

SUPPLEMENTAL INFORMATION

TITLE: DNAPL Architecture and Dissolution in Discretely Fractured Sandstone Blocks

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Supplemental Data

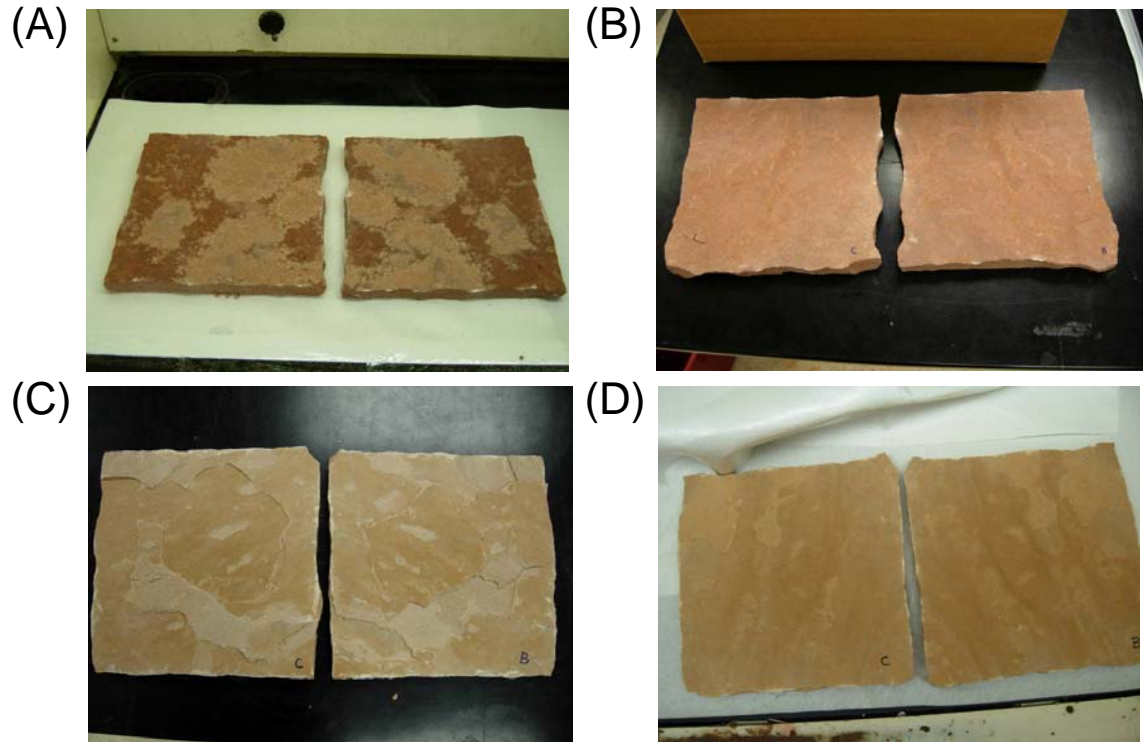


Figure S1. Inside views of the fracture faces for: (A) Colorado rock 1, (B) Colorado rock 2, (C) Arizona rock 1, and (D) Arizona rock 2. Each rock was approximately 29 cm long (L) x 29 cm wide (W).

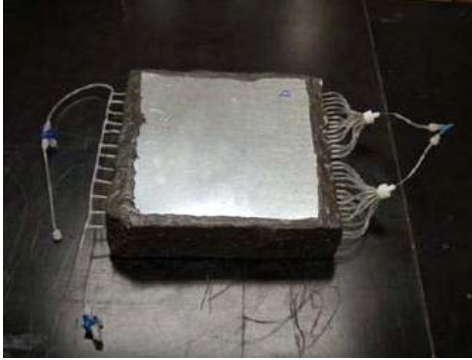
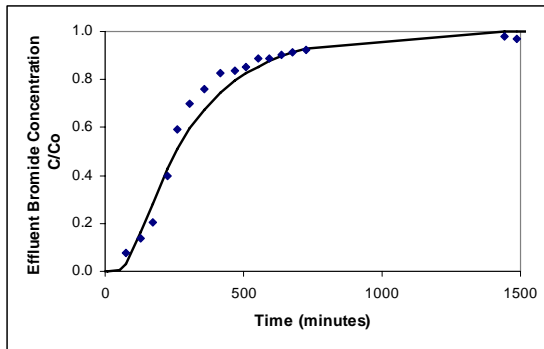


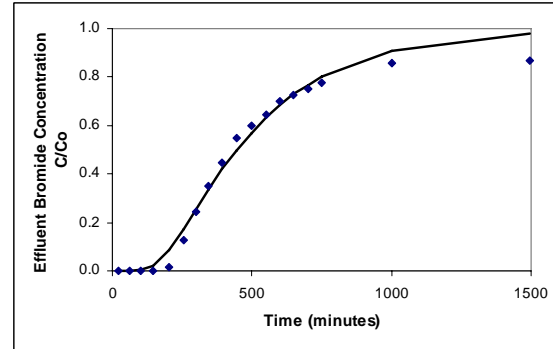
Figure S2. Experimental fracture system.

