Adsorptive Transport of Noble Gas Tracers in Porous Media

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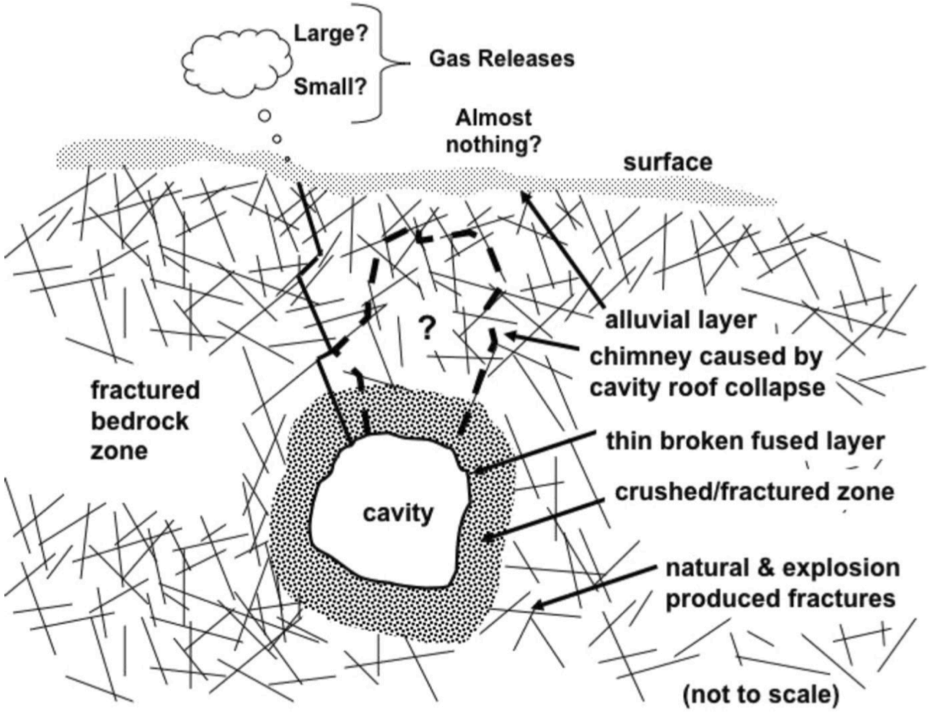
Introduction

Transport processes significantly affect the quantity of radioactive noble gases that reach the surface in an underground nuclear explosion (UNE)

Transport through the a homogeneous media depends on intrinsic properties including:

- Porosity
- Tortuosity
- Permeability
- Barometric conditions
- Water saturation

Heterogeneity can be modeled by varying material properties or dual porosity/fracture-matrix models



C. Carrigan and Y. Sun, "Detection of Noble Gas Radionuclides from an Underground Nuclear Explosion During a CTBT On-Site Inspection", Pure and Applied Geophysics, vol. 171, no. 3-5, pp. 717-734, 2012.

Background

In fully advective flow, all tracers arrive at the same time with the same dilution. However, diffusion disperses material, reducing the concentration arriving at the surface.

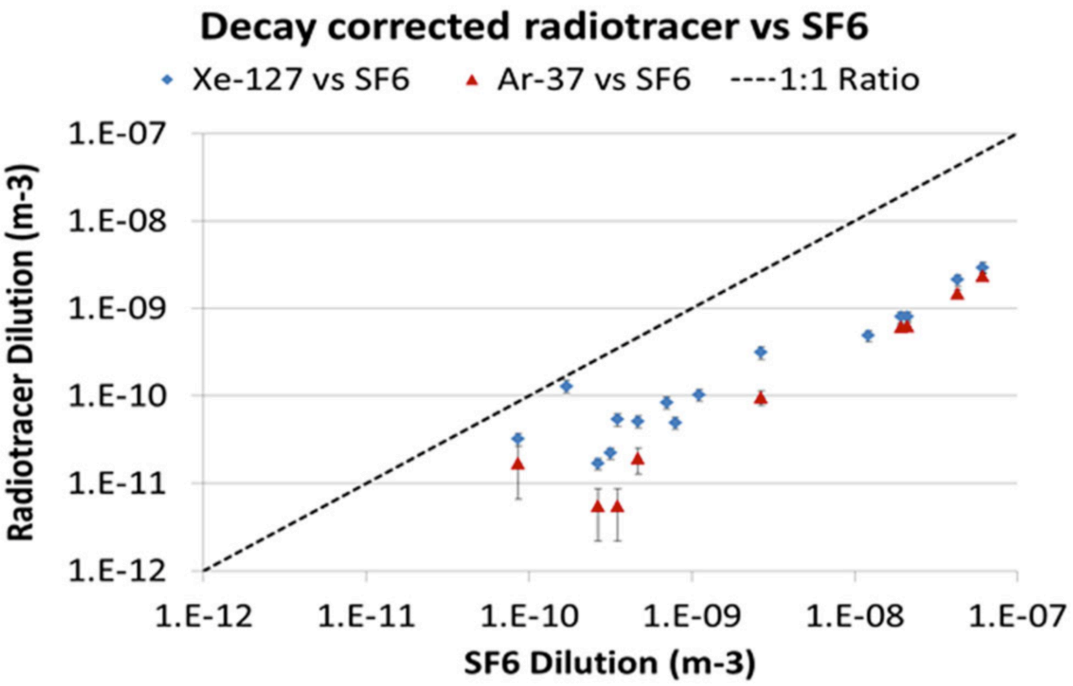
In field tests, the quantity of noble gas radionuclides reaching the surface falls below the stable reference, Sulfur Hexafluoride, SF_6

