB Column.⁽⁴⁾ The second used a pulse column geometry and feed composition similar to that that might be used in the B-Plant IC column⁽⁶⁾ and investigated the effect of stream compositions, flow rates, and temperature on cerium-rare earth separation. The third investigated the extraction kinetics of rare earths from an HEDTA-complexed feed, using $\text{Eu}^{152-154}$ as a tracer representative of the slower extracting rare earths.

SUMMARY

The proposed process for continuously separating cerium from the other rare earths was successfully demonstrated in a dual-purpose IC column. Satisfactory separation was achieved with 2M HNO_3 strip solutions (ICX)

containing either 0.2M persulfate with 0.02 to 0.03M silver catalyst or 0.3M persulfate with 0.0012 to 0.012M silver. The latter composition was preferred because of the lower chemical cost and a lesser sensitivity to the reducing normality of the solvent. Typical cerium contamination in the rare earth product (ICP) was less than 0.3% of that entering the column with ICX flows ranging from 10 to 20% of the solvent feed (ICF) flow. Corresponding rare earth losses in the effluent solvent (ICW) were 3% or less with a 10 ft tall stripping section.

A short scrub section, about 2 to 4 ft tall, was required to remove residual Ce(IV) from the aqueous product. The scrub flow of fresh solvent (ICS) was arbitrarily set at 20% of the solvent feed flow.

Other operating conditions contributing to high cerium separation and low rare earth losses included operating at elevated temperatures (30 to 50 °C) and using a top interface to increase the aqueous phase residence time (typically 80 to 180 min). The process was insensitive to the diluent used for the D2EHPA [normal paraffin hydrocarbon (NPH) and Soltrol-170*] and to solvent pretreatment procedures, provided that nitrous acid extracted during the cerium stripping step was destroyed by sulfamic acid before reuse of the solvent.

The adverse effect of HEDTA-complexing on rare earth extraction kinetics at pH 3.8 was overcome by operating the IA column at 50 °C with the aqueous phase continuous to

maximize the aqueous phase residence time. More than 99% of the europium was extracted under these conditions. The recovery actually exceeded that obtained in room temperature runs at low feed pH's where the rare earths were not significantly complexed by HEDTA.

EQUIPMENT

The preliminary tests (Series 1) were conducted with a 3 in. diam stainless steel pulse column equipped with sample ports at 4- to 8-in. intervals. These ports could be used as alternate feed points for the ICF. The ICX and ICS streams entered in the top and bottom disengaging sections, respectively. The remaining tests (Series 2 and 3) were conducted in a three column battery of 3-in.-diam glass pulse columns previously described in Reference (6). The three columns provided the functions of a IA column (rare earth extraction), a dual-purpose IC column [rare earth stripping and Ce(IV) re-extraction], and a IO column [Ce(IV) reduction and stripping]. The latter column was used primarily as a service column, and no special effort was made to optimize its performance.

Stainless steel nozzle plate* cartridges were used in all columns. The cartridge geometries are presented in Table I.

A 1 in. amplitude pulse was supplied to the IC and IO columns by sinusoidally driven bellows pulsers.

* Sieve plates with the holes indented by punching to form tiny jetting nozzles extending about 0.04 in. below the bottom surface of the plate.

* Phillips Petroleum Co.

TABLE I PULSE COLUMN CARTRIDGE
GEOMETRIES

	Series 1	Series 2 and 3		
	IC	IA	IC	IO
Overall Height, ft	16	10	14	9
Scrub Section Height, ft	0 to 8.5	0	4	0
Plate Spacing, in.				
Extraction (Stripping)	4	4	4	4
Scrub	4	--	2	--
Hole Diameter, in.	1/8	1/8	1/8	3/16
Percent Free Area	10	10	10	23

The IA column used an air pulser, which provided a variable pulse amplitude. Temperature control was achieved by heating the IA and IC column feed streams (IAF and ICF) and monitoring the resulting column temperatures by internal and skin thermometers.

FLWSHEET CONDITIONS

Feed solutions for the three run series were prepared to simulate IAF and/or ICF compositions that might

be used in the Strontium Semiworks and B-Plant. The Series 1 ICF was prepared by quantitatively extracting the rare earths from a concentrated aqueous solution at pH 2 to 3. The Series 2 ICF was prepared by using the IA column as a service contactor to extract rare earths from a dilute water solution. No pH adjustment was necessary since only the bottom few inches of the IA column operated at an unfavorably low pH for rare earth extraction. The IAF in the Series 3 runs simulated a lead-contaminated feed with HEDTA added to prevent lead extraction. The objective in the latter series of runs was to demonstrate conditions under which rare earths and Sr⁹⁰ could be coextracted. Detailed feed compositions are presented in Table II.

