Differentiated influence of the double porosity of the chalk on solute and heat transport

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Abstract: The chalk porosity plays a decisive role in the transport of solutes and heat in saturated chalk. From a geological point of view, there are at least two types of porosities: the porosity of pores corresponding to the micro-spaces between the fossil coccoliths that form the chalk matrix, and the porosity due to the micro- and macro-fractures (i.e., secondary porosity). For groundwater flow, the fracture porosity is a determining factor at the macroscopic scale. The multi-scale heterogeneity of the porous/fractured chalk is inducing different effects on solute and heat transport. For solute transport considered at the macroscopic scale, tracer tests have shown that the 'effective transport porosity' is substantially lower than the 'effective drainable porosity'. Moreover, breakthrough curves of tracer tests are showing an important influence of diffusion in a large portion of 'immobile water' ('matrix diffusion') together with quick preferential advection through the fractures. For heat transport, the matrix diffusion in the 'immobile water' of the chalk is hard to distinguish from conduction within the saturated chalk.

Chalk aquifers are considered as excellent groundwater reservoirs (among others: Foster & Milton 1974; Price 1987; Dassargues *et al.* 1988; Price *et al.* 1993; Dassargues & Monjoie 1993; Younger & Elliot 1995; MacDonald & Allen 2001; Nativ *et al.* 2003; William *et al.* 2006) but at the same time, the saturated chalk of which they are composed is one of the most complex geological media due to multi-scale heterogeneity (Fig. 1). Groundwater quality issues in chalk aquifers have been studied and discussed for a very long time (among others: Gray & Morgan-Jones 1980; Jackson *et al.* 1984; Hallet 1998; Nativ *et al.* 1999; Gooddy *et al.* 2001; Brouyère *et al.* 2004; Batlle-Aguilar *et al.* 2007; Orban *et al.* 2010; Hakoun *et al.* 2017; Boudjana *et al.* 2019). A detailed understanding of solute transport in the chalk aquifers is thus an important issue.

More recently, the increasing consideration of renewable energies is resulting in a huge expansion of the interest on the quantification of heat transfer in partially and fully saturated aquifers including chalk aquifers. Site specific values for heat transport properties/parameters are needed to design shallow geothermal reservoirs and heat storage systems (i.e. Borehole Thermal Energy Storage (BTES) and Aquifer Thermal Energy Storage (ATES) systems) in chalk aquifers. They will influence the short-, mid- and long-term performances of the systems, as well as the estimated impacts on the groundwater resources.

For groundwater quality as for geothermal applications, it could be very important to have a realistic quantification of the highly heterogeneous groundwater flow and transport processes in porous/fractured chalk formations. This information is important for modelling doublets in a double porosity context (Barker *et al.* 2010). Groundwater quantity and quality assessments and the subsequent protection and remediation measures should be based on a sound and

accurate understanding of the processes and their quantification at the scale under consideration. Flow and solute transport are mainly driven by open fractures as preferential paths with very high velocities, while matrix processes can also have a strong influence on contamination duration (among others: Bloomfield 1996, Brouyère *et al.* 2000, Brouyère *et al.* 2004, Weiss *et al.* 2006, Massei *et al.* 2006, El Janyani *et al.* 2014, Tamayo-Mas *et al.* 2018, Hoffmann *et al.* 2020). Thermal storage properties could also be strongly dependent on the multi-scale heterogeneity of the chalk as shown by studies recently published for other geological media (Molson *et al.* 1992, Wagner *et al.* 2014, Wildemeersch *et al.* 2014, Klepikova *et al.* 2016, De La Bernardie *et al.* 2019).

