TID-11098

MICHIGAN CHEMICAL CORPORATION
Saint Louis, Michigan
Research Department
June 30, 1959

cc T. Marvin
F. A. DeMaestri (6)
A. J. Romanski (2)
C. W. Dunbar
H. S. Lawton (3)
J. R. Gump
D. Williams
R. J. Knapp
C. B. Hollabaugh
A. M. Gammill
10 extra copies

Report 258
Project 942
Work by L. D. McCowen
Supervised by J. R. Gump
Author: L. D. McCowan
Notebook Reference: No. 246, pp 1-17
Period: May 15, 1958 to June 11, 1958

PURIFICATION OF YTTRIUM OXIDE--BY ACID EXTRACTION

Abstract

The investigation of an aqueous acid scrub solution for the purification of the yttrium oxide from the primary contactor has been successful while using either 0.4 normal hydrochloric acid or 0.2 normal sulfuric acid. The yttrium oxide was extracted with the aqueous scrub, and the heavy rare earths remained in the organic phase consisting of kerosene, n-decanol, and monododecylphosphoric acid.

Introduction

Pilot plant experiments performed by Lockwood (1) showed that the 21-stage liquid-liquid extraction unit was capable of upgrading 63% yttrium oxide to 87%. Further purification of the 87% Y_2O_3 could be accomplished with an aqueous acid solution. It was decided to set up experiments using either dilute hydrochloric acid or sulfuric acid as the aqueous scrub solution.

This report includes information obtained from the 9-stage laboratory acid back extraction unit using either hydrochloric acid or sulfuric acid as the aqueous scrub.

Apparatus

The laboratory 9-stage, mixer-settler system was described by Lockwood in Research Report 167.

Experimental

The 9-stage laboratory acid extractor was operated countercurrently with an aqueous scrub against an organic solution. The organic solution consisted of 3 parts kerosene, 1 part normal decanol, and 1 part monododecylphosphoric acid. This organic solution was obtained from stage 1 of the 21-stage primary contactor unit. The concentration of Y_2O_3 and the heavy rare earths in this organic solution was between 4.5 and 5.0 grams per liter. The organic contacted the aqueous scrub which entered the laboratory 9-stage unit at stage 1 and extracted the yttrium oxide into the aqueous phase. The heavy rare earths remained in the organic phase.

In the first set of experiments the aqueous phase was prepared with hydrochloric acid at concentrations between 0.2 to 1.0 normal. The solutions were added to the 9-stage laboratory unit at a ratio of 4 to 1, organic to aqueous until the system reached equilibrium. Samples were taken of both phases and the rare earths were precipitated with oxalic acid, filtered, and burned at 750°C to the oxides.

Report 258
June 30, 1959

The aqueous scrub was changed to sulfuric acid solutions at various concentrations between 0.1 to 0.6 normal in the second set of experiments. The flow conditions were maintained at the rate given in the first set of experiments.

Results

In the first set of experiments, the aqueous hydrochloric acid concentrations of 0.3 and 0.4 normal upgraded 84% yttrium feed to 97% Y_2O_3. The principal impurities remaining in the final yttrium concentrate were 0.46% erbium, 0.18% dysprosium, and 2.1% cerium. The results are tabulated in Table I. The higher hydrochloric acid concentrations stripped the organic solution under the conditions tried in the laboratory.

In the second set of experiments, the aqueous sulfuric acid concentrations of 0.1 and 0.2 normal upgraded the yttrium concentrate feed to 94% Y_2O_3. The cerium oxide (5.8%) was the major impurity while using 0.1 normal sulfuric acid scrub. The impurities in the yttrium product at 0.2 normal sulfuric acid scrub were lutecium, erbium, and dysprosium. The differences in the final yttrium product purity with the above aqueous scrub concentrations can be attributed to the amount of these elements in the feed used for each extraction. The results are presented in Table II.

Conclusions and Recommendations

(1) Yttrium oxide of 97% purity can be produced from a 82-87% yttrium concentrate in the organic phase by a 9-stage discontinuous liquid-liquid acid extractor using either hydrochloric acid or sulfuric acid scrub.

(2) Yttrium oxide product yields of 95% of the yttrium oxide fed to the acid extractor can be expected under steady operating conditions.