TABLE II PILOT PLANT IAF AND ICF MOLAR COMPOSITIONS

	Series 1	Series 2		Series 3	
	ICF	IAF	ICF	IAF ^(a)	ICF
Total Rare Earths ^(b)	0.0084	0.020	0.0040	0.0064	0.0062
La	0.0041	0.011	0.0022	0.0027	0.0027
Ce	0.0027	0.0055	0.0011	0.0023	0.0023
Nd	0.0010	0.0020	0.0004	0.0008	0.0008
Pr	0.0003	0.0006	0.0001	0.0002	0.0002
Sm	0.0002	0.0003	0.00007	0.0001	0.0001
Na	-----	0	-----	1.53	~0.065 ^(c)
Ca	-----	0.0027	(0.0005)	0	0
Sr	-----	0	-----	0.0012	~0.0012 ^(c)
Pb	-----	0	-----	0.0336	(0)
Fe(III)	-----	0	-----	0.0088	(0)
Nitrate	-----	0.065	-----	1.16	-----
Sulfate	-----	0	-----	0.080	-----
Na ₃ HEDTA	-----	0	-----	0.11	-----
Hydroxyacetic Acid	-----	0	-----	0.26	-----
Rare Earth Tracer	Ce-Pr ¹⁴⁴	Ce-Pr ¹⁴⁴	Ce-Pr ¹⁴⁴	Eu ¹⁵²⁻¹⁵⁴	Eu ¹⁵²⁻¹⁵⁴

(a) Portions of the IAF were adjusted to pH's of 1.8, 2.3, and 3.8.

(b) A mixture of Lindsay Chemical Co. rare earth nitrates (Code 350) and lanthanum nitrate.

(c) At IAF pH = 3.8.

Two solvents were tested in the pilot plant studies. The first, obtained from the Strontium Semiworks, used an NPH diluent (a mixture of long-chain normal paraffin hydrocarbons); the other was diluted with Soltrol-170 and had been used in previous pilot plant studies.⁽⁶⁾ Both solvents contained 0.3M D2EHPA and 0.12 to 0.16M tributyl phosphate (TBP). As described later, the solvents were given a variety of washes before use or reuse. The nominal flow rates of the IAX (IA column extractant) and ICF streams were 1 ± 0.2 liters/min; the ICS (solvent scrub stream) rate was 0.2 liters/min. These rates are compatible with Strontium Semiworks and B-Plant requirements.

The ICX stream was divided into two portions to avoid premature reduction of the persulfate by reaction with the silver catalyst. The silver was added as a concentrated solution of AgNO_3 at a flow rate of 0.6 to 6 ml/min. The remainder of the ICX contained 2M HNO_3 and nominally 0.2 to 0.4M persulfate added variously as the potassium, ammonium, and sodium salts. Stability studies, to be described later, indicated that actual persulfate concentrations entering the IC column were 15 to 25% lower than the make-up values. Combined ICX flow rates ranged from 70 to 230 ml/min.

OPERATING PROCEDURE

The IC column runs normally lasted about 5 to 6 hr, long enough to allow about two to three displacements of the continuous phase. Several of the runs, however, were terminated as soon as the cerium loss trends were clearly

established to conserve feed and times. The approach to steady-state was monitored by counting effluent and intermediate samples while the run was still in progress. (The ICP samples were recounted later after Pr^{144} decay.) Successful runs in the glass IC column were also visually marked by rather vivid color changes; the solvent picked up the characteristic yellow color of Ce(IV) and the aqueous phase turned various shades of amber, orange, and rose, apparently produced by higher silver valences and accentuated in some cases by the presence of trace quantities of manganese in the solvent.

Pulsing conditions were set to give tight, efficient dispersions in the stripping section. The corresponding dispersion in the scrub section (Series 2 runs) was usually quite loose but composed of very fine droplets. Flooding, when it occurred, started near the top of the column.

RESULTS AND DISCUSSION

IC Column Studies

The assumed mechanism for the separation of cerium from the other rare earths in a countercurrent solvent extraction column involves the following steps:

- (1) The rare earths, including cerium, are stripped from the solvent by the 2M HNO_3 in the ICX (fast).
- (2) The cerium is oxidized in the aqueous phase to Ce(IV) by silver-catalyzed persulfate (relatively slow).
- (3) The Ce(IV) is re-extracted into the solvent phase

(relatively fast).

- (4) The extracted Ce(IV) is reduced by the solvent to Ce(III) in an undesired side reaction (slow).

Factors that should improve the separation include:

- Using a long aqueous phase residence time (low ICX for rate and aqueous-continuous operation) to provide adequate time for cerium oxidation
- Using a short solvent phase residence time to minimize Ce(IV) reduction by the solvent
- Adding a scrub section below the ICF feed point to recover that small fraction of cerium that will be pulled below the feed point before it can be oxidized and re-extracted
- Operating the system at an elevated temperature to improve the kinetics of mass transfer and cerium oxidation.

These premises proved correct in the early runs and were used to set the conditions of the succeeding runs.

The results discussed in the following sections were obtained in both Series 1 and Series 2 runs. Detailed operating conditions and results of these runs are presented in Tables A-I and A-II in the Appendix.

