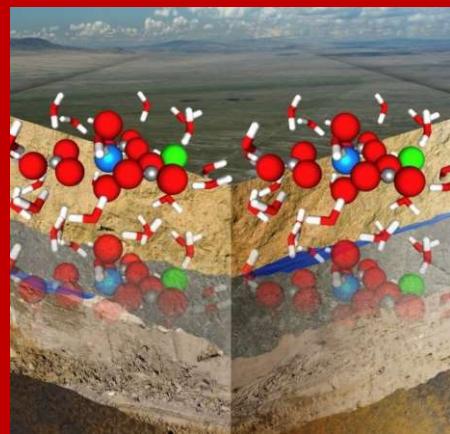


# **Geochemical Fate and Transport of Radionuclides in Groundwater**



**“One thing, however, caused us great uneasiness—our water reserve was already half exhausted.”**

**—Henry Lawson in “Journey to the Center of the Earth” by Jules Verne.**

# **Environmental Impacts**

The environmental movement of radionuclides in air, water, soil—and to the biosphere depends on:

1. The chemical properties of the specific radionuclide.
2. The geological, hydrogeological, and meteorological characteristics of the area impacted.

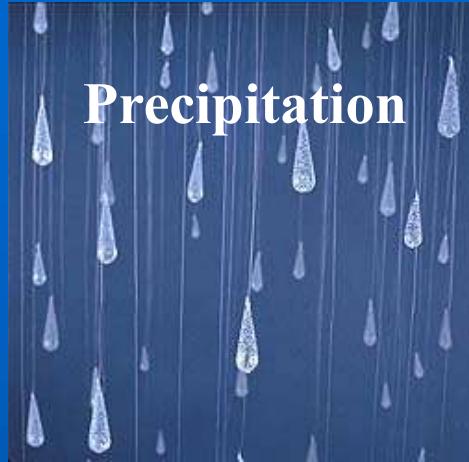
# **Environmental Pathways**

The hydrogeology and climate determines water availability and movement.

Atmospheric dispersion depends on meteorological conditions, topography, plume depletion caused by precipitation, radioactive decay, and interaction with the ground.

# **Environmental Pathways**

Ideally, wastes should be unreactive, but if groundwater reaches the waste package, some radionuclides may dissolve or leach and move from the disposal area.



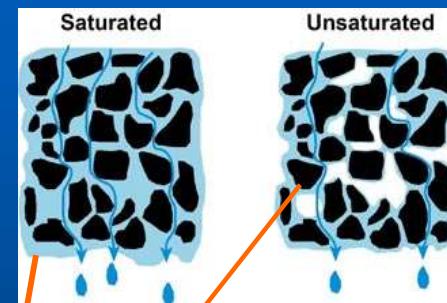
Wet and dry deposition

Volatilization



Leaching

Monitoring well



Sorption

Chemical  
Precipitation

Dilution  
Diffusion

Unsaturated zone

“water table”

Contamination

Groundwater flow

Oxidized

plume

Reduced

Bioconcentration



# Attenuation Mechanisms

Diffusion: the spontaneous movement of radionuclides (or any chemical or molecule) from an area of greater concentration to that of a lesser concentration.

Diffusion will occur if there is a concentration gradient (the Second Law of Thermodynamics: entropy increases).

# **Transport by Diffusion**

At some (molecular) level nothing is completely impermeable.

**1. Diffusion from waste packages:**

**Steel barrels and canisters**

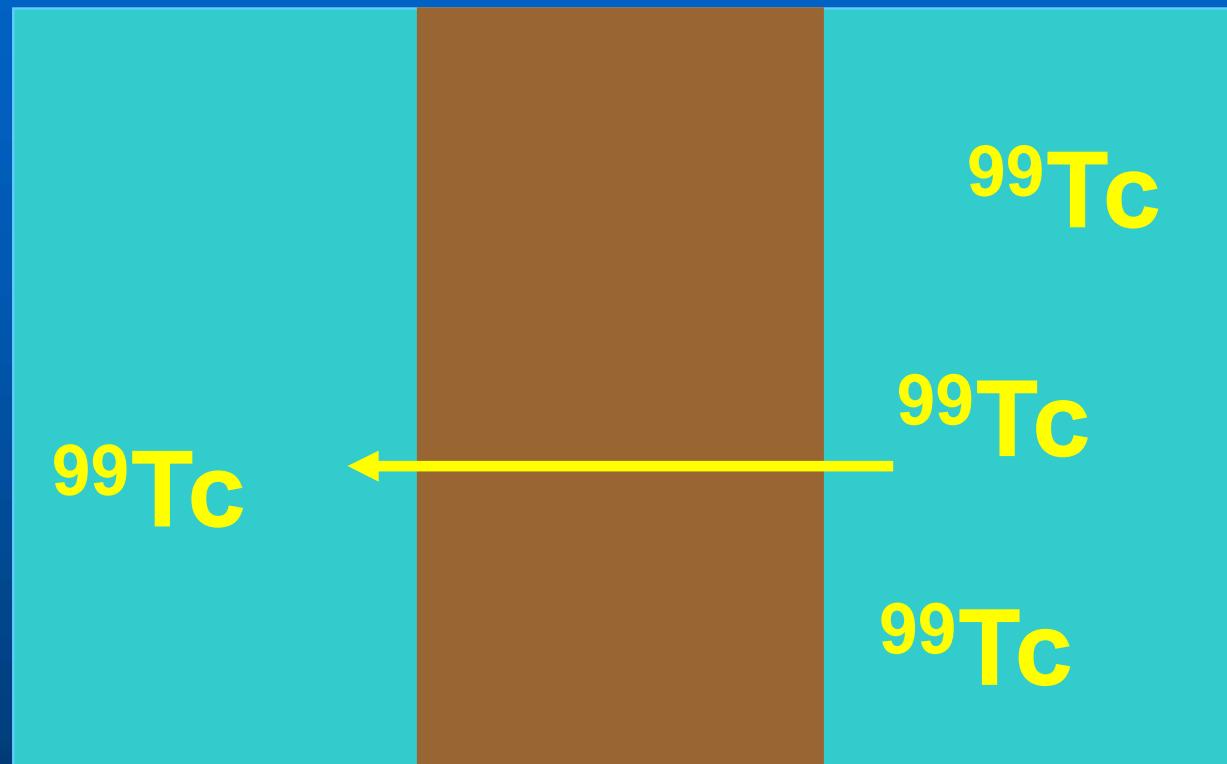
**Ceramic and vitrified waste forms.**

**2. Diffusion from disposal sites:**

**Movement through compacted clays and soils,  
and rock formations.**

**3. Movement in groundwater even when the  
water is not moving.**

# Diffusion through a solid mass



Thickness  $d$ , and area  $A$ , and donor reservoir volume  $V_d$

# Diffusion coefficients (cm<sup>2</sup>/sec)

Examples:

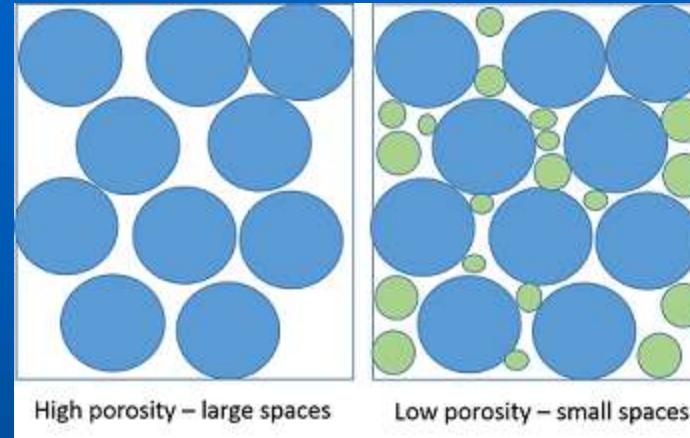
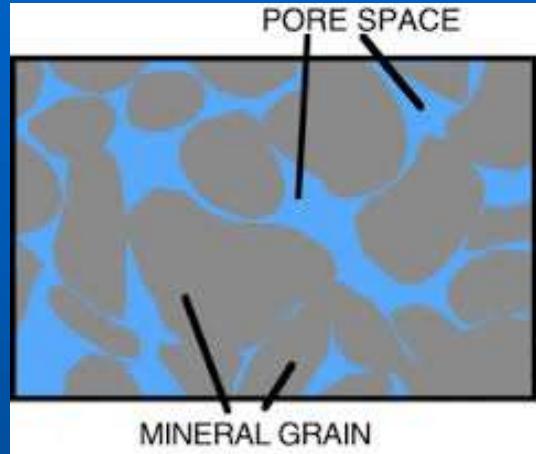
Cement and concrete (lab measurements)

$^{36}\text{Cl}$ :  $3.0 \times 10^{-7}$

$^{137}\text{Cs}$ :  $2.71 \times 10^{-15}$

How can diffusion coefficients be used?

**Porosity: volume of void spaces divided by the volume of mass.**



**Tortuosity: the ratio of the diffusion path in air to the diffusion path in a solid.**

**Radionuclides would have longer paths in solids to move through as they diffuse around particles or along fractures.**

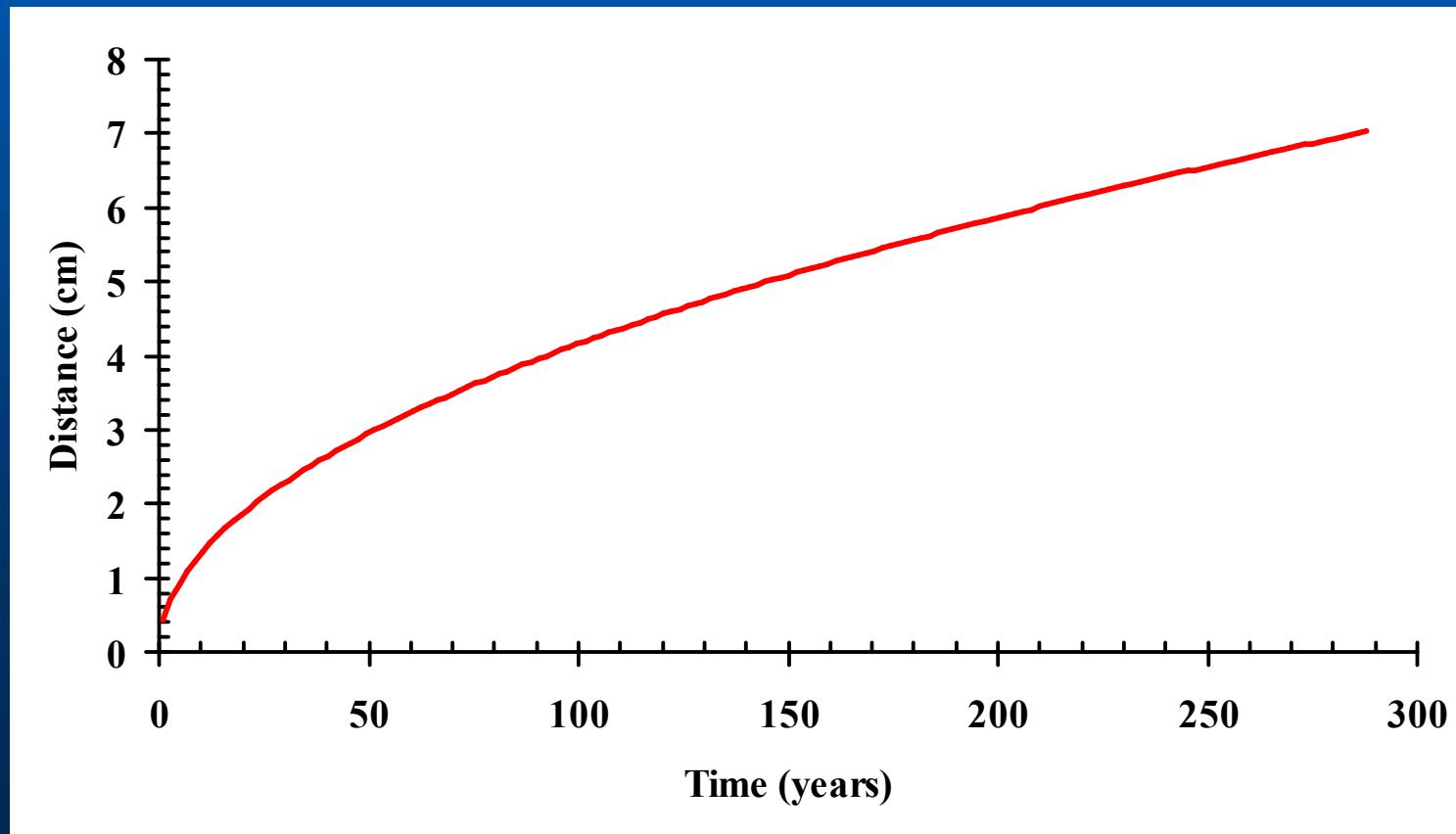
# Tortuosity



**Go to:**

[http://www.earthwardconsulting.com/diffusion  
calculator.htm](http://www.earthwardconsulting.com/diffusion_calculator.htm)

