



UNCONVENTIONAL RESERVOIR ENGINEERING PROJECT

COLORADO SCHOOL OF MINES



Progress Report

Membrane Properties of Shale and Osmosis in Porous Media

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UNCONVENTIONAL RESERVOIR ENGINEERING PROJECT

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Background

Behavior of argillaceous low-permeability media is analogous to semipermeable membranes due to the membrane properties of shale layers

[Kemper and Rollins, 1966; Olsen, 1969; Horseman and McEwen, 1996, and Neuzil, 2000]

The membrane properties of weakly permeable media are associated with the existence of the gradient-driven coupled flows

[Katchalsky & Curran, 1967; Bolt, 1979; Revil, 1999]

In argillaceous media, chemical osmosis is one of the main coupled flows

[Kemper & Quirk, 1972; Keijzer et al., 1999; Neuzil, 2000; Malusis & Shackelford, 2002; Gonçalves et al., 2004 & 2007].

The capacity of the membrane to behave as a semipermeable boundary is defined by the chemical-osmosis coupling coefficient



Background

Thermodynamics in nano-porous media can lead to different molecular compositions of the gas and liquid phases in different-size nano-pores.

Concentration gradients in heterogeneous nanoporous media cause diffusion. If the pore-throat sizes approach the scale of membrane pores, osmosis can also take place.

- Darcy's Law alone cannot describe the fluid flow in weakly permeable media demonstrating membrane behavior.
- Diffusion and osmosis take place in opposite directions with respect to the concentration gradient
- It is important to know the prevailing mechanism at a given point to determine the correct direction of transport.



Background

Fluid composition vs. pore size

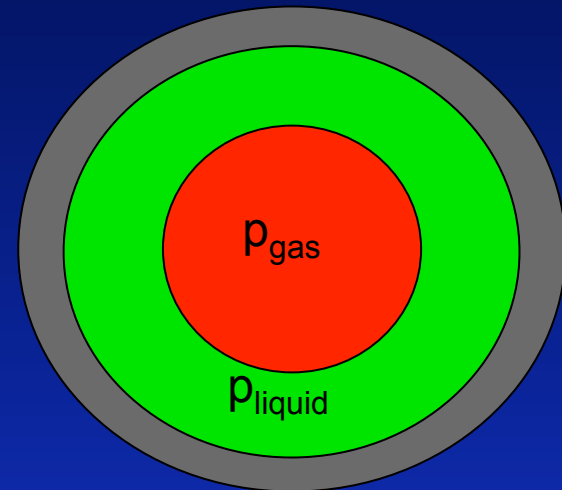
Phase behavior in nano-pores depends on capillary pressure and surface forces; thus, it depends on the sizes and the distribution of pores

In Confined Environment

The interface is curved

$$P_{gas} - P_{liquid} = P_c + \Pi_{surface}$$

$$P_c = \frac{2\sigma}{r}$$



Note: Capillary pressure is negligible in large pores

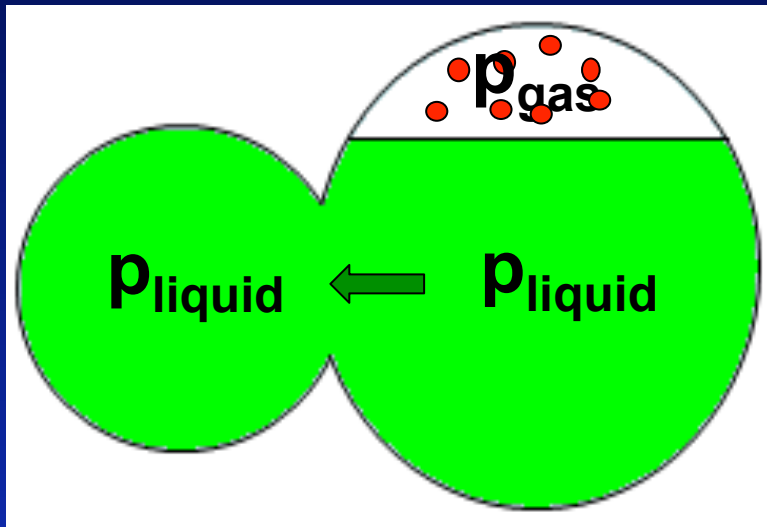


Background

Diffusion and Osmosis for different cases

Diffusion

Large connection between two different-size pores



- Concentration difference between pores
- Diffusion to establish equilibrium
- Heavier fluid molecules will go from the large pore to the small pore

