

BRINE EVOLUTION AND MINERAL DEPOSITION IN HYDROLOGICALLY OPEN EVAPORITE BASINS

WARD E. SANFORD and WARREN W. WOOD

U. S. Geological Survey, MS 431, National Center,
Reston, Virginia 22092

ABSTRACT. A hydrologic analysis demonstrates the critical importance of basin leakage on brine evolution and the consequent evaporite-mineral suite and thickness. Solute loss from evaporite basins can be either by ground water or surface water, and although the flux is often small, it nevertheless can play a significant role in the evolution of evaporite brines and the formation of evaporite deposits. The leakage ratio, the ratio of water outflow to water inflow, is an important factor in this analysis. A lumped-parameter, solute mass-balance model is developed to define the role of water outflow from a well-mixed basin. A mass-balance model is analyzed with a geochemical model designed for waters with high ionic strengths. Two typical waters, seawater and a Na-HCO₃ ground water, are analyzed to illustrate the control that the leakage ratio (or hydrologic openness of the basin) has on brine evolution and the suite and thicknesses of evaporite minerals deposited. The analysis suggests that brines evolve differently under different leakage conditions. Even the smallest of leakages will have an effect on a brine's evolution. For any finite value of the leakage ratio, a steady-state condition will develop with respect to the solute fluxes in the brine (assuming a constant volume) after a given amount of time. Given the predicted residence times of solutes in such basins, the condition of steady-state solute flux may often predominate during the formation of evaporite deposits. The mineral suite and thicknesses are also controlled by the leakage ratio, and some minerals will only precipitate in significant quantities at certain leakage ratios. Model results indicate that brine evolution and evaporite formation should be a strong function of leakage in both continental and marine environments.

INTRODUCTION

The solute chemistry and minerals of evaporite basins in both continental and marine environments have been intensely studied (Jones, 1966; Braitsch, 1971; Jones and others, 1977; Eugster and Jones, 1979; Al-Droubi and others, 1980; Sonnenfeld, 1980; Eugster and others, 1980; Harvie and Weare, 1980; Harvie and others, 1980, 1982, 1984; Brantley and others 1984; Sonnenfeld, 1984; Last, 1989; Jankowski and Jacobson, 1989; among many others), and many fundamental geochemical problems related to the chemistry and evolution of brines in evaporative basins have been resolved. However, several problems are still encountered, including the discrepancy between predicted and observed mineral suites, the presence of nonequilibrium-mineral thicknesses, and the apparent lack of mass balance between solute input and accumulated evaporite deposits (Alderman, 1983; Spencer and others, 1985a,b).

The nonequilibrium assemblages of evaporite minerals in many marine basins provide a classic example of the discrepancies observed between predicted and observed amounts of mineral precipitation. Argu-

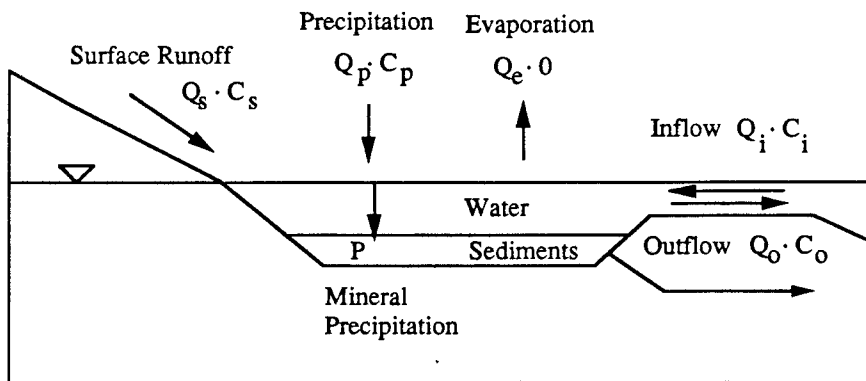
ments have been made by Lowenstein and others (1989) and Hardie (1990) that some of these discrepancies can be attributed to variable chemistry in the source waters. Hardie (1990) describes how many marine evaporite deposits in the world are low in magnesium sulfates compared to what thermodynamic models predict. King (1947) proposed that exchange of water between a restricted evaporating body of water and the ocean was one possible way to produce nonequilibrium thicknesses and unusual mineral suites observed in many marine evaporite deposits. He proposed that continued redilution of the evolving brine by the source water (in this case seawater) would limit the increase in salinity and allow continual precipitation of only the more insoluble minerals. Sonnenfeld (1980, 1984) has expanded this concept by developing an equation to show the salinity in a restricted body of water as a function of the flux of seawater out of and into a basin undergoing evaporation.

