Geochemistry, Groundwater and Pollution: "Learning by Modeling"

C.A.J. Appelo[1], A. Dimier[2]

[1]*Hydrochemical Consultant, Amsterdam, Netherlands, appt@xs4all.nl*

[2]*Andra, Chatenay Malabry, France*

1 INTRODUCTION

Predicting the fate of chemicals that leach from waste deposits and deciphering their transport in the invisible subsoil must rely on 1) understanding the pattern of groundwater flowlines and travel times, 2) insight in the chemical reactions which retard the solutes, and 3) the quality of the database of the geochemical model. Inhomogeneities in an aquifer can be deduced from tritium/helium age profiles with depth, and otherwise from costly tracer experiments. The retardation of heavy metals is illustrated for a case of acid mine drainage from a former uranium mine. In addition to retardation by sorption, U(6) may disperse into confining layers where it reduces to U(3) and precipitates. Lastly, a model is presented for the release of arsenic in Bangladesh groundwater. With a recently defined carbonate surface complex in the database, carbonate appears important for displacing sorbed arsenic to poisonous aqueous concentrations.

2 TRANSPORT, tritium/helium age dating unravels irregularities

The flowlines in a phreatic aquifer may follow the pattern shown in Figure 1. In the homogeneous case, the age of water varies with depth according to:

$$t = \frac{-D\varepsilon_w}{P}\ln\left(1 - \frac{d}{D}\right)$$

where t is time (yr), D is thickness of the aquifer (m), ε_w is water-filled porosity (-), P is recharge (m/yr), and d is depth (m) (Appelo and Postma, 2004). However, the ages calculated from radioactive decay of ^3H to its daughter ^3He in borehole DFG1 deviate from the ideal line for a homogeneous aquifer (fig. 1). The water is too old in the upper part and too young in the lower part, and seems mixed over depth. Clearly, the aquifer is not homogeneous, although the sediment samples indicate a uniform sand. We can, with a few simple formulas, derive the flow properties of the inhomogeneity that may explain the observed ages. For example,
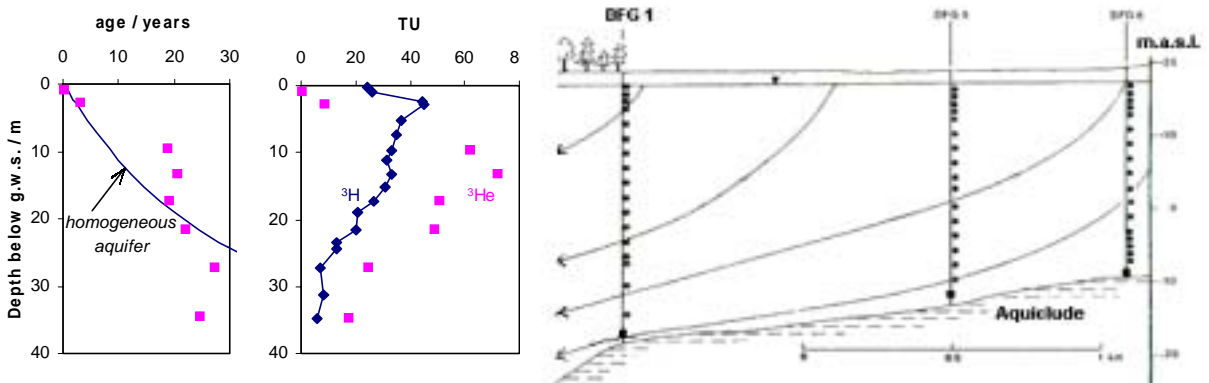

Figure 1. Regular flowlines in a phreatic aquifer (right) are contradicted by the age profile calculated from tritium/helium measurements in borehole DFG 1 (modified from Leuchs, 1988).

mixing over half of the depth in borehole DFG1 (about 18 m) requires a flowpath of $L = (18/2)^2 / 2\alpha = 810$ m, for a (vertical) transversal dispersivity $\alpha = 0.05$ m. We can also estimate that the zone upstream, where mixing takes place, has a permeability that is $(D - z) / z$ larger than of the average sediment, z being the thickness of the permeable layer. These numbers are useful for initiating a hydrogeological model in which irregularities are tried out and distributed over the section to simulate the observed age pattern. However, an exact and detailed flowpattern requires a much denser net of boreholes.