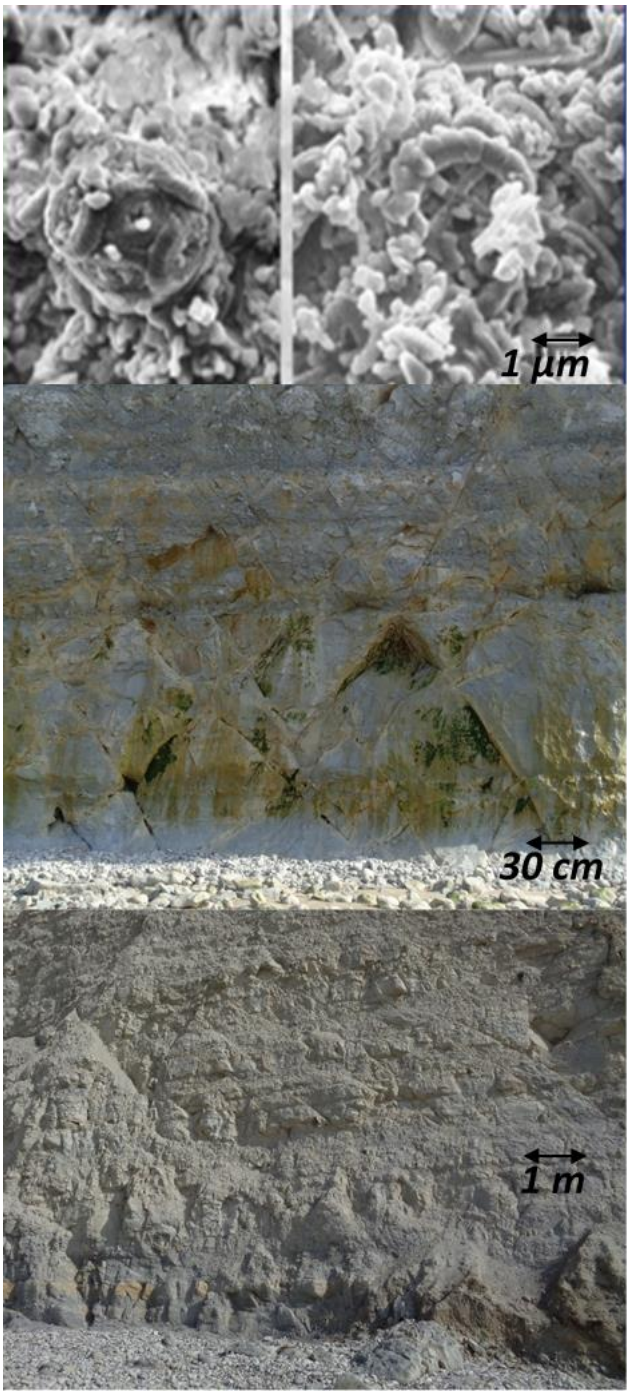

Fig. 1. Multi-scale heterogeneity of the chalk, from the micro-scale with coccoliths forming the chalk matrix showing a pore porosity (above) towards macro-scales at which the porosity is also influenced by cracks and fractures (center and below).

Porosity definitions

The *total porosity* is defined as:

$$n = V_v/V_t \quad (1)$$

where V_v is the void volume and V_t the total volume with respect to a defined representative elementary volume (REV). Here, the void volume includes the pores but also all kind of fractures, cracks, channels, and bedding planes. The porosity is indeed the result of various processes (i.e., physical and chemical) having induced changes in the chalk throughout its geological history. In geology, the terms *primary porosity* and *secondary porosity* are used to describe, respectively, the initial porosity of the chalk, and the acquired additional porosity due to diagenesis, fracturing or deformation, and then dissolution. This latter can often be considered as the dominant process for enhancing permeability (Price 1987, Price *et al.* 1993, Foster 1993). In chalks, the secondary porosity consists most often of a fracture porosity as opposed to interstitial or matrix porosity. This fracture porosity can have more influence on groundwater flow and the storage properties than the primary porosity. In fact, chalks can be considered as dual porosity media with fracture network and matrix porosities, even if a part of this matrix porosity can be reduced by cementing materials in the pore spaces.

The definition of porosity implies conceptually that a given volume of the chalk is considered, which is big enough to yield a value considered as representative at that scale. In practice, the REV concept is always implicitly considered even though this is not necessarily acknowledged (de Marsily 1986). Behind this concept lies the fact that an equivalent value is used (Bachmat and Bear 1986, Bear and Verruijt 1987) that is the result of a homogenization process at that REV scale. The size of the later is chosen essentially according to the aims of the study.

