International Journal of Mineral Processing 119 (2013) 89–92

Contents lists available at SciVerse ScienceDirect

International Journal of Mineral Processing

journal homepage: www.elsevier.com/locate/ijminpro

Extraction of rare earth metals from deep sea nodule using H_2SO_4 solution

P.K. Parhi [a,b], K.H. Park [a], C.W. Nam [a], J.T. Park [a,*], S.P. Barik [a,c]

[a] Mineral Resources Research Division, Korea Institute of Geoscience & Mineral Resources (KIGAM), Daejeon, 305-350, Republic of Korea
[b] Hydro and Electro Metallurgy Department, CSIR-Institute of Minerals and Materials Technology, Bhubaneswar-751013, India
[c] Resources Recycling, University of Science and Technology, Daejeon, 305-333, Republic of Korea

ARTICLE INFO

Article history:
Received 17 September 2012
Received in revised form 7 January 2013
Accepted 20 January 2013
Available online 28 January 2013

Keywords:
Deep sea nodule
Rare earth metals
Leaching
H_2SO_4 solution

ABSTRACT

Leaching of rare earth (RE) metals from the Pacific Ocean sea nodule was carried out in H_2SO_4 medium. Preliminary study was performed to ascertain the existence of rare earth elements in the sea nodule crust. Concentration of H_2SO_4 and temperature were found as the key factors which enhance the dissolution rate of rare earth metals. The maximum average RE leaching efficiency of 83.03% was obtained using 3 M H_2SO_4. At the above condition, leaching of most of the RE was ≥90% and the remaining metals were; Ce 44.6%, La 55.3%, Nd 84.7%, Eu 85.8%, Pr 76.4% and Th 78.8%, in which the co-extraction of other base metals like Fe, Co, Ni, Cu was high. Dilute acid i.e. 0.2 M of H_2SO_4 and temp. 45 °C was found to be best for optimum extraction (57.6%) of total rare earth, where the co-extractions of other base metals (Cu, Co, Ni, Mn and Fe) are very less.

1. Introduction

Deep sea nodule crust has ~500–1000 ppm of total rare (RE) earth metal in addition to other valuable metals such as nickel (1.25–1.5%), copper (1–1.4%), cobalt (0.2–0.25%) and Mo (~0.05%) (Fuerstuenau and Han, 1977; Monhemius, 1986). In spite of low RE content, the sea nodule is still considered to be an attractive future source of rare earth metals. Previous studies (Jung, 1993; Koschinsky et al., 2011; Fuerstuenau and Han, 1977) have shown that the rare metals are located in the lattice of manganese and iron phase (major content of sea nodule). Rare earth metals can be recovered either by reductive dissolution of the primary phase of sea nodule or by direct leaching with mineral acids.

Many researchers (Nam et al., 2003; Das et al., 1986; Anand et al., 1988; Senanayake, 2011) have suggested several processing routes. Most of them followed hydrometallurgical methods e.g. glucose-ammoniacal (Das et al., 1986), reduction-ammoniacal leaching (Acharya et al., 1999), pressure leaching (Anand et al., 1988), and sulphuric acid leaching (Zhang et al., 2001). These approaches are successful on quantitative leaching of metals from the sea nodules, but they still have limitations such as high energy consumption, multistage operations, lack of selectivity etc. (Senanayake, 2011). In spite of a few disadvantages, direct sulphuric acid leaching process can be a suitable option for selective recovery of rare earth metals while minimizing leaching of Mn, Fe, Cu, Co and Ni. Accordingly the number of processing stages and overall energy consumption can be minimized. H_2SO_4 was found as suitable lixiviant compared to HCl with high extraction efficiency, while leaching the rare metals namely Ir and Y from the computer monitor scraps (Resende and Morais, 2010). Lokshin et al. (2002) have also used H_2SO_4 for leaching of lanthanides from Khibiny apatite concentrate mineral. The majority of the published literatures discuss the processing of deep sea nodules for the recovery of valuable metals such as Cu, Co, Zn, and Ni; however, until now none of the studies has reported on the recovery of rare earth metals from sea nodules.