Effect of Scrub Section Height

The effect of varying the scrub section height on cerium separation was investigated in Series 1. The results, summarized in Table III, show that a scrub section height of 2 ft was generally adequate to achieve the goal of extracting over 95% of the cerium. The results also show that 97 to 99% of the rare earths were stripped from the feed at 50 °C with stripping section heights of 7.5 to 10 ft. The present Strontium Semi-works IB column has a cartridge height of 16 ft, and the overall

TABLE III EFFECT OF SCRUB SECTION HEIGHT ON CERIUM SEPARATION

Temperature, °C	Scrub Section Height, ft	Extraction Section Height, ft	Cerium in ICP, %	Trivalent Rare Earths in ICW, (a)%
25	0	16	31	----
50	0	16	18	----
50	1.0 ^(b)	14.2	≤7.1	----
50	1.3 ^(b)	10.8	1.2	----
50	1.8	14.2	≤8.5	----
50	2.0 ^(b)	7.5	0.4	----
50	2.5	13.5	≤3.7	0.53
50	4.0 ^(c)	10.0	≤1.7	0.55, 2.2
50	5.2	10.8	0.2	----
50	8.5	7.5	≤0.5	1.1

(a) Separate runs using Ce(III) tracer; no silver or persulfate in ICX

(b) Based on intermediate scrub section samples

(c) From Series 2 runs using similar operating conditions

height available for the IC column cartridge in B-Plant is 14 ft. Thus, a 4 ft scrub section was considered to be near optimum for both columns, leaving 10 to 12 ft of the available cartridge height for the rare earth stripping section.

Effect of Interface Position

Moving the interface from the top of the column to the bottom increased the cerium loss to the ICP from $\leq 3.7\%$ to 79% of the entering cerium. This result demonstrated that long aqueous phase residence times are required for quantitative cerium oxidation and re-extraction, since the immediate effect of the move was to decrease the aqueous phase residence time from 120 to 17 min. (A converse argument can also be made that the long solvent residence time obtained with the bottom interface favored the reduction of extracted Ce(IV) by the solvent.)

Effect of ICX Flow Rate

The ICX flow rate also affects the aqueous phase residence time, but rate variations over the range of 90 to 230 ml/min (aqueous residence times of

80 to 200 min) did not appear to affect the cerium separation performance. The effect was unexpected but may merely reflect the lack of sufficient runs to properly define the effect. Certainly, under some conditions, a high aqueous rate would not provide enough residence time for complete cerium oxidation; and an unusually low aqueous rate might not only permit destruction of the persulfate before it reached the feed point but also be inadequate to strip all of the trivalent rare earths from the ICF.

From the equilibrium data of Bray and Roberts,⁽¹⁾ the lower limit for aqueous-to-organic flow ratios (A/O) still providing good cerium and promethium stripping should be about 0.1. Results of tests made in the current series of runs (summarized in Table IV) agree with this conclusion. The flowsheet was adjusted as indicated to permit Ce¹⁴⁴ tracer to be used to follow the trivalent rare earth behavior. Sulfuric acid, added to simulate the effect of persulfate decomposition, appeared to lower the rare earth losses.

TABLE IV EFFECT OF TEMPERATURE AND ICX FLOW RATE ON RARE EARTH STRIPPING

(ICX = 2M HNO₃, 0 to 0.094M H₂SO₄;
Stripping Section Height = 10 ft)

ICX Flow Rate, ml/min	A/O, ICX/(ICF+ICS)	Temperature, °C	H ₂ SO ₄ in ICX, M	Cerium in ICW, (a) %
71	0.057	54	0 ^(b)	7.3
73	0.058	50	0.082	2.2
73	0.058	30	0.082	3.1
110	0.090	51	0.094	0.55
110	0.090	41	0.094	≥ 0.61

(a) Ce(III) used to follow rare earth behavior

(b) 0.1M persulfate in ICX: no silver added.

Effect of Silver and Persulfate Concentrations

The observed rate law for the silver-catalyzed persulfate oxidation of many reducing agents, including cerous ion and water, is

$$-d[S_2O_8^{=}] / dt = k_2 [S_2O_8^{=}] [Ag^+].$$

The rate at any instant is proportional to the persulfate and silver ion concentrations and independent of the reducing ion concentration.⁽⁸⁾ Since the silver ion concentration for a given ICX composition remains constant, the rate law in effect corresponds to a first order reaction in which the half-life of the persulfate ion is inversely proportional to the silver ion concentration:

$$t_{1/2} = \frac{0.693}{k_2 [Ag^+]}$$

Most of the persulfate used up in the column will be lost by side reactions with water, solvent, and solution impurities; hence it is important to use low silver concentrations to increase the persulfate life and to maintain the desired reaction rate by starting with high persulfate concentrations. In the present application, the maximum persulfate concentration will be restricted by the stability of the resulting rare earth sulfates, as discussed under "ICP Solution Stability," page 9.