In many different aquifers, but especially in chalk aquifers, observations at the scale of lab tests (up to a few decimetres) or at the scale of field tests (e.g., pumping tests) imply that a part of the groundwater in the aquifers can be considered as immobile in the pores of the matrix. In all textbooks about hydrogeology an effective porosity is distinguished from the total porosity.

In saturated conditions and for groundwater flow problems, an *effective porosity* is usually defined as the drainable porosity under the in-situ pressure conditions:

$$n_e = V_m/V_t \quad (2)$$

where V_m is the volume of mobile water in the REV. This corresponds to the specific yield (S_y). This specific yield or drainable effective porosity gives also a reliable value for the storage coefficient in unconfined aquifers (i.e., as consolidation effects can be neglected in unconfined conditions).

If solute transport is considered, it remains difficult to know accurately which part of the saturated porosity is occupied by mobile water, on which the transport velocity is based (Dassargues 2018). In particular, in aquifers where a fracture porosity is usually lower or around 1 %, very rapid transport (advection) velocities are observed (Worthington 2015). On the basis of all observations from tracer tests and contaminations, distinction must be made systematically between the effective drainable porosity and an effective transport porosity which takes typically a lower value than the former one (Hallet & Dassargues 1998, Brouyère

et al. 2000, Payne *et al.* 2008, Hadley & Newell, 2014). In addition, Worthington et al. (2019) have recently demonstrated that the transient nature of effective porosity and specific yield is of importance for an unconfined chalk aquifer, highlighting that these values should not necessarily be treated as similar, time-invariant values.

The advection velocity is defined as:

$$\boldsymbol{v_a} = \boldsymbol{q}/n_m \tag{3}$$

where $\boldsymbol{q}$ is the groundwater Darcy flux, and n_m is the *effective transport porosity* (Dassargues 2018). This later is in theory very dependent on what is actually defined as mobile and immobile groundwater in the REV. In practice however, if experimental results (i.e., pumping tests and tracer tests results) have to be reproduced by model results, a lower value for the effective transport porosity is to be chosen than for the effective drainable porosity.

Especially in the chalk, if the Darcy flux were divided by the total porosity n (or even by the effective drainable porosity n_e), this would lead to a kind of averaged velocity which can be misleading (i.e., leading to underestimation of actual velocities). However, one can argue that this could be partially and artificially compensated in models by considering larger values of the longitudinal dispersivity, but it is also misleading as it only counterbalances a correlation between parameters and not improve the model conceptualisation towards an accurate parameterisation (Dassargues 2018).

Dual porosity and hydraulic conductivity of chalk

The dual porosity concept, with micro-pores in the solid porous matrix and macro-pores corresponding to fractures or bedding, was already considered by Gerke & van Genuchten (1993). If it is applied at larger scale, subzones of low and high hydraulic conductivity also form a dual permeability medium (Dassargues 2018).

Indeed, a dual or triple porosity of the chalk could be considered as a result of the geological processes having led to these pores, micro- and macro-fractures (Fig. 1 and Fig. 2). The influence of this multi-scale heterogeneity can be considered differently in function of the studied processes (i.e., groundwater flow, solute transport and heat transport). In each case, the parameter values are considered at a given scale (i.e., the scale of the REV) depending on the problem to be solved.

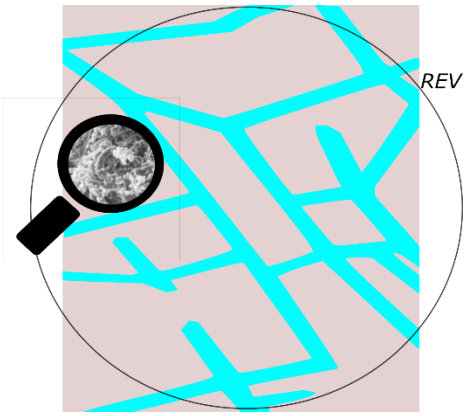

Fig. 2. Porosity of the pores in the matrix made up of coccoliths and fracture network porosity at the macroscopic REV scale.

