Desalination and Water Treatment
www.deswater.com

12 (2009) 28–33

doi: 10.5004/dwt.2009.940

Recent developments in studies on separation process in order to obtain nuclear grade dysprosium oxide

M. Anitha, M.K. Kotekar, H. Singh*

Rare Earths Development Section, Bhabha Atomic Research Centre, Mumbai – 400085, India
Tel. +91 (22) 25554949; Fax +91 (22) 25505151; email: hsingh@barc.gov.in

Received 28 July 2008; Accepted in revised form 12 October 2009

ABSTRACT

Separation of nuclear grade dysprosium oxide is a technically challenging task. The separation process adopted is dual cycle counter current solvent extraction. The extractant is 2-ethyl hexyl phosphonic acid mono-2-ethyl hexyl ester (EHEHPA). Scrubbing is incorporated to enhance the separation performance of the cascade before the stripping operation. A 54 stage mixer-settler cascade was operated in dual cycle mode. In the first cycle, Y, Ho and Er were separated from Dy and lighter rare earths (LRE) and in the second cycle, Gd and Tb were separated from Dy. Salient separation results including material balance are presented in this paper. Results show that high purity product analyzing $Dy_2O_3 > 97\%$, $Gd_2O_3 < 0.2\%$, $Tb_4O_7 \leq 1\%$ and $Y_2O_3 < 1\%$ is obtained, as required for nuclear reactor application.

Keywords: Separation; Solvent extraction; Dysprosium oxide; AHWR

1. Introduction

Boron is often used for nuclear reactor control applications. But it has the disadvantage of accumulation of large radiation induced damages caused by (n,α)-reactions on B-10 isotope leading to helium formation and swelling which causes fuel instability. As an alternative, rare earths such as Dy and Gd involving (n,γ) reactions are considered to replace (n,α)-absorbers. In Russian power water reactors (VVER-1000, MIR), boron carbide and boron steel were replaced by dysprosium titanate [1]. To extend the fuel cycle length from 12 to 24 months of PWR in France, Gd_2O_3 was successfully used as burnable absorber for controlling the increased reactivity due to enriched U-235 in the reactor [2]. For TAPS 3 and 4 in India, gadolinium nitrate has been used for reactivity control through moderator liquid poison system as well as for reactor shut down system [3]. In India, the advanced heavy water reactor (AHWR) was designed for a future nuclear power program based on thorium-U-233 fuel cycle [4]. Dysprosium oxide admixed and pelletised with zirconium oxide, is considered for the AHWR central rod, for the purpose of maintaining negative void coefficient. Gadolinium is used as burnable absorber in PHWR because of its large thermal neutron absorption cross-section of 49,000 barns while dysprosium with cross-section of 930 barns is preferred in AHWR as a slow burning absorber to reduce the thermal neutron flux generated on voiding of the coolant.

The natural dysprosium consists of seven stable isotopes. Dy-156 with content of 0.06% has thermal neutron-absorption cross-section of 33 barns. Similarly Dy-158 (0.1%) has 43 barns, Dy-160 (2.34%) has 56 barns, Dy-161 (19%) has 600 barns, Dy-162 (25.5%) has 194 barns, Dy-163 (24.9%) has 124 barns and Dy-164 (28.1%) has 2840 barns [5]. The end products in a nuclear reactor are Ho

---

* Corresponding author.

Presented at the Symposium on Emerging Trends in Separation Science and Technology (SESTEC-2008)
March 12–14, 2008, University of Delhi, Delhi, India

and Er. All the radionuclides have a low gamma activity and a short half-life period. Dysprosium oxide has a high chemical resistance. It does not interact with cladding material. Dy_2O_3 can be used in control rods as pellets due to its favourable physical properties such as density of 7.8 g/cc, high melting point 2340°C, radiation stability, and simple fabrication. Dy_2O_3 control rods can be used safely for longer lifetime because the non-radioactive waste produced after irradiation is easily reprocessed [1].

