

PREDICTION OF THE CHEMICAL EVOLUTION OF NATURAL WATERS
DURING EVAPORATION



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Abstract - Chemical evolution of natural waters concentrated by evaporation can be predicted using a computer program designed to calculate the distribution of aqueous species and the precipitation of minerals on basis of equilibrium reactions. Total molality of elements, pH and alkalinity of solutions fluctuate during the evaporation processes. These fluctuations can be interpreted by the use of the concept of generalized residual alkalinity.

I - A COMPUTER MODEL FOR WATER CONCENTRATION BY EVAPORATION

A computer program called EVAPOR calculates the evolution of the chemical composition of solutions submitted to evaporation, on the basis of the equilibrium reactions proposed by GARRELS and MACKENZIE (1967). The program and the model, already described by FRITZ (1975), AL-DROUBI *et al.* (1976 a, 1976 b), AL-DROUBI (1976) and GAC *et al.* (1977), are applied to the Euphrate river (Syria). Some of the results are presented in Fig. 1 and Table 1. Starting from the initial chemical composition of the river, the model simulates a theoretical evaporation by successive small increments of concentration. At each step, ionic strength, activity coefficients, activity of the free ions and complex aqueous species as well as degree of the solution saturation with respect to salts, are computed. After reaching saturation with respect to one mineral, the number of moles of this mineral precipitated is then calculated as function of the concentration factor.

In Euphrate system, the following minerals are formed : calcite (CaCO_3) Mg-montmorillonite ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$), magnesite (MgCO_3), gypsum ($\text{CaSO}_4, 2\text{H}_2\text{O}$) thenardite (Na_2SO_4) and sylvite (KCl) for concentration factors respectively equal to : 1, 2, 3.5, 48.6, 3735 and 5680.

As shown on Fig. 1, the sense of variation of alkalinity, pH, Ca, Mg or SO_4 in solution, can change with respect to concentration factor when the precipitation of a new mineral occurs in the sequence. pH, for example increase after precipitation of calcite, Mg-montmorillonite or gypsum but decreases after formation of magnesite or thenardite. Direction and magnitude of these variations

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differ for each case analyzed.

II- PREDICTED CHEMICAL EVOLUTION OF SOME NATURAL WATERS

Different natural waters were concentrated by simulated evaporation : Euphrate (Syria), Jordan (Jordan), Chari (Chad) and sea water. Calculated chemical evolutions are schematically reported on Fig. 2, where changes of log total molality of elements (ordinates) are shown as function of log concentration factor (abscissae), with $f\text{CO}_2$ of initial water maintained constant : $10^{-2.36}$ for Euphrate, $10^{-3.05}$ for Jordan, $10^{-2.9}$ for Chari and $10^{-3.2}$ for sea water .

Before concentration by evaporation, the relative amounts of anions and cations in these four natural solutions are the following :

Euphrate river : $\text{HCO}_3 > \text{Ca} > \text{Na} > \text{Cl} > \text{Mg} > \text{SO}_4 > \text{K}$ and $3\text{SiO}_2 < 4\text{Mg}$
 Jordan river : $\text{HCO}_3 > \text{Na} = \text{Mg} > \text{Ca} = \text{Cl} > \text{K} > \text{SO}_4$ and $3\text{SiO}_2 < 4\text{Mg}$
 Chari river : $\text{HCO}_3 > \text{Na} > \text{Ca} > \text{Mg} > \text{K} > \text{Cl} > \text{SO}_4$ and $3\text{SiO}_2 < 4\text{Mg}$
 Sea water : $\text{Cl} > \text{Na} > \text{Mg} > \text{SO}_4 > \text{Ca} > \text{K} > \text{HCO}_3$ and $3\text{SiO}_2 < 4\text{Mg}$

It can be seen on Fig. 2 that before precipitation of the first mineral the pH and all molalities increase with concentration factor. Therefore after formation of successive minerals, the pH, alkalinity and molalities may increase slower or decrease and sometimes increase again. pH for example rises continuously even after precipitation of sylvite and trona (Jordan and Chari), falls after the magnesite saturation point (Euphrate and sea water) and rises again after gypsum precipitation (Euphrate). In the case of sea water, magnesium molality increases continuously, but for Chari and Jordan it decreases after Mg-montmorillonite and magnesite precipitations. Magnesium molality fluctuates frequently in the case of the Euphrate. Such considerations can be emphasized for each element involved. It is now tempting to consider an approach for predicting such patterns.