As an example, if only groundwater flow properties are considered in the chalk aquifer of Hesbaye (Cretaceous chalks of the Maastrichtian and Campanian ages of the Geer basin in Belgium), different values (see below) were found according to the considered size of the REV (Dassargues 2018).

At the *microscopic scale* (up to a few centimeters), one considers essentially the matrix of a chalk sample. Aggregated coccolith fossils of a few microns are forming this chalk matrix. The measured porosity may vary depending on localized calcium carbonate ($CaCO_3$) precipitation. The overall spatial distribution of voids seems relatively homogeneous in the samples of a few centimeters, so they are apparently adequate REVs to measure a reliable pore porosity. The following values have been measured: $n = 0.40 - 0.42$ and $n_e = 0.35$. Consequently, the hydraulic conductivity values are quite low $K \cong 1.0\ 10^{-8}$ (m/s).

At the *macroscopic scale* (up to a few decimeters), any REV actually includes conjugate micro-fractures networks (or micro-fractures) and chalk layering. The effective drainable porosity (i.e., to be considered for a groundwater flow through this REV and influencing the hydraulic conductivity at this scale) is now strongly dependent the porosity of these micro-fractures: $n = 0.42 - 0.45$ and $n_e = 0.01 - 0.03$. Accordingly, larger values of hydraulic conductivity are found with $1.0\ 10^{-5} \leq K \leq 1.0\ 10^{-4}$ (m/s).

At the *megascopic* scale (scale of field tests such as pumping tests, up to a few hundred meters), it is observed (through interpretation of tests and inverse modelling) that 'homogenization' in a large REV ensures that all fractures, faults and discontinuities should be considered as interconnected, which increases the effective porosity and the hydraulic conductivity values: $n = 0.42 - 0.45$ and $n_e = 0.05 - 0.10$; $1.0\ 10^{-4} \leq K \leq 1.0\ 10^{-3}$ (m/s).

Now if solute or heat advection is considered, the n_m values are systematically lower than the $n_e$values, representing a more accurate assessment of the actual mobile water volume for advective mass transport. For example, for solute transport, on the basis of 47 different tracer tests in Belgian unconfined chalk aquifers performed for delineation of protection zones around pumping wells, the arithmetic mean, geometric mean and median values for n_m were found to be 0.0187, 0.0058, and 0.008, respectively (Briers *et al.* 2017).

In summary, this concept of dual porosity is at the origin mostly influenced by the chalk geological conditions and history. Its relative importance for possible consideration in the quantification of solute and heat processes is largely dependent on the scope of the study and the associated scale of consideration.

Solute transport in chalk accounting for matrix diffusion/immobile water effect

Adding the contribution of the different solute mass processes, the solute conservation equation for mobile groundwater can be written for a REV in aquifers (Dassargues 2018):

$$R\frac{\partial C}{\partial t} = -\boldsymbol{v_a}\cdot\nabla C + \nabla\cdot(\boldsymbol{D_h}\cdot\nabla C) - R\lambda C - \frac{q_s}{n_m}(C - C_s) \quad (4)$$

where C is the volume concentration (kg/m^3) in the mobile groundwater, $\boldsymbol{D_h}$ is the hydrodynamic dispersion tensor(m^2/s) including the mechanical dispersion and the diffusion in the mobile water, R is the retardation factor due to adsorption-desorption processes (-), λ is a first-order (linear) decay constant (s^{-1}), q_s is the source/sink volumetric flow rate per unit volume of porous medium (s^{-1}) flowing into ($q_s > 0$) or flowing out from ($q_s < 0$) the control volume and C_s is the associated concentration (kg/m^3). In this equation, diffusion is considered only in the mobile water fraction of the saturated media.

In reality, diffusion occurs between mobile water and immobile water as a result of solute concentration differences. Especially in a porous/fractured chalk, the concentration (C) first rises in the very mobile groundwater in the fractures (Fig. 3). In contact with the immobile water at a concentration (C_{im}) in the matrix pores, diffusion occurs (i.e., assuming $C > C_{im}$). On the contrary, when the peak in mobile water concentration C has passed, back diffusion can take place from the immobile into the mobile water (i.e., assuming $C < C_{im}$).