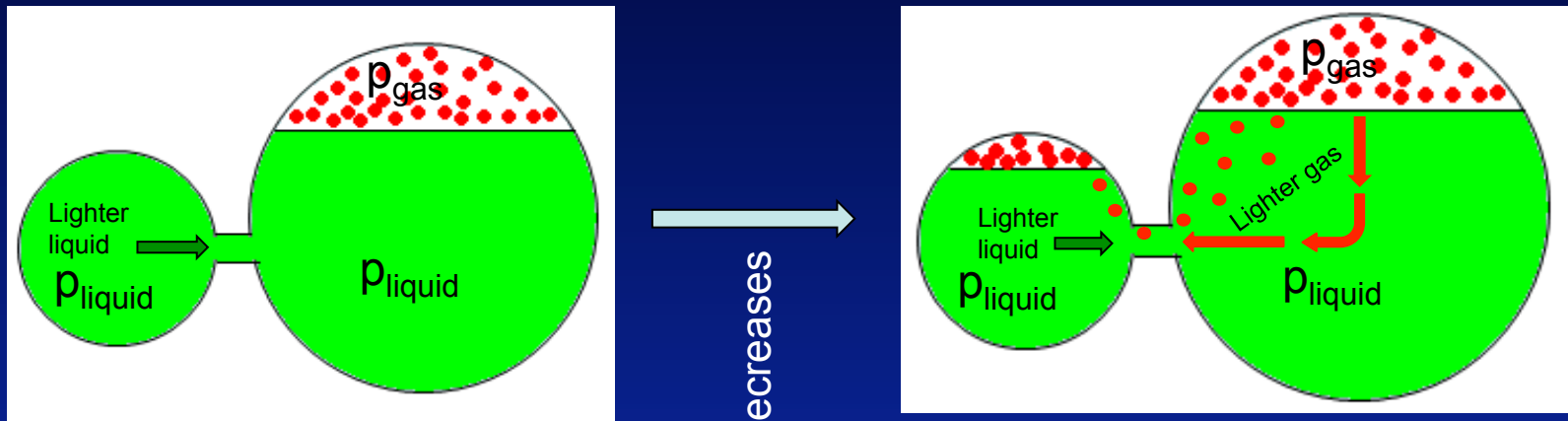


Background

Diffusion and Osmosis for different cases

Osmosis

Narrow pore throat between two different-size pores.



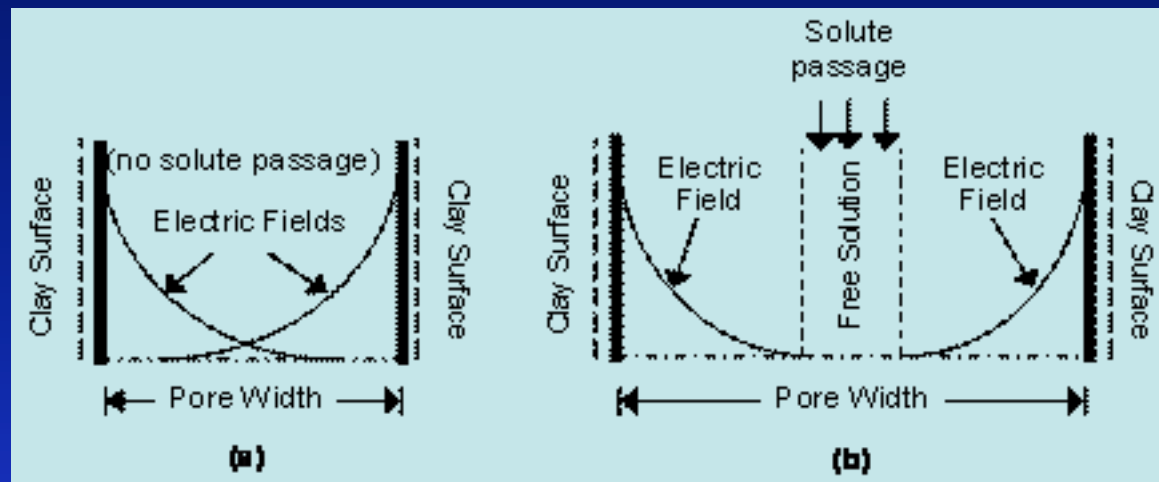
- While large molecules can not pass through small pore throat, small molecules can do.
- Osmosis will be from small pore to large pore.