**Diffusion of  $^{90}\text{Sr}$  in soil. 1% concentration.  
Porosity = 0.2. tortuosity = 0.8**



# Attenuation Mechanisms

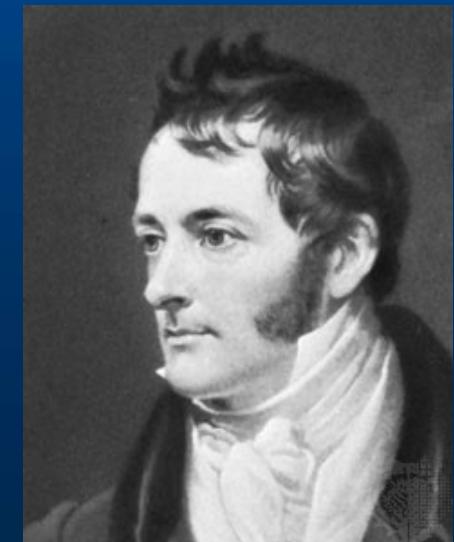
In unsaturated/saturated groundwater flow:

Water-air partitioning (Henry's Law)  
(Dr. William Henry: English Chemist)

Vapor-phase concentration =  $K_H \times S$

where  $K_H$  = chemical-specific  
constant

$S$  = solubility in water



# Chemical reactions

## Precipitation-dissolution reactions

Example strontium-90:  $^{90}\text{Sr}^{2+} + \text{SO}_4^{2-} = ^{90}\text{SrSO}_4\downarrow$   
(celestite)

Equilibrium constant  $K_T = ^{90}\text{SrSO}_4 / (^{90}\text{Sr}^{2+})(\text{SO}_4^{2-})$

$(^{90}\text{Sr}^{2+})(\text{SO}_4^{2-})$  = Ion activity product (IAP)

At equilibrium, IAP =  
reaction constant ( $K_T$ )

When  $\text{IAP} > K_T$

celestite precipitates

When  $\text{IAP} < K_T$

celestite dissolves (if present)



# Attenuation Mechanisms

## Ion exchange

Exchange between ions in solution with those on a stationary solid phase.

Process used to purify chemicals and decontaminate liquids.

# Ion Exchange Resin



# **Ion Exchange by Geological Materials**

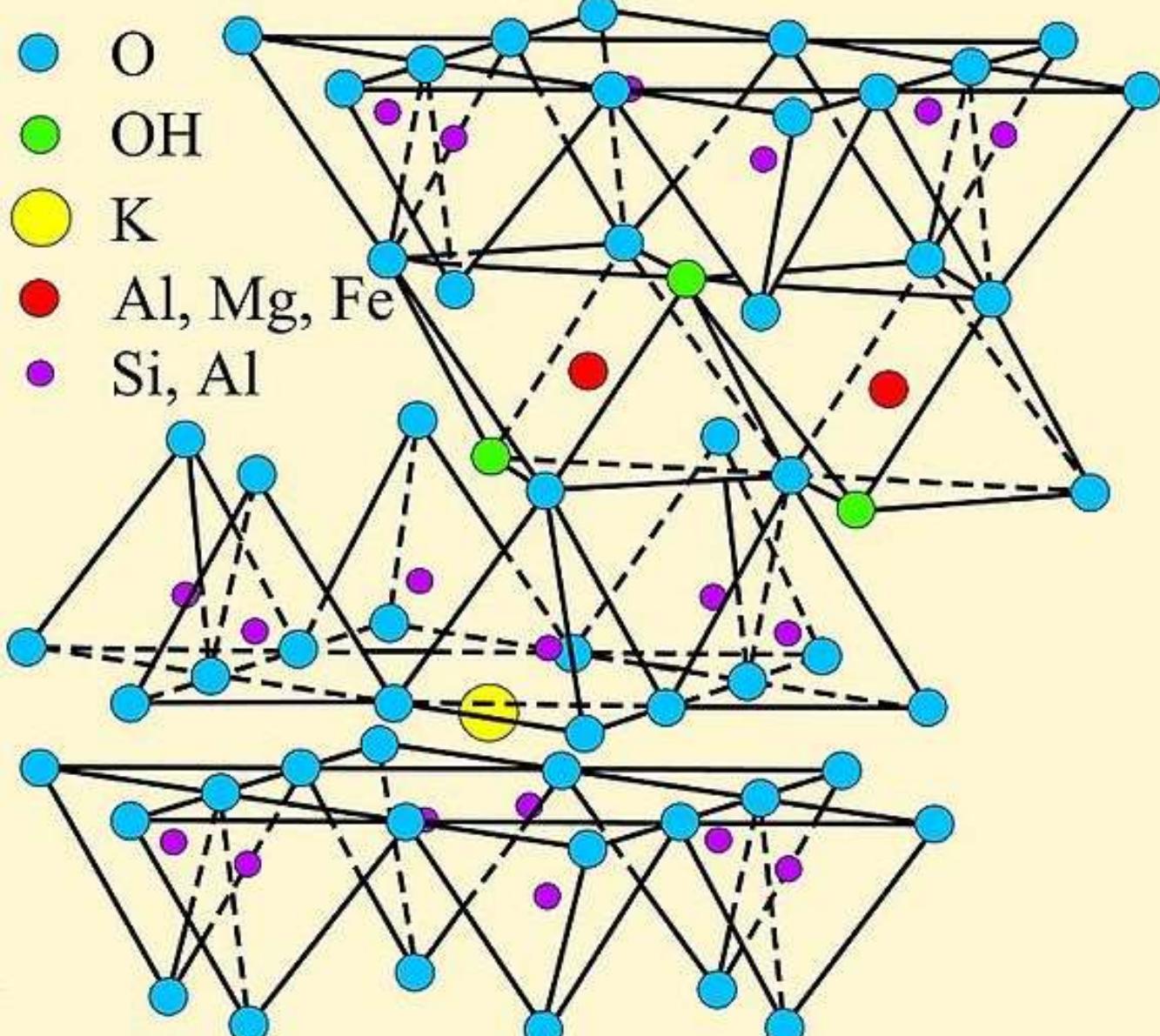
Soils, clay minerals and soil organic matter can also remove ions from solution by ion exchange.

Ion exchange is a type of (ad)sorption reaction.



Surfaces of clay minerals often have a negative charge resulting from isomorphous substitution within the clay structure.

# STRUCTURE OF ILLITE



MODIFIED FROM GRIM (1962)

# Sorption

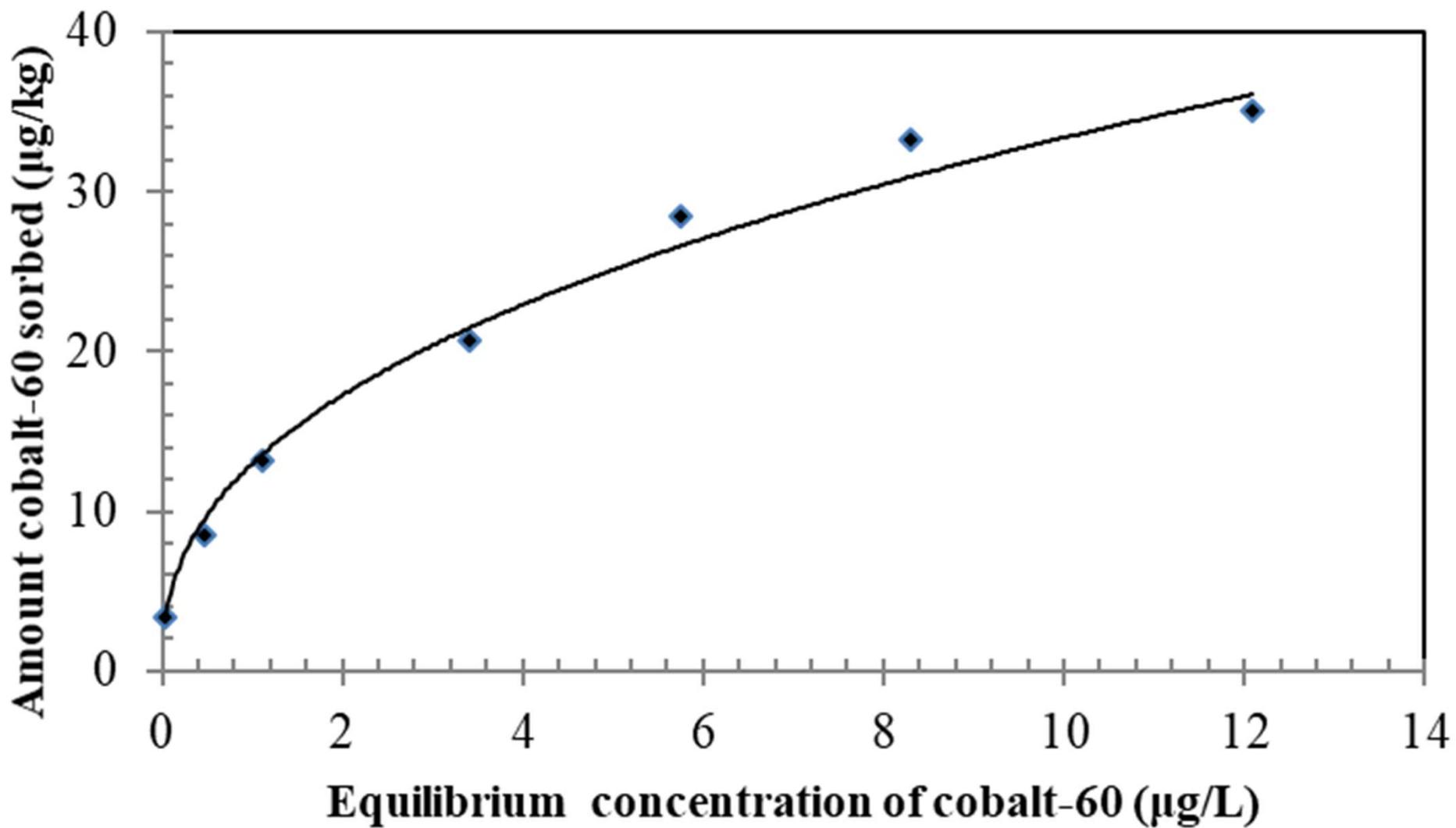
Cations are concentrated on the surfaces to balance the negative charge. Hence, the cation is removed from solution and it immobilized.

Natural organic matter in soil also has positive and negative functional groups (sites) that can sorb ions.

# Sorption

Sorption of radionuclides cannot be predicted *a priori* but must be measured experimentally.

The experimental results are usually generalized as an sorption isotherm, a plot of the amount sorbed versus the equilibrium concentration.



# **Attenuation Mechanisms**

If the sorption isotherm is linear, the data can be generalized as

$$x/m = K_d C$$

where  $x$  = mass sorbed

$m$  = mass of sorbent

$K_d$  = partition coefficient  
(volume/mass)

$C$  = concentration (mass/volume)

# Attenuation Mechanisms

Partition or sorption coefficients give an idea about the mobility of a radionuclide subsurface environments.

If  $K_d = 0$ , no retention. The radionuclide moves at the same rate as groundwater.

