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Simultaneous recovery of yttrium and uranium using D2EHPA–TBP and DNPPA–TOPO from phosphoric acid

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ABSTRACT

A method to simultaneously recover yttrium and uranium from phosphoric acid using DNPPA + TOPO and D2EHPA + TBP solvent systems has been developed. The solvent mixture DNPPA + TOPO is employed for merchant grade phosphoric acid, while the D2EHPA + TBP solvent system is employed for wet process phosphoric acid to recover uranium and yttrium. In the method, four steps are involved for the yttrium recovery: (1) yttrium is co-extracted with uranium using the two organic systems; (2) yttrium is selectively stripped from the loaded organic solutions; (3) yttrium is recovered from the strip liquor by double sulphate salt precipitation; (4) yttrium double sulphate salt is dissolved and precipitated with oxalic acid to generate pure yttrium product. Selective stripping of yttrium from the loaded organic solutions with various strip solutions was tested. It was found that 10% (w/v) Na_2SO_4 + 30% H_2SO_4 and H_2SO_4 (30 to 40%) are the most preferable conditions with more than 95% of yttrium recovered and less than 0.2% of uranium lost in the yttrium strip liquor. From the resultant strip liquor, more than 98% of yttrium was precipitated in the form of sodium yttrium double sulphate salt under the optimized conditions of 10% (w/v) Na_2SO_4, 60 ± 1°C and aging time of 45 min. Pure yttrium oxide with more than 99% was obtained after dissolution of the resultant double sulphate salt, precipitation with oxalic acid and calcination at a high temperature. Sodium contained in the yttrium oxide product was removed by washing steps using distilled water and it could be completely removed under the conditions of liquid to solid ratio of 50, 80 ± 5°C and washing for 30 min. A conceptual process flowsheet has been proposed to recover yttrium as a by-product of uranium from phosphoric acid.

Keywords: Yttrium; DNPPA; TOPO; D2EHPA; TBP; Rare earths double sulphate; Strip solution; Yttrium oxide

1. Introduction

Large amounts of rare earths (0.1–0.8%) present in the phosphate rock becomes attractive to recover them as by-product of uranium [1]. Phosphate rock has been chemically processed worldwide to produce fertilizers and it is also considered to be an important secondary source of uranium. A part or all of the rare earths were leached out by the acid depending on the different acid (H_2SO_4/HNO_3) used for treating the rock. In wet process of phosphoric acid, normally 5–6 M H_3PO_4 containing 25–30% P_2O_5 was generated by sulphuric acid leaching of the rock in which ≈25% of the rare earths are reported to the leach solutions. Rare earths were completely leached out with nitric acid [2]. Even with sulphuric acid leaching, the concentration of rare earths in the leach solutions

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is much higher than that of uranium. Generally, the concentration of yttrium in wet phosphoric acid (WPA) is in the range of 0.2 to 0.5 g/l while uranium concentration is in the range of 0.1–0.2 g/l [3]. WPA is often concentrated to merchant grade acid (MGA), which is about 12–14 M H_3PO_4 (≈55% P_2O_5), for commercialization, and for the production of di-ammonium phosphate fertilizer. Yttrium is a very valuable rare earth which finds application in superconductors, lasers, phosphors, electronic devices etc. The extraction of lanthanides and uranium using different extractants such as di-2-ethyl hexyl phosphoric acid (D2EHPA), di-octyl phenyl phosphoric acid (DOPPA), nonyl phenyl phosphoric acid (NPPA) etc in combination of neutral oxodonors such as tri-n-octyl phosphine oxide (TOPO), di-butyl butyl phosphonate (DBBP), tri-n-butyl phosphate (TBP) from various types of sources obtained from the treatment of phosphatic rock have been reported [3–10]. Mishra et al. [11] has studied the extraction behavior of uranium from aqueous acidic solutions of nitrate, perchlorate, sulphate, chloride and phosphate with dinony phenyl phosphoric acid (DNPPA) in combination of TOPO. They have reported $[UO_2(HR_2)_2.TOPO]$ type of complexes in the organic phase irrespective of aqueous media, where $(HR)_2$ is a dimer of DNPPA. Recently our group has developed and demonstrated two novel processes to recover uranium using 1.5 M D2EHPA + 0.2 M TBP from WPA and 0.6 M DNPPA + 0.3 M TOPO from MGA [11,12]. Both the processes have two cycle solvent extraction operation. While the first cycle is for the concentration of uranium from mg/l level to g/l, the second cycle pertains to the purification of uranium. Investigations on the extraction behaviour of yttrium with DNPPA + TOPO from phosphoric acid medium were carried out in our laboratory [13]. Though several studies are reported on the use of organophosphorous extractants for the extraction of uranium, rare earths from phosphoric acid medium, relatively scanty reports are available to simultaneously recover rare earths as by-product of uranium.