In this paper we describe a model and present results of model simulations which suggest that even a small amount of continual outflow from a restricted, evaporating body of water may significantly affect solute concentrations, brine evolution, and potential mineral precipitations. These small seepage fluxes out of evaporative basins can explain the abundance of the less soluble minerals observed in many basins relative to the amount of soluble minerals. The leakage ratio (ratio of water outflow to inflow) is the controlling factor, and it has a profound effect on both the suite and thicknesses of minerals deposited in basins. Knowledge of the leakage ratio also allows the compositions of the brine in both the surface and subsurface to be predicted as a function of time. We have generalized and quantified these ideas by developing a lumped-parameter conceptual model of an open basin. The lumped-parameter model is analyzed by means of the geochemical-reaction model PHRQPITZ (Plummer and others, 1988). Calculations are made of ionic concentrations, mineral suites, and mineral thicknesses for different leakage ratios and source waters.

CONCEPTUAL MODEL

Models developed to explain the observed mineral suites in evaporite deposits of marine origin often incorporate as a principal feature a strait or narrow passage of surface water connecting the body of more saline water to the sea (fig. 1A). Solute and water-flux components of such a model include a water influx and associated solute concentrations, Q_i and C_i , respectively, and a water outflow and associated solute concentrations, Q_o and C_o . Outflow continually removes the brine by either density-driven flow through the strait in an undercurrent (King, 1947) or through the subsurface by seepage reflux (Adams and Rhodes, 1960). In addition, rainfall and surface runoff can add components of water and solute fluxes, Q_p , C_p , Q_s , and C_s , respectively. Evaporation removes water at a rate, Q_e , that is larger than the precipitation rate, Q_p . The concentration of water in the basin, C_o , increases above the input concentration, C_p ,

A



B

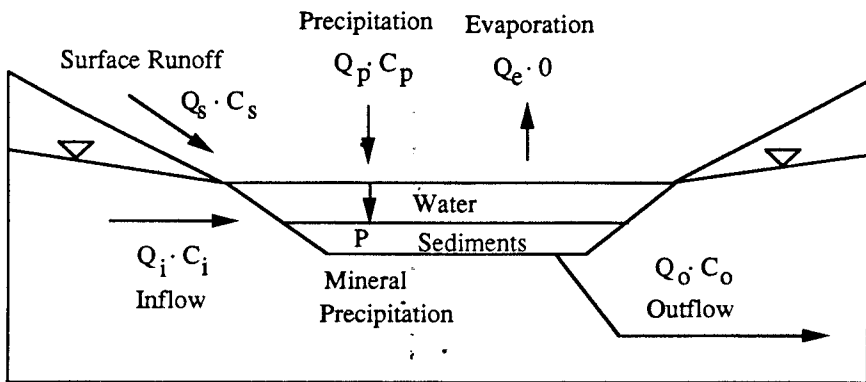


Fig. 1 Water and solute budget components of an evaporative basin in (A) a coastal-marine environment and (B) a continental playa-lake environment.

but continuous redilution of the evolving brine by inflow keeps the basin-water solute concentration at a limited value.

We propose that many evaporite deposits of continental origin have been affected significantly by seepage losses to ground water (Wood and Sanford, 1990). The major components of the water and solute fluxes are the same as for the marine case, except we propose that in the continental environment outflow is strictly by seepage loss to ground water (fig. 1B). In our continental model the inflow has a significant, if not dominant, ground-water component. In our marine model, seepage loss to ground water would tend to be less than the loss through surface-water outflow, but either seepage or surface-water outflow would have the same general

effect on the brine evolution and mineral precipitation. Such seepage losses from continental playa lakes have been suggested by Hutchinson (1957) and described by Sanford and others (1989). Losses can occur by molecular diffusion, density-driven flow, and simple advection through underlying rocks. In the case of a marine environment, we propose that a continuous variation is likely to exist between two endmembers—the first endmember being a basin with a large strait and a large outflow, and the second endmember being a basin with little or no outflow through either surface or subsurface outlets.

