Minerals Engineering 49 (2013) 121–127

Contents lists available at SciVerse ScienceDirect

Minerals Engineering

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

Application of ocean manganese nodules for the adsorption of potassium ions from seawater

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ARTICLE INFO

Article history:
Received 11 December 2012
Accepted 20 May 2013
Available online 13 June 2013

Keywords:
Ocean manganese nodules
Potassium ionic sieve
Sea brine
Potassium adsorption
Seafloor resources

ABSTRACT

Extracting potassium from seawater has great economic potential, although conventional methods offer low separation capacity and selectivity. In this study, a series of novel potassium ionic sieves (PISs) were synthesized using ocean manganese nodules (OMN) as raw materials. The PISs were characterized by XRD, SEM, and nitrogen adsorption–desorption. The potassium adsorption capacities and separation factors of PISs and OMN in KCl solution and sea brine showed that $KMnO_4$ treatment will result in the highest adsorption and separation performance. The resulted sample OMN-C exhibit major composition of birnessite-type potassium manganese oxides and high micropore volumes. The adsorption capacities of OMN-C to K^+ in KCl solution and sea brine were 35.2 mg g^{-1} and 22.1 mg g^{-1}, respectively. The separation factor of OMN-C was $\alpha(K^+/Na^+) = 108.6$ and the sieve did not adsorb Mg^{2+}, indicating its relatively high separation selectivity to K^+. Therefore, OMN-C can selectively extract potassium from sea brine effectively. This study not only utilized the abundant OMN resources, but also prepared effective PISs, which showed great potential in the utilization of seawater.

1. Introduction

Potassium which is the 6th abundant metal ion in seawater is one of the three major plant nutrients. Average ratio of nitrogen fertilizers, phosphates, and potassium carbonate in the world is 1:0.5:0.4, while the consumption of potassium carbonate is 60 million tons per annum (Dave and Ghosh, 2006; Perucca, 2003). The distribution of potassium on land is uneven and 90% potassium is distributed in Canada, Russia, Ukraine, Germany, Israel, and America. Due to the low abundance of potassium in other countries, research on extracting potassium from seawater has attracted great attention (Wang et al., 2007). The potassium content in seawater is as high as 0.399 g L^{-1}. However, the potassium content in sea brine is 2 g L^{-1} which is five times higher than that in seawater. Therefore, previous studies considered extracting potassium from sea brine (Li and Li, 2010). The methods of extraction include chemical precipitation (Dave and Ghosh, 2006; George et al., 1968), solvent extraction (Hanson and Murthy, 1969), and extraction by potassium ionic sieve (PIS) (George et al., 1968). Natural clinoptilolite (a zeolite $(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O_{36}\cdot 12(H_2O)$) is an example of PIS which shows great technical feasibility (Ji et al., 2011; Yuan et al., 2011, 2007). However, there are several issues to be resolved. First, the ion exchange capacity of PIS to potassium in seawater is below 20 mg g^{-1}, which led to large ion-exchange equipment; second, as the separation selectivity of natural clinoptilolite to K^+ is relatively unfavorable, it is difficult to separate K^+ from Na^+ and Mg^{2+} in seawater.

Ocean manganese nodules (OMN), also known as iron-manganese nodules, or polymetallic nodules, were first discovered in 1873 during the voyage of the HMS Challenger (Post, 1999). They are of commercial interest because they contain abundant valuable metals such as Cu, Ni, Co, and other strategic metals in addition to Mn (Senanayake, 2011). It is estimated that the total reserves of OMN are more than 3 trillion tons (Post, 1999). On the initial stage of development, the main focus was the leaching of valuable metals from OMN (Zhang et al., 2000; Luo et al., 2004; Kumari and Natarajan, 2002). For example, Niinae et al. (1996) and Vu et al. (2005) had reported the leaching process in detail. In recent years, investigations using transmission electron microscopy, powder X-ray, and neutron diffraction methods have provided important new insights into the structures and properties of OMN (Post, 1999). OMN has been found to be an effective catalysts and adsorbent in reactions such as oxidation, reduction, decomposition, and de-metallisation (Dominguez et al., 2009; Zhang et al., 2008; Sauvage et al., 2009). For instance, OMN residue after treatment can decolourize methylene blue effectively (Satapathy et al., 2012). Han et al. (2009) synthesized manganese ferrite ($MnFe_2O_4$) from OMN. The ferrite exhibits excellent magnetic susceptibility performance and reaches saturation magnetization state. Sun et al.

