International Journal of Minerals, Metallurgy and Materials
Volume 20, Number 8, August 2013, Page 713
DOI: 10.1007/s12613-013-0788-2

Solvent extraction and recovery of Y(III) and Yb(III) from fluorspar mineral

Y.A. El-Nadi[1,2], *N.E. El-Hefny*[1], *and H.F. Aly*[1]

1) Hot Laboratories Centre, Atomic Energy Authority, 13759, Egypt

2) Faculty of Science, Jazan University, Jazan 2097, Saudi Arabia

(Received: 3 November 2012; revised: 22 November 2012; accepted: 23 November 2012)

Abstract: Yttrium and ytterbium were extracted from sulfuric acid medium using triphenylarsine (TPAs) dissolved in kerosene. The influence of different factors, such as shaking time, extractants, metal ions, sulfate ion concentrations, as well as temperature, was studied in detail. From the slope analysis method and IR measurements, the structure of the extracted species was suggested as $MSO_4(HSO_4)\cdot TPAs$, where M refers to Y(III) or Yb(III). The equilibrium constants (K_{ex}) and thermodynamic parameters, such as the change in enthalpy (ΔH), free energy (ΔG), and entropy (ΔS), were calculated. The method of extraction and stripping was applied to obtain the aforementioned metals from a sample of fluorspar mineral giving a recovery yield of 88.2% and 83.5% for yttrium and ytterbium, respectively.

Keywords: yttrium; ytterbium; extraction; fluorspar; triphenylarsine

1. Introduction

Fluorspar is the commercial name of fluorite (CaF_2), which is the principal source of the element fluorine [1]. Crystalline fluorite has a very low index of refraction and an unusual ability to transmit UV light [2]. Fluorite comes in a variety of colors, which ranges from colorless through white, yellow, green, and purple to blue, but purple is the most common. The mineral is brittle and has a hardness of 4.0 (on the Mohs scale) and a density of 3.0 to 3.25 g/cm^3. It is used as a fluxing agent in steelmaking and in iron and steel foundries [3]. Fluorine compounds from fluorspar are used in water treatment to suppress dental caries and used to make fluoropolymers (such as Teflon), lubricants, and refrigerants [4]. In addition, it is used in aluminum fluoride manufacturing, primary aluminum production, glass manufacturing, enamels, ceramic, and hydrofluoric acid [5]. Major producing and exporting countries of fluorspar are China, Mexico, Kenya, Namibia, and South Africa [6-7]. Some fluorspar deposits offer potential for rare earth elements (REE) production from associated minerals or from the fluorite in which REE that substitute for some calcium [8]. For instance, fluorspar mining at Naboomspruit, South Africa, produced a small amount of monazite in the 1980s [9]. About 65 t of bastnasite concentrate were produced from a fluorspar deposit in the Gallinas mountains, New Mexico, in the 1950s [10].

Ideally, fluorite contains 51.1% calcium and 48.9% fluorine. Small quantities of rare earth elements and strontium may substitute for calcium within the crystal structure. Processing of fluorspar for production of hydrofluoric acid is generally carried out by acidulation with sulfuric acid, where hydrogen fluoride gas is released [11]; calcium sulfate is precipitated; and REE, if present, are transferred into the sulfate solution.

With the increasing demand for REE and their compounds in new materials and technology, the separation and purification of these elements from different resources have drawn extensive attention in recent years. Solvent extraction undoubtedly represents one of the recommended separation techniques for rare earths separation because of its simplicity, rapidity, applicability to various concentration ranges, and purity of the products. In this concern, the solvent extraction of several rare earth ions from sulfate solutions was extensively reported. Prominent extractants that were employed are high molecular weight amines [12-13], carboxylic acids [14], tri-*n*-butyl phosphate (TBP)

Corresponding author: Y.A. El-Nadi E-mail: yael_nadi@yahoo.com

[15], di-(2-ethylhexyl) phosphoric acid (D2EHPA) [16-17], and trialkylphosphine oxides (Cyanex 923) [18-19]. Furthermore, synergistic effect is a noticeable phenomenon in the solvent extraction of REE and was also studied widely [20-26].

The trialkylarsenic compounds (R_3As, R refers to alkyl group) have an unshared pair of electrons on the arsenic atoms, so they function as Lewis bases toward metal ions. Consequently, there are many coordination compounds in which R_3As molecules are ligands [27]. Many organoarsenic compounds are prepared by reactions of $AsCl_3$ with alkyl group transfer agents, such as Grignard reagents, lithium alkyls, or aluminum alkyls. R_3As species possess pronounced σ-donor and π-acceptor properties. This leads to their proliferation in coordination chemistry and, hence, their extensive use as ligands for many metals [28].