- While lighter fluid molecules pass through from small pore to large pore, lighter gas molecules pass through from large pore to small pore.
- Osmosis will be in both direction.



Clay as a membrane

- *Electrostatic exclusion (charged solutes)*
 - ✓ In an ideal membrane (i.e., $\omega = 1$), electric fields associated with the DDLs of adjacent clay particles overlap within the pore space (Fig. 1a). Ions attempting to pass through the membrane are repelled across the entire width of the pore space.
 - ✓ Conversely, pore spaces of a non-ideal membrane (i.e., $0 < \omega < 1$) are sufficiently large that the electric fields do not overlap and contain an area of neutral or "free" solution through which ions can pass (Fig. 1b).



Clay as a membrane

- *Steric hindrance*
 - ✓ the geometric restriction that occurs when the size of the solute exceeds the pore size
 - ✓ It represents a geometric restriction rather than an electrostatic restriction, exclusion of uncharged solutes (e.g., nonpolar organic solutes), particularly those with high molecular weight, may be possible.



Osmotic efficiency in shale (ω)

- The ability of a material to act as an osmotic membrane is quantitatively characterized by the osmotic efficiency, also called the reflection coefficient.
- Its value ranges between two extremes: 0 for a non-perm selective material and 1 for a material with the perfect or ideal membrane behavior.
- the membrane efficiency of a soil will depend on the *effective* size of the pores, or the size of the free-solution channels.
- In general, ω increases with the effective stress and decreases with the solute charge and/or solute concentration



Coupled Flows

- If clays are subjected to flows of fluid, electrical charge, chemicals, or heat, in most cases, flows of different types occur simultaneously, even if only one driving force is acting. These are so-called coupled flows.
- These process involve the simultaneous flows of fluid, electricity, chemicals and heat under hydraulic, electrical, chemical and thermal gradients.
- Net transport of fluid and chemicals depends on number of complex interactions.
- Quantitative evaluation and prediction of the flows require that these interactions be accounted for appropriately.



Coupled Flows

The types of interrelated coupled flow that can occur under the influences of hydraulic, electrical, chemical and thermal gradients are given in table 1.

Flow J	Gradient X			
	Hydraulic	Electrical	Chemical	Thermal
Fluid	Hydraulic conduction (Darcy's Law)	Electro-osmosis	Normal osmosis	Thermal osmosis
Electric Current	Streaming potential	Electric conduction	Diffusion and membrane potentials	Seebeck effect
Ion	Streaming current	Electrophoresis	Diffusion (Fick's Law)	Soret effect
Heat	Isothermal heat transfer	Peltier effect	Dufour effect	Thermal conduction



Coupled Flows

- Coupled flows occur when a flow of one type is induced by a driving force or gradient of another type. Thus the total flow of type i is the sum of contributions from flows caused by gradients of type j according to

$$\vec{J}_i = \sum_{j=1}^n L_{ij} \vec{X}_j$$

$i=1,2,\dots,n$ and is a coupling coefficient that relates flows of the type i to gradient of type j .



Generalized Theory for the coupled Flows of Fluid

Coupled fluxes under isothermal conditions are defined by a dissipation function, Φ ,
(Mitchell and Soga,2005)

$$\Phi = \sum_{i=1}^N J_i X_i$$

More concisely, as

$$\vec{J}_i = \sum_{j=1}^n L_{ij} \vec{X}_j$$

L_{ij} are phenomenological coefficients that relate the flux of type i to the gradient of type j .