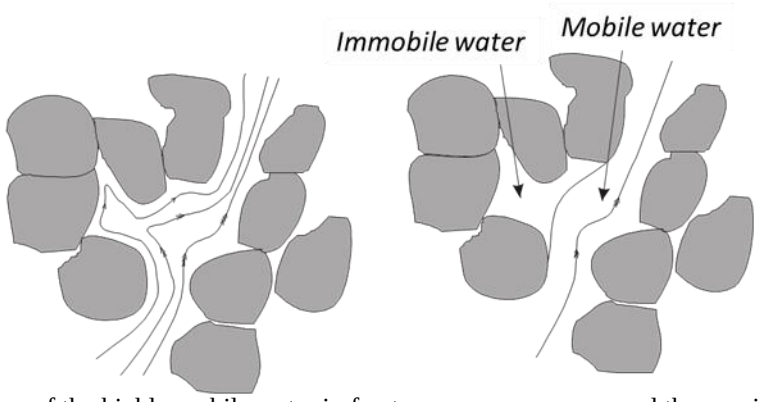

Fig. 3 Schematic view of the highly mobile water in fractures or macro-pores and the quasi immobile water in the pores of the chalk.

This immobile water effect on the solute transport is often referred to as 'matrix diffusion' in the literature (Rasmusen & Neretnieks 1981, Wood *et al.* 1990, Carrera *et al.* 1998). It was detected by tracer tests showing longer tailing of the breakthrough curve (BTC). One of the way to take this matrix diffusion into account is to express a classical linear exchange relationship as (Coats & Smith 1964, Bear & Verruijt 1987, Brouyère 2001):

$$f_m^{im} = \alpha_d^m(\rho C - \rho_{im} C_{im}) \quad (5)$$

where f_m^{im} is the diffusive solute mass flux (kg/m^{3}s) from mobile to immobile water (or vice-versa), ρ and ρ_{im} are the density of mobile and immobile water respectively, α_d^m is defined as the matrix diffusion coefficient or immobile water diffusion coefficient (s^{-1}), similar to a diffusion coefficient (m^2/s) divided by a surface area (m^2) intended to describe the mobile water - immobile water contact area. This flux could be added to the solute conservation equation expressed for the mobile water in the REV (equation 4). In practice, to obtain the net gain or loss of solute mass in the mobile water at each time step (i.e., dual-domain mass transfer), a solute mass balance equation in the immobile water must also be considered. Values for the matrix diffusion coefficient (α_d^m) are inferred from lab and field tracer tests results and diffusion coefficient values. As studied by Brouyère (2001), this value can have a crucial influence on the simulated BTC (Fig. 4).

A few examples of BTC from tracer tests performed in the unconfined chalk aquifer of Hesbaye (Geer basin, Belgium) show the wide diversity of the obtained BTC in function of the local multi-scale heterogeneity of the chalk (Fig. 5).

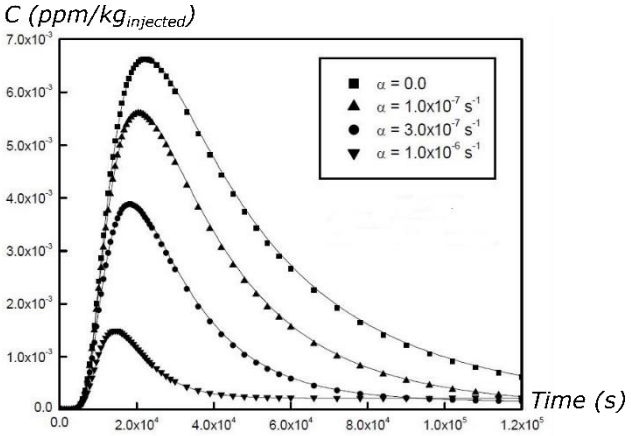

Fig. 4 Calculated BTCs in a pumping well for a saturated chalk with 30 % of immobile water and n_m= 1 %, with different values for the matrix diffusion coefficient (from Brouyère 2001).