An attempt has, therefore, been made in the present work to develop a method to effectively recover yttrium from a loaded strip liquor generated from 0.6 M DNPPA + 0.3 M TOPO–MGA and 1.5 M D2EHPA + 0.2 M TBP–WPA processes. The recovery of yttrium as by-product of uranium in these processes will not only improve the economics of the process, but would also be a step towards the conservation of natural resources.

2. Experimental

2.1. Reagents and solutions

DNPPA was synthesized in our laboratory containing 87–90% diester, 4–5% mono ester and 7–8% neutral, which was further purified to >95% diester and <0.5% monoester by the method described elsewhere [13]. TOPO (American Cyanamid Co. USA, >95% pure), TBP (BDH, >95% pure) and D2EHPA (HWB, India, >95% pure) were used as received. Petrofin (an aliphatic fraction of refined kerosene) with flash point 102°C was used as the diluent to prepare desired concentration, extractant solutions. Industrially produced phosphoric acids, WPA (≈6M) and MGA (≈12M), were used as aqueous feed. These acids were treated with activated carbon to remove organic impurities prior to solvent extraction studies. Stock solutions of uranium and yttrium were prepared by dissolving required quantities of uranium metal (≈99.9% purity) and yttrium oxide (>99.9% purity) in hydrochloric acid. After evaporating the excess acid, the solutions were diluted to 250 ml with distilled water. Synthetic loaded organic phases of 0.6 M DNPPA + 0.3 M TOPO containing 3.0 g/l U_3O_8 and 3.0 g/l Y_2O_3 and 1.5 M D2EHPA + 0.2 M TBP containing 6.5 g/l U_3O_8 + 2.5 g/l Y_2O_3 + 2.3 g/l Fe were prepared for studies on selective stripping of yttrium. Stripping reagents such as Na_2SO_4, H_2SO_4, HCl, oxalic acid, HF and HNO_3 used were of analytical reagent grade. Na_2SO_4 solution was prepared in water and its concentration has been represented as % (w/v) through out the text.

2.2. Procedures

Solvent extraction/stripping studies were carried out by equilibrating aqueous and organic phases for 5 min in a glass beaker using a magnetic stirrer or in separating funnel and thereafter phases were allowed to settle for phase separation. Independent extraction/stripping experiment as a function of time suggested that 5 min duration was sufficient for achieving equilibrium condition. The concentrations of uranium, yttrium and iron were determined using ICP-AES (JY-Ultima 2). The concentrations of these metal ions in the organic phase were estimated by mass balance. Distribution ratio (D) is the ratio of metal ion concentration in the aqueous to organic phase. For temperature variation effect, care was taken to keep the temperature constant through out the studies by monitoring at regular intervals using a thermometer and also by preheating the solutions. A digital pH meter (LI 127 of Elico make) was used to monitor the pH of the aqueous solution with an accuracy of ±0.03 pH units. In all the experiments each data point represents a mean value of at least three independent measurements with standard deviation of ≈5%.

3. Results and discussion

3.1. Yttrium stripping from DNPPA + TOPO system

In DNPPA + TOPO process it was found that rare earths were co-extracted with uranium [12]. Based on this study, a synthetic loaded organic solution of 0.6 M DNPPA + 0.3 M TOPO containing 3.0 g/l Y_2O_3 and

Table 1
Effect of various reagents on the stripping of Y(III)

Reagent	Stripping (%)	
	Y(III)	U(VI)
Saturated oxalic acid	4.23	<0.17
50% HCl	7.26	<0.10
30% HNO_3	0.80	<0.05
30% H_2SO_4	48.26	<0.15
40% H_2SO_4 (Temp. 28°C)	72.29	<0.20
40% H_2SO_4 (Temp. 60°C)	87.35	<0.20
10% Na_2SO_4 + 30% H_2SO_4	71.96	<0.15

3.0 g/l U_3O_8 was prepared by equilibrating the organic solution with an aqueous feed containing 1.6 g/l Y_2O_3 and U_3O_8 each at O/A of 1:2.5. Different reagents were tested for selective stripping of yttrium from the synthetic loaded organic solution at phase ratio of O/A 1:1 and a room temperature (28 ± 1°C). The contact time for these tests was 5 min. The results are summarized in Table 1.

The stripping of Y(III) with the mixture of Na_2SO_4 and H_2SO_4 resulted in precipitation of rare earths-sodium double sulphate. The chemical composition of resultant double salt precipitate was reported to be $Na_2SO_4 \cdot Y_2(SO_4)_3 \cdot xH_2O$ [14]. The precipitation of lanthanum and neodymium with a mixture of Na_2SO_4 + H_2SO_4 system has also been reported [8]. The stripping of yttrium with 40% H_2SO_4 at a high temperature of 60°C was found to be 87% in a single contact. For all tested reagents for yttrium stripping, the loss of uranium was less than 0.2%. Jaronsinski et al. [7] reported rare earth sulphate precipitation from rare earth loaded 0.5 M NPPA/kerosene when stripped with ≈45% sulphuric acid. Contrary to this no such precipitation of rare earths sulphate has been observed in the present study. The cause for this is not well understood and at present it is difficult to offer a valid explanation to this. As yttrium stripping with the mixture of Na_2SO_4 + H_2SO_4 forms precipitation leading to difficult operation, 40% sulphuric acid was used in this study. Yttrium stripping from 0.6 M DNPPA + 0.3 M TOPO loaded with 3.0 g/l of Y_2O_3 and U_3O_8 with 40% sulphuric acid under various conditions are shown in Table 2.