To quantify our conceptual model of an open basin, the assumption is made that the evolving brine stays “well-mixed” within the finite region occupied by the lake or inland sea. The constant volume of well-mixed brine may also include that brine present in the pore water in the top several meters of sediment. In cases when the surface water is shallow and often dries up all together, the volumes of brine considered in our calculations does not reduce to zero but remains as the finite volume in the sediment pores. This “well-mixed” assumption allows space to be removed as a variable, and a lumped-parameter equation can then be developed to describe the evolution of the solutes and mineral precipitation through time. Others have used this lumped-parameter type of model to look at the evolution of isotopes in evaporative lakes—for example, Dincer (1968), Zimmermann (1977), and Phillips and others (1986). In this paper, the terms “basin water” and “basin volume” are used frequently and refer to this finite volume of well-mixed, evolving brine upon which our lumped-parameter equation is based. A distributed-parameter model of the system would allow the analysis of the spatial distribution of mineral and precipitation across a basin, but such a model is more complex and is beyond the intent of this paper.

If the solute fluxes illustrated in figure 1A or B are summed, the following first-order differential equation of the solute mass balance is obtained:

$$Q_p C_p + Q_s C_s + Q_i C_i - Q_o C_o - P = \frac{d(V C_o)}{dt}, \quad (1)$$

where P is the mineral precipitation rate, in mass/time, V is the volume occupied by the basin water, and t is time. Dimensionless parameters can be introduced to simplify the analysis, including (1) the length of time relative to that required to evaporate one basin volume, t_o , (2) the ratio of water outflow to water inflow (or leakage ratio), Q_o/Q_i , and (3) the ratio of the basin solute concentration to the input (and initial) concentration, C_o/C_i . This equation development has been described in more detail in Wood and Sanford (1990) and expands upon a similar development made by Sonnenfeld (1980, 1984) for the marine environment. If there is no mineral precipitation in such a basin, then the solution of the solute

mass balance eq (1) becomes:

$$\frac{C_o}{C_i} = \frac{Q_i}{Q_o} - \left(\frac{Q_i}{Q_o} - 1 \right) \exp \left[\frac{-Q_o t_o}{Q_e} \right]. \quad (2)$$

For cases where the leakage ratio is small, Q_e and Q_i are nearly identical, and eq (2) can be plotted as a function of the leakage ratio and dimensionless time (fig. 2). The baseline in figure 2 represents a closed basin (a leakage ratio of 0), where salinity of the brine would increase indefinitely if no mineral precipitation occurred. Any other horizontal line above the baseline defines the increase in brine salinity over time for that particular leakage ratio. From eq (2) it can be seen that, as time becomes large, the exponential term goes to zero, and eq (2) becomes:

$$\frac{C_o}{C_i} = \frac{Q_i}{Q_o}. \quad (3)$$

Eq (3) indicates that, at steady-state, the salinity of the brine will remain steady at a level above the input salinity that is a direct function of the