3 RETARDATION of U(6) and Zn from acid mine drainage

After closure of the uranium mine at Königstein (G), the acid mine drainage will enter the aquifer above the mine and flow towards the Elbe river (Bain et al., 2001). We like to predict how quickly the heavy metals and uranium advance and whether they are retarded with respect to water flow, $v_i = v_{H_2O} / R$. 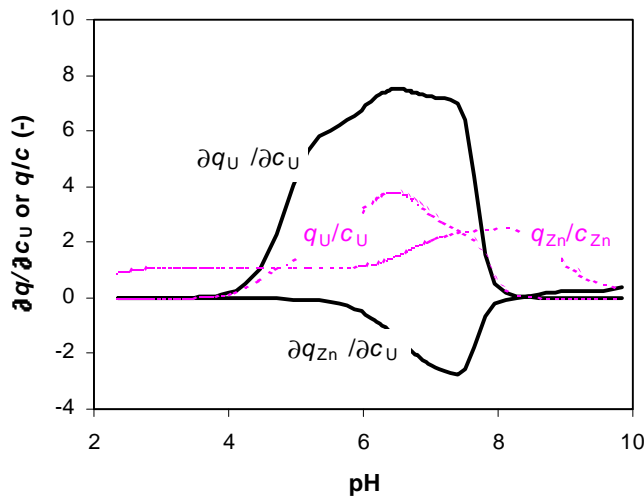Traditionally, retardation is calculated from $R = 1 + q/c$, where q is sorbed and c is solute concentration (mol/L). However, for transport the flushing factors given by $(\partial q_i / \partial c_j)_{i \neq j}$ should be considered (the slope of the isotherm if $j = i$), rather than the distribution coefficient $K_d = q/c$.

In the Königstein case the distribution coefficients differ markedly from the flushing factors, shown for Zn and U(6) as function of pH in Figure 2. In the calculations, the mine water composition of Bain et al. was used and the WATEQ4F database of PHREEQC (Parkhurst and Appelo, 1999), with the exchange and surface complexation capacity set to $X^- = 50$ mM, Hfo_w = 2 mM and Hfo_s = 0.05 mM.

The distribution coefficient of Zn is determined by ion exchange at low pH, increases at intermediate pH's by sorption on iron-oxyhydroxides, and dwindles again at high pH through aqueous complexation. The distribution coefficient of U(6) shows the same pattern but is zero at low pH since the element is not exchanged (at least not in the WATEQ4F database). The slope $(\partial q_U / \partial c_U)_{i \neq U}$ is higher than K_d, indicating a concave isotherm for U(6) (at a fixed pH). Consequently, the U(6) front will be sharpening when concentrations decrease. On the other hand, for Zn

Figure 2. Distribution coefficients (q_i/c_i, dotted lines) and flushing factors (($\partial q_i / \partial c_U)_{i \neq U}$, full lines) for Zn and U(6) in acid mine drainage as function of pH.
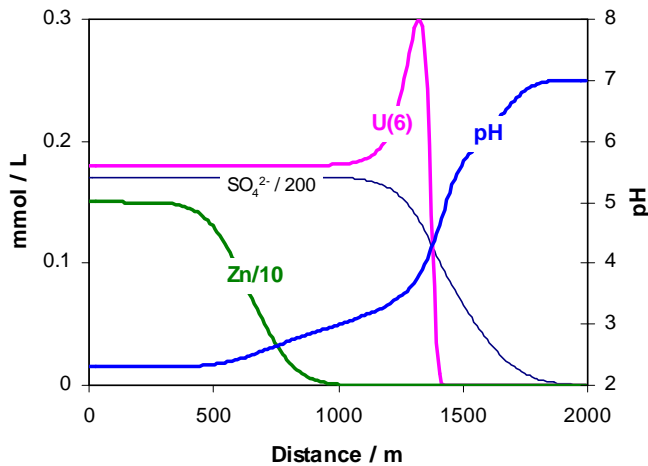

Figure 3. Concentrations of SO_4^{2-}, Zn^{2+}, U(6) and pH from acid mine drainage along a flowline calculated with PHREEQC-2.

the slope $(\partial q_{Zn} / \partial c_U)_{i \neq U}$ is negative in the pH range where U competes with Zn for sorption sites with an even stronger effect than of Zn itself.

The calculated concentrations along a flowline (fig. 3) show almost conservative behavior for SO_4^{2-} and a retardation of 2.1 for Zn by ion exchange (the retardation is not affected by U in the low pH range, cf. Figure 2). The concentration of U shows an increase as if a heap of snow is pushed up in front of a snowplough. The typical shape is related to the pH variation at the front. Uranium is sorbed at neutral pH, but as the pH decreases to below 4 in the acid mine water, U is desorbed again, and the decreasing concentration gives a sharp front.
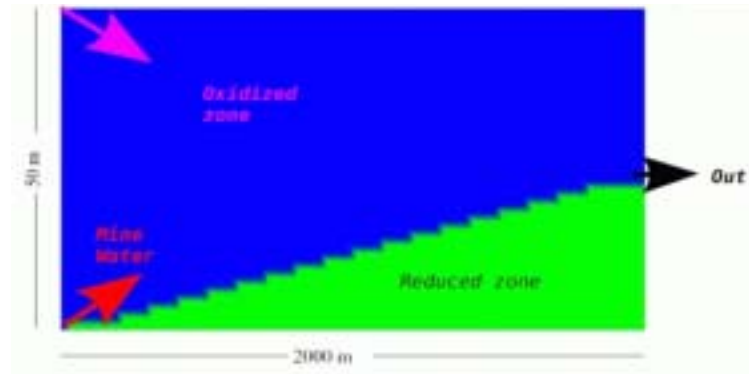

Figure 4. Outline of the model aquifer. The reduced zone contains pyrite.

