Separation and Purification Technology 168 (2016) 161–167

Contents lists available at ScienceDirect

Separation and Purification Technology

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

An environmental friendly Na_2CO_3-roasting decomposition strategy for the mixed rare earth concentrate

Junmei Zhao *, Feng Pan, Huizhou Liu *

Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

ARTICLE INFO

Article history:
Received 11 February 2016
Received in revised form 19 April 2016
Accepted 27 May 2016
Available online 27 May 2016

Keywords:
Mixed RE concentrate
Na_2CO_3
Decomposition
Bastnaesite
Monazite
H_2SO_4-leaching
Sintering

ABSTRACT

The decomposition of the mixed RE (rare earth) concentrate bastnaesite ($RECO_3F$) and monazite ($REPO_4$) has been investigated extensively for a few decades. In this work, a novel environmental friendly Na_2CO_3-based roasting decomposition strategy for the mixed RE concentrate has been proposed. It is a two-step strategy combining air-oxidation and Na_2CO_3-roasting. In the first step of air-oxidation, almost all of bastnaesite decomposes. While more than 95% of monazite decomposes in the second Na_2CO_3-roasting step. Thus, the consumption of Na_2CO_3 in the current proposed process would decrease greatly. The Na_2CO_3-roasting phenomena were compared among the reactions of Na_2CO_3-mixed RE concentrate, Na_2CO_3-pure bastnaesite and Na_2CO_3-the first leaching residue by H_2SO_4. The air-roasting temperature was optimized. In particular, the roasting temperature for the reaction of Na_2CO_3 and H_2SO_4-leaching residue has been optimized according to P- and Ce-leaching percents. Finally, following the proposed flowsheet under the optimized conditions, taking 50 g of mixed RE concentrate as feedings, the final solid residue occupies around 2.4%. In addition, about 70% of F and 87% of P can be transferred into H_2SO_4-leaching liquor and H_2O-leaching liquor, respectively. 93.7% of Th and 96.6% of RE can be leached. Finally, a H_2SO_4-leaching liquor containing Th, Ce(IV), RE(III) and F can be obtained for the subsequent separation.

1. Introduction

Baiyunobo ores in Baotou, Inner Mongolia, China, possesses abundant rare earth (RE) resources deposits, particularly light REs. It contains bastnaesite ($RECO_3F$) and monazite ($REPO_4$) as main RE bearing minerals. For the separation of bastnaesite and monazite from Baiyunobo ores, conventional physical beneficiation methods, such as flotation, gravity, magnetic, and electrostatic separation, were carried out to obtain mixed RE concentrate mainly composed of bastnaesite and monazite [1]. Generally, the ratio of bastnaesite to monazite in the mixed RE concentrate is about 9:1–1:1 with a grade of 45–65% REO [2]. The value varies with the mining year by year. Furthermore, there are some important non-RE valuable resources besides RE, such as 5–7% fluoride, 4–6% phosphorus and 0.1–0.2% thorium. In addition, it also contains a certain amount of Fe, Mn, Mg, Zn, Pb and Si, etc. So far, it is very difficult to comprehensively recover valuable elements from the mixed RE concentrate due to its complicated components.

However, several acidic, basic and air-roasting processes have been developed for the isolation of rare earth elements (REEs) from rare earth metal ores [3–13]. Among them, the concentrated H_2SO_4-roasting method, developed by General Research Institute for Nonferrous Metals, Beijing, has been extensively applied in decomposing Baotou mixed RE concentrate [9]. Although this concentrated H_2SO_4-roasting process has contributed a lot to Chinese rare earth production and worldwide rare earth supplies, it exposes more and more problems, in particular, the recovery of some bearing valuable elements and environmental contamination. For example, this process does not refer to how to recovery of F, P and Th. While radioactive thorium finally was transferred into the solid waste, which leads to severe environmental problems and finally hurts human's health. In fact, Na_2CO_3-decomposition process for the mixed RE concentrate is an old and relative cleaner technique [14], where thorium has been transferred into the leaching liquid. Thus, the recovery of thorium is possible. On the other hand, Na_2CO_3-roasting process belongs to an oxidation process just like air-roasting process, where cerium (Ce) can remain tetravalent during the subsequent leaching by H_2SO_4. It is well known that tetravalent Ce can be easily separated from the other RE(III) adopting the traditional solvent extraction technology not like trivalent Ce. In addition, $\Sigma CeO/\Sigma REO$ (mass ratio of total cerium/total rare earths) is about 50% in Baotou mixed RE concentrate. Therefore, if most of cerium remains tetravalent

