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Preparation of Na specific absorbent and application of sodium removal from ammonium tungstate solution

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Abstract: An adsorbent, $Na_{1.6}Al_{0.6}Ti_{1.4}(PO_4)_3$ (or NATP), was prepared by controlled crystallization of glasses in the $Na_2O-Al_2O_3-CaO-TiO_2-P_2O_5$ system. The crystalline phases characterized by X-ray diffraction (XRD) show that the sample glasses crystallizes into two phases, i.e. NATP and $Ca_9Al(PO_4)_7$, while the $Ca_9Al(PO_4)_7$ phase can be leached selectively with HCl, leaving a massive number of pores in the material. Through the experimental research, the effects of contact time, solution pH, and the initial concentration of Na^+ on the cation exchange properties were investigated. The batch sorption kinetics and equilibria can be described by Pseudo-second-order kinetic equations and Langmuir isotherm equations respectively. Furthermore, the experiments with an industrial solution show that the removal rate of sodium from industrial $(NH_4)_2WO_4$ is higher than 97%. Cycle experiment also shows that the NATP has a good cyclic performance.

Key words: Na specific adsorbent; sodium removal; ammonium tungstate; purification

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1 Introduction

Ammonium paratungstate (APT), as an intermediate product of tungsten metallurgy and tungsten chemical [1−3], is used to manufacture many terminal products, such as cemented carbide, tungsten metal material, ammonium metatungstate. Generally, almost all the tungsten raw materials should be firstly converted to sodium tungstate for recovering tungsten [4,5]. To transform from sodium tungstate to ammonium tungstate, ion-exchange and/or solvent extraction methods is frequently used in industrial $(NH_4)_2WO_4$ production [6,7]. But in practice it is found that timely trace sodium still contaminates the $(NH_4)_2WO_4$ owing to physical entrainment, misoperation, which leads to exceeding level of sodium content in APT, and makes it unable to meet higher application requirements.

In order to obtain products of APT-0 grade (as per Chinese standard GB 10116−88), the Na^+ concentration in $(NH_4)_2WO_4$ solutions must be lower than 10 mg/L [8]. In factories, to control the sodium content in APT some measures have to be adopted. Firstly, a large volume of pure water should be used to wash off most of the entrained sodium impurities. Secondly, purified desorption reagents should be used to avoid bringing extra sodium in $(NH_4)_2WO_4$ solution. These processing steps are generally labor intensive and complicated, and produce substantial volume of waste water with low concentrations of tungstate, which is difficult to recover. The removal of Na^+ is more difficult compared with other harmful elements in the $(NH_4)_2WO_4$ solution, and has become a difficult problem in tungsten metallurgy industry. In $(NH_4)_2WO_4$ solution, the predominant monovalent cation is NH_4^+, and the separating method employed should show a high selectivity for Na^+ in order to remove Na^+ efficiently. Methods for Na^+ removal are precipitation [9], adsorption and ion exchange. The selectivity of precipitation and adsorption obtained is generally low, and therefore its application is limited to a few particular cases [10].

It was reported that NASICON-type materials have stable skeleton structure, in which PO_4 tetrahedron share their corners with TiO_6 octahedra to form a 3D network structure [11], and sodium ion can transfer through the channels freely. There has been some research about the cation exchange properties of some NASICON-type materials [12−15], which has shed some light on Na^+

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removal from $(NH_4)_2WO_4$ solution.

In the present study, we prepared NASICON-type $Na_{1.6}Al_{0.6}Ti_{1.4}(PO_4)_3$ (NATP) as a Na^+ ion-sieve, and the exchange properties of this material were studied.

