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SORPTION OF NICKEL ON CERIUM(IV)-BASED ION-EXCHANGERS

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Sorption of nickel on the oxide, phosphate, antimonate, and tungstate of cerium has been studied at pH 4.0 as a function of nickel ion concentration. The absorption on cerium tungstate and hydrous cerium oxide was linearly related to the nickel ion concentration up to 0.08 M.

Hydrous oxides of polyvalent metals can serve both as cation and anion exchangers.[1)] Ceric phosphate behaves as a cation exchanger in basic media[2)] and its absorption of amine and ethylenediamine complexes of Cu^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} at different external ionic concentration and pH has been studied.[3)] This paper attempts to compare the absorption properties of four cerium-based ion-exchangers by comparing their sorption isotherms of nickel ions.

Hydrous ceria was precipitated from saturated ammonium ceric nitrate solution with ammonia solution.[4)] Ceric phosphate was prepared by the reaction of saturated ammonium ceric sulphate solution with 6.0 M H_3PO_4 at room temperature.[3)] Ceric antimonate and ceric tungstate were prepared by the addition of 200 ml of saturated ceric sulphate solution in 1.0 M H_2SO_4 to a well stirred 200 ml solution (1.0 M) of antimony pentachloride and sodium tungstate, respectively. The precipitates were kept in contact with the mother liquor for 24 h at room temperature. They were washed several times with demineralised water till the filtrate was neutral. Finally they were filtered off under suction and dried at 40 °C. The products, except the hydrous ceria, were kept in 2.0 M HNO_3 for 24 h with intermittent shaking to convert them into the hydrogen form and were finally washed with demineralised water till the filtrate was neutral and dried at 40 °C. For sorption studies the samples were ground in a porcelain mortar and sieved to 100 - 200 mesh size.

To examine the reversibility of the exchange, the sodium ion capacity was determined on the exchanger in the hydrogen form by the batch technique. A 1.0 g portion of the samples was immersed in 50 ml of a 2.0 M sodium chloride solution with intermittent shaking for 24 h. It was then filtered and washed with 30 ml of the 2.0 M sodium chloride solution. The amount of hydrogen ions released by the exchanger was calculated by titrating potentiometrically the filtrate and washing with a standard sodium hydroxide solution.

To 0.5 g of each of the samples, 25 ml of the nickel ion solution were added. The initial concentration was varied between 0.01 and 0.1 M and the pH was 4.0. The solid-solution mixture was equilibrated for 24 h at about 28 °C with intermittent shaking. It was found that equilibrating for 24 h gave steady state values. The mixture was then filtered and the nickel ion concentration determined complexometrically.5) The amount sorbed by the samples was then calculated.

Figure 1 shows the amount of nickel ions absorbed by the four samples as a function of the nickel ion concentration. Sorption properties of hydrous oxides arise from the presence of, and the pH dependent dissociation of, the surface hydroxyl groups. Their acidic nature is reflected in their point of zero charge (PZC). Expressed in pH units, it is the pH beyond which the hydrous oxides behave as cation exchangers. For CeO_2 the PZC is approximately 7.6) The absorption of nickel ions by hydrous ceria at pH 4 is presumably due to the formation of a Ni - O bond between sorbed species and the surface oxygen group. The sorption of nickel ions on the hydrogen form of cerium phosphate, antimonate, and tungstate can be represented by the following exchange mechanism:

$$n\mathrm{CeXH} + \mathrm{Ni}^{n+} \rightleftharpoons (\mathrm{CeX})_n\mathrm{Ni}^{n+} + n\mathrm{H}^+ \qquad (1)$$

where XH stands for the phosphate, antimonate, or tungstate. The amount of nickel ions absorbed will depend on the pH of the solution. With increase in pH the absorption of nickel ions is expected to increase. Aqueous solutions of Ni(II) not containing strong complexing agents contain the green hexaquonickel(II) ion, $[Ni(H_2O)_6]^{2+}$. In the case of hydrous ceria and cerium tungstate, the absorption of nickel ions varied linearly with the nickel ion concentration in the solution up to about 0.08 M. Thereafter the sorption tended towards a maximum value. For cerium tungstate and hydrous ceria this maximum is about 0.27 mmol/g and 0.23 mmol/g respectively. The absorption maximum for cerium antimonate is about 0.43 mmol/g.