A completely different picture is predicted for the aquifer, where the confining layers contain pyrite that reduces U(6) to U(3). The latter forms insoluble compounds which generates an infinite retardation for U. A rectangular cross-section of the aquifer, 50 * 2000 m above the Kˆnigstein mine was discretized in 40 * 100 cells for modeling with MT3D/PHREEQC (fig. 4). Acid mine water enters the section from the lower left corner and is accompanied by an equal flow of natural water from the upper left corner. The water leaves the section in the middle right. The lower right quarter, from the mine until the outflow cell contains pyrite.

The solute concentrations of U indicate the loss towards the reduced zone where coffinite precipitates, while at the front the snowplough effect appears (fig. 5). The contact with pyrite is determined by the vertical dispersivity, here taken to be 1 m. Probably, the translation towards the reduced zone enriched the strata with uranium in the geological past.
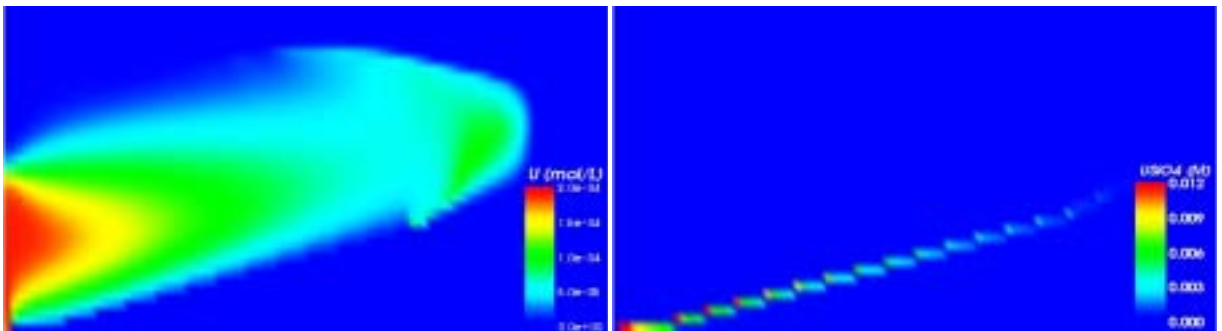

Figure 5. Modeled concentrations of U(6) in acid mine drainage entering an aquifer (left) and precipitation of USiO$_4$ (coffinite, right) at the border of the reduced zone. Calculated with Alliances, an MT3D/PHREEQC combination developed at Andra.
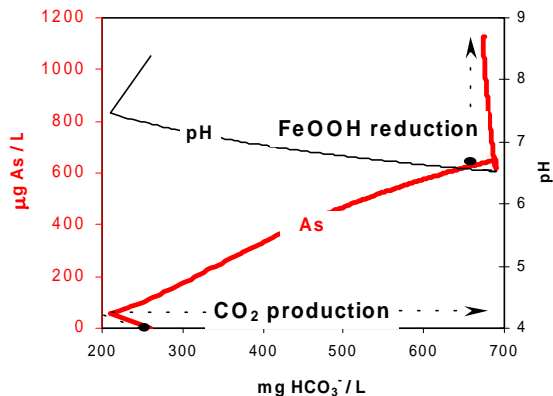
4 DATABASE, modeling the source of As in groundwater

Figure 6. Increasing HCO_3^- concentrations will desorb As from iron-oxyhydroxide (Appelo et al., 2002).

The model results crucially depend on the validity of the chemical reactions and associated constants in the database. The surface complex of HCO_3^- has been avoided by experimenters and was neglected in databases, but it is rather essential for modeling sorption variations of heavy metals in nature since it is the dominant anion in groundwater and competes with other solutes for surface sites. The release of As in Bangladesh aquifers has been explained by the reductive dissolution of iron-oxyhydroxide (Kinniburgh and Smedley, 2001). However, if we consider a flowline that infiltrates in a soil where organic matter is oxidized aerobically, the HCO_3^- concentration strongly increases and it may displace As from iron-oxyhydroxides which have sorbed the element from surface water, but at a much smaller HCO_3^- concentration (fig. 6). The figure shows that the increase of HCO_3^- by CO_2 production in the soil can be accompanied by increase of As to 600 ppb, far above the drinking water limit (cf. details in Appelo et al., 2002). In this case, the effect is only notable in the model calculations if the surface complexes of carbonate are included in the database.

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