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Synthesis of neodymium phosphate from iron-neodymium solution using sodium sulfite

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A B S T R A C T

Iron-neodymium alloys are generally used for producing magnets. Neodymium falls under the class of rare earth elements, which are precious and expensive, and are thus often recovered by recycling processes as a cost saving measure. There are a few reported processes for the recycling of rare earth elements; however, these processes have disadvantages, including the requirement for high temperatures and the use of harmful gases. In this study, a novel technique for recovery of neodymium while circumventing the difficulties reported in previous methods is presented. Because rare earth phosphates are the main components of rare earth ore, a novel phosphate process is suggested in this work. In this process, an iron-neodymium solution was mixed with phosphoric acid solution and then adjusted to several different pH values using sodium hydroxide solution and nitric acid. The precipitates were filtered and dried. The ratio of neodymium to iron in the precipitates and filtered solutions was estimated by the inductively coupled plasma (ICP) method. As an ideal phenomenon, neodymium phosphate was filtered off and the cationic iron species were contained in the filtrate. The Fe/Nd and P/(Fe + Nd) ratios, concentrations of neodymium, iron, and phosphoric acid, and pH were varied to study precipitation of the neodymium compounds. The neodymium cation was recovered from the iron-neodymium solution using phosphoric acid. This novel process was demonstrated to be useful for the recovery of neodymium, and may find applications in the recycling and recovery of other rare earth elements of interest.

1. Introduction

Currently, neodymium-iron-boron permanent magnets are used in hard disk drives, in the motors of hybrid cars, and in magnetic resonance imaging (MRI) machines, etc. [1,2]. Recently, the use of these magnets has increased dramatically. In the process to produce neodymium-iron-boron magnets, a certain degree of scrap is formed by cutting and mill ends [3]. Neodymium tends to coexist with other rare earth elements in natural ores [4]. The separation of neodymium from other rare earth elements requires energy consuming procedures; therefore, there is an industrial demand for the recycling of neodymium from scrap to save time and energy [5].

Rare earths are potential candidates for various functional materials, although there are several difficulties related to the supply of these elements to industries [6,7]. Rare earth ores tend to be localized, and often include radioactive elements [8]. Since the mining of rare earth ores leads to environmental issues, recycling of rare earth elements from scrap may be a suitable alternative [9]. There are some reported processes for the recycling of rare earth elements. For example, transition metals have been removed from rare earths by solvent extraction with an undiluted ionic liquid [10,11]. This process requires a high concentration of acid and particular reagents. As another method, neodymium was recovered from the sludge of an iron-neodymium magnetic alloy by a chemical vapor transport method [12,13]. This method requires high temperature and special apparatus. These processes have several disadvantages. Therefore, the development of a novel technique to improve the current recycling methods is desirable.

Rare earth phosphates are the main components of rare earth ore, and they are known to be stable in acidic and basic solutions [14]. However, there are very few reports of recycling processes using phosphoric acid. Precipitation is one of the most useful techniques for the separation of the target metals from other metals in a matrix [15,16]. Precipitation using inorganic reagents is particularly convenient because harmful organic solvents are not employed and treatment of the wastewater generated during the process is relatively simple. Generally, metal hydroxides are used in the precipitation technique because they allow for the efficient recovery of a large amount of metal cations [17,18]. However, metal

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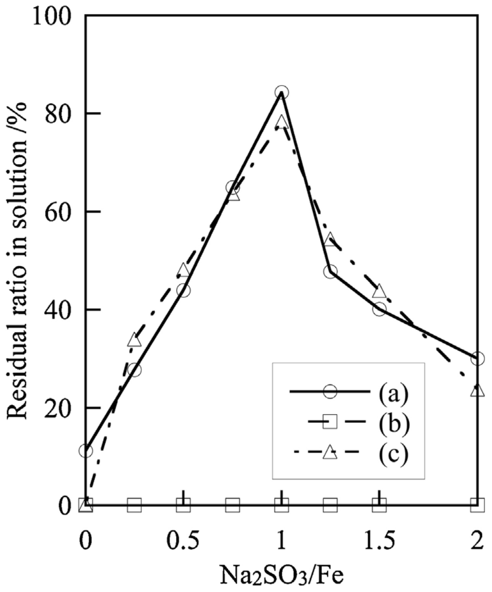

Fig. 1. Residual ratio of each element in solution at various Na_2SO_3/Fe ratios: (a) phosphorus, (b) neodymium, and (c) iron (pH 2.8, P/(Fe + Nd) = 1, Fe/Nd = 9).

hydroxides have poor selectivity for formation of precipitates in the presence of the precipitant. In a previous study, a novel recycling process in which neodymium phosphate was recovered with phosphoric acid and ascorbic acid from iron-neodymium solution was reported [19]. This process was relatively simple and did not require the use of harmful organic solvents. Ascorbic acid works as a reducing agent to convert Fe^{3+} to Fe^{2+}; thus, formation of iron phosphate became difficult and neodymium phosphate was precipitated with a smaller amount of iron phosphate. Since there are many kinds of reducing agents, separation of neodymium and iron may be achieved with other reducing agents. In the present work, a recycling process with phosphoric acid and sodium sulfite is employed to recover neodymium phosphate from iron-neodymium solution.

