



Separation of cobalt, neodymium and dysprosium using amorphous zirconium phosphate

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ABSTRACT

The purpose of this study was to investigate the separation of Co, Nd and Dy from a ternary Co-Nd-Dy solution using amorphous zirconium phosphate (am-ZrP). Am-ZrP was synthesized by a precipitation method at room temperature and subsequently characterized by Fourier transform-infrared spectrometry, thermogravimetry, scanning electron microscopy, X-ray diffraction, solid-state ³¹P magic angle spinning nuclear magnetic resonance spectrometry and sodium hydroxide titration (with and without background salt). The ion exchange kinetics of am-ZrP that were determined in ternary 1 mM equimolar solutions at equilibrium pH 2.5. The effect of pH on the adsorption was studied in ternary 1 mM equimolar solutions and the uptakes of the metals increased with increasing pH until approximately pH 3.5. The adsorption isotherms of Co, Nd and Dy were tested in a series of ternary equimolar solution, the total uptake amounted to 4.13 meq/g at pH ~3.0. The preference of am-ZrP for these metals occurred in decreasing order Dy > Nd >> Co. The separation of Co, Nd and Dy from their 1 mM equimolar ternary mixture was investigated on an am-ZrP column. Effects of loading (7.8%, 62% and 100%) on the separation were compared by measuring the corresponding HNO₃ elution fractions. It was found that with a lower metal loading of 7.8%, three clear elution bands were obtained. Am-ZrP exhibited selective separation properties towards the ternary Co-Nd-Dy system, which contribute to the future scale-up studies for the recycling of NdFeB magnets.

1. Introduction

Neodymium-iron-boron (NdFeB) permanent magnets have been widely used in computer hard-disk drives, hybrid and electric vehicles, wind turbines, household electrical appliances and small electronic devices (Binnemans et al., 2013). Quantities of end-of-life (EOL) NdFeB permanent magnets have been accumulating year by year, due to their long lifecycles that range up to 30 years. EOL NdFeB magnets contain about 31–32% rare-earth elements (REEs) such as Nd, Pr, Dy, Tb and Gd (Yang et al., 2008). In addition, Co is added to NdFeB magnets with a comparable content of Dy (El-Moneim et al., 2002). The purpose of adding Co is to improve corrosion resistance of NdFeB magnets (El-Moneim et al., 2002). Recycling of REEs from EOL NdFeBs has become a significant activity in the NdFeB market and will play an important role in the future supply of REEs in the magnet sector (Rademaker et al., 2013).

Recently, many researches using physical or chemical way to

recycle REEs from EOL NdFeB magnets took place. The processes for REEs separation from computer hard disk drives have been well developed to produce demagnetized hydride alloy powder in atmospheric pressure hydrogen (Sheridan et al., 2014; Walton et al., 2015). In order to obtain the individual REEs, the NdFeB alloy powder is usually first leached by mineral acids into aqueous solution. However, the high concentration of Fe ion in acid leaching solution is the big problem for the further REEs separation. Hence, an ionic liquid with homomorphic behavior was used for a roasted magnet for Fe ion removal to achieve an efficient separation. Those authors extracted Fe into the ionic liquid phase, whereas Nd, Dy and Co remained in the aqueous phase. (Dupont and Binnemans, 2015).

For commercial REEs production, they are firstly extracted from ores using mineral acids leaching. The obtained pregnant leaching solution is then treated by solvent extraction (SX) for the separation of REEs. During the SX operation, REEs are transferred to an organic phase using REE-selective extractants. Apart from the demerit of using volatile

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organic solvent as a diluent, the separation efficiency of individual REE is not satisfying. Due to the similarity of the REEs, often hundreds of separation stages (utilising mixer-settler units) and complicated flow-sheets with reflux are needed in the actual industrial scale separation to obtain individual REE. In fact, the REEs are still present in the strip liquor/raffinate after many stages even though the extraction rate is higher than 99% (Brown and Sherrington, 1979; Morais and Ciminelli, 2004; Nakamura et al., 2007). In this case, the separation process of ion exchange could be a viable supplement to the continuous REEs recycling after solvent extraction in industry.

Ion exchange technology is commonly used to purify solutions by removing the dissolved ions by electrostatic adsorption onto the internal and external surfaces of ion exchange materials of various physical forms. Before the 1960s, the separation process of ion exchange was the dominated method to obtain the individual REE. Nowadays, ion exchange method is still used industrially to prepare high purity REEs even though solvent extraction plays the key role on the large scale REEs production (Inamuddin and Luqman, 2012; Xie et al., 2014).

Inorganic ion exchangers are generally much more selective than organic resins for metal ions. Typically such high selectivities arise from their porous and ordered, rigid structures that exhibit ion sieve functionality (Yang, 2011). Inorganic ion exchangers have been used on a large scale mainly for water purification and removal of radionuclides from nuclear waste effluents (Lehto and Harjula, 1999). Zirconium phosphates (ZrPs) have received wide attention because of their excellent properties, such as high Brønsted acidity, very high thermal and chemical stability, insolubility in acids and resistance to ionizing radiation. The use of ZrPs has been promising for the following areas: catalysts (Emig and Hofmann, 1983; Rao et al., 2006), cation ion exchangers (Clearfield, 1984), matrices (Bestaoui et al., 2006) and solid electrolytes (Cook and Sammells, 1991). However, crystalline ZrP granules tend to form submicron particles and are thus difficult to be used in a fixed-bed column (Xu et al., 2017). It is worthy to mention that amorphous ZrP (am-ZrP) has a relatively larger specific surface area and a sufficient content of micropores, which can enhance its function as ion exchangers, catalysts and adsorbents (Sydoruk et al., 2011). Amorphous ZrP (Am-ZrP) has been thoroughly studied in thermodynamics of alkali metal ion exchange (Kullberg and Clearfield, 1981), heavy metals removal (Zhang et al., 2008), radioisotope adsorption (Dyer et al., 1997). Nevertheless, little is known about their adsorption and separation behavior on cobalt and the REEs.