Dysprosium oxide for AHWR application needs to conform to specifications such as lighter rare earths or LRE (which include La, Ce, Pr, Nd and Sm) < 0.1%, Gd_2O_3 < 0.2%, Tb_4O_7 < 1%, Dy_2O_3 ~95%, Y_2O_3: < 3%, Ho < 0.5% and Er < 0.5%. The source material for feed is phosphates which include monazite and also fertilizer phosphates from which uranium and rare earths get co-extracted by mixture of di-2-ethyl hexyl phosphoric acid and tri-n-butyl phosphate, D2EHPA+TBP [6] and di-nonyl phenyl phosphoric acid in combination with tri-n-octyl phosphine oxide, DNPPA+TOPO, patented systems [7]. The overall difficulty of separation, for obtaining a pure product from a given feed, can be indicated by a decontamination factor (DF), which is defined as the ratio of impurity to Dy_2O_3 in feed, to the ratio of impurity to Dy_2O_3 in product. The DF values for required separation of Dy_2O_3 are shown in Table 1.

1.1. Separation flowsheet

The separation of individual rare earths element (REE) with similar chemical properties is a challenging task. It is achieved by using the process of solvent extraction (SX) with a large number of separation stages in a complex process circuit. The overall separation scheme selectively separates one REE after another, while producing by-products that form feed-stock for further separations. The separations are based on extraction of REE from an aqueous phase into an organic phase containing an extractant of liquid cation exchanger type: 2-ethyl hexyl phosphonic acid mono-2-ethyl hexyl ester (EHEPHA). The extraction mechanism at low loading, [REE]/[EHEPHA] < 0.14 and < 5 M HCl in feed can be described as:

$$REE^{3+}_{(aqueous)} + 3(HR)_{2\,(organic)} = REE\,(HR_2)_{3\,(organic)} + 3H^{+}_{(aqueous)}$$

where $(HR)_2$ is the dimeric form of EHEHPA, REE^{3+} is a trivalent rare earth ion and subscripts aqueous and organic denote the phase in which species are present.

The sequence in which various individual REE are extracted by EHEHPA is as follows:

La < Ce < Pr < Nd < Sm < Eu < Gd < Tb < Dy < Ho < Y < Er < Tm <Yb < Lu

Extraction increases with decrease in ionic radii of REE. This sequence provides the logic for development of a 'dual-cycle extraction' process. It is schematically shown in Fig 1. In this process the desired element of interest is the Dy. The heavier rare earths or HRE (Ho, Y, Er, etc.) have better extraction than Dy and are selectively extracted in the first cycle. The Dy element along with lighter REE (Gd, Tb etc) is left in the aqueous raffinate phase of the first cycle, which forms the feed to a second cycle. Between the two extraction cycles, the operations of oxalate precipitation, calcination to oxide and re-dissolution are incorporated as needed for water and acidity control. In the second cycle, the Dy^{3+} is preferentially extracted into the organic phase while leaving the less extracted lighter REE in the aqueous raffinate phase.

Each of the two cycles has cascades of counter-current stages of extraction, scrubbing and stripping. The primary parameter governing the separation between two rare earths (e.g. Dy and Tb) in the solvent extraction is separation factor (β) defined as the ratio of distribution ratio of individual rare earth elements (D_{Dy}/D_{Tb}). Typical separation factors are $\beta_{Dy/Tb}$ = 2.7 and $\beta_{Ho/Dy}$ = 1.8 with EHEPHA as an extractant [8]. As a result of low β, scrubbing in a number of stages is essential to back-wash the co-extracted element into the aqueous phase. Scrubbing medium is diluted hydrochloric acid (1–2.5 M). Where very high purity is needed, scrubbing medium also contains part of the pure product in an operation called 'refluxing'. Refluxing is adopted in second cycle where final product is obtained. This is considered when purity needed is ~99% [9].

From a description of the generic process it is evident that there are a large number of process variables that need to be optimized. These include for each cycle of operation:

1. Total rare earth oxide concentration in feed (TREOF)
2. Aqueous feed acidity (FA)

Table 1
Decontamination factors (DF) for cycle-1 and cycle-2

Rare earth element	Feed-1		
	Feed (%)	Product (%)	DF
LRE	0.3	0.12	12
Gd	4.6	0.18	119
Tb	4.4	0.95	22
Dy	20.9	97.60	
Ho	1.8	0.45	19
Y	65.1	0.25	1216
Er	2.9	0.45	30
	Feed-1A		
LRE	0.12	0.11	1.20
Gd	0.11	0.09	1.34
Tb	1	0.95	1
Dy	88.77	97.60	
Ho	1.5	0.50	3
Y	8	0.25	35
Er	0.5	0.50	1.10

