

GYPSUM PRECIPITATION/DISSOLUTION DURING SEAWATER INTRUSION

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Abstract

The precipitation of gypsum during the intrusion of seawater in a coastal aquifer has been shown as a possible cause of the decrease in sulphate concentration with respect to the conservative freshwater/seawater mixing observed in many field studies. Results of laboratory column experiments of salt water intrusion previously obtained (Gomis *et al.*, 1997) and the application of a multicomponent reactive transport model (Gomis *et al.*, 1996) have shown that precipitation of gypsum during the early stages of the advance of the seawater front causes a decrease in sulphate concentration (Gomis *et al.*, 2000). This process could occur when cations of seawater (mainly sodium and magnesium) displace calcium ions on sediment exchange sites. The increase in dissolved calcium together with the high sulphate concentration of the seawater could produce a saturation index (SI) > 0 and consequently gypsum precipitation could be expected. If gypsum precipitation is produced, the amount of sulphate transported by the intrusion front will decrease, the water will be under-saturated in gypsum and will have a deficit of sulphate with respect to the conservative mixture freshwater / seawater. In this paper, several sets of results obtained in laboratory column experiments are analysed. The experimental set-up consisted of a column of stainless steel or glass connected to a HPLC pump. In the experiments, the columns were filled either with natural sediment or a cationic resin saturated in calcium. The porous media was initially equilibrated either with synthetic freshwater or with a calcium chloride solution. Laboratory intrusion experiments started when seawater flushed continuously from the bottom to the top through the column. In each of the experiments the effluent was collected in small fractions and analysed to obtain the variations of concentration of the major ions versus time in the effluent. The influence of the transport parameters (Péclet number), the characteristics of the sediment (Cation Exchange Capacity) and the nature of exchangeable medium (natural clay or artificial resin) in the precipitation of gypsum are studied.

Keywords: seawater intrusion, column experiment, dissolution, precipitation, gypsum

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Introduction

In recent years, a great number of multicomponent reactive transport models have been formulated to describe the displacement of ions in groundwater. Sullivan *et al.* (2003) provides a description of some them (Valocchi *et al.*, 1981a, 1981b; Appelo and Postma, 1993; Appelo, 1994, 1996; Parkhurst and Appelo, 1999; Robinson *et al.*, 2000). It is necessary to understand the reactive transport behaviour of inorganic chemical species when dealing with environmental problems such as fresh- or seawater intrusions into aquifers, landfill leaching plumes, or transport of heavy metals in soils and aquifers (Voegelin *et al.*, 2000).

Seawater intrusion is a particular case of multicomponent reactive transport with a more complicated solution: a great number of ions at very high concentration (high ionic strength) and different type of reactions such as cation exchange and precipitation/dissolution are involved. In order to validate the application of the models to the particular case of seawater intrusion, it is necessary to have a set of experimental data available on the evolution of the composition of water while seawater intrusion is produced. This set of data should contain all physical and chemical parameters necessary to properly validate a multicomponent transport model.

In this work, several sets of experimental data have been obtained by flushing seawater through columns packed either with natural sediment or with a cationic resin saturated in calcium which had previously been equilibrated with freshwater. The required sets of data contain the ion concentrations of the outflow and the physical and chemical parameters needed for the theoretical simulation of marine intrusion using a hydrogeochemical code. The results obtained permit the analysis of changes in concentrations produced by cation exchange reactions (the most studied reactions in groundwater systems, Sardin *et al.*, 1998, Vulava *et al.*, 2002, Carlyle *et al.*, 2004) and, especially, by dissolution / precipitation reactions of solid phases like gypsum.

Description of the experiments

Five column experiments were carried out to obtain values of the changes in the concentration of the different ions during seawater intrusion in the laboratory. The columns were filled either with natural sediment or with resin that were first saturated in batch with synthetic freshwater (Table 1) or with a CaCl₂ solution of Ca = 1.5 mmol/L (Table 1). After the porous media was conditioned with solutions, the columns were continuously flushed with a constant flow of seawater. Then, small volumes of the effluent were collected at the column outlet. The water samples were analysed to determine the variation of major ion concentrations versus time. The experiments finished when the concentrations in the effluent were equal to those of seawater (Table 1).