The technology developed by KIGAM (Nam et al., 2003, 2004) for deep sea nodule processing consists of smelting-acid leaching of matte- and SX-EW of Cu, Co and Ni. During smelting, all the rare earth metals are transferred to slag phase which presents a challenge for subsequent recovery of rare earth metals. In other words, it is quite difficult and not economic to recover REE from this slag. Thus, our objective was to find a simple process to recover REE with a low recovery of other metals before smelting of raw manganese nodules. Therefore, the present investigation is focused on the leaching of total rare metals including Y, Th and U, from deep sea nodule using H_2SO_4 solution.

2. Experimental

2.1. Materials and reagents

The sea nodule samples were procured from the Clarion–Clipperton fracture zone (Korea mining site) of the north east Pacific Ocean. They were ground in a ball mill to obtain a suitable size fraction. The fine ground fraction of the average particle size of ~75 μm was used for leaching study. After the standard digestion procedure,

---

* Corresponding author. Tel.: +82 42 868 3655.
E-mail addresses: jtpark@kigam.re.kr (J.T. Park), parhi_pankaj@yahoo.co.in (P.K. Parhi).

0301-7516/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.minpro.2013.01.005

Table 1
Chemical composition of deep sea nodule.

Name of elements	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U	Mn	Fe	Cu	Co	Ni
[M],mg/kg	94.03	100	298	37.7	148	37.9	10.3	37.5	6.63	32.6	6.71	16.7	2.68	16.1	2.7	27.6	4.91	2392000	373000	8800	1530	10200

the deep sea nodule was analyzed by ICP-MS (JOBIN-YVON JY 38) and the chemical composition is given in Table 1.

2.2. Method

Leaching tests were carried out using a three necked 500 ml round bottom flask. Heating and stirring were provided by temperature controlled mantle heater (accuracy ± 1 °C) and externally placed variable speed stirrer motor, respectively. Before each experimental lixiviant was heated at a desired stirring rate. After reaching a set leaching temperature a requisite quantity of sea nodule sample was charged into the reactor containing 250 ml of lixiviant. The samples were withdrawn at the end of each experiment and then filtered, diluted and analyzed for metal content by ICP-MS. At the end of leaching tests, the slurry was filtered followed by in-situ washing of the residues with de-ionized water. The washed residues were dried at 100 °C, weighed and analyzed for metal content. Dissolution extent of metals was calculated based on both solution and solid analysis. Most of the leaching experiments were duplicated in order to determine the variance. The experimental error was observed to be within ±4%. The stirring rate and pulp density were kept fixed at 500 min^{-1} and 10%, respectively in all the cases of experimentation.

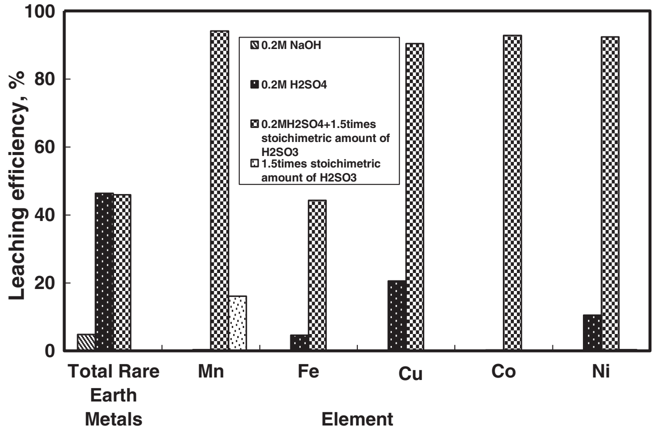

Fig. 1. Relative elemental distribution for leaching of total rare earth metals with other base metals from sea nodules using different reagents, conditions: time 2 h., temp. 30 °C, and stirring speed: 500 rpm.