Process that may result in selective separation include:

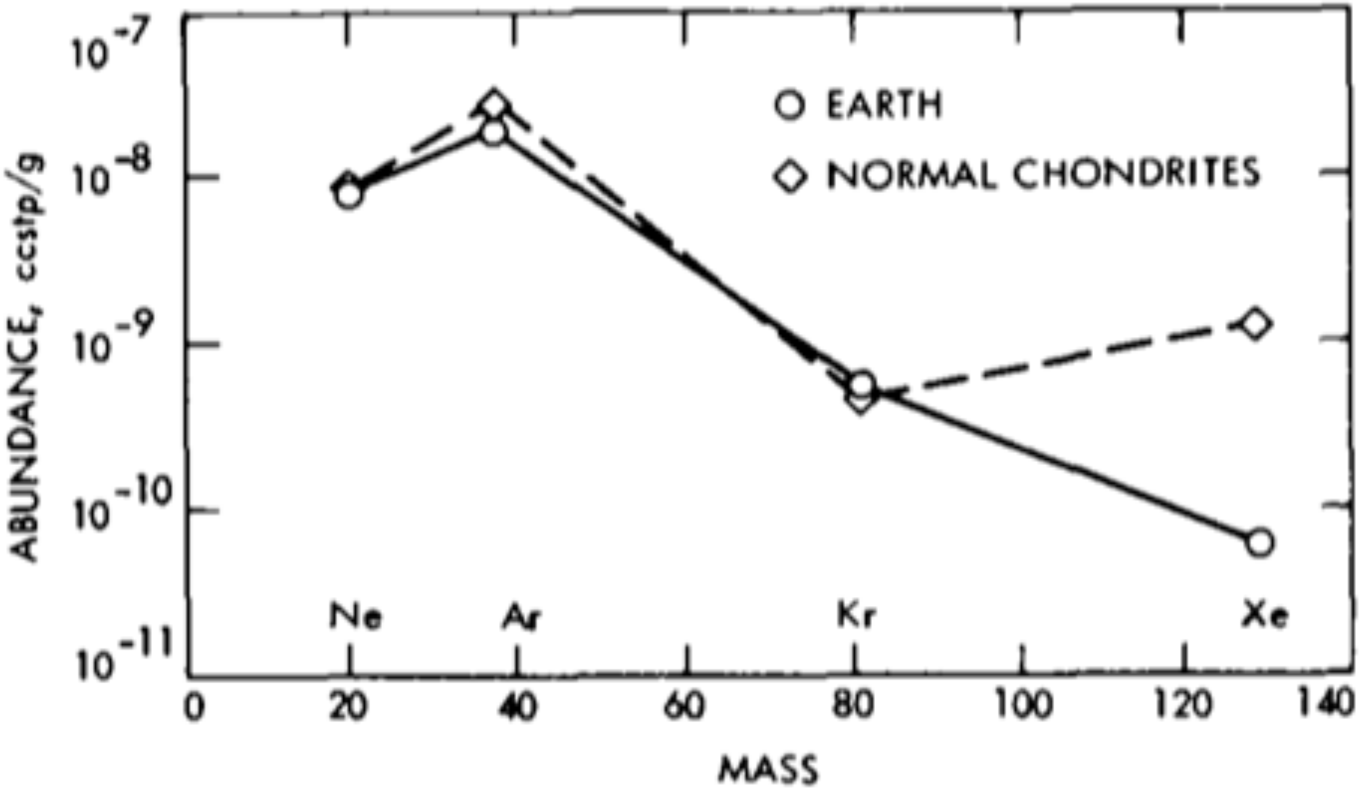
- Diffusivity
- Radioactivity
- Chemical Reactivity
- Sorption Affinity

Diffusive losses into the surrounding matrix may explain the dilution of argon, but cannot for xenon

Negligible chemical reactions for both noble gases and saturated fluorides



Olsen, K. B., et al. "Noble gas migration experiment to support the detection of underground nuclear explosions." *J Radioanal Nucl Chem* 307 (2016): 2603-2610.