The experimental equipment (Figure 1) consisted of a stainless steel column connected to a HPLC Shimadzu LC-5A pump. In experiments 1-4 (Table 2), sediment from the Javea Quaternary aquifer (to the north of Alicante province, SE Spain) was utilised. The length of the stainless steel column was 1 m and its internal diameter was 3.16 cm. Two fritting glass diffusers (porosity=1) were placed into the column, one at the top, to prevent the migration of sediment particles, and the other on the bottom, to distribute the

Table 1. Composition of the fresh and seawater used.

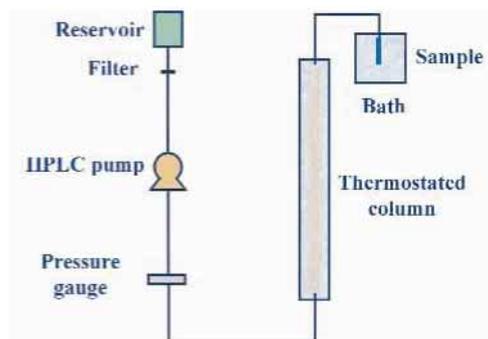
Ion	Freshwater		Seawater	
	mg/L	mmol/L	mg/L	mmol/L
Na ⁺	50	2.17	12000	522
K ⁺	3.4	0.0872	400	10.3
Ca ²⁺	125	3.13	450	11.3
Mg ²⁺	15	0.617	1500	61.7
Cl ⁻	105	2.96	21500	606
SO ₄ ²⁻	165	1.72	2900	30.2
HCO ₃ ⁻	200	3.28	130	2.13

influent water into the column. Two stainless steel screw caps closed the column and were connected to the rest of the equipment with high-pressure connections. The columns were long enough as to increase the peaks of concentration of some ions and to study their effect on the others ions. The HPLC pump permitted a small constant flow of water to be introduced so as to achieve the local chemical equilibrium with the sediment and, on the other hand, to simulate the low velocity of seawater intrusion processes. This low velocity and the large size of the column resulted in some of the experiments lasting almost four months.

Table 2. Characteristics of the sediment (porosity (ϵ), cation exchange capacity (CEC), dispersivity (α) and Péclet number (Pe)); flow rate, and column type (stainless steel (ss) or glass) used in the experiments (Exp).

Exp	Flow rate ($\mu\text{L}/\text{min}$)	Col. type	Length (cm)	Diam (cm)	Porous medium	CEC (meq/100g)	ϵ	α (cm)	Pe
1	82	ss	100	3.16	sediment	7	0.40	20	5
2	35	ss	100	3.16	sediment	7	0.30	0.7	150
3	20	ss	100	3.16	sediment	7	0.30	0.7	150
4	20	ss	100	3.16	sediment	10	0.30	0.7	150
5	50	glass	19	2.50	resin	235	0.50	0.2	95

In experiment 5, the porous medium was a strong cation exchanger (Duolite C20) saturated in calcium. In this case the glass column OMNIFIT[®] was used. It is 2.5 cm internal diameter and its length reached 19 cm. The great cation exchange capacity of the resin could produce a high concentration of calcium that would produce gypsum precipitation inside the column.

**Figure 1.** Configuration of the column experiments.

Transport parameters

The mean residence time, initial porosity and initial dispersion coefficient were obtained by fitting the experimental data corresponding to the breakthrough curve for the conservative ion Cl^- through modeling. In all the experiments a multicomponent transport model (Gomis *et al.*, 1996) was applied. The equation used was:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x}$$

where:

- C = concentration of chloride in water
- ϵ = sediment porosity
- D = dispersion coefficient
- u = Darcy velocity of the effluent
- x = distance
- and t = time

With the two initial and boundary conditions:

For $x=0$ and $t=0$, $C=C_0$, the concentration of chloride in freshwater.

For $x=L$ and for every $t>0$, $C=C_S$, the concentration of chloride in seawater.

To carry out the calculations, a finite difference representation using the Crank-Nicholson method (Costa *et al.*, 1986) was used to solve the partial differential equation.

The dispersion coefficient can be written as a contribution of two members:

$$D=D_d+\alpha v$$

where D_d is the diffusion coefficient and α is the dispersivity. When the flow velocity in the column is high enough to cause a dispersion-dominated spreading, D_d can be ignored (Appelo and Postma, 1993).

