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## **EQUILIBRIA IN SUBSURFACE FLUIDS WITH LINEAR INTERACTION BETWEEN DECAY AND SORPTION**

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*There are many situations in groundwater transport where sorption processes act at the same time. Equilibria of components in a decay chain, which are known for a single phase system, may remain valid in a multi-phase environment - but under certain circumstances only: the conditions are noted below. Analytical solutions are given for systems in which the single process idealization is not valid. Solutions are derived for cases of the coupled regime (1) of phase-dependent first order decay or degradation and (2) of linear phase exchange. In the description of two-phase equilibria, R-factors as a generalization of retardation factors are introduced. A mathematical relationship is derived between R-factors, decay-constants and concentration equilibria. For radionuclides, this allows the determination of retardation ratios from measured concentration ratios.*

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### **INTRODUCTION**

Equilibria between various components in a decay chain play a significant role in studies in geochemistry. Comparisons between measured and theoretically derived equilibria lead to a fundamental insight in complicated systems. In textbooks on isotope geochemistry only single-phase-systems are presented (Durrance, 1986, Lieser, 1989), despite the fact that geological processes almost always take place in multi-phase environments. The gap is filled by this paper. The following analysis is carried out for three phases: solid, fluid and gaseous. Interaction is considered between the solid and fluid phases only.

The equilibrium concept for components in a decay chain is generalized for multiphase systems with an interaction between decay and phase exchange. Special focus lies on concentrations in porous

media, where slow and fast desorption and adsorption interact with degradation processes. Degradation in this paper is understood as a generalized idea of decay as mass loss of first order. Thus, in the mathematical analysis decay-constants are assumed to be phase-dependent.

Section I tackles the differential equations governing multiphase transport processes. Section II provides analytical solutions with special focus on component equilibria. Separately treated are the cases of two components with equilibrium (Section II.1) and non-equilibrium (Section II.2) sorption, and of decay chains with more than two components (Section II.3). In the latter section some components may decay slowly and some quickly relative to the sorption processes.

## I. THEORETICAL BACKGROUND

The general theory for coupled processes of advection, diffusion, dispersion, sorption, decay, degradation and even reaction is very well established. The transport equation for a chain of  $n$  components in subsurface fluid flow is given by:

$$\begin{aligned} \varphi S \rho_f \frac{\partial c_f^1}{\partial t} &= L_T(c_f^1) - \varphi S \rho_f \lambda_f^1 c_f^1 + q^1 \\ \varphi S \rho_f \frac{\partial c_f^i}{\partial t} &= L_T(c_f^i) - \varphi S \rho_f \lambda_f^i c_f^i + \varphi S \rho_f \lambda_f^{i-1} c_f^{i-1} + q^i \end{aligned} \tag{I.1}$$

for  $i \in \{1, \dots\}$ .

The operator  $L_T$  contains all terms which are related to transport in a narrow sense: advection, dispersion and diffusion. They need not to be given in detailed form for the purpose of this paper (see Bear and Bachmat, 1991, Dagan, 1989). In this work the focus lies on systems in which transport processes are negligible:  $L_T \equiv 0$ .

The intermediate terms on the right hand sides of equations (I.1) are attributed to decay of the components  $i$  and  $i-1$ . The former is a loss, the latter a gain for the mass of component  $i$ . Component 1 is the mother component and is not produced by decay of another substance. There are various processes that can be described by these terms. Radioactive decay is just one in which component  $i$  is the daughter nuclide and component  $i-1$  denotes the mother nuclide. The decay constant for a radionuclide is universal. It undergoes no changes, not temporal, not spatial and not from one phase to the other. This does not hold for the other decay processes, such as biological or chemical degradation, which depend strongly on the geochemical environment.

The general sink/source term,  $q$ , contains various different processes. In this paper,  $q$  describes the phase interaction or the exchange between fluid and solid phase. It is a quantitative description of the balance between adsorption and desorption. In the case of dominant adsorption  $q$  is negative, in the case of dominant desorption  $q$  is positive. The concentration change in the solid phase thus is given by the equations:

$$\begin{aligned} (1 - \varphi) f(S) \rho_s \frac{\partial c_s^1}{\partial t} &= -(1 - \varphi) f(S) \rho_s \lambda_s^1 c_s^1 - q^1 \\ (1 - \varphi) f(S) \rho_s \frac{\partial c_s^i}{\partial t} &= -(1 - \varphi) f(S) \rho_s \lambda_s^i c_s^i + (1 - \varphi) f(S) \rho_s \lambda_s^{i-1} c_s^{i-1} - q^i \end{aligned} \tag{I.2}$$

The function  $f(S)$  (compare Bear and Bachmat, 1991) depends on the way liquid and gas fill the pore space in the unsaturated case. The nearby assumption is that the contact interface between fluid and the porous medium decreases proportionally with  $S$ ; then:  $f(S)=S$ . If the pore space is structured in a different way, such that even for low saturations the wetting phase covers the surfaces of the solid, the function  $f$  becomes almost constant:  $f=1$ .

Both equations (I.1) and (I.2) are derived from the mass conservation principle. They form the basis for all following analyses which differ only in additional assumptions. Note that decay or first order degradation may be different in both phases.

