Dept. Renewable Energy Sci. /4th Stage

Dr. Saadi Sattar Shahadha

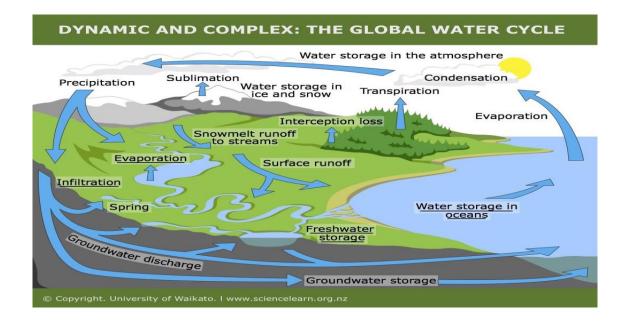
Lecture (1)

The hydrologic cycle

The Water Cycle just like all sources of water on Earth, groundwater comes directly from and is a large part of the water cycle. It begins with precipitation.

- Water falls from condensed clouds and collects on the surface, which then will move down whatever surface it is on due to gravity. This is called runoff. Runoff can either collect in larger streams and rivers, which will eventually flow into lakes or oceans, or runoff can move underground through percolation.
- Percolated water will first move through surface soils, because they are often the top strata, and they easily absorb water. After it moistens the soil, it will move through any permeable strata below, until it reaches an aquifer, aquitard, or aquiclude.
- The movement of water from the surface to the ground is called infiltration.
- The area of the ground filled with water, either in an aquifer or an aquitard, is the saturated zone. Conversely, the area above the saturated zone, where the ground is not filled with water, is called the vadose zone. The line separating these areas, above which there is little to no water, below which there is saturated strata, is the water table.

Water Hydraulics



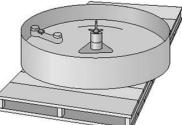
Elements of Hydrological Cycle

1. Evaporation the process by which an element or compound transitions from its liquid state to its gaseous state below the temperature at which it boils; in particular, the process by which liquid water enters the atmosphere as water vapour.

- Controlling factors

- a. Humidity
- b. Temperature
- c. Wind

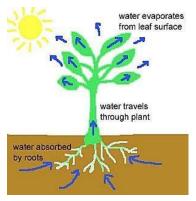




Class A evaporation pan, a cylinder with a diameter of 47.5 in (120.7 cm) that has a depth of 10 in (25 cm).

2. Transpiration is the process of water movement through a plant and its

evaporation from aerial parts, such as leaves,stems and flowers. Water is necessary for plantsbut only a small amount of water taken up bythe roots is used for growth and metabolism.The remaining 97–99.5% is lost by transpirationand guttation.

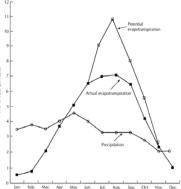


- Controlling factors are

Evaporation + *Transpiration* = *Evapotranspiration* (*ET*)

Evapotranspiration (ET) is a combined process of evaporation and transpiration.

- Potential ET (PET) = amount of water evaporating or transpiring from a surface if water were unlimited
- Actual ET < PET (except for open bodies of water)
- PET is often estimated empirically as a function of temperature and other variables
- **3. Precipitation** is any product of the condensation of atmospheric water vapor that falls under gravity from clouds.



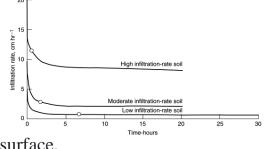
4. Infiltration is the process by which water on the ground surface enters the soil. It is commonly used in both hydrology and soil sciences. The infiltration capacity is defined as the maximum rate of infiltration.



Two forces are controlling the infiltration: gravity (drainage) and capillary (imbibition)

Infiltration rates are a measure of how fast water enters the soil and are

typically expressed in cm per hour. For initial in-field assessments, however, it is more practical to express **infiltration** time in the number of minutes it takes soil to absorb each cm of water applied to the soil surface.



• Reasons for infiltration rate decreasing with time:

- Diminishing of capillary forces.
- Closing of cracks and macropores.

• Conditions in favor of a high infiltration rate:

- Coarse soils
- Well-vegetated land
- Low soil moisture
- Cracks and macropores

How to increase rainwater infiltration in an urban environment?