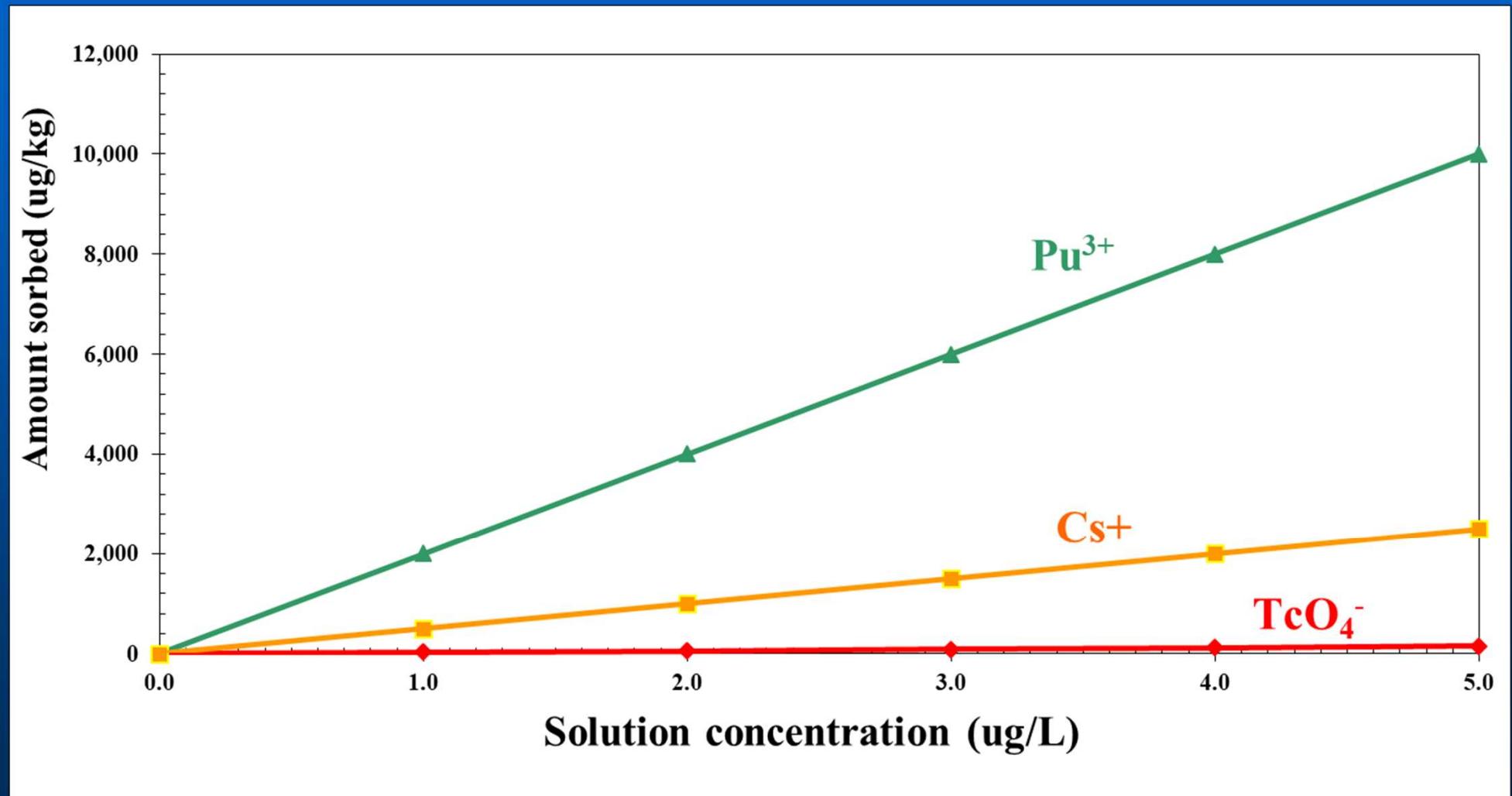
In general, anionic radionuclides are more mobile than cationic radionuclides.

# Sorption Coefficients

Default  $K_d$  values used in modeling studies ( $\text{cm}^3/\text{g}$ ) from Argonne National Laboratory's "User's Manual for RESRAD Version 6"

$^{3}\text{H}$	0
Sr	30
Tc	0
Cs	500
I	0.1
Ra	70
Th	60,000
Np	0
Pu	2,000
Am	20

# Sorption isotherms for Pu, Cs, and Tc



# How does $K_d$ relate to transport by advection?

Retardation ( $R$ ) = velocity of groundwater/velocity of radionuclide.

$$R = 1 + [\rho_b (K_d)/\theta]$$

where

$\rho_b$  = dry bulk density

$\theta$  = volumetric water content

# How does $K_d$ relate to transport by advection?

Distance traveled =  $t(K_{sat})i/Rn_e$

where

$t$  = time

$K_{sat}$  = saturated hydraulic conductivity

$i$  = hydraulic gradient

$n_e$  = water-conducting porosity  
(effective porosity).

# Movement in sand away from a leaking tank

If we let

Dry bulk density = 1.7 g/cm<sup>3</sup>

Volumetric water content = 0.30 cm<sup>3</sup>/cm<sup>3</sup>

K<sub>sat</sub> = 10<sup>-3</sup> cm/sec (sand)

Gradient = 0.1 cm/cm

Water-conducting porosity = 0.3

# Distance traveled in 30 days

Radionuclide	R (unitless)	Distance
$^{3}\text{H}$	1	28 feet 8.53 m
$\text{TcO}_4^-$	1	28 feet 8.53 m
$\text{Cs}^+$	2,830	0.8 inch 2.0 cm
$\text{Pu}^{3+}$	11,330	0.2 inch 0.5 cm

# Attenuation Mechanisms

## Reduction-Oxidation reactions

These are chemical reactions in which oxidation state of a radionuclide is changed by adding or removing electrons.

Chemically reduced systems are typically oxygen-poor systems such as deep groundwater.

# Reduction-Oxidation

Reduction-Oxidation reactions

Example:

Oxidizing (aerated) conditions

$\text{TcO}_4^-$  (Tc VII), a mobile anion  
( $K_d = 0$ ).

Under reducing conditions

$\text{TcO}_2$  (Tc IV) which precipitates as a solid phase.

## In surface water

Contamination groundwater discharges into a river or lake:

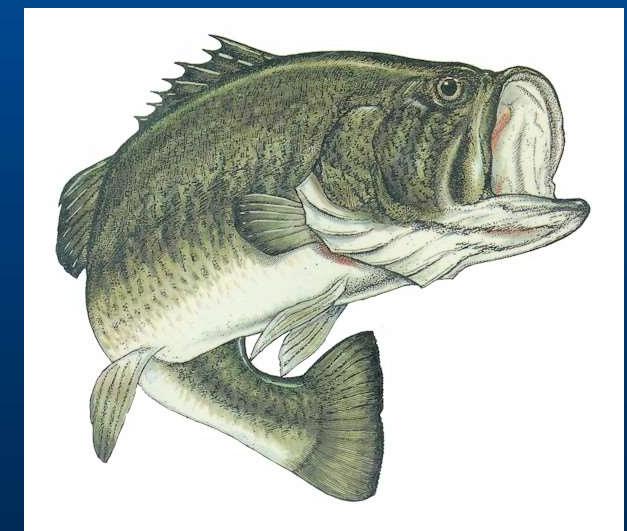
Dilution

Bioconcentration by aquatic organisms; the increase in concentration of a radionuclide in an organism resulting from tissue absorption levels exceeding the rate of metabolism and excretion.

# BCF

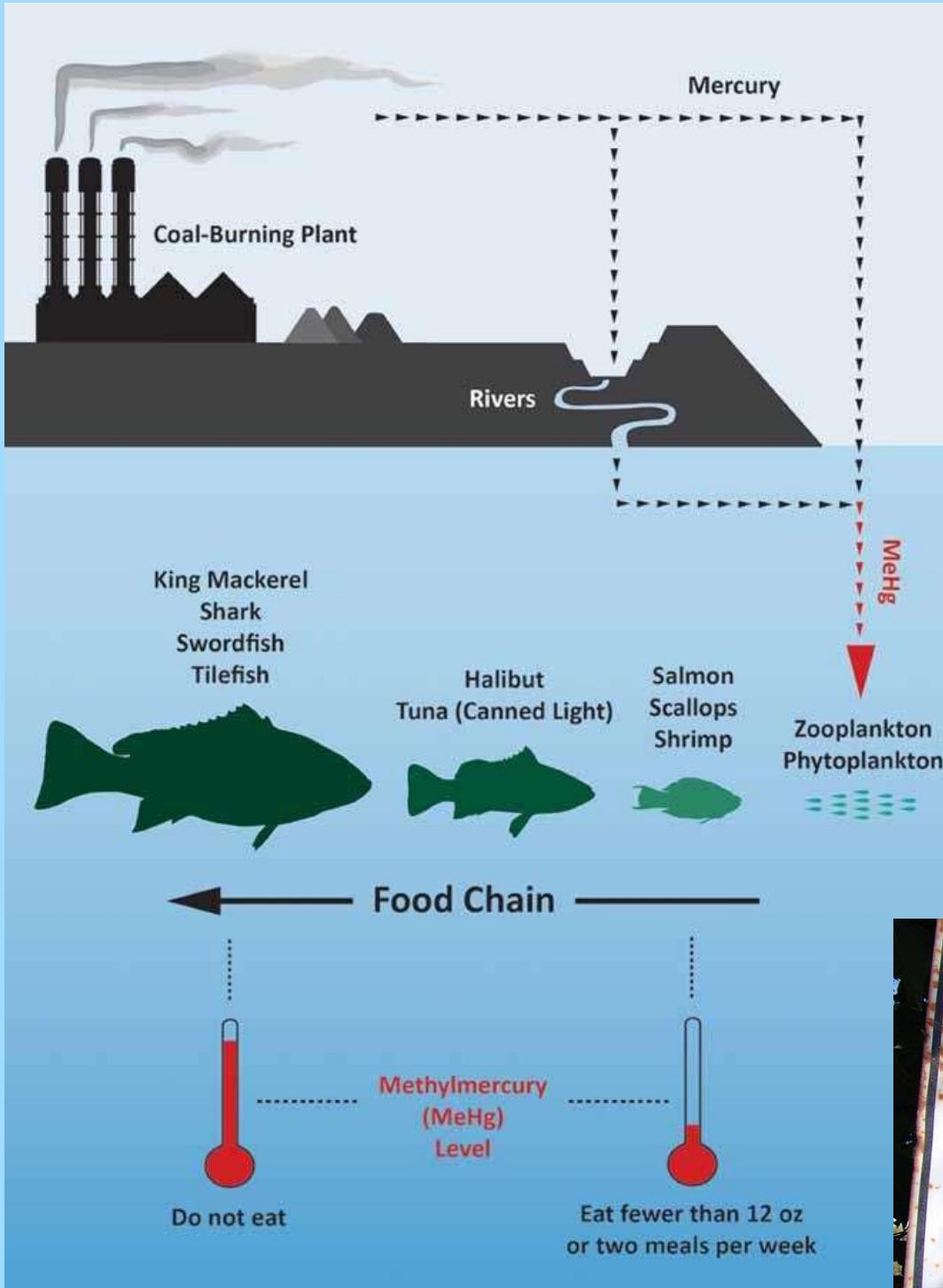
Bioconcentration Factor (BCF) =  
Concentration of a radionuclide in  
an organism divided by the  
concentration of same radionuclide  
in water.

At equilibrium and often  
for aquatic organisms.



# Examples of BCFs

Radionuclide	BCF	Organism
Americium	2,500	Bass
	4,200	Catfish
Strontium	2,400 to 63,000	Fish bones
Plutonium	10 to 40	Fish
	1,000	Algae
Mercury	10,000 to 40,000	Oysters



# **Atmospheric Dispersion**

All gases and particulates released to atmosphere are progressively diluted in the course of travel downwind as result of diffusion and deposition processes (dry and wet).

Radionuclides are subject additionally to radioactive decay.

# Persistent Radionuclides

Some radionuclides found in airborne effluents from nuclear facilities have extremely long radioactive half-lives.

Some long-term radionuclides are not efficiently removed from the plume by other processes such as wet and dry deposition.