Herein, am-ZrP was investigated in our present study for its potential in the separation and recovery of Co, Nd and Dy from a Co-Nd-Dy ternary solution system. The synthesis and characterizations of the am-ZrP material in addition to the identification of its acidity, selectivity, and isothermal adsorption for Co, Nd and Dy ions. The kinetic mechanism of am-ZrP material and preliminary batch elution using mineral acids were also investigated. Our aim was to avoid the use of organic complexing agents by using simple mineral acids to separate Nd and Dy from each other and Co by relying on the separation capability of the ZrP material itself. Finally, column loading and eluting using only HNO₃ was tested.

2. Experimental

2.1. Chemicals

Zirconium tetrachloride (ZrCl₄, > 99.5%), hydrochloric acid (HCl, > 37%), phosphoric acid (H₃PO₄, 85%) were used as precursors for the material synthesis. Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 98%), neodymium nitrate hexahydrate (Nd(NO₃)₃·6H₂O, 99.9%), dysprosium nitrate hydrate (Dy(NO₃)₃·xH₂O 99.9%), sulfuric acid (H₂SO₄, 95%–97%), nitric acid (HNO₃, 67%–69%), hydrochloric acid (HCl, > 37%), phosphoric acid (H₃PO₄, 85%) were used in the ion exchange experiments. All chemicals were purchased from Sigma-Aldrich except for the H₂SO₄, which was purchased from J. T. Baker

and used without further purification. Milli-Q water (Merck Millipore) with the resistivity of 18.2 MΩ cm was used in the experiments.

2.2. Instrumentation and analyses methods

X-ray powder diffraction (XRD) patterns of am-ZrP were recorded by a Philips PW3710 X-ray powder diffractometer with the setting of: 40 kV, 40 mA, Cu-Kα radiation ($\lambda = 1.54056 \text{ \AA}$). Fourier transform infrared (FT-IR) spectra (400–4000 cm⁻¹) were recorded on a Perkin Elmer Spectrum one FT-IR spectrometer fitted with Universal Attenuated Total Reflectance sampling accessory. Thermogravimetry (TG) was performed on a Mettler Toledo TGA850 in N₂ flow with a heating rate of 10 °C min⁻¹. Scanning electron microscope (SEM) images were collected using a Hitachi Hi-Tech S-4800 FESEM. A digital pH meter (Orion model 920A) was used for the pH measurements. Solid-state ³¹P magic angle spinning nuclear magnetic resonance (³¹P MAS NMR) spectra were obtained with a Bruker Avance III NMR spectrometer operating at 500 MHz for protons. The spectra were externally referenced to 85% H₃PO₄. A microwave plasma-atomic emission spectrometer (MP-AES) Agilent 4200 was used for analysis of metal ions. The element content of P/Zr was measured by MPAES by dissolving weighed am-ZrP powder in a mixture of 65% HNO₃ and 1% HF using a CEM MARS 5 microwave digestion system.

2.3. Synthesis of am-ZrP by precipitation

Am-ZrP was prepared via room-temperature precipitation synthesis method at room temperature according to the method described by Krogh Andersen et al. (1998). First, 30.7 g of ZrCl₄ was carefully dissolved in 430 mL of 2 M HCl. Then, 400 mL of 1.25 M H₃PO₄ was added to the previous solution. The resulting precipitated solid was allowed to stand over night and was then filtered using a filter paper (2.5 μm (Particle retention)). The white solid was then washed with 1 L of 2 M H₃PO₄ in order to remove the unbound Cl⁻ ions. Subsequently, 1 L of 1 M HNO₃ was poured over the filtrate to purify the product and to ensure full conversion to H-form. Finally, the am-ZrP product was rinsed with deionized water until the pH of the filtrate reached 3, and dried in an oven at 60 °C for 48 h.

2.4. Preparation of ternary Co-Nd-Dy solution

The ternary Co, Nd, and Dy solution was prepared by mixing their corresponding nitrate salts and the solution pH was adjusted by 1 M HNO₃. Solutions containing 0.01 to 10 mM of each metal were prepared at pH 3 for batch ion exchange experiments. A feed solution containing 1 mM of each metal was prepared at pH 1.8 for column studies.

2.5. Potentiometric titration

The direct titration (from H to Na form) of the prepared am-ZrP was conducted in a series of batch experiments where 100 mg of am-ZrP was placed into 19 mL of deionized water or 1.0 M NaNO₃ solution and adding different amounts (250–1050 μL) of 1 M NaOH solution. The samples were equilibrated for three days in a rotary mixer (60 rpm) and their equilibrium pH values were measured.

2.6. Effect of pH studies

A 100 mg quantity of am-ZrP was placed into a 20 mL polyethylene vial filled with 20 mL of 1 mM equimolar Co, Nd and Dy at different pHs (1–6). The vials were equilibrated in a rotary mixer (60 rpm) for three days. After the initial 24 h, the pH value of each solution was checked and adjusted when necessary with 1 M NaOH. Phase separation was achieved by centrifugation at 4000 rpm (3000 g) for 15 min after which the pH of the supernatants were measured and finally metal concentration determination with MP-AES.

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