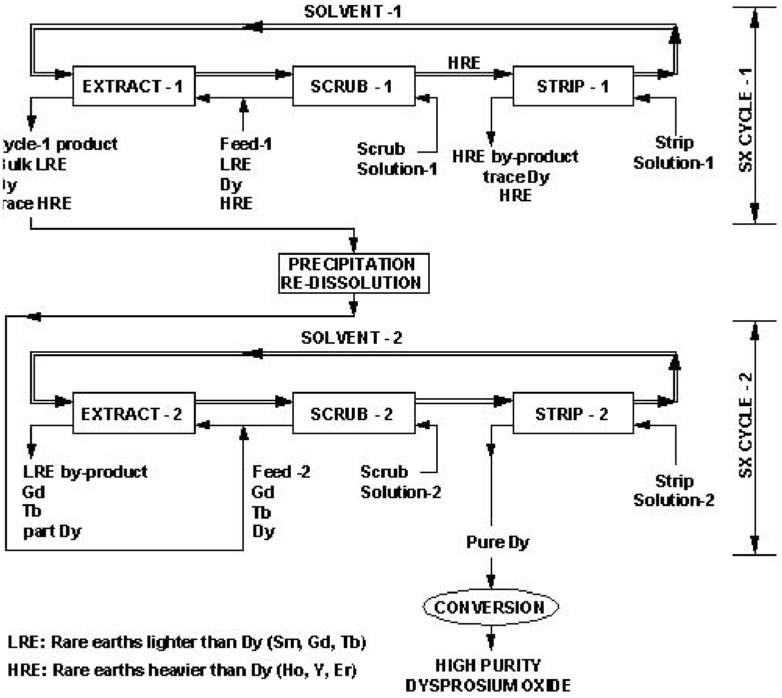


Fig. 1. Generic dual cycle solvent extraction separation process for dysprosium purification.

3. Extract to aqueous phase ratio (OAET)
4. Number of stages in extraction (NET)
5. Scrubbing solution acidity (SCA)
6. Organic to scrub phase ratio (OASC)
7. Number of stages in scrubbing (NSC)
8. Strip solution acidity (STA)
9. Strip to organic phase ratio (OAST)
10. Number of stages in stripping (NST)

Mathematical models are used to aid process simulation and optimization of complex REE processes. In particular ‘artificial neural network’ (ANN) based models have been tested and found superior to the conventional models for predicting the equilibrium distribution ratio as a function of aqueous phase composition in the field of rare earths. The ANN models combined with material balance models in a spread-sheet format such as Excel have been earlier successfully demonstrated on industrial scale for Nd-Pr separation [10]. Based on process modelling, the operation of separation cascades has yielded the high purity oxides of required purity in bulk tonnage amounts. Similar approach is adopted for Dy_2O_3. The process parameters for the flowsheet are shown in Table 2.

Table 2
Process parameters for purification of Dy

Parameter	Cycle-1(feed-1)	Cycle-1(feed-1A)	Cycle-2
TREOF (g/l)	25	25	30
FA (HCl, M)	0.3	0.2	0.2
OAET	2.08	2.11	1.49
NET	12	8	8
SCA (HCl, M)	1.5	2.5	1.3
OASC	5.43	5.58	5.88
NSC	10	8	16
STA (HCl, M)	3.5	3.5	3.5
OAST	4.03	3.96	2.77
NST	4	4	4

2. Experimental

2.1. Materials

Mixed rare earths oxide containing Dy_2O_3: 20–25%, Y_2O_3: 60–67%, Gd_2O_3: 3–4%, Tb_4O_7: 3–4%, Sm_2O_3: 1%, Er_2O_3: 3–4%, Ho_2O_3: 2–3% were obtained from monazite processing unit of Indian Rare Earths Limited. This was dissolved in concentrated HCl and diluted to obtain a solution of 25 g/L total rare earth oxide (TREO) with 0.3 M free acidity, represented as feed-1 for the first cycle. The raffinate solution obtained from the first cycle operation was precipitated as rare earth oxalate and calcined to rare earth oxide. This oxide was dissolved in concentrated HCl and diluted to 30 g/L TREO with free acidity of 0.2 N HCl for use as feed solution for the second cycle (feed-2). During mixer settler operations with feed-1, we obtained an off grade product consisting Dy_2O_3 (< 89%), Y_2O_3 (> 7%) and Ho_2O_3 (> 1.5%). This was an alternative feed material (feed-1A) for first cycle operations where Dy is further purified with regard to Y and Ho. Commercially available EHEHPA of >95% purity was used as supplied and diluted with aliphatic hydrocarbon diluent. All other chemicals used were of analytical reagent grade. HCl was used as the medium since it is cheaper than nitric acid and EHEHPA works efficiently with this medium for separation of rare earths [11]. Rare earths separation in chloride media is a well established plant practice in India, China, Japan, etc.

