

SEPARATION AND RECOVERY OF RARE EARTHS AFTER RED MUD LEACHING BY CATION - EXCHANGE CHROMATOGRAPHY

Lamprini-Areti TSAKANIKΑ, Maria OCHSENKÜHN-PETROPOULOU

Laboratory of Inorganic and Analytical Chemistry, School of Chemical Engineering, National Technical University of Athens, Iroon Polytechniou 9, Zografou Campus, 15780 Athens, GR

btsakanika@gmail.com, oxenki@central.ntua.gr

Abstract

In this study the selective separation and recovery of rare earths from the main elements in the leachate after red mud treatment, were investigated. An ion exchange process was developed using a suitable industrial strong cation exchanger and multiple successive elutions by selective eluents. The absorption and elution conditions for both rare earths - especially Sc- and Fe including the residence time, the bed volume, the flow rate, the kind, the concentration of eluents and their appropriate volumes were investigated and optimised firstly in lab scale. The aim was to improve rare earths' recovery and their separation of the main elements, especially Fe. The developed ion exchange process was successfully applied on pilot plant and a good agreement with the lab scale experiments was found.

Introduction

Scandium (Sc) and other rare earth elements (REEs), such as yttrium (Y) and lanthanides (Ln), are elements of high techno-economical interest, especially in high purity, due to their large variety of modern technological applications.¹⁻⁴ The main minerals hosting these elements are monazite [(REE)PO₄], bastnaesite [(REE)(CO₃)F] for the lighter REEs and xenotime [YPO₄] for the heavier REEs, where they are usually associated in ores with often radioactive natural minerals,¹⁻³ while scandium's main mineral is the very rare thortveitite [(Sc, Y)₂Si₂O₇].⁵ As REEs are usually found together, their individual recovery is difficult due to their similar chemical properties derived of their same valence and similar ionic radii. Therefore, to their purification from the matrix as well as their separation as individual elements chromatographic and solvent extraction techniques have been developed.⁶⁻¹¹

The commercial prices of REEs and Sc, especially in high purity, are high due to their increasing demand as well as the difficulty in their recovery and the rarity of economical exploitable resources, especially for scandium.^{2,12,13} As China controls by

its production 97 % of the global market³ the discovery and utilisation of alternative resources, such as apatite mining, uranium tailings etc. seems to be attractive. Among them, it has been found that red mud (RM) the insoluble, fine grained alkaline byproduct of the alumina production after Bayer process is enriched in scandium, yttrium and lanthanides, having a total uniform concentration over more than 20 years of 0.1 %.^{11,14} Especially the content of Sc $\sim 130 \text{ g}\cdot\text{tn}^{-1}$ dry RM (0.02 % Sc_2O_3), is close to the content in its main resources.^{10,11,14} The bauxitic residue consists mainly of oxides of Fe (about 45 %), Ca, Al, Si, Ti, Na, containing also minor concentrations of V and Zr. Its global production is estimated ~ 120 million tonnes/year, while in Greece the industry “Aluminium of Greece” produces annually 700,000 tonnes.¹⁵

In the present work, the selective separation and recovery of REEs and Sc from RM was achieved by an ion exchange procedure. The developed technique was based on a preliminary study using an analytical grade ion exchanger.⁶ In this study an industrial strong acid cation exchanger was used and the optimum absorption and elution conditions were investigated in lab and pilot plant scale.¹⁶ Different inorganic acids (HNO_3 , HCl , H_2SO_4) of industrial grade were used as eluents, firstly for the removal of the main elements (ME) and secondly for the quantitative recovery of Sc and REEs. The absorption and elution conditions for rare earths -especially Sc - and Fe including the residence time, the bed volume and the flow rate were optimised. In addition, the required volumes of the eluents, necessary for the quantitative removal of main elements and mainly Fe as well as the highest possible recovery of Sc and REEs, were also investigated and optimised. The developed ion exchange procedure was applied to red mud samples from the alumina production, after their appropriate leaching.^{16,17}