# Persistent Radionuclides

Well-known and important radionuclides that are persistent and mobile:

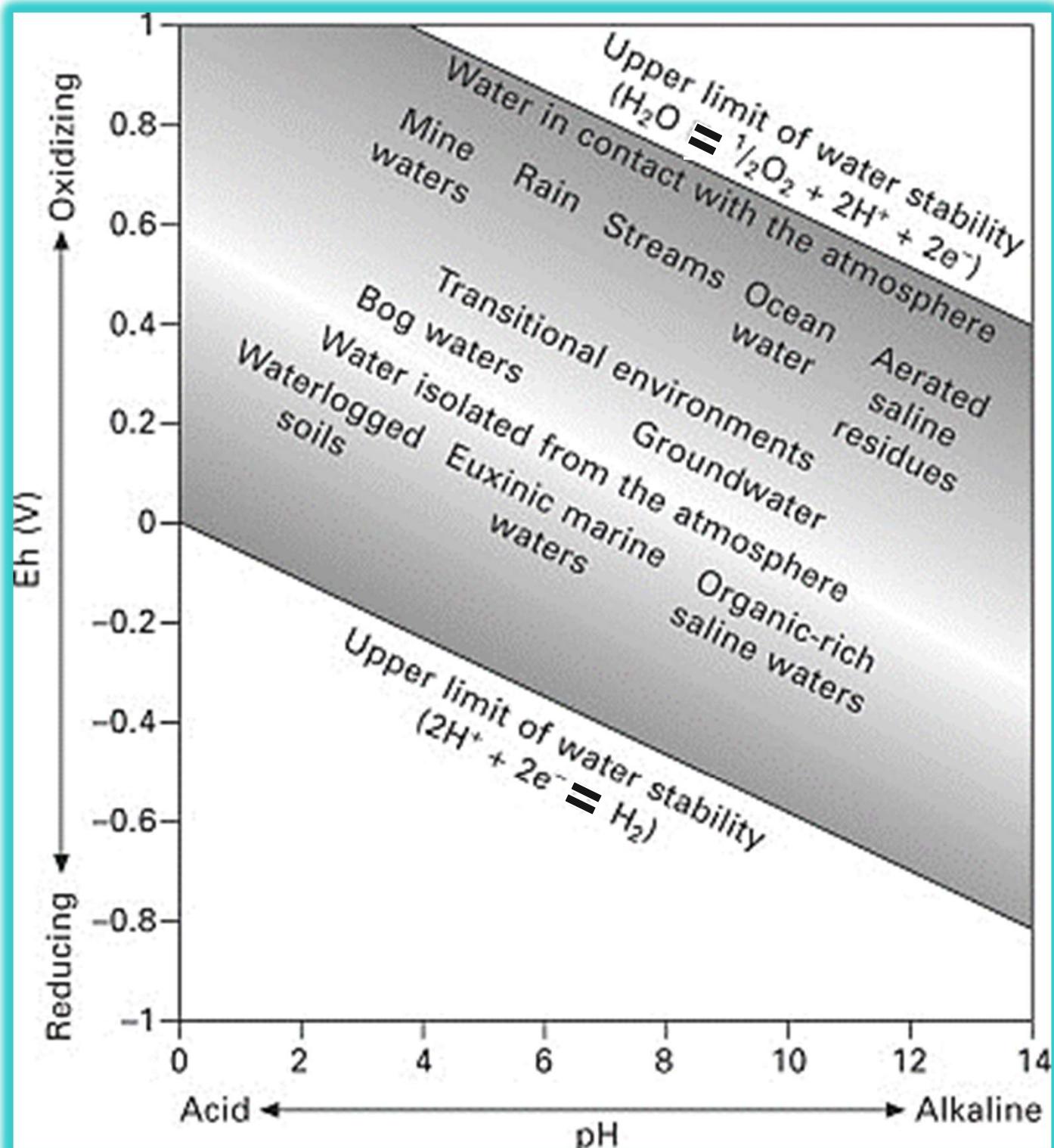
$^3\text{H}$  ( $t_{1/2} = 12.3$  yr)

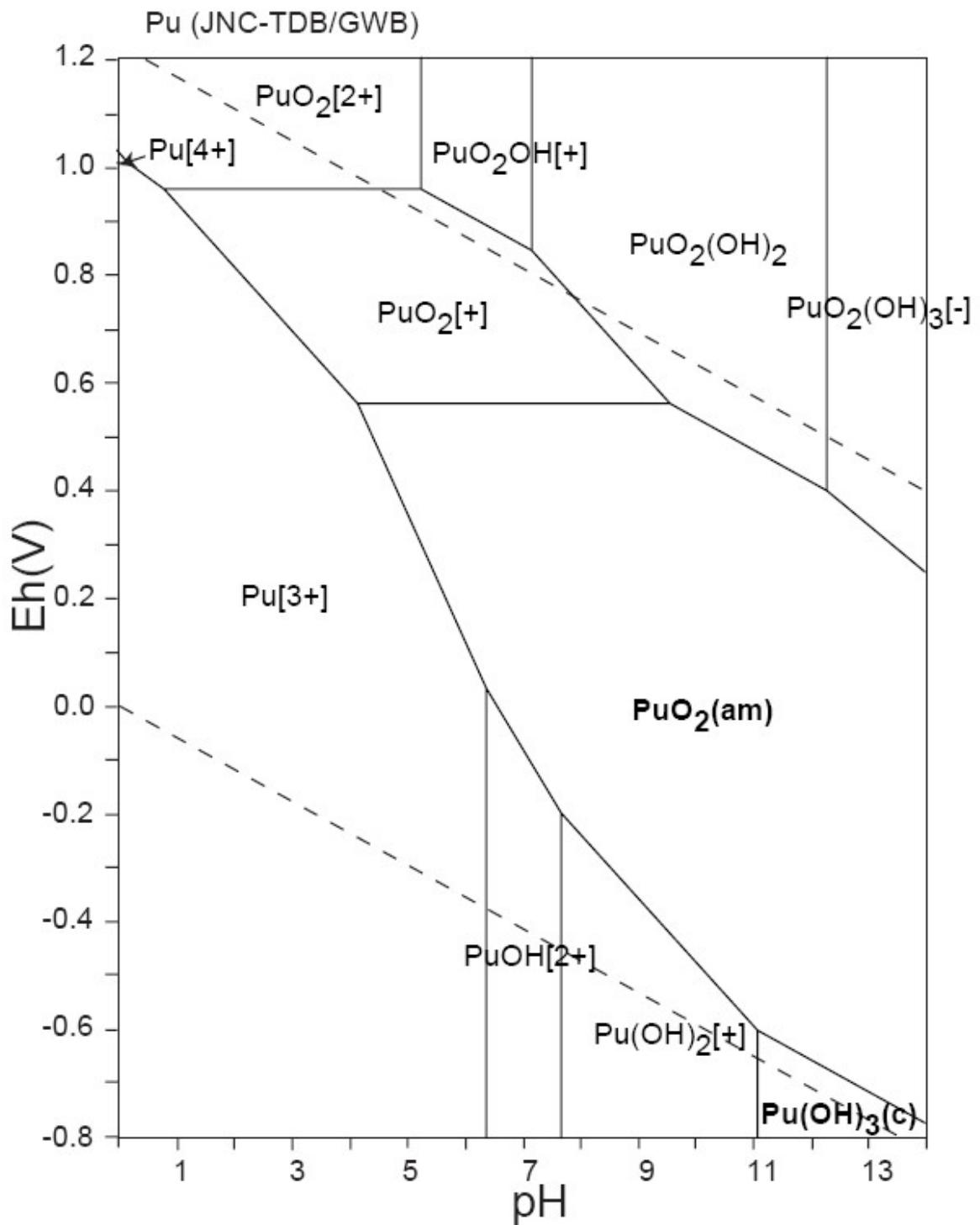
$^{14}\text{C}$  ( $t_{1/2} = 5,730$  yr)

$^{85}\text{Kr}$  ( $t_{1/2} = 10.7$  yr)

$^{129}\text{I}$  ( $t_{1/2} = 1.57 \times 10^7$  yr)