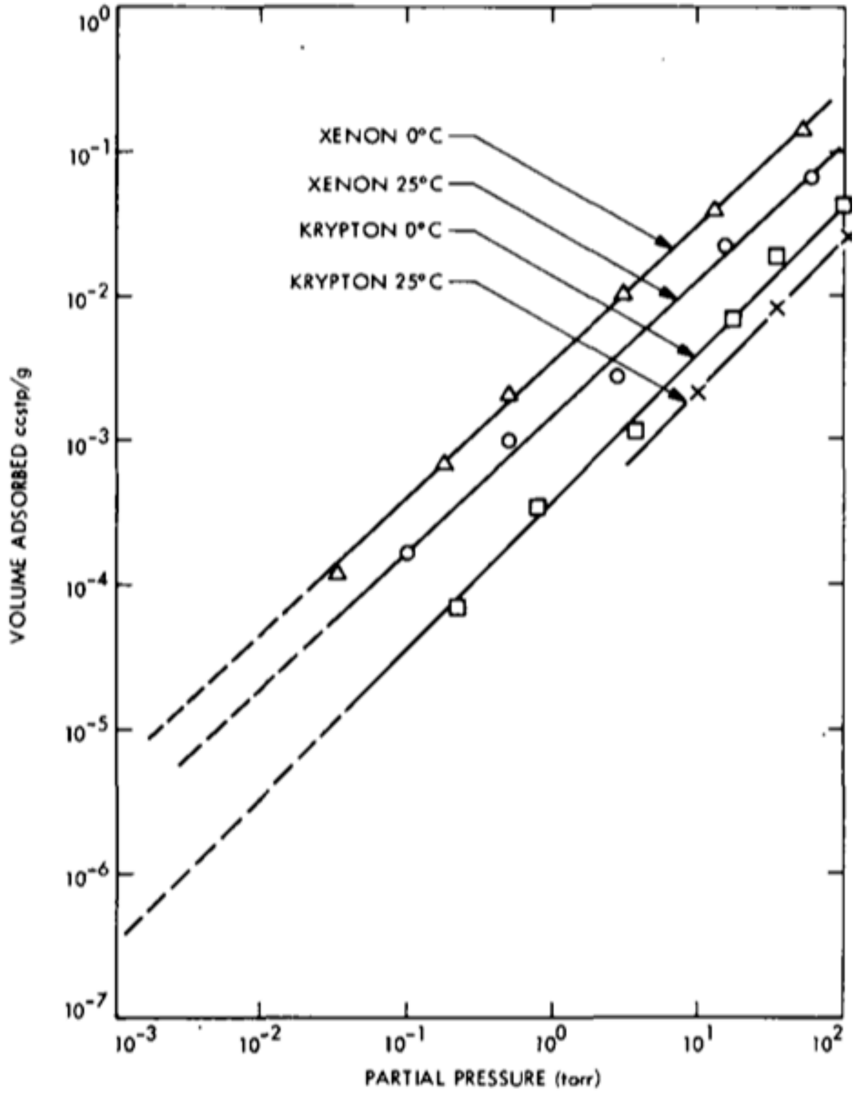


The Missing Xenon Question

F.P. Fanale and W.A. Cannon, ”Physical adsorption of rare gas on terrigenous sediments”, Earth and Planetary Science Letters, vol. 11, no. 1-5, pp. 362-268, 1971.

Noble Gas Adsorption Literature Data on Geological Materials

- Limited data previously available of xenon adsorption on general geological materials
  - Linear to 100 torr
  - Henry's Law is valid extrapolation to much lower partial pressures
- Measured in terms of mass of adsorbent



F.P. Fanale and W.A. Cannon, "Physical adsorption of rare gas on terrigenous sediments", Earth and Planetary Science Letters, vol. 11, no. 1-5, pp. 362-268, 1971.

Three-phase Material Balances

- Three volumes:
  - Gas ε(1-S)V
  - Liquid εSV
  - Solid (1-ε)V
- Six interfacial surfaces fluxes:
  - Gas-Gas defined by advective/ diffusive flows
  - Liquid-Liquid and Solid-Solid assumed legible
  - Gas-Liquid defined by absorption
  - Gas-Solid and Liquid-Solid defined by adsorption
- Radioactive kinetics independent of phase
- Capacity factor with an adsorbed phase

$$\kappa_i = 1 + \frac{RT}{P}\frac{\rho_s K_i}{(1-S)}\left(\frac{1}{\varepsilon} - 1\right)$$

$$\frac{\partial}{\partial t}\int_{\varepsilon(1-S)V} c_{i,g}\,dV = -\oint_{\varepsilon(1-S)V} N_i \cdot dA + \int_{\varepsilon(1-S)V} r_i\,dV$$

$$\frac{\partial}{\partial t}\int_{\varepsilon SV} c_{i,l}\,dV = -\oint_{\varepsilon SV} N_i \cdot dA + \int_{\varepsilon SV} r_i\,dV$$

$$\frac{\partial}{\partial t}\int_{(1-\varepsilon)V} c_{i,s}\,dV = -\oint_{(1-\varepsilon)V} N_i \cdot dA + \int_{(1-\varepsilon)V} r_i\,dV$$

$$\frac{\partial}{\partial t}\left(\kappa_i c_i\right) = -\nabla \cdot N_i + r_i$$

Three-phase Material Balance

$$\frac{\partial}{\partial t}\left(\kappa_i c_i\right) = -\nabla \cdot N_i - \kappa_i \lambda_i c_i + \sum_{j \neq i}^{n} f_{i,j} \kappa_j \lambda_j c_j$$

$$\kappa_i \frac{\partial c_i}{\partial t} = \frac{\varepsilon(1-S)}{q^2} D_i \nabla^2 c_i$$

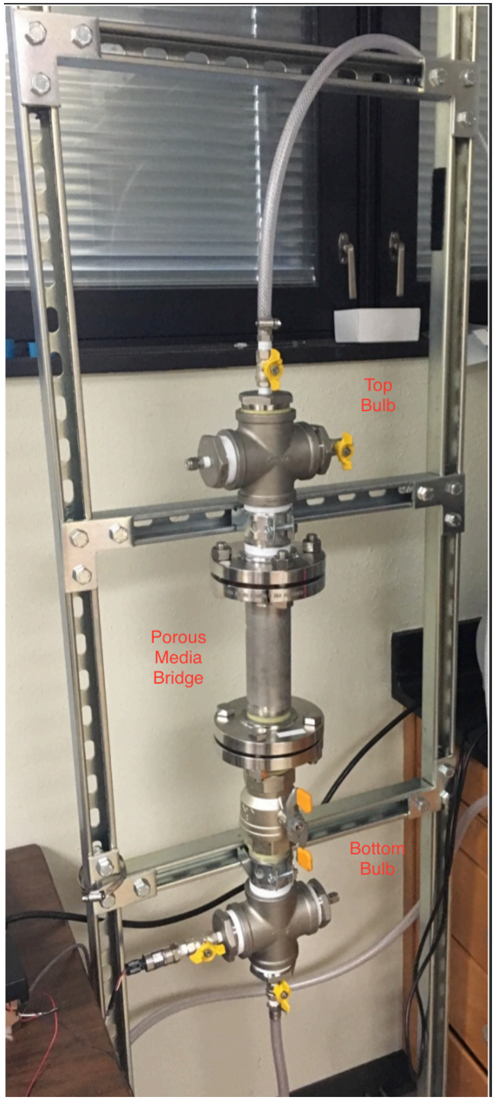
- In the field:
  - Barometric pumping
  - Dilute
  - Homogenous decay
  - Inhomogeneous sources
- In the laboratory:
  - Isothermal
  - Isobaric
  - Dilute
  - Stable (when using GC-MS)

