Specific Features of Rhenium Desorption from Weakly Basic Anion Exchangers Purolite A170 and Purolite A172 with Ammonia Solutions

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Abstract—Equilibrium, kinetics, and dynamics of rhenium desorption from weakly basic macroporous (Purolite A170) and gel anion (Purolite A172) exchangers with ammonia solutions were studied. The effective diffusion coefficients of rhenium in its desorption from these anion exchangers and the activation energy of rhenium desorption from the gel anion exchanger were estimated.

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The choice of an ion exchanger in development of an ion-exchange process for recovery of a particular component is determined not only by its selectivity and capacity for the ion being recovered, but also by the ease and completeness of desorption of this ion. Comparatively recently, Purolite Int. Ltd has purposefully synthesized weakly basic anion exchangers selective toward rhenium. These anion exchangers are presently manufactured under brand names Purolite A170 (macroporous anion exchanger) and Purolite A172 (gel anion exchanger), which have the same functional groups and differ in the matrix morphology [1]. The anion exchangers have exhibited advantage in selectivity toward rhenium over other, not only weakly, but also strongly basic anion exchangers in rhenium sorption from solutions of various compositions [2–4].

An important advantage of weakly basic anion exchangers is that rhenium can be desorbed with ammonia solutions, which enables recovery of ammonium perrhenate, the final product of hydrometallurgical processing of rhenium from eluates without any intermediate procedures [5]. At the same time, there are no systematic data on rhenium desorption from Purolite A170 and Purolite A172 anion exchangers with ammonia solutions.

The goal of our study was to comparatively examine the rhenium desorption from the weakly basic macroporous and gel Purolite A170 and Purolite A172 anion exchangers with ammonia solutions.

EXPERIMENTAL

Purolite A170 and Purolite A172 anion exchangers (in what follows, A170 and A172, respectively) were converted to the sulfate form. For experimental studies of the kinetics of rhenium desorption, the anion exchangers were sieved into 0.25–0.5-and 0.5–0.63-mm (A172) and 0.63–0.8- and 1.0–1.5-mm (A170) fractions in the air-dry state.

When studying the desorption of rhenium, we preliminarily saturated the anion exchangers with rhenium to a prescribed capacity by bringing weighed portions of the anion exchangers in contact with a rhenium-containing solution. The initial content of rhenium in the solution was chosen experimentally so as to reach a prescribed saturation of the anion exchangers with rhenium upon equilibration. After equilibrium was attained (in 5–7 days), the solutions were separated from the anion exchangers and analyzed for rhenium. Further, the saturated anion exchangers were thoroughly washed with water and dried on paper.
filters, and then were subjected to rhenium desorption.

When studying the desorption of rhenium under equilibrium conditions, we brought weighed portions of the anion exchangers (0.2 g in terms of an absolutely dry anion exchanger) saturated with rhenium to a prescribed capacity in contact with 20 mL of an ammonia solution of certain concentration under agitation in a thermostated Memmert ONE 14 shaker at a prescribed temperature for 40–90 h (depending on temperature). Preliminary experiments demonstrated that this time of contact is sufficient for equilibration. After the time specified above elapsed, the solutions were separated from the anion exchangers and analyzed for rhenium. In separate experiments, the residual capacity of the anion exchangers for rhenium was in parallel determined by direct analysis of the anion exchanger phase. For this purpose, weighed portions of the anion exchangers were washed with water upon desorption of rhenium, dried at a temperature of 105°C, mixed with an Eschka mixture, and burnt in a muffle furnace at 800°C. The resulting cake was dissolved in dilute sulfuric acid and the rhenium concentration in solution was determined.

The kinetics of rhenium desorption was analyzed by the limited-volume method [6]. When studying the kinetics of rhenium desorption, we charged a vessel with a 100-mL portion of an ammonia solution of certain concentration, placed the vessel in a thermostat, and kept it there until a prescribed temperature was reached. Then, a weighed portion of an anion exchanger (1 g in terms of dry mass) with certain grain size was placed in a cell with apertures, whose design was described in [6]. The cell was attached to the axis of a mechanical stirrer and brought in contact with the solution, immediately after which agitation was switched on. Under the action of the centrifugal force, the solution was sucked into the cell through its bottom and then was discharged into the vessel through side apertures, passing in the process through the anion exchanger bed. Then the solution was sampled at regular intervals of time to make an analysis for rhenium. The amount of rhenium desorbed by any instant of time was calculated with consideration for the change in the solution volume upon sampling. The degree $F$ of equilibration was found as the ratio between the amount of rhenium desorbed by instant of time $\tau$ to that desorbed upon equilibration.

As shown below, the rate of rhenium desorption is limited by the internal diffusion in all the systems studied. We calculated the effective diffusion coefficients by the Boyd–Adamson–Mayers equation [6]. Using the experimental values of $F$ from the tabulated data of [7], we found the dimensionless time parameter $B\tau$ and then calculated the effective rhenium diffusion coefficients.

Experiments on rhenium desorption under dynamic conditions were performed in glass columns filled with 20 mL of an anion exchanger at a 10 : 1 ratio between the height of the anion exchanger bed and the inner column diameter. The solution delivery rate was 0.65 sp.vol. h$^{-1}$ in all experiments.

The rhenium concentration in solutions was determined by photocolorimetry on a KFK-2MP photoelectrocolorimeter from the coloration intensity of the reduced form of a yellow complex of rhenium with the rhodanide ion [8].

In the first stage of the study, we examined the rhenium desorption under equilibration conditions. Depending on the composition of a solution from which rhenium is recovered, the capacity of the anion exchangers for rhenium may reach various values. The completeness of desorption of ions frequently depends on the degree of anion exchanger saturation with these ions. Therefore, we first examined how the degree of saturation of anion exchangers with rhenium affects the degree of rhenium desorption from these. Rhenium was desorbed from anion exchanger saturated to a particular capacity with a 6 M aqueous ammonia solution at a temperature of

![Fig. 1. Degree $D$ of rhenium desorption from (1) A170 and (2) A172 anion exchangers with a 6 M aqueous ammonia solution at a temperature of 20°C vs. the degree $E$ of their saturation with rhenium.](image-url)