Do you know other elements of hydrologic cycle?

References:

Fetter, C.W., 2018. Applied hydrogeology. Waveland Press.

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Lecture (2)

Water balance

• Inflow – outflow = change in storage (ΔS)

1- Global Scale (for land):

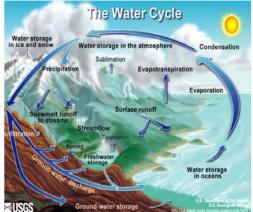
– Inflow: Precipitation (P)

– Outflow: Evaporation (E), Transpiration (T),and Runoff (RO)

- Groundwater discharge equation

 $P - E - T - RO = \Delta S$

2- Basin scale is more our focus



(basin can be either a watershed or a structural/sedimentary basin)

Inflow:

Precipitation (P); Surface water inflow (Si); Groundwater inflow (Gi)

Outflow:

Evapotranspiration (ET); Surface water outflow (So); Outflow from groundwater (Go)

Changes in storage:

Surface water; soil moisture; temporal depression storage; plant surface; groundwater

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Basin-scale equation: $P + Si + Gi - ET - So - Go = \Delta S$

• What is hydrogeology?

It is a study of water in the subsurface (primarily groundwater)

• "Ground water" or "Groundwater"?

Hydrogeology is a very recent and important field of science. It is the combination of Hydrology, the study of movement, quality, and other properties of water around the world, and geology, the study of the composition and processes of the Earth.

Hydrogeologists study the properties of water under the Earth's surface, and how it affects other systems (the study of groundwater).

• What is groundwater?

It is a subsurface water in the saturated zone (where all pores are filled with

water (more about this later)

• Why do we care about groundwater?

Groundwater as a resource

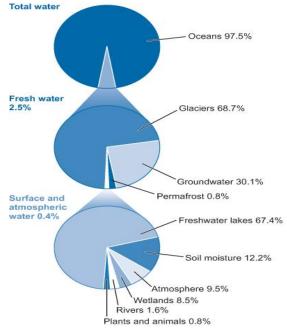
Distribution of water by volume on Earth: oceans 97.5 %,

ice/snow 2.14 %,

ground water 0.61 %,

surface water and soil moisture <0.05%

• Groundwater = **30.1%** of available fresh water.



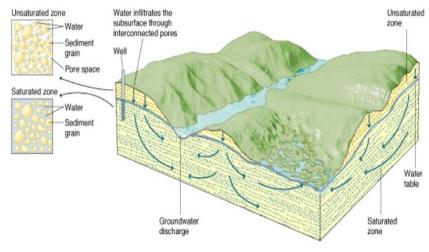
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Zones of subsurface water

- soil-water zone
- vadose (unsaturated) zone
- saturated zone

• What separates the unsaturated and saturated zones?

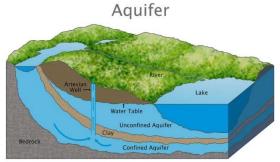


The **watershed** is a drainage basin. It consists of surface water (lakes, streams, reservoirs, and wetlands, and all the underlying groundwater. Larger **watersheds** contain many smaller **watersheds**. It all depends on the outflow point; all of the land that drains water to the outflow point is the **watershed** for that outflow location.

Aquifers

An aquifer is a geologic unit that can yield water to wells or springs. It

is an underground layer of water-bearing permeable rock, rock fractures or unconsolidated materials (gravel, sand, or silt). Groundwater can be extracted using a water well.



The study of water flow in **aquifers** and the characterization of **aquifers** is called hydrogeology.

• Groundwater can sustain streamflow during dry periods (provides baseflow)

• About 79.6 billion gallons of groundwater is withdrawn everyday in U.S., accounting for 26% of total water withdraws.

• Irrigation is the largest groundwater use in the U.S. and about 53.5 billion gallons of groundwater are used daily for agricultural irrigation.

• 44% of the U.S. population depends on groundwater for its drinking water.

Groundwater as a nuisance

- Control of groundwater is important in dams, excavations, and waste-disposal facilities
- Role of groundwater in slope failure, solution collapse, and soil salinization



References:

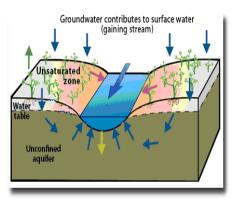
Fetter, C.W., 2018. Applied hydrogeology. Waveland Press.