Two-bulb Quasi-steady State Method

- Ney-Armistead developed the two-bulb quasi-steady state method of measuring diffusivity
- Deviation from original method as the bridge is packed with porous media
    - Used #10-30 mesh Ottawa sand
    - Filled with ordinary atmosphere
    - Supports wet media
    - Maximum tracer concentration is roughly 100 ppm
- Apparatus designed to support gas chromatograph-mass spectrometer (GC-MS) sampling times
- Analytical solution to two-bulb system with bridge of negligible volume:

$$\tau = \frac{1}{D_i}\frac{q^2}{\varepsilon(1-S)}\frac{L}{A}\frac{V_1V_2}{V_1+V_2} \qquad \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = c_\infty \begin{bmatrix} 1 \\ 1 \end{bmatrix} + c_0 \begin{bmatrix} -V_2 \\ +V_1 \end{bmatrix} e^{-t/\tau}$$

- Four unknowns in a set of inhomogeneous, nonlinear system of equations
    - Volumes may vary by species as the adsorbed volume is species dependent



Ney, Edward P., and Fontaine C. Armistead. "The Self-Diffusion Coefficient of Uranium Hexafluoride." Physical Review 71, no. 1 (Jan 1947): 14-19.

Quantitative Method

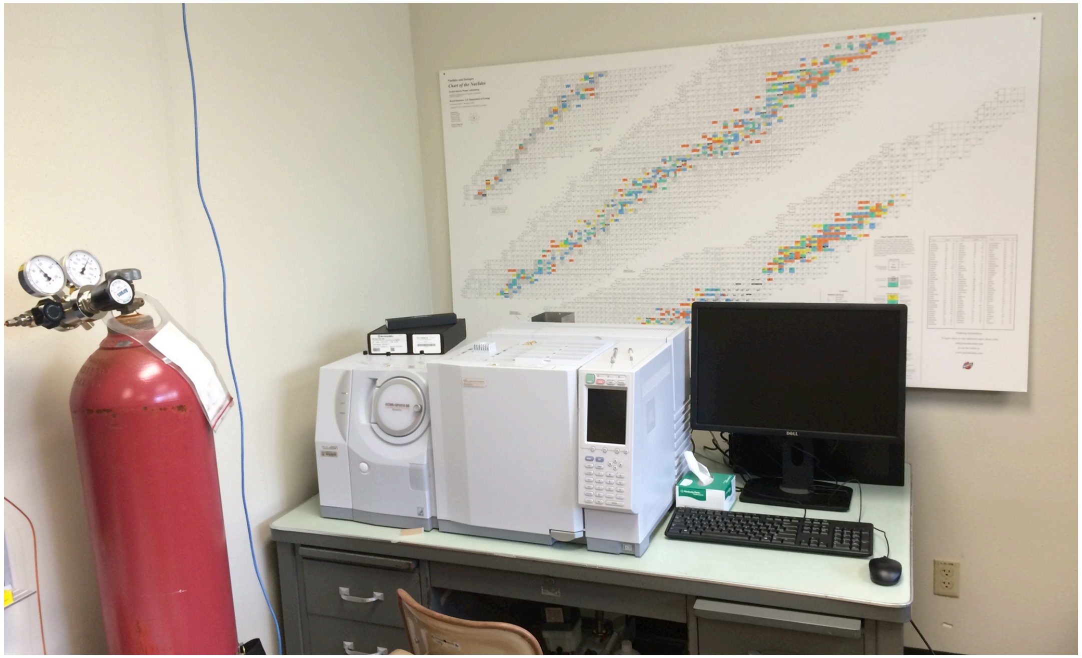
2 He 4.003
10 Ne 20.18
18 Ar 39.95
36 Kr 83.79
54 Xe 131.3
86 Rn (222)
118 Og (294)

- Noble gases are monatomic
  - – No infrared, visible, or ultraviolet interactions
- Must benchmark to SF_6
  - – No suitable gamma-emitting radioisotopes of S or F
- Dilute concentrations are required
  - – Thermal conductivity or capacitance are insensitive
- Gas Chromatography-Mass Spectrometry chosen
  - + Detects dilute, stable, and monatomic tracers
  - – Samples are invasive
  - – Analysis time takes minutes

Quantitative Method

A GC-MS instrument was required on-site due to:

- Vial permeation
- Configuration management
- Increased availability



Employed the Shimadzu GCMS-QP2010 SE

- Electron Impact (EI) ion source
- Single-quadrupole mass analyzer

Numerical Method

- Because the bulbs are converging exponentially,
  - Requires three digits of precision or more
  - Small systematic error or permeation losses results in large differences in relaxation times
- Numerical estimation of equilibrium concentration
  - Homogenize vector components using equilibrium concentration estimate
  - Maximum likelihood estimate (MLE) of exponential parameters
  - Iterate using bisection method until common relaxation time is found