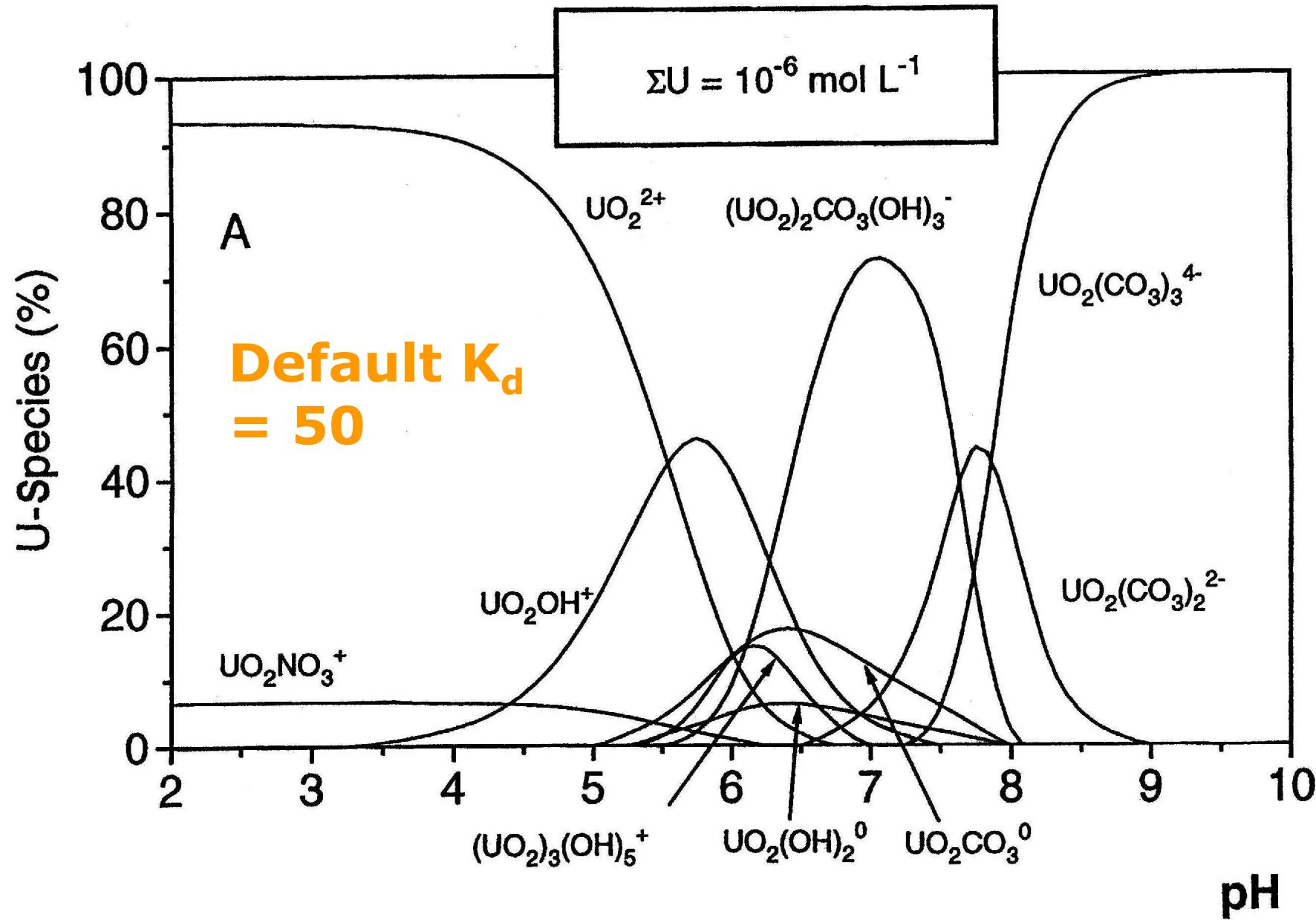


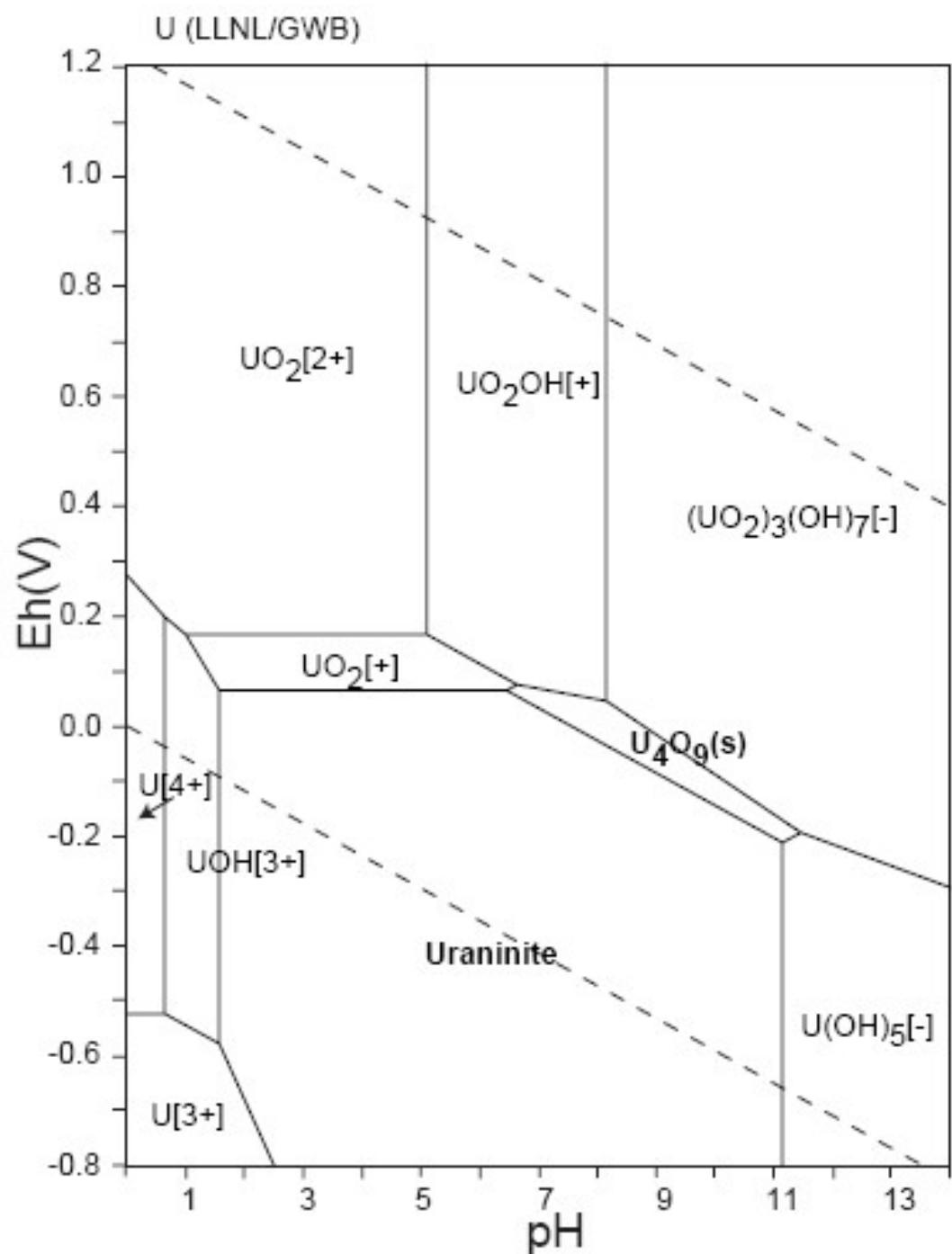
# Fate Chemistry of Plutonium

Plutonium solubility is limited in a wide pH range by the formation of amorphous plutonium hydroxide  $[Pu(OH)_4]$  or plutonium oxide ( $PuO_2$ ).

$$12.93 \pm 2.54 \text{ } \mu\text{g/L}$$

All things considered, if Pu escapes from the disposal area, it will not move far (relatively immobile) because of sorption and precipitation (default  $K_d = 2,000$ ).





# Fate Chemistry of Neptunium

Np solubility in water:

pH 7, 25° C, Eh<sub>Z</sub> = 431 mV in 0.18 M  
NaClO<sub>4</sub>    **45.5 ± 4.98 µg/L**

In geomedia, Np is generally mobile  
(default K<sub>d</sub> = 0), but dependent both  
on pH and the oxidation state.

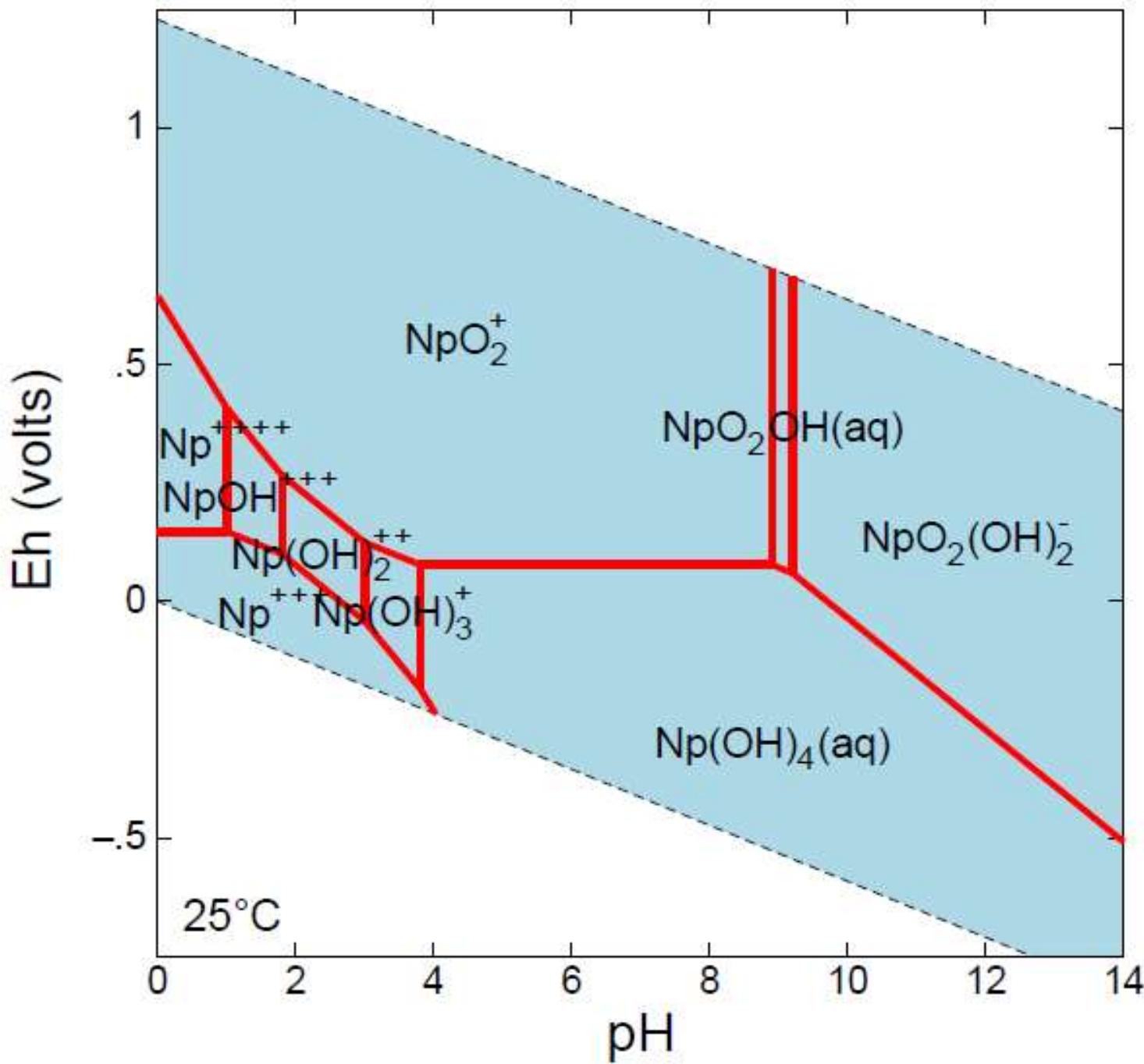
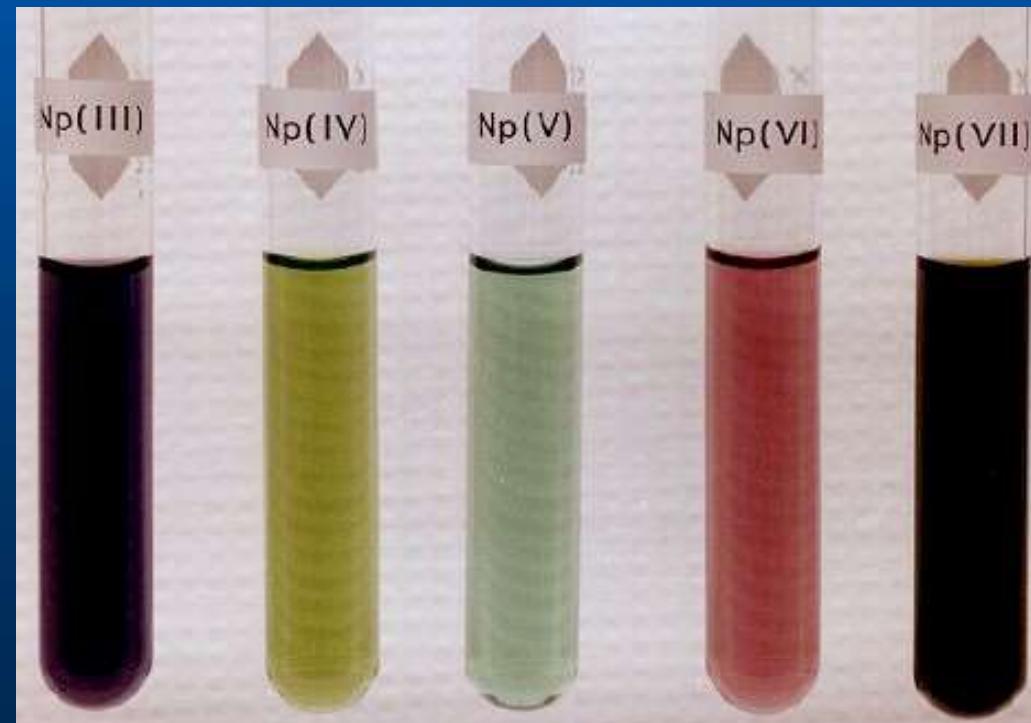


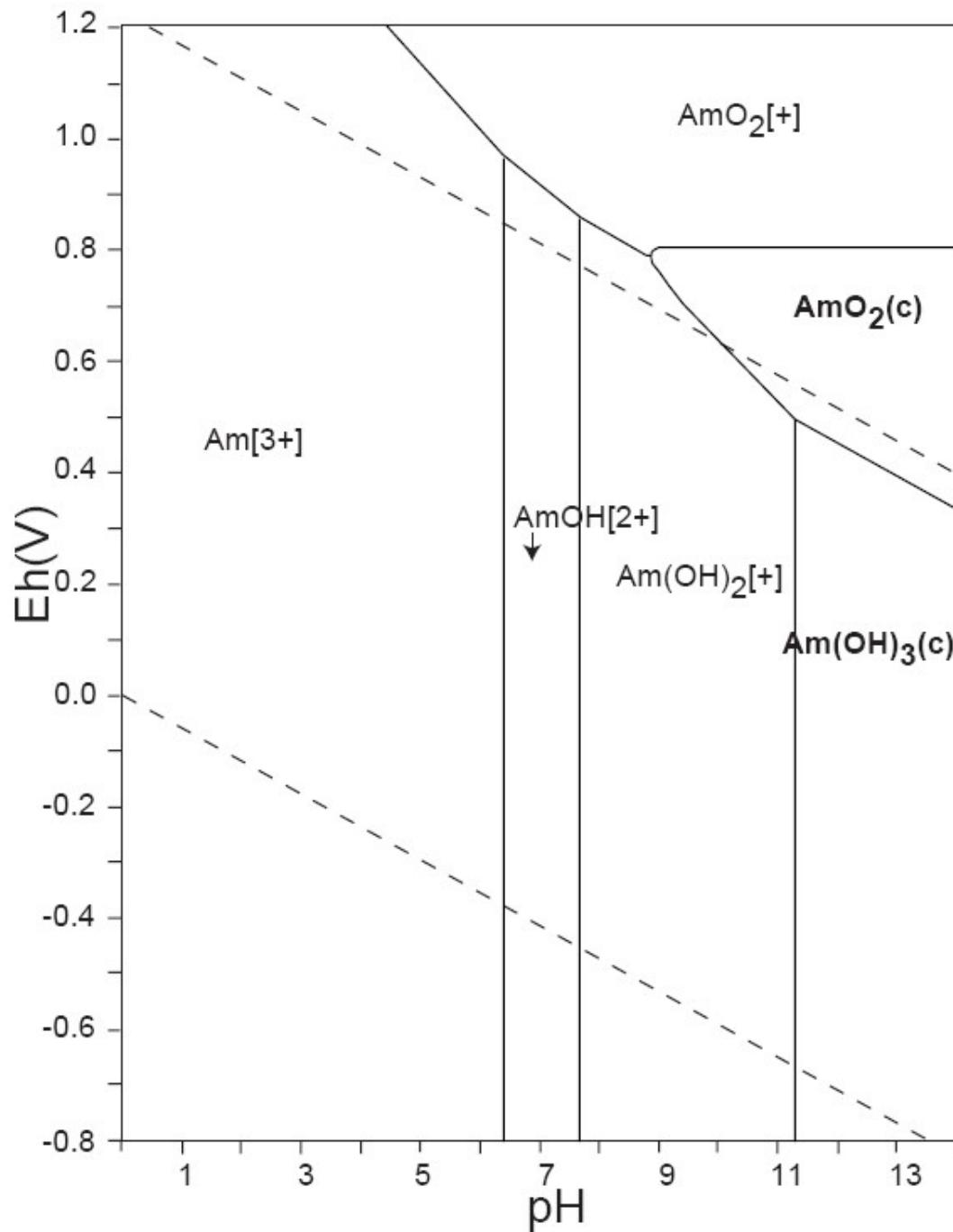
Diagram Np<sup>++++</sup>, T = 25 °C, P = 1013 bars, a[marl] = 10<sup>-8</sup>, a[H<sub>2</sub>O] = 1; Suppressed: {1122 species}