The validity of the above analysis was confirmed by the pilot plant results shown in Figure 1, where the amount of cerium left in the rare earth product is plotted as a function of silver and persulfate concentrations in the ICX. (The data for the

FIGURE 1. EFFECT OF SILVER AND PERSULFATE CONCENTRATION ON CERIUM LOSS
(Scrub Section Ht = 4 to 5 ft. Aqueous Residence Time = 80 to 235 min.)

full test range of ICX flow rates was included in the absence of any definite effect of such rates on cerium behavior.) The data show that optimum performance was obtained at 0.3M persulfate concentration with as little as 0.0012M Ag^+ present. Acceptable cerium losses were also obtained at 50 °C with 0.18M persulfate and 0.02 to 0.03M silver; however, the losses appeared to be quite sensitive to the silver concentration: high losses at 0.04M silver were attributed to premature persulfate destruction, while high losses at 0.01M silver were tentatively attributed to an inadequate oxidation rate. Runs with 0.1M persulfate or less were completely unsuccessful.

Effect of Temperature

The reaction rate of persulfate ion is highly dependent on temperature. For example, the rate constants for the thermal decomposition of acidic persulfate solutions increase three to four fold with each 10 °C rise in temperature.⁽⁸⁾ The poor performance observed at 40 °C using 0.18M persulfate (illustrated in Figure 1) can thus be explained as an adverse effect of low temperature on the cerium oxidation rate. This effect could be overcome either by increasing the temperature to 50 °C or by increasing the silver concentration to about 0.04M. The temperature effect at 0.3M persulfate was much less pronounced, and low cerium losses were obtained at temperatures ranging from 30 to 53 °C.

The data presented in Table IV show that rare earth losses were reduced about one-third by increasing

the column temperature from 30 to 50 °C. A similar effect was also reported in Reference (6).

Effect of Diluent and Solvent Pretreatment

Comparable performance was obtained with solvents containing either Soltrol-170 or NPH as diluents. Bray and Roberts, however, have shown that Ce(IV) is more stable in NPH solvent than in Soltrol solvents under radiation and have recommended that NPH be used as the diluent when extracting Ce^{144} .

A qualitative pilot plant test showed that small amounts of Soltrol-170 degradation products could be tolerated in the solvent without adverse effects. Approximately 1.5 liters of Soltrol-based solvent was degraded by digesting it for 4 hr at 80 to 90 °C in contact with nitrite-saturated 6M HNO_3 . The nitrite was then destroyed by sulfamic acid and the solvent washed with 6M NaOH. Both the wash and the degraded solvent were added to about 300 liters of solvent during Run 29 without increasing cerium losses to the ICP.

Several solvent washing procedures were tested during the pilot plant program, but the only one that appeared to be essential was a sulfamic acid treatment to destroy nitrous acid remaining from the standard HNO_3 - NaNO_2 cerium-removal step. About 0.02 to 0.04 g-moles of sulfamic acid per liter of solvent (added as a concentrated solution in dilute HNO_3) proved sufficient. No attempt was made to decant the small amount of associated aqueous

phase before using the treated solvent.

The solvent used in the Series 1 runs was washed with ICX (2M HNO₃, 0.02M AgNO₃, 0.2M K₂S₂O₈) before use to assure the absence of reducing impurities. There were no apparent ill effects when this wash was discontinued.

Schulz has reported that Ce(IV) distribution ratios were lowered by solvents washed in basic solutions.⁽⁹⁾ This phenomenon was tentatively explained by assuming that nitro-paraffin degradation products were converted to the more reactive enol form by the basic wash. Several such washes ^{were} ~~was~~ tested in the current study, however, without affecting the cerium performance. The solvent was used as IAX and ICS directly after the following washes shown in Table V were made. (Successive washes are listed in order.)

Third-phase formation was observed with the NPH solvent during basic wash studies whenever the equilibrium sodium concentration in the aqueous

phase was less than 1.8 to 2M. This was about three fold more sodium than required to prevent third-phase formation with Soltrol-170 diluent⁽⁶⁾ and may indicate a considerably lower solubility for the sodium salt of D2EHPA in straight-chain hydrocarbon diluents.

ICP Solution Stability

Precipitates found in several rare earth product samples upon standing were tentatively identified as the double sulfate salts of sodium or potassium and rare earths. The sulfate was produced from persulfate decomposition by the overall reaction:

Apparent threshold conditions, determined from the pilot plant runs and laboratory studies, are shown in Table VI.

The data indicate that rare earths are much more stable in sulfate solutions derived from ammonium persulfate than in the corresponding sodium

TABLE V BASIC SOLVENT WASH PROCEDURES
(Organic/aqueous volume ratios = 3; contact time = 0.5 to 1 hr)

Diluent	Wash Composition (a)	Runs in which Washed Solvents were used
NPH	3.5M NaOH 2M HNO ₃ - 0.2M KMnO ₄ ; 50 °C (b) H ₂ O	13a, 13b, 14a
NPH	2.5M NaOH-0.25M Na ₂ CO ₃ -0.2M tartaric acid 2M HNO ₃	22, 23a, 23b
Soltrol-170	3M NaOH-0.2M tartaric acid 2M HNO ₃	27 through 29b

(a) Before solvent neutralization. Na⁺ and H⁺ concentrations were lowered about 1M by exchange with the solvent.

(b) 0.5M oxalic acid added after 1 hr to destroy the excess permanganate and MnO₂.