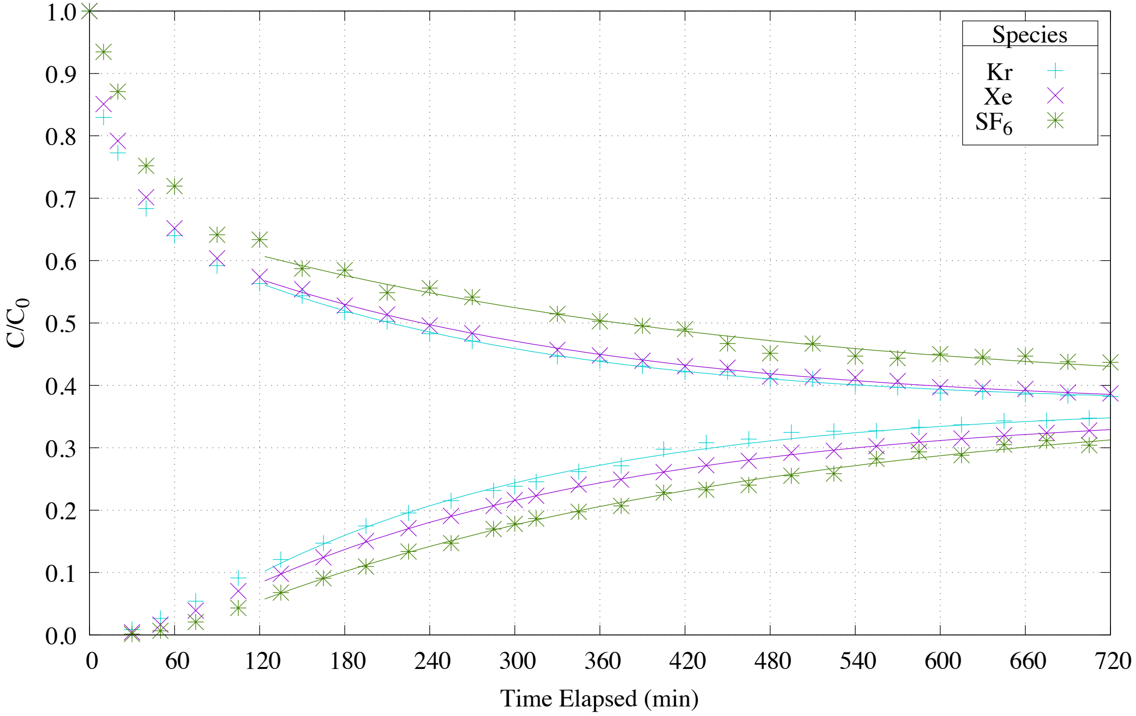
$$Ae^{Bx_i} + \varepsilon_i = y_i = c_i - c_\infty$$

$$P(A,B) = \prod \frac{1}{\sqrt{2\pi\sigma}} e^{-\frac{(y_i - Ae^{Bx_i})^2}{2\sigma^2}}$$

$$\ln A = \frac{\sum x_i^2 y_i^2 \sum y_i^2 \ln y_i - \sum x_i y_i^2 \sum x_i y_i^2 \ln y_i}{\sum y_i^2 \sum x_i^2 y_i^2 - \left(\sum x_i y_i^2\right)^2} = \ln c_o V$$

$$B = \frac{\sum y_i^2 \sum x_i y_i^2 \ln y_i - \sum x_i y_i^2 \sum y_i^2 \ln y_i}{\sum y_i^2 \sum x_i^2 y_i^2 - \left(\sum x_i y_i^2\right)^2} = \frac{1}{\tau}$$

$$\Delta B(c_\infty) = B_1(c_\infty) - B_2(c_\infty) = 0$$



Example Trial Results

Time-dependent concentration of three-species released simultaneously, normalized to the initial concentration.

Diffusivity Results

- Using measured bulb volumes, the relaxation time is related to the effective diffusivity – including porosity and tortuosity

- Dividing the observed effective diffusivity by literature values for diffusivity in nitrogen provides the estimate of the porosity-tortuosity factor

Trial	Gas	τ(min)	$D_i \varepsilon/q^2$ (cm^2/s)	ε/q^2	
1	Kr	229.6	0.0400	0.270	0.276
	Xe	269.2	0.0341	0.280	
	SF_6	359.0	0.0256	0.279	
2	Kr	232.9	0.0394	0.266	0.265
	Xe	278.6	0.0329	0.270	
	SF_6	387.7	0.0237	0.258	
3	Kr	222.5	0.0413	0.279	0.270
	Xe	281.8	0.0326	0.267	
	SF_6	376.7	0.0244	0.265	

Marrero, T. R., and E. A. Mason. "Gaseous Diffusion Coefficients." J. Phys. Chem. Ref. Data. 1, no. 1 (1972): 3-118.