The few published papers on the treatment of fluorite mineral from one side and the limited use of TPAs as extractant from another side, as well as the growing attention for development of new extraction systems for the separation of REE as a group or from one another, make us to study the extraction and separation of Y(III) and Yb(III) from sulfuric acid medium by TPAs with application to their recovery as by product from a sample of fluorspar mineral.

2. Experimental

2.1. Reagents and apparatus

TPAs was obtained from Aldrich-Sigma and dissolved in kerosene. Stock solutions of yttrium and ytterbium were prepared from their oxides (Fluka, 99.99%) by dissolving in 9 mol/L sulfuric acid (BDH) and diluting with distilled water as required. All the other chemicals used were of analytical grade.

A Hanna digital pH meter was used for pH measurements. Shimadzu UV-160A spectrophotometer was employed for spectrophotometric determinations of metal concentrations, while infrared spectra were performed using FT-IR JASCO 6300 instrument.

2.2. Fluorspar sample

The fluorspar sample (1 kg) was obtained by hand picking from Jabel Dembeir, North Kordofan, Sudan, which lies at north latitude $12°34'30''$and east longitude $30°47'35''$. The fluorspar occurs in this area as veins or as replacement deposit in the marble. The sample used in the present work was purple in color and taken from the fissure filling veins tending NE-SW. The sample was milled and sieved to give a particle size of 74 μm (–200 mesh). The XRD of a representative sample indicated that the mineral is mainly fluorspar ($\geq$ 90 %) and contains minor amounts of quartz, calcite, kaolinite, and hematite. Table 1 shows the main crystallographic data of JCPDS and the fluorite sample.

2.3. Extraction procedures

Liquid-liquid extraction/stripping was carried out by shaking equal volumes (5.0 mL) of aqueous and organic phases in glass tubes using a mechanical shaker at 25°C for 30 min, which is found sufficient to reach equilibrium.

2.4. Measurements

Yttrium and ytterbium ions concentrations were separately determined by Arsenazo-III method [29]. Confirmatory simultaneous determinations of the metals concentrations were carried out using ICPS-7500 Shimadzu sequential plasma spectrometer.

The distribution ratio, D, was calculated from the relation:

$$D = \frac{C_o - C}{C} \tag{1}$$

where C_o is the original metal concentration in the aqueous phase before extraction, and C is the metal concentration in the aqueous phase after extraction.

Table 1. Selected crystallographic data of the standard (JCPDS) and fluorite sample

Peak No.	JCPDS			Fluorite		
	2θ / (°)	d / nm	I/I_0	2θ / (°)	d / nm	I/I_0
1	28.2726	0.31540	99	28.2416	3.15739	100
2	47.0101	0.19314	100	46.9727	1.93285	27
3	55.7664	0.16471	30	55.7303	1.64808	7
4	87.3854	0.11151	16	87.3247	1.11572	4

Note: JCPDS—International Centre for Diffraction Data(No.88.2301), PCPDFWIN v. 2.2 (2001).

3. Results and discussion

Using EDAX technique, the fluorspar sample under investigation was found to consist mainly of CaF_2 with small amounts of iron, yttrium, and ytterbium (Fig. 1). A complete assay of the sample is presented in Table 2.

3.1. Extraction investigations

As the dissolution of fluorspar minerals is usually performed by sulfuric acid, it is necessary to elucidate the extraction behavior of yttrium and ytterbium from such medium. In this respect, different extractants including thenoyltrifluoroacetone (HTTA), Cyanex 272, Cyanex 471x, Cyanex 301, Triphenyl arsine, Tridodecyl amine, Acetylacetone, and Lix 84 were tested to extract Y and Yb from 3 mol/L H_2SO_4 solution, to find out the most appropriate one. The extraction percent for Y and Yb

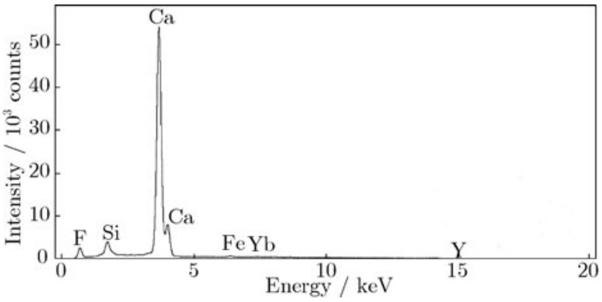

Fig. 1. EDAX spectrum of the fluorspar sample.

Table 2. Composition of the fluorspar sample using EDX technique %

Ca	F	Si	Fe	Y	Yb
62.71	31.44	4.19	0.66	0.57	0.43

by 0.2 mol/L of each extractant in kerosene was found as follows: 11% Y and 26% Yb by HTTA; 15% Y and 33% Yb by Cyanex 272; 8% Y and 16% Yb by Cyanex 471x; 1.5% Y and 10% Yb by Cyanex 301; 16% Y and 48% Yb by TPAs; 5% Y and 26% Yb by Tridodecyl amine; 2% Y and 11% Yb by acetylacetone; and 6% Y and 18% Yb by Lix 84. Accordingly, Triphenylarsine (TPAs) gave the highest extraction percent compared to the other extractants for both metal ions, and therefore, it was used throughout the present work.