Experimental

Instrumentation

A peristaltic pump (IsmaTec, Switzerland) and a dosimetric pump (Prominent GmbH, Germany) were used to adjust the flow rates in lab and in pilot plant experiments respectively. The ion exchanger (resin) was packed in glass columns with a resin bed volume of 25 ml (lab scale) and 5l (pilot plant scale, operating in multiple stages). For the determination of ME and especially Fe in the leachates and eluates, a flame atomic absorption spectrometer (AAS, Varian Model AA240FS) was used. The selected elements' wavelengths were: Fe 238.204 nm, Ca 422.7 nm, Na 589.0 nm, Al 309.3 nm, Si 251.6 nm, Ti 364.3 nm and V 318.5 nm. Sc and REEs were analysed by inductively coupled plasma-optical emission spectrometry (ICP-OES, Optima 7000DV Perkin Elmer). The conditions were: power 1450 W, cooling gas flow (Ar) $12 \text{ l}\cdot\text{min}^{-1}$,

sheath gas flow (Ar) 0.2 l min^{-1} , nebulisation pressure 2.0-2.5 bar, sample uptake $1.5 \text{ ml}\cdot\text{min}^{-1}$ and the selected elements' wavelengths: Sc 361.384 nm, Yb 328.937 nm, Er 369.265 nm, Y 360.073 nm, Eu 381.967 nm, Nd 430.358 nm, Ce 418.660 nm, La 398.852 nm.

Reagents-samples

Concentrated acids such as HNO_3 68 wt%, HCl 32-33 wt% and H_2SO_4 98 wt%, were of industrial grade (Kalogeropoulos Chemicals S.A. Greece). The eluents were prepared by dilution of the appropriate amounts of acids in de-ionised water (Ionel S.A.). Stock standard solutions of Sc and REEs in the range of $10^3 \text{ mg}\cdot\text{l}^{-1}$ in 2 % HNO_3 of 99.999 % purity, were supplied by CPI Int, USA. The corresponding stock solutions of the ME such as Fe, Ca, Na, Al, Si, Ti, V in the range of 10^3 or $10^4 \text{ mg}\cdot\text{l}^{-1}$ were supplied by Fluka Chemika. Working solutions in the range of $0.5\text{-}10 \text{ mg}\cdot\text{l}^{-1}$ for REEs and $1\text{-}100 \text{ mg}\cdot\text{l}^{-1}$ for the ME, were prepared daily by dilution of the appropriate amounts of stock standard solutions in HNO_3 (65 %, p.a., Merck).

Analytical Procedure

Preparation of feed solution

The feed solution enriched in Sc and the other REEs with a low content of Fe about 2 %, coming from an optimised hydrometallurgical treatment of red mud by a selective acidic leaching under ambient conditions, is described elsewhere.^{16,17}

Ion exchange procedure

For the first batch experiments a portion of 50 ml (or 50 l in a pilot plant scale) of the filtered liquid (feed solution) was passed through the cation exchanger using a dosimetric pump. All elements were retained totally in the column except Na, Si, V, which were found in a range 10-100 % in the effluent. The ME were firstly eluted and removed from the column using appropriate solutions of HNO_3 or HCl . A second elution using HNO_3 , HCl , H_2SO_4 as eluents in a range of 1-7 M was followed for the recovery of Sc and REEs. The elutions were carried out at a flow rate of $1 \text{ ml}\cdot\text{min}^{-1}$ in lab scale and $0.2 \text{ l}\cdot\text{min}^{-1}$ in pilot plant scale respectively. The appropriate conditions in pilot plant scale such as the volume of ion exchanger and the flow rate of the eluents, were selected so as to keep same the residence time τ about 25 min in both laboratory and pilot plant experiments.¹⁶

Results and Discussion

Absorption

Resin bed volume and flow rate effects

The absorption behavior of the ion exchanger was investigated in lab scale by varying the resin bed volume (15 ml – 25 ml) and the flow rate of the feed solution (1-2 ml·min⁻¹). It was found that a resin bed volume of 25 ml and the flow rate of 1 ml·min⁻¹ were the most appropriate conditions.¹⁰

Ion exchanger capacity

As a feed solution the filtered liquid after the acidic leaching was used. In the following absorption procedure (flow rate of 1 ml·min⁻¹) a total of 53 fractions, 25 ml each, was collected. The results are shown in the diagrams of Figures 1, 2. Iron appears in the effluent firstly after the 17th fraction of the feed solution, while Y and Sc after the 32nd and the 37th fraction, respectively. It results that the selected ion exchanger retains stronger Sc and Y in comparison to Fe, which causes the breakthrough of Fe much faster than of the investigated REEs.