One assumption, which in many cases is justified, is that the sorption processes are fast compared with transport processes. Subsurface flow is mostly so slow that an equilibrium between fluid and solid phase is established everywhere at all times. If decay processes are slow as well, the equilibrium condition (isotherm)

$$c_s^i(c_f^i) \quad \text{for} \quad i \in \{1, \dots, n\} \tag{I.3}$$

is used to simplify the system of two differential equations. The isotherm does not depend on saturation as long as the solid phase concentration is defined for the solid medium in contact with water only. If  $c_s^i$  is defined for the entire solid phase, the equilibrium becomes saturation dependent (Bear and Bachmat 1991). In that case several conditions concerning the concentration in the solid phase which is not connected to water have to be fulfilled additionally.

Under the noted condition the corresponding equations (I.1) and (I.2) (after division by  $S$  and  $\rho_f$  and  $\rho_s$ ) are summed which results in:

$$\varphi R^1 \frac{\partial c_f^1}{\partial t} = L_T(c_f^1) - \tilde{R}^1 \lambda_f^1 c_f^1 \tag{I.4}$$

$$\varphi R^i \frac{\partial c_f^i}{\partial t} = L_T(c_f^i) - \tilde{R}^i \lambda_f^i c_f^i + \tilde{R}^{i-1} \lambda_f^{i-1} c_f^{i-1}$$

with

$$R^i = 1 + \frac{1-\varphi}{\varphi \gamma} \frac{\partial c_s^i}{\partial c_f^i} \quad \text{where} \quad \gamma = \frac{S}{f(S)} \frac{\rho_f}{\rho_s}$$

$$\tilde{R}^i = 1 + \frac{1-\varphi}{\varphi \gamma} \frac{\lambda_s^i}{\lambda_f^i} \frac{c_s^i}{c_f^i} \quad \text{for} \quad i \in \{1, \dots\} \tag{I.5}$$

The factors  $R^i$  and  $\tilde{R}^i$  are generalized retardation factors (in the following referred to as R-factors for component  $i$ ). In fact equation (I.4) shows that under the regime of sorption and decay there always occurs something more complicated than just retardation (in a strict sense the name is justified only when there is no decay or degradation).

Further simplifications are allowed under certain conditions. For example, if the linear isotherm describes the equilibrium between the fluid and solid phases

$$c_s^i = K_d^i \rho_f c_f^i \tag{I.6}$$

Equation (I.6) is the porous media analog to Henry's Law, which was set up for two-phase gas-fluid mixtures (Baehr and Stephan, 1993). The factor  $\rho_f$  has to be introduced, for  $c_f^i$  is given as mass ratio here, not mass/volume.

In order to determine concentrations as function of space and time from equations (I.1) and (I.2) directly, the exchange term has to be specified. In the simplest form  $q$  is a linear function of the concentration difference between the phases (with other coefficients, compare Corapcioglu, 1987):

$$q = \alpha^i S \rho_f (c_s^i - K_d^i \rho_s c_f^i) \quad (\text{I.7})$$

Note that  $K_d^i$  in (I.7) determines the interphase equilibrium state in correspondence with the linear isotherm. In unsaturated flow the transfer coefficient  $\alpha^i$  may depend on fluid saturation, but the concept is consistent for low saturations even if it is constant.

In the case of the linear isotherm (I.6) both R-factors are constant, in contrast to nonlinear isotherms where generalized retardations become dependent on concentration (Kinzelbach 1992):

$$R^i = 1 + \frac{1-\phi}{\phi} \rho_s K_d^i \quad \tilde{R}^i = 1 + \frac{1-\phi}{\phi} \frac{\lambda_s^i}{\lambda_f^i} \rho_s K_d^i \quad (\text{I.8})$$

The following remarks can be made.

1. These definitions make sense not only for the equilibrium sorption case. They can be used for slow sorption as well. If the interphase exchange term is defined as in (I.7) the  $K_d$ 's specify the equilibrium state independent of the sorption dynamics.

2. A special case is given when the adsorbed phase is not subject to any chemical transformation. In this case set  $\lambda_s^i = 0$  and the entire distribution of concentrations is identical to the case without any sorption but with reduced decay constant  $\lambda_f^i / R^i$  (this has already been noted by Wexler, 1992).

3. Of course, both definitions can be made for saturated and unsaturated flow. It is notable that their significance is the same under the given circumstances. In the linear sorption case there is no dependence of retardation on saturation.

Another assumption is that decay constants are not phase dependent. In fact this is true for radioactive decay, whereas it is usually not valid considering chemical or biological degradation processes. If both mentioned conditions are fulfilled then the following equation holds:

$$R^i = \tilde{R}^i = 1 + \frac{1-\phi}{\phi} \rho_s K_d^i \quad (\text{I.9})$$

This equation can be found in many textbooks as the *retardation factor* (Bear and Bachmat, 1991). As mentioned above, the term is not justified if there is a relevant degradation process. This can be easily demonstrated in the example of a single mother nuclide: the solutions for the pure decay and for the decay-sorption situations are the same, namely  $c_{f0} \exp(-\lambda^i t)$ . Thus there is no retardation.

