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Research paper

Determination of gas diffusion coefficients in saturated porous media: He and CH_4 diffusion in Boom Clay

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A B S T R A C T

Boom Clay is presently studied as the reference host formation for the disposal of high-level and long-lived radioactive waste in Belgium. In a geological repository, the production of gas is unavoidable. Gas is produced by different mechanisms: anaerobic corrosion of metals in waste and packaging, radiolysis of water and organic materials in the packages and microbial degradation of various organic wastes. Corrosion and radiolysis yield mainly hydrogen while microbial degradation leads to methane and carbon dioxide. The generated gas will dissolve in the ground water. As transport in Boom Clay is dominated by diffusion, the dissolved gas is transported away from the repository by diffusion as dissolved species. If the rate of gas generation is larger than the diffusive flux into Boom Clay, the pore water within the disposal gallery will become oversaturated and a free gas phase might form. If the gas pressure keeps increasing, free gas ingress into Boom Clay will occur, most likely through creation of new pathways. In order to make a good evaluation of the balance between gas generation and gas dissipation through engineered barriers and host formation, good estimates for the gas diffusion coefficients of the gases are needed. The currently available gas diffusion parameters for hydrogen in Boom Clay suffer from a large uncertainty, and by application of conservative values for both the source term and the gas migration term the formation of a free gas phase can presently not be excluded for some waste types. In this study a versatile method was developed to determine more precisely the gas diffusion coefficient for dissolved gases in Boom Clay. For the development of the technique, He and CH_4 were used.

The proposed method is based on a through diffusion methodology and allows for two dissolved gases to diffuse through a clay sample at the same time. From the evolution of the diffusant concentration in both compartments, the apparent diffusion coefficients of dissolved He and CH_4 were obtained: 12.2×10^{-10} and 2.42×10^{-10} m^2/s, with uncertainties of 10%, respectively.

1. Introduction

Boom Clay is presently studied as the reference host formation for the disposal of high-level and long-lived radioactive waste in Belgium. This formation has favourable properties such as a low hydraulic conductivity (Wemaere et al., 2008), high adsorption capacity for many radionuclides (Maes et al., 2004) and self-sealing properties due to its elasto-plastic behaviour (Van Geet et al., 2008). All these properties help to retard the migration of radionuclides escaping from the waste after breaching of the waste container package (Yu and Weetjens, 2009).

The production of gas is unavoidable within a geological repository. Gas is produced by different mechanisms: anaerobic corrosion of metals in waste and packaging, radiolysis of water and organic materials in the packages and microbial degradation of various organic wastes. Corrosion and radiolysis yield mainly hydrogen while microbial degradation leads to methane and carbon dioxide (Rodwell et al., 1999; Yu and Weetjens, 2009). At the time of gas generation, the repository near field is considered to be saturated with pore water, and the water pressure is assumed to be almost recovered to the equilibrium hydrostatic pressure (Weetjens et al., 2009).

The gas generated predominantly at steel surfaces of waste and barriers and inside the waste packages will dissolve in the pore water and will be transported away from the repository by diffusion as dissolved species. If the rate of gas generation is larger than the diffusive flux into Boom Clay, the pore water within the disposal gallery will become oversaturated and a free gas phase might form. It is assumed that desaturation will occur in materials with (relatively) low gas-entry pressure such as the cementitious backfill. For Boom Clay, tests indicate that the gas entry pressure exceeds the lithostatic pressure (Le et al., 2008 and Lima et al., 2012). If the gas pressure should reach this value, evidence (Harrington et al., 2012) suggests that gas flow will happen through dilatant pathways, corresponding to newly formed

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porosity. Whether Boom Clay will ever be subject to such high gas pressures depends on many factors: a.o. the gas generation source term, the (dissolved) gas diffusion coefficient, gas entry value of the concrete EBS materials and total storage volume, characteristics of the seals etc.

The currently available gas diffusion parameters for hydrogen in Boom Clay were obtained from the MEGAS project (Modelling and Experiments on Gas Migration in Repository Host Rocks) (Volckaert et al., 1994). During this project, 2 types of diffusion experiments with H_2 were performed: in-diffusion experiments and through diffusion experiments. The in-diffusion experiments suffered from H_2 leakages, and the through-diffusion experiments were disturbed by CO_2-outgassing of the clay samples. These experimental problems lead to an uncertainty of up to 2 orders of magnitude (diffusion coefficient expressed as D_{app}) (4.2×10^{-12} m^2/s < D_{app} < 1.6×10^{-10} m^2/s). A recent re-evaluation of this MEGAS experiments by Aertsens (2009) showed that the applied technique indeed did not allow a more precise determination of the diffusion coefficient. Due to different experimental problems like outgassing of the clay, occurrence of a H_2 leak and a too short duration of the experiment compared to the length of the samples, only the lumped parameter nR√D could be fitted from which only estimations of D_{app} could be made. Finally this re-evaluation lead to an estimated D_{app} between 5×10^{-12} m^2/s and 4×10^{-10} m^2/s (Aertsens, 2009).

Sensitivity calculations varying the diffusion coefficient for hydrogen (Weetjens and Sillen, 2006) showed that with this uncertainty on the diffusion coefficient — combined with the uncertainty on the gas source term, the formation of a free gas phase cannot be excluded for some waste types.

Methods to determine gas diffusion coefficients of different gases in saturated porous media are limited in literature and are often very complicated and not suited to measure diffusion coefficients of different gases (He, CH_4, H_2, Ar).