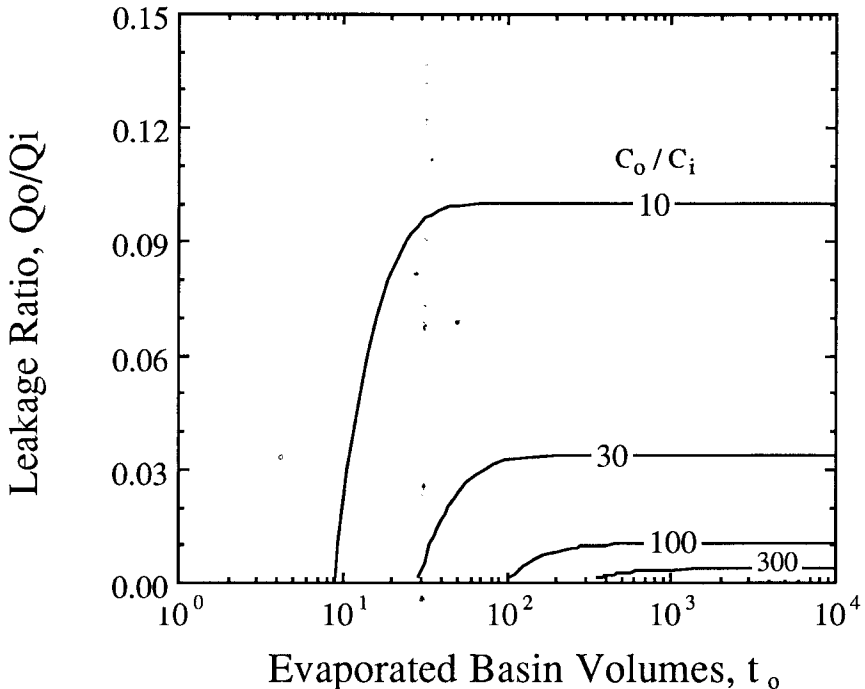


Fig. 2. The ratio of a conservative solute concentration relative to the input (and initial) concentration, C_o/C_i , during brine evolution in an open basin as a function of the leakage ratio and the number of evaporated basin volumes, t_o .

leakage ratio. Large outflows (or leakage ratios) will keep the restricted waters at low or moderate salinities. Smaller outflows will allow higher (but still finite) salinities to develop. This relation is illustrated in figure 2, where at a leakage ratio of 0.01, the ratio of C_o/C_i reaches a maximum of 100, and at a leakage ratio of 0.10, the ratio of C_o/C_i only reaches 10.

For a restricted basin with a source of marine water, where water depth is a few meters and the net evaporation rate is about 1 m per yr, the time required to evaporate one "basin volume" is a few years. Similarly, the average residence time of the solutes in the basin water (which will be the water residence time multiplied by the ratio C_o/C_i) will be relatively short—tens of years, because the ratio C_o/C_i for marine evaporite brines is likely to be on the order of ten (solubility constraints make it impossible for C_o to exceed about 400 g/L). Thus, considering the thousands to millions of years required for thick evaporite deposits to form, the basin must be nearly continuously in conditions of steady-state with respect to water and solute fluxes. This steady-state condition may also be true in many semiarid continental environments where a lake maintains a relatively constant volume (or a relatively large reservoir or pore water exists) because of a large ground-water component of inflow. Steady-state would less likely be maintained in an ephemeral continental lake with a large surface-water component of inflow and/or a small reservoir of pore water.

For basins that do attain steady-state conditions, changes in mineral precipitation over time will occur only as the leakage conditions of the basin change over time. In fact, as salts are deposited and compacted, the permeability of a basin floor is likely to decrease over time, causing a probable decrease in the leakage ratio, and the appearance of the soluble salts only near the top of an evaporite sequence (an order of evaporite deposition commonly observed). Our model assumes the water in the basin remains at a constant volume—a condition where water input to the lake is in balance with evaporation losses and flow of water from the basin. Accordingly, in order to maintain this constant volume, a marine basin (whose input is tied to sealevel) would be expected to sink at the same rate that precipitated minerals accumulate on the basin floor.

GEOCHEMICAL MODEL

Eqs (2) and (3) are based on the assumption that no mineral precipitation is occurring. In reality, many different solute concentrations evolve simultaneously in the basin and precipitate as a variety of different minerals (Eugster and Jones, 1979). Conditions with multiple solute constituents and mineral precipitation create mass-balance equations that are too complex for the development of analytical solutions, and thus, numerical methods must be used. In this study, the geochemical equilibrium-reaction model PHRQPITZ by Plummer and others (1988) is used. PHRQPITZ contains the virial-coefficient approach of Pitzer (1973, 1975) for calculating the thermodynamics of minerals in

solutions with high ionic strength. Thus, it is ideally suited for calculating mineral equilibrium in waters typically found in an evaporative saline basins. The Pitzer treatment in PHRQPITZ is based largely on the aqueous model as presented by Harvie and Weare (1980) and Harvie and others (1984).

Our numerical simulations of hydrologically open evaporative basin systems assume a constant lake volume and fractional crystallization of the minerals that are deposited. By assuming fractional crystallization, we explicitly require that previously precipitated minerals are sealed off from the body of brine and do not back react. This is a reasonable assumption in shallow lacustrine systems and may also be applicable in certain deep-basin systems. Evidence of back-reactions have been widely observed in the field, for example Hardie (1984) and Lowenstein (1988), but because we believe a basin is usually in a condition of steady-state with respect to solute fluxes, the long-term precipitation rates calculated are not largely affected by assuming that no back reactions occur. In fact, it is demonstrated later that certain minerals that have typically been predicted to back-react during brine evolution can remain in equilibrium under certain steady-state conditions and precipitate in significant quantities.