3.1.1. Effect of extractant concentration

The variation of TPAs concentration on the extraction of Y(III) and Yb(III) from 3 mol/L sulfuric acid within the range 0.05-0.3 mol/L was studied. It was found that the extraction of both metals increased by increasing the extractant concentration. The slopes of lg-lg linear relations within TPAs concentration (up to 0.2 mol/L) with the corresponding distribution ratios were found to be about 1; Fig. 2 indicates that each metal ion is coordinated by 1 mol of TPAs.

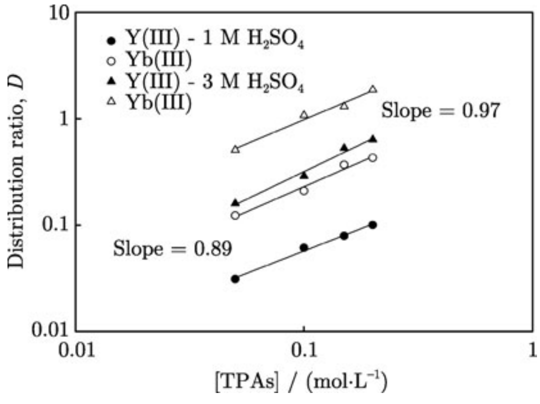

Fig. 2. Effect of TPAs on the extraction of Y(III) and Yb(III) from 3 mol/L H_2SO_4 at phase ratio (O/A) = 1 and 25°C.

3.1.2. Effect of sulfuric acid concentration

The effect of sulfuric acid concentration on the extraction of Y(III) and Yb(III) was investigated in the range 0.5-9 mol/L using 0.2 mol/L TPAs in kerosene. The relations between the sulfuric acid concentration in the aqueous phase and the respective distribution ratios (D) are represented in Fig. 3. It was found that the distribution ratio increases with the increase in sulfuric acid concentration, reaching a maximum value at $[H_2SO_4] = 3$ mol/L and then decreases with further increase in the acid concentration. The decrease in the extraction beyond 3 mol/L may be attributed to the probable extraction of sulfuric acid by TPAs at a higher acidity. On the other hand, Fe(II) and Ca(II), which represent the main impurities, were poorly extracted from such medium using TPAs as extractant.

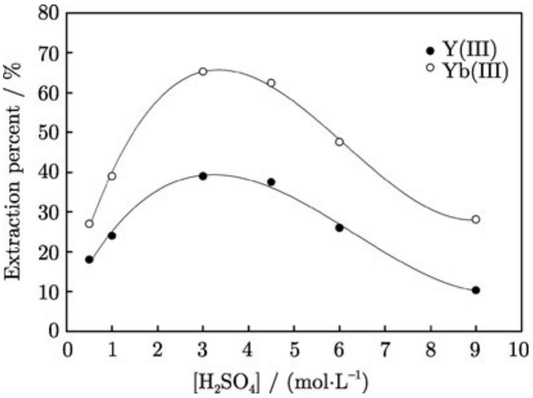

Fig. 3. Effect of sulfuric acid on the extraction of Y(III) and Yb(III) by 0.2 mol/L TPAs at phase ratio (O/A) = 1 and 25°C.

To understand the extraction of Y and Yb from sulfuric acid by TPAs, we have to consider the ionization of sulfuric acid in the solution:

$$H_2SO_4 \xrightarrow{k_{a1}} H^+ + HSO_4^- \tag{2}$$

$$HSO_4^- \overset{k_{a2}}{\rightleftharpoons} H^+ + SO_4^{2-} \tag{3}$$

where the ionization constants of H_2SO_4, k_{a1}, is very large, and $k_{a2} = 10^{-1.92}$ [30].

On the other hand, the stability constants (β_1) of Y and Yb with SO_4^{2-} are equal to $10^{3.47}$ and $10^{3.58}$, respectively [30]. When sodium sulfate was used to study the effect of sulfate ions in the aqueous phase on the extraction and regarding the complexes of Y^{3+} and Yb^{3+} with SO_4^{2-}, it is sufficient to consider only the first complex under the experimental conditions used as defined by

$$M^{3+} + SO_4^{2-} \xrightarrow{\beta_1} (MSO_4)^+ \tag{4}$$

Then, the total metal ions in the aqueous phase (M_t) are given by

$$M_t = M^{3+} + (MSO_4)^+ = [M^{3+}] + \beta_1[M^{3+}][SO_4^{2-}] = [M^{3+}](1 + \beta_1[SO_4^{2-}]) \tag{5}$$