The values of the dispersivity (α) and porosity (ϵ) are shown in Table 2. Parameters such as interstitial velocity (v), mean residence time (t_m) and the Péclet number (Pe) can be obtained using the following equations:

$$v = \frac{u}{\epsilon} \quad t_m = \frac{\epsilon L}{u} \quad \text{Pe} = \frac{v L}{D} = \frac{L}{\alpha}$$

where L is the length of the column.

Results and discussion

The influence of the Péclet number has been studied in three experiments (1, 2 and 3). In the first experiment (Figure 2), the effect of a small Pe (high dispersivity) causes the elution curves of the different ions to tend to typical breakthrough curves, where the several maxima and minima produced by different reactions of cation exchange, precipitation / dissolution, are very smooth.

Experiments 2 and 3 were carried out with a different flow rate but with the same Pe (figures 3 and 4). Figure 5 shows the perfect coincidence of the curves of each ion in dimensionless time (v^*t/L), very different to those of Experiment 1. Obviously, the shape of the experimental curves is basically affected by dispersion. Moreover, and contrarily to Experiment 1, in Experiments 2 and 3 it can be observed that there is a great peak of calcium (maximum concentration 60 mmol/L in Experiment 1, and more than 200 in Experiments 2 and 3), that could produce gypsum precipitation. A delay of sulphate with respect to the chloride curve can also be observed. The later dissolution of gypsum would cause the concentration of sulphate to be higher than that of seawater.

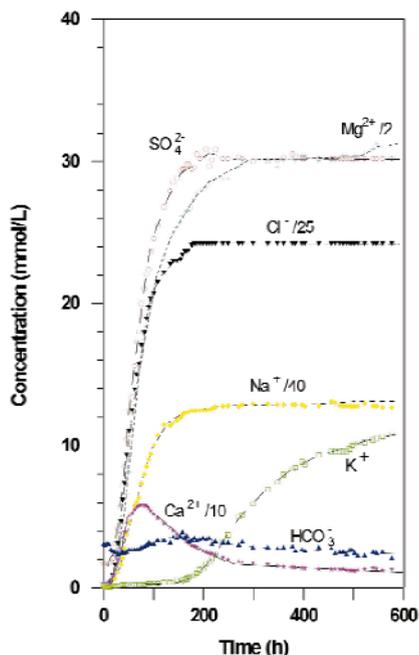


Figure 2. Concentration of the different ions versus time obtained in Experiment 1.

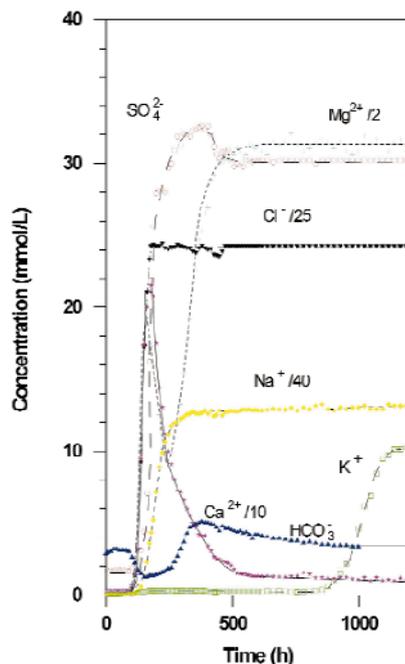


Figure 3. Concentration of the different ions versus time obtained in Experiment 2.

The influence of the cation exchange capacity has been studied in Experiments 3 and 4, which were carried out using similar sediment but with different CEC (figures 4 and 6). Great changes in the height of the calcium peak (320 mmol/L) and in the difference between the maximum and minimum of the magnesium are noticed. The concentration wave of sodium and potassium is delayed with respect to that of chloride, and these curves have a perfect coincidence in both experiments. The exchange selectivity coefficients for the potassium/sodium are probably equal in both sediments, but those for magnesium/calcium and sodium/calcium exchange are probably different.

In Experiment 4 (Figure 6), the sulphate curve presents a delay with respect to the chloride curve similar to that of Experiment 3 (Figure 4). The proposed cause is that high concentrations of calcium and sulphate in the first stages of the intrusion could produce a precipitation of gypsum. Its subsequent dissolution causes the concentration of sulphate to be higher than in seawater.