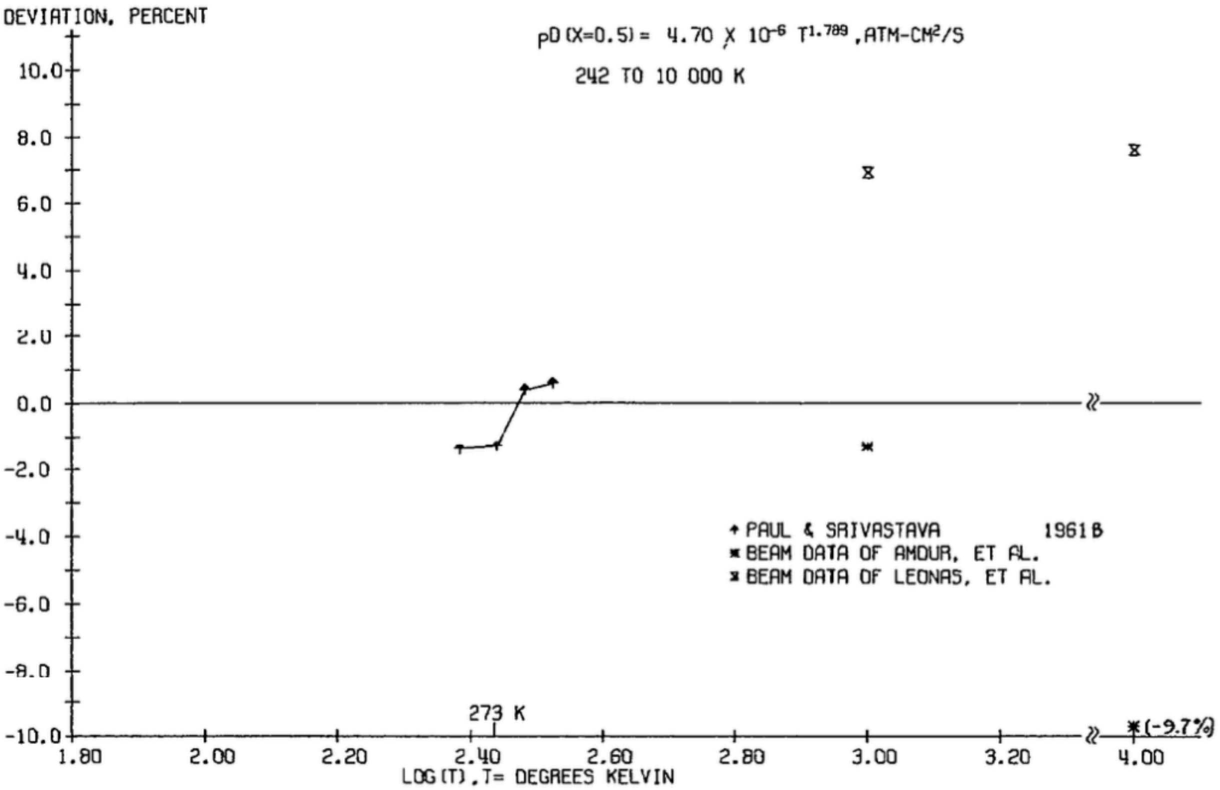


FIGURE 62. *Deviations of diffusion coefficients from reference equation.*

Nitrogen—Xenon

Spread in Literature Values for Xe-N_2 Diffusion

Marrero, T. R., and E. A. Mason. "Gaseous Diffusion Coefficients." J. Phys. Chem. Ref. Data. 1, no. 1 (1972): 3-118.

Apparent Volume Results

Gas	C_∞/C_0	$V_i(cm^3)$	$V_i-V_{Ar}(cm^3)$	$K_i(cm^3@STP/g/torr)$
Kr	0.3650	2052	89	1.11E-04
Xe	0.3645	2055	92	1.14E-04
SF_6	0.3706	2021	58	7.22E-05

- Using the measured high concentration bulb volume and the fraction at equilibrium yields the total apparent volume
- Comparing the apparent volume of the tracer species to argon – presumed inert – yields an indirect estimate of the adsorption isotherm

Discussion

- Porosity-tortuosity factor adequately described diffusion after initial transient
- Yet a difference in the final apparent volume is present
  - Capacity factor has no impact on (quasi)steady-state systems of stable tracers
- To scale to larger systems, the non-dimensional numbers must match
  - Fourier number necessarily large for quasi-steady state method to apply

$$\kappa_i \frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i - \kappa_i \lambda_i c_i$$

$$\mathrm{Fo} = \frac{D_i}{\kappa_i} \frac{t}{L^2}$$

Infinite Medium

- E.g. Stable tracer of fixed concentration diffusing into an infinite adsorbing medium