Table 2
Effect of phase ratio (O/A) on stripping of Y(III)

Phase ratio (O/A)	% Stripping of Y(III)
2:1	60.86
1:1	72.40
1:2	76.54
1:3	82.20
1:4	85.86

It is evident that the stripping of Y(III) increased from 60.86 to 85.86 with the decrease in O/A from 2:1 to 1:4 under ambient condition (28°C). The increase in % stripping may be due to increase in sulphuric acid volume.

3.2. *Stripping studies of yttrium in D2EHPA + TBP system*

Based on the literature [11], uranium, yttrium and some iron was co-extracted with D2EHPA + TBP system. Accordingly, 1.5 M D2EHPA + 0.2 M TBP contained 6.5 g/l U_3O_8, 2.5 g/l Y_2O_3 and 2.3 g/l Fe was prepared by contacting with WPA for yttrium stripping study. Various stripping reagents such as H_2SO_4 (10–40%), oxalic acid, HCl, 30% H_2SO_4 + 10% Na_2SO_4, 30% H_2SO_4 + 5% HF were tested to selectively strip yttrium from loaded organic at O/A ratio of 1 at temperature 28 ± 1°C. Based on the results shown in Table 3, 30% H_2SO_4, 40% H_2SO_4, 30% H_2SO_4 + 10% Na_2SO_4 and 6 M HCl were found to be effective, as quantitative stripping of yttrium was achieved from loaded extract in a single contact at O/A = 1. Substantial impurities of uranium and iron are strip together with yttrium in the loaded strip liquor as shown in Table 3 using the tested reagents. In contrast stripping with H_2SO_4 and H_2SO_4 + Na_2SO_4 resulted in high yttrium stripping and relatively lower uranium and iron contamination. Considering yttrium double sulphate precipitation by 30% H_2SO_4 + 10% Na_2SO_4, 30% H_2SO_4 was selected for the yttrium stripping tests. The above single contact experiments at elevated temperature of 55°C gave similar results for yttrium stripping but with increase in impurities comprising of uranium and iron. Hence, room temperature stripping was preferred in further experiments. Fig. 1 shows the variation in D values for uranium and yttrium with increase in sulphuric acid concentration from a synthetic loaded extract containing 6.5 g/l U_3O_8 and 2.48 g/l Y_2O_3.

Table 3
Yttrium (III) stripping test with various reagents from synthetic loaded D2EHPA + TBP. Loaded extract composition – U_3O_8: 6.5 g/l, Y_2O_3: 2.5 g/l, Fe: 2.3 g/l, O/A: 1

Stripping reagent	% Stripping at RT (28°C)		
	Y_2O_3	U_3O_8	Fe
10% H_2SO_4	29.8	<0.1	ND
20% H_2SO_4	33.4	0.5	2.7
30% H_2SO_4	95.7	3.0	8.3
40% H_2SO_4	98.7	6.9	9.2
30% H_2SO_4 + 10% Na_2SO_4	93.4	1.0	<0.5
30% H_2SO_4 + 5% HF	94	5.34	7.2
50% HCl	93	<0.5	28%
7.5% Oxalic acid	38.5	ND	87%

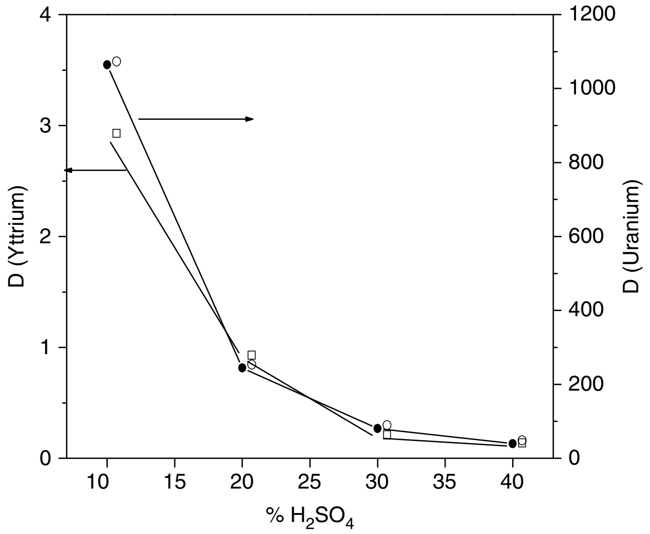

Fig. 1. Effect of sulphuric acid concentration on stripping of uranium and yttrium from synthetic loaded D2EHPA + TBP.