2 Experimental

2.1 Preparation of porous NATP

All reagents used in the experiment were in analytical grade and the solutions were prepared with distilled water. The base glass in the system $Na_{1.6}Al_{0.6}Ti_{1.4}(PO_4)_3$+$0.5Ca_3(PO_4)_2$ (molar ratio) was prepared with Na_2CO_3, Al_2O_3, TiO_2, $CaCO_3$ and H_3PO_4(85%) as starting materials. Stoichiometric starting materials were placed in a Teflon beaker and stirred completely, and a slurry was obtained. Then the slurry was dried at 240 °C for 10 h, and the resulting cake was ground to powders. The powders were then melted in a corundum crucibles at 1300 °C for 1 h. The melts were poured into a stainless steel mold to form glass. The mold was removed and the glass was annealed at 620 °C. The glass was heated up to 690 °C and maintained at the same temperature for 24 h. Subsequently, the specimens were heated at 800 °C without cooling down to room temperature and kept for 20 h. The resulting dense glass ceramics were crushed to produce a certain particle size distribution. Then the particles were leached with 1 mol/L HCl with stirring for 6 h and then filtered, washed, and dried. In this way, the soluble phase was selectively leached while the NATP phase was converted into the H^+-form.

The crystal structures of samples were characterized with a Rigaku D/max TTRIII X-ray diffractometer (XRD) at room temperature. The morphologies of the samples were observed with a JEOL JSM−6360LV SEM.

2.2 Ion-exchange properties of NATP

2.2.1 pH experiments

In order to study the influence of the pH on the Na^+−H^+ exchange, 100 mL of 50 mg/L Na^+ solution was placed in a sealed polyethylene bottle. The pH was then adjusted to 0.5−12.0 with HCl or $NH_3 \cdot H_2O$ solutions and 1.0000 g of the dry prepared NATP in H^+-form was added to the solution. The experiments were carried out at 298 K, and the final pH was measured after reaction for 24 h. The Na^+ concentrations in solution were determined by AAS (atomic absorption spectrometry, Persee of Beijing, China).

2.2.2 Adsorption dynamics and isotherm experiments

Kinetic and isotherm experiments were conducted at a constant temperature of 298 K. The NATP particles used in the kinetic experiments are 38−50 μm. For each experiment, 1.0 g prepared exchanger was added to 1000 mL Na^+ simulant solution (pH=11.0), and samples were taken from the reactor at regular time intervals. Na^+ solutions (50 mL) of different concentrations with increments of 50 mg/L (50−350 mg/L) were equilibrated for a specific period of time with 0.1 g of exchanger in conical flasks with stopper. The chemical compositions of the solutions were carried out via atomic absorption spectroscopy (WFX−120, Thermo Electron Corporation). The Na^+ concentration adsorbed into the exchanger was calculated by the mass balance relationship shown in Eq. (1).

$$q = (\rho_o - \rho_t)V/m \tag{1}$$

where q is the Na^+ concentration in the ion exchanger phase (mg/g); ρ_0 and ρ_t are the initial Na^+ concentration in the solution and one at time t, respectively; V is the solution volume (L); m is the ion exchanger mass in dry form (g).

3 Results and discussion

3.1 Characterization of porous NATP

Figure 1 shows the XRD patterns of the glass−ceramics before and after the acid leaching treatment. It can be observed that the sample crystallizes into NATP and $Ca_9Al(PO_4)_7$ phase. The acid dissolves $Ca_9Al(PO_4)_7$ phase selectively, leaving NATP with a number of pores which are distributed uniformly in the sample. It is obvious that the material is essentially composed of dense glass (Fig. 2(a)) before leaching, and a massive number of pores are left (Fig. 2(b)) after the $Ca_9Al(PO_4)_7$ phase being leached out with HCl. The schematic of the formation process of porous NATP glass−ceramics can be seen from Fig. 3.

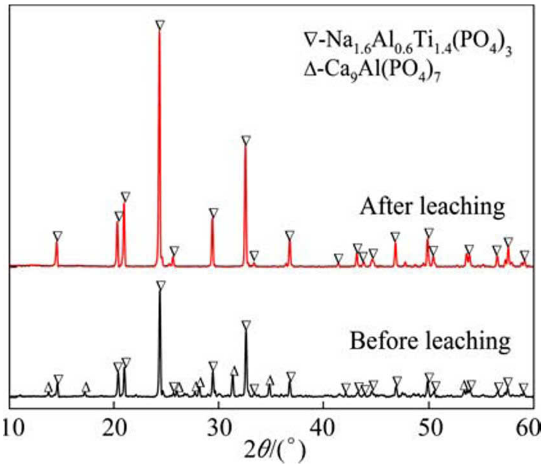

Fig. 1 XRD patterns of glass−ceramics before and after leaching