TABLE VI THRESHOLD CONDITIONS FOR RARE EARTH PRECIPITATION IN THE ICP
(All solutions contain $2M$ HNO_3 and 0 to $0.03M$ $AgNO_3$.)

Pilot Plant Runs				
Run ^(a)	Persulfate Cation	$SO_4^{=}$, M ^(b)	Rare Earths, M	Appearance of ICP Samples
21	NH_4^+	0.8	0.050	Clear
27	Na^+	0.8	0.026	Thin layer of precipitate cake ^(d)
17b	K^+	0.4	0.032	Clear
10b	K^+	0.4	0.058	Few pale yellow crystals
Laboratory Studies ^(c)				
--	NH_4^+	0.78	0.03	Clear
--	NH_4^+	0.72	0.10	Clear
--	Na^+	0.58	0.03	A few white precipitate flakes
--	Na^+	0.78	0.005	Clear
--	Na^+	0.78	0.01	Trace of white precipitate
--	Na^+	0.78	0.02	A few white precipitate flakes
--	Na^+	0.78	0.03	Thin white precipitate layer
--	K^{+1}	0.38	0.057	Clear
--	K^{+1}	0.58	0.03	Clear
--	K^{+1}	0.78	0.03	A few white crystals

(a) Representative runs

(b) Assuming complete reduction of the persulfate; the sulfate and persulfate-cation concentrations were identical.

(c) Simplified system with sulfate added as H_2SO_4 ; lanthanum substituted for rare earth mixture.

(d) A similar precipitate formed as a brownish-gray film on the column wall and plates.

or potassium solutions and that the potassium system is slightly more stable than the sodium. Unfortunately, the potassium persulfate concentration at 25 °C is limited to $0.28M$ by its solubility in $2M$ HNO_3 ,⁽²⁾ and the use of ammonium salts in separations plants is avoided whenever possible because of the potential for pluggage of the off-gas filters by the deposition of ammonium nitrate solids.

Gross precipitation occurred in the IC column during the Series 3 runs in sufficient quantity to plug the ICF

line at the inlet to the column and to preclude obtaining any meaningful IC column data during that series. A spectrographic analysis indicated that the precipitate was "strong" in sodium, lanthanum, and strontium and moderate-to-strong in lead and silver. These results strongly suggest that sulfate precipitates were formed as a combined result of aqueous entrainment from the IA column and partial neutralization of the HNO_3 in the IC column by exchange with extracted sodium in the ICF. The addition of scrub column to

treat the solvent product from the IA column (employing a low pH scrub solution to remove sodium) would have alleviated the problem.

Persulfate Solution Stability

The decomposition of uncatalyzed persulfate ion in $2M$ HNO_3 followed a first-order rate law with a half-life of 11 to 12 days when stored at room temperature in either glass bottles or stainless steel tanks. The results, plotted in Figure 2, indicated that the decomposition rate was independent of the persulfate cation. The rate constant calculated from these data was $4 \times 10^{-5} \text{ min}^{-1}$, agreeing reasonably well with published results for similar conditions.⁽⁸⁾

The persulfate stability study also revealed that several of the freshly

prepared silver-free ICX solutions had only 75 to 85% of the expected persulfate concentration. The loss probably occurred when hot, distilled water was used for the make-up.

Estimates of the persulfate concentrations actually entering the IC column are included in Tables A-I and A-II. These estimates may be slightly in error in some of the early runs because of an inadequate history of the ICX make-ups.

IO Column Studies

The ICW from most of the Series 2 runs was routed to the IO column to remove the cerium by contact with an aqueous solution of $0.1M$ $NaNO_2$ in $2M$ HNO_3 . The operation demonstrated that continuous reduction of the cerium was feasible but that the IO

FIGURE 2. PERSULFATE STABILITY IN SILVER-FREE ICX
(ca. 22 °C)

column was too short to permit quantitative cerium stripping. Typical cerium losses in the effluent solvent leaving the 9 ft tall column ranged from 11 to 18% (bottom interface, A/O flow ratio = 0.4) to 50 to 70% (top interface, A/O = 0.2). The higher losses with top interface were probably due to the short solvent residence time (about 2.5 min versus 10 min with the interface at the bottom). In either case, most of the remaining cerium in the solvent was removed by a batch wash with 2M HNO_3 , indicating complete reduction of cerium to Ce(III) .

IA Column Studies

The Series 3 runs were made to study the kinetics of rare earth extraction from an HEDTA-complexed feed. Bray⁽¹⁰⁾ has shown that HEDTA decreases the rate of rare earth extraction as well as the magnitude of the distribution ratios. The rate reduction was negligible at low pH's but became quite pronounced at pH's above 2.5. The rate of extraction decreased with increasing atomic number with $\text{Ce} > \text{Pm} > \text{Eu}$; thus, a $\text{Eu}^{152-154}$ tracer was used in the pilot plant runs to assure applicability of the results to the

extraction of promethium in the Strontium Semiworks.