$$\kappa_i \frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i$$

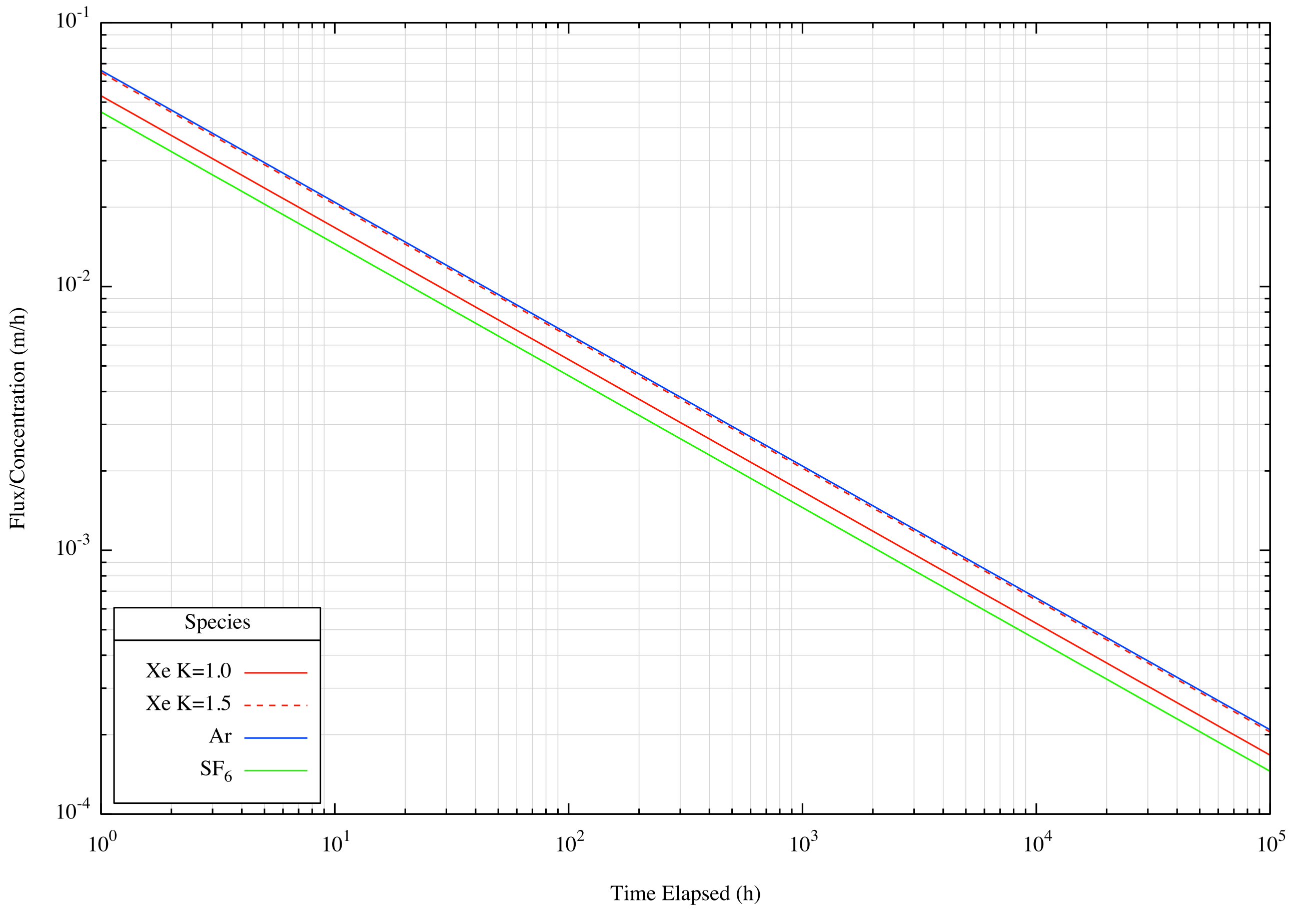
$$c(x,0) = 0 \quad c(0,t) = c_0 \quad c(\infty,t) \rightarrow 0$$

- Concentration profile approaches steady state via the error function

$$c(x,t) = c_0 \operatorname{erfc}\left(\frac{|x|}{2} \sqrt{\frac{\kappa_i}{D_i t}} \right)$$

- Applying Fick's Law at the interface (x=0) reveals the diffusive flux is enhanced by sorption
  - Counter to "retardation" factor moniker

$$J_0(t) = c_o \sqrt{\kappa_i D_i} \frac{1}{\sqrt{\pi t}}$$



Diffusive Flux into an Infinite Sorbent Matrix

With a capacity factor of 1.5, the diffusive flux of Xe is virtually indistinguishable from the diffusive flux of Ar.

Finite Medium

- E.g. Stable tracer of fixed concentration diffusing into a finite adsorbing medium
  - No flux condition at length L

$$\kappa_i \frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i$$

$$c(x,0) = 0 \quad c(0,t) = c_0 \quad \frac{\partial c}{\partial x}(L,t) = 0$$

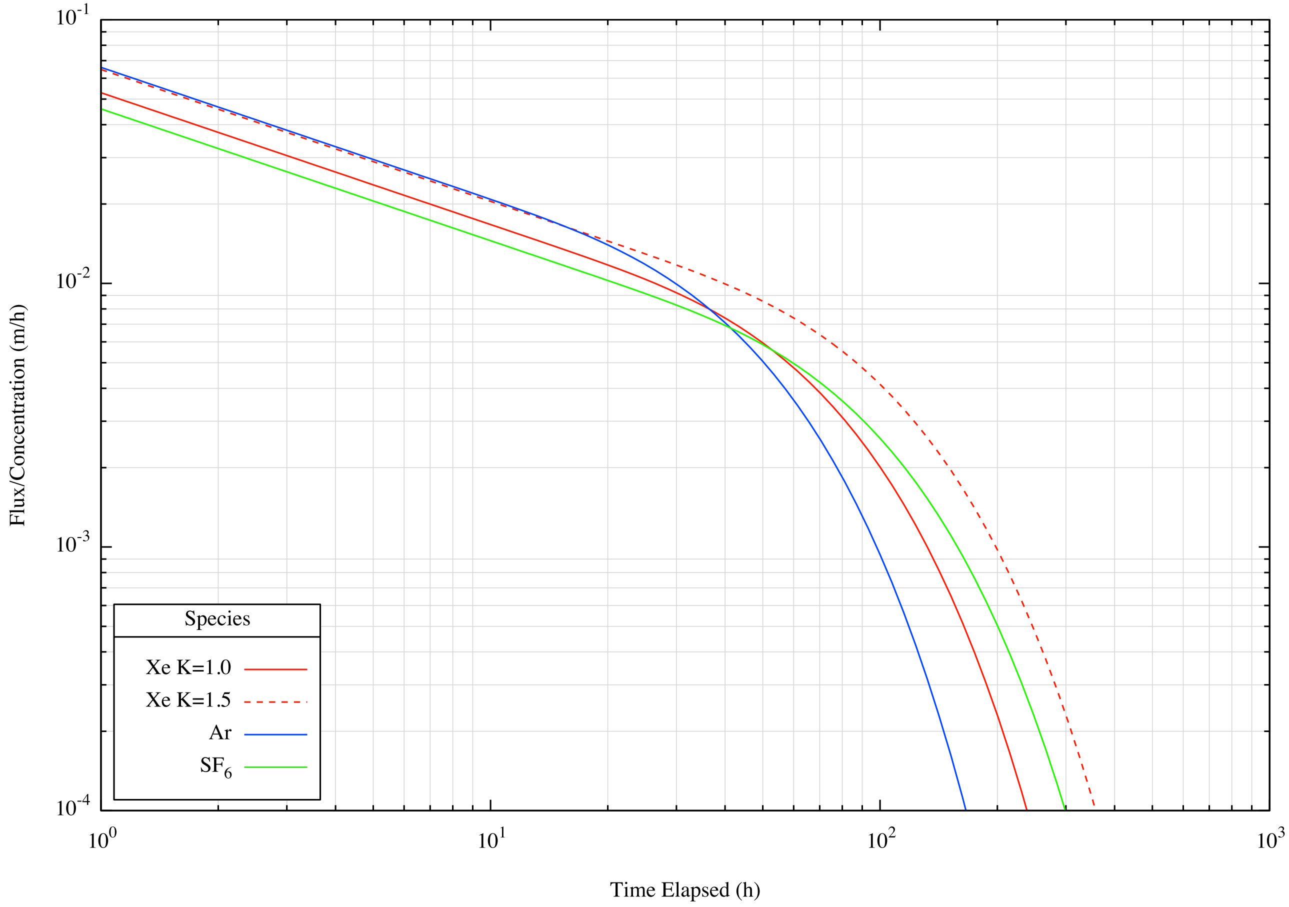
- Concentration profile approaches steady state via Fourier series