In general, 3 types of methods are used to determine gas diffusion coefficients. The first method is the outgassing of clay samples or boreholes: clay samples are stored in a vacuum container and the concentration of gas released by the sample is measured. For boreholes the concentration of gas released into the borehole is measured. Based on these gas concentration measurements, the diffusion coefficient is determined. This method has been used by Bigler et al. (2005) and Gomez-Hernandez (2000). Bigler et al. (2005) performed an ^{4}He outgassing experiment with a spherical sample of the Callovo–Oxfordian Shale. With the best fit between the experimental result and the analytical solution, $D_p = 7.5 \times 10^{-10}$ m^2/s was obtained with an uncertainty of 20%. As the sample is spherical, the obtained diffusion coefficient is actually a mixed diffusion coefficient with respect to bedding plane orientation. In addition, the sample was not a perfect sphere and might have been disturbed by cutting. It is reported that this value has to be considered as a maximum value, affected by experimental artefacts (Bigler et al., 2005).

Bigler et al. (2005) also modelled an in-situ pore diffusion coefficient based on the natural He profile in the Callovo–Oxfordian shale. The obtained value is $D_p = 2.4 \times 10^{-10}$ m^2/s with a range of uncertainty from 0.8×10^{-10} to 7.2×10^{-10} m^2/s (Bigler et al., 2005). This range of uncertainty is almost 1 order of magnitude, and the experimentally obtained value for D_p does not fall within this range.

An in-situ in- and out-diffusion experiment with He parallel to the bedding plane was performed on Opalinus Clay in the Mont-Terri underground laboratory by Gomez-Hernandez (2000). The best fit for $D_{eff}(He) = 2.1 \times 10^{-10}$ m^2/s was obtained for an out-diffusion experiment but a porosity of 30% was used which is double of the typical reported porosity values for Opalinus Clay. This can be explained by the fact that during the drilling of the experimental borehole an EDZ was created, leading to a higher permeability and increased porosity (Gomez-Hernandez, 2000). However, this porosity value has not been confirmed by other measurements and is thus an estimate. As the fit for D_{eff} is based on this estimated porosity, the precision of D_{eff} is questionable. The other out- and in-diffusion experiments performed by Gomez-Hernandez (2000) could not confirm this value for D_{eff} without adapting parameters like the circulation volume or the initial concentration of ^{4}He.

The second method is calculating the diffusion coefficient, based on the concentration profile as natural tracer. This profile is obtained by outgassing boreholes or samples. This technique has been used by Rübel et al. (2002) and Bensenouci et al. (2011).

Rübel et al. (2002) fitted D_{app} for He (D_{app} = 3.5 × 10–11 m^2/s) in Opalinus Clay based on the natural profile of helium obtained at Mont Terri URL (Switzerland). However, according to Mazurek et al. (2011), this D_{app} value is likely too small because of an overly simplified model. Bensenouci et al. (2011) obtained a He profile for samples collected from 2 vertical drilled boreholes in the Toarcian/Domerian Shale in Tournemire URL (France). The He content in the pore water was determined by outgassing in high-vacuum containers. Based on the obtained He profile, D_p was calculated to be in a range between 2.4 and 12.7×10^{-11} m^2/s. But for 3 samples a discrepancy between the measured ^{4}He concentration and the model simulation was noticed (Bensenouci et al., 2011).

Calculating diffusion coefficients for naturally present gases, based on their concentration profile is an interesting technique, but it has two major disadvantages. The technique is only applicable for gases which are naturally present in the clay and basically limited to He, Ar and CH_4. So this method cannot be used to determine the diffusion coefficient for hydrogen.

The second disadvantage is that experimental results, obtained by outgassing of clay samples have to be interpreted with care. The treatment of the samples after coring has to be done very carefully: cores will degas immediately after sampling, or they can take up gas from the atmosphere. This uncertainty on the initial state of the sample increases the uncertainty on the obtained diffusion coefficient. Mazurek et al. (2011) stated that the core outgassing of noble gases requires sophisticated equipment and there is a possibility of gas leakage at several stages.

The third method to determine diffusion coefficients for gases is by performing lab experiments based on the in- or through-diffusion technique. This method has been used by Krooss and Schaefer (1987) and by Rebour et al. (1997). Krooss and Schaefer (1987) used a through diffusion set-up where the upstream reservoir was filled with a gas. The gas composition of the downstream reservoir was analysed on a regular base, and the diffusion coefficient was calculated by using the time-lag method. The described set-up has some disadvantages: due to its design gas pressure should be equal to atmospheric pressure and consequently sample thickness should be small (between 2 and 10 mm) in order to obtain the diffusion coefficient within a reasonable time period and due to the treatment of the sample during the loading into the diffusion cell, the natural pore structure might have changed. The reported maximum error on the diffusion coefficient is 20%. Rebour et al. (1997) also used a through diffusion set-up but the upstream reservoir was a water phase saturated with gas. This method is interesting as it describes a through-diffusion experiment with dissolved gases so similar to our concept. However as the set-up involves many valves, controllers, pumps and some very specific equipment like tailor-made pressure accumulators and a He-extraction system, the construction and operation of this set-up is not straightforward. Despite the fact that this set-up could be used for different gases, only data for He diffusion on Callovo–Oxfordian Clay were reported ($D_{app} = 5 \pm 1 \times 10^{-11}$ m^2/s) (Rebour et al., 1997). The interpretation of the data suffered from complications such as anisotropy effects which were not taken into account and the measured porosity (23%) did not correspond to the porosity value needed to obtain a good fit (16%) (Bigler et al., 2005).

Therefore a more versatile method, using a simple set-up and suitable for a suite of gases, was developed to determine more precisely the gas diffusion coefficient for dissolved gases (especially dissolved hydrogen) in Boom Clay. This should allow a more realistic assessment of the diffusive gas flux out of a repository as a function of the estimated gas generation rates.