The variables investigated were feed pH, interface position, and temperature. The synthetic feed composition was typical of a Strontium Semiworks feed after lead sulfate treatment to remove sulfate-soluble cations.⁽²⁾ Detailed results are presented in Table A-III in the Appendix.

Effect of Feed pH

The europium loss was highly dependent on the feed pH, increasing by a factor of 17 as the pH was increased from 1.8 to 3.8. A summary of the results of room temperature, bottom interface runs is shown in Table VII.

Laboratory kinetic studies made with the same feeds gave comparable extraction results.⁽¹⁰⁾ For example, 99% of the europium was extracted within 2 min at pH 2.3 while only 63% was extracted at pH 3.8. In the latter case, the europium extraction was increased to 96% with a 5 min contact.

The stability of the column was also affected by the pH, with lower pH's favoring increased stability.

TABLE VII EFFECT OF FEED pH ON EUROPIUM EXTRACTION
(Bottom interface; 25 °C; A/O = 1)

pH	Amplitude times Frequency, in./min ^(a)	Aqueous Residence Time, min	Europium in IAW, %
1.8 ^(b)	45	2.7	≤2.1
2.4	32	2.6	3.7
3.8	18	2.5	36

(a) Near maximum stable pulsing conditons

(b) A white precipitate, apparently lead and strontium sulfates, formed on standing.

Effect of Temperature and Interface Position

The increased aqueous-phase residence time obtained by moving the interface from the bottom of the column to the top lowered the europium loss by three fold at pH 3.8 and 25 °C. A still greater factor of improvement was obtained by heating the column to 50 °C, as shown in Table VIII. The europium loss of 0.39% at optimum operating conditions indicated a transfer unit height (HTU_{OR}) of 1.8 ft, about as low as reported for the D2EHPA extraction of strontium and cerium under less severe complexing conditions⁽⁶⁾ and approaching the 1.2 to 1.4 ft cerium HTU's observed during Series 2 1A column service runs with uncomplexed feed.

STRONTIUM SEMIWORKS PROCESS DEMONSTRATION

A satisfactory demonstration of the continuous persulfate process was recently completed in the Strontium Semiworks by the Chemical Processing Department of the General Electric Company.⁽¹¹⁾ The equilibrium loss of promethium in the cerium product (ICW) was 1% and that for cerium in the promethium-rare earth product (ICP) was less than 1%. The respective cerium and promethium equilibrium losses to the IAW were 1 and 4%. The overall

cerium and promethium losses were somewhat higher than this because of deliberate process upsets and the usual start-up and shut-down losses. A total of 150 kCi of Pm^{147} were recovered from an input of 170 kCi and 860 kCi of Ce^{144} were recovered from an input of 908 kCi.

Both the IA and IC columns were dual-purpose columns. The IA column contained a 15 ft tall scrub section above a 10 ft tall extraction section; the IC column contained a 10 ft tall stripping section above a 6 ft tall scrub section. The columns were operated at 35 to 40 °C with a bottom interface in the IA column and a top interface in the IC column.

The feed for the run was prepared from Purex waste that had been treated with a lead sulfate precipitation and a D2EHPA solvent extraction cycle to remove most of the impurities. The IAF contained 0.0048M rare earths, including 0.0015M cerium, and was complexed with 0.06M HEDTA and buffered at a pH of 1.8 with 0.2M hydroxyacetic acid. (Radiolysis increased the feed pH slightly during the run and may have contributed to the relatively high promethium loss in the IAW.) The IA scrub stream (IAS) contained 0.025M HNO_3 , and the ICX (after blending the separate silver and persulfate

TABLE VIII EFFECT OF TEMPERATURE AND INTERFACE POSITION ON EUROPIUM EXTRACTION
(Feed pH = 3.8, A/O = 1)

<u>Column Temperature, °C</u>	<u>Interface Position</u>	<u>Aqueous Residence Time, min.</u>	<u>Europium in IAW, %</u>	<u>Europium HTU_{OR}, ft</u>
25	Bottom	2.5	36	10
25	Top	10	12	4.7
50	Bottom	2.5	13	4.9
45-50	Top	12	0.39-0.94	1.8-2.2

streams) contained $2M$ HNO_3 , $0.2M$ $K_2S_2O_8$, and $0.02M$ $AgNO_3$. The solvent was nominally $0.4M$ D2EHPA- $0.2M$ TBP in NPH diluent and had been used in previous Strontium Semiworks runs. It was reused during the run after stripping the cerium out with a nitric acid-sodium nitrite solution and destroying the residual nitrite with sulfamic acid. Relative flow ratios IAF/IAS/IAX/ICX/ICS were $1.05/0.25/1.0/0.2/0.2$. The superficial volume velocities were the same as those used in the pilot plant runs. The radiation power density in both the IAF and ICF was about 1.2 W/liter, mostly attributable to Ce^{144} .

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APPENDIX

DETAILED PILOT PLANT RUN SUMMARIES

TABLE A-1 IC COLUMN RUN SUMMARIES: SERIES 1

(General Conditions: Overall cartridge height = 16 ft; Top interface except in Run 7; 2M HNO₃ in ICX; Solvent pretreated with ICX before use; Pulse amplitude = 1 in.; Pulse frequency normally = 55 ± 10 cycles/min [about 80 to 90% of flooding]; detailed ICF composition in text.)

