Supplying Information

Dilution Effect On Concentration Measurements

Figure S1 illustrates the effect of sampling-induced dilution on experimental diffusion measurements. The estimated impact of dilution ranges from 0.2 to 3.7% standard deviation in C/C_0 values over the considered diffusion timescale (up to 100 minutes). Therefore, the established experimental procedure, with a sampling rate of 0.2 mL/minute, has a negligible impact on the accuracy of diffusion coefficient measurements.

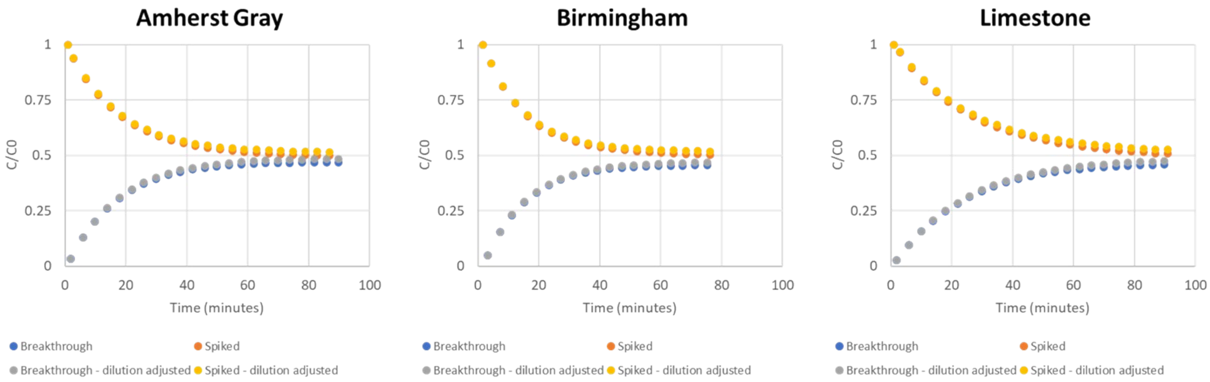

Figure S1: Ambient temperature breakthrough showing the impact of dilution over the < 100-minute diffusion experiment.

Diffusion in a Two-Bulb Cell

The general equation for advection-diffusion is [73]

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c) - \nabla \cdot (vc) + R \tag{S1}$$

where c is the concentration, t is the elapsed time for transport, D is diffusion coefficient, v is the velocity field and R is the source or sink term of H_2 molecules.

In the system of interest, constant-pressure flow mode is achieved and thereby pure diffusion is established. Then Eq. (S1) reduces to

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c) \quad . \qquad \text{(S2)}$$

A solution of the concentration within the connecting tube is a function of position and time. With the assumption of a quasi-steady state and linear concentration profile within the tube, Fick's first law [74] can be applied to predict concentration changes as a function of time for either bulb:

$$V\square_2 \frac{\partial c_2}{\partial t} = - DA(c_2 - c_1)/L \quad , \qquad \text{(S3)}$$

where $V\square_2$ is the volume of the breakthrough bulb, $(c_2 - c_1)/L$ is the linear concentration gradient across the connecting tube and A is the cross-sectional area of the tube.

In the quasi-steady state, there is no accumulation in the connecting tube, establishing a mass balance in the two bulbs,

$$V\square_2 c_2 + V_1 c_1 = (V_1 + V_2) c_\infty , \qquad \text{(S4)}$$

Where V_1 is the volume of the spiked chamber, c_∞ is the stabilized concentration obtained at diffusion equilbirum conditions.

Combining the diffusivity equation with the mass balance equation gives:

$$\frac{\partial c_2}{\partial t} = - \frac{DA(V_1 + V_2)}{L V_1 V\square_2} (c_2 + c_\infty) \quad . \qquad \text{(S5)}$$

The time-series concentration of the bulb is found by substituting the initial concentration of c_o, measured immediately after H_2 injection into the solution of Eq. (S5), which is given by [35-37]

$$\frac{c(t)}{c_o} = \left(1 - \frac{c_\infty}{c_o}\right) e^{-\frac{DA(V_1 + V_2)}{LV_1 V_2} t} + \frac{c_\infty}{c_o}. \tag{S6}$$

In the above formula, $c(t) \rightarrow c_\infty$ for sufficiently large diffusion time (i.e., time to reach equilibrium conditions). A linear relationship can be found by log-transformation of the concentration solution, i.e.,

$$\ln\left(c_\infty - c(t)\right) = -\frac{DA(V_1 + V_2)}{LV_1 V_2} t + \ln\left(c_\infty - c_o\right). \tag{S7}$$

The effective diffusion coefficient of the rock samples can be determined from the slope of the semi-log plot of $(c_\infty - c)$ against diffusion time. $(c_\infty - c)$ is the concentration change in the spiked or breakthrough bulb, monitored through continuous sampling and mass spectrometry analysis.

Simulation Model in CMG-GEM

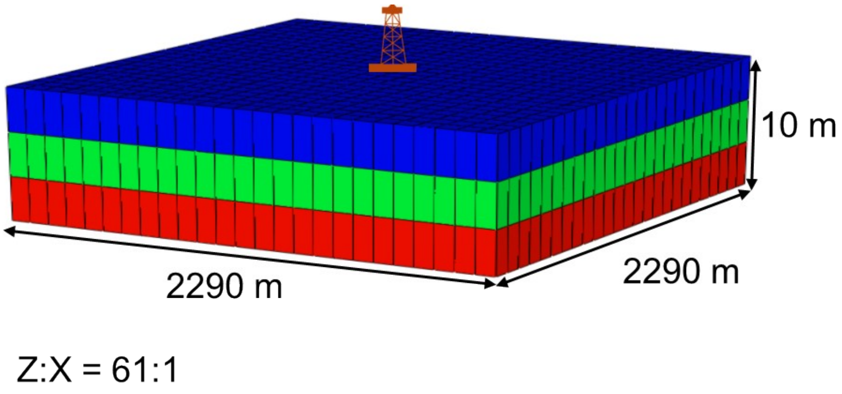

Figure S2: Numerical model used to simulate H_2 plume migration in reservoir layers under advective and diffusive flow, with injection well placed in the center. Vertical direction is scaled 61 times more than horizontal direction.