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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)₂WO₄ 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

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 (NH₄)₂WO₄ production [6,7]. But in practice it is found that timely trace sodium still contaminates the (NH₄)₂WO₄ 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

sodium impurities. Secondly, purified entrained desorption reagents should be used to avoid bringing extra sodium in (NH₄)₂WO₄ 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 (NH₄)₂WO₄ solution, and has become a difficult problem in tungsten metallurgy industry. In (NH₄)₂WO₄ 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 TiO₆ 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 (NH₄)₂WO₄ 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 Na₂CO₃, Al₂O₃, TiO₂, CaCO₃ and H₃PO₄(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 $38-50 \mu m$. 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).

$$q = (\rho_0 - \rho_t) V/m \tag{1}$$

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 Ca₉Al(PO₄)₇ phase. The acid dissolves Ca₉Al(PO₄)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 Ca₉Al(PO₄)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



Fig. 2 SEM images of sample before (a) and after (b) HCl leaching



Fig. 3 Schematic of formation process of porous NATP glass-ceramics

Figure 4 shows the ion-exchange properties of the prepared porous NATP glass-ceramics under different pH conditions. It can be seen from Fig. 4, the exchange rate increases with an increase in solution pH, which shows an S-shape. According to report by ZHANG and LIU [16], the exchange process is cation ion exchange, i.e. H^+ -Na⁺ exchange mechanism. Furthermore, the sorption is practically zero under acidic conditions pH<1.5, while the exchange rate during sorption can reach higher than 97% at pH>5.5. This means that



Fig. 4 Exchange rate-pH graph

 Na^+ uptake cannot be performed completely in solutions with pH<5.5 due to the strong association of hydrogen ions with the active sites of the ion sieves under acidic conditions.

3.2 Adsorption isotherms

In this work, the uptake equilibrium data can be described by the Langmuir isotherm model [17]. The isothermal equation can be expressed as follows:

$$\frac{\rho_{\rm e}}{q_{\rm e}} = \frac{\rho_{\rm e}}{q_{\rm m}} + \frac{1}{K_{\rm L}q_{\rm m}} \tag{2}$$

where ρ_e is the equilibrium concentration (mg/L); q_e is the uptake amount at equilibrium (mg/g); q_m is the theoretical maximum of adsorption capacity (mg/g); K_L is the Langmuir empirical constants.

The relationship between ρ_e/q_e and ρ_e is illustrated in Fig. 5. The results show that the plot has a good linear relation with a correlation coefficient of 0.998, which demonstrates that a monolayer coverage of Na was adsorbed on the surface of NATP adsorbent. The values of q_m and K_L are calculated to be 24.82 mg/g and 0.1124 L/mg, respectively. However, the equilibrium exchange capacity of Na⁺-H⁺ does not reach its theoretical value (90.89 mg/g). This can be attributed to the structure of the material, namely, in NATP there are two different sites running throughout the lattice structure for the sodium ion, in which the M1 site is fully occupied and the M2 site is partially occupied (Fig. 6) [14]. But the sodium in the M1 site is not fully exchanged, which will result in incomplete exchange of the sodium in NATP.



Fig. 5 Langmuir isotherms for Na⁺ uptake by NATP



Fig. 6 Crystal structure of NATP

3.3 Adsorption kinetics

The study on ion-exchange kinetics is also important because it demonstrates the solute uptake rate. And the uptake rate in turn will control the residence time of ion exchange at the solid–solution interface, and represent the exchange efficiency of the NATP, thereby determining the potential applications. As shown in Fig. 7, the equilibrium uptake capacity increases with increasing the Na⁺ concentration. And the maximum amount of adsorption reaches after 10 min, which shows that equilibrium time is independent on initial adsorbate concentration. Therefore, the time mentioned above is sufficient to attain equilibrium at the maximum removal rate of sodium from aqueous solutions of $(NH_4)_2WO_4$.

In order to investigate the sorption rate law of ion exchange, the kinetic data obtained from batch



Fig. 7 Effect of contact time on Na⁺ uptake by NATP at various initial Na⁺ concentrations

experiments were analyzed using the pseudo-second order equation [18,19]. The kinetic rate law can be rewritten as follows:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{3}$$

where k is the rate constant of sorption (g/(mg·s)); q_e is the amount of metal adsorbed at equilibrium (mg/g); q_t is the amount of metal adsorbed on the surface of the sorbent at a certain time t (mg/g).

The straight-line plots of t/q_t vs t for all cases were obtained by introducing the experimental data into Eq. (3) and shown in Fig. 8. Based on the equations and the obtained linear plots, the q_e , k and R^2 were calculated and listed in Table 1. The correlation coefficients of the pseudo-second-order rate model for the linear plots are very close to 1, indicating that the process essentially follows the pseudo-second order rate equation. HO and MCKAY [18] reported that the exchange may be the rate-limiting step involving valence forces through exchange of electrons between sorbent and sorbate.