---

* Corresponding authors.
E-mail address: jmzhao@ipe.ac.cn (J. Zhao).

http://dx.doi.org/10.1016/j.seppur.2016.05.036
1383-5866/

and can firstly be isolated from the leaching liquid, it will greatly simplify the separation process of other RE(III) and decrease the separation cost [15]. However, Na_2CO_3-roasting process has not been applied in industry so far just because there are some fatal problems in this process. In particular, the sintering problem during the Na_2CO_3-roasting process has never been effectively solved until now due to the formation of possible melted salts. Sintering can form lumps, which would lead to the sticking and clogging walls of the roasted equipment rotary kiln, and further prevent roasting operation from running smoothly. In addition, the distribution of some valuable elements, such as F, P, Th and RE, are not clear in this Na_2CO_3-roasting process. Therefore, exploring a clean and feasible strategy for the comprehensive recovery of these valuable metal resources from the mixed RE concentrate is still a big challenge until now [9].

In this work, a novel environmental friendly two-step strategy for the decomposition of Baiyunobo mixed RE concentrate was designed through combining air-oxidation roasting at the first step and then Na_2CO_3-decomposition of the residue. It can be expected that most of bastnaesite ($CeCO_3F$) in the mixed RE concentrate would decompose while the remaining portion is mainly composed of monazite ($REPO_4$). Therefore, most of F can be transferred into the H_2SO_4-leaching liquors during the subsequent H_2SO_4-leaching process. On the other hand, chemical attacking monazite with Na_2CO_3 at a higher temperature has been extensively reported [16]. In this way, it is possible to recover phosphate and rare earths during the Na_2CO_3-decomposition process at the second step, respectively. Thus, this novel strategy can make fluorine and phosphate keeping separation. In addition, both air-oxidation-roasting and Na_2CO_3-roasting belong to oxidation process. Thus, cerium can remain tetravalent in the H_2SO_4-leaching liquors, which can effectively simplify the subsequent extraction separation process. More importantly, there are no bumps found during these roasting processes. Furthermore, compared with the original Na_2CO_3-roasting process, the consumption of Na_2CO_3 in the current proposed process would decrease greatly due to the removal of about 60% ore during the air-oxidation roasting and leaching process. Furthermore, compared with the alkali-liquid calcinations [3], it is easier for the current solid-state high-temperature roasting to be operated continuously although it needs a higher temperature. Hence, it can be expected that the novel two-step decomposition strategy for the mixed RE concentrate is an environmental friendly process due to the possible separation and recovery of F, P, Th, Ce(IV) and RE(III), respectively.

2. Experimental section

2.1. Materials

Baotou Baiyunobo mixed RE concentrate was provided by Baotou Iron & Steel Rare-Earth Hi-Tech Co., Ltd. in China. Pure bastnaesite with a purity of 70% was provided by Sichuan Mianning Fangxing rare-earth Co., Ltd. Na_2CO_3 powder, concentrated H_2SO_4 and HCl were of analytical grade.