## II. ANALYTICAL SOLUTIONS AND EQUILIBRIA

### II.1 Equilibrium sorption

There is a vast literature about analytical solutions for systems with coupled transport, decay and linear sorption (Kinzelbach, 1992). All solutions are derived under special conditions such as

uniform flow and single species. General cases can be treated by numerical methods only. Other authors, who focus on two or more component systems, neglect transport as the third major process (for example Lieser, 1980). In order to get an understanding of the main interaction between sorption processes and first order degradation/decay processes, this restriction is made for the following parts of this paper as well.

The simplest case is when there is fast linear sorption and global decay in a single porosity environment. If for a component in question there is no decaying mother component, the analytical solution for the concentration in a porous medium is just the same as in pure fluids or anywhere else. It is exponential decay described by the exponential function  $\exp(-\lambda_f^1 t)$ . If decay constants are different in both phases the generalized formula holds:

$$c_f^1 = c_{f0}^1 \exp\left(-\lambda_f^1 \frac{\tilde{R}^1}{R^1} t\right) \tag{II.1}$$

As a next step the concentration in presence of a mother component is studied.

The solution can be obtained under the assumption that  $c_f^2$  is a linear combination of

$\exp(-\lambda_f^2 \frac{\tilde{R}^2}{R^2} t)$  and  $\exp(-\lambda_f^1 \frac{\tilde{R}^1}{R^1} t)$ . Under the condition that both components are determined by their initial concentrations only, the explicit equation follows:

$$c_f^2 = \frac{\lambda_f^1 \tilde{R}^1}{\lambda_f^2 \tilde{R}^2 - \lambda_f^1 R^2 \frac{\tilde{R}^1}{R^1}} c_{f0}^1 \left( e^{-\lambda_f^1 \frac{\tilde{R}^1}{R^1} t} - e^{-\lambda_f^2 \frac{\tilde{R}^2}{R^2} t} \right) + c_{f0}^2 e^{-\lambda_f^2 \frac{\tilde{R}^2}{R^2} t} \tag{II.2}$$

The dynamics of the solution is given by two exponential functions in which the exponents are determined by the decay constants and the R-factors. Note that the influence of the R-factors in the exponents is only given when  $\lambda_f^j \neq \lambda_s^j$  for  $j \in \{1,2\}$ . But the coefficients of the exponential functions are affected even if decay constants in both phases are identical. Equation (II.1) can be used to rewrite equation (II.2) in the following way:

$$c_f^2 = \frac{\lambda_f^1 \tilde{R}^1}{\lambda_f^2 \tilde{R}^2 - \lambda_f^1 R^2 \frac{\tilde{R}^1}{R^1}} c_{f0}^1 \left( 1 - e^{-\left(\lambda_f^2 \frac{\tilde{R}^2}{R^2} - \lambda_f^1 \frac{\tilde{R}^1}{R^1}\right) t} \right) + c_{f0}^2 e^{-\lambda_f^2 \frac{\tilde{R}^2}{R^2} t} \tag{II.3}$$

If, in the initial state, the daughter-component is not present, the second term in the equation can be omitted. The ratio between daughter and mother concentration component becomes:

$$\frac{c_f^2}{c_f^1} = \frac{\lambda_f^1 \tilde{R}^1}{\lambda_f^2 \tilde{R}^2 - \lambda_f^1 R^2 \frac{\tilde{R}^1}{R^1}} \left( 1 - e^{-\left(\lambda_f^2 \frac{\tilde{R}^2}{R^2} - \lambda_f^1 \frac{\tilde{R}^1}{R^1}\right) t} \right) \tag{II.4}$$

The equilibrium between daughter and mother concentration which is approached after long times is thus given by:

$$\frac{c_f^2}{c_f^1} = \frac{\lambda_f^1 \tilde{R}^1}{\lambda_f^2 \tilde{R}^2 - \lambda_f^1 R^2 \frac{\tilde{R}^1}{R^1}} \quad (\text{II.5})$$

For radioactive decay ( $R^j = \tilde{R}^j$  for  $j \in \{1,2\}$ ) and the (transient) equilibrium becomes:

$$\frac{c_f^2}{c_f^1} = \frac{\lambda^1 R^1}{(\lambda^2 - \lambda^1) R^2} \quad (\text{II.6})$$

In generalization of the concept for radionuclides, the secular equilibrium can be defined for components with  $\lambda_f^1 \tilde{R}^1 / R^1 \ll \lambda_f^2 \tilde{R}^2 / R^2$ . Under this condition the equilibrium equations (II.5) and (II.6) can be simplified to:

$$\frac{c_f^2}{c_f^1} = \frac{\lambda_f^1 \tilde{R}^1}{\lambda_f^2 \tilde{R}^2} \quad \text{and} \quad \frac{c_f^2}{c_f^1} = \frac{\lambda^1 R^1}{\lambda^2 R^2} = \frac{R^1 \tau^2}{R^2 \tau^1} \quad \text{for radionuclides} \quad (\text{II.7})$$

Some comments on these results:

1. The equilibrium between mother and daughter component concentrations in the fluid phase is influenced by sorption in any case, where R-factors for both components are different. For radioactive decay this result was already formulated by Hadermann and Petry (1980).

2. The result is derived under the assumption that there is no transport. The R-factors are defined in the same way as retardation factors in the transport description.

3. In general, equilibria are determined by:  $\lambda_f^1 / \lambda_f^2, K_d^1, K_d^2, \lambda_s^1 / \lambda_f^1, \lambda_s^2 / \lambda_f^2$ .