Fig. 8 Pseudo-second order kinetic plots for Na⁺ uptake by NATP at various initial Na⁺ concentrations

 Table 1 Kinetic parameters of pseudo-second order model for

 Na⁺ uptake by NATP at different concentrations

Concentration of $Na^+/(mg \cdot L^{-1})$	$k/(g \cdot mg^{-1} \cdot s^{-1})$	$q_{\rm e}/({\rm mg}\cdot{\rm g}^{-1})$	R^2
50	1.73×10^{-3}	17.86	0.9990
100	1.77×10^{-3}	23.26	0.9998
150	2.96×10 ⁻³	25.64	0.9999

For the investigation of the Na^+-H^+ exchange mechanism, the intraparticle diffusion model [20] was used and fitted with the experimental data. The equation can be written as follows:

$$q_t = k_{\rm id} t^{1/2} \tag{4}$$

where $q_t (mg/g)$ is the amount adsorbed at time t (s), and k_{id} (mg/(g·s)) is the rate constant of intraparticle diffusion. Figure 9 presents the plots of q_t vs $t^{1/2}$ obtained for the Na⁺-H⁺ exchange at different Na⁺ concentrations, 50, 100 and 150 mg/L. The plots show two stages of sorption, and the first plot was linear but did not pass through the origin. It is concluded that the double stage of the curves were attributed to the fact that the adsorption in the initial stages was due to the boundary layer diffusion whereas in the later stages adsorption was due to the intraparticle diffusion [21,22]. On the other hand, the increased sorption rate with the increase of initial concentration can be ascribed to the improved chances of contact between Na⁺ and the surface of the NATP with increasing Na⁺ concentration, which results in a larger amount of Na⁺ diffusion through the boundary layer in unit time [23].



Fig. 9 Intraparticle diffusion plots for Na⁺ uptake by NATP at different Na⁺ concentrations

3.4 Na⁺ removal from (NH₄)₂WO₄ solution

In order to verify the effect of Na⁺ removal with the prepared NATP materials, a series of experiments were practiced by adding certain amount of the NATP to the industrial $(NH_4)_2WO_4$ solution $(WO_3 275 \text{ g/L}, \text{pH } 9.6)$ with stirring. After about 10 min of contact, the $(NH_4)_2WO_4$ solution was separated from the ion exchanger by filtering and the ion sieve was recovered for regeneration and reuse. The APT products were obtained by evaporation of filtrate. The recycle tests for ion sieve were conducted with 1 mol/L HCl solution to immerse the Na⁺-loaded NATP for 10 min.

The removal results are listed in Table 2. The $(NH_4)_2WO_4$ solution can act as a NH_3 – NH_4Cl buffer solution, and the pH is not changed after exchange reaction. In all cases the removal rate was higher than 97% and the results were consistent with the above. Generally, in order to prepare a APT which can meet the APT-0 (GB/T10116–2007) grade, the m_{Na}/m_{WO_3} in $(NH_4)_2WO_4$ solution should be lower than 5×10^{-4} before crystallization [24]. According to the experimental results in this work, the w_{Na}/w_{WO_3} is much lower than the requirement and the spectrographic analysis of sodium concentrations shows that all the products meet the APT-0 grade.

Figure 10 shows the cycling performance of the Na⁺ removal by NATP materials. The results indicate that the

Table 2 Results of deep removing sodium from commercial $(NH_4)_2WO_4$ solution

$(m_{\rm Na}/m_{\rm WO_3})/10^{-6}$		Removal	Sodium content	
Before purification	After purification	rate/%	of APT/%	
183	5	97.27	< 0.001	
356	7	98.03	< 0.001	
547	12	97.81	< 0.001	
675	8	98.81	< 0.001	
764	13	98.30	< 0.001	
1109	14	98.74	< 0.001	
1505	15	99.00	< 0.001	



Fig. 10 Cycle performance of NATP

adsorbent could be regenerated easily with 1 mol/L HCl solution and its capacity and activity remain after 17 cycles, indicating an excellent cyclic performance of the adsorbent for Na⁺ removal from $(NH_4)_2WO_4$ solution.

4 Conclusions

1) The adsorbent $Na_{1.6}Al_{0.6}Ti_{1.4}(PO_4)_3$ can be partially exchanged and the primary exchange mechanism can be described as H^+ – Na^+ exchange.

2) The exchange rate during sorption can reach higher than 97% at pH>5.5, while practically zero at pH<1.5.

3) The adsorbent exhibits a high efficiency for removing sodium from the $(NH_4)_2WO_4$ solution, and the removal rate of sodium is higher than 97% under optimum conditions. Meanwhile the NATP maintains a good cyclic performance for application.

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特性 Na 离子吸附剂的制备及其 从钨酸铵溶液深度除钠

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摘 要:在 Na₂O-Al₂O₃-CaO-TiO₂-P₂O₅体系中通过控制结晶合成了多孔吸附剂 Na_{1.6}Al_{0.6}Ti_{1.4}(PO₄)₃(NATP)。XRD 分析表明,合成的玻璃体会弥散结晶为 NATP 和 Ca₉Al(PO₄)₇两相;通过酸浸可将 Ca₉Al(PO₄)₇相溶出,从而使主 相 NATP 中留下大量孔道。实验研究了平衡时间、溶液 pH 和 Na⁺浓度对吸附剂离子交换性能的影响。吸附动力 学和平衡热力学研究表明,吸附过程可以很好地用准二级动力学方程和 Langmuir 等温方程进行描述。此外,在 工业钨酸铵溶液中深度除钠的实验表明,除钠率高于 97%,且循环实验表明该吸附剂具备良好的循环性能。 关键词:特性 Na 吸附剂;除钠;钨酸铵;净化

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