The concentration of the anionic species, $[SO_4^{2-}]$ and $[HSO_4^-]$, in the aqueous phase can be calculated according to Eqs. (2)-(4), as well as the electric charge and material balance. The slope of the plot in Fig. 4, representing the relation of lg $[D(1+\beta_1[\mathrm{SO_4^{2-}}])]$ versus lg$[\mathrm{SO_4^{2-}}]$, is almost 1, suggesting the involvement of one $\mathrm{SO_4^{2-}}$ion in the extracted species, which is in agreement with that reported by Wang *et al.* [19], who studied the extraction of Yb(III) from H_2SO_4 medium by Cyanex 923. Since TPAs is a neutral extractant, metal ions are expected to be transferred into the organic phase as neutral species. Thus, $\mathrm{HSO_4^-}$ can act as another counter ion to balance of electric charge. This is supported by the slope resulting from the plotting of lg$[D(1+\beta_1[\mathrm{SO_4^{2-}}])]$ against lg$[\mathrm{HSO_4^-}]$, as seen in Fig. 4. To verify these findings, the FTIR spectrum of the extracted Yb-TPAs complex was measured and shown in Fig. 5. A stretching vibration of $\mathrm{SO_4^{2-}}$ appeared as a strong band at 1077 cm^{-1}, which indicates that $\mathrm{SO_4^{2-}}$ takes part in the coordination of the extracted complex. While a medium band at 465 cm^{-1}, which is due to $\mathrm{HSO_4^-}$, suggests that $\mathrm{HSO_4^-}$ is also coordinated to the extracted species resulting in the process of extraction.

3.1.3. Extraction equilibrium

Based on the slopes resulted in Figs. 2 and 4, as well as the IR spectrum (Fig. 5), the extraction equilibrium of Y(III) and Yb(III) from sulfate solutions with TPAs may be written as

$$\mathrm{M^{3+}} + \mathrm{SO_4^{2-}} + \mathrm{HSO_4^-} + \overline{\mathrm{TPAs}} \rightleftharpoons \overline{\mathrm{M(SO_4)HSO_4\cdot TPAs}} \tag{6}$$

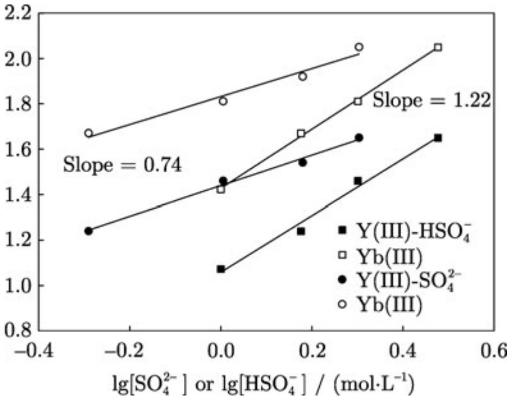

Fig. 4. Effect of sulfate ions on the extraction of Y(III) and Yb(III) by 0.2 mol/L TPAs at phase ratio (O/A) = 1 and 25°C.

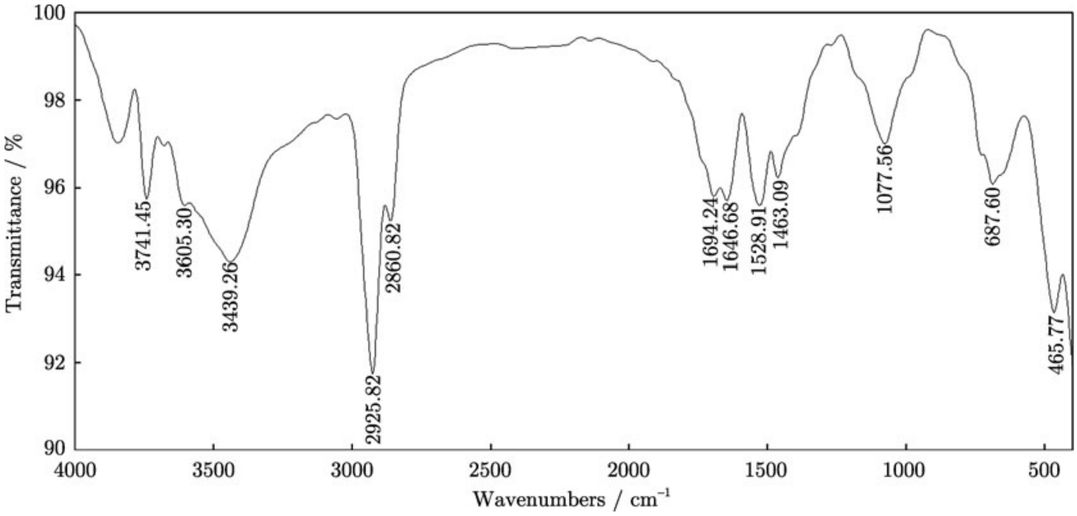

Fig. 5. IR spectrum of the ytterbium-TPAs complex.

