Using a generalised Power Law for simulating the feedback effect of dissolution/precipitation on diffusive transfer in ToughReact

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USING A GENERALISED POWER LAW FOR SIMULATING THE FEEDBACK EFFECT OF DISSOLUTION/PRECIPITATION ON DIFFUSIVE TRANSFER IN TOUGHREACT

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ABSTRACT

In the case of variable porosity calculations (due to precipitation/dissolution in a calculation coupled with chemistry), the permeability and diffusion coefficients in different porous media vary with porosity. In the case of nuclear waste storage, solute transport is supposed to be diffusion-controlled because of the extremely low permeability of surrounding materials, like concrete or clay. Various experiments and also different reactive transport modeling show a possible clogging due to the alkaline perturbation at the concrete/bentonite or concrete/clay interfaces (Gaucher et al., 2004; Burnol et al. 2006; Trotignon et al., 2007; De Windt et al., 2008). The decrease of porosity will therefore impact the extent of diffusion of all chemical elements, including the radionuclides, through the engineered and geological barriers. Taking into account the feedback effect of porosity change due to the chemical reactivity is therefore an important issue to simulate the migration of radionuclides out of the disposal drift. The chemical conditions found in deep nuclear waste storage rise some concern about the migration of radionuclides at the interface between the engineered and geological barriers where the alkaline perturbation could cause a "clogging" and therefore could impact the diffusion-controlled process itself.In this poster, a new general "Power Law" which connects the effective diffusion coefficient and the porosity evolution is described and tested. The conclusion is that if the version V1.0/V1.2 is used to study the diffusion of radionuclides in the surrounding zone of a waste nuclear disposal, the effective diffusion could be overestimated even with the Millington Law. A modified version of TouhgReact with diffusion harmonic weighting gave the same results as HYTEC code, both in the case of weak feedback(power=1/3) or strong feedback (power=2) in the new "Power Law". It should be noticed that the Power Law described in this poster is only verified for the aqueous phase but the same kind of law was developed for the gaseous phase in a two-phase system.

STATE OF ART AND THE NEW PROPOSED POWER LAW

The law of Millington and Quirk (1961) is implemented in TOUGHREACT V1.0 (YMP Q V3.1). The user has to set a "virtual" null value for the tortuosity parameter in flow.inp file in order to introduce a so-called "tortuosity" τ value equal to the porosity power 1/3. In saturated conditions, the effective diffusion coefficient De is written as a product of the porosity ω, the "tortuosity" τ and the free-water diffusion D_0 :

$$D_e = \omega.\tau.D_0, \qquad \tau = (\omega)^{1/3} \qquad (E1)$$

Some limits of this specific law are: the porosity power 4/3 is not the experimental cementation factor for cementious materials like the CEM I paste (Trotignon et al., 2007) ; it is not possible to consider different tortuosities if the feedback effect with Millington law is taken into account. The effective diffusion coefficient may be very different between materials, eg about 2 orders of magnitude for chloride effective diffusion between clay and concrete (Trotignon et al., 2007). To overcome these limitations and in the absence of better information on physical characteristics of perturbated CEMI cement, MX80 bentonite or Callovo-Oxfordian clay, a general Power Law similar to the Archie law (Archie, 1942) as modified by Winsauer et al. (1952) has been chosen to describe the relation

between the effective diffusion and the porosity evolution (Lagneau, 2002):

$$D_e = \omega.\tau.D_0, \quad \tau = \left(\frac{\omega - \omega_{min}}{\omega_o - \omega_{min}} \right)^p .\tau_0 \quad (E2)$$

With : ω_{min}, the critical porosity under which diffusion is supposed to stop (percolation threshold) ; p, the power coefficient (e.g. 0.3 for a non-consolidated sand, 1.2 for a limestone and 2 for a cement paste chosen by Trotignon et al. (2007)).

Test-Case I : verification case for power coefficient p=1/3 (Millington and Quirk)

In test-case I, the objective is not yet to validate the new law but only to verify that the old law (E1) is equivalent to the new law (E2) with a power 1/3 and with a tortuosity parameter in the new law in both media.

Two media with a different porosity in a 2m-length 1D geometry were considered. The effective diffusion coefficients are initially very similar in both media, the small difference is only due to the difference of porosity. The physical characteristics of both media are presented in table 1.

Table 1. Physical parameters of both media.