2.2. Equipment

First cycle experiments were carried out using polypropylene mixer settlers of capacity 800 ml settler and 200 ml mixer. Each mixer had a vari-speed DC motor. The solutions were fed by peristaltic pump into four points of the circuit. These solutions were feed, organic, scrubbing and stripping solutions. Flow rates of aqueous and organic phases were maintained using electronic metering pumps. The system stability was monitored by analyzing for TREO in exit flows periodically. Bench scale experiments were carried out using laboratory glass separatory funnels fitted with motorized agitators for second cycle.

2.3. Analysis

Free acid content in rare earth chloride solution was determined by precipitating it with sodium oxalate followed by titration with standard NaOH using phenolphthalein indicator. The TREO concentration was determined by gravimetric method using oxalic acid as precipitant. The individual rare earths were analyzed by a sequential inductively coupled plasma atomic emission spectrometer (ICP-AES). An instrument with high resolution of 0.005 nm, JY Ultima 2 was commissioned and used for analysis. It enables superior analysis of the complex spectrum of rare earths in rare earth matrix which has several lines and has an intense background continuum. In particular, it was found that Gd impurity could be analysed to a detection limit of 0.01%.

3. Results and discussion

3.1. Separation factors

Separation factor is a complex function of equilibrium composition of aqueous and organic phases. Acidity is one of the factors. The extraction of TREO decreases with increase in HCl concentration in aqueous feed solution. The percentage extraction of TREO reported was 50% with rare earth chloride solution similar to feed-1 at 0.3 M HCl free acidity using 1 M EHEHPA[12]. The optimized feed acidity used in our experiments was 0.3 M HCl. The stage to stage acidity was monitored in extraction as well as scrubbing stages as shown in Fig. 2. In cycle-1 extraction, the stage to stage acidity varied from 0.2 to 0.7 M HCl, which was suitable for separation of Dy and Y. In cycle-1, the separation factors of Y with respect to Dy ($\beta_{Y/Dy}$) with 1M EHEHPA were evaluated experimentally and were found to decrease marginally with increase in feed acidity. Typical $\beta_{Y/Dy}$ values observed were 3.78 and 3.05 at 0.2 M and 1 M HCl free acidity respectively for a feed containing of Dy_2O_3(65%) and Y_2O_3(20%). A similar trend was observed in the stage to stage analysis of first cycle of continuous operation of off-grade product as shown in Fig. 2.

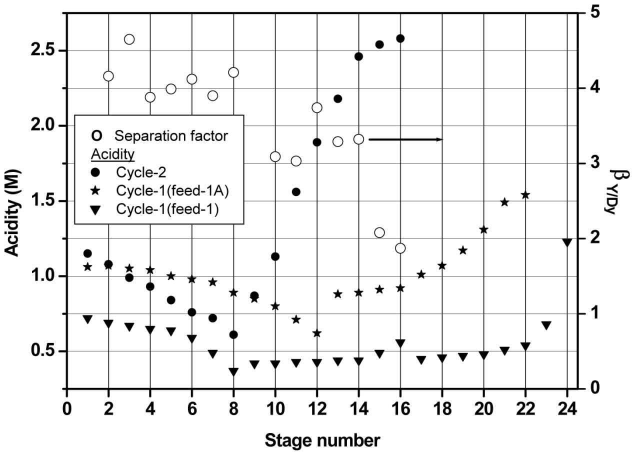


Fig. 2. Stage to stage variation of acidity and separation factor.