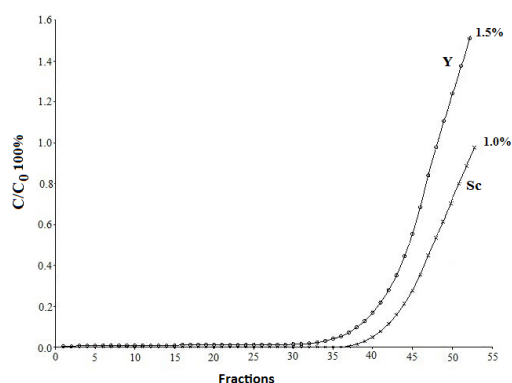


Figure 1: Breakthrough curve of Sc and Y (Column vol.25 ml, flow rate 1 ml·min⁻¹)¹⁰

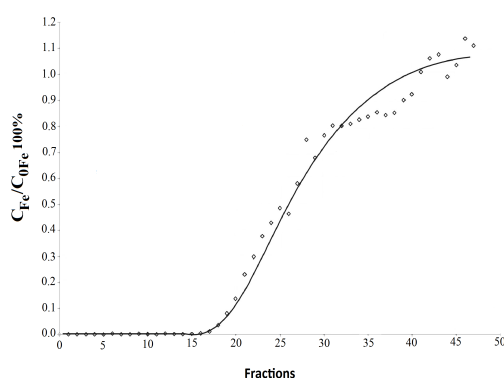


Figure 2: Breakthrough curve of Fe (Column vol.25 ml, flow rate 1 ml·min⁻¹)¹⁰

Elution

Iron and 'other' main elements removal

According to previous experiments, the concentration of 1.75M HNO₃ was proposed for the elution and removal of ME from the analytical grade cation exchanger DOWEX 50XW8.¹⁶ By using the industrial strong cation exchanger, it was found that for the same eluent the ME were eluted with the first 25 ml (or L pilot plant) of 1.75M HNO₃, while Fe was removed slowly from the column and higher volumes of eluent (ratio of eluent to feed solution 3:1) were required for its quantitative

removal. Furthermore, losses of Sc and Y were observed about 1.5-14.0 %. Aiming to reduce the required eluents' volumes for Fe total removal and minimising Sc and Y losses, HCl was used as an alternative eluent. The comparison of the effectiveness of the two investigated acids is shown in Figure 3. It resulted that by using 1.75 M HCl a lower ratio of eluent to feed solution about 2:1 was appropriate for the quantitative removal of iron (100 %). In addition, Sc and Y losses by elution with 1.75M HCl were restricted to a percentage of 2-3 %.

The above elution process was applied also on pilot plant scale. By the comparison of % removal of iron and % losses of Sc and Y a good agreement of the results was obtained in both lab and pilot plant scale processes. The same tendency was found for the other ME.¹⁰

Scandium and other Rare earths

Representative elements of REEs were selected such as La, Nd, Ce from the light REEs, Y and Eu from the middle REEs, Er and Tb from the heavy REEs. For the elution and their quantitative recovery from the cation exchanger, different eluents such as HNO₃, HCl, H₂SO₄ were tested firstly in lab scale. It resulted that nearly quantitative recovery of Sc and REEs as a group was achieved using 6 M HNO₃. Thus, scandium was recovered in a percentage higher than 99 %, while the elution of the other REEs was observed in a range of 82-97 %. A slightly higher recovery of the other REEs in the range of 86-100 % was obtained using 5 M HCl as eluent, but smaller amounts of about 72 % of Sc were recovered. By using higher concentrations of HCl in order to increase the % recovery of Sc and REEs no improvement was achieved.¹⁰ Furthermore, a selective elution of Sc, was achieved with H₂SO₄. Especially, using 1M H₂SO₄, scandium was recovered in a percentage of 80-100 %, while yttrium was co-eluted in a percentage of 4-24 %. Applying higher flow rates the recovery of Sc is decreased, as it is presented in Figure 4.

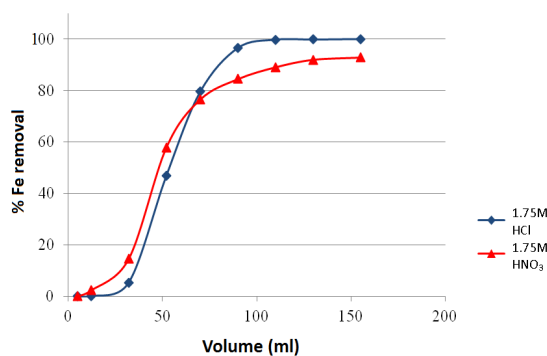


Figure 3: % removal of Fe in 1.75 M HNO₃ and 1.75 M HCl ($V_{\text{feed solution}} = 50\text{ml}$)¹⁰

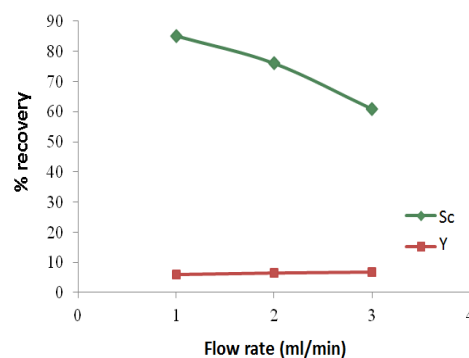


Figure 4: % recovery of Sc and Y in 1M H₂SO₄ vs flow rate of the eluent (eluent to feed solution 1.5:1)¹⁰

The developed procedure was applied on pilot plant scale. The results are in good agreement with the results obtained in laboratory scale, succeeding both high recoveries of Sc and REEs with the lower volume of the eluents.