4. A generalization of the equilibria states for nuclide chains with more than two components is given below.

5. In order to distinguish the equilibria given by equation (II.7) from the single phase equilibrium (compare Lieser, 1980 or equation (II.18)) in the following, this will be referred to as porous medium equilibrium (for fluid phase).

6. For linear fast sorption, the steady state ratio of concentrations in the solid phase can be derived from equation (II.7) by using the defining equations (I.8) for the R-factors:

$$\frac{c_s^2}{c_s^1} = \frac{K_d^2 c_f^2}{K_d^1 c_f^1} = \frac{K_d^2 \lambda_f^1 \tilde{R}^1}{K_d^1 \lambda_f^2 \tilde{R}^2} = \frac{\lambda_s^1 (\tilde{R}^2 - 1) \tilde{R}^1}{\lambda_s^2 (\tilde{R}^1 - 1) \tilde{R}^2} \approx \frac{\lambda_s^1}{\lambda_s^2} \quad (\text{II.8})$$

The last equality holds approximately if retardations are much greater than 1 (which is fulfilled for most radionuclides in several porous media). Thus the solid phase equilibria are the same in single-phase and in two-phase environments.

7. In contrast to the single-phase case, two-phase equilibria have to be “corrected” by the ratio of retardations. If the retardation of the daughter nuclide is greater than the retardation of the mother nuclide, the daughter concentration will be smaller in the two-phase situation and vice versa. Ratios discovered as “disequilibria” in single-phase systems may thus in reality be equilibria in two-phase systems.

## II.2 Non-equilibrium sorption

The former results were derived under the assumption that sorption is a fast process compared to other regimes, especially decay. This may not be true in some applications. Radioactive decay in all decay chains spreads over various timescales (see example in Section II.3).

The question is whether the equilibria derived above remain valid for very fast decaying daughters as well or if they are changed by the different nature of the processes. For an answer the starting point is equations (I.1) to (I.3). If transport can be neglected the following system of two linear equations results:

$$\frac{\partial}{\partial t} \begin{pmatrix} c_f^i \\ c_s^i \end{pmatrix} = \begin{pmatrix} -\left( \lambda_f^i + \frac{\alpha^i K_d^i \rho_f}{\phi} \right) & \frac{\alpha^i}{\phi} \\ \frac{\lambda^i \alpha^i \gamma K_d^i \rho_f}{1-\phi} & -\left( \lambda_s^i + \frac{\alpha^i \gamma}{1-\phi} \right) \end{pmatrix} \begin{pmatrix} c_f^i \\ c_s^i \end{pmatrix} + \begin{pmatrix} \lambda_f^{i-1} c_f^{i-1} \\ \lambda_s^{i-1} c_s^{i-1} \end{pmatrix} \quad (\text{II.9})$$

The eigenvalues of the matrix on the right hand side are given by:

$$\mu_{1,2}^i = \frac{1}{2} \left[ -\left( \lambda_f^i + \lambda_s^i + \alpha^i \left( \frac{K_d^i \rho_f}{\phi} + \frac{\gamma}{1-\phi} \right) \right) \pm \sqrt{\left( \lambda_f^i - \lambda_s^i + \alpha^i \left( \frac{K_d^i \rho_f}{\phi} - \frac{\gamma}{1-\phi} \right) \right)^2 + \frac{4(\alpha^i)^2 \gamma K_d^i \rho_f}{\phi(1-\phi)}} \right] \quad (\text{II.10})$$

In the following, the assumption will be made that halflives in solid and fluid phases are equal.

Under this condition the decay constants can be written simply as  $\lambda^i$  and R-factors as  $R^i$  (for  $i \in \{1, \dots\}$ ). Then one of the eigenvectors given by equation (II.10) becomes equal to  $\lambda^i$ . The other one (denoted simply  $\mu^i$ ) is given by:

$$\mu^i = \lambda^i + \alpha^i \left( \frac{K_d^i \rho_f}{\phi} + \frac{\gamma}{1-\phi} \right) = \lambda^i + \frac{\alpha^i \gamma R^i}{1-\phi} \quad (\text{II.11})$$

Obviously the relation  $\lambda^i \leq \mu^i$  is valid under all circumstances. The general solution of the homogeneous system can be formulated by use of the eigenvectors:

$$\vec{c}_{\text{hom}}^i = c_1^i \begin{pmatrix} 1 \\ K_d^i \rho_f \end{pmatrix} e^{-\lambda^i t} + c_2^i \begin{pmatrix} 1 \\ \frac{-\phi \gamma}{1-\phi} \end{pmatrix} e^{-\mu^i t} \quad \text{for } \vec{c} = \begin{pmatrix} c_f \\ c_s \end{pmatrix} \quad (\text{II.12})$$

$c_1^i$  and  $c_2^i$  are constants which have to be determined by the boundary conditions.

While the solution in the fast sorption case is a linear combination only from the first exponential function, in the slow sorption case another exponential term is added. Note that this additional term decays faster than the former one.