3. Results and discussions

3.1. Preliminary study of rare earth leaching

Preliminary leaching tests were performed to ascertain the presence of rare earth metal in the sea nodule crust. As it is well known that the major phases of the sea nodule crust are of Fe_2O_3 and MnO_2, the rare earth metals can be in either of the above phases.

Leaching of rare earth metals from sea nodule was carried out using different reagents namely NaOH, H_2SO_4, H_2SO_3 and $H_2SO_4 + H_2SO_3$. The concentration of the NaOH and H_2SO_4 is kept fixed at 0.2 M and the H_2SO_3 concentration was 1.5 times of the stoichiometric amount. Other parameters were: stirring speed 500 rpm, temp. 30 °C, and time 2 h. About 46.4% and 45.9% of total rare earth metals are dissolved with 0.2 M H_2SO_4 and 0.2 M H_2SO_4 + 1.5 times stoichiometric amount of H_2SO_3, respectively, as shown in Fig. 1. As expected, Mn extraction was significantly high (94.06%) using 0.2 M H_2SO_4 + 1.5 times stoichiometric amount of H_2SO_3 and leaching of other metals such as Cu, Co and Fe is trace quantity. On the other hand, 32% of copper and 10.6% of nickel were leached with 0.2 M H_2SO_4 with a very low co-extraction of Mn, Fe and Co. Thus, the extraction efficiency of rare earth metals with respect to each of the reagents can be ordered as: $H_2SO_4 > H_2SO_3 + H_2SO_4 >$ NaOH $> H_2SO_3$. As can be seen from the results of Fig. 2, leaching of cerium (Ce) lanthanum (La) and thorium (Th) was found to be low and in contrast, and the recovery of Neodymium (Nd) was comparatively good with 0.2 M H_2SO_4. The leaching behavior of the rest of the rare earth metals followed the same trend. Substantial recovery of total rare earth was comparatively low due to low leaching rate of Ce

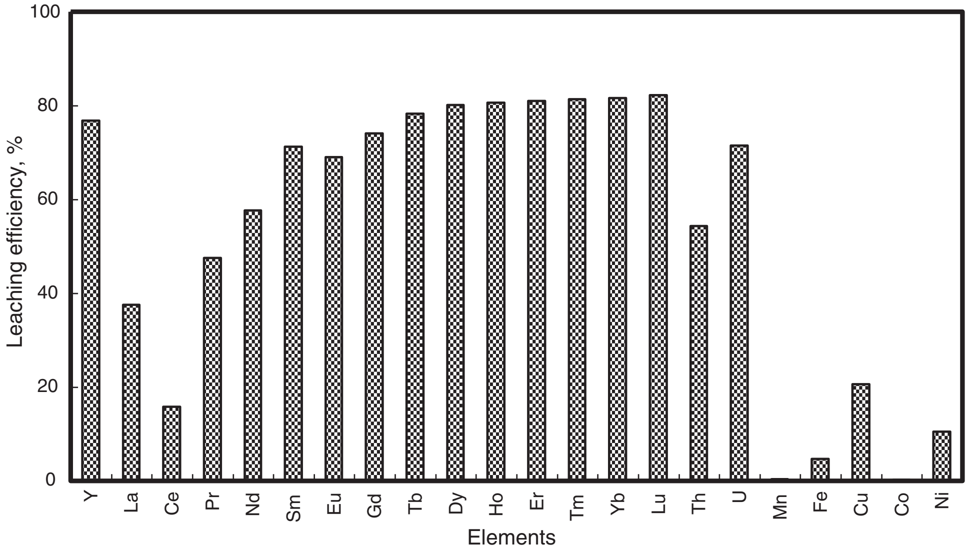

Fig. 2. Relative elemental distribution for leaching of rare earth and base metals from sea nodules using 0.2 M H_2SO_4, conditions: time 2 h., temp. 30 °C, and stirring speed: 500 rpm.