III- BEHAVIOUR OF ELEMENTS IN SOLUTION DURING PRECIPITATION OF SALTS

During evaporation, the behaviour of elements in solution after reaching the saturation point with respect to a given salt is easily predictable, only when the salt in question is a simple strong electrolyte. This is the case of NaCl, for example ; total molality of Na or Cl, written (Na) and (Cl), rise together in solution until the saturation point with respect to halite. At this point, three possibilities are offered, depending on the ratio $(\text{Na})/(\text{Cl})$ in the initial solution. If $(\text{Na}) > (\text{Cl})$, (Na) will go on to increase and (Cl) to decrease as function of concentration factor ; if $(\text{Cl}) > (\text{Na})$, the contrary is observed. Molalities of Na and Cl will not change if they are equal in the initial solution. This problem can simply be treated, using the mass action law and mass balance equations, disregarding activity coefficients and complex aqueous species.

If (Na^{**}) and (Cl^{**}) are the molalities at a saturation point with respect to NaCl, we have : $(Na^{**})(Cl^{**}) = K_{sp}$

After a small step of evaporation, corresponding to a concentration factor of $(1 + d\xi)$ and precipitation of dx moles of NaCl, it follows that :

$$(Na) = (Na^{**})(1 + d\xi) - dx ; (Cl) = (Cl^{**})(1+d\xi) - dx, \text{ with : } (Na)(Cl) = K_{sp}$$

The direction of variation of (Na) and (Cl) are given by the signs of :

$$\frac{d(Na)}{d\xi} = (Na^{**}) - \frac{dx}{d\xi} \text{ and } \frac{d(Cl)}{d\xi} = (Cl^{**}) - \frac{dx}{d\xi}$$

By deriving the mass action law equation $(Na)(Cl) = K_{sp}$, we obtain :

$$\frac{1}{(Na)} \frac{d(Na)}{d\xi} + \frac{1}{(Cl)} \frac{d(Cl)}{d\xi} = 0$$

$$\text{Thus : } \frac{d(Na)}{d\xi} = \frac{(Na^{**}) [(Na^{**}) - (Cl^{**})]}{(Na^{**}) + (Cl^{**})} \text{ which is positive if } (Na^{**}) > (Cl^{**})$$

$$\frac{d(Cl)}{d\xi} = \frac{(Cl^{**}) [(Cl^{**}) - (Na^{**})]}{(Na^{**}) + (Cl^{**})} \text{ which is positive if } (Cl^{**}) > (Na^{**})$$

If we have now a salt with three or more components, the expression of the derivative is much more complicated. For a fictive $NaKCl_2$ salt, for example the expressions calculated above would become :

$$\frac{d(Na)}{d\xi} = \frac{(Na^{**}) [4(Na^{**})(K^{**}) + (Na^{**})(Cl^{**}) - 3(K^{**})(Cl^{**})]}{(K^{**})(Cl^{**}) + 4(Na^{**})(K^{**}) + (Na^{**})(Cl^{**})}$$

$$\frac{d(K)}{d\xi} = \frac{(K^{**}) [4(Na^{**})(K^{**}) + (K^{**})(Cl^{**}) - 3(Na^{**})(Cl^{**})]}{(K^{**})(Cl^{**}) + 4(Na^{**})(K^{**}) + (Na^{**})(Cl^{**})}$$

$$\frac{d(Cl)}{d\xi} = \frac{(Cl^{**}) [(K^{**})(Cl^{**}) + (Na^{**})(Cl^{**}) - 4(Na^{**})(K^{**})]}{(K^{**})(Cl^{**}) + 4(Na^{**})(K^{**}) + (Na^{**})(Cl^{**})}$$

Thus, after reaching saturation point with respect to $NaKCl_2$, (Na) will go on to increase if $(Na^{**})(K^{**}) + (Na^{**})(Cl^{**}) - 3(K^{**})(Cl^{**}) > 0$ that is : $(Na^{**}) > \frac{3(K^{**})(Cl^{**})}{4(K^{**}) + (Cl^{**})}$

During the same time, (Cl) will continue to increase if $(Cl^{**}) > \frac{4(Na^{**})(K^{**})}{(Na^{**}) + (K^{**})}$

Prediction of such behaviour will be more accurate if calculations of complex ions and activity coefficients are taken into account. However, when a mineral precipitates, the higher the concentration of one of its components in the initial solution, the greater the chance that the concentration of this components will rise during the evaporation steps.

