IMPROVED INORGANIC ION-EXCHANGERS

II. AMMONIUM MOLYBDOPHOSPHATE — SILICA GEL SYSTEM

J. DOLEŽAL, J. STEJSKAL, M. TYMPL, V. KOUŘÍM

Nuclear Research Institute, 25068 Řež (Czechoslovakia)

The possibility of using the sol - gel method for preparation of inorganic ion-exchangers with a silica gel matrix has been demonstrated on the ammonium molybdophosphate — silica gel (AMP — SG) system. For the preparation of the ion-exchanger a sodium silicate solution, containing AMP and components to cause gelling to silica gel after increase of the temperature of the solution, is poured into a hot stirred silicone oil. The solution forms droplets, which are filtered off after their gelling, washed and dried. Beads containing 65 wt.% of AMP per gram of dry material have been prepared by this method and tested in ion-exchange columns for caesium removal from nitric acid solutions. Caesium may easily be desorbed with ammonium chloride at nitrate solution. The ion-exchanger is suitable for long-time reversible column operation, having not only good chemical, thermal and radiation stabilities but also good mechanical and hydrodynamic properties and resistance to abrasion. It combines the advantage of the good kinetics of ion-exchange obtained with microparticles of precipitated inorganic ion-exchanger, with the low flow resistance of large particles.

Introduction

In a previous paper\(^1\) a method of preparation of granulated inorganic ion-exchangers has been described using an organic polymer as binding material. The method solves well the problem of the hydrodynamic properties of inorganic ion-exchangers, but nevertheless the materials are of limited use when applications at higher temperature are demanded; another disadvantage might be the lower radiation stability of the granules in comparison with the original inorganic substance.

We have therefore been looking for an inorganic material capable of replacing organic binding polymers and stable under the working conditions of the highly radioactive solution treatment.

Such a suitable material seemed to be silica gel, which has sufficient chemical, thermal and radiation stability, a porous structure allowing relatively fast transport of ions and solutions inside the particles, and suitable mechanical properties, and which, moreover, may easily be prepared in the form of spherical particles using the sol - gel method.\(^2,3\) Instead of an inorganic ion-exchanger being precipitated on the surface and inside the channels of the silica gel structure, the application of the sol - gel process has further the advantage of allowing a dispersion of the
exchange particles into the silica gel matrix. The channels are thus left free, which might improve the kinetics of the ion-exchange, and the loss of the active component due to peptization and surface abrasion during column operation should also be lower.

Having been interested in caesium recovery from high-level radioactive waste solutions, we began studying exchangers with the silica gel matrix on the ammonium molybdophosphate - silica gel (AMP-SG)* system, expecting that the resulting material might possess the ion-exchange properties of the original AMP, i.e. its high selectivity for caesium even in concentrated nitric acid solutions, good ion-exchange capacity, high radiation stability, and the possibility of caesium desorption.5,6

Experimental

Reagents

Except for the technical grade sodium silicate solution and "pure" phosphomolybdic acid, all reagents used were of analytical purity. Phosphomolybdic acid solutions had to be filtered before use, as the commercial reagent contained some white insoluble material. The caesium nitrate solutions were labelled with $^{137}$Cs, the radiochemical purity of which was checked by $\gamma$-spectrometry.

Preparation of AMP

Equal volume of 0.1M phosphomolybdic acid and 0.5M ammonium nitrate solutions were mixed, and the AMP precipitate was washed three times with 0.1M ammonium nitrate solution, filtered off and dried at 110 °C for 3 hrs. The theoretical ratio of the AMP components is $\text{NH}_4: \text{P}:\text{Mo} = 3:1:12$, according to the formula $(\text{NH}_4)_3\text{PMO}_{12}\text{O}_{40} \cdot 2\text{H}_2\text{O}$, and the ratio found was 2.95 : 1 : 11.4.** The difference is probably caused by a partial decomposition of the phosphomolybdic acid used for the preparation.

Preparation of silica gel matrix exchangers

One of the techniques used for preparation of the silica gel matrix exchangers resembles the technique of preparation of organic resin pearl polymers. The sodium silicate solution, containing inorganic exchanger and components causing gelling to silica gel after increase of the temperature of the solution, is poured into a hot stirred bath filled with a liquid immiscible with aqueous solutions. The sodium

*Experiments on various insoluble ferrocyanide - SG exchangers have recently been successfully carried out.4

**The analysis was performed by Dr. M. Santarová of N.R.I.