$V = 0.097 \text{ cm/min}; D = 0.61 \text{ cm}^2/\text{min}$



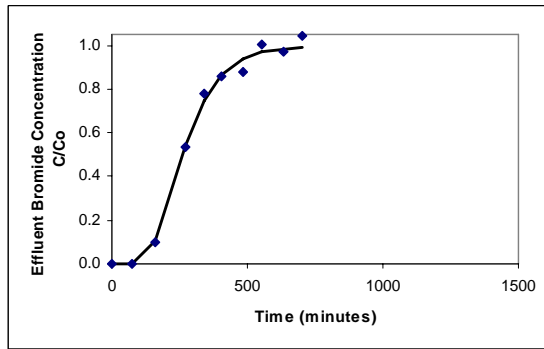
(a)

$V = 0.055 \text{ cm/min}; D = 0.31 \text{ cm}^2/\text{min}$



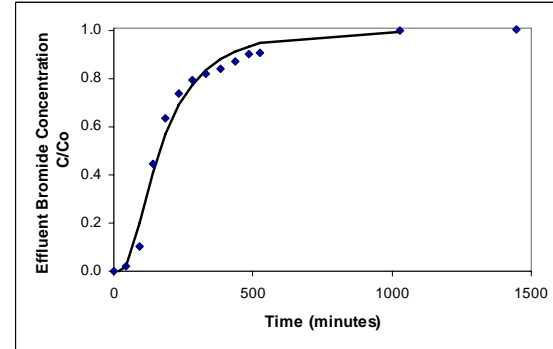
(b)

$V = 0.010 \text{ cm/min}; D = 0.25 \text{ cm}^2/\text{min}$



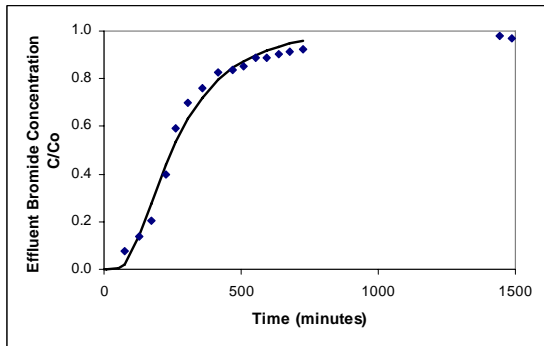
(c)

$V = 0.14 \text{ cm/min}; D = 1.2 \text{ cm}^2/\text{min}$



(d)

$V = 0.087 \text{ cm/min}; D = 0.77 \text{ cm}^2/\text{min}$



(e)

Figures S3a through S3e. Bromide elution curves in rock: a) C1 (no residual PCE), b) A1 (no residual PCE), c) C1 (residual PCE present), d) A1 (residual PCE present), and e) C1 (no residual PCE). Elution curves were regressed to Equation 1 using CXTFIT. Regressed values of the water velocity and dispersion coefficient are shown above each figure. The volumetric flow rate for the experiment shown in Figure S3c was only $0.6 \text{ cm}^3/\text{min}$, compared to approximately $0.1 \text{ cm}^3/\text{min}$ for the experiments shown in the other figures.