In order to get a special solution of the inhomogeneous system (II.9) assumptions have to be made concerning the concentration development of the mothernuclide. For the following, the case will be treated that component 1 is the first component of a chain and reaches equilibrium between phases:

$$c_f^1 = c_{f0}^1 e^{-\lambda^1 t} \quad \text{and} \quad c_s^1 = K_d^1 \rho_f c_{f0}^1 e^{-\lambda^1 t} \quad (\text{II.13})$$

Then a solution for the inhomogeneous system can be derived as a combination of the eigenvectors:

$$\bar{c}_{in\,hom}^2 = \left[ \frac{\lambda^1}{\lambda^2 - \lambda^1} \frac{R^1}{R^2} \begin{pmatrix} 1 \\ K_d^2 \rho_f \end{pmatrix} + \frac{\lambda^1}{\mu^2 - \lambda^1} \frac{R^2 - R^1}{R^2} \begin{pmatrix} 1 \\ -\frac{\phi\gamma}{1-\phi} \end{pmatrix} \right] c_{f0}^1 e^{-\lambda^1 t} \quad (\text{II.14})$$

For the daughter component the general solution is given by the sum of equations (II.12) and (II.14). If at initial time  $t=0$  there is a separation of nuclides, i.e. the concentration of the daughter is zero, the solution can be written as follows:

$$\bar{c}^2 = c_{f0}^1 \left[ \frac{\lambda^1}{\lambda^2 - \lambda^1} \frac{R^1}{R^2} (e^{-\lambda^1 t} - e^{-\lambda^2 t}) \begin{pmatrix} 1 \\ K_d^2 \rho_f \end{pmatrix} + \frac{\lambda^1}{\mu^2 - \lambda^1} \frac{R^2 - R^1}{R^2} (e^{-\lambda^1 t} - e^{-\mu^2 t}) \begin{pmatrix} 1 \\ -\frac{\phi\gamma}{1-\phi} \end{pmatrix} \right] \quad (\text{II.15})$$

From equations (II.13) and (II.15) a equation for the transient equilibrium follows:

$$\frac{c_f^2}{c_f^1} = \frac{\lambda^1}{\lambda^2 - \lambda^1} \frac{R^1}{R^2} + \frac{\lambda^1}{\mu^2 - \lambda^1} \frac{R^2 - R^1}{R^2} = \frac{\lambda^1}{R^2} \left( \frac{R^1}{\lambda^2 - \lambda^1} + \frac{R^2 - R^1}{\mu^2 - \lambda^1} \right) \quad (\text{II.16})$$

The secular equilibrium is given by:

$$\frac{c_f^2}{c_f^1} = \frac{\lambda^1}{R^2} \left( \frac{R^1}{\lambda^2} + \frac{R^2 - R^1}{\mu^2} \right) \quad (\text{II.17})$$

It is easy to see that there are two extreme cases of equilibria:

(i) Exchange between phases is fast. Then the transfer coefficient is quite high and  $\lambda^2 \ll \mu^2$ .

That is, in equations (II.15) and (II.16), the second term can be omitted. Consistent with the results obtained above, these equilibria are identical to the ones described in equations (II.6) and (II.7).

(ii) There is no connection between solid and fluid phase, which results in  $\lambda^2 = \mu^2$ . For the transient and the secular equilibrium:

$$\frac{c_f^2}{c_f^1} = \frac{\lambda^1}{\lambda^2 - \lambda^1} \quad \text{and} \quad \frac{c_f^2}{c_f^1} = \frac{\lambda^1}{\lambda^2} \quad (\text{II.18})$$

These equations obviously describe the no-sorption or single-phase case for which equilibria given by (II.18) are well-known (see Lieser 1989).

Generally the value of  $\mu^2$  as defined in equation (II.11) determines the equilibrium state. The relation between decay constant on one side and the ratio  $\alpha^i \gamma R^i / (1 - \phi)$  on the other side (both have physical dimension [1/time]) is relevant here. If both are equal, the secular equilibrium is reached in the middle between the special cases (i) and (ii). To see this easily, equation (II.16) is rewritten as:



$$\frac{c_f^2}{c_f^1} = \frac{\lambda^1}{\lambda^2 - \lambda^1} \left[ \beta + \frac{R^1}{R^2} (1 - \beta) \right] \quad \text{with} \quad \beta = \frac{\lambda^2 - \lambda^1}{\lambda^2 + \frac{\alpha^2 \gamma R^2}{1 - \phi} - \lambda^1} \quad (\text{II.19})$$

Concerning the situation mentioned above,  $\beta$  becomes 0.5. In Figure 1 the equilibrium is presented as function of  $\beta$ . Note that for a secular equilibrium,  $\beta$  is given by the ratio  $\lambda^2/\mu^2$ .