3.2. Cycle-1: separation of Dy from HRE

The primary objective of the first cycle was to purify dysprosium with regard to holmium and yttrium. This is achieved in 12-stage extraction and 10-stage scrubbing in continuous mixer settlers under operating conditions given in Table 2. The feed consisting Dy_2O_3 (~21%) and Y_2O_3 (~65%) was fed to extraction stage at a rate of 2.22 l/h. Dysprosium and other LRE are scrubbed into aqueous phase at a flow rate of 1.38 l/h which was mixed with feed solution. The out going raffinate which was obtained at the extraction end was found to consists of Dy_2O_3 (~68%), Y_2O_3 (~0.15%), Gd_2O_3 (~15%), Tb_4O_7 (~14%) and LRE (<3%). The stage-to-stage data with regard to percentage Dy and Y after operation of over 400 h is plotted in Fig. 3. The percentage recovery of Dy is ~94% and purity is ~68%. Kilogram quantity of Dy_2O_3 was thus produced for the second cycle operation. The overall material balance for the process is shown in Fig. 4. Interestingly, the strip solution obtained contains 92% pure Y_2O_3. This can be further processed to obtain high purity yttrium for phosphor application as developed in our laboratory [13].

Optimization of process parameters for feed-1A was carried out to improve the purity of the off grade product with respect to Y. Fig. 5 shows that at low acidity considerable amount of Dy gets extracted and separation is achieved with respect to Tb and LRE rather than Dy and HRE. This is shown by the trend of Tb in raffinate which is 5% at 1.5 M scrub acidity and also by Y in strip solution

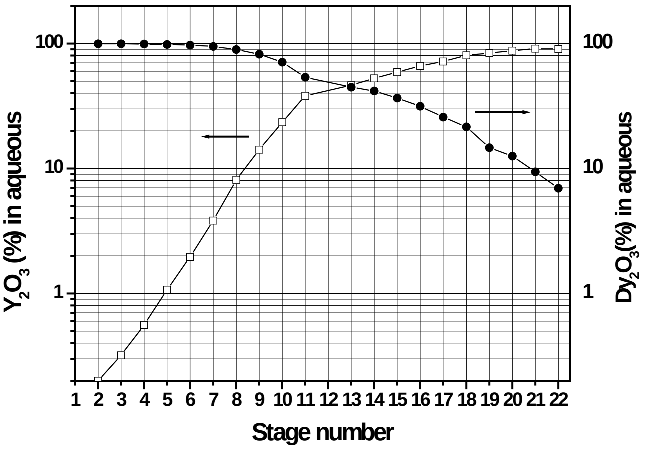
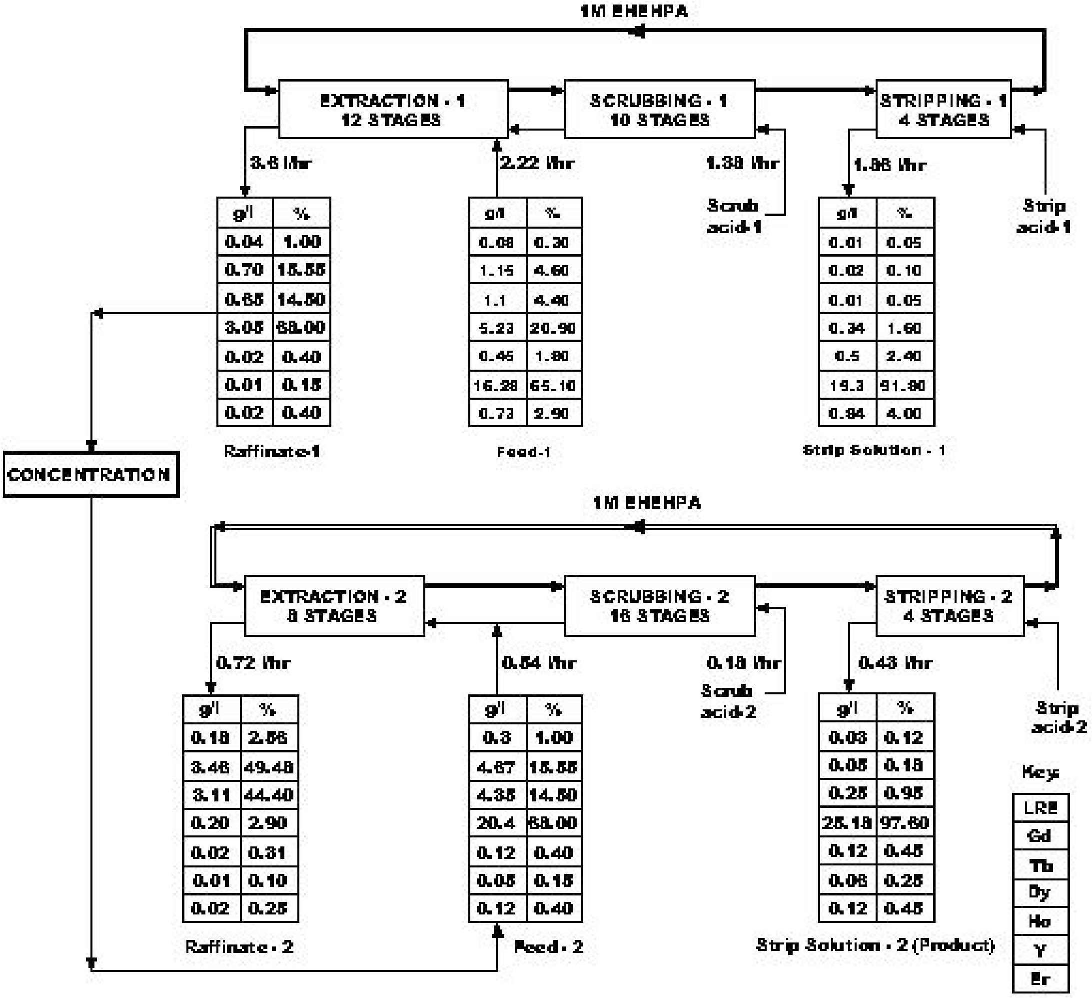