# Fate Chemistry of Neptunium

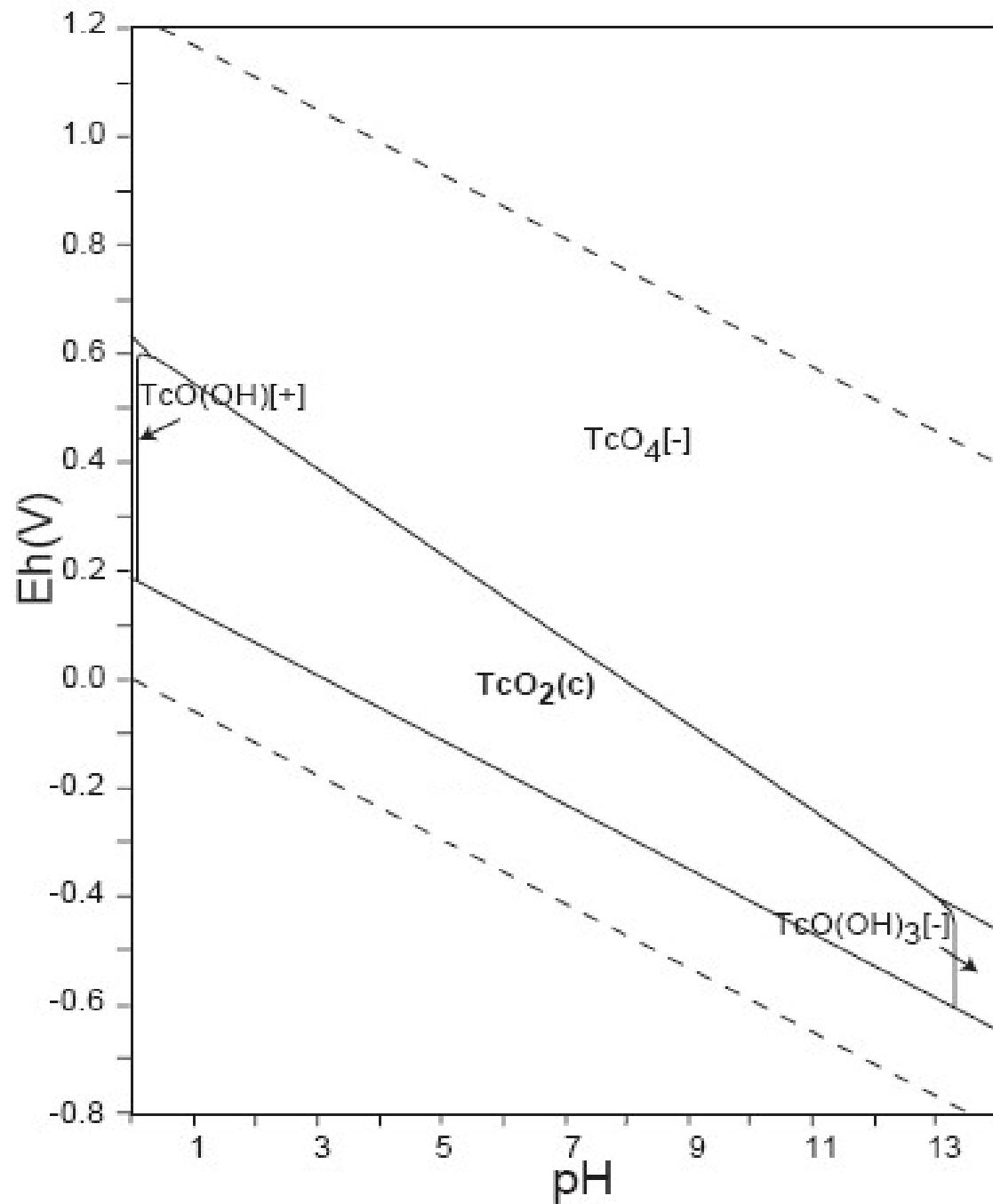
Np can exist in five oxidation states: +3, +4, +5, +6, and +7. The +5 state is the most stable ion in aqueous solution.

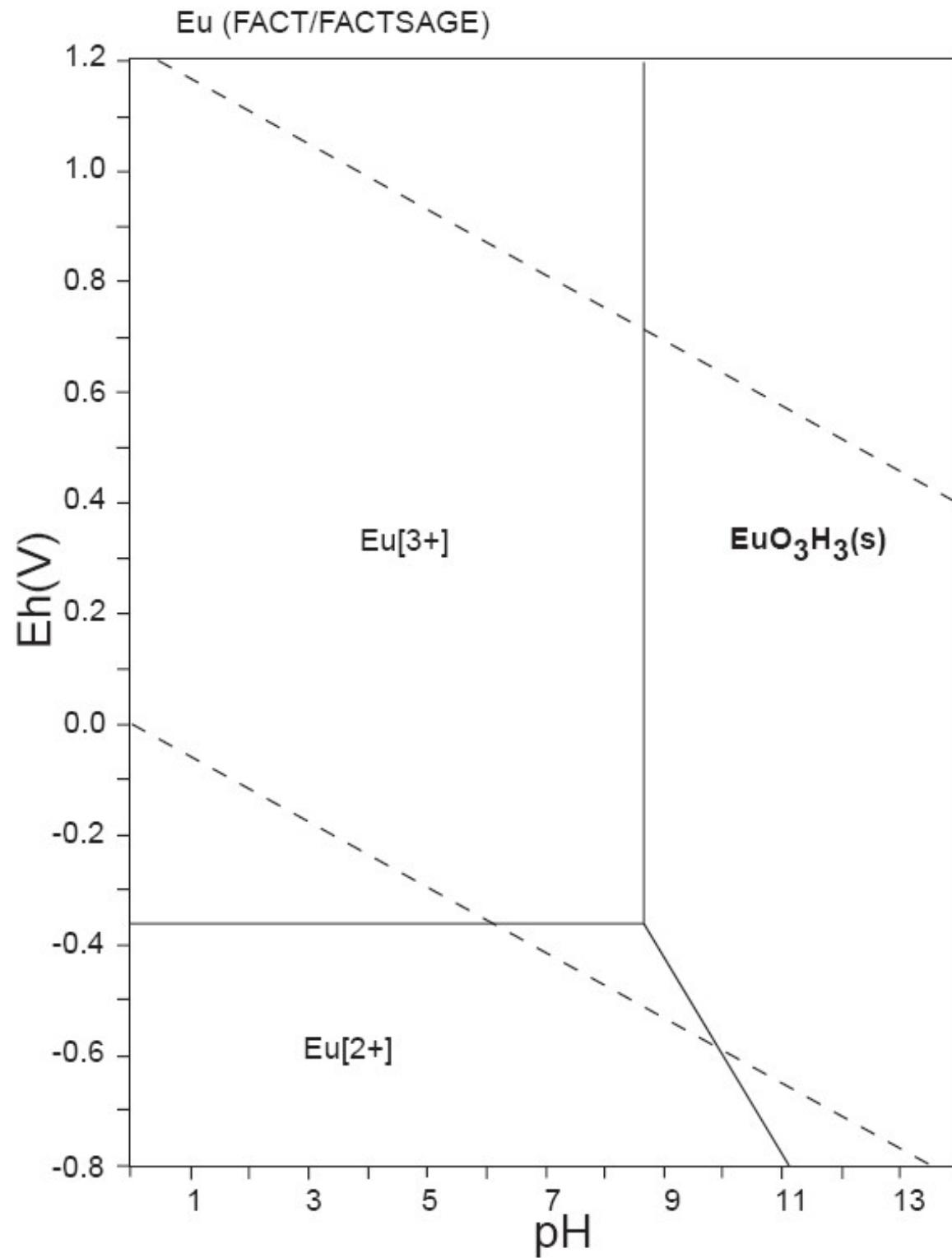


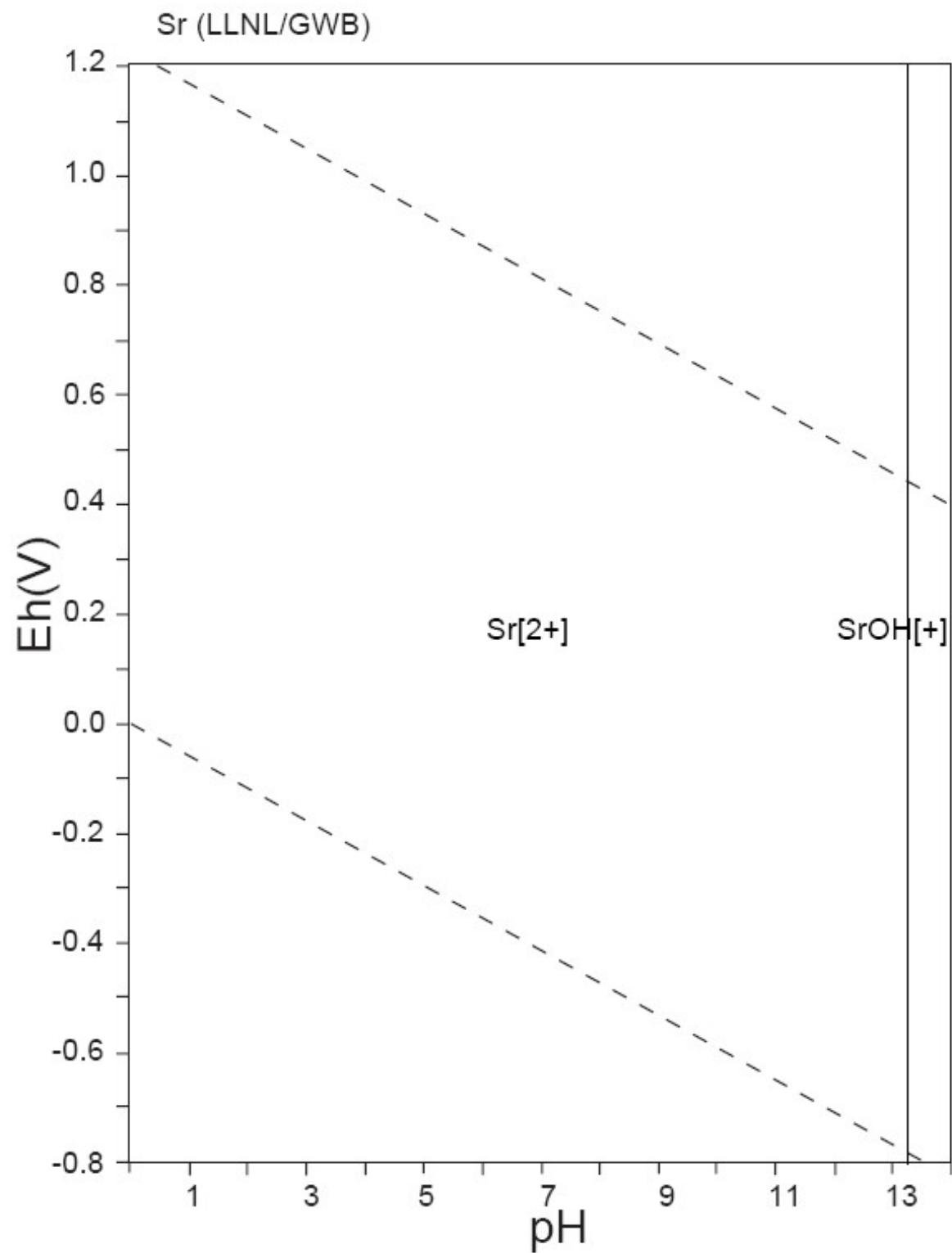
Am (OECD-NEA/FLASK-AQ)