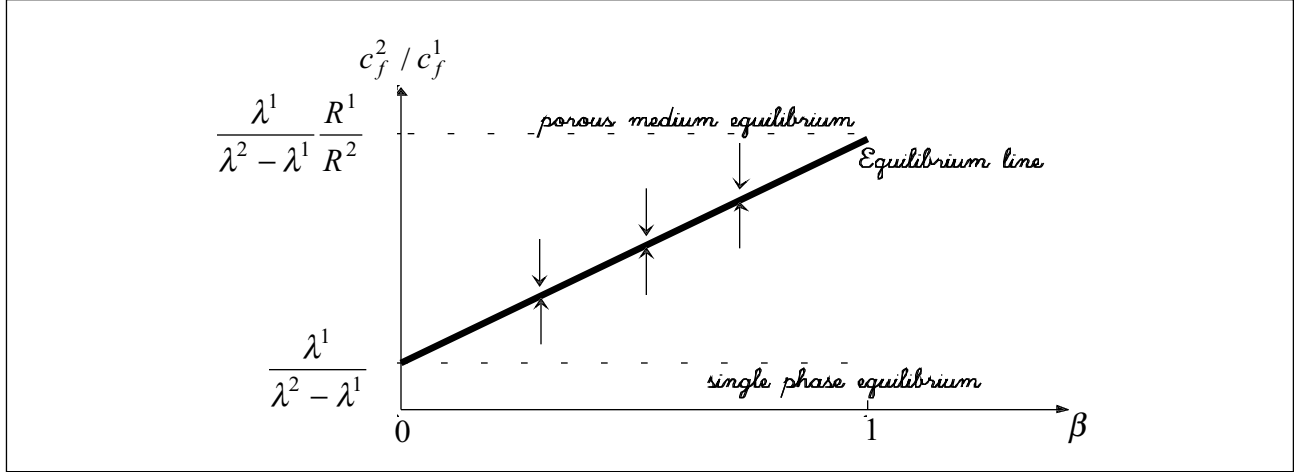


Figure 1. Concentration ratio at equilibrium as a function of  $\beta$  (see equation II.19) for daughter-components with decay and sorption at the same timescale.

In order to get a more obvious criterion, the obtained functions are now compared with the solution for the case of pure slow sorption, which is:

$$\bar{c} = c_1 \left( \frac{1}{K_d \rho_f} \right) + c_2 \left( \frac{1}{-\phi \gamma} \right) e^{-\frac{\alpha \gamma R}{1 - \phi} t} \quad (\text{II.20})$$

The first term obviously specifies the equilibrium state, while the second describes the transient dynamics. In analogy to the halflife concept for decay processes, a “half-decline-time”  $\hat{\tau}_{1/2}$  can be introduced for non-equilibrium sorption as well:

$$\hat{\tau}_{1/2} = \frac{(1 - \phi) \ln(2)}{\alpha \gamma R} \quad (\text{II.21})$$

Then the above described equilibrium state  $\beta = 0.5$  is equivalent to

$$\tau_{1/2}^2 = \hat{\tau}_{1/2}^2 \quad (\text{II.22})$$

Thus halflife and slow sorption “half-decline time” can be compared directly and the following criteria for the secular equilibria states are obtained:

$$\begin{aligned} \text{If } \tau_{1/2}^2 \ll \hat{\tau}_{1/2}^2 & \text{ then eq. (II.18) applies} \\ \text{If } \tau_{1/2}^2 \gg \hat{\tau}_{1/2}^2 & \text{ then eq. (II.7) applies} \end{aligned} \quad (\text{II.23})$$

### II.3 Decay chains

As a next step, the validity of the equilibria state descriptions will be analyzed for a linear chain of decaying components. The halflife of the (first) mother component may be largest of all. Thus a

solution of equation (II.9) has to be found where the component  $i-1$  for long times can be described as:

$$\bar{c}^{i-1} = \begin{pmatrix} A_f^{i-1} \\ A_s^{i-1} \end{pmatrix} e^{-\lambda^1 t} \quad (\text{II.24})$$

Note that for  $i=2$  and  $i=3$  this representation has been proven already: see equations (II.1) and (II.14) and neglect terms in equations (II.2) and (II.12) under the condition  $\lambda^1 < \lambda^2$ . Thus, for the following argument, coefficients  $A_f^{i-1}, A_s^{i-1}$  may be given. In order to solve equation (II.9) the approach (II.12) can be made again, which finally leads to the following recursion equations for  $A_f^i, A_s^i$ :

$$A_f^i = \frac{\lambda^{i-1}}{R^i} \left( \frac{A_f^{i-1} + \frac{1-\varphi}{\varphi} A_s^{i-1}}{\lambda^i - \lambda^1} + - \frac{A_f^{i-1}(R^i - 1) - \frac{1-\varphi}{\varphi} A_s^{i-1}}{\mu^i - \lambda^1} \right)$$

$$A_s^i = \frac{\lambda^{i-1}}{R^i} \frac{\varphi}{1-\varphi} \left( \frac{A_f^{i-1} + \frac{1-\varphi}{\varphi} A_s^{i-1}}{\lambda^i - \lambda^1} (R^i - 1) - \frac{A_f^{i-1}(R^i - 1) - \frac{1-\varphi}{\varphi} A_s^{i-1}}{\mu^i - \lambda^1} \right) \quad (\text{II.25})$$

Applying the relations  $c_s^{i-1} / c_f^{i-1} = A_s^{i-1} / A_f^{i-1} = (R^{i-1} - 1)\varphi / (1 - \varphi)$ , which are derived from the equilibrium state, there results a recursion equation for  $c_f^i$  and  $c_s^i$ . For the concentration ratios at equilibria results:

$$\frac{c_f^i}{c_f^{i-1}} = \frac{A_f^i}{A_f^{i-1}} = \frac{\lambda^{i-1}}{R^i} \left( \frac{R^{i-1}}{\lambda^i - \lambda^1} + \frac{R^i - R^{i-1}}{\mu^i - \lambda^1} \right) \quad (\text{II.26})$$

$$\frac{c_s^i}{c_s^{i-1}} = \frac{A_s^i}{A_s^{i-1}} = \frac{\lambda^{i-1}}{R^i (R^{i-1} - 1)} \left( \frac{R^{i-1}(R^i - 1)}{\lambda^i - \lambda^1} - \frac{R^i - R^{i-1}}{\mu^i - \lambda^1} \right) \quad (\text{II.27})$$

Using equations (II.26) and (II.27), an equation for transient and secular equilibria can be obtained for chains where, for some components, halflives are greater than sorptive transfer times and for some others, smaller. Only some special cases will be treated in the following.