Feed (WPA) containing 50 mg/l Y_2O_3 and 130 mg/l U_3O_8 was processed using D2EHPA (1.5 M) + TBP (0.2 M) in an eight-stage counter current extraction at an O/A of 1:2. A lot of 180 contacts were given to obtain sufficient loaded extract-I (LE-I). Stripping of LE-I with MGA containing 15 g/l iron resulted in 1.3 l strip solution. The resultant strip solution containing 3062 mg/l U and 902 mg/l Y was diluted to 2.6 l and oxidized with hydrogen peroxide (emf > 600 mV). The above strip solution was further processed in the second cycle, comprising eight-stage counter current extraction with D2EHPA (1.5 M) + TBP (0.2 M) at an O/A of 1:2. About 350 ml of loaded extract-II (LE-II) was obtained in 32 contacts. LE-II containing 652 mg/l Y_2O_3 and 2665 mg/l U_2O_3 was stripped with 30% H_2SO_4 at an O/A of 2.5 in a four-stage of counter current set-up. After 11 contacts, raffinate and extract (stripped with 12 M H_3PO_4 + 10 g/l Fe) were analysed for uranium and yttrium. Results showed that the extract contained 4.3 mg/l yttrium and 2335 mg/l uranium, while raffinate contained yttrium (1620 mg/l) and uranium (55 mg/l). Inter-stage stripping analysis data is shown in Table 4. Almost quantitative stripping of yttrium was achieved in four-stages while ≈1% uranium was stripped out.

Table 4
Second cycle counter current stripping: Inter-stage analysis data. Loaded organic – Y_2O_3 : 652 mg/l, U_3O_8 : 2665 mg/l

Stage No.	Organic phase (mg/l)		Aqueous phase (mg/l)	
	U_3O_8	Y_2O_3	U_3O_8	Y_2O_3
1	2357	91.5	55	1620
2	2357	33.9	55	218
3	2356	5.9	55	34
4	2335	2.6	53	14

The stripping tests of yttrium from organic phases of DNPPA + TOPO and D2EHPA + TBP systems indicated that 40% and 30% sulphuric acid respectively are best suited to bring the yttrium into the aqueous phase with <0.15% loss of uranium.

3.3. Optimization of conditions for yttrium double sulphate precipitation

The feasibility of recovering yttrium from sulphuric acid solutions generated in both the processes has been tested. Recovery of rare earths as double sulphate precipitation method in presence of Na_2SO_4 is reported [14]. However, the conditions for obtaining rare earth double sulphate from such a highly acidic solution are not reported so far and also the conditions for precipitation are seldom mentioned in literature. Hence, process conditions were optimized to get maximum recovery of rare earths in the product with respect to parameters such as amount of Na_2SO_4, temperature, digestion time, yttrium concentration etc in both the processes (D2EHPA + TBP–WPA and DNPPA–TOPO–MGA).

3.3.1. Effect of sodium sulphate concentration

Effect of concentration of Na_2SO_4 on the recovery of yttrium as precipitate of sodium yttrium double sulphate from 30% sulphuric acid solution containing 2.5 g/l Y_2O_3 was studied at constant temperature of 50°C and digestion time of 45 min. The % recovery of yttrium as a function of Na_2SO_4 concentration is shown in Fig. 2. It was observed that with increase in Na_2SO_4

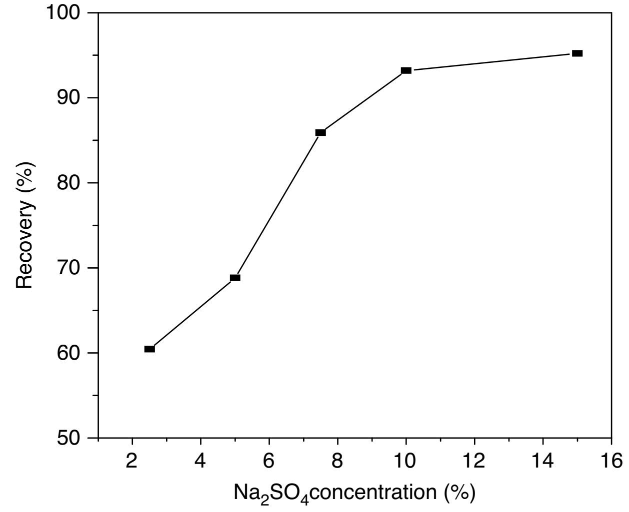

Fig. 2. Effect of sodium sulphate concentration on the recovery of yttrium.

concentration from 2.5 to 15%, the recovery of yttrium in precipitate increased from 60 to 95%. However, beyond 10% concentration of sodium sulphate, the recovery was found to be constant. Accordingly a 10% Na_2SO_4 concentration was selected for all the studies in the present investigation. The % recovery of yttrium as double sulphate has been evaluated based on the analysis of aqueous solution for yttrium content by ICP-AES.