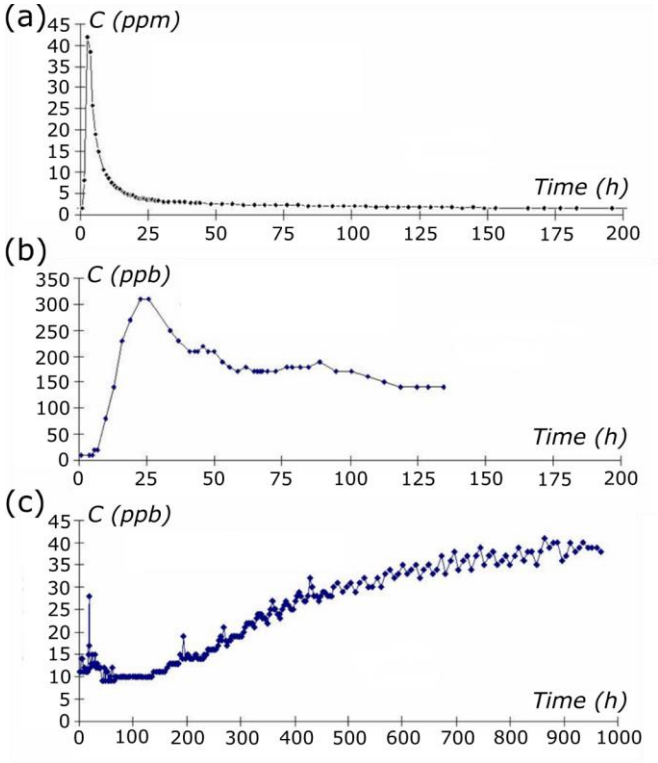

Fig. 5 Examples of measured breakthrough curves for different tracer tests tracers performed in in the unconfined chalk aquifer of Hesbaye (Geer basin in Belgium) showing the diversity of the solute transport behaviour.

More details about the tracing conditions (Hallet 1998) and interpretation:

(a) 52 kg of potassium, injected (in depth-averaged conditions) during 2h at a distance of 93 m from the pumping well with a discharge rate of 9 m^3/h. Local hydraulic conductivity values were assessed between 4.0 and 20.0 10^{-4} m/s in the fractured zones and about 8.5 10^{-5} m/s in the less fractured chalk from pumping tests interpretation. The clear advection dominated solute behaviour with a moderate tailing is due to preferential flow through open fractures or conduits.

(b) 22.9 kg of iodide, injected (in depth-averaged conditions) during 9h45 at a distance of 54 m from a drainage gallery (BTC was measured in the gallery). Local hydraulic conductivity values were assessed between 3.0 and 10.0 10^{-4} m/s in the fractured zones and between 0.1 and 8.0 10^{-5} m/s in the less fractured chalk from pumping tests interpretation. The long tailing with relatively high concentrations clearly shows a strong immobile water effect with occurrence of matrix diffusion and back-diffusion.

(c) 4.1 kg of lithium, injected (in depth-averaged conditions) during 30h at a distance of 110 m from the pumping well with a discharge rate of 4.4 m^3/h. Local hydraulic conductivity values are assessed between 1.0 and 10.0 10^{-3} m/s in the fractured zones and between 0.3 and 1.0 10^{-5} m/s in the less fractured chalk from pumping tests interpretation. The atypical BTC can be interpreted as showing a limited first advection arrival at very short times corresponding to a preferential flowpath through a

fractured zone detected previously by geophysics, and a quite delayed second peak due to the solute pathway through the less fractured chalk matrix.

Heat transport in chalk

Heat can be transported through both the pore/fracture space and the solid matrix of the chalk, whereas solutes in groundwater are transported only through the pores and fractures. The main processes for heat transfer in a saturated chalk are thermal conduction, advection and dispersion. The corresponding heat conservation equation can be written:

$$\frac{\partial \rho_b c_b T}{\partial t} = -\nabla \cdot [\rho_w c_w \boldsymbol{q} T - (\lambda_b + c_b \rho_b \boldsymbol{D}) \cdot \nabla T] + Q_T \quad (6)$$