Run	Cartridge Strip	Height, in. Scrub	Column Temperature, °C	Flow Rates, ml/min				Aqueous Residence Time, min (a)		ICX Composition, M			% of ICF in ICF	Cerium in ICP	Run Length min
				ICF	ICS	ICX	A/O, Stripping	Overall	Strip Only	Ag +	Nominal	Actual			
											K ₂ S ₂ O ₈	S ₂ O ₈ ⁼ (b)			
1	192	0	25	1000	0	200	0.20	120	120	0.02	0.2	0.16	59	31	330
2	192	0	50	1000	0	200	0.20	120	120	0.02	0.2	0.16	80	18	75
3	90	102	50	800	200	200	0.20	120	70	0.02	0.2	0.15	111	≤0.74	135
	90	24(c)	--	----	---	---	----	80	---	----	-----	----	-	0.42	-
4	90	102	50	800	200	200	0.20	120	70	0.02	0.2	0.16	99	≤0.53	360
	90	24(c)	--	----	---	---	----	80	---	----	-----	----	-	0.42	-
5	170	22	50	800	200	200	0.20	120	110	0.02	0.2	0.15	102	≤8.5	320
	170	12(c)	--	----	---	---	----	110	---	----	-----	----	-	≤7.1	-
6	162	30	50	800	200	200	0.20	120	100	0.02	0.2	0.19	114	≤3.7	195
7	162	30	50	800	200	200	0.20	17(d)	14(d)	0.02	0.2	0.18	11	79	275
8	162	30	50	800	200	200	0.20	120	100	0.02	0.2	0.17	84	3.1	285
9	130	62	50	800	160	200	0.21	120	90	0.02	0.2	0.19	101	0.21	270
	130	16(c)	--	---	---	---	----	100	---	----	-----	----	-	1.2	-
10a	130	62	50	800	150	100	0.11	240	180	0.02	0.2	0.18	92	0.27	270
	130	16	--	----	---	---	----	190	---	----	-----	----	-	1.1	-
10b	130	62	50	800	0	100	0.13	240	180	0.02	0.2	0.18	51	≥8.5	155
11a	130	62	50	1000	200	200	0.17	120	90	0.01	0.1	(0.04)	≤5.7	≥92	180
	130	16(c)	--	----	---	---	----	100	---	----	-----	----	-	101	-
11b	130	62	50	1000	200	200	0.17	120	90	0.02	0.1	(0.04)	≥12	103	150
	130	16(c)	--	----	---	---	----	100	---	----	-----	----	-	105	-
CS-1	90	0	50	1000	0	200	0.20	70	70	0	0	0	1.1	≥83	325
CS-2	162	0	50	1000	0	200	0.20	100	100	0	0	0	0.53	>91	285

(a) Based on column volume from interface to ICP sample point and to ICF entry point, assuming 85% aqueous holdup

(b) Estimated from 12 day persulfate half-life. (Silver added in separate stream)

(c) Intermediate aqueous sample at indicated distance below ICF feed point

(d) Bottom interface, residence time based on assumed 15% aqueous holdup between ICX entry point and interface (or ICF entry point)

TABLE A-II IC COLUMN RUN SUMMARIES - SERIES 2

(General Conditions: Cartridge Heights: Stripping section = 10 ft, scrub section = 4 ft; Top interface; 2M HNO₃ in ICX; Pulse amplitude = 1.0 in.; Pulse frequency = 50 ± 5 [about 80 to 90% of flooding].)

