Brackish springs in coastal aquifers and the role of calcite dissolution by mixing waters

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CHAPTER 7: GENERAL CONCLUSIONS
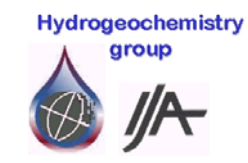
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Chapter 7

General conclusions

This chapter is a summary of the main contributions provided by this thesis.

In the first part of the thesis we study the mechanisms of salinization in brackish springs. We use simple hydraulic models to characterize the basic physics of the mechanisms of salinization at the conduit branching, and to reproduce the field salinity and discharge observations. The equations governing turbulent flow for variable-density fluids have been derived and solved with an iterative algorithm programmed in FORTRAN (called TURBOCODE). The solver was programmed to simulate both turbulent and Darcyan flow and transport of variable-density fluids in well developed coastal kast systems. The response of the spring concentration to the variation of freshwater flow rate from the aquifer is evaluated for two scenarios: a conduit branching connected to the sea through an open karst conduit, or a single karstic conduit contaminated by seawater from the surrounding fissured matrix. The solution reveals the distinctive features of every conceptual model, in terms of freshwater-seawater curve and relationship of spring concentration and discharge. For low freshwater flow rates, the spring concentration is controlled by the weight of the water column of the conduit connecting to the spring mouth. For this situation, the solution is sensitive to the depth of the conduit branching. For higher freshwater flow rates in the conduit branching, the energy loss in the vertical becomes the controlling factor since it increases quadratically with the flow. Thus, the solution shows high sensitivity to the resistance to flow in the vertical conduit for high freshwater flow rates and to the resistance in the conduit connected to the sea for medium freshwater flow rates.

When comparing the results for both conceptual models, those present similarities for medium spring discharges, although the dependency of spring salinity with discharge is more

linear for the Turbulent-Porous case. Additionally, for very low spring discharges, the concentration for the Turbulent-Turbulent case becomes constant when the spring discharge tends to zero. This points out that, for this situation the solution depends only on the water column weight in the vertical conduit. In fact, the spring dries up when the excess in elevation of the spring mouth is balanced by the excess in of density of seawater with respect to that of the mixed water in the conduit connected to the spring mouth. The depth of the conduit branching can be then approximated from the elevation of the spring mouth and from spring salinity for very low spring discharges.

The prediction curves of freshwater-seawater ratio and the relationship of spring discharge and salt mass fraction are compared with field data from Pantan spring, Almyros of Heraklion spring and S'Almadrava spring. The simulation results show a good agreement with the field data available, and provide insights to identify the conceptual model governing every particular springs. The analysis highlights the importance of using field data encompassing the whole range of spring discharges for a sound understanding of the spring functioning.

The freshwater-seawater curve is specific to all brackish springs and it is representative of the dimensions of the karst system and the salinization mechanism. In the light of our findings an analysis based on the freshwater-seawater ratios rather than on the relationship of spring concentration and discharge proves to be more suitable for identifying the salinization mechanisms of some brackish springs.

In Chapter 3 we propose a revision of the hydraulic a revised hydraulic conceptual model for S'Almadrava spring (+8 m.a.s.l., Mallorca, Spain). This model assumes the existence of a conduit branching at a minimum depth of -540 m.a.s.l. (based on field observations) and connection with sea through an open karst conduit of reduced section. The mixed water flows up mainly through a karst open conduit, thus resulting in a fast response of the system to the rainfall events. TURBOCODE solver was used to reproduce this single conduit conceptual model for S'Almadrava spring with satisfactory results. The model reproduces the variation of the spring concentration with the discharge in 1996 in both dry and wet seasons and this conceptual model is therefore capable to explain the basic physics of the system controlling S'Almadrava spring response. However this model was not able to explain the two most distinctive features of S'Almadrava: the double high salinity peak after the first rainfall event after summer and the secondary peak in the middle of every salinity drop following the recharge events.

To explain these especial features, diverse conceptual models could be suggested. We propose a dual permeability model, where the mixed water flowing from the conduit branching to the spring mouth divides into a fast turbulent flow component in an open conduit, and a low flow through a fractured matrix. Simulation results for this complex model are able to reproduce the field observations, including the formation of secondary salinity peaks. The solution is

extremely dependent on the difference in water column weight of the two media and therefore requires the use of transient simulations. The formation and extent of the secondary salinity peaks depends on the section and hydraulic permeability of the porous matrix.

This dual permeability model is analyzed also using reactive transport model in the Chapter 4. A high-frequency sampling campaign was performed during the first 50 days after the summer dry season of 2004, and samples were analyzed for $\delta^{18}O$ and $\delta^{34}S$ stable isotopes as well as major ions. Isotope values allowed to confirm that alternative salinity sources (like evaporates dissolution from Keuper materials or contamination by fertilizers) other than seawater, are practically negligible at any stage of the spring functioning. The availability of detailed geochemical data (major ions) allows the identification of different water-rock interaction processes for the different behaviours of the spring. Thus, reactive transport simulations show that the chemical signal at the secondary salinity peaks is a consequence of ion exchange reactions. Ion exchange increases the proportion of Ca and Sr, and reduces that of Mg, Na, and K with respect to the conservative mixing between fresh and seawater. These exchange reactions are likely to occur in clay minerals in fissured matrix. During high flow circumstances, most of the flow upwards occurs through the karst conduit while the proportion of flow from the fissured matrix increases for saltier mixtures reported. The inverse exchange process is predicted to occur during a very short period of high spring discharges. The dissolution of calcite due to water mixing is also predicted to occur is not recognizable from the composition of the spring discharge neither on the field measurements nor on the simulation results. However, this result is a bit disappointing since it prevents from the identification of calcite dissolution at depth, from the chemistry of the discharge of brackish springs.