where λ_b is the heat (or thermal) conductivity (W/(m°K)) of the bulk saturated chalk, ρ_b is the bulk density (kg/m^3), c_b is the bulk heat capacity (J/(kg°K)) ($\rho_b c_b$ is the bulk volumetric heat capacity J/(m^3°K)), ρ_w is the water density (kg/m^3), c_w is the water heat capacity (J/(kg°K)) ($\rho_w c_w$ is the water volumetric heat capacity in J/(m^3°K)), $\boldsymbol{q}$ is the total water flux vector (m/s) from Darcy's law and including the possible temperature effect on the water density and viscosity (natural convection), $\boldsymbol{D}$ is the thermal dispersion tensor (m^2/s), ∇T the temperature gradient (°K/m), Q_T is the heat source (if $Q_T > 0$) or sink (if $Q_T < 0$) term.

In aquifers, most often, the thermal dispersion is considered as negligible compared to the thermal conduction term and compared to the advection-convection term (Anderson 2005, Irvine *et al.* 2015). Then, the equation is accordingly simplified and divided by the bulk volumetric heat capacity ($\rho_b c_b$) to obtain (Dassargues 2018):

$$\frac{\partial T}{\partial t} = -\nabla \cdot \left[\frac{\rho_w c_w}{\rho_b c_b} \boldsymbol{q} T - \frac{\lambda_b}{\rho_b c_b} \nabla T\right] + Q_T/(\rho_b c_b) \quad (7)$$

where the coefficient $\lambda_b/(\rho_b c_b)$ is named thermal diffusivity (m^2/s) and the term $Q_T/(\rho_b c_b)$ (°K/s) can also be understood as the temperature associated with a groundwater flux entering or exiting 1 m^3 of the domain

For heat transport the 'effective heat transport porosity' could probably be considered as equal to the 'effective solute transport porosity' in the advection term. On the contrary, the 'diffusive term' in the heat transport equation corresponds to conduction (as heat dispersion is often considered as to be neglected with regards to conduction) that occurs in solid matrix and both mobile and immobile water. So, the total porosity is required to assess the values of the bulk saturated chalk matrix heat capacity (c_b) and density (ρ_b) that are considered in the heat transport equation. Conduction is actually boosted by the temperature difference between the mobile water and the immobile water, and also between the mobile water and the solid matrix. These effects are fully included in the diffusive term of the heat solute transport equation (equation 7). This last term is most often three orders of magnitude higher than a solute diffusion term in a solute transport equation. Thus, looking at equation (7), the immobile water effect on the heat transfer is clearly integrated in the thermal diffusivity term describing conduction in the bulk saturated media.

Usual values for bulk thermal conductivities (λ_b) are comprised between 0.5 and 2.5 (W m^{-1}°K^{-1}) for a dry chalk and between 0.57 and 0.60 for water. Usual values for bulk heat capacity (c_b) and volumetric heat capacity ($\rho_b c_b$) for a dry chalk are about 0.90 10^3 (J kg^{-1}°K^{-1}) and 2.2 – 2.25 10^6 (J m^{-3}°K^{-1}) respectively, and 4.18 10^3 (J kg^{-1}°K^{-1}) and 4.18 10^6 (J m^{-3}°K^{-1}) for water.

An example of a temperature BTC from a tracer test performed in a continuous chalk fracture isolated between packers is shown in Fig. 6. The injection well (i.e. with the isolated fracture between packers at 35 m of depth) is located at 7.55 meters from the pumping well in the unconfined chalk of the Mons basin (Belgium) (more details in the Fig. 6 legend). It shows clearly heat advection and then the combined effect of the conduction and possibly matrix diffusion in the delayed answer of heat evolution with time. As long as the injection of hot water is in progress the curve rises showing essentially advection, but as soon as the injection is stopped, apart from a small and temporary drop in temperature (due to the drop in temperature in the fracture itself), a new but slow temperature rise is observed by conduction and possibly matrix diffusion (Fig. 6). Interestingly, the finally measured temperature change in the recovery well is 0.44 °C, and thus already 10 % higher than the peak measured during the active injection of hot water. Due to the stop of the hot water injection, but the ongoing pumping in Pz1 during this period, heat stored in the rock matrix around the injection well and around the fractures between the injection and pumping wells, is probably progressively released from the rock matrix to the colder water circulating in the fractures towards the pumping well. In contrast, the comparison with the solute (uranine) behavior is striking with a very quick advection of solute, as expected, since the injection was performed in the fracture between packers.