The equilibrium constant of the extraction is given by

$$K_{\mathrm{ex}} = \frac{[\overline{\mathrm{M(SO_4)HSO_4\cdot TPAs}}](1+\beta_1[\mathrm{SO_4^{2-}}])}{[\mathrm{M^{3+}}][\mathrm{SO_4^{2-}}][\mathrm{HSO_4^-}][\overline{\mathrm{TPAs}}]} \tag{7}$$

$$K_{\mathrm{ex}} = \frac{D(1+\beta_1[\mathrm{SO_4^{2-}}])}{[\mathrm{SO_4^{2-}}][\mathrm{HSO_4^-}][\overline{\mathrm{TPAs}}]} \tag{8}$$

where bars indicate the species in the organic phase.

Taking the lg of Eq. (8), Eq. (9) is obtained:

$$\mathrm{lg}K_{\mathrm{ex}} = \mathrm{lg}(D(1+\beta_1[\mathrm{SO_4^{2-}}])) - \mathrm{lg}[\mathrm{SO_4^{2-}}] - \mathrm{lg}[\mathrm{HSO_4^-}] - \mathrm{lg}[\overline{\mathrm{TPAs}}] \tag{9}$$

The average value of K_{ex} calculated at different sulfate, bisulfate, and extractant concentrations were found to equal 3.26 × 10^3 for Y(III) and 1.24 × 10^4 for Yb(III).

3.1.4. Effect of temperature

The effect of temperature on the extraction of Y(III) and Yb(III) (1 g/L each) was investigated in the range 15-45°C using 0.2 mol/L TPAs in kerosene from 3 mol/L H_2SO_4 solutions. The increase of the temperature was found to slightly decrease the extraction. Using the Van't Hoff equation [31], the enthalpy change was calculated from the relation:

$$\mathrm{ln}K_{\mathrm{ex}} = -\frac{\Delta H}{RT} + C \tag{10}$$

where R is the universal gas constant (8.314 J·mol^{-1}·K^{-1}), and C is a constant.

The plot of $\ln K_{ex}$ versus $1/T$ for the extraction of each metal ion gave straight line as shown in Fig. 6. The negative values of the enthalpy change for the extraction calculated from the slopes of the linear relations indicate the exothermic nature of the extraction process (Table 3). The free energy change (ΔG) and the entropy change (ΔS) were calculated using the equations:

Table 3. Thermodynamic functions of the extraction of Y(III) an Yb(III) from 3 mol/L H_2SO_4 medium by 0.2 mol/LTPAs in kerosene at phase ratio = 1

Metal ion	ΔH / (kJ·mol^{-1})	ΔG / (kJ·mol^{-1})	ΔS / (J·mol^{-1}·K^{-1})
Y(III)	−77.6	−20.1	−192.9
Yb(III)	−52.8	−23.4	−98.6

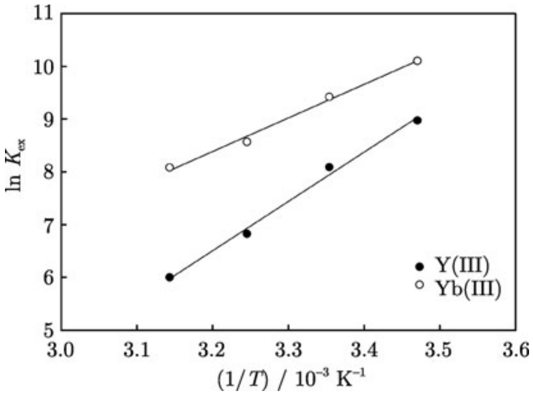

Fig. 6. Effect of temperature on the extraction of Y(III) and Yb(III) from 3 mol/L H_2SO_4 by 0.2 mol/L TPAs at phase ratio (O/A) = 1.

$$\Delta G = -RT\ln K_{ex} \tag{11}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{12}$$

As shown in Table 3, the negative value of ΔG for the extraction of Y(III) and Yb(III) by TPAs from sulfuric acid medium refers to the spontaneous nature of the extraction reaction, while the negative values of entropy change indicate the decrease in the disorder upon the extraction reaction. It is interesting to mention that in organic solvents, solvation generally is weaker than in aqueous solutions. Consequently, the desolvation reaction may result in small values of ΔH_{sol} and ΔS_{sol} (for solvation). Therefore, ΔH_{com} and ΔS_{com} (for combination of the metal and ligand) are $\geq \Delta H_{sol}$ and ΔS_{sol}, respectively [32]. This suggests that $\Delta H_{reaction}$ is often negative, whereas $\Delta S_{reaction}$ may be positive or negative, which is consistent with the values obtained and presented in Table 3.

3.2. Development of extraction process

To develop the initial parameters for extraction process, the effect of phase ratio on the extraction of metal ions as well as the selection of suitable stripping reagent are required.

