

CHROMOSYMP. 1642

Note

Calculation of column performance in nitrate removal from water supplies by anion exchange

RONG-JIN LEU, YNG-LONG HWANG and FRIEDRICH G. HELFFERICH*

Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802 (U.S.A.)

Contamination of drinking water supplies by nitrate from agricultural run-off is a serious environmental problem and health hazard. Anion exchange suggests itself as an effective means of nitrate removal and has been studied by several investigators^{1–3}. The present communication addresses calculation of column performance in such operations on the basis of independently determined parameters.

In practice, nitrate removal by anion exchange is a multicomponent problem because the water usually also contains chloride, sulfate, and carbonate in comparable concentrations. Moreover, in most cases, the stepwise dissociation equilibrium of carbonic acid and, if weak-base resins are used, the association equilibrium of the fixed ionogenic groups, must be accounted for.

The most detailed previous study has been by Clifford and Weber^{1,4}. A promising procedure was found to be a two-column operation. The water is acidified in a cation-exchange column in H⁺ form, and is then passed through an anion-exchange column in free-base form. Breakthrough occurs in the sequence of increasing affinity of the anions for the ion exchanger: carbonate, chloride, nitrate, sulfate. The column is run to nitrate breakthrough. Best economics are obtained with weak-base resins because they can be regenerated with carbonate.

Clifford⁴ was able to account for much of the effluent history by using independently determined separation factors of the anions and the Helfferich–Klein theory of multicomponent chromatography⁵. This theory does not include dissociation–association equilibria and so cannot predict early column behavior involving pH variation from alkaline to acidic and protonation of carbonate and fixed weak-base groups. However, from chloride breakthrough onward, the acidity of the feed guarantees complete protonation of the fixed groups and thus approximately constant pH and carbonate association. This allows the remainder of the effluent history to be calculated in good approximation, beginning with chloride breakthrough.

The present communication demonstrates calculation of the entire effluent history, based on a recent extension⁶ of the original theory. The theory as presented postulates local equilibrium and absence of dispersive effects and so gives no information on the sharpness of the breakthrough waves.

THEORY

The multicomponent theory of Helfferich and Klein⁵ operates with the concept of "coherence" of waves (concentration variations). Coherence is an asymptotically stable state in which the waves of all species present at the respective location and time travel at the same velocity and so do not separate from one another. In the case at hand, with an acidic feed entering a column with anion exchanger in free-base form, all waves are shocks, *i.e.* would be concentration discontinuities under conditions of local equilibrium and absence of dispersive effects. For systems without reactions, the velocity $v_{\Delta x_i}$ of a concentration discontinuity Δx_i (shock) of a species i can be related to the concentration variations across the shock by a material balance argument (notation follows ref. 6):

$$v_{\Delta x_i} = v^0/[1 + \gamma(\Delta y_i/\Delta x_i)] \quad (1)$$

For the shock to be coherent, this velocity must be the same for all species present, *i.e.*,

$$\Delta y_i/\Delta x_i = A \quad \text{for all } i \text{ present} \quad (2)$$

where A has the same value for all species.

The extended theory allowing for reactions⁶ views the system as composed of "moieties", which are conserved with respect to the reactions. For example, the species CO_3^{2-} , HCO_3^- , H_2CO_3 , and H^+ are considered as composed of the moieties CO_3 and H in different proportions. Eqns. 1 and 2 remain formally valid for moieties even if reactions occur. The normalized concentrations of moieties (s_k and q_k) and species are interrelated as follows:

$$s_k = \sum_i \mu_{ki} x_i \quad q_k = \sum_i \bar{\mu}_{ki} y_i \quad (3)$$

where μ_{ki} and $\bar{\mu}_{ki}$ are reaction-coupling factors of species i with respect to moieties k in the solution and ion exchanger, respectively. Combination of these factors and the stoichiometric coefficients of the reactions leads to a reaction matrix for each phase as a compact representation of the reactions. For the system considered here, the reaction matrices are listed in Table I. As these matrices show, sulfate is assumed to be entirely in the form of SO_4^{2-} ion and its association is disregarded as in the work of Clifford and Weber^{1,4}. The calculation here will focus on the early effluent history involving the protonation of carbonate and fixed weak-base groups of the resin.