In the case of calcium carbonate, the problem was approached by EATON (1950) and treated by EUGSTER (1970). Van BEEK and Van BREEMEN (1973) introduced the concept of residual alkalinity for predicting the behaviour of alkalinity and pH in alkali soils formation.

IV- GENERALIZED RESIDUAL ALKALINITY CONCEPT

AL-DROUBI (1976) extended the concept of residual alkalinity of Van BEEK and Van BREEMEN (1973).

Alkalinity of natural solutions can be defined as :

$$(Alk.) = (K)_t + (Na)_t + 2(Ca)_t + 2(Mg)_t - (Cl)_t - 2(SO_4)_t$$

$$(\text{Alk.}) = (\text{HCO}_3)_t + 2(\text{CO}_3)_t + (\text{OH})_t - (\text{H})$$

in which $(\text{HCO}_3)_t$ is the total molality, including the molality of the free ion HCO_3^- as well as the molality of complex bound HCO_3 , i.e. NaCO_3^0 , MgHCO_3^+ , CaHCO_3^+ etc ... ; Or $(\text{OH})_t$ includes the molality of the free ion $(\text{OH})^-$ as well as molality of $\text{Mg}(\text{OH})^+$, $\text{Ca}(\text{OH})^+$ etc ... (STUMM and MORGAN, 1970).

Residual alkalinity for calcite, after reaching calcite saturation is defined as :

$$(\text{Res. Alk.}) \text{ calcite} = (\text{Alk.}) - 2(\text{Ca})_t$$

Residual alkalinity for calcite and magnesite after precipitation of these two minerals is defined as :

$$(\text{Res. Alk.}) \text{ calcite} + \text{magnesite} = (\text{Alk.}) - 2(\text{Ca})_t - 2(\text{Mg})_t$$

If $f\text{CO}_2$ is constant during the evaporation, the sign of residual alkalinity will determine :

- a) the behaviour of calcium, pH and alkalinity during the precipitation of calcite,
- b) the behaviour of calcium, magnesium, pH and alkalinity during coprecipitation of calcite and magnesite.

After precipitation of calcite, calcium concentration increases, pH and alkalinity decrease, if $(\text{Res. Alk.}) \text{ calcite}$ is negative. If positive, calcium concentration decreases, pH and alkalinity rise. At the stage of precipitation of magnesite, after calcite, magnesium and calcium concentrations increase, pH and alkalinity decrease if $(\text{Res. Alk.}) \text{ calcite} + \text{magnesite}$ is negative ; if $(\text{Res. Alk.}) \text{ calcite} + \text{magnesite}$ is positive, magnesium and calcium concentrations decrease, pH and alkalinity rise together.

It must be emphasized that if the sign of $(\text{Res. Alk.}) \text{ calcite}$ is positive and the sign of $(\text{Res. Alk.}) \text{ calcite} + \text{magnesite}$ is negative, calcium concentration decreases after calcite precipitation but increases again after magnesite precipitation. This is what happens in the case of the Euphrate river (Fig. 2)

Application to other binary salts

When, after calcite and magnesite precipitation, other salts are formed, it can be shown that the above expression of Residual Alkalinity is still valid.

After reaching saturation point with respect to gypsum, for example :

$$\begin{aligned} &(\text{Res. Alk.}) \text{ magnesite} + \text{calcite} + \text{gypsum} = \\ &(\text{Alk.}) - 2(\text{Mg})_t - 2(\text{Ca})_t + 2(\text{SO}_4)_t = \\ &(\text{Na})_t + (\text{K})_t - (\text{Cl})_t \end{aligned}$$

If (Res. Alk.) is positive, Alkalinity and pH will increase, $(\text{Ca})_t$ and $(\text{Mg})_t$ will decrease and by the way $(\text{SO}_4)_t$ will rise. If negative, the opposite evolution is observed.