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http://dx.doi.org/10.1016/j.mineng.2013.05.019

(2010) synthesized nanocrystalline potassium manganese oxide mineral with formula $K(Mn^{4+}, Mn^{2+})_8O_{16}$ from reduction–ammoniacal leaching residue ($MnCO_3$) of OMN, which could effectively reduce the preparation costs of nanocrystalline cryptomelane.

In this study, novel PISs were synthesized from OMN using the method described by Zahi et al. (2007), Cheng et al. (2009), Jiang and Tatsumi (1998), Chen et al. (2010) and Suib (2008). Ionic sieves were synthesized using different reagents to introduce K^+ to the tunnels of OMN to provide charge balance and stabilize the structure. The K^+ ions were then replaced by H^+ ions in the K–Mn–O compound oxides structure which resulted in screening and memory capacity to the original target ion K^+ (Jiang et al., 2007). The obtained PIS presented excellent adsorption capacity and separation selectivity for K^+ from KCl solution or sea brine.

2. Experimental

2.1. Materials

The OMN samples used in this experiment were supplied by China Ocean Mineral Resources R&D Association. They were collected from the China Pioneer Area in July 2001 during the voyage of DY105-11 at 7–10°N, 144–147°W (Zhu, 2001). These brown-black samples are subspherical–botryoidal blocks with diameter of 0.5–25 cm. Contents of measurable metals in the OMN are shown in Table 1 (Han et al., 2009).

The sea brine used in this work was prepared according to the following compositions: Mg^{2+} 6.386 g L^{-1}, Cl^- 23.45 g L^{-1}, SO_4^{2-} 2.25 g L^{-1}, Na^+ 2.98 g L^{-1}, K^+ 1.70 g L^{-1} (Dave and Ghosh, 2006).

Chemical reagents KNO_3, KOH, $KMnO_4$, and $(NH_4)_2S_2O_8$ were supplied by Sinopharm Chemical Reagent Co., Ltd. All reagents used in this study are of analytical grade purity and were used without further purification.

2.2. Preparation of potassium ionic sieve (PIS)

The OMN samples were pretreated by soaking in standard seawater with pH value of 8.0 for 48 h. Then the samples were ground to less than 130 μm, dispersed into distilled water under ultrasonic treatment for 5 min and centrifuged at 1000 rpm for 4 min. The products were collected and dried at room temperature for 24 h.

A sample of OMN powder (5 g) and 0.02 mol of each potassium reagent (KOH, KNO_3 or $KMnO_4$) were mixed and homogenized with 10 mL distilled water. The mixture was heated at 1000 °C for 6 h at the heating rate of 95 °C min^{-1}.

The obtained products were submerged in 300 mL of 0.5 mol L^{-1} $(NH_4)_2S_2O_8$ aqueous solution at 25 °C for 40 min. $(NH_4)_2S_2O_8$ will react with Mn in OMN according to the following reaction:

$$\begin{aligned}&2MnO_2 + 3(NH_4)_2S_2O_8 + 4H_2O\\&= 3(NH_4)_2SO_4 + 3H_2SO_4 + 2HMnO_4 \qquad (1)\end{aligned}$$

The suspension (PIS) was filtered and washed with distilled water until the filtrate became neutral and dried in a temperature controlled oven at 110 °C for 3 h. According to the different potassium reagents, the products were named OMN-A (treated by KOH), OMN-B (treated by KNO_3), and OMN-C (treated by $KMnO_4$), respectively.

