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Hyperfiltration of potassium nitrate through clay membranes under relatively low-head conditions

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Abstract—Much like reverse osmosis membranes, clays have been shown to exhibit reverse osmosis properties at high hydraulic heads. To determine if reverse osmosis was possible at lower hydraulic heads, potassium nitrate solutions were passed through thin clay layers at heads of 1.30 to 1.42 m. In each experiment, concentrations significantly increased due to partial solute rejection by the clay membranes. Concentration increases within the experimental cells were between 131% and 184%. Calculated values of the reflection coefficient ranged between 0.55 to 0.70, suggesting that these thin clay layers exhibited membrane effects. The results of these experiments suggest hyperfiltration may concentrate some dissolved contaminants from below to above regulatory limits in shallow aquifers bounded by a membrane-functioning aquitard or relatively low hydraulically conductive geologic strata. Hyperfiltration may also control nutrient distributions, creating subsurface microbial “hotspots”. Consideration of hyperfiltration effects may ultimately lead to a clearer understanding of many subsurface processes, both shallow and deep, including contaminant fate and transport, subsurface microbiology, natural bioremediation and attenuation, redox, rock–water interaction, and groundwater chemistry. *Copyright © 2005 Elsevier Ltd*

1. INTRODUCTION

Two field studies found nitrate concentrations increased with depth in perched or shallow aquifers (Schulmeister et al., 2003b; Schulmeister et al., 2004; Smith et al., 1991) and three studies found an increase in chloride concentrations with depth towards bounding clay layers (Smith et al., 1991; Johnson and Chou, 1998; Ronen et al., 1987). Although several explanations, such as different water sources and differing levels of microbiological activity, can be offered for such solute concentration increases, hyperfiltration by clay-rich aquitards (relatively impermeable geologic strata) should also be considered as a possible mechanism for such solute concentration profiles.

Hyperfiltration, also known as solute-sieving or reverse osmosis, occurs when flow of solution, with an initial solute concentration c_i (Fig. 1A), through a membrane-functioning aquitard causes a build-up of solute on the high-pressure side of the membrane (Fig. 1B) due to rejection of some of the solute by the membrane. This zone of increased concentration is known as the concentration polarization layer (CPL), and c_o is defined as the maximum solute concentration located immediately adjacent to the membrane. As solute concentrations increase near the high-pressure membrane face, the membrane efficiency or ability to selectively reject solutes decreases due to exposure to increasing concentrations of dissolved solutes. Eventually, the solute concentration at the membrane ultimately reaches a maximum steady-state value, assuming no chemical or biological reactions occur (Fritz and Marine, 1983).

Numerous laboratory experiments have demonstrated that clays and shales can exhibit hyperfiltration effects at high hydraulic heads (Fritz and Marine, 1983; Kharaka and Berry, 1973; Benzel and Graf, 1984; Fritz and Whitworth, 1994; Liangxiong et al., 2003). Osmotic and diffusion membrane properties of clays have also been shown in many laboratory experiments (Low, 1955; Kemper and Evans, 1963; Kocherginsky and Stucki, 2001). A number of field studies have also alluded to subsurface clay membrane effects based on regional water chemistry measurements, (Phillips et al., 1986; Hitchon and Friedman, 1969; Nuezil, 2000; Becker, 1892). Geologic processes thought to involve clay membrane processes include 1) sedimentary ore formation (Becker, 1892; Mackay, 1946; Lueth and Whitworth, 2001), 2) cementation and diagenesis (Fothergill, 1955; Fritz and Eady, 1985), 3) fractionation of solute isotopes (Benzel and Graf, 1984; Fritz and Whitworth, 1994; Coplen and Hanshaw, 1973; Fritz et al., 1987), 4) groundwater sampling (Fritz and Whitworth, 1994), 5) subsurface petroleum accumulation (Magara, 1974), and 6) thrust faulting (Hanshaw and Zen, 1965). Acceptance of subsurface geologic membrane effects have been slow to emerge in the geosciences—in part because hydraulic heads used in the laboratory (50.7 to 2062 m, Fritz and Marine, 1983; Kharaka and Berry, 1973; Fritz and Whitworth, 1994; Milne et al., 1963) are much greater than those thought to commonly exist in the subsurface (Nuezil, 1986) and hyperfiltration effects have not been previously demonstrated to occur at lower heads.

One natural scenario where lower head hyperfiltration may occur is in perched aquifers underlain by clay-rich aquitards. In a perched aquifer the water depth is equal to the head across the lower bounding aquitard. Water depths of one to two meters are common in shallow perched aquifers. Similar subsurface head differences across clay bounding layers have previously been reported. Pressures in artesian aquifers (often bounded by shales or clays) can be quite high. For example, a well drilled in 1841 in the Paris Basin to a depth of 1798 feet into an artesian aquifer produced a column of water many feet into the air (Tolman, 1937). This represents a head across the aquitard