Parameters	Medium I	Medium II
De (m^2 s^{-1})	2.92 10^{-12}	5.10^{-12}
ω_0 (-)	0.2	0.3
w_{min}	0	0
p	1/3	1/3
τ_0 (-)	0.585	0.669
Length, L (m)	1.05	1.05
Δx (m)	0.05	0.05

Initially, aqueous $SrCl_2$ (10^{-1} mol kgw^{-1}) and a non-reactive tracer (10^{-6} mol kgw^{-1}) were supposed present in medium I whereas only SO_4Na_2 (10^{-1} mol kgw^{-1}) without tracer is supposed to be present in medium II. The chemical parameters used for calculation are summarized in Table2. The diffusion of the strontium and sulphates ions will lead to the precipitation of celestite ($SrSO_4$) at the interface: $SrSO_4(s) = SO_4^{2-} + Sr^{2+}$ with log K = -6.632. In order to increase the porosity variation, and therefore the feedback effect of celestite precipitation on the diffusion of the tracer, the precipitation is not

treated under kinetic constraints but at local equilibrium and the molar volume of the solid phase is arbitrarily increased (10 L/mol instead of 46.25 cm^3/mol).

Table 1. Chemical parameters of both media.

Parameters	Medium I	Medium II
pH	7	7
tracer (mol kgw^{-1})	10^{-6}	10^{-20}
Sr (mol kgw^{-1})	10^{-1}	10^{-10}
Cl (mol kgw^{-1})	5×10^{-2}	5×10^{-9}
S(6) (mol kgw^{-1})	10^{-10}	10-1
Na (mol kgw^{-1})	5×10^{-9}	5×10^{-2}

The result is presented in the Figure 1. As it could be expected, (E1) and (E2) are rigorously equivalent if the tortuosity $\tau_0 = (\omega_0)^{1/3}$ is chosen in the new law in both media (Table 1).
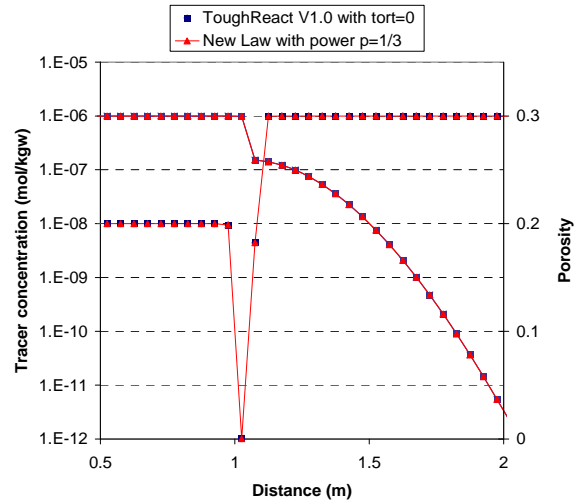

Figure 1. Porosity variation and tracer concentration after 10 years calculated with the old law (E1) and new law (E2).

Test-Case II : comparison case of TOUGHREACT V1.0 with HYTEC V3.3 for weak (p=1/3) and strong (p=2) feedback

The aim of this test-case II is to compare the results of two different codes for different values of the power p. The results of V1.0 with the new law are compared with the results given by HYTEC 3.3, a french code (van der Lee et al., 2003) which is also able to simulate the reactive transport with variable porosity.

The HYTEC retroaction law is the same as the power law described in Equation (E2). The physical parameters are the same parameters as in Test-Case I except for the effective diffusion with a difference of one order at the interface.

For the limit conditions, the 1D system is supposed to be closed in both codes, ie no mass flux at X=0 m X=2 m.

Table 2. Physical parameters of both media in Test-case II (see Table 1 for the other parameters).

Parameters	Medium I	Medium II
D_e (m^2 s^{-1})	10^{-12}	10^{-11}
$\tau_0 D_0$ (m^2 s^{-1})	$1/2 \ 10^{-11}$	$10/3 \ 10^{-11}$
ω_0 (-)	0.2	0.3
p	1/3, 2	1/3, 2

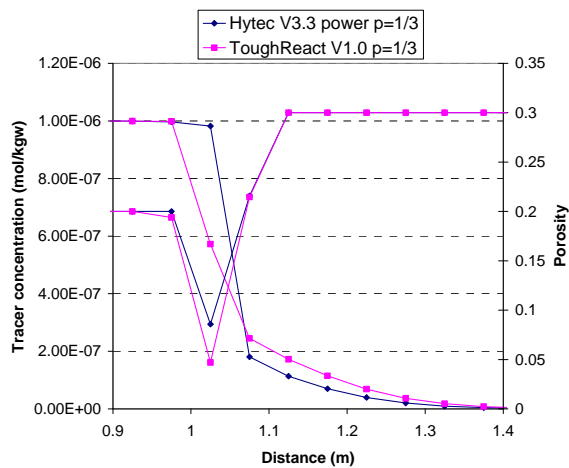

Figure 2. Comparison of tracer concentration and porosity after 10 years between TOUGHREACT V1.0 or HYTEC V3.3 with power p=1/3.