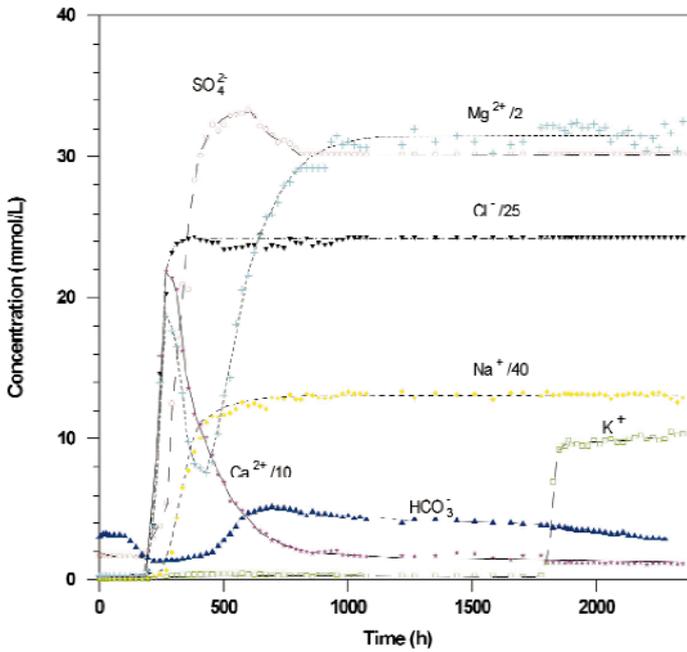


Figure 4. Concentration of the different ions versus time obtained in Experiment 3.

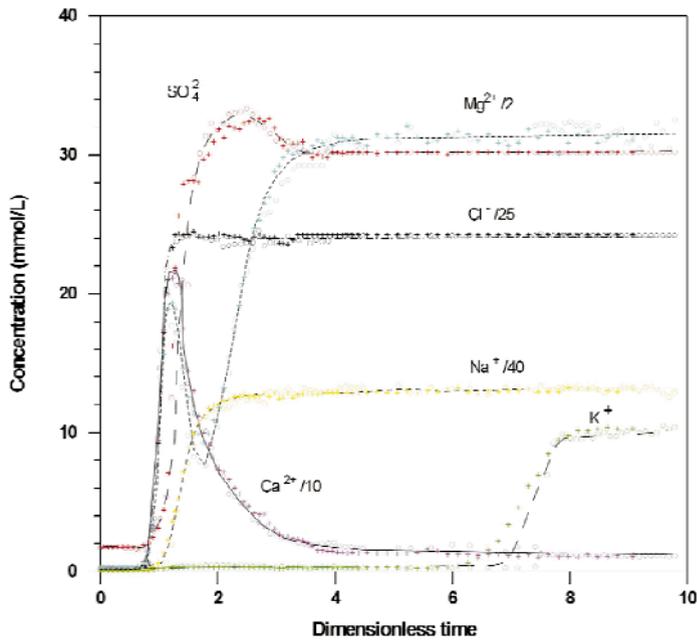


Figure 5. Concentration of the different ions in Experiments 2 and 3 versus dimensionless time.

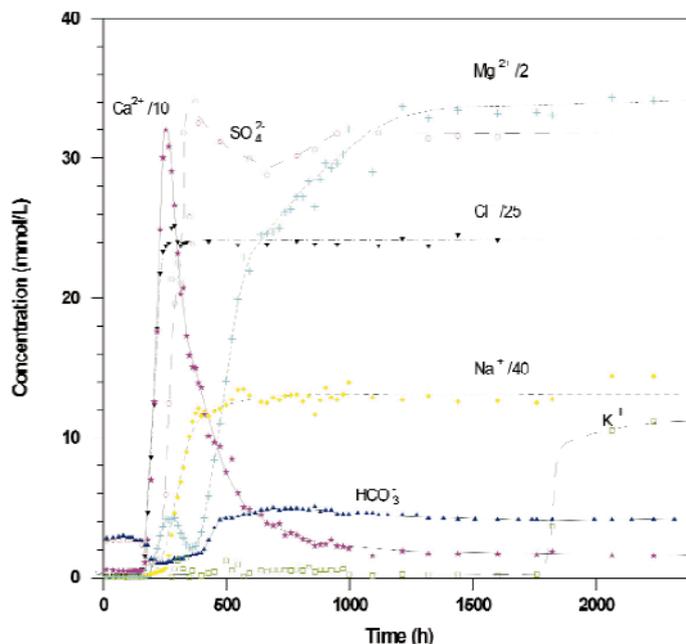


Figure 6. Concentration of the different ions versus time obtained in Experiment 4.