In case of DNPPA + TOPO–MGA system, 40% sulphuric acid was effective for stripping of yttrium from organic phase. Accordingly, the conditions for obtaining yttrium double sulphate precipitate were arrived at in the light of the conditions suitable for 30% sulphuric acid solution. It was observed that with 14% of Na_2SO_4, temperature (70°C) and digestion time (45 min), the % recovery of yttrium from the aqueous strip solution was >98%.

3.3.2. *Effect of digestion time*

The effect of digestion time on the recovery of yttrium from 30% sulphuric acid solution containing 2.5 g/l Y_2O_3 and 10% Na_2SO_4 obtained in D2EHPA + TBP–WPA system was investigated at 28°C as well as at 50°C. The results obtained are depicted in Fig. 3. It is evident that at room temperature (28°C), the digestion time has no significant effect as the % recovery increased in the range of 40 to 44% with increase in digestion time from 15 to 240 min. At 50°C it was observed that 45 min digestion time is effective for recovering >90% yttrium from strip solution. Similarly results were obtained using 40% sulphuric acid strip solution obtained in DNPPA + TOPO–MGA system.

3.3.3. *Effect of temperature*

The effect of temperature on % recovery of yttrium from 30% sulphuric acid solution is shown in Fig. 4. The concentration of yttrium and sodium sulphate in feed was 2.5 g/l Y_2O_3 and 10% Na_2SO_4 respectively. The digestion time for the reaction mixture was fixed at 45 min while the temperature was varied from 28 to 70°C. The % recovery of yttrium in the precipitate increased almost linearly with an increase in temperature and at 70°C, the recovery was ≈97%. The % recovery of yttrium was found to follow the following empirical relationship with temperature in the range from 30 to 70°C, (correlation coefficient >98.5%).

$$\% \text{ Recovery} = (15.1 \pm 5.6) + (1.19 \pm 0.10) \times T \quad (1)$$

3.3.4. *Effect of yttrium concentration*

After optimizing experimental variables such as digestion time, temperature, concentration of sodium sulphate in the solution, the recovery of yttrium from 30% H_2SO_4 solution was investigated as a function of yttrium concentration in the aqueous solution at fixed temperature (50°C), digestion time (45 min) and Na_2SO_4 (10%). From the plot of % recovery vs yttrium concentration, it is evident that there is an increase in recovery from 88 to 99% for a ten-fold increase in yttrium concentration (Fig 5).

Under optimized conditions several test runs with synthetic as well as stripped solution of yttrium obtained from first cycle of DNPPA + TOPO–MGA and second cycle of D2EHPA+TBP–WPA processes rendered reproducible results with >95% recovery of yttrium in the precipitate.

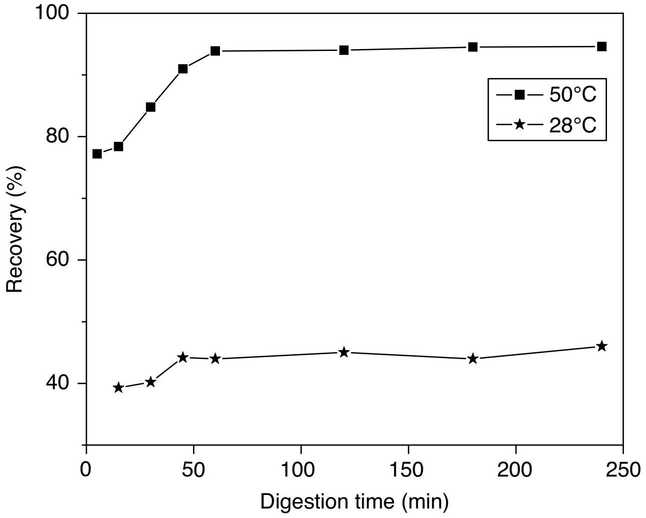

Fig. 3. Effect of digestion time on effective recovery of yttrium from sulphuric acid solution.

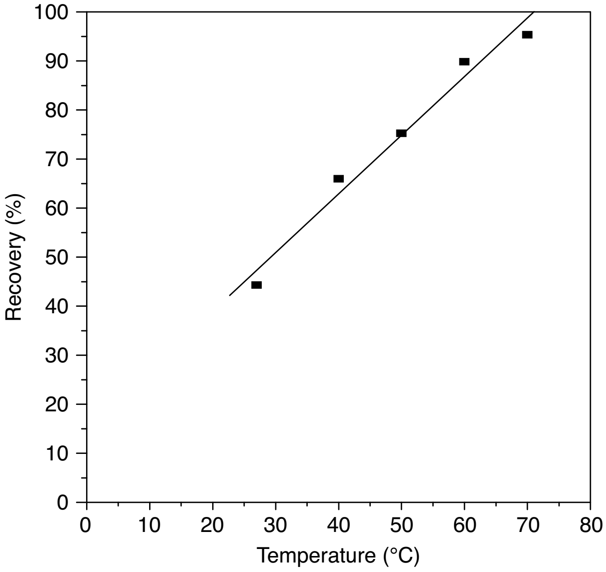

Fig. 4. Effect of temperature on recovery of yttrium from sulphuric acid solution.