2. Experimental

A 280 mL portion of iron-neodymium solution (Fe: 0.09 mol/L, Nd: 0.01 mol/L), prepared from iron nitrate and neodymium chloride, was mixed with 140 mL of phosphoric acid (P: 0.2 mol/L). Sodium sulfite (formula: Na_2SO_3) was added to the iron-neodymium solution at various Na_2SO_3/Fe ratios before mixing. The standard iron/neodymium ratio was determined in reference to the permanent magnet composition, $Nd_2Fe_{14}B$. To determine the optimum conditions for neodymium recovery, the concentrations of iron, phosphoric acid, and sodium sulfite were varied (Fe: 0.045, 0.14, 0.19, 0.24, 0.29 mol/L; P: 0.02, 0.1, 0.3, 0.4 mol/L; Na_2SO_3: 0, 0.0225, 0.045, 0.0675, 0.09, 0.1125, 0.135, 0.18 mol/L). The mixed solution was adjusted to pH 2.3–4.3 with a highly concentrated sodium hydroxide solution. The precipitates were then filtered off and dried at room temperature over three days.

Table 1
Fe/Nd and Nd/(Nd + Fe) ratios in the precipitate at various Na_2SO_3/Fe ratios (pH 2.8, P/(Fe + Nd) = 1, Fe/Nd = 9 in original solution).

Na_2SO_3/Fe	Fe/Nd	Nd/(Nd + Fe)
0	9.47	0.096
0.25	5.71	0.149
0.5	4.30	0.189
0.75	2.81	0.263
1	1.60	0.385
1.25	3.45	0.255
1.5	4.74	0.174
2	6.65	0.131

The residual ratio of iron, neodymium, and phosphoric acid in the filtered solutions was calculated from the ideal concentrations and the ICP results obtained using an inductively coupled plasma–atomic emission spectrometer (Model SPS1500VR; Seiko Instruments, Inc.) [20]. A portion of the precipitate was dissolved in nitric acid solution. The ratios of phosphorus, iron, and neodymium in the precipitates were also calculated based on the ICP data for these solutions. The phase compositions of the precipitates were analyzed using X-ray diffraction (XRD); the XRD patterns were recorded on a MiniFlex Rigaku Corporation X-ray diffractometer using monochromated Cu-Kα radiation. A part of the precipitates was heated at 700 °C for 1 h in air, and the thermal products were analyzed by XRD.

3. Results and discussion

3.1. Na_2SO_3/Fe ratio

Fig. 1 shows the residual ratio of each element in solution at various Na_2SO_3/Fe ratios (pH 2.8, P/(Fe + Nd) = 1, Fe/Nd = 9). As shown in this figure, for all conditions, the residual ratio of neodymium in solution was 0%. The residual ratios of iron and phosphorus were low without the addition of sodium sulfite (Na_2SO_3/Fe = 0). Neodymium phosphate and iron phosphates were precipitated under this condition. With the addition of sodium sulfite, the residual ratios of iron and phosphorus in solution increased to Na_2SO_3/Fe = 1. However, at Na_2SO_3/Fe > 1, these residual ratios became lower. In a previous study [19], Fe^{3+} that was reduced to Fe^{2+} by ascorbic acid for conversion to iron phosphate ($FePO_4$) became difficult to precipitate, and the recovery ratios of iron and phosphorus decreased. Because sodium sulfite also works as a reducing reagent, the precipitation of iron phosphate became difficult due to reduction of the iron cation.

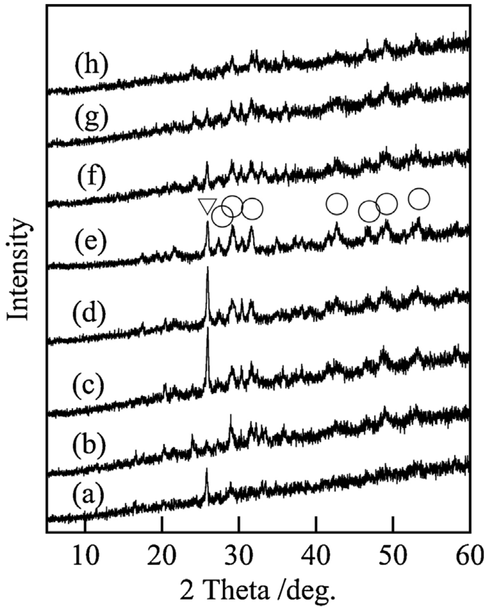

Fig. 2. XRD patterns of samples prepared at various Na_2SO_3/Fe ratios with subsequent heating at 700 °C: (a) 0, (b) 0.25, (c) 0.5, (d) 0.75, (e) 1, (f) 1.25, (g) 1.5, and (h) 2 (pH 2.8, P/(Fe + Nd) = 1, Fe/Nd = 9), ○: $NdPO_4$, ▽: $FePO_4$.