Assumptions used in the non-equilibrium thermodynamics formalism:

1. Local equilibrium
2. Linear phenomenological equations
3. Validity of Onsager's reciprocal relations



Coupled Flux Equations

$$\Phi = -q \frac{\partial p}{\partial x} - I \frac{\partial \psi}{\partial x} - \sum_{i=1}^M J_i^d \frac{\partial \mu_i}{\partial x}$$

q : liquid (solution) flux, P : liquid pressure, I : electric current, ψ : electrical potential, μ_i : chemical potential of solute i , J_i^d : molar diffusive flux of solute i , M : number of solute species.

$$q = -L_{11} \frac{\partial p}{\partial x} - L_{12} \frac{\partial \psi}{\partial x} - \sum_{i=1}^M L_{1,j+2} \frac{\partial \mu_i}{\partial x}$$

$$I = -L_{21} \frac{\partial p}{\partial x} - L_{22} \frac{\partial \psi}{\partial x} - \sum_{i=1}^M L_{2,j+2} \frac{\partial \mu_i}{\partial x}$$

$$J_i^d = -L_{j+2,1} \frac{\partial p}{\partial x} - L_{j+2,2} \frac{\partial \psi}{\partial x} - \sum_{i=1}^M L_{j+2,i+2} \frac{\partial \mu_i}{\partial x} : \dots j = 1, 2, \dots M$$

If the chemical solution is dilute such that ideal solution relationships are valid,

$$\frac{\partial \mu_i}{\partial x} = \frac{RT}{C_i} \frac{\partial C_i}{\partial x}$$



Noncharged Solute Formulation

$$\Phi = -J_w V_w \frac{\partial p}{\partial x} - \sum_{i=1}^M J_i^d \frac{RT}{C_i} \frac{\partial C_i}{\partial x}$$

Where J_w is the flux of solvent (H_2O), V_w is the partial molar volume of solvent, J_s^d is the diffusive solute flux, and C_s is the molar solute concentration. For dilute solutions, $J_w V_w \approx q$.

$$\Phi = -q \frac{\partial p}{\partial x} - \sum_{i=1}^M J_i^d \frac{RT}{C_i} \frac{\partial C_i}{\partial x}$$

$$q = -L_{11} \frac{\partial p}{\partial x} - \sum_{i=1}^M L_{1,i+2} \frac{RT}{C_i} \frac{\partial C_i}{\partial x}$$

$$J_s^d = -L_{21} \frac{\partial p}{\partial x} - \sum_{i=1}^M L_{j+2,i+2} \frac{RT}{C_i} \frac{\partial C_i}{\partial x}$$



Single-noncharged solute formulation

It is given by Manassero and Dominijanni (2003)

For single solute system, $M=1$ and for dilute solutions $V_w \approx 1$

$$\begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} = \begin{bmatrix} \frac{k_h}{\gamma_w} & -\frac{\omega C_s k_h}{\gamma_w} \\ -\frac{\omega C_s k_h}{\gamma_w} & \frac{nD_s^* C_s}{RT} + \frac{C_s^2 k_h \omega^2}{\gamma_w} \end{bmatrix}$$

$$q = -\frac{k_h}{\gamma_w} \frac{\partial p}{\partial x} + \frac{\omega k_h}{\gamma_w} RT \frac{\partial C_s}{\partial x}$$

$$J_s^d = \frac{\omega C_s k_h}{\gamma_w} \frac{\partial p}{\partial x} - \left(\frac{nD_s^*}{RT} + \frac{\omega^2 C_s k_h}{\gamma_w} \right) RT \frac{\partial C_s}{\partial x}$$



Planned Work

Set up a coupled flow model to demonstrate the significance of osmosis in nanoporous unconventional reservoirs

Start experimental study to observe osmosis in non-uniform and nanoporous unconventional reservoir samples

Choose (and improve) the constitutive relations appropriate to model transport by osmosis in unconventional reservoirs

Quantify the phenomenological coefficients in coupled flow equations

Integrate osmosis (couple flows) into COZsim