The satisfactory performance of the simulation reproducing the field observations allow to further validate the dual permeability conceptual model for S'Almadrava spring. This conclusion reveals the importance of applying techniques to complement the purely hydraulic studies to further validate the conceptual models proposed for brackish springs. High frequency geochemical data appears to be a powerful tool for this purpose.

In the second part of this thesis, we perform numerical simulations of mixing of calcite-saturated waters of different salinities. Results reveal that the variation of the saturation of the mineral is not always a good indicator of the real potential for calcite dissolution of a mixture. For end-member solutions reproducing a coastal carbonate aquifer affected by seawater intrusion, the maximum subsaturation is expected to occur for mixing ratios of about 15%-salty, while the expected dissolved calcite reaches its maximum for 50% of mixing. This apparent inconsistency can be explained by the strong influence of the pH in the carbonate speciation, the relative lower activity of CO_3^{2-} compared to that of Ca^{2+} in solution, and the dependency of the activity coefficients with the mixing ration (i.e., with the salinity variation). Therefore, the capacity of a certain mixture to dissolve calcite should be addressed in terms of calcite

dissolution, rather than on the variation of calcite saturation with the mixing ratio as done in previous literature.

This situation is tested through a series of flow-through experiments carried out with end-members of different salinity and pCO_2, and for different flow rates and a range of mixing ratios of 0-50%-salty. Diffusion of CO_2 at the reactor cell allows testing the effect that minor variations of CO_2 in the aquifer may have in the potential for dissolution of mixing waters. Experiments clearly show a strong dependency of the dissolution with the mixing ratio and with minor variations of CO_2 at the reaction place. Experiments results are consistent with the calcite dissolution predicted from obtained with the geochemical modelling, and confirm the discrepancy between saturation and actual dissolution patterns.

Aquifers often present unallocated buckets of organic matter that may alter the geochemistry of groundwater (and specially the CO_2 pressure). However, P_{CO2} measurements in the field are difficult to obtain and often generate the highest uncertainties when modelling seawater intrusion field cases. Therefore, the high sensitivity demonstrated by the geochemical model to the CO_2 content in solution can explain the variety and "contradictory" field observations (dissolution vs. lack of dissolution), and is of great importance for future modelling of natural systems, especially when the modelling results are scaled into geological time.

These results motivated the study on Chapter 6, which provides insights on the interplay between chemistry and transport in the mixing zone of coastal carbonate aquifers. Simulations performed of one dimensional mixing (diffusion) show that it is the transport of minor acidity constituents ($CO_2(aq)$ and H^+) what largely controls the system. They are depleted by calcite dissolution, which increases their diffusion rate, further increasing dissolution. This causes maximum dissolution rates to concentrate at the freshwater end. As expected, the amount of calcite dissolved is larger for the fully coupled than that for the two-step method, which only converges for time steps sufficiently small. The interaction between reactions and transport also explains the somewhat paradoxical dependence of dissolution rates on the P_{CO2} of end members. The most interesting situation occurs when the P_{CO2} of saltwater is high, where undersaturation increases with decreasing P_{CO2} of the freshwater end member. However, the opposite occurs to dissolution rates near the freshwater end member, because the transport of acidity can be larger for high freshwater P_{CO2}. On the other hand, near the saline end member, diffusion distances are long, so that the effect of saturation index prevails and dissolution is largest for low freshwater P_{CO2}. These results suggest that indeed the interplay between transport and reactions is non-trivial. Saturation index calculations are needed but do not indicate how much calcite is dissolved, which is controlled by mixing rate, nor necessarily where dissolution rate is maximum. This supports our conjecture about the need for fully coupled reactive transport.

Results in a 2-D vertical cross-section of a hypothetical coastal carbonate aquifer appear to be qualitatively similar to those obtained by Sanford and Konikow (1989) from a two-step method, which that their approach works better than we had anticipated. Still, our results allow one to gain some additional insights into the process. Two locations of maximum dissolution rates are found: one near the aquifer bottom and one near the discharge area, with some residual dissolution occurring throughout the rest of the mixing zone. In general, dissolution tends to concentrate at the freshwater side of the mixing zone, except at the discharge area, where dissolution is maximum near the saline side. This contrasts with Sanford and Konikow's results, but agrees with calcite subsaturation observed in some blue holes from Bahamas (Whitaker and Smart, 1997). Dissolution rates in this area are consistently larger than elsewhere and can be very high. Results are relatively robust with respect to dispersivity, which is fortunate because of the uncertainties in assigning this parameter. Moreover, heterogeneities would cause dissolution to be uneven along the coast. This would lead to three-dimensional effects, causing flow from adjacent flow lines to concentrate in the locations of initial dissolution. The result would be dissolution rates even higher than those predicted here.