In order to simulate the evaporation conditions with PHRQPITZ, a certain combination of options in the model is used. In the first step, evaporation is simulated not by the removal of water from the solution, but by using an equivalent method—the addition of salt that is representative of the solutes in the input water. In the second step, a large fraction of the evolving brine (for example, 0.9, which corresponds to a leakage ratio of 0.1) is mixed with a small fraction of the input water (in this case, 0.1). This mixing is equivalent to losing 10 percent of the brine to leakage and replacing the lost brine by the input water. This two-step sequence of adding salt and mixing is repeated until the brine reaches a condition of steady state. PHRQPITZ can also be run so that a solution (in this case, the evolving brine) can be kept in equilibrium with a designated set of minerals. The model keeps track of how much of each mineral precipitates or dissolves. For our study, we ran the model so that minerals would only precipitate, not dissolve. This is not an option built into PHRQPITZ but was achieved by running the model through the series of evaporation steps a number of times for each leakage ratio. During each series of evaporation steps, the saturation state of minerals of interest were observed so that the point in time could be identified when any new mineral would begin to precipitate. That particular mineral would then be added at that point in the evaporation series during the run of the next series. Also, any mineral that changed from a state of precipitation to dissolution was removed at that point from the list of precipitating minerals during the next run (thus eliminating back reaction). In this way, the final run for each solute input and leakage ratio would produce a unique sequence of mineral precipitation corresponding to those conditions.

The numerical procedure used, which incorporates the geochemical model into the lumped-parameter model, is explicit in nature—that is, the equations are solved at each time step with information only from the previous time step. Therefore, results obtained from these types of simulations are a function of the time-step size (or number of basin volumes evaporated per time step). Thus, if large time steps are used, the solution to the equations will become unstable and will diverge from the true solution. If, on the other hand, very small time steps are used, the solutions will appear nearly identical for each successive smaller time-step size as the numerical solution approaches the stable value. Such small time steps, however, require additional computation time, which may then become the limiting factor for running the model. For these simulations, different time steps that depended on the concentration of the input water were used. For our example of a dilute input ground water from Idaho, we chose a time-step size of 50 evaporated basin volumes. We found this was adequate to generate with an accuracy suited to illustrate the effects of interest and found that smaller time steps only slightly refined the resulting concentrations and mineral thicknesses. For seawater, time-step sizes of 0.5 and 1.0 basin volumes were used, depending on the leakage ratio. These small time steps were necessary because of the high concentration of seawater as an input solution.

Output from PHRQPITZ is given in moles and was converted to the thicknesses of minerals deposited by using the molecular weights and densities of the individual minerals. The column of basin water was assumed to be 1 m deep, and porosity in the minerals deposited was assumed to be zero. Although initial porosities in saline mineral layers formed by crystal settle-out are typically about 50 percent, we were interested in putting our results in the context of ancient evaporite sequences, where porosities have been significantly reduced. Our results could be reinterpreted for 50 percent porosity simply by multiplying all thicknesses by a factor of two.

Other assumptions had to be made in our simulations about equilibration of certain minerals. We specified that dolomite, rather than calcite, would be the stable carbonate phase, because we believe that calcite is likely to be converted to dolomite as the magnesium to calcium ratio increases with evaporation in many basins. Thus, we specified an immediate precipitation of dolomite instead of permitting the precipitation of calcite and its subsequent conversion to dolomite as evaporation proceeded. For the Na-HCO₃ ground water, we allowed both calcite and dolomite to precipitate. For both example waters and throughout the simulations we precipitated gypsum rather than anhydrite even though we recognize that anhydrite may be the stable phase at high temperatures and in highly saline environments. Our model also assumes that bromide is conservative. In nature, bromide is coprecipitated to a small degree in the halides. We have not considered any silicate mineral in our analyses nor have we addressed the role of many of the trace elements. In addition, CO₂ was specified to be at an atmospheric partial pressure of 10^{-3.5}, though it is recognized that CO₂ partial pressures can vary in such

basin waters. All these choices of mineral and aqueous phases made only minor differences in the amounts of the remaining minerals that precipitate. This does not imply that the processes we chose are the only ones that may be important in nature. Rather, these choices were made to expedite the computational procedure to illustrate the effect of leakage on solute evolution and mineral precipitation.