If, following gypsum, thenardite (Na_2SO_4) precipitates :

$$\begin{aligned} &(\text{Res. Alk.}) \text{ magnesite} + \text{calcite} + \text{gypsum} + \text{thenardite} = \\ &(\text{Alk.}) - 2(\text{Mg})_t - 2(\text{Ca})_t + 2(\text{SO}_4)_t - (\text{Na})_t = (\text{K})_t - (\text{Cl})_t \end{aligned}$$

the same rule can be applied i.e. $(\text{Na})_t$ will increase if $(\text{SO}_4)_t$ decreases which happens when (Res. Alk.) is negative.

After halite (NaCl) precipitation :

$$\begin{aligned} &(\text{Res. Alk.}) \text{ magnesite} + \text{calcite} + \text{gypsum} + \text{thenardite} + \text{halite} = \\ &(\text{Alk.}) - 2(\text{Mg})_t - 2(\text{Ca})_t + 2(\text{SO}_4)_t - (\text{Na})_t + (\text{Cl})_t = (\text{K})_t \end{aligned}$$

The residual Alkalinity is obviously positive; in this case $(\text{K})_t$, $(\text{Cl})_t$, $(\text{SO}_4)_t$, (Alk.) and pH will rise and $(\text{Na})_t$, $(\text{Ca})_t$ and $(\text{Mg})_t$ will decrease.

Finally after sylvite (KCl) precipitation :

$$\begin{aligned} &(\text{Res. Alk.}) \text{ magnesite} + \text{calcite} + \text{gypsum} + \text{thenardite} + \text{halite} + \text{sylvite} = \\ &(\text{Alk.}) - 2(\text{Mg})_t - 2(\text{Ca})_t + 2(\text{SO}_4)_t - (\text{Na})_t + (\text{Cl})_t - (\text{K})_t = 0 \end{aligned}$$

(Res. Alk.) is equal to zero, alkalinity, pH and concentration of other elements in solution will not change and remain constant according to the phase rule, the number of phases which control the system becoming sufficiently high.

When a strong electrolyte is formed two possibilities are offered :

- a) if any of the two components (anion or cation) was already involved in a previous precipitation, the formation of the new mineral does not modify the Residual Alkalinity ;
- b) when one of the two components (anion or cation) was already involved, the total molality of the other must be added (if anion) or subtracted (if cation) from the previous Residual Alkalinity, to calculate the new one.

If the salt formed is a weak acid salt, the concentration of the cation only, must be subtracted, the weak acid anion being already counted in the Alkalinity.

Derivative of Alkalinity

A mathematical formulation is now developed for the simple case of a solution saturated with respect to calcite and reaching gypsum precipitation point, in conditions of fCO_2 fixed. Without taking into account of activity coefficients and complex species, following equations can be derived from the mass balance and the mass action law equations.

For a small step of evaporation $(1 + d\xi)$, dx and dy are respectively the number of moles of calcite and gypsum formed :

$$(Alk.) = (1 + d\xi) [(Na^{**})_t + (K^{**})_t + 2(Mg^{**})_t - (Cl^{**})_t] + 2(Ca^{**})_t (1 + d\xi) - 2 dx - 2 dy - 2(SO_4^{**})_t - (-2 dy)$$

$$(Alk.) = (Alk^{**})(1 + d\xi) - 2 dx \text{ and } \frac{d(Alk.)}{d\xi} = (Alk.^{**}) - \frac{2 dx}{d\xi}$$

$$(Res. Alk.) \text{ calcite} + \text{gypsum} = (1 + d\xi) [(Na^{**})_t + (K^{**})_t + 2(Mg^{**})_t - (Cl^{**})_t]$$

$$(Res. Alk.) \text{ calcite} + \text{gypsum} = (1 + d\xi) (Res. Alk.^{**}) \text{ calcite} + \text{gypsum}$$

$$\frac{d (Res. Alk.) c + g}{d \xi} = (Res. Alk.^{**}) c + g$$

(* stars indicate the initial values)

According now to mass action law for CO_2 , HCO_3^- , H_2O , $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ equilibrium reaction, it comes :

$$\frac{d [H^+]}{d \xi} = \frac{[H^+]}{2 [Ca^{2+}]} \frac{d [Ca^{2+}]}{d \xi}, \quad \frac{d [CO_3^{--}]}{d \xi} = - \frac{[CO_3^{--}]}{[Ca^{2+}]} \frac{d [Ca^{2+}]}{d \xi}$$

$$\frac{d [HCO_3^-]}{d \xi} = - \frac{[HCO_3^-]}{2 [Ca^{2+}]} \frac{d [Ca^{2+}]}{d \xi}, \quad \frac{d [OH^-]}{d \xi} = - \frac{[OH^-]}{2 [Ca^{2+}]} \frac{d [Ca^{2+}]}{d \xi}$$

$$\frac{d [SO_4^{--}]}{d \xi} = - \frac{[SO_4^{--}]}{[Ca^{2+}]} \frac{d [Ca^{2+}]}{d \xi}$$