If decay is slow compared to sorption for all components in the chain the recursions can be simplified. The second terms in the brackets can be omitted (for  $\mu^i \rightarrow \infty$ ).

$$\frac{c_f^i}{c_f^{i-1}} = \frac{\lambda^{i-1}}{\lambda^i - \lambda^1} \frac{R^{i-1}}{R^i} \quad (\text{II.28})$$

From this it can easily be proven that the following equations hold for the transient and secular equilibrium of component  $i$ :

$$\frac{c_f^i}{c_f^1} = \frac{\lambda^1 \dots \lambda^{i-1}}{(\lambda^2 - \lambda^1) \dots (\lambda^i - \lambda^1)} \frac{R^1}{R^i} \quad \text{and} \quad \frac{c_f^i}{c_f^1} = \frac{\lambda^1 R^1}{\lambda^i R^i} \quad (\text{II.29})$$

For nuclide chains in terms of activities, it means that the product of retardation and activity is the same for all components of the static fluid filling the pore space. They are generalizations of equations (II.6) and (II.7), i.e. they are the porous medium equilibria for decay chains. For transient and secular equilibria of two ( $i > j$ ) components in the chain, it follows from (II.29):

$$\frac{c_f^i}{c_f^j} = \frac{\lambda^{j+1} \dots \lambda^{i-1}}{(\lambda^{j+1} - \lambda^1) \dots (\lambda^i - \lambda^1)} \frac{R^j}{R^i} \quad \text{and} \quad \frac{c_f^i}{c_f^j} = \frac{\lambda^j R^j}{\lambda^i R^i} \quad (\text{II.30})$$

If for one element there are two components in a chain, the secular equilibrium remains the same as in the single process case, for retardations are dependent on the chemical characteristic of a component only ( $R^i = R^j$ ). Thus disequilibria of uranium or thorium (mentioned by Rosholt, 1959, Fleischer and Raabe, 1978, Osmond, 1980) cannot be explained by the presented approach.

Equation (II.29) is valid, if for all components in the chain, decay is much slower than phase exchange. How equilibria change if this is not true for only one component is demonstrated by the following example.

The chain Ra-228, Ac-228, Th-228 is considered, for which half-lives are given in Table 1.

Table 1. Half-lives for example radionuclides

Component	Half-life
Ra-228	5.75 a
Ac-228	6.13 h
Th-228	1.19 a

In the following it is assumed that in a porous medium the sorption equilibrium for Ac-228 cannot be reached within some days. Thus, for the first two components, a single phase equilibrium according to equation (II.18) will be reached in long times. The Th-228 equilibrium can be calculated using recursion equation (II.26):

$$\frac{c_f^{Th}}{c_f^{Ra}} = \frac{c_f^{Th}}{c_f^{Ac}} \frac{c_f^{Ac}}{c_f^{Ra}} = \frac{\lambda^{Ac}}{\lambda^{Th} - \lambda^{Ra}} \frac{R^{Ac}}{R^{Th}} \frac{\lambda^{Ra}}{\lambda^{Ac}} = \frac{\lambda^{Ra}}{\lambda^{Th} - \lambda^{Ra}} \frac{R^{Ac}}{R^{Th}} \quad (\text{II.31})$$

In comparison with equation (II.29), the ratio of R-factors becomes different. Obviously retardation ratios do not cancel all as they do in the step from equation (II.28) to equation (II.29). Nevertheless by use of equation (II.26), equilibria can be determined for general chains of decaying components, if half-lives and special retardation factors are given.

If there is just one fast decaying component  $j$  in a chain from a mother nuclide down to component  $i > j$ , the recursion equation (II.25) can be applied several times and the secular equilibrium becomes:

$$\frac{c_f^i}{c_f^1} = \frac{\lambda^1 R^1}{\lambda^2 R^2} \cdots \frac{\lambda^{j-2} R^{j-2}}{\lambda^{j-1} R^{j-1}} \cdot \frac{\lambda^{j-1}}{\lambda^j} \cdot \frac{\lambda^j R^j}{\lambda^{j+1} R^{j+1}} \cdots \frac{\lambda^{i-1} R^{i-1}}{\lambda^i R^i} = \frac{\lambda^1 R^1}{\lambda^i R^i} \frac{R^j}{R^{j-1}} \quad (\text{II.32})$$

Generalized retardations for components with fast decay are hard to determine. Thus the equations derived in this work may not be useful for the determination of equilibria in long chains. However it is important to know that concentration ratios at equilibrium depend on the R-factors. Moreover, besides the decay constants they depend *only* on the R-factors.