Required in addition are equations describing ion-exchange equilibria of the species. Here, binary separation factors α_{ij} are assumed to be constant:

$$y_i x_j / y_j x_i \equiv \alpha_{ij} = \text{constant} \quad (4)$$

Such a set of equilibrium equations in terms of $\{x_i\}$ and $\{y_i\}$ can be converted to a set of relations between $\{s_k\}$ and $\{q_k\}$ with eqns. 3, the reaction matrices, the equilibrium constants of the reactions and the electroneutrality conditions.

In the case at hand, a "frontal analysis" pattern^{1,4,7} is known to develop:

TABLE I
SPECIES, REACTIONS, MOIETIES AND REACTION MATRICES OF NITRATE REMOVAL SYSTEM

Moiety/reaction	Species ^a									
	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	CO ₃ ²⁻	HCO ₃ ⁻	H ₂ CO ₃	OH ⁻	H ⁺	-B	-BH ⁺
<i>Solution phase</i>										
Cl	1	0	0	0	0	0	0	0	0	0
NO ₃	0	1	0	0	0	0	0	0	0	0
SO ₄	0	0	1	0	0	0	0	0	0	0
CO ₃	0	0	0	1	1	1	0	0	0	0
H	0	0	0	0	1	2	-1	1		
H ₂ O ↔ H ⁺ + OH ⁻	0	0	0	0	0	0	1	1		
H ₂ CO ₃ ↔ H ⁺ + HCO ₃ ⁻	0	0	0	0	1	-1	0	1		
HCO ₃ ⁻ ↔ H ⁺ + CO ₃ ²⁻	0	0	0	1	-1	0	0	1		
HSO ₄ ⁻ ↔ H ⁺ + SO ₄ ²⁻	0	0	1	0	0	0	0	1		
<i>Exchanger phase</i>										
Cl	1	0	0	0	0	0	0	0	0	0
NO ₃	0	1	0	0	0	0	0	0	0	0
SO ₄	0	0	1	0	0	0	0	0	0	0
CO ₃	0	0	0	1	1	1	0	0	0	0
H	0	0	0	0	1	2	-1	1	0	1
B	0	0	0	0	0	0	0	0	1	1
H ₂ O ↔ H ⁺ + OH ⁻	0	0	0	0	0	0	1	1	0	0
H ₂ CO ₃ ↔ H ⁺ + HCO ₃ ⁻	0	0	0	0	1	-1	0	1	0	0
HCO ₃ ⁻ ↔ H ⁺ + CO ₃ ²⁻	0	0	0	1	-1	0	0	1	0	0
-BH ⁺ ↔ -B + H ⁺	0	0	0	0	0	0	0	1	1	-1

^a Species -B and -BH⁺ denote the fixed base group and its ionic conjugate, respectively.

traversing the column in the direction of flow, an observer sees one moiety disappear at each successive wave; specifically, of the moieties left, each time that with highest affinity for the ion exchanger disappears. This makes it possible to calculate the velocities of the shock waves one by one, starting with the slowest, the sulfate front, at which the SO₄ moiety disappears. Upstream of that wave the column is in equilibrium with the feed, and downstream of it no SO₄ in any form is present. Accordingly, for this moiety, the concentration differences Δs_{SO_4} and Δq_{SO_4} across the wave equal the feed concentration $s_{SO_4,0}$ and exchanger concentration $q_{SO_4,0}$ in equilibrium with feed, respectively. With these substitutions, the value of A is obtained from eqn. 2 and the velocity of the sulfate front can then be calculated from eqn. 1. Now, the concentrations of the other species in the plateau zone downstream of the front can be calculated from eqn. 2 and the equilibrium equations. The procedure is then repeated for the other waves in succession, first for the nitrate front, at which sulfate is entirely absent and NO₃ now is the moiety with highest affinity for the exchanger; then for the chloride front, etc. From the column inlet to the chloride front the fixed weak-base groups of the resin can be assumed to be completely protonated, so their deprotonation reaction can be disregarded in the calculations. That reaction, however, becomes essential in the calculation of the carbonate front (that of the CO₃ moiety), across which the resin is converted from its initial free-base to its ionic form.