Conclusions

An ion exchange process using an industrial strong cation exchanger was developed for the selective separation of REEs and Sc from Fe and other ME coexisting in the leachate after the hydrometallurgical treatment of red mud. HCl at a concentration of 1.75 M was found to be a suitable eluent for the selective removal of ME and especially iron with minimal losses of Sc and Y. REEs and Sc can be recovered afterwards either as a group using 6M HNO₃ or dilute H₂SO₄ for the selective recovery of Sc and afterwards 5M HCl for the quantitative recovery of the other REEs as a group. The further separation of the individual REEs can be achieved by an appropriate extraction-backstripping process.¹¹ The above procedure was successfully applied on pilot plant scale too.

References

1. M. Humphries, "Rare Earth Elements: The Global Supply Chain", *CRS Report*, 1-26 (2011).
2. Walters and P. Lusty, "Rare Earth Elements", *British Geological Survey*, Minerals UK (2011).
3. Hurst, "China's Rare Earth Elements Industry: What Can the West Learn?", *Institute for the Analysis of Global Security*, 1-42 (2010).
4. F. Feyerabend, J. Fischer, J. Holtz, F. Witte, R. Willumeit, H. Dröcker, C. Vogt and N. Hort, "Evaluation of Short-Term Effects of Rare Earth and Other Elements Used in Magnesium Alloys on Primary Cells and Cell Lines", *Acta Biomaterialia*, **6** 1834-42 (2010).
5. <http://www.3rd1000.com/elements/Scandium.htm>.
6. M. Ochsenkühn-Petropulu, Th. Lyberopulu and G. Parissakis, "Selective Separation and Determination of Scandium from Yttrium and Lanthanides in Red Mud by a Combined Ion-Exchange-Solvent Extraction Method", *Anal. Chim. Acta*, **315** 231-7 (1995).
7. L. Tsakanika, M. Ochsenkühn-Petropoulou and L. Mendrinou, "Investigation of the Separation of Rare Earth Elements from Red Mud by Use of Reversed-Phase HPLC", *Anal Bioanal Chem*, **379** 796-02 (2004).
8. T. Suzuki, K. Itoh, A. Ikeda, M. Aida, M. Ozawa and Y. Fujii, "Separation of Rare Earth Elements by Tertiary Pyridine Type Resin", *Journal of Alloys and Compounds*, **408-412** 1013-16 (2006).
9. V. Belova, A. Voshkin, A. Kholkin and A. Payrtman, "Solvent Extraction of Some Lanthanides From Chloride and Nitrate Solutions by Binary Extractants", *Hydrometallurgy*, **97** 198-03 (2009).
10. L.A. Tsakanika, PhD thesis, "Separation and Recovery of Lanthanides from Red Mud by Use of Selective Extraction and Chromatographic Techniques", NTUA, Greece, 2013.
11. M. Ochsenkühn-Petropoulou, L. Tsakanika and Th. Lymperopoulou, "Process Control of an Innovative Method for the Recovery and Separation of Rare Earths from Red Mud by Different Analytical Techniques", in *Proceedings of ERES 2014*, Milos Island, Greece, 2014.
12. <http://www.lynascorp.com/page.asp?category>.
13. <http://www.mineralprices.com/>.

14. M. Ochsenkühn-Petropulu, Th. Lyberopulu and G. Parissakis, "Direct Determination of Lanthanides, Yttrium and Scandium in Bauxites and Red Mud From Alumina Production", *Anal. Chim. Acta*, **296** 305-13 (1994).
15. www.alhellas.com/default.asp?siteID=3&pageid=3&langid=2.
16. M. Ochsenkühn-Petropoulou, <http://pubs.acs.org/doi/abs/10.1021/ie011047b-ie011047bAF1> K. Hatzilyberis, L. Mendrinou, C. Salmas, "Pilot-Plant Investigation of the Leaching Process for the Recovery of Scandium from Red Mud", *Ind. Eng. Chem. Res.*, **41** 5794–01 (2002).
17. EPET II Project from GSRT, "Application and Demonstration in Pilot Scale of a Novel Method for the Treatment and Exploitation of Red Mud: Waste of Metallurgical Activity of a Greek Industry" NTUA (coordinator: M.Ochsenkuehn-Petropoulou) and Aluminum of Greece, Final report, pp. 160, 2001.