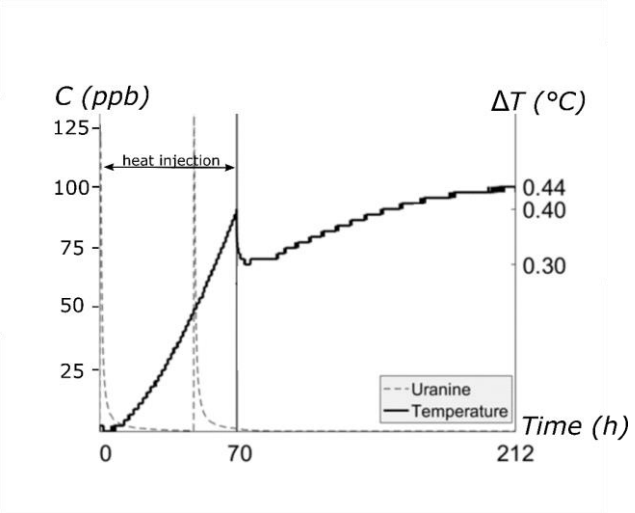

Fig. 6 Observed concentration of uranine and temperature change at a recovery pumping well 7.2 m^3/h) located at a 7.55 m distance from the injection well. Both wells are crossing an identified sub-horizontal fracture connecting them at a depth of 35 m. A 70 h injection of hot water (ΔT = + 40 °C) was complemented by two 10 minutes uranine pulse injections within an inflatable double packer system isolating the sub-horizontal chalk fracture of interest. The uranine tracer was injected simultaneously with the start of the hot water injection. During the first period (i.e., continuous hot water injection period during the first 70 h), both uranine injections show first arrival times of about 10 minutes at the recovery well. In contrast, the first measured temperature increases of 0.01 °C is observed after 12.5 h. The followed observed heat increasing increments are always 0.01 °C and the time between two increments is getting shorter till the peak is reached. After 70 h of hot water injection, the measured temperature change in the recovery well is 0.40 °C, far from having reached a steady-state temperature value. After the stop of hot water injection, the temperature decreases first rapidly to 0.33 °C, before a further temperature rebound.

Conclusion and perspectives

In chalk aquifers, it could be particularly recommended to distinguish between the different kinds of porosity. A pumping test in an unconfined chalk aquifer in transient conditions allows to deduce interpreted values for hydraulic conductivity and effective drainable porosity (specific yield), while a tracer test (with an ideal solute tracer) would confirm that this latter is

not the adequate porosity to calculate advection groundwater velocity. In reality, a systematic difference is observed between the portion of mobile water for flow calculation and the portion of mobile water actually transporting the solute by advection. This is particularly true in chalk aquifers showing a multi-scale heterogeneity with pores and various micro- and macro-fractures.

For solute transport, the matrix diffusion in the immobile water should be accounted for to obtain a reasonably realistic quantification and characterisation. For heat transport on the contrary, possible matrix diffusion is masked and thus can be included in thermal conduction that is active through both the pore/fracture space and the solid matrix of the chalk.

Finally, determining the breakthrough curve of a solute contaminant at a given pumping well (i.e., mainly influenced by advection, dispersion and matrix diffusion) is completely another problem then assessing efficiency of an ATES geothermal system that will be mainly dependent on advection and conduction). Each process should be investigated and calculated with its corresponding specific behaviour in the multi-scale heterogeneity context of the chalk. This is requiring a lot of characterisation work involving well designed in situ solute and heat tracer tests.

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Data Availability

The data set of the joint heat-solute experiment is stored on the H+ Network database (http://hplus.ore.fr/en/hoffmann-et-al-2020-hydrogeology-of-the-chalk-data). The access will be free 6 months after publication. The authors express their special thanks to N. Guihéneuf by assisting the data upload to the H+ database.

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