2.2. Analysis

The content of related elements in the mixed RE concentrate or leach residue were analyzed by either X-ray fluorescence analysis (XRF, Axios mAX, PANalytical) or chemical methods. The total rare earth oxides (ΣREO) in the acidic solutions were analyzed by standard oxalate gravimetric method. That is, 5 ml of 1:1 HCl and 2 ml of concentrated HNO_3 were added into 5 ml of leaching liquor with RE. Then, the obtained mixture was evaporated to be dried under a low temperature condition on the electric hot plate. This step can remove Si from the leaching liquor. After that, 10 ml of 1:1 HCl was used to dissolve the obtained salts together with a few drops of H_2O_2. As the solution became clear, it was diluted to be 100 ml with the deionized water and 3 g of NH_4Cl was added inside. The obtained solution was heated to be boiling. Inside this boiling solution, 1:1 ammonia was added until a large amount of precipitation produced with an excess of 20 ml of 1:1 ammonia. Then, 2–3 drops of H_2O_2 was added to completely oxidize Ce(III) to be Ce(IV), keeping boiling for 2 min. Subsequently, the suspension was filtered via the rapid qualitative filter paper. This step can remove Al, Fe, F and P from the leaching liquor. The precipitation and beaker were washed by 2% hot NH_4Cl solution for three times, then the precipitation was dissolved by 1:1 hot HCl. The filter paper was also washed until there was no yellow on it. The obtained solution was diluted by deionized water to be 100 ml, and then heated to be boiling, in which 10% hot oxalate solution and 2–3 drops of Cresol red indicator were added. Subsequently, 1:1 ammonia was used to adjust the solution color to be yellow from red (pH = 1.8–2). This suspension was heated to be boiling again and keeping warm for 1 h, then cooled by cold water, and filtered by slow speed quantitative filter paper. This step can remove Ca, Mg, etc. and the pure RE oxalates were obtained. The obtained precipitation and the beaker were washed by 1% oxalate solution for three times. The precipitation together with filter paper was placed in a porcelain crucible to ash, then calcined for 40 min at 800–850 °C in a muffle furnace. After the crucible was cooled to be room temperature and the mass of precipitation (REO) was weighed.

The concentration of F in the leaching liquors was measured by fluorine electrode. And the concentrations of P and Th were analyzed by ICP-OES (OPTIMA 7000DV, PerkinElmer, USA). The contents of F, P, Th and REO in the concentrate or leach residue can be analyzed via the above said method by completely transferring 0.2 g solid concentrate into a 25 ml solution following the procedure below:

A. Mixing 0.2 g solid concentrate with 0.2 g Na_2CO_3 powder and milling;
B. Covered the above powder by 1/4 ashless filter and calcined for 1 min at 900 °C in a nickel crucible;
C. After cooled, the calcined products were completely dissolved by 1:1 hot HCl into a solution of 25 ml.
D. The contents of F, P, Th and REO in this 25 ml solution corresponding to their contents in 0.2 g solid concentrate.

2.3. Chemical composition in mixed RE concentrate

In general, the mixed RE concentrate mainly contains ~55% bastnaesite ($RECO_3F$), ~15% monazite ($REPO_4$), ~7% fluorite (CaF_2), ~5% iron mineral (Fe_2O_3), and ~3% apatite ($Ca_3(PO_4)_2$) [17]. The chemical composition of mixed RE concentrate analyzed by XRF is listed in Table 1. Results show that light rare earth elements, such as Ce, La, Nd and Pr, occupied approximately 50% of the total elemental mass and other non-rare earths were mainly found to be manganese (Mn), calcium (Ca), fluorine (F), ion (Fe), phosphorus (P) and magnesium (Mg). Furthermore, it contained around 0.44% Th.

In addition, the percent contents of F, P, Th and REO occupied in the concentrate were also analyzed through chemical analysis methods (see Experimental Section). The results show that F, P, Th and REO are (6 ± 0.5)%, (4.1 ± 0.1)%, (0.145 ± 0.005)% and (55 ± 5)%, respectively. The leaching percents of F, P, Th and REO will be calculated according to the values from chemical analysis methods.