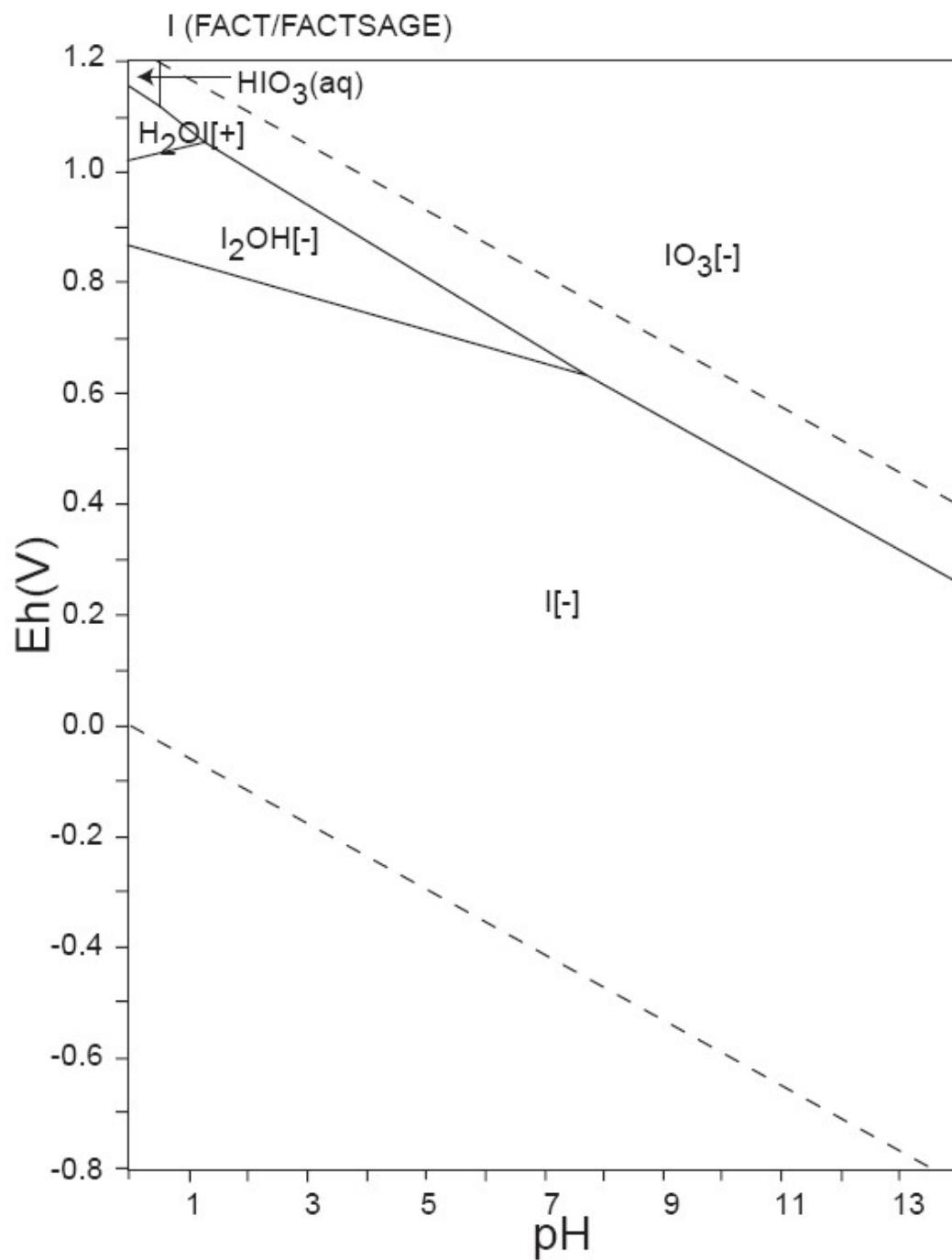


Tc (OECD-NEA/FLASK-AQ)









# Hydrogeology of groundwater

Groundwater flows through porous geological media at a rate that depends on the driving force (gravity), the gradient (change in elevation), and the ability of the material to transmit water (saturated hydraulic conductivity). Henry Darcy generalized that, for a volume of homogeneous, isotropic material ...

# Darcy's law

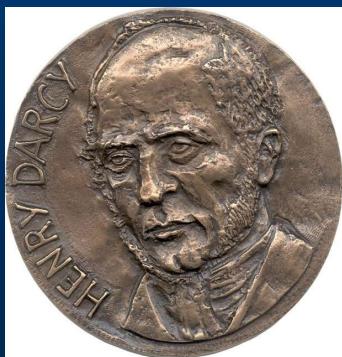
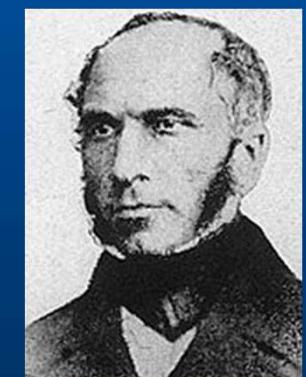
$$(K_{\text{sat}} A \Delta h)/L = Q$$

where  $K_{\text{sat}}$  = saturated hydraulic conductivity  
A = cross-sectional area of the volume of porous material

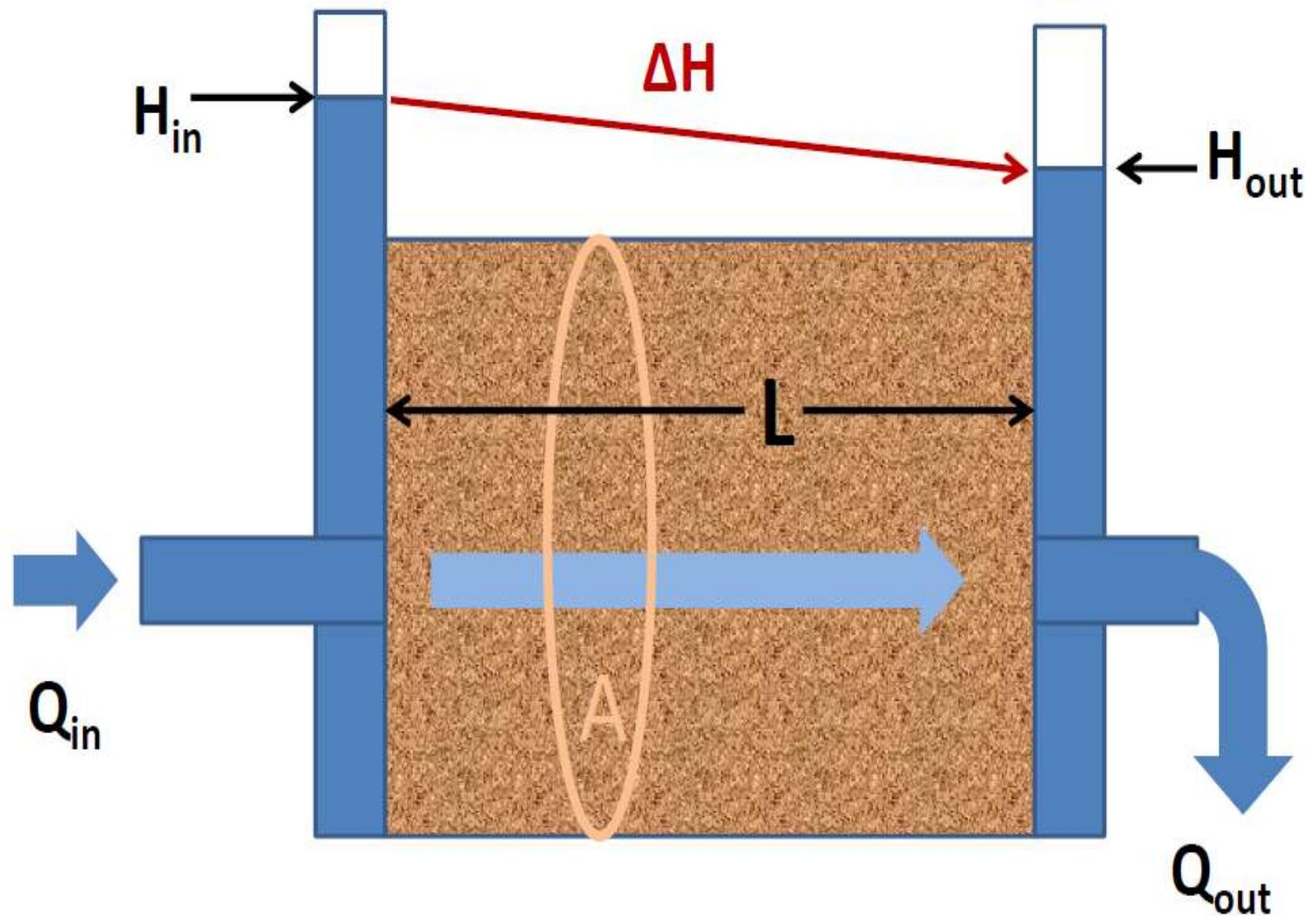
$\Delta h$  = change in elevation or hydraulic gradient (i)

L = distance of the flow path

Q = flow rate



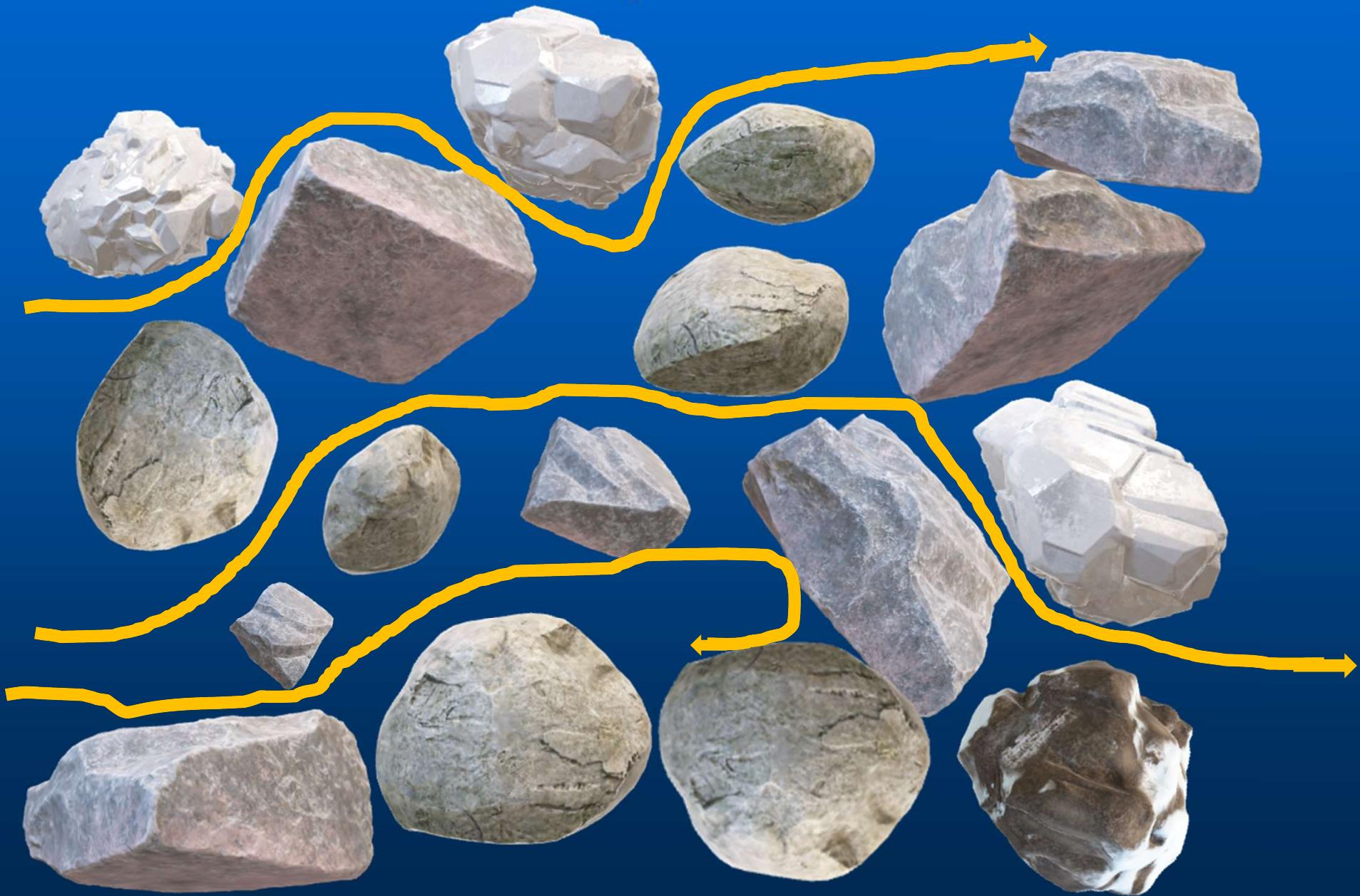
Henry Darcy  
French Engineer



# **Transport by dispersion**

Dispersion is a process in which radionuclides spontaneously spread out in porous media in flowing groundwater. At the microscopic level, dispersion results from the flow through different pore sizes and flow paths around particles of different sizes and shapes.