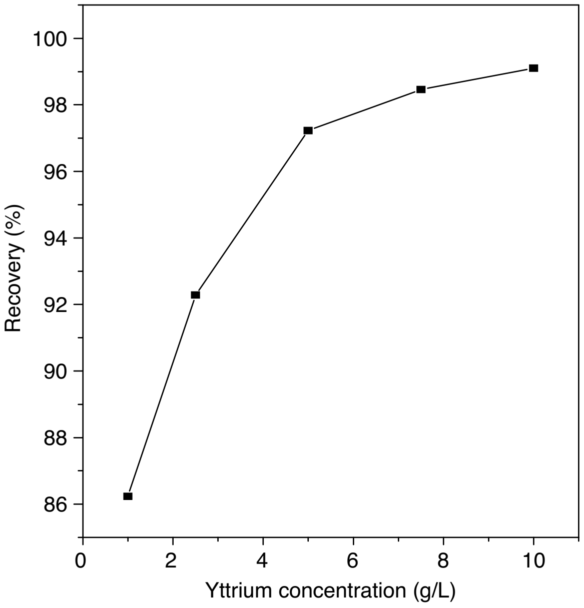

Fig. 5. Effect of yttrium concentration in aqueous solution on its recovery by double sulphate precipitation method.

3.4. *Recovery of yttrium as oxide from double sulphate precipitate*

The precipitate obtained during stripping of yttrium from both the schemes was washed thoroughly with 10% Na_2SO_4 and re-dissolved in distilled water. A representative solution containing 8.0 g/l Y_2O_3 was taken separately in 100 ml batches for the preparation of yttrium oxide by various routes. Three precipitation routes based on sodium carbonate, ammonium oxalate and oxalic acid were evaluated for precipitation of yttrium followed by ignition (at 850°C for one hour) to yield product Y_2O_3. The results obtained are tabulated in Table 5.

From the data shown in Table 5, ammonium oxalate and oxalic acid precipitation routes were found to be comparable with respect to purity of yttrium in the product oxide, while the carbonate route rendered only 30% pure product, remaining being sodium. Oxalic acid precipitation route has been adopted for rest of the work in the present investigation as it is practiced industrially to produce rare earth oxides from various sources [15,16]. Accordingly, the conditions for obtaining >98% recovery of yttrium in the corresponding oxalate were optimized. It was observed that the temperature and digestion time did not have any significant effect on the recovery, so the amount of oxalic acid used for precipitation purposes has been optimized. Fig. 6 shows the effect of amount of oxalic acid (7.5%) on % recovery of yttrium as yttrium oxalate from a solution containing 8.0 g/l Y_2O_3 (pH = 0.61) of yttrium. The temperature was fixed at 50°C and the digestion time at 30 min. The pH of the precipitation reaction was maintained at 2.0 by the addition of alkali. Stoichiometrically 11.3 ml of 7.5% oxalic acid is required for precipitation. From the graph it was observed that thrice the stoichiometric amount is essential for almost complete precipitation of yttrium.

The main impurity in the product oxide was found to be sodium. Sodium removal was observed to be feasible with hot water treatment of the oxide. Accordingly, experimental conditions were optimized with respect to solid to liquid ratio, digestion time and temperature to remove sodium contamination efficiently from the product Y_2O_3.

Table 5
Effect of different precipitation route on grade of yttrium in the product Y_2O_3

Precipitation route	Initial quantity of Y_2O_3 taken for precipitation (g)	Quantity of product obtained after ignition (g)	Grade of yttrium in the product Y_2O_3 (%)
Sodium carbonate	0.8	2.66	30
Ammonium oxalate	0.8	1.33	60
Oxalic acid	0.8	1.29	62

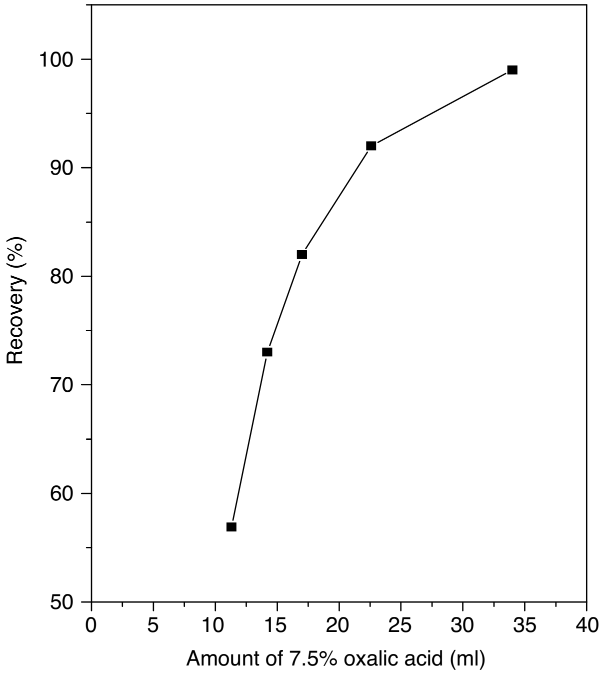

Fig. 6. Effect of amount of oxalic acid on the precipitation of yttrium.