Lecture (3)

Interaction Between Streams and Groundwater:

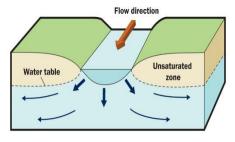
1- Gaining streams: Streams that maintain flow essentially year-

round and have flows that are wellsustained or increase in а direction downstream are called gaining streams. The water along **gaining** table streams is generally at or above stream level, and ground water generally moves toward and into the **stream**.

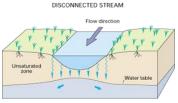


2- Losing streams are those that lose a significant part of their flow

into the groundwater system. Like sinkholes, they are discrete recharge features that allow surface water to rapidly enter the subsurface. The water table along losing streams is below stream elevation.



- **3- A gaining** stream can temporary become a losing stream during floods.
- **4- Disconnected** streams also recharge groundwater, but through the unsaturated zone.



More about gaining and losing streams

- Streams can be gaining in some locations and losing in others
- At a particular location, a stream can be gaining at some *times* and losing at others
- Perennial stream—flows year-round
- Intermittent stream—flows seasonally
- Ephemeral stream—flows only after storms

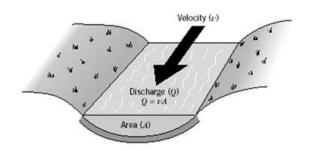
Measure Stream Discharge:

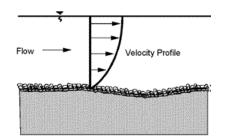
Q = VA

Q: discharge (L3/T)

A: cross-section area (L2)

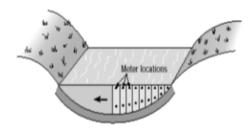
V: Average velocity (L/T)





Measure Stream Discharge:

- 1- current meter
 - $Q = \Sigma qi = \Sigma viai = \Sigma vidiwi$
 - qi: discharge of a section (L3/T)
 - *a*i: =*d*iwi cross-section area of a section (L2)
 - *d*i: depth of the midpoint of a section (L)
 - wi: width of a segment (L)
 - vi: Average velocity of a section (L/T)



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Aquifers

Aquifers a geologic unit that can STORE and TRANSMIT water at rates fast enough to supply reasonable amounts to wells. It is an underground layer of water-bearing permeable rock, rock fractures or unconsolidated materials (gravel, sand, or silt). Groundwater can be extracted using a water well. The study of water flow in **aquifers** and the characterization of **aquifers** is called hydrogeology.

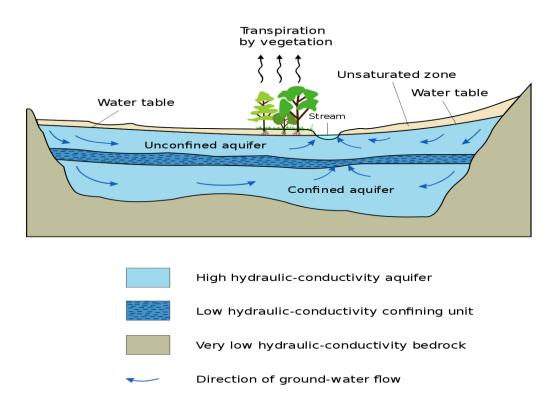
- A Unit with very low permeability is called a **confining layer** ($K < 10^{-5}$ cm/s, arbitrary).

A confining layer also transmits water but with a slower rate.

- Aquifer Types
- Unconfined aquifers
- Confined aquifers
- Perched aquifers (less common)

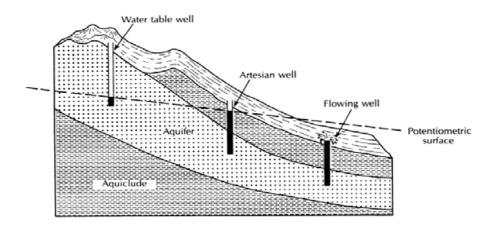
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There are two general types of aquifers: confined and unconfined.

1- A confined aquifer is an aquifer below the land surface that is saturated with water. Layers of impermeable material are both above and below the aquifer, causing it to be under pressure so that when the aquifer is penetrated by a well, the water will rise above the top of the aquifer



• Overlain by a confining layer;

• Water level of a well in a confined aquifer is above the top of the aquifer. What if the water level is above the land surface?