Run	Column Temperature °C	Flow Rates, ml/min			A/O, Stripping	Aqueous Residence Time, min (a)		Solvent Pretreatment (b)	ICX Composition, M			% of ICF Cerium in ICF	Run Length min	
						Overall	Strip Only		Nominal		Actual			
		ICF	ICS	ICX					Ag ⁺	K ₂ S ₂ O ₈	S ₂ O ₈ ^{=(c)}			
12a	50	930	210	110	0.094	170	120	A	0.039	0.2	0.15	≤27	≥75	310
12b	50	1100	210	190	0.15	90	70	A	0.025	0.2	0.19	98	0.46	375
13a	52	1040	180	220	0.18	80	60	D	0.011	0.2	(0.08)	1.2	88	280
13b	55	1070	200	190	0.15	90	70	D	0.01	0.2	(0.08)	1.9	97	180
14a	55	1070	200	190	0.15	90	70	D	0.021	0.2	0.20	99	≤1.7	90
14b	52	970	200	200	0.17	90	60	B	0.029	0.2	0.20	61	≥47	255
14c	52	970	200	200	0.17	90	60	C	0.029	0.2	0.20	97	0.23	120
15a	52	1010	230	230	0.18	80	60	C	0.026	0.2	0.18	99	≤6.6	75
15b	40	1010	230	120	0.095	150	110	C	0.025	0.2	0.18	58	≥2.6	~90
15c	54	1010	230	120	0.095	150	110	C	0.025	0.2	0.18	≥84	≤6	45
16a	≥54	1020	200	120	0.096	150	110	C	0.047	0.2	0.17	≤23	>54	220
16b	40	1020	200	120	0.096	150	110	C	0.047	0.2	0.17	101	≤29	175
17a	39	970	200	110	0.095	160	120	C	0.011	0.2	0.16	<17	>48	195
17b	50	970	200	110	0.095	160	120	C	0.011	0.2	0.16	4.2	≥86	155
18	51	910	200	100	0.093	170	120	C	0.012	0.4(NH4 ⁺)	0.33	97	0.25	345
19	53	1000	200	110	0.088	170	120	C	0.0061	0.4(NH4 ⁺)	0.28	99	0.16	365
20	20	1000	200	100	0.084	180	130	C	0.006	0.4(NH4 ⁺)	0.26	<15	>8	45
21	54	1030	200	71	0.057	250	180	B	0	0.2	0.11	7.3	≥70	345
22	53	1030	200	110	0.091	160	110	E	0.0049	0.4(NH4 ⁺)	0.31	100	≤0.043	310
23a	40	1010	200	120	0.096	150	110	E	0.0012	0.4(NH4 ⁺)	0.29	89	0.30	170
23b	52	1010	200	120	0.096	150	110	E	0.0012	0.4(NH4 ⁺)	0.29	91	≤0.13	90
24	42	940	200	100	0.088	180	130	E	0	(e)	(e)	11	84	365
25a	51	1050	200	110	0.090	160	110	E	0	0 (d)	0	0.55	86	330
25b	41	1050	200	110	0.090	160	110	E	0	0 (d)	0	≥0.61	>75	100
26a	50	1070	200	73	0.058	240	180	E	0	0 (d)	0	2.2	96	270
26b	30	1070	200	73	0.058	240	180	E	0	0 (d)	0	3.1	96	150
27	50	1030	180	110	0.088	170	120	E (f)	0.0013	0.4(Na ⁺)	0.34	97	≤1.0	390
28a	50	1030	140	97	0.083	180	130	E (f)	0.0077	0.4(Na ⁺)	0.31	99	0.17	140
28b	30	1030	140	97	0.083	180	130	E (f)	0.0078	0.4(Na ⁺)	0.30	100	0.28	300
29a	30	1110	200	90	0.069	200	140	E (f)	0.0078	0.4(Na ⁺)	0.30	104	0.25	75
29b	30	1110	200	90	0.069	200	140	E (f) (g)	0.0078	0.4(Na ⁺)	0.30	103	0.15	240

- (a) Based on aqueous volume assuming 85% aqueous holdup
 (b) Solvent treatment codes (see text for wash details)
 A = None (ICW from Run 11, no nitrite present)
 B = HNO₃ + nitrite only
 C = Same as B but followed with sulfamic acid wash to destroy nitrite
 D = NaOH followed by HNO₃ + KMnO₄; (oxalic acid added after 1 hr to destroy MnO₄⁻), H₂O
 E = NaOH (Na₂CO₃) + tartaric acid followed by HNO₃
 (c) Estimated from 12 day persulfate half-life (silver added in a separate stream)
 (d) 0.08 to 0.09M H₂SO₄ added to simulate persulfate decomposition product
 (e) Composition of ICX in doubt; believed to be 0.4M (NH₄)₂ S₂O₈
 (f) Soltrol-170 diluent. All other runs used NPH diluent
 (g) Added 0.5% highly degraded diluent to IAX-ICS while running 29a (see text)

TABLE A-III IA COLUMN RUN SUMMARIES: SERIES 3

(General Conditions: Cartridge Height = 10 ft [no scrub section]; pulse amplitude 0.5 to 0.8 in.; Soltrol-170 diluent; $\text{Eu}^{152-154}$ tracer added to IAF 1 to 2 hr before run. Detailed IAF composition in text.)

Run	Column Temperature, °C	Interface Position	Amplitude Times Frequency in./min ^(a)	Flow Rates, ml/min		A/O	Aqueous Residence Time, min ^(b)	pH		% Europium in		Run Length min
				IAF	IAX			IAF	IAX	IAW	IAP	
30	25	Bottom	18	1110	1000	1.1	2.5	3.8	3.5	36	56	90
31	50	Bottom	28	1130	1030	1.1	2.5	3.8	3.6	13	89	80
32	25	Top	34	1120	970	1.2	10	3.8	3.4	12	92	90
33	50	Top	35	900	1000	0.9	12.5	3.8	3.4	0.94	100	80
34	45	Top	37	1000	880	1.1	11	3.6	3.4	0.39	97	170
35a	25	Bottom	32	1100	1090	1.0	2.6	2.4	2.4	3.7	97	120
35b	25	Bottom	45	1040	1090	1.0	2.7	1.8	1.7	≤2.1	<115	45

(a) Adjusted to ca. 90% of flooding

(b) Assuming dispersed phase occupied 20% of the volume.

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