### CONCLUDING REMARKS

Equilibria in two-phase systems may be different from single phase systems. Steady state concentration ratios are not determined solely by decay constants, but as well by retardation factors. Additionally the timescale in approaching the equilibrium state may be different. Formulae for concentration ratios, as obtained above, can be applied to calculate component equilibria for two-phase systems in which exchange processes are faster or slower than degradation processes.

Tables 2 and 3 give an overview on transient and secular concentration ratios in the equilibrium state. The line labeled “slow decay” contains results for systems where decay is slower than sorption, as usually assumed in equilibrium sorption applications. The line labeled “fast decay” presents results for systems where decay is faster than sorption. In Table 3 phase dependent decay constants are considered, while ratios in Table 2 are derived for constant degradation. Labels of equations in the text above are given in brackets.

Table 2. Transient equilibria for a two nuclide system (1 : mother, 2 : daughter)

System	$c_f^2 / c_f^1$	$c_s^2 / c_s^1$	$a_f^2 / a_f^1$	$a_s^2 / a_s^1$	Timescale
Single phase No exchange	$\lambda^1 / (\lambda^2 - \lambda^1)$ (II.18)	$\lambda^1 / (\lambda^2 - \lambda^1)$	$\lambda^2 / (\lambda^2 - \lambda^1)$	$\lambda^2 / (\lambda^2 - \lambda^1)$	$\exp(-(\lambda^2 - \lambda^1)t)$
Two phase Slow decay	$\lambda^1 R^1 / (\lambda^2 - \lambda^1) R^2$ (II.6)	$\lambda^1 / (\lambda^2 - \lambda^1)$	$\lambda^2 R^1 / (\lambda^2 - \lambda^1) R^2$	$\lambda^2 / (\lambda^2 - \lambda^1)$	$\exp(-(\lambda^2 - \lambda^1)t)$
Two phase Fast decay	$\lambda^1 / (\lambda^2 - \lambda^1)$ (II.16)	$\lambda^1 / (\lambda^2 - \lambda^1)$	$\lambda^2 / (\lambda^2 - \lambda^1)$	$\lambda^2 / (\lambda^2 - \lambda^1)$	$\exp(-(\lambda^2 - \lambda^1)t)$

Table 3. Secular equilibria for a two component system (1 : mother, 2 : daughter)

System	$c_f^2 / c_f^1$	$c_s^2 / c_s^1$	$a_f^2 / a_f^1$	$a_s^2 / a_s^1$	Timescale
Single phase No exchange	$\lambda_f^1 / \lambda_f^2$ (II.18)	$\lambda_s^1 / \lambda_s^2$	1	1	$\exp(-\lambda_f^2 t), \exp(-\lambda_s^2 t)$
Two phase No exchange	$\lambda_f^1 \tilde{R}^1 / \lambda_f^2 \tilde{R}^2$ (II.7)	$\lambda_s^1 / \lambda_s^2$ (II.8)	$\tilde{R}^1 / \tilde{R}^2$	1	$\exp(-(\lambda_f^2 \tilde{R}^2 / R^2) t)$
Two phase Fast decay	$\lambda_f^1 / \lambda_f^2$ (II.17)	$\lambda_s^1 / \lambda_s^2$	1	1	$\exp(-(\lambda_f^2 \tilde{R}^2 / R^2) t)$

In the solid phase equilibria of components in a decay chain,  $c_s^2 / c_s^1$  are not different from ratios in single phase systems. Fluid phase equilibria of components are different, because mostly retardation factors and R-factors are not the same. The results of this paper may explain measured concentrations, which do not agree with classical concentration ratios, if a fluid phase is involved in the pathline of the measured components.

For example, it is very unlikely for radioactive hot spring deposits or oil- and gas-field brines to contain concentrations in ratios equal to the equilibria at their subsurface origin. Rosholt (1959) classifies this phenomenon as a “disequilibrium type”. As shown above, the measured values could be explained as a two-phase equilibrium.

Moreover the analysis of this paper can be useful in reverse. Observed concentration ratios in groundwater provide hints on the value of retardations which are effective in a subsurface system.

### **Explanation of Terms:**

$a_f^i$	radioactivity of nuclide $i$	[Bq]
$c_f^i$	fluid phase concentration of component $i$	[mol/kg]
$c_s^i$	solid phase concentration of component $i$	[mol/kg]
$K_d^i$	fast sorption distribution coefficient for component $i$	[m <sup>3</sup> /kg]
$q^i$	phase exchange for component $i$	[mol/s]
$R^i$	retardation factor for component $i$	[1]
$R^i$	generalized retardation factor for component $i$	[1]
$S$	saturation	[1]
$\alpha^i$	slow sorption transfer coefficient for component $i$	[1/s]
$\varphi$	porosity	[1]
$\lambda^i$	radioactive decay constant for nuclide $i$	[1/s]
$\lambda_f^i$	fluid phase decay constant for component $i$	[1/s]
$\lambda_s^i$	solid phase decay constant for component $i$	[1/s]
$\rho_f$	fluid phase density	[kg/m <sup>3</sup> ]
$\rho_s$	solid phase density	[kg/m <sup>3</sup> ]
$\tau^i$	half-life for radionuclide $i$	[s]
$\hat{\tau}^i$	half-decline time for non-equilibrium sorption of comp. $i$	[s]

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