EXPERIMENTS WITH A SODIUM-ION ELECTRODE AS A MEANS OF STUDYING CATION-EXCHANGE RATES*

by

VANCE C. KENNEDY and THOMAS E. BROWN†

EXTENDED ABSTRACT

THE EXCHANGE capacity of stream sediments is believed to be a significant factor in stabilizing the chemical composition of stream water against short-term changes, especially with regard to minor elements. The rate at which cation exchange occurs is a factor in determining the time required for chemical equilibrium to be achieved between sediment and stream water. A method for measuring the rate of exchange of a divalent cation for a monovalent cation sorbed on stream sediments has been developed and is described herein.

A sodium-ion electrode was inserted into a continuously stirred suspension containing 100 ml. of distilled water and 4 g of sodium-saturated sand-size material from Brandywine Creek in Delaware. Sufficient calcium chloride solution was then added rapidly to give a ratio of about 3 : 1 meq Ca : meq Na. As calcium displaced the sorbed sodium, the sodium activity in solution increased, causing a change in the e.m.f. of the sodium-ion electrode. This e.m.f. provided the input for a pH meter whose output was connected to a potentiometric strip-chart recorder. In this way, a continuous record of sodium activity versus time was obtained. About 90 per cent exchange on 0.12–0.25 mm and 0.25–0.50 mm sand fractions occurred in 3 min and 7 min respectively.

A modification of the method consisted of inserting the sodium-ion electrode into a stirred magnesium chloride solution and then adding a sodium-saturated sample, either dry or as a slurry. This modification gave smoother curves during the early part of an exchange reaction than did the first version of the method.

Sodium-saturated Brandywine Creek sands were placed in magnesium solutions using the modified method. Time for 90 per cent exchange on 0.25–0.50-mm and 0.50–1.0-mm sand fractions was about 7 min and 12 min respectively.

When 0.2–0.4 g of sodium-saturated clays (kaolinite from Bath, S.C.; Fithian illite and montmorillonites from Polkville, Miss., and Clay Spur, Wyo.) were placed in 60 ml. of 0.17 N magnesium chloride solution, 50 per cent exchange occurred within 0.1–0.3 sec and 90 per cent exchange within 1–2 sec. Detailed knowledge of the rate of exchange between 90 and 100 per cent is difficult to obtain because the rate of electrode response decreases as the electrode approaches equilibrium with the solution.

The increase in time required for sand to approach equilibrium as compared to clay-size materials is attributed to the fact that the divalent cations must diffuse into the sand grains and the sodium must diffuse out before the sodium ions can be detected by the specific-ion electrode. Stream sands commonly contain fine-grained rock fragments,

---

* Publication authorized by the Director, U.S. Geological Survey.

† Geologists, U.S. Geological Survey, Denver, Colorado.

so a significant part of the exchange capacity of sand grains may be inside the grains.

Specific-ion electrodes should be useful in following exchange reactions of many monovalent–divalent cation pairs in addition to those mentioned in this study. Such electrodes can be used to determine not only sodium but also potassium, ammonia, lithium, silver, and cesium in the presence of divalent cations.