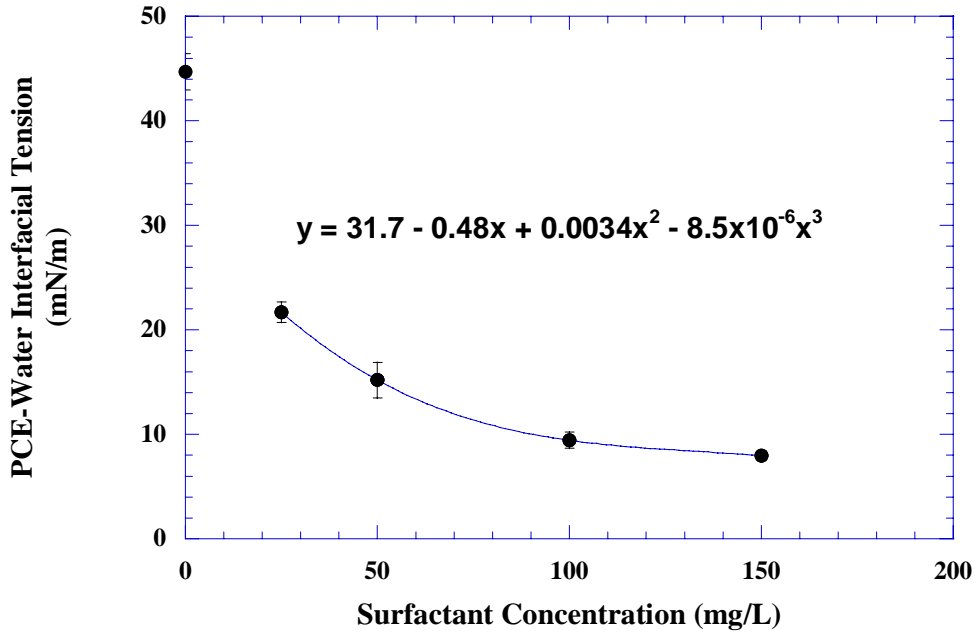


Figure S4. PCE-water interfacial tension as a function of SDBS concentration in water.

The polynomial regressed to the data was used to compute the derivative in Equation 5.

Regressed Values of R from CXTFIT.

The standard error for each regressed value of R from Eq. 1. The standard error for R calculated for the replicate experiments (δ_R) also is shown in the table.

Rock	Retardation Factor (R)
C1	1.20 / 1.15 / 1.16 ($\delta_R = 0.015$)
C2	1.42 / 1.33 / 1.34 / 1.39 ($\delta_R = 0.021$)
A1	1.45 / 1.47 ($\delta_R = 0.010$)
A2	1.22 / 1.22 / 1.10 ^a / 1.23 ($\delta_R = 0.003$)

^a Outlier

Error Calculation for DNAPL-water Interfacial Area

The standard regression error associated with R (Eq. 4) is less than or equal to 1.5% (based on standard error of replicate regressions performed using CXTFIT). The standard error associated with K (Eq. 5) is less than 10%, which is derived from the derivative of the polynomial regression ($\frac{\partial \sigma}{\partial C}$) shown in Figure S4. The standard error associated with θ (Eq. 4) is less than 12%, which is derived from the error associated with the determination of the fracture volume (FV) and DNAPL volume of each rock. Error propagation for calculating the DNAPL-water interfacial area was performed using the generalized propagation of error formula (NIST/SEMATECH e-Handbook of Statistical Methods, <http://www.itl.nist.gov/div898/handbook/>, 2006):

$$\delta_a = \sqrt{\left(\frac{\partial a}{\partial K}\right)^2 \delta_K^2 + \left(\frac{\partial a}{\partial \theta}\right)^2 \delta_\theta^2 + \left(\frac{\partial a}{\partial R}\right)^2 \delta_R^2} \quad \text{Eq. S1}$$

where δ is the standard error associated with the interfacial area (a), SDBS sorption coefficient (K), volumetric water content (θ), or retardation factor (R). The resultant value of δ_a is <28%.

An additional Monte Carlo simulation was performed to verify results for the C1 rock. For the simulation, it was assumed that θ was sampled over a normal distribution with a mean of 0.76 and a standard deviation of 0.06. K was sampled over a normal distribution with a mean of 0.0061 and a standard deviation of 0.00061. R was calculated as the mean of the three experimental results for C1, but each of the three results were independently sampled over a normal distribution with means of 1.2, 1.15, and 1.16, and standard deviations of 6 % (derived from the regression error for individual SDBS tracer tests from CXTFIT).

The calculation (using Eq. 4) was repeated 5000 times. Each time a value for a_i was calculated based on independent and randomly selected values of R , θ , and K , constrained by the distributions defined above. The software package Crystal Ball (Ver 7.3 for EXCEL spreadsheets) was used for the analysis. Results are shown below. Results are in good agreement with those using Eq. S1.

Statistic	Forecast values
Trials	5,000
Mean	21.41
Median	21.06
Standard Deviation	5.927
Variance	35.13
Skewness	0.347
Kurtosis	3.33
Coeff. of Variability	0.2768
Minimum	-3.233
Maximum	46.94
Mean Std. Error	0.0838