RESULTS

To demonstrate the application of this model, we selected seawater and a ground-water sample typical of continental semiarid environments for solute input to our evaporating basin (table 1). Seawater was selected for two reasons. First, many geochemists are familiar with the sequence of minerals deposited from the closed basin evaporation of seawater and will recognize the differences in brine evolution, mineral suites, and thicknesses as leakage from the basin is varied. Second, a dilute input of aerosol sea salts is a reasonable input to an evaporating continental basin in either a coastal environment or to one in which the soluble minerals in the drainage basin have been largely depleted because of previous cycles of weathering. The ground-water sample selected as a source input (table 1) is ground water from the welded tuffs in Owyhee County, Snake River basin Idaho (Wood and Low, 1986). This sample is typical of a sodium bicarbonate water from a volcanic terrain that yields an alkaline brine and sodium carbonate minerals during evaporation. Temperatures of all the simulations are 25°C. Table 2 is a listing of all the minerals that

TABLE 1

Concentrations of solute constituents used in the input solutions for the model simulations

	Example 1 (Sea Water) mg/L	Example 2 (Na-HCO ₃ Ground Water) mg/L
Ca	412.3	27
Mg	1,292	4.8
Na	10,768	173
K	399	9.8
Cl	19,353	29.8
HCO₃	141.7	338
SO₄	2,712	79.6
Br	67.3	.78
F	0	10.6
B	0	.2
TDS	35,145	674
pH	8.22	7.62

TABLE 2

List of the minerals and chemical formulas considered in this study, along with the densities and equilibrium constants used in the calculations

Mineral Name	Mineral Formula	Density (gm/cc)	log K 25 °C
Anhydrite	CaSO ₄	2.94	-4.362
Aphthitalite	NaK ₃ (SO ₄) ₂	2.70	-3.803
Bischofite	MgCl ₂ ·6H ₂ O	1.60	4.455
Borax	Na ₂ B ₄ O ₇ ·8H ₂ O	1.71	12.464
Burkeite	Na ₆ CO ₃ (SO ₄) ₂	2.57	-.772
Calcite	CaCO ₃	2.71	-8.406
Carnallite	KMgCl ₃ ·6H ₂ O	1.60	4.330
Dolomite	CaMg(CO ₃) ₂	2.85	-17.083
Fluorite	CaF ₂	3.18	-10.960
Gaylussite	CaNa ₂ (CO ₃) ₂ ·5H ₂ O	1.99	-9.421
Glauberite	Na ₂ Ca(SO ₄) ₂	2.85	-5.254
Gypsum	CaSO ₄ ·2H ₂ O	2.32	-4.581
Halite	NaCl	2.16	1.570
Hexahydrate	MgSO ₄ ·6H ₂ O	1.75	-1.635
Kainite	KMgClSO ₄ ·3H ₂ O	2.15	-.193
Kieserite	MgSO ₄ ·H ₂ O	2.57	-.123
Pirssonite	Na ₂ Ca(CO ₃) ₂	2.35	-9.234
Polyhalite	K ₂ MgCa ₂ (SO ₄) ₄	2.85	-13.744
Sylvite	KCl	1.99	.900
Trona	Na ₃ H(CO ₃) ₂ ·2H ₂ O	2.14	-11.384

appear in the simulations, along with their chemical formulas and the densities and equilibrium constants used in the calculations.

Example 1: seawater.—The first example presented is of seawater as it undergoes evaporation with a leakage ratio of 0.001 (that is, where 1 L of water is leaking out for every 1000 L entering the basin). Figure 3 illustrates changes in concentration of the solutes as the basin water undergoes evaporation. The reference ion in all these simulations is bromide, which does not form a precipitate under the ranges of concentrations considered. Thus, because we have assumed it is a conservative ion, its change in concentration illustrates the effect of leakage as the basin water evaporates. The bromide curve would be linear in the simulation of evaporation in a closed basin (leakage ratio of 0), but it is curved when leakage occurs, and it becomes horizontal once steady state is reached. The bromide curve in figure 3 shows that a steady-state solute flux is not reached for a conservative solute after 1000 basin volumes are evaporated at a leakage ratio of 0.001. It can be seen, however, that all other solute fluxes are very near a steady-state condition once the last soluble mineral (bischofite) begins to precipitate. In effect, a leakage ratio