(3) The best flow rates and conditions used in laboratory work were:

Organic 400 ml 3 to 1 to 1, kerosene, n-decanol, and Dowsol 12 (containing 3.7 to 4.4 grams Y_2O_3 per liter with a purity of 82 to 87%.

Scrub 100 ml 0.4 normal hydrochloric acid or 0.1-0.2 normal sulfuric acid.

(4) The low sulfuric acid concentration would be recommended for future use because of its cost advantage.

Author L. D. McCowen

fh Supervisor F. R. Zump

Reference

(1) Lockwood, D. A., Michigan Chemical Corporation, Research Report 167, June 30, 1958

Report 258
June 30, 1959

Table I Extraction Data from the 9-Stage Back Extraction System

Organic Phase - 400 ml 3.7 to 4.4 g Y_2O_3 per liter with a purity of 82 to 87%
Aqueous Phase - 100 ml 1.0 to 0.2 normal hydrochloric acid

Phase	Normality	pH	X-ray Analyses Y	Lu	Yb	Tm	Er	Dy	Gd	Ce	Percent of orig. oxide wt
Aqueous soln.	1.0	0.00									
Organic feed			85	2.7	5.1	1.1	2.6	1.5	0.29	-	
Organic ext.			4.7	<1	<1	<1	<1	0.54	2.9	72	1.0
Raffinate		0.65	87	2.8	5.3	1.3	2.9	1.6	0.06	-	99
Aqueous soln	0.8	0.00									
Organic feed					Same as above						
Organic ext.					No analysis						1.0
Raffinate		0.40	88	2.7	5.3	1.5	2.8	1.8	0.08	<1	99
Aqueous soln.	0.6	0.00									
Organic feed			87	2.5	4.9	1.1	2.4	1.4	0.10	2.3	
Organic ext.					No analysis						1.0
Raffinate		0.40	90	2.3	4.4	1.2	2.7	1.6	0.11	<1	99
Aqueous soln.	0.4	0.40									
Organic feed			84	1.5	5.8	1.0	0.40	0.24	0.09	9.8	
Organic ext.			4.0	1.9	5.6	<1	0.25	0.56	-	71	3.3
Raffinate		1.00	98	<1	<1	<1	0.48	0.13	0.04	1.5	96.7
Aqueous soln.	0.3	0.40									
Organic feed					Same as above						
Organic ext.			42	3.2	20	1.9	1.6	0.38	<1	24	17.7
Raffinate		1.00	97	<1	<1	<1	0.44	0.22	0.06	2.7	82.3
Aqueous soln.	0.2	0.70									
Organic feed			82	1.6	7.3	1.4	1.1	0.21	0.41	5.1	
Organic ext.			66	2.0	11	2.9	3.9	0.19	-	9.8	59
Raffinate		1.7	95	<1	<1	<1	1.0	0.33	0.50	4.3	41

Report 258
June 30, 1959

Table II Extraction Data from the 9-Stage Back Extraction System

Organic Phase - 400 ml 3.8 to 4.4 g Y_2O_3 per liter with a purity of 84 to 87%
Aqueous Phase - 100 ml 0.6 to 0.1 normal sulfuric acid

			X-ray Analyses								Percent of
Phase	Normality	pH	Y	Lu	Yb	Tm	Er	Dy	Gd	Ce	orig. oxide wt
Aqueous soln.	0.6	0.40									
Organic feed			87	2.5	4.9	1.1	2.4	1.4	0.10	2.3	
Organic ext.					No analyses						1.0
Raffinate		1.25	92	1.9	3.2	1.2	3.6	1.6	0.01	<1	99
Aqueous soln.	0.4	0.40									
Organic feed					Same as above						
Organic ext.					No analyses						1.0
Raffinate		2.0	93	1.7	1.1	<1	2.3	1.8	0.21	1.8	99
Aqueous soln.	0.2	0.5									
Organic feed					Same as above						
Organic ext.					No analyses						1.7
Raffinate		2.5	94	1.0	<1	<1	1.9	2.4	0.32	<1	98.3
Aqueous soln.	0.1	0.6									
Organic feed			84	1.5	5.8	1.0	0.40	0.24	0.09	9.8	
Organic ext.			80	1.8	8.0	1.0	0.70	0.26	0.07	10	26.7
Raffinate		2.3	94	<1	<1	<1	0.29	0.15	0.10	5.8	73.3