Table 1
Contents of measurable metals in the OMN samples (all in mass percent %).*

Mn	Fe	Ni	Co	Cu	Zn
20.73	11.50	0.73	0.28	0.47	0.15

* Data source: Han et al. (2009)

2.3. Adsorption performance of PISs

Adsorption experiments were carried out in a series of 250 mL flasks containing 0.5 g of PIS or OMN and 100 mL of 0.04 mol L^{-1} KCl solution. The mixture was continuously stirred by a magnetic stirrer at 200 rpm. The K^+ concentrations were determined every 2 h (0, 2, 4, 6, 8, 10, 12, 14 h). Every experiment was repeated three times and the mean values were taken. The adsorption capacities were calculated according to the K^+ concentrations before and after experiments. To investigate the K^+ adsorption performance of PIS for sea brine, the KCl solution was replaced by sea brine while other conditions were kept constant.

2.4. Characterizations

The crystal structures of OMN samples and PISs were studied by X-ray diffraction. The XRD data were collected by a D/max 2550 X-ray diffractometer (Riguaku, Japan) with Cu Kα radiation (λ = 0.15406 nm) from 5° to 75°. The operation voltage and current were maintained at 40 kV and 34 mA, respectively. The micromorphologies of OMN and derived PISs were investigated by scanning electron microscope (SEM) and were examined by a Hitachi S-4800 electron microscope at an accelerating voltage of 5 kV and working distance of 8.8–8.9 mm. Nitrogen adsorption and desorption analyses were conducted to investigate the surface area and pore characteristics of OMN and PISs. The data were recorded at 77 K using a Coulter OMNISORP surface area and pore analyzer. Adsorption experiments were carried out to evaluate the K^+ ion exchange capacities of OMN and PISs. The concentrations of K^+, Na^+, and Mg^{2+} were measured by atomic absorption spectrometry (AAS).

3. Results and discussion

3.1. XRD analyses

As shown in Fig. 1, the untreated OMN-D sample and the three PIS products obtained after treating with KOH (A), KNO_3 (B) and $KMnO_4$ (C) exhibit different XRD patterns. Major composition of OMN and PISs are listed in Table 2. The major components of untreated OMN-D are todorokite and birnessite. Small amounts of buserite, quartz, and feldspar can also be found in the XRD pattern of OMN. This result is consistent with the mineralogy of deep sea

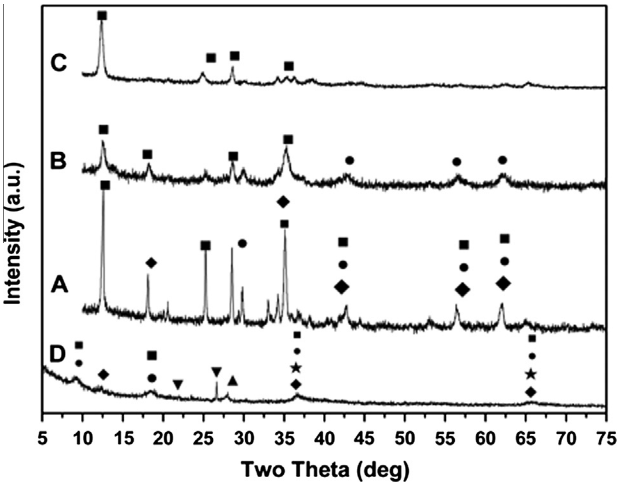

Fig. 1. XRD patterns of sample OMN and PISs (A-OMN treated with KOH, ■-birnessite-type potassium manganese oxides (BPMO), ◆-jacobsite, ●-pyrolusite; B-OMN treated with KNO_3, ■-lepidocrocite, ●-pyrolusite; C-OMN treated with $KMnO_4$, ■-BPMO; D-OMN, ■-todorokite, ●-birnessite, ◆-vernadite, ▼-quartz, ▲-feldspar, and ★-buserite).