R & D NOTES

Effects of Flow Instabilities on Ion Exclusion Operations

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The purpose of this note is to present specific data which show that the concentration profiles which develop in certain fixed bed sorption operations can be very markedly affected by hydrodynamic instabilities, if such exist. We also wish to indicate how one may estimate a priori what operating conditions are necessary to avoid such effects.

The hydrodynamic instabilities which occur when a less viscous fluid is used to displace a more viscous fluid from a porous medium are well known, especially in connection with the secondary recovery of petroleum via water-flooding. Even minor heterogeneities can trigger the growth of fingers of the less viscous driving fluid into the fluid being displaced. If the displacement is vertically downward, however, the flow can often be stabilized by operating at sufficiently low velocities. This is true because the upper fluid is, if it is less viscous, usually also less dense than the lower fluid. At sufficiently low velocities the favorable density difference has more effect than the unfavorable viscosity difference, and a stable flow pattern will exist. The critical superficial velocity v_c dividing the stable and unstable regimes is given approximately by the expression (Dumore, 1964)

$$v_c = kg(\rho_1 - \rho_2)/(\mu_1 - \mu_2) \tag{1}$$

where ρ and μ are densities and viscosities; 1 and 2 refer to the upper and lower fluids, respectively; g is the gravitational acceleration; and k is the permeability of the porous medium.

In certain sorption operations (for example, ion exclusion—a well-studied process of practical importance) the viscosity and density variations associated with the concentration profiles in the sorbent bed are frequently large enough to cause significant instabilities. Asher and Simpson (1956) noted such behavior during the separation of glycerine and sodium chloride in beds of Dowex 50-X8 ion exchange resin. Their data, shown in Figure 1, indicate the severe contamination of the glycerol product zone which resulted from flow instabilities. It might be mentioned that Asher and Simpson were not certain as to the origin of the effect and suggested three possibilities, one of which was (as we know now) correct.

The writer has also observed the effects of viscous fingering in the same kinds of processes [for example, glycerine/NaCl separation (Cooney, 1966), blood and lymph purification (Cooney et al., 1967)] and has examined them systematically (Cooney, 1966). Figure 2 shows effluent curves obtained during the elution, with pure water, of a bed [5 cm in diameter times 150 cm initial height] of 50-100 mesh Dowex 50w-X8 resin (Na^+ form) which had previously been fully saturated using an aqueous feed containing 10 wt. % sodium chloride and 30 wt. % glycerine. Data for superficial velocities of 0.034, 0.011, 0.0034, and 0.0017 cm^3/cm^2-s are shown. The dashed line shows what the rest of the glycerine effluent curve should look like in the absence of any flow instabilities. This line is schematic only, and does not represent either a theoretical or experimental result.

From Equation (1), the critical velocity can be estimated to be about ~0.002 cm^3/cm^2-s [actually a v_c range exists (Dumore, 1964), since Equation (1) should more properly be written in terms of $d\rho/d\mu$, a quantity which is usually concentration-dependent]. Hence, only the lowest flow rate run would be expected to be stable with certainty. Note that since the times at which the midpoints of the effluent curves exit from the bed would be roughly inversely proportional to the flow rates, we have plotted the four curves on a dimensionless time basis in order to permit their comparison (the midpoint times for the four

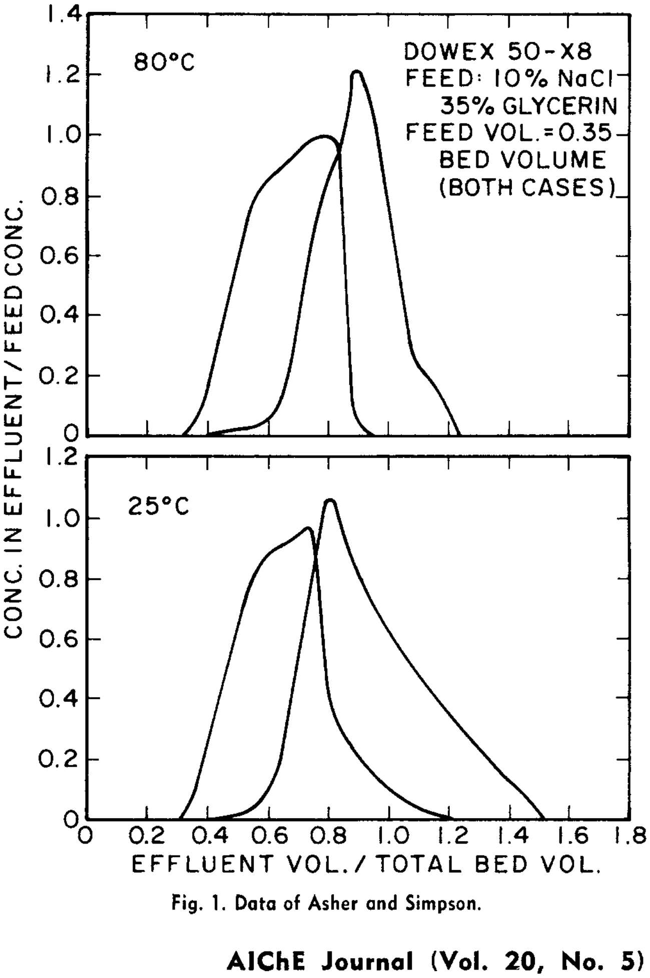

Fig. 1. Data of Asher and Simpson.

runs were roughly 32, 94, 312, and 601 min).

