Process tomography of diffusion, using PET, to evaluate anisotropy and heterogeneity

J. KULENKAMPFF*, M. GRÜNDIG, A. ZAKHNINI, R. GERASCH AND J. LIPPMANN-PIPKE

Helmholtz-Zentrum Dresden-Rossendorf, Permoserstr. 15, 04318 Leipzig, Germany

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ABSTRACT: Anisotropy and compositional and structural heterogeneity in clays are causes of considerable deviations from homogeneous diffusion, in particular in terms of direction-dependent transport rates and preferred transport zones. Conventional diffusion experiments, in which the sample is treated as a homogeneous black box in a concentration gradient, are interminable and insensitive to spatial effects. In contrast, tomographic imaging methods are capable of both reducing the amount of observation time required and revealing space-dependent features of the diffusion process.

In the present study, positron-emission-tomography (PET) was applied as the most sensitive quantitative spatiotemporal tomographic modality for direct observation of positron-emitting radio-tracers in opaque media at reasonable resolution (1 mm) on a laboratory scale (100 mm).

Geoscientific applications of PET, or GeoPET, have revealed anisotropic and heterogeneous effects in diffusion experiments that have been conducted on Opalinus clay samples of different sizes, as well as on other rock types. Applying the Comsol Optimization Module to 2D-image sections of the PET tomograms, effective parameter values were derived, thereby quantifying the anisotropic diffusion.

KEYWORDS: Opalinus clay, diffusion, tomography, positron emission tomography, heterogeneity, anisotropy.

Molecular diffusion is the dominant transport mechanism of dissolved species in clays, complemented by species interactions with the large internal surface area along the propagation pathways. Due to small pore sizes (in the nm range), advective flow processes play only a minor role. Diffusion in clays is based on Fickian diffusion (Altmann et al., 2012) of some species in a concentration gradient, restricted by the pore-space geometry of the material and the sorption of the diffusing species on the portion of the internal surface area that comes in contact with the species.

Van Loon et al. (2004) designed a conceptual model for mudrocks (which consist of layered clay platelets that are oriented preferentially by overburden pressure). The oriented heterogeneity on the sub-micrometer scale causes anisotropy in many properties of clay on the sub-millimetre scale. Heterogeneities on the larger, millimetre scale such as intercalations of silty or sandy laminations or lenses cause anisotropic behaviour on a larger scale. The diffusion pathways in such laminations are less tortuous and thus establish a quicker route to the less penetrable clay-rich zones. Also, the specific surface area, and thus the density of the sorption sites, is smaller in these zones than in the pure clay. Such heterogeneities are present in Opalinus clay samples of drill-core size and distinguishable in the µCT-image of a comparable sample (Fig. 1). The heterogeneities may also be observed on the field scale as homogeneous anisotropic behaviour with modified diffusion parameters compared to values from the smaller scale.

These multi-scale material characteristics cause complex diffusion pathways that are difficult to predict with simple homogeneous models. In the range below the centimetre scale, which is the size of the largest...
distinguishable features in the µCT image (Fig. 1), the propagation is not homogeneous but fluctuates spatially; this is due both to the effects of platelet orientation on the microscale and layering on the millimetre scale. Some of the internal surface area is not affected immediately by the diffusing species because zones with large sorption capacity are frequently bypassed through less tortuous pathways. These multi-scale heterogeneity effects modify the macroscopic diffusion parameters, and thus anisotropic diffusion parameters with strongly increased transport in the direction of the largest axis have to be considered.

The second Fickian diffusion equation in its general form is:

$$\frac{\partial c(r, t)}{\partial t} = \nabla(D_a(r) \cdot \nabla c(r, t))$$

(1)

where $c$ is the concentration and $D_a$ [m$^2$/s] is the apparent diffusion tensor, $r$ is the position vector and $t$ is time. The apparent diffusion tensor groups together geometrical effects (porosity, internal surface area, tortuosity) and chemical parameters (chemical-state variables, surface complexation and exchange). The scalar geometrical parameters must be considered as effective quantities, including only the portion that is involved in the diffusion process. Whether diffusive propagation of species is predictable on the basis of a small number of parameters thus appears questionable.