3.2.1. Effect of phase ratio and metal ion concentration

When the organic/aqueous phase ratio (O/A) increased from 1/3 to 3/1, the increasing tendency of the extraction from 3 mol/L H_2SO_4 solution by 0.2 mol/L TPAs in kerosene was almost the same for Y(III) and Yb(III) (Fig. 7). In addition, the effect of change in both metals concentration (0.25 g/L to 1.25 g/L) on the extraction process was investigated. A McCabe-Thiele diagram [33] was constructed as a relation between the metal ions transferred to the organic phase to that remained in the aqueous phase after extraction. This was performed to predict the number of stages required for extraction of Y and Yb contained in fluorspar sample. As shown in Fig. 8, three stages are sufficient for almost the complete extraction of Y, while two steps are required in the case of Yb.

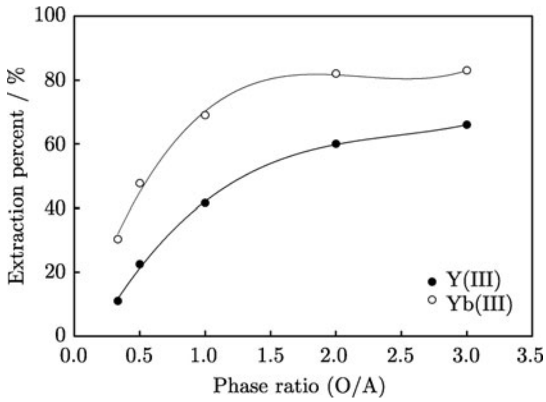

Fig. 7. Effect of phase ratio on the extraction of Y(III) and Yb(III) from 3 mol/L H_2SO_4 by 0.2 mol/L TPAs at 25°C.

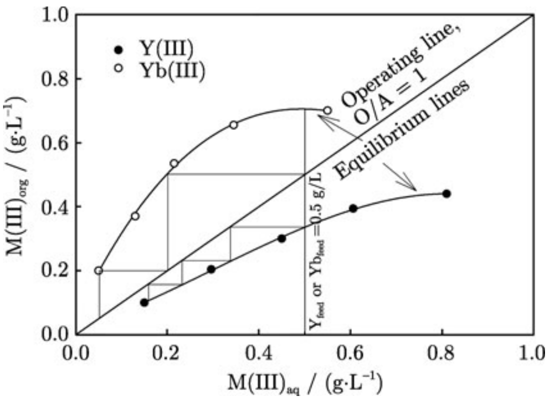

Fig. 8. McCabe-Thiele diagram for the extraction of Y(III) and Yb(III) from 3 mol/L H_2SO_4 by 0.2 mol/L TPAs at phase ratio (O/A) = 1 and 25°C.

3.2.2. Stripping investigations

Stripping investigations were carried out on the organic solution consisting of TPAs in kerosene and containing Y(III) and Yb(III) after extraction from 3 mol/L H_2SO_4 solution. The effect of different concentrations of mineral acids on the stripping of metal ions from the loaded organic solvents was studied at 25°C and phase ratio = 1. The results given in Fig. 9 show that sulfuric acid (0.01 mol/L) can be considered as a promising stripping agent since it leads to better stripping of yttrium over ytterbium. Two stripping steps were found sufficient to recover most of yttrium from the loaded organic phase. In the case of ytterbium, using 0.1 mol/L hydrochloric acid solution can help in its separation from the solution.

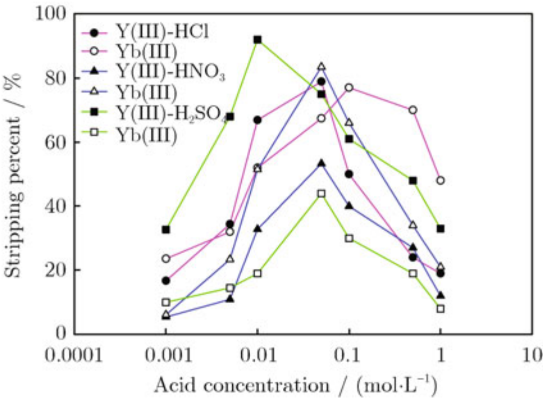

Fig. 9. Effect of different mineral acid solutions on the stripping of the organic TPAs phase loaded with Y(III) and Yb(III) after extraction at 25°C.