CALCULATIONS

For demonstration, the calculation of column performance in one of the experiments by Clifford and Weber¹ is presented. Their run No. 10 was selected because of its low flow-rate, ensuring a reasonably close approximation to local equilibrium as evident from its relatively sharp waves. Data on the ion exchanger, column, flow-rate, and feed composition are summarized in Table II. The total normality of the solution and the ion-exchange capacity of the resin are chosen as reference concentrations for the purpose of normalization.

The values of the separation factors and reaction equilibrium constants are shown in Tables III and IV. As far as available, values independently determined by Clifford⁴ were used. In addition, the fractional water content and the $\text{Cl}^-/\text{HCO}_3^-$ separation factor was assumed to be the same as for the similar anion exchanger Amberlite IRA-93 (ref. 8); the $\text{HCO}_3^-/\text{OH}^-$ separation factor was taken to be 1.00 as ideal Donnan equilibrium would demand. The column void volume, not reported by Clifford, was estimated from his calculated effluent history for another run⁴ with the same resin. The dissociation constants in solution were taken from the literature⁹ and converted to the concentration scale used here (normalized molarity). The dissociation constants in the resin were assumed to have the same values as in solution if expressed in terms of molalities; the values in Table IV are those after conversion to the normalized-molarity scale.

RESULTS

Fig. 1 shows a comparison of the measured and calculated effluent concentration histories. The agreement is quite good, except for the lack of ideal sharpness of

TABLE II
DATA FOR EXPERIMENT OF NITRATE REMOVAL

Weak-base resin (Duolite ES-368)	pK _b	6.2
	Exchange capacity (equiv./l)	1.54
	Fractional water content	0.57 ^a
Ion-exchange bed	Length (cm)	61
	Diameter (cm)	2.54
	Flow-rate (ml/min)	100
	Fractional void volume	0.57 ^b
Simulated water supply	NO ₃ ⁻ (mequiv./l)	1.5
	Cl ⁻ (mequiv./l)	1.5
	SO ₄ ²⁻ (mequiv./l)	1.5
	HCO ₃ ⁻ (mequiv./l)	1.0 ^c
	pH	6.5
	Total normality (mequiv./l)	5.5 ^d

^a Value from ref. 8 for Amerlite IRA-93 is used here for Duolite ES-368 because of similar resin characteristics.

^b Estimated from calculated effluent history (using the original Helfferich-Klein theory) in ref. 4 for another run with the same resin.

^c Total carbonate (CO₃ moiety) expressed in terms of the normality of HCO₃⁻ ion^{1,4}.

^d Total normality of simulated water supply containing calcium, magnesium, and iron.

TABLE III
SEPARATION FACTORS OF NITRATE REMOVAL SYSTEM

Counterion pair ij	Separation factor α_{ij}
SO_4^{2-}/NO_3^-	2.83
NO_3^-/Cl^-	3.87
Cl^-/HCO_3^-	4.00 ^a
HCO_3^-/OH^-	1.00 ^b

^a Value from ref. 8 for Amberlite IRA-93 is used here for Duolite ES-368 because of similar resin characteristics.

^b Based on ideal Donnan equilibrium.

TABLE IV
REACTION CONSTANTS OF NITRATE REMOVAL SYSTEM

Reaction	Normalized equilibrium constant
<i>Solution</i>	
$H_2O \leftrightarrow H^+ + OH^-$	$3.31 \cdot 10^{-10}$
$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$	$8.36 \cdot 10^{-5}$
$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	$8.00 \cdot 10^{-9}$
<i>Exchanger</i>	
$H_2O \leftrightarrow H^+ + OH^-$	$1.37 \cdot 10^{-15}$
$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$	$1.70 \cdot 10^{-7}$
$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	$1.63 \cdot 10^{-11}$
$-BH^+ \leftrightarrow -B + H^+$	$5.87 \cdot 10^{-9}$

the observed waves and slight discrepancies in the carbonate breakthrough and nitrate concentration after its breakthrough. Specifically, the breakthroughs of the various fronts and the compositions of the intermediate plateau zones match the observations satisfactorily.