• Sometimes also called artesian aquifers.

2- Unconfined aquifer: Where groundwater is in direct contact with the atmosphere through the open pore spaces of the overlying soil or rock, then the aquifer is said to be unconfined.

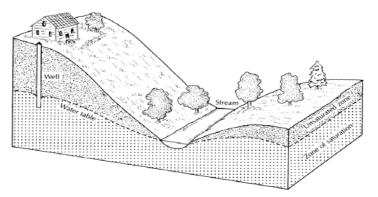
The upper groundwater surface in an **unconfined aquifer** is called the *water table*. **Unconfined aquifers** are typically below major water courses such as rivers. These systems provide a constant source of water that seeps down to **form** the **aquifer**.

• Permeable materials extend from the base to the land surface;

• A water table forms the upper boundary;

• Can receive direct recharge from unsaturated zone.

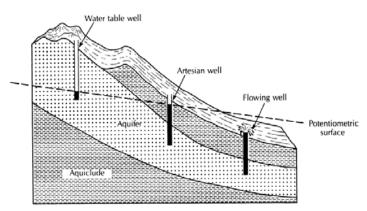
• Sometimes also called water-table aquifers.



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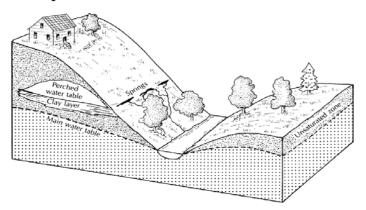
Potentiometric Surface

- Represent the water level of a confined aquifer.
- Above the top of the aquifer.
- Normally constructed from water levels measured in wells.



Perched Aquifers

- Lens of low permeability in more permeable materials.
- Usually very small.



Aquifers Terms:

- Confining Layer geologic unit with little or no intrinsic permeability.
- Aquifuge Absolutely impermeable unit that will not transfer water.
- Aquitard a layer of low permeability that can store ground water and transmit it slowly from one aquifer to another.
- Unconfined/Confined Aquifer an aquifer without/with a confining layer on top.
- Leaky Confined Aquifer a confined aquifer with an aquitard as one of its boundaries.
- Perched Aquifer a layer of saturated water that forms due to accumulation above an impermeable lens (e.g. clay).
- Water Table depth where the soil becomes completely saturated

<u>References:</u>

Fetter, C.W., 2018. Applied hydrogeology. Waveland Press.

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Lecture (4)

Properties of Aquifers

- Aquifers are essentially porous media and so the **properties** relate to the **properties** of *porous* media
- Porosity is the ratio of the volume of voids to the total volume
- 0<n<1, although sometimes we express it as a percentage by multiplying by 100

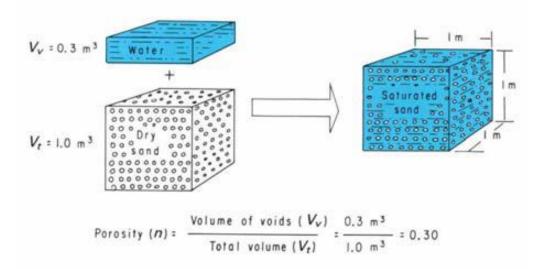
•
$$n = \frac{V_v}{V_T}$$

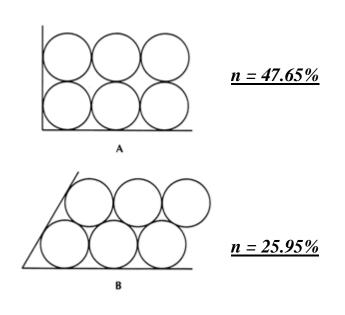
Porosity *n* (dimensionless)

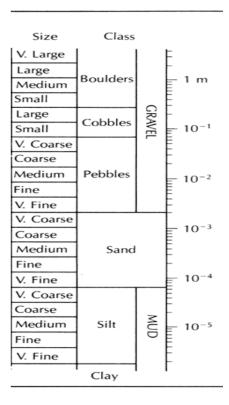
- *Vv* : volume of voids
- *VT* : total volume of a porous medium

$$VT = Vv + Vs$$

Vs : volume of solids







Porosity range for sediments:

for Sediments
25-50%
20-35%
10-20%
35-50%
33-60%

Based on Meinzer (1923a); Davis (1969); Cohen (1965); and MacCary and Lambert (1962).