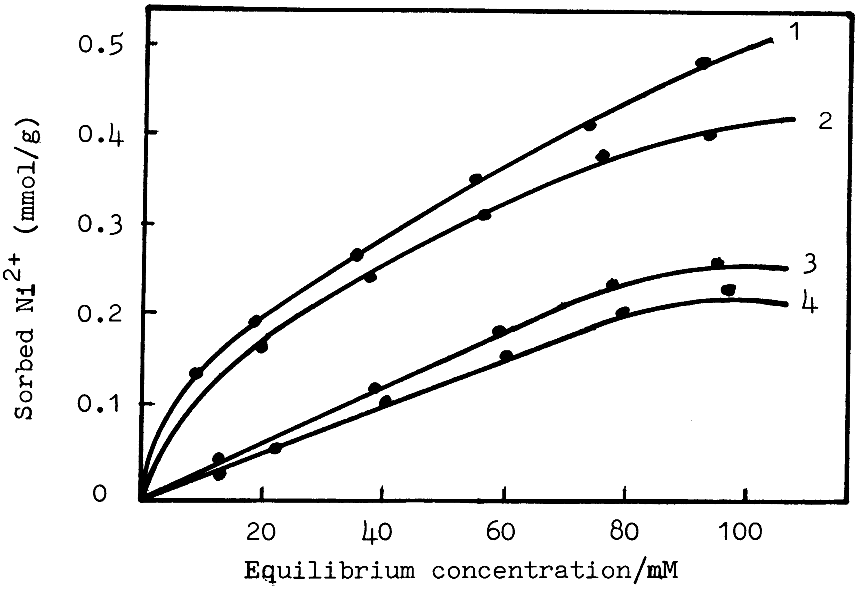

Fig. 1. Sorption of nickel on the phosphate (1), the antimonate (2), the tungstate (3), and the hydrous oxide (4), of cerium.

Table 1. Ion-exchange capacities of cerium-based exchangers and their sorption maximum for nickel ions

Exchanger	Ion-exchange capacity mequiv./g	Nickel absorption mequiv./g
Cerium phosphate	1.46	----
Cerium antimonate	0.58	0.43
Cerium tungstate	0.45	0.27
Hydrous ceria	----	0.23

An important factor in determining the ion-exchange capacity of inorganic ion-exchangers is the first ionisation constant of the acid. Qureshi and co-workers[7)] found that the ion-exchange capacity of titanium molybdate, antimonate, and tungstate decreases in that order. Qureshi and co-workers again found that the ion-exchange capacity of zirconium phosphate, molybdate, and tungstate decreases in that order.[8)] Table 1 gives the capacities of the samples. It is clear that cerium phosphate has the highest ion-exchange capacity. This is in conformity with the fact that phosphoric acid is more acidic than antimonic or tungstic acid. The capacity decreases in the order phosphate, antimonate, and tungstate.

The capacity for hydrous ceria was found to be very small. This may be due to the fact that at the pH employed for the capacity determination (about pH 7), hydrous ceria is neither a strong cation exchanger nor a strong anion exchanger and its affinity for sodium ions is weak. From equation 1 it can be inferred that the amount of nickel ions that can be absorbed by the exchanger is proportional to the number of exchangeable hydrogen on the exchanger, viz. the capacity of the exchanger. From Figure 1 and Table 1 it can be seen that the amount of nickel ions absorbed by the samples is proportional to the capacity values of the samples.

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