3.4.1. Effect of solid to liquid (S/L) (g/ml) ratio

The impure yttrium oxide obtained through oxalic acid precipitation route was taken for sodium removal study. A known quantity of impure Y_2O_3 was taken in a glass beaker (100 ml) having different volumes of water. The resultant mixture was stirred on magnetic stirrer for 30 min at 85 ± 1°C. After filtration, the alkaline filtrate and the precipitate were analyzed for yttrium content. The results are shown in Fig. 7. The graph shows that S/L ratio had no significant effect. Consequently, S/L ratio of 0.02 was selected for further studies.

3.4.2. Effect of temperature and digestion time of sodium removal

After optimizing the conditions for solid to liquid ratio, important variables like temperature and digestion time were optimized to remove the sodium contamination effectively from the product yttrium oxide. The temperature was varied from 28 to 100°C keeping digestion time constant at 30 min. In the case of digestion time effect, the temperature was kept constant at 85°C, while digestion time was varied from 5 to 60 min. The results obtained in both the experiments are shown in Fig. 8. From the results, it is observed that with increase in temperature from 28 to 100°C, the purity of Y_2O_3 increased from 78 to 99.8%, while even 5 min digestion time was found to render 85% pure Y_2O_3, however it increased to 99.8% at 30 min.

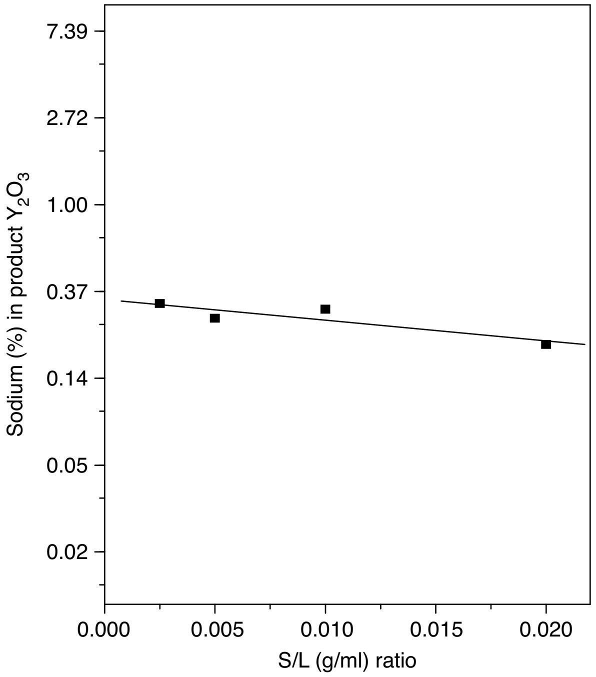

Fig. 7. Effect of solid to liquid ratio (g/ml) on removal of sodium contamination from Y_2O_3.

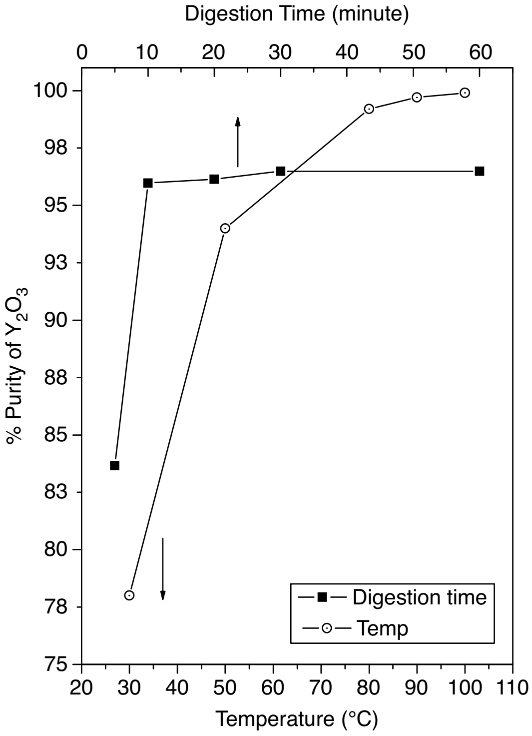

Fig. 8. Effect of temperature and digestion time on purity of Y_2O_3 in the product.