Types of porosity

• **Primary** porosity: created at time of deposition or *crystallization* of porous media.

• Secondary porosity: created by jointing, *faulting, and weathering*.

• Effective porosity (ne): ratio of *interconnected* void volume to total volume of porous media.

Gravimetric water content: gravimetric water content. It is simply the ratio of water weight to soil weight.

 $\theta_g = \frac{W_w}{W_s}$ (dimensionless) (g/g)

Ww Mass of water in the soil.

Ws Mass of solid particles

***** Volumetric water content:

Volumetric water content is a numerical measure of soil moisture. It is simply the ratio of water volume to total volume.

 $\theta_{v} = \frac{V_{w}}{V_{T}}$ (dimensionless) (vol/vol)

✓ When the pores in a porous medium contain some air, i.e. unsaturated, $\theta_v < n$

- ✓ When the porous media is saturated, $\theta_v = n$
 - Both θg and θv are dimensionless.

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Bulk density:

Bulk density is dependent on soil organic matter, soil texture, the density of soil mineral (sand, silt, and clay) and their packing arrangement. As a rule of thumb, most rocks have a density of 2.65 g/cm^3 .

Bulk density $\rho b = Ms/VT$: density of dry soil or rock sample

Particle density $\rho s = Ms/Vs$ density of solids.

For most earth materials, $\rho s = 2.65 \text{ g/cm}^3$

Relationship among porosity, bulk density, and particle density

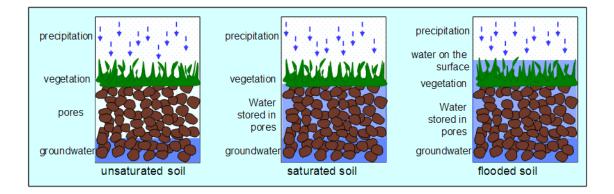
$$n=1-\frac{\rho_b}{\rho_s}$$

Saturation ratio:

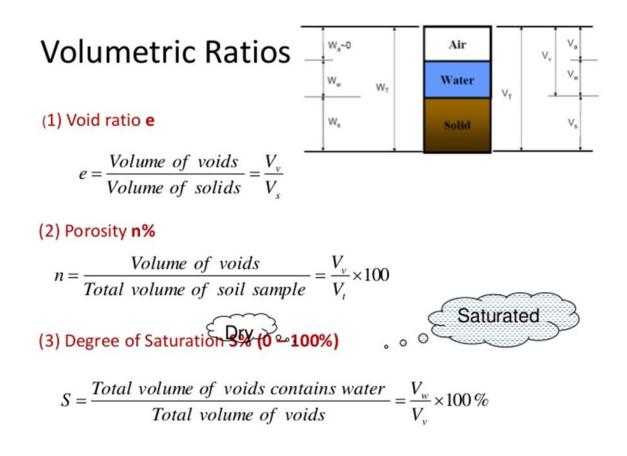
Saturation - refers to a soil's water content when practically all pore spaces are filled with water. This is a temporary state for well-drained soils, as the excess water quickly drains out of the larger pores under the influence of gravity, to be replaced by air.

$$R_s = \frac{Vw}{Vv}$$

When the porous media is saturated: *Rs*=1



Water Hydraulics



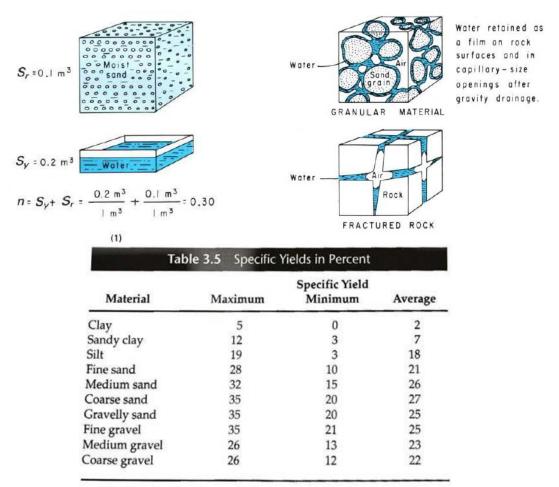
Specific Yield:

 $n = S_y + S_r$

 S_y -- specific yield, the ratio of the volume of water that drains from a saturated rock, owing to gravity, to the total rock volume.