If activities [] are confused with total molalities and combining these equation with the above ones, one has :

$$\frac{d (Alk.)}{d \xi} = - \frac{1}{2 (Ca^{**})} \frac{d (Ca)}{d \xi} \underbrace{[(HCO^{**}) + 4(CO^{**}) + (OH^{**}) + (H^{**})]}_{\alpha > 0}$$

Because $(Res. Alk.) \text{ calcite} + \text{gypsum} = (Alk.) - 2(Ca)_t + 2(SO_4)_t$, it comes :

$$\frac{d (Alk.)}{d \xi} = \frac{d (Res. Alk.) \text{ calcite} + \text{gypsum}}{d \xi} + 2 \frac{d (Ca)}{d \xi} - \frac{2 d (SO_4)}{d \xi}$$

and finally :

$$\frac{d(\text{Alk.})}{d\xi} = \left[\frac{1}{1 + 4 \frac{1}{\alpha} [(Ca^{2+}) + (SO_4^{2-})]} \right] (\text{Res. Alk.}) \text{ calcite + gypsum}$$

always positive

Thus, the derivative of Alkalinity has the sign of Residual Alkalinity defined for the minerals involved.

Limitations for the use of Residual Alkalinity

Two major limitations were found in the use of Residual Alkalinity for predicting behaviour of elements in solution when salts precipitate.

The first one comes from the direction of variation of Alkalinity in connection with pH at constant fCO_2 . The equilibrium $HCO_3^- + H^+ \rightleftharpoons CO_2 + H_2O$ or $CO_3^{2-} + 2H^+ \rightleftharpoons CO_2 + H_2O$ indicates that activities of HCO_3^- or CO_3^{2-} increases when pH increases. Therefore in brines, because molalities can be very different from activities, it is possible to find cases in which Alkalinity varies in a different direction of pH.

Furthermore when the salts involved are of three or more components, the expression and the use of Residual Alkalinity become complex. This is, for example, the case when dolomite or montmorillonite are the first minerals formed.

CONCLUDING REMARKS

During evaporation, concentration of soluble species can fluctuate, depending on the nature of salts precipitating and of the relative amount of these species in solution. Prediction of such behaviour may be approached by the use of Residual Alkalinity extended concept. However this method is limited to relatively simple cases. A computer approach seems then necessary to solve correctly the problem.

Table 1. Chemical composition of Euphrate waters, (concentrations in mmols/kg H₂O, Alkalinity in meq/kg H₂O) before evaporation (1) and after evaporation for a concentration factor of 5680 (2), maintaining fCO₂ = 10^{-2.36}.

Conc. fact.	Alk	SO ₄	Cl	Na	K	Ca	Mg	SiO ₂	Ionic str.
(1) 1	3.051	0.701	0.875	1.266	0.072	1.270	0.725	0.115	0.007
(2) 5680	16.28	564.6	4969.9	5702.1	408.9	0.89	1.3	1.15	5.19