# Dispersion



# Transport by diffusion

$$D = a_l V + D^*$$

where  $D$  = dispersion coefficient

$a_l$  = longitudinal dispersivity of the media

$V$  = average linear groundwater velocity

$D^*$  = effective diffusion coefficient

The longitudinal dispersivity component is best estimated from laboratory measurements of flow in soil columns using a non-reactive tracer.

# **Transport by Advection-Dispersion-Reaction**

$$\frac{\partial C}{\partial t} = D_x \left( \frac{\partial^2 C}{\partial x^2} \right) - V_x \left( \frac{\partial C}{\partial x} \right) - \left( \frac{\rho_b}{\theta} \right) \left( \frac{\partial S}{\partial t} \right)$$

**where C = concentration of the radionuclide in solution**

**$D_x$  = the effective dispersion coefficient along flow path x**

**$V_x$  = mean convective flow along flow path x**

**$\rho_b$  = bulk density of the geomedia**

**$\theta$  = volumetric water content**

**S = amount of sorbate per mass of sorbent**

**t = time**

# Transport by Advection-Dispersion-Reaction

The analytical solution of this second-order differential equation is

$$\frac{C}{C_0} = 0.5 \left\{ \operatorname{erfc} \left( \frac{(x - Vt^*)}{2(D_x t^*)^{0.5}} \right) + \exp \left( \frac{Vx}{D_x} \right) \operatorname{erfc} \left( \frac{(x + Vt^*)}{2(D_x t^*)^{0.5}} \right) \right\}$$

where  $C/C_0$  = ratio of the radionuclide concentration in groundwater at time  $t$  and distance  $x$  to the initial concentration  $C_0$ ,

$\operatorname{erfc}$  = complimentary error function

$V$  = average linear pore-water velocity

$D_x$  = dispersion coefficient

$T^*$  = retarded time (actual time divided by the retardation factor  $R$ )

$x$  = distance of migration

# Groundwater monitoring for radionuclides

Gross alpha and gross beta measurements indicate the combined amount of radioactive substances in air, soil, and water.

Used for many years because of their ease, speed, and small analytical cost. However, these measurements do not identify the specific source(s) of the activity.

# Gross counting

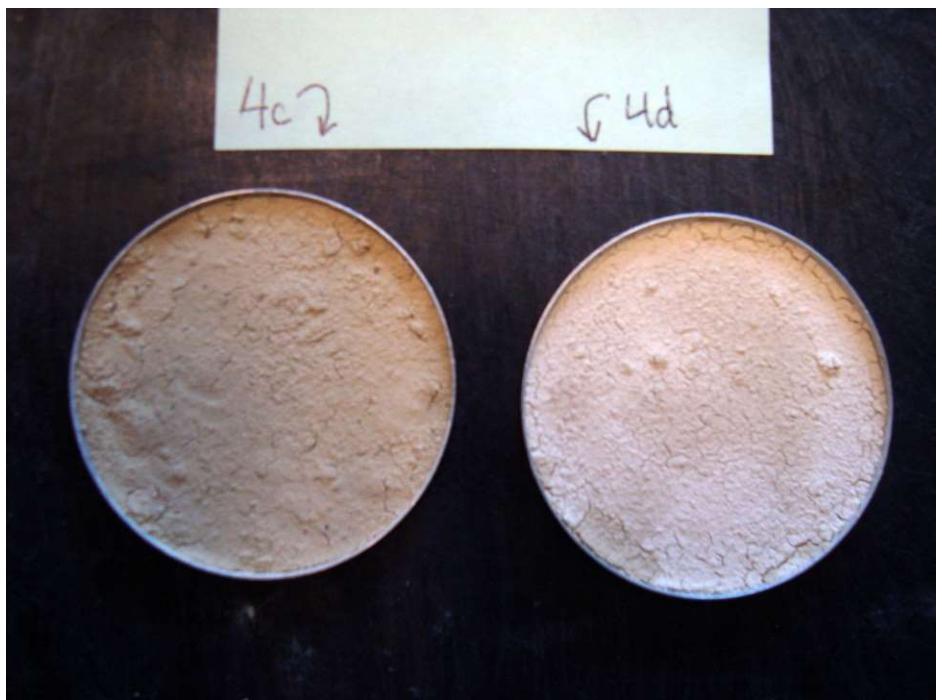
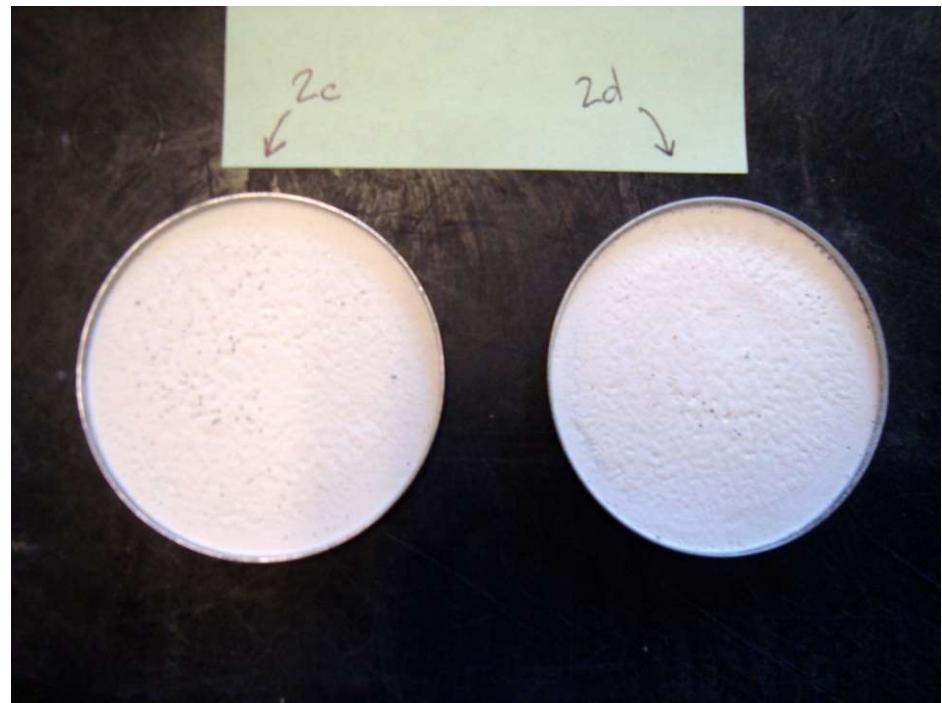
Gross counting is commonly applied as a screening tool to identify situations in which there may be a need to determine the specific radionuclides using other analytical methods.

# Likely natural sources of alpha and beta activity in groundwater

Element	Isotope	Activity
Uranium	U-234	alpha
	U-235	alpha
	U-238	alpha
Thorium	Th-228	alpha
	Th-230	alpha
	Th-232	alpha
Potassium	K-40	beta
Radium	Ra-226	alpha
	Ra-228	beta
Radon	Rn-222	alpha

# **Gross counting**

Gross measurements of water samples for a groundwater monitoring program are commonly made by first evaporating the water, then counting the alpha and beta particles emitted from the solid residue using a gas-flow proportional counting system.





# Example of interpreting gross count data (EPRI project)

Leachate sample collected in an coal ash pond.

Gross  $\alpha$  = 13.3 pCi/L.



Common radionuclides determined:  $^{226}\text{Ra}$  = 0.49 pCi/L and  $^{238}\text{U}$  = 0.88 pCi/L.

Clearly  $13.3 \neq 1.37$  pCi/L

What was missing?

# Example of interpreting gross count data (EPRI project)

Radium decays into short-lived radon, polonium, and lead radionuclides,

$^{226}\text{Ra} \rightarrow ^{222}\text{Rn} + \alpha$  ( $^{226}\text{Ra}$  half-life of 1,620 years)

$^{222}\text{Rn} \rightarrow ^{218}\text{Po} + \alpha$  ( $^{222}\text{Rn}$  half-life of 3.8 days)

$^{218}\text{Po} \rightarrow ^{214}\text{Pb} + \alpha$  ( $^{218}\text{Po}$  half-life of 3 minutes)

# Interpretation of gross data

The additional sources of alpha particles were from the decay of  $^{226}\text{Ra}$  that formed before the sample was analyzed before gross counting (i.e., the sample holding time was exceeded).

The results were not valid.



# Interpretation of gross data

Another example: Gross  $\beta = 561 \text{ pCi/L}$

Oh no!

The sample contained  $637 \text{ mg/L K}$  (unexpected!)

$\text{mg/L K} \times 0.852 = \text{pCi/L} {}^{40}\text{K}$

The sample contained  $\sim 534 \text{ pCi/L} {}^{40}\text{K}$

$$561 \text{ pCi/L} \approx 534 \text{ pCi/L}$$

Conclusion: sample contaminated by K-containing waste

Roy, W. R., B. Hensel, and B. Hennings. 2008. Gross Alpha and Gross Beta Measurements in Coal Combustion Product Leachate. Electric Power Research Institute, report number 1015546, EPRI, Palo Alto, CA.

# **Class Assignment 3**

**Read Chapter 2.**

**Answer Review Questions 2, 3, 4, and 6.**

**Rubric:**

**This assignment is worth 20 points.**

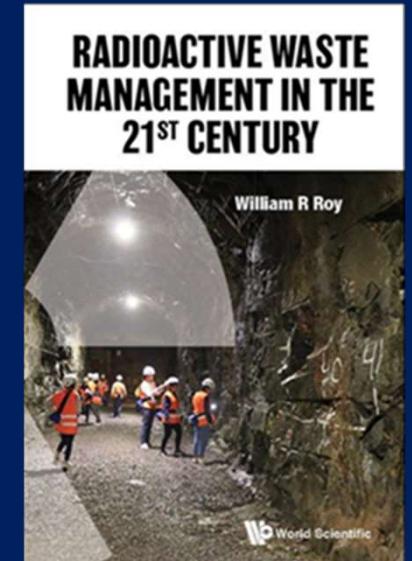
**Question 2 is worth 4 points.**

**Question 3 is worth 2 points.**

**Question 4 is worth 5 points.**

**Question 6 is worth 9 points.**

**Typed or handwritten. Do not send by email as an attachment.**



# **Release of Radionuclides**

**Davis–Besse Nuclear Power Station  
at Oak Harbor, Ohio.**

**“Boric acid in the reactor coolant had leaked from cracked control rod drive mechanisms directly above the reactor and eaten through more than six inches (150 mm) of the carbon steel reactor pressure vessel head over an area roughly the size of a football.”**

# Release of Radionuclides



Air filters had to be changed weekly and no one asked why at first. First Energy, the owner of Davis-Besse, acknowledged a series of safety violations. The company paid \$28 million under a settlement with the Justice Department \$23.7 million of that were fines. Repairs and upgrades cost \$600 million.

# Questions?