 S_r -- specific retention, the ratio of the volume of water a rock can retain against gravity drainage to the total rock volume.

- Specific yield decreases with decreasing grain size.
- Specific retention increases with decreasing grain size.



Source: Johnson (1967).

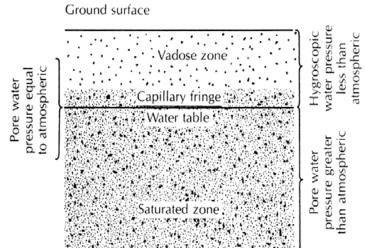
Water Table

The surface at which pore water pressure is equal to atmospheric pressure.

- The water table generally follow the general shape of the topography, but with less relief.
- A sloping water table indicates the groundwater is flowing.

What if the water table is flat?

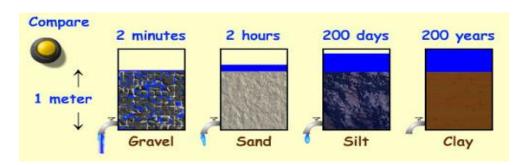
• In general, porous media below the water table are saturated with water.



Permeability

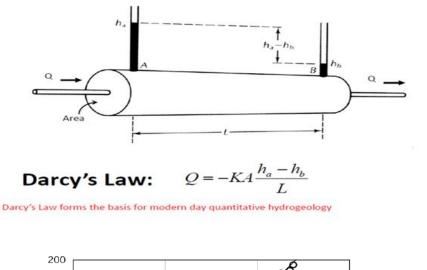
Permeability is the property of rocks that is an indication of the ability for fluids (gas or liquid) to flow through rocks. **High permeability** will allow fluids to move rapidly through rocks.

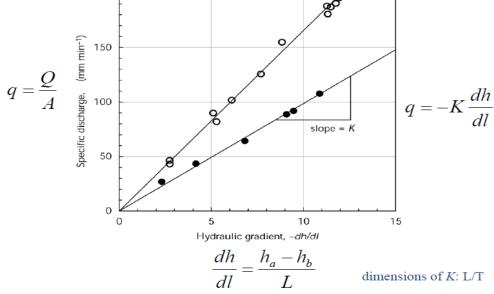
Permeability is largely **dependent on** the size and shape of the pores in the substance and, in granular materials such as sedimentary rocks, by the size, shape, and packing arrangement of the grains.



Darcy's Law

• Basic question: how does discharge through porous media relate to water levels along the flow path?





References:

Fetter, C.W., 2018. Applied hydrogeology. Waveland Press.

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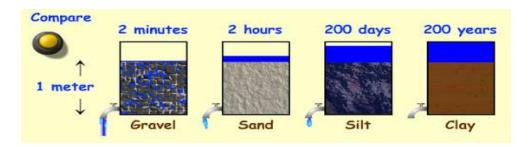
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Lecture (5)

Permeability and Darcy's Law

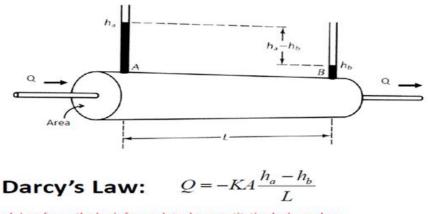
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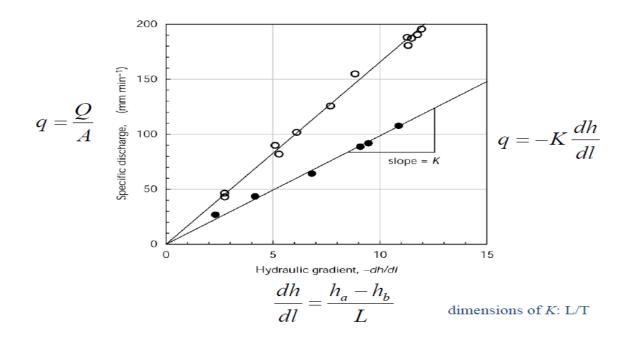


Darcy's Law

• Basic question: how does discharge through porous media relate to water levels along the flow path?