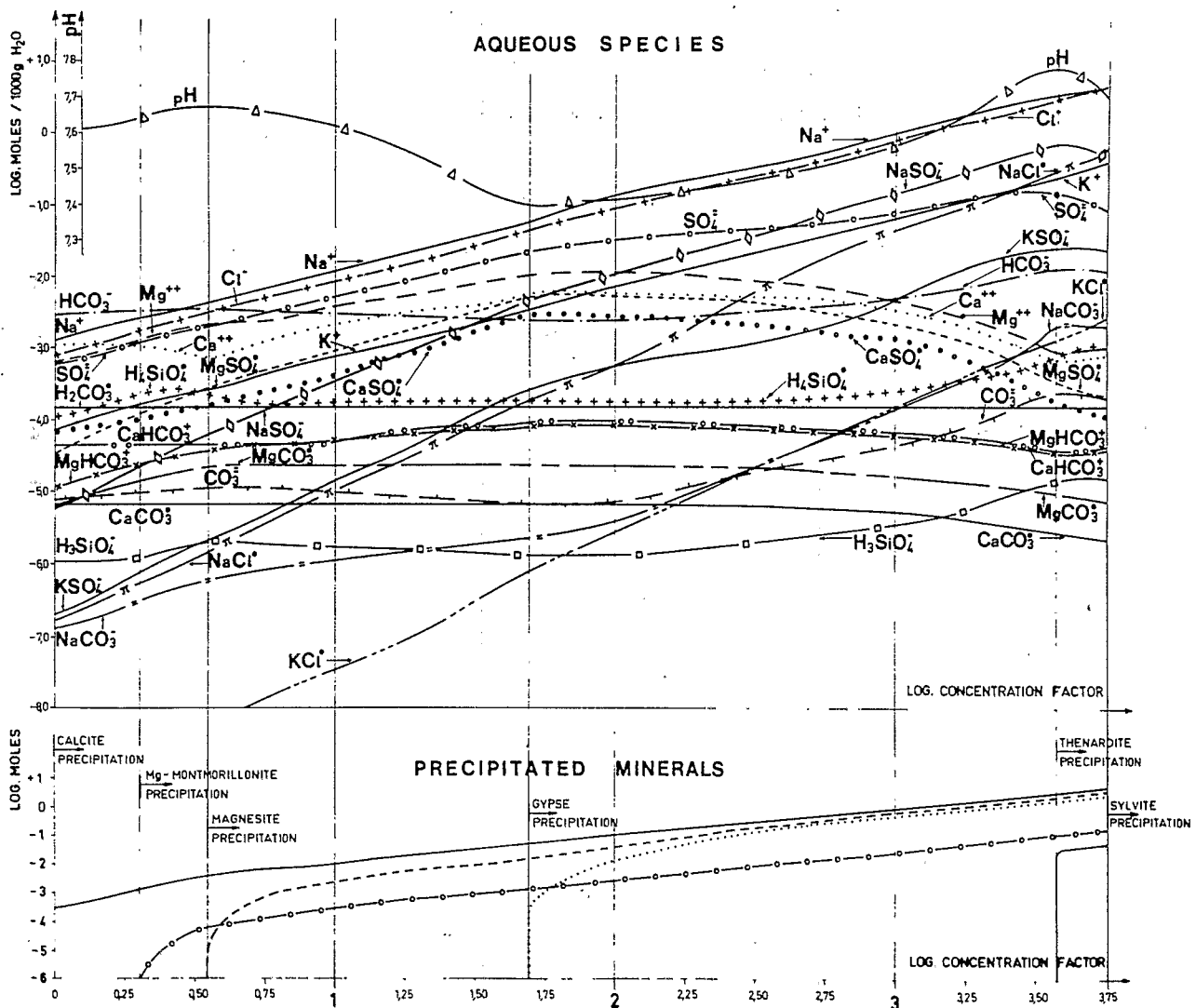
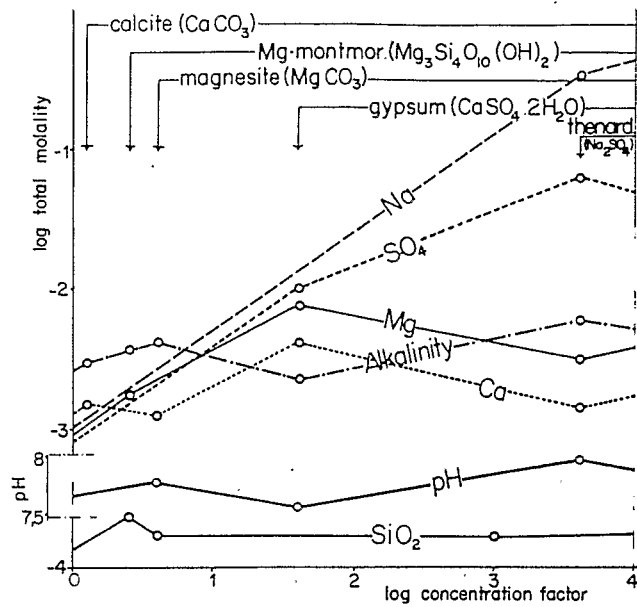
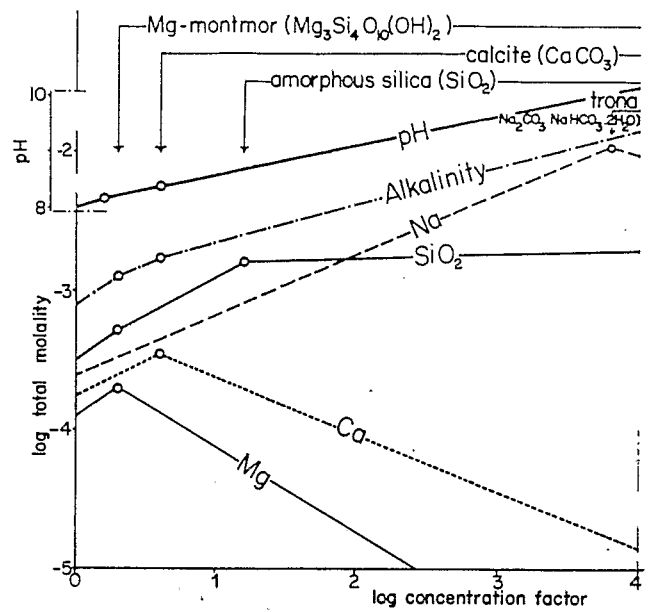