Fig. 3. Stage to stage variation of Dy and Y in cycle-1.

which is as low as 7.6%. As the acidity increases, bulk of Dy reports into raffinate. This results in an increase in TREO in the raffinate as well as percentage Dy in the raffinate. It is accompanied by an increase in percentage of Y in the strip solution. The final raffinate product obtained also meets the required specification for AHWR. This study illustrates experimentally the importance of the control over the acidity of scrub solution in overall process performance.

3.3. Cycle-2: separation of Dy from LRE

The raffinate of the first cycle consists of Gd_2O_3 (~15%), Tb_4O_7 (~14%) and LRE (<3%) apart from Dy_2O_3 (~68%). The impurities such as Gd and Tb are separated from dysprosium in the second cycle. The separation factor $\beta_{Dy/Tb}$ = 2.82 is lower than $\beta_{Gd/Dy}$ (16.52). The required decontamination factor (DF) of Gd with respect to Dy is higher than Tb because the Dy product specification for Gd and Tb are different which are Gd < 0.2% and Tb < 1%. Hence, there is a need for careful optimization and experimentation. It is observed experimentally in counter current 8-stage extraction, 16-stage stubbing, the scrub acid played a major role in recovery and purity of product obtained. A series of second cycle operations were car-



Raffinate-1

g/l	%
0.04	1.00
0.70	15.55
0.65	14.50
3.05	68.00
0.02	0.40
0.01	0.15
0.02	0.40

Feed-1

g/l	%
0.08	0.30
1.15	4.60
1.1	4.40
5.23	20.90
0.45	1.80
16.28	65.10
0.73	2.90

Strip Solution - 1

g/l	%
0.01	0.05
0.02	0.10
0.01	0.05
0.34	1.60
0.5	2.40
19.3	91.80
0.84	4.00

Raffinate - 2

g/l	%
0.18	2.56
3.46	49.48
3.11	44.40
0.20	2.90
0.02	0.31
0.01	0.10
0.02	0.25

Feed - 2

g/l	%
0.3	1.00
4.67	15.55
4.35	14.50
20.4	68.00
0.12	0.40
0.05	0.15
0.12	0.40

Strip Solution - 2 (Product)

g/l	%
0.03	0.12
0.05	0.18
0.25	0.95
25.18	97.60
0.12	0.45
0.08	0.25
0.12	0.45

Fig. 4. Material balance for 54-stage mixer settler cascade for separation of high purity Dy_2O_3.