3.2.3. Application to fluorspar sample

As shown in Fig. 10, the application of the studied method of extraction is performed as follows: 10 g of the ground fluorspar sample was attacked by 100 mL of 9 mol/L sulfuric acid solution at 100°C for 2 h with stirring, where $CaSO_4$ precipitated; HF gas evolved; and rare earth contents were released in the solution. This solubilizes about 97.8% of the rare earths contents [34] and releases HF, which could be converted into high purity CaF_2 by bubbling the gas in $CaCO_3$ solution. The dissolved rare earths were removed from the leach liquor by filtration from the precipitated CaF_2. The filtrate containing Y(III) and Yb(III) with some other impurities was diluted with water to reach 3 mol/L H_2SO_4 solution. The solution was shaken with 0.2 mol/L TPAs in kerosene to extract Y(III) and Yb(III), leaving other impurities in the aqueous phase. The loaded organic solution was washed with water and treated with 0.01 mol/L H_2SO_4, followed by the addition of 0.1 mol/L HCl to strip Y and Yb, respectively. The resulted lanthanides were precipitated as oxalate by using oxalic acid solution, giving a recovery yield of 88.2% for yttrium and 83.5% for ytterbium.

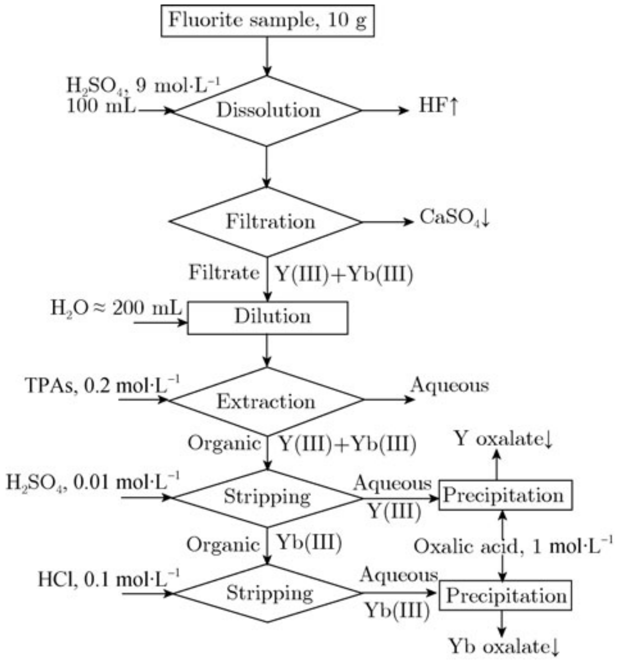

Fig. 10. Flowsheet for the process of extraction and recovery of yttrium and ytterbium from the fluorspar sample.

4. Conclusion

The extraction of yttrium and ytterbium from sulfuric acid medium was performed by using of triphenylarsine in kerosene. The extracted species was suggested as $MSO_4(HSO_4)\cdot TPAs$, where M refers to Y(III) or Yb(III) based on the slope analysis method and IR measurements. The temperature had a retarding effect on the extraction process of both metals. The extraction process proceeded exothermically, spontaneously, and associated with decreasing in the disorder. The method of extraction and stripping was successfully applied to recover Y and Yb from a sample of fluorspar mineral.

References

[1] S.E. Manahan, *Environmental Science and Technology: A Sustainable Approach to Green Science and Technology,* 2nd Ed., CRC Press, Florida, 2007, p. 307.

[2] R.B. Fulton and G. Montgomery, *Industrial Minerals and Rocks,* 5th Ed. American Institute of Mining Metallurgical and Petroleum Engineers, New York, 1983, p. 723.

[3] P.W. Harben and R.L. Bates, *Industrial Minerals: Geology and World Deposits*, Industrial Minerals Division, Metal Bulletin plc, London, 1990, p. 11.

[4] T.W. Swaddle, *Inorganic Chemistry: An Industrial and Environmental Perspective,* Academic Press, USA, 1997, p. 12.

[5] M.M. Miller, *Mineral Commodity Summaries*, U.S. Bureau of Mines, 1995, p. 58.

[6] M.M. Miller, *Minerals Yearbook: Vol. 1, Metals and Min-*

erals, U.S. Bureau of Mines, 1992, p. 487.

[7] U.S. Bureau of Mines, *Randol Mining Directory 1994/199*5, Randol International Ltd, Golden, CO, 1994, p. 165.

[8] S.B. Castor and J.B. Hedrick, *Industrial Minerals and Rocks*, 7th Ed, Society for Mining Metallurgy, 2006, p. 778.

[9] J.B. Hedrick and D.A. Templeton, *Rare Earth Minerals and Metals*, USBM, Washington, DC, 1989.

[10] J.W. Adams, *Mineral and Water Resources of New Mexico*, Bulletin 87, New Mexico Bureau of Mines and Mineral Resources, Socorro, 1965, p. 234.

[11] J.W. Sutter and D.M. Burt, Hydrofluoric acid generation in mine dumps and tailing: experimental determination of reaction rates, [in] *Proceedings of GSA Annual Meeting*, Vol. 151, 2001.

[12] D.D. Desai and V.M. Shinde, Liquid anion-exchange extraction and separation of yttrium, neodymium and samarium, *Anal. Chim, Acta*, 167(1985), p. 413.