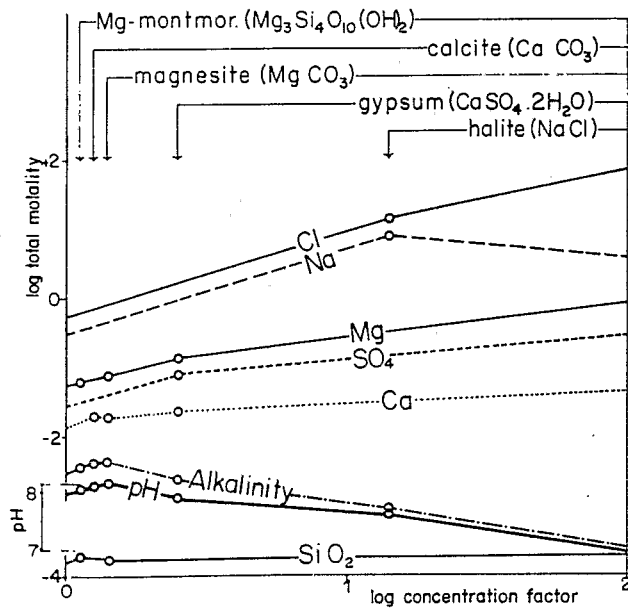
Fig. 1 - Evolution of chemical composition of solutions and amount of salt precipitated during evaporation of Euphrate water, as function of concentration factor (ξ).



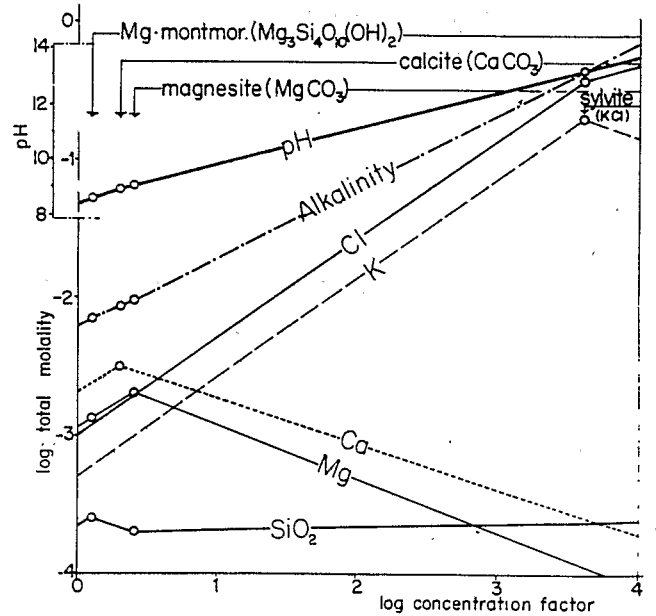
EVAPORATION OF EUFRATE WATER



EVAPORATION OF CHARI WATER



EVAPORATION OF SEA WATER



EVAPORATION OF JORDAN WATER

Fig.2 - Schematic computed chemical evolution of Euphrate, Chari, sea water and Jordan waters, during concentration by evaporation.

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