Darcy's Law forms the basis for modern day quantitative hydrogeology



Hydraulic conductivity (K)

Hydraulic conductivity is a physical property, which measures the ability of the material to transmit fluid through pore spaces and fractures in the presence of an applied **hydraulic** gradient

• Constant of proportionality in Darcy law (dimensions of L/T), Empirical relationship

- Measure of permeability of porous media to water
- Recall that *n* values range from ~ 0 to 60%
- *K* values can range over 12 orders of magnitude

```
(10^{-14} \text{ m/s to } 10^{-2} \text{ m/s})
```

Soil Layer	Saturated K _{soil} (cm/s)	Permeability Class
Pavement	0	Very low
Silty loam	1.9×10^{-4}	Low
Loam	3.7×10^{-4}	
Fine sandy loam	5.2×10^{-4}	
Sandy loam	7.2×10^{-4}	Moderate
Loamy fine sand	1.0×10^{-3}	
Loamy sand	1.7×10^{-3}	High
Sandy gravelly soils	5.8×10^{-3}	Very high

✓ How does K relate to parameters such as n or d (grain size)?

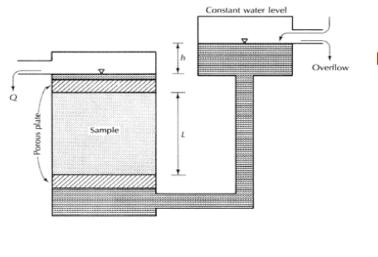
Hydraulic conductivity (K) Saturated **hydraulic conductivity** is a quantitative measure of a saturated **soil's** ability to transmit water when subjected to a **hydraulic** gradient. Saturated hydraulic conductivity is affected by both soil and fluid properties. It depends on the soil pore geometry as well as the fluid viscosity and **density**. The hydraulic conductivity for a given soil becomes lower when the fluid is more viscous than **water**.

How to measure the hydraulic conductivity?

A ring infiltrometer is a thin-walled open-ended cylinder inserted into the **soil** to a specific depth (typically around 5 cm) **to measure** field saturated **hydraulic conductivity**. Water infiltrates through the ring(s) using either the constant or falling head techniques.

1- Constant-head permeameter

Constant-head permeameter



From Darcy's law:

$$Q = -KA \frac{(h_a - h_b)}{L}$$

$$Q = \frac{V}{t}$$

$$h = -(h_a - h_b)$$

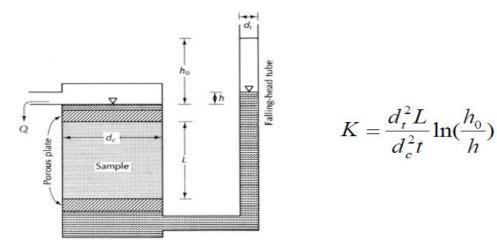
$$VI$$

$$K = \frac{VL}{Ath}$$

What's the flow direction in the sample?

2- Falling-head permeameter

Falling-head permeameter



Falling-head permeameter is suitable for materials with low *K*.

Homogeneity and Heterogeneity of Hydraulic Cconductivity

- Homogeneity: *K* is the same at all locations in a geological formation.
- Heterogeneity: *K* changes spatially in a formation.
- Common (simplistic) assumption: *K* is

homogeneous

• Usual case: *K* is heterogeneous





Isotropy and anisotropy

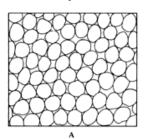
- *K* is a vector and tensor quantity (magnitude can vary with direction)
- **Isotropy**: Kx = Ky = Kz
- Anisotropy:

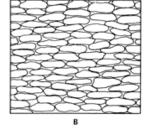
 $Kx \neq Ky$,

 $Kx \neq Kz$,

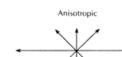
 $Ky \neq Kz$

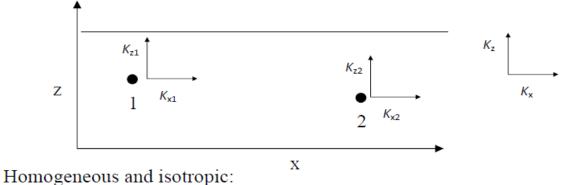
- Common (simplistic) assumption: *K* is isotropic
- Usual case: *K* is anisotropic











$$K_{\rm x1} = K_{\rm x2}; \, K_{\rm z1} = K_{\rm z2}; \, K_{\rm x1} = K_{\rm z1}; \, K_{\rm x2} = K_{\rm z2}$$