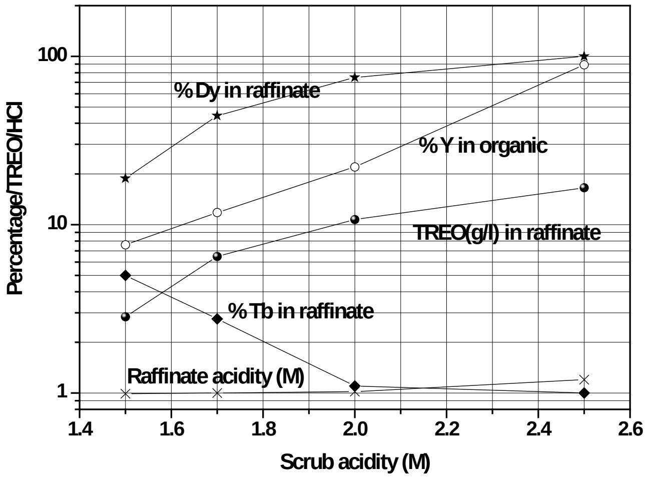


Fig. 5. Effect of scrub acidity on purity of Dy.

ried out by varying scrub acidity. The recovery of total oxide in product decreased from 75% to 44% as the scrub acidity increased from 1.3 M to 1.6 M HCl. Similarly, the purity of Dy decreased from 97% to 90% with increase in acidity. With the information thus available, the process conditions were further optimized. A typical data of a test run with SCA = 1.3 M HCl, OAET = 1.49 and OASC = 5.88, STA = 3.5 M HCl OAST = 2.77, NST = 4, shows that TREO in loaded organic is almost constant after 60 contacts and the average value is 9.52 g/l. The analysis for Tb in the scrubbing section of cycle-2 is important in determining the overall purity of the product. The Tb in aqueous phase of scrubbing cycle increased from ~3% to ~24%. As a result Tb in the loaded organic decreased to <1% from 10%. Equilibrium acidity remained almost constant at 0.45 M HCl except in one or two stages of scrubbing. The product thus obtained is Dy_2O_3 (~97%) pure with a recovery of ~99%.

4. Conclusion

A two cycle solvent extraction process based on EHEHPA has been experimentally tested for producing nuclear grade Dy_2O_3. The percentage recovery of Dy_2O_3 in the first cycle raffinate was ~94% of purity ~68%. In the second cycle, the product obtained was ~97% pure Dy_2O_3 with ~99% recovery. The overall recovery was ~93%. Experimentally, scrub acidity has been shown to be a key parameter for efficient separation. Analytical methods were developed to analyse Gd_2O_3 and Tb_4O_7 in Dy_2O_3 matrix and the purity of the product was confirmed. The product samples are being further evaluated by the user divisions of BARC.

References

[1] V.D. Risovany, E.E. Varlashova and D.N. Suslov, J. Nucl. Mat., 281 (2000) 84–89.
[2] M. Asou and J. Porta, Nucl. Engg. Des., 168 (1997) 261–270.
[3] S.L. Mishra and H. Singh, BARC Newsletter, 270 (2006) 35–37.
[4] R.K. Sinha and A. Kakodkar, Nucl. Engg. Des., 236 (2006) 683–700.
[5] V.F. Sears, Neutron News, 3(3) (1992) 29–37.
[6] H. Singh, S.L. Mishra, M. Anitha, R. Vijayalakshmi, A.B. Giriyalkar, M.K. Kotekar and T.K. Mukherjee, US Patent No. 7,192,563, March 20, 2007.
[7] H. Singh, S.L. Mishra, R. Vijayalakshmi, A.B. Giriyalkar and C.K. Gupta, US Patent No. 6645453, Nov 11, 2003.
[8] S.L. Mishra, H. Singh and C.K. Gupta, Hydromet., 56 (2000) 33–40.
[9] S.L. Mishra, N.S. Iyer, M.K. Kotekar and H. Singh, BARC Internal Report, BARC/2004/I/012, 2004.
[10] M. Anitha and H. Singh, Desalination, 232 (2008) 59–70.
[11] C.A. Morais and V.S.T. Ciminelli, Hydromet., 73 (2004) 237–244.
[12] D.K. Singh, M.K. Kotekar and H. Singh, Desalination, 232 (2008) 49–58.
[13] M. Anitha, Preparation and characterization of rare earth based luminescent materials in borates and related systems, PhD thesis, Mumbai University, Feb. 2006.