In the simplest form these are equilibrium distribution coefficient, $K_d$ [cm$^3$/g] from sorption batch experiments, total porosity $\varepsilon$, bulk density $\rho_b$ [g/cm$^3$] and the scalar diffusion coefficient in water $D_{aq}$ [m$^2$/s]:

$$\frac{\partial c(x, t)}{\partial t} = D_a \cdot \frac{\partial^2 c(x, t)}{\partial x^2}$$

(2)

with

$$D_a = \frac{D_{aq}}{\alpha \cdot F}$$

(3)

where the capacity factor, $\alpha$

$$\alpha = \varepsilon + \rho \cdot K_d$$

(4)

considers sorption effects and the formation factor $F$ considers pore geometry. The Archie’s equation

$$F = \varepsilon^{-m}$$

(5)

with an empirical Archie coefficient of $m \approx 2$ may be applied as a simple approximation, or better, a more sophisticated tortuosity model (Boving & Grathwohl, 2001). It is proposed here that effective porosity $\varepsilon_{\text{eff}} < \varepsilon$,
thus $F_{\text{eff}} > F$ and an effective distribution coefficient $K_{d, \text{eff}} < K_d$, taking into account the smaller effective surface area, because some of the bulk material is not involved in the process. Assuming spatial independence of $D_a$, it follows that:

$$D_a = \frac{D_{aq}}{F_{\text{eff}}(e_{\text{eff}}) \cdot \alpha_{\text{eff}}(e_{\text{eff}}, K_{d, \text{eff}})}$$

(6)

Approaches which are more dependable than simple assumptions about the effective parameters are based on empirical observations of the distributional propagation of a tracer in an undisturbed material under controlled laboratory conditions. Examples of such experiments are in-, out-, and through-diffusion experiments, conducted in diffusion cells with periodic fluid sampling in the fluid reservoirs (Van Loon et al., 2004). The sample is regarded as a black box, and the diffusion coefficient is derived from the input and output tracer concentration. In the case of slow propagation, these experiments can be extended by destructive analysis of the tracer distribution in the sample (Van Loon & Eikenberg, 2005). These experiments yield exact data for $D_a$ in one direction; they are elaborate, however, and ignore spatiotemporal effects which could be caused by the natural heterogeneity of the sample or by damage caused during preparation.

These inconveniences can be reduced by applying non-destructive tomographic methods for observing tracer propagation within the sample because the impact of withdrawal of in situ conditions and preparation damage can be minimized. For quantitative imaging of tracer concentrations, positron emission tomography (PET) is particularly suitable. The so-called PET is known from medical applications as a tomography (PET) is particularly suitable. The so-called PET is known from medical applications as a...
Fig. 2. Activity concentration distribution of the $^{22}$Na$^+$ tracer after 3 h, 10 days, 16 days and 27 days after injection (from top to bottom, respectively). Vertical slices oriented in the direction of the major axes, scaled with reference to the actual data range (colour scale on the left), horizontal image at the bottom showing the projection of the mean value over all slices in vertical direction (colour scale on the right).

Fig. 3. Isosurfaces (100, 150, 200 Bq/voxel) and projections onto the $xy$ plane of the $^{22}$Na$^+$ activity concentration distribution, 10 days after tracer injection.
physically sealed source. The sample was then stored at 20°C.

Beginning daily, with increasing time lag, a sequence of 20 PET images was produced over a period of 150 days until the tracer was roughly equally distributed throughout the core. In the following, an initial period of 1 month was considered, before the spreading tracer reached the sample circumference.