In Experiment 5, the influence of the exchangeable medium was studied (Figure 7). A strong cation exchanger (Duolite C20) increases the value of the CEC of the sediment more than 20 times. This was used to study the precipitation of gypsum in seawater intrusion experiments. The shape of the calcium curve is similar to that of the other experiments, but the maximum concentration is only 50 mmol/L greater. The other cations are delayed with respect to conservative chloride, but the shape of the breakthrough curves is different. Probably there are great differences between the exchange selectivity coefficients of the natural clay and these of the cation resin.

In this experiment the increase in dissolved calcium together with the high sulphate concentration of the seawater produces gypsum over-saturation. However, the sulphate front is not retarded with respect to conservative chloride, indicating that gypsum precipitation does not occur in the first stage. The precipitation/dissolution of gypsum is probably not fast enough as to maintain local equilibrium.

Conclusions

Gypsum precipitation is a possible cause to explain a deficit in sulphate concentration with respect to conservative freshwater/seawater mixing in seawater intrusion.

Five experiments with different conditions have been compared. The influence of the Péclet number modifies the shape of the elution curves of the major ions. If Pe is small (high dispersivity), the curves tend to typical breakthrough curves, where the several maxima and minima produced by different reactions of cation exchange and precipitation/dissolution are very smooth.

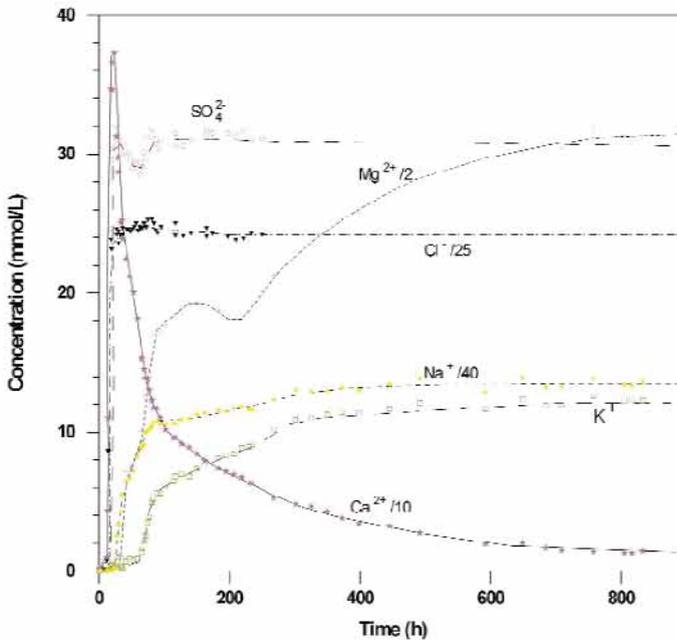


Figure 7. Concentration of the different ions versus time obtained in Experiment 5.

The influence of the cation exchange capacity of the sediment produces changes in the height of the calcium peak and in the maxima and minima of magnesium, probably because the exchange selectivity coefficients for several cations have varied. The sulphate curve of several experiments presents a delay with respect to the chloride curve. The high concentrations of calcium and sulphate in the first stages of the intrusion could produce precipitation of gypsum. Its subsequent dissolution could cause the concentration of sulphate to be higher than that of seawater.

The nature of the exchangeable medium has different influences in the pattern of the chromatographic curves. In the resin experiment, the shape of the calcium curves is similar to the other experiments, but the shape of other curves is different. There are probably great differences between the exchange selectivity coefficient of the natural clay and the cation resin. As far as the sulphate curve is concerned, several differences can be observed with respect to other experiments. The high sulphate concentration of seawater together with the increase in dissolved calcium produces a gypsum saturation index $SI > 0$. However, the sulphate front is not retarded with respect to conservative chloride, indicating that the gypsum precipitation does not occur in the first stage. The precipitation/dissolution processes of gypsum are probably not fast enough to maintain local equilibrium and, in addition, other factors (porosity, length of the column, grain size of resin, nature of the resin, etc.) may have different influences in the process of precipitation/dissolution of gypsum.

Acknowledgements

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