The parameter p is either fixed to 1/3 for a "weak" feedback and to 2 for a "strong" feedback. In both cases, there are significant differences between the results of the two codes (Figure 2 and Figure 3).
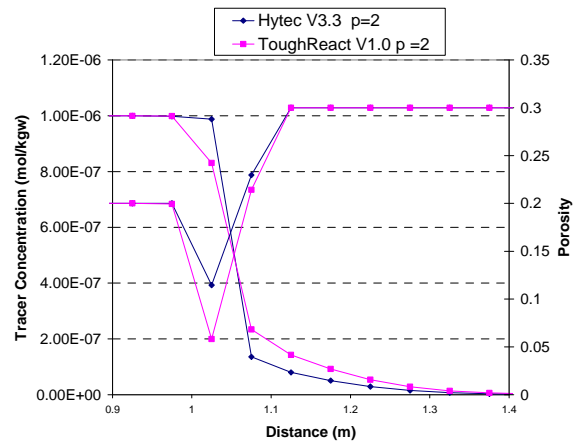

Figure 3. Comparison of tracer concentration and porosity after 10 years between V1.0 and HYTEC V3.3 with power p=2.

It is well known that for a single-phase flow, the appropriate interface weighting scheme for the effective diffusion coefficient is a harmonic weighting. In TOUGHREACT V1.0, the effective diffusion at the interface is the product of D_0 with two terms : the first term of (E1), ie the porosity ω, is calculated as a harmonic mean at the interface, and the second term, ie the tortuosity τ, is a weighted mean (the weights are the nodal distances from the interface).

A new version of TOUGHREACT with harmonic weighting of the effective diffusion coefficient at the interface, gives much better results as shown in Figure 4.
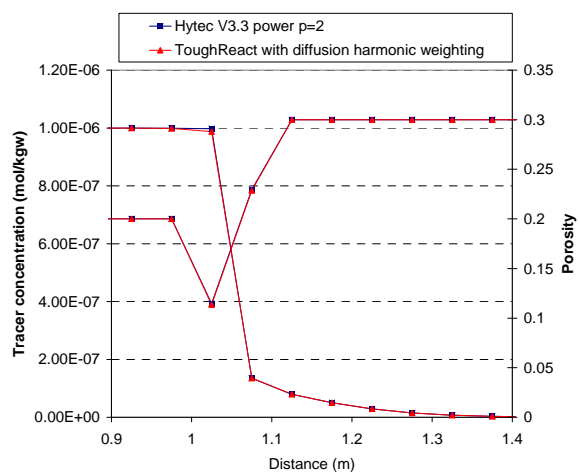

Figure 4. Same as Figure 3 but with diffusion harmonic weighting added (see text).

The interface diffusion coefficient calculation used in TOUGHREACT V1.0 is roughly valid without feedback effect of porosity variation, departing from true diffusion values as porosity decreases and the error in case of low or strong feedback could be significant as shown in Figure 2 and Figure 3.

CONCLUSION

The chemical conditions found in deep nuclear waste storage rise some concern about the migration of radionuclides at the interface between the engineered and geological barriers where the alkaline perturbation could cause a "clogging" and therefore could impact the diffusion-controlled process itself.

In this study, a new general "Power Law" which connects the effective diffusion coefficient and the porosity evolution is described and tested. The conclusion is that if the version V1.0 is used to study the diffusion of radionuclides in the surrounding zone of a waste nuclear disposal, the effective diffusion could be overestimated even with the Millington Law. A modified version of TouhgReact with diffusion harmonic weighting gave the same results as HYTEC code, both in the case of weak feedback(power=1/3) or strong feedback (power=2) in the new "Power Law".

It should be noticed that the Power Law described in this poster is only verified for the aqueous phase but the same kind of law was also developed for the gaseous phase in a two-phase system.

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