The raw data (projections) were corrected for attenuation and scattering of the photon pair. The tomographic image was reconstructed using the iterative OSMAPSO algorithm supplied by Open-source STIR-software (Thielemans et al., 2012). The remaining concentric-ring artefacts, caused by large gaps between the detector modules, were reduced using image-processing methods. The images were decay-corrected, and the total activity was calibrated with respect to the administered activity, thus yielding quantitatively activity concentrations per voxel.

The accuracy of the method was evaluated with the help of Monte Carlo PET simulations. The initial tomogram (image taken at 3 h after the start of the experiment) was reproduced successfully by the Monte-Carlo simulation (Zakhnini et al., 2013). However, imaging artefacts were still present in the tomograms, caused by multiple factors including tracer distribution, spatial distribution of the signal-to-noise ratio, and the precision of applied corrections. Improvements of imaging quality are more elaborate in dense geomaterials than in light biomaterials of medical PET applications. Further success at eliminating artefacts is being achieved on an ongoing basis.

The sample had to be considered as damaged by stress and fluid-pressure release during coring, fluid-loss during transport and storage before the experiments, and by preparation. In principle, it is possible to minimize these effects by conducting the experiments in a pressure vessel and by reducing the preparation impact. However, the aim of the present study was to optimize the measurement procedure and to develop evaluation methods.

RESULTS AND DISCUSSION

The diffusive propagation of the tracer is shown in four time steps as orthogonal slices of spatial activity concentration, from the initial image to that taken after 27 days, when the tracer reached the circumference (Fig. 2). At the bottom of each image, the respective projections in the axial direction of the mean value are shown. Isosurfaces of activity concentrations of the tomogram taken after a period of 10 days are shown in Fig. 3. At this time step, a transversely isotropic finite-element model (FEM) was fitted to the data collected, applying the Comsol Optimization module (Fig. 4). This method (Schikora, 2012; Gerasch, 2015) yielded the apparent diffusion coefficients in the principal directions, \( D_{a,xx} = D_{a,zz} = 1.1 E-10 \, m^2/s \) and \( D_{a,yy} = 3.4 E-11 \, m^2/s \), which is in accordance with results.

Fig. 4. Optimum fit of the PET tracer distribution (left) with a Comsol Multiphysics FEM model (right) (scaled in molar concentrations).
from through-diffusion experiments parallel and perpendicular to the bedding (Van Loon et al., 2004).

Distant from the source, in the range of low activity, the axial projections are smooth and elliptically shaped, in accordance with the FEM result. These low-activity values are more affected by background noise than the higher-activity values adjacent to the source. In the zones with higher-activity values, local structures become visible which deviate from the smooth elliptical shape. In particular, the perimeter of the isosurfaces appears oblate, in the shape of rounded planes, which also are slightly eccentric from the bore (Fig. 5). These deviations from simple anisotropic propagation are indications of heterogeneity, probably because of a fine silty layer adjacent to the bore. The diffusional transport appears to be controlled by laminations, lenses and other structural heterogeneities that are present in the OPA clay, causing preferential diffusion pathways at the cm scale.

**CONCLUSIONS**

Compared to input-output methods for deriving diffusion parameters, process tomography of diffusion in clays has certain advantages: continuous sampling of fluid samples containing radioisotopes is not required, the complete spatio-temporal evolution of the tracer distribution pattern is recorded and samples with representative sizes with respect to major structural features can be investigated non-destructively at simulated temperature and pressure conditions.

Meaningful anisotropic diffusion coefficients were derived. In addition, indications of heterogeneity effects were found, i.e. alignment of zones with greater concentrations of tracer in contrast to blank zones with small concentrations of tracer. The nature of these zones will be clarified after decay of the tracer, using µCT and destructive methods.

This spatial variance of diffusion at the cm scale will have implications for our understanding of the fundamental process and for diffusional transport modelling. Zones of the material which are dominated by high tortuosity and a larger surface-to-volume ratio are less effective for diffusional transport than zones with lower tortuosity and a smaller specific surface area. Thus, total transport is amplified and retention is reduced with respect to homogeneous conditions.
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