In ion exclusion systems, electrolyte distribution isotherms tend to be concave in nature (that is, the ratio of the resin phase concentration to the external phase concentration, at equilibrium, tends to increase with increasing concentration level). This causes higher concentration portions of electrolyte solute fronts to travel through the system at lower speeds than the lower concentration portions of such fronts. For nonelectrolytes, the reverse is generally true because the isotherms (which are affected by interference effects) are convex. Therefore, in the region of rising glycerine concentration and falling sodium chloride concentration, the solute profiles tend to remain fairly steep (such profiles are often termed *self-sharpening*).

For the experiments performed in the present study, it can be shown (Cooney, 1966; Cooney and Lightfoot, 1965) that the particle diffusion resistance is in all cases much larger than the external film resistance. Also, it has been demonstrated (Cooney and Lightfoot, 1965) that the bed which was used was long enough to ensure a close approach to asymptotic or constant-pattern behavior (a state in which the sharpening effects of the solutes' isotherm shapes are exactly counterbalanced by the broadening effects of axial dispersion and finite mass transfer rates). Therefore, in the absence of flow instabilities all four experimental curves should be identical and should closely match the solid line drawn through the points for the 0.0017 cm^3/cm^2-s run. This line is a theoretical prediction based on constant-pattern theory [details of the theoretical solution are given elsewhere (Cooney and Lightfoot, 1965)].

Clearly, severe instabilities exist at the two higher flow rates, causing large-scale penetration of fingers of water into the more viscous glycerine/NaCl zone. At the highest flow rate, the theoretically expected rise of glycerine to $\sim$ 42 wt. % [this results from interference effects (Asher and Simpson, 1956; Cooney, 1966)] is completely washed out, and no rise occurs at all. For a velocity of 0.0034 cm^3/cm^2-s, which is in the range of the system's critical velocities, nearly stable behavior occurs. And, for a velocity of 0.0017 cm^3/cm^2-s, which is below the critical range, complete stability appears to exist.

These data show clearly that hydrodynamic instabilities can cause the behavior of such systems to be completely different from what one would expect, and that separations carried out under unstable flow conditions will often be poor. Moreover, if one is unaware that such phenomena are possible, great confusion will exist when one attempts to interpret data from such systems. (The viscous fingers in the present system, normally undetectable by eye, can be made visible by addition of dye to the eluant, as shown in Figure 3.)

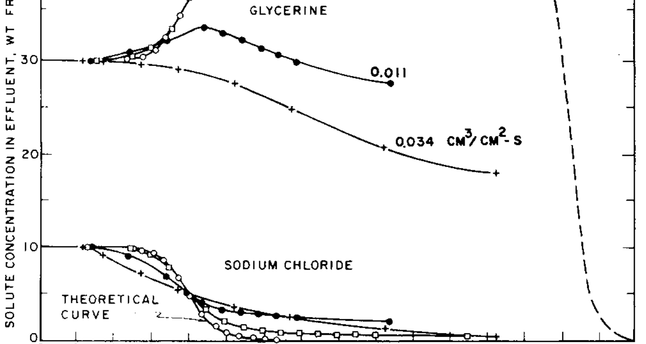

Fig. 2. Experimental ion exclusion effluent curves.

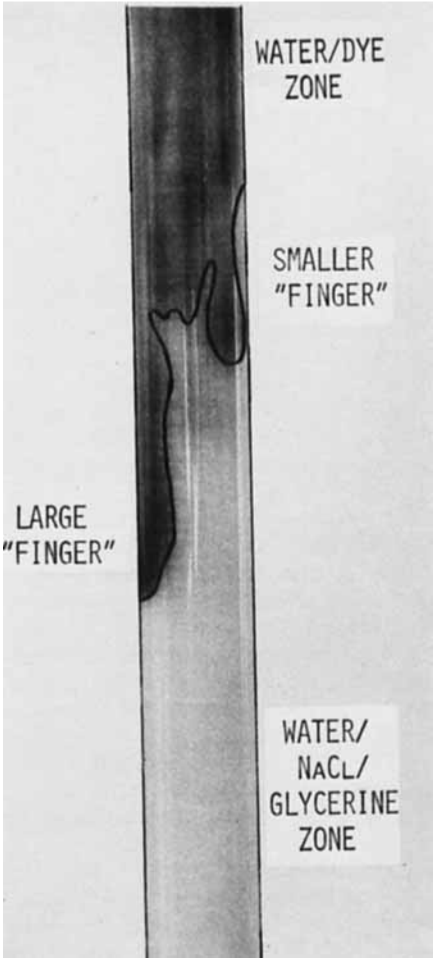

Fig. 3. Unstable flow patterns, with outer boundaries of fingers accented.

The possibility exists in all fixed bed separation processes that flow instabilities may be present and may greatly reduce separation efficiencies. Equation (1), we have shown, seems to be satisfactory for estimating what the critical velocities in such systems will be. One can then deliberately operate in the stable regime. It might be noted, however, that if $(\mu_2 - \mu_1)$ and $(\rho_2 - \rho_1)$ are both small, a finite v_c value can exist and yet flow instabilities will be inconsequential. This is because the rate of growth of viscous fingers depends strongly on the magnitudes of $(\mu_2 - \mu_1)$ and $(\rho_2 - \rho_1)$, and not only on their ratio.

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