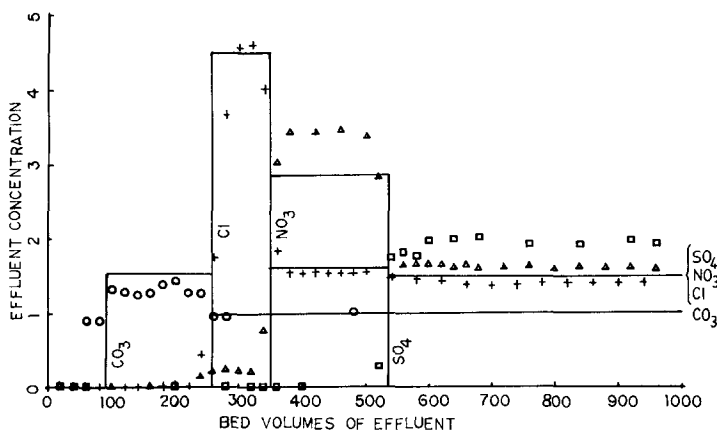


Fig. 1. Comparison of observed and calculated effluent concentration histories (observed histories are from Clifford and Weber¹; following them, total sulfate and total carbonate are presented in terms of the normalities of SO_4^{2-} and HCO_3^- ions, respectively). — = Predicted; \circ = HCO_3^- ; + = Cl^- ; Δ = NO_3^- ; \square = SO_4^{2-} . Effluent concentration is in mequiv./l.

DISCUSSION

It is to be noted that the calculation was carried out with best available input data and without any adjustment of parameters. It is possible that the use of $\text{Cl}^-/\text{HCO}_3^-$ and $\text{HCO}_3^-/\text{OH}^-$ separation factors experimentally determined for the ion exchanger used and of more accurate values for the fractional water content and column void volume might improve the agreement between observed and calculated effluent histories. Moreover, since SO_4^{2-} is divalent, a selectivity coefficient rather than the separation factor measured by Clifford should be used for the $\text{SO}_4^{2-}/\text{NO}_3^-$ exchange equilibrium.

For practical purposes, an accurate prediction of the point of breakthrough of first traces of nitrate will require the relaxation of the premise of local equilibrium, to account for the lack of ideal sharpness of the waves. However, this need be done only for the nitrate front and can be applied as a correction after the approximate effluent history with ideally sharp shocks has been calculated with the premise of local equilibrium.

SYMBOLS

q_k	=	normalized concentration ^a of moiety k in exchanger
s_k	=	normalized concentration ^a of moiety k in solution
v^0	=	linear velocity of bulk flow of solution
$v_{\Delta x_i}$	=	wave velocity of shock Δx_i
x_i	=	normalized concentration ^a of species i in solution
y_i	=	normalized concentration ^a of species i in exchanger
α_{ij}	=	separation factor of counterion i to counterion j
γ	=	$\frac{\text{(fractional exchanger volume) (exchanger capacity)}}{\text{(fractional column void volume) (total normality of solution)}}$
Λ	=	eigenvalue of coherent shocks
μ_{ki}	=	reaction-coupling factor of species i with respect to moiety k in solution
$\bar{\mu}_{ki}$	=	reaction-coupling factor of species i with respect to moiety k in exchanger

ACKNOWLEDGEMENT

The financial support by the National Science Foundation under Grant CBT-8511956 is gratefully acknowledged.

REFERENCES

- 1 D. A. Clifford and W. J. Weber, Jr., *Report EPA-600/2-78-052*, U.S. Environmental Protection Agency, Cincinnati, OH, 1978.
- 2 R. P. Lauch and G. A. Guter, *J. Am. Water Works Assoc.*, 5 (1986) 83.
- 3 M. Cox and D. Murgatroyd, in P. A. Williams and M. J. Hudson (Editors), *Recent Developments in Ion Exchange*, Elsevier Applied Science, London, New York, 1987.

^a "Normalized concentration" is defined as the ratio of the respective molarity to the total normality in the solution phase, or to the exchanger capacity (normality) in the exchanger phase.

- 4 D. A. Clifford, *Ind. Eng. Chem. Fundam.*, 21 (1982) 141.
- 5 F. G. Helfferich and G. Klein, *Multicomponent Chromatography—Theory of Interference*, Marcel Dekker, New York, 1970.
- 6 Y.-L. Hwang, F. G. Helfferich and R.-J. Leu, *AIChE J.*, 34 (1988) 1615.
- 7 S. Claesson, *Ark. Kemi Mineral. Geol.*, A20 (1945) No. 3.
- 8 D. A. Skoog and D. M. West, *Fundamentals of Analytical Chemistry*, Holt, Rinehart and Winston, NC, New York, NY, 1969.