[13] O.A. Desouky, A.M. Daher, Y.K. Abdel-Monem, and A.A. Galhoum, Liquid-liquid extraction of yttrium using primene-JMT from acidic sulfate solutions, *Hydrometallurgy,* 96(2009), p. 313.

[14] D.K. Singh, H. Singh, and J.M. Mathur, Extraction of rare earths and yttrium with high molecular weight carboxylic acids, *Hydrometallurgy*, 81(2006), p. 174.

[15] J.N. Mathur and G.R. Choppin, Paraffin wax as a diluent for extraction of actinides and lanthanides with TBP, *Solvent Extr. Ion Exch.*, 16(1998), p. 459.

[16] E. Panturu, D.P. Georgescu, F. Aurelian, and N. Udrea, Selective separation of yttrium from chemical concentrate of rare earth, *Dev. Miner. Process. C*, 13(2000), p. 6.

[17] J.Z. Zhou, W.H. Duan, X.Z. Zhou, and C.Q. Zhang, Application of annular centrifugal contactors in the extraction flowsheet for producing high purity yttrium, *Hydrometallurgy*, 85(2007), p. 154.

[18] B. Gupta, P. Malik, and A. Deep, Solvent extraction and separation of tervalent lanthanides and yttrium using Cyanex 923, *Solvent Ext. Ion Exch.*, 21(2003), No. 2, p. 239.

[19] W.W. Wang, X.L. Wang, S.L. Meng, H.F. Li, and D.Q. Li, Extraction and stripping of ytterbium(III) from H_2SO_4 medium by Cyanex 923, *J. Rare Earths*, 24(2006), p. 685.

[20] S. Tachimori and H. Nakamura, Application of synergistic MEHPA-DEHPA mixed solvent to the extraction of lanthanides(III), *J. Radioanal. Nucl. Chem.*, 44(1978), No. 1, p. 37.

[21] B.V. Reddy, L.L. Reddy, A.S. Reddy, M.L.P. Reddy, S. Sujatha, T.R. Ramamohan, and A.D. Danodaran, Synergistic solvent extraction of Eu(III) and Tb(III) with mixtures of various organophosphorus extractants, *J. Radioanal. Nucl. Chem.*, 178(1994), No. 1, p. 109.

[22] S. Jing and D.Q. Li, Study of synergistic extraction of rare earth element (III) with BTMPPA and HBMBP, *Appl. Chem.*, 11(1994), No. 3, p. 49.

[23] Y. Xiong, X.L. Wang, and D.Q. Li, Synergistic extraction and separation of heavy lanthanide by mixtures of bis(2,4,4-trimethylpentyl) phosphoric acid and 2-ethylhexyl phosphinic acid mono-2-ethylhexyl ester, *Sep. Sci. Technol.*, 40(2005), p. 2325.

[24] X.W. Huang, J.N. Li, Z.Q. Long, X.X. Xue, Y.Q. Zhang, and Z.W. Zhu, Synergistic extraction of rare earth by mixtures of 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester and di-(2-ethylhexyl) phosphoric acid from sulfuric acid medium, *J. Rare Earths*, 26(2008), No. 3, p. 410.

[25] Y.Q. Zhang, J.N. Li, X.W. Huang, C.M. Wang, Z.W. Zhu, and G.C. Zhang, Synergistic extraction of rare earths by mixture of HDEHP and HEH/EHP in sulfuric acid medium, *J. Rare Earths*, 26(2008), No. 5, p. 688.

[26] Y.A. El-Nadi, Lanthanum and neodymium from Egyptian monazite: Synergistic extractive separation using organophosphorus reagents, *Hydrometallurgy,* 119-120(2012), p. 23.

[27] J.E. House, *Inorganic Chemistry*, Academic Press, Canada, 1998, p. 410.

[28] Ch. Elschenbroich and A. Salzer, *Organometallics: A Concise Introduction*, 2nd Ed, VCH Verlagsgesellschaft, Weinheim, 1992, p. 206.

[29] Z. Marczenko, *Spectrophotometric Determination of Elements*, Ellis Harwood Ltd., Chichester, 1976, p. 438.

[30] J.G. Speight, *Lange's Handbook of Chemistry*, 16th Ed, McGraw-Hill, Inc, New York, 2005, p. 330.

[31] D.W. Rogers, *Concise Physical Chemistry*, John Wiley & Sons, Inc., New Jersey, 2011.

[32] J. Rydberg, C. Musikas, and G.R. Choppin, *Principles and Practices of Solvent Extraction*, 2nd Ed., Marcel Dekker Inc., New York, 1992, p. 584.

[33] M. Benedict, T.H. Pigford, and H.W. Levi, *Nuclear Chemical Engineering*, 2nd Ed., McGraw-Hill Book Company, New York, 1982.

[34] T.M.M. Ibrahim and O.M. El-Hussaini, Production of anhydrite-gypsum and recovery of rare earths as a by-product, *Hydrometallurgy*, 87(2007), p. 11.