Under the optimized conditions of S/L ratio (0.02), temperature (85°C) and digestion time (30 min), the purity of the yttrium oxide obtained was found to be >99.8% with <0.2% sodium. The sodium removal study was tested on larger batches (1000 ml capacity). The results were found to be reproducible.

3.5. Conceptual flow-sheet

A conceptual flow–sheet (Fig. 9) has been proposed to incorporate separation schemes in both the processes [11,12] to recover the rare earths as by-product of uranium from fertilizer grade phosphoric acid. Rare earths are stripped out by sulphuric acid solutions in the first cycle of 0.6 M DNPPA + 0.3 M TOPO–MGA and second cycle of 1.5 M D2EHPA + 0.2 M TBP–WPA processes. The rare earths are precipitated as rare earths double sulphate, which upon re-dissolution and re-precipitation with oxalic acid rendered rare earths oxide following ignition. The impure rare earths oxide when treated with hot water under optimized conditions yielded sodium-free pure rare earths oxide (>99.8%). The proposed flow-sheet has been tested for DNPPA–TOPO–MGA process for the recovery of rare earths. A loaded extract comprising of 0.6 M DNPPA + 0.3 M TOPO + 1.27 g/l RE_2O_3 + 2.8 g/l U_3O_8 + ≈6.0 g/l iron was prepared by equilibrating MGA containing 0.095 g/l Y_2O_3,

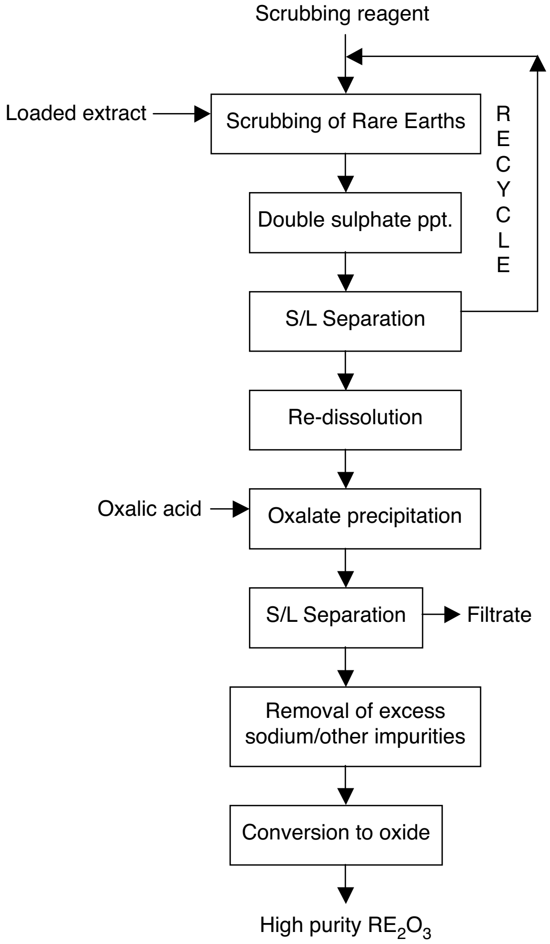

Fig. 9. Conceptual flow-sheet for rare earths recovery from MGA and WPA by DNPPA + TOPO and D2EHPA + TBP processes respectively.

0.028 g/l Er_2O_3, 0.0066 g/l Yb_2O_3, 0.0037 g/l Dy_2O_3, 0.29 g/l U_3O_8 and ≈2.0 g/l iron with 0.6 M DNPPA + 0.3 M TOPO dissolved in petrofin in a cross current manner. Experiments carried out under optimized conditions yielded >99% recovery of rare earths from the loaded extract (Table 6). Thus the feasibility of recovering rare earths from MGA has been established. Similar results were obtained with WPA as starting material.

Table 6
Recovery of rare earths in DNPPA + TOPO–MGA system

Sample	Composition (%)						
	Y_2O_3	Er_2O_3	Yb_2O_3	Dy_2O_3	U_3O_8	Iron	Sodium
Impure RE_2O_3 (Step 2)	40.6	16.27	3.8	2.3	ND	ND	≈38
RE_2O_3 after Na removal (Step 3)	67.5	23.5	5.6	3.3	ND	ND	<0.2

ND = not detected.

4. Conclusions

Stripping reagents such as 10% Na_2SO_4 + 30% H_2SO_4 and H_2SO_4 (30–40%) were found to be effective for selective separation of yttrium from uranium in DNPPA + TOPO and D2EHPA + TBP processes. The percentage stripping increased with decrease in phase ratio (O/A). Conditions for recovering rare earths as double sulphate in the presence of sodium sulphate from highly acidic strip solutions in both the processes have been optimized. Oxalic acid precipitation route was found to be optimum for obtaining high purity rare earths oxide from double sulphate. Sodium contamination from rare earths oxide product was removed by hot water treatment under optimized conditions. An effective process for the recovery of yttrium from strip solutions has been developed and tested. Feasibility of obtaining high purity rare earth oxide from phosphoric acid has been established.

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