$$Fo = \frac{D_i}{\kappa_i}\frac{t}{L^2} \quad k_n = \frac{(2n+1)\pi}{2}$$

$$c(x,t) = c_0\left(1 - 2\sum_{n=1}^{\infty}\frac{\sin(k_n \frac{x}{L})}{k_n} e^{-k_n^2 \mathrm{Fo}}\right)$$

- Applying Fick's Law at the interface (x=0) demonstrates
  - Initial flux is unaffected by sorption, but
  - The capacity factor "retards" the the Fourier number with increasing time
  - I.e. Higher flux for a longer time period

$$J_0(t) = 2c_o D_i \sum_{n=0}^{\infty} e^{-k_n^2 Fo}$$



Diffusive Flux into an Finite Sorbent Matrix

The characteristic length used is 1 m. While the flux response is similar to the infinite case initially, the response diverges as the system reaches capacity.

Conclusions

- Porosity-tortuosity adequately describes the steady-state transport of noble gases and SF_6 in macroporous media, however
- Gas adsorption/absorption has a measureable impact, reducing the gas phase concentration.
  - This effect is most pronounced for Xe.

- The capacity or "retardation" factor decreases the Fourier number, without decreasing the corresponding flux
- Consequently, the flux response of a less diffusive species may match that of a more diffusive species into an approximately infinite sorbent media but
- It is not generally possible to match the flux response in finite media for all times

- Knowledge of both the diffusivity (well known) and capacity factor (poorly known) are necessary to scale the diffusive flux of different chemical tracer gas species

Acknowledgments

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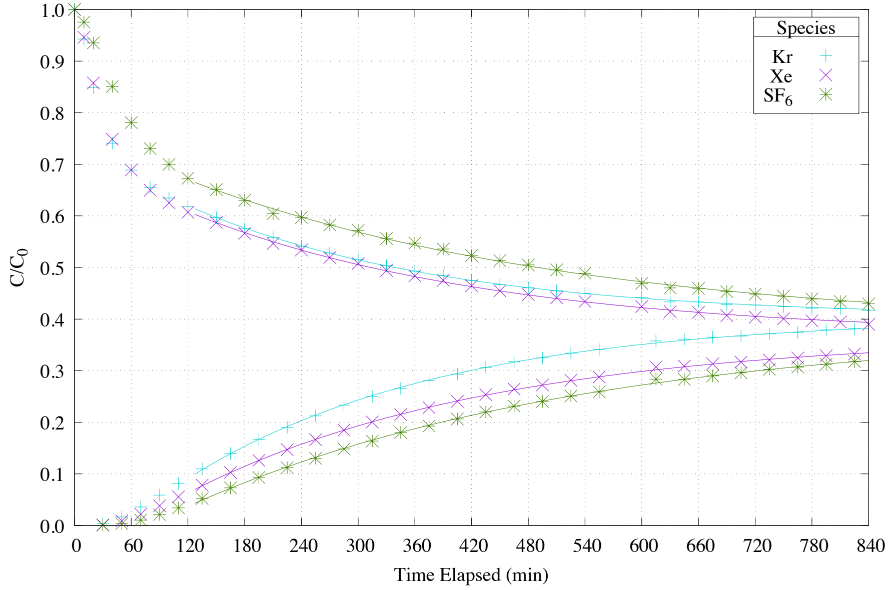
QUESTIONS?

Wet Trial Results



Trial	Gas	τ(min)	D_i (cm^2/s)	$\varepsilon(1-S)/q^2$
Dry	Kr	228.3	0.0352	0.237
	Xe	276.5	0.0290	0.239
	SF_6	373.4	0.0215	0.234
Wet	Kr	270.5	0.0297	0.200
	Xe	323.6	0.0248	0.204
	SF_6	416.9	0.0193	0.210

- The porous media was filled to 40% volumetric saturation with deionized water
- The relaxation time increased, but not linearly so with saturation
- The equilibrium fraction of Xe relative to SF_6 was further depressed