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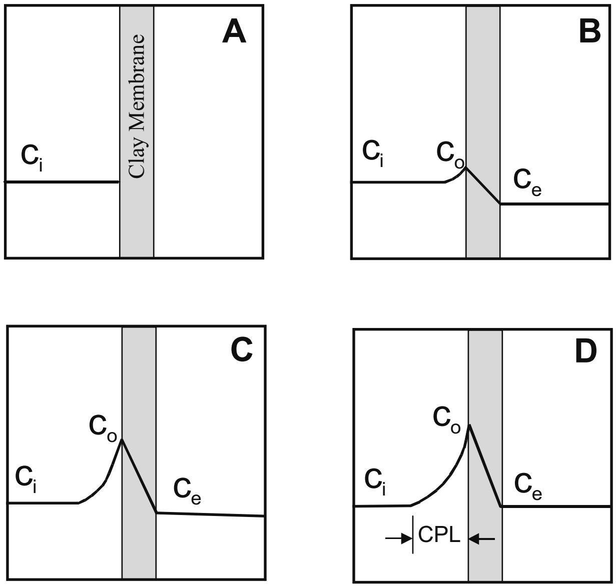

Fig. 1. Conceptual CPL development. This assumes that the solute is conservative and no ion exchange is occurring. Initially, (A) the solute is all on the high-pressure side of the membrane and no solute is contained within the pore fluids within the membrane. After flux commences, (B) the concentration at the high-pressure membrane face c_o increases due to solute rejection. Effluent samples contain some solute now. (C) C_o has increased further as has the effluent concentration c_e. At steady-state (D) the input concentration c_i is now equal to the output c_e and the value of c_o is constant. (Redrawn from Fritz and Marine, 1983).

of at least 548 meters and a hydraulic head of 312 (Tolman, 1937). High hydraulic gradients occur throughout the Normandy Bathonian aquifer (Delhomme, 1979). Other wells in the lower portions of the alluvial fans in southwestern U. S. alluvial basins produce artesian flows that extend from less than a meter to as much as 115 meters above the ground across very thin clay lamellae of 2.5 cm to 1 m thick, which represent gradients from 115 to 46,000 (Paulsen, 1949).

Previous modelling has predicted that hyperfiltration effects can be significant with only one or two meters of hydrostatic head (Whitworth, 1998). Therefore we experimentally tested hyperfiltration effects of thin (0.0011 to 0.0025 m) smectite and kaolinite clay layers using constant heads of 1.30 to 1.42 m to determine whether a significant hyperfiltration-induced concentration build-up of potassium nitrate is possible.

We chose nitrate as the solute for these experiments because nitrate is a significant drinking water contaminant in the U.S. (Nolan and Stoner, 2000), as well as in many other parts of the world (Gleick, 1993). Excessive nitrate ingestion can cause diseases such as methemoglobinemia (blue baby syndrome), nasopharyngeal cancer, stomach cancer, and numerous other cancers (Nolan and Stoner, 2000). Methemoglobinemia is the most prevalent disease associated with excessive nitrate consumption from contaminated drinking water (Nolan and Stoner, 2000). At sufficiently high levels, nitrate poisoning, or methemoglobinemia can be lethal (Nolan and Stoner, 2000).

2. METHODS

We used commercial Na-smectite (Wyoming Bentonite) as well as kaolinite collected from an outcrop located on the south side of Highway 60E (33°53'22"N, 106°44'21" W) east of San Antonio, New Mexico. Both clays were identified via X-ray diffraction. In these experiments dilute potassium nitrate solutions, prepared from reagent grade chemicals, were passed through thin kaolinite and Na-smectite membranes contained within experimental cells similar to those used in previous experimental work (Fig. 2; Fritz and Whitworth, 1994).

The clay was prepared for use by first separating out any sand and silt by settling. The clay was then filtered from the supernatant liquid using vacuum filtration through a 0.45-μm filter. The clay was then removed from the filter paper, reslurried, and dialyzed using Spectra/POR 6-8000 MWCO dialysis tubing to remove any dissolvable contaminants. Once dialysis was complete, the clay was freeze-dried using a Labconco Model 4500 freeze dryer and stored in doubled Zip Lock bags.

Clay was weighed and rehydrated with approximately 60 mL of deionized water to form a clay slurry. This slurry was placed within the assembled acrylic experimental cell. The cell was then connected to the high-performance liquid chromatography pump, which forced deionized water into the experimental cell and caused the clay to sediment onto a MFS brand 0.1-μm filter paper supported by two Whatman #2 paper filters using an applied hydraulic compaction pressure of 100 psi. By initially overcompacting the clays, compaction due to applied hydraulic gradient could not occur during the experiment.

Initially deionized water was passed through the assembled experimental cells in order to determine water permeation (L_p) (Fritz and Whitworth, 1994). The deionized water was removed from the experimental cell and replaced with the potassium nitrate solution. The experiments began immediately after insertion of stock solution to the cell in order to observe the entirety of the reverse osmotic process. During each experiment, effluent samples were collected at intervals and the time, date, interval seconds (sample intervals initially started with approximately 90 s and increased to several days as the experiment progressed towards steady-state), and weight (to ± 0.01 g) of each effluent sample were recorded (Figs. 3–5).

Evaporation control by means of keeping headspace at 100% humidity was used to prevent effluent evaporation between sampling times (Fritz and Whitworth, 1994). Each sample was analyzed for nitrate concentration using a Dionex DX-120 ion chromatograph. Every fifth effluent sample, all reservoir and cell solutions were analyzed in triplicate. The cell solution was also saved and analyzed at the end