Homogeneous and anisotropic:

 $K_{\mathtt{x1}} = K_{\mathtt{x2}}; \; K_{\mathtt{z1}} = K_{\mathtt{z2}}; \; K_{\mathtt{x1}} \neq K_{\mathtt{z1}}; \; K_{\mathtt{x2}} \neq K_{\mathtt{z2}}$

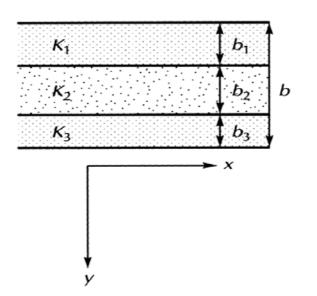
Heterogeneous and isotropic

 $K_{\rm x1} \neq K_{\rm x2}; \ K_{\rm z1} \neq K_{\rm z2}; \ K_{\rm x1} = K_{\rm z1}; \ K_{\rm x2} = K_{\rm z2}$

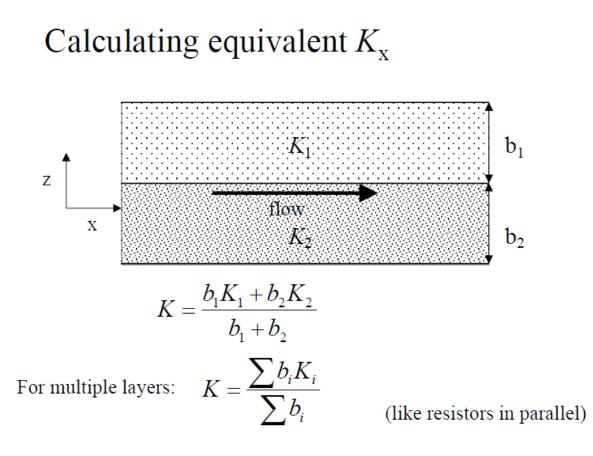
Heterogeneous and Anisotropic

 $K_{\mathtt{x1}} \neq K_{\mathtt{x2}}; \ K_{\mathtt{z1}} \neq K_{\mathtt{z2}}; \ K_{\mathtt{x1}} \neq K_{\mathtt{z1}}; \ K_{\mathtt{x2}} \neq K_{\mathtt{z2}}$

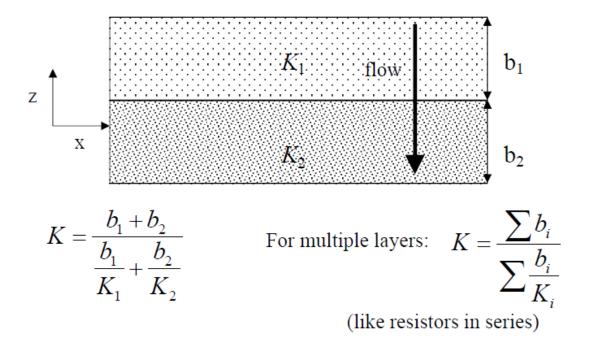
Equivalent hydraulic conductivity







Calculating equivalent Kz



References:

Fetter, C.W., 2018. Applied hydrogeology. Waveland Press.

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<u>Lecture (6)</u>

Hydraulic gradient and flow direction

Groundwater flows down-gradient (from high to low hydraulic head). As is the case with surface water, or a ball rolling down a hill, the water flows in the direction of the steepest gradient, meaning that it flows perpendicular to equipotentials.

General **flow** directions are **determined** from contour maps of the *water table and potentiometric surface*, or from information on water levels, boundaries, and locations of recharge and discharge areas.

The **hydraulic gradient** is the **slope** of the water table or potentiometric surface, that is, the change in water level per unit of distance along the direction of maximum head decrease. ... For example, if the difference in water level in two wells 1000 m apart is 2 m, the **gradient** is 2/1000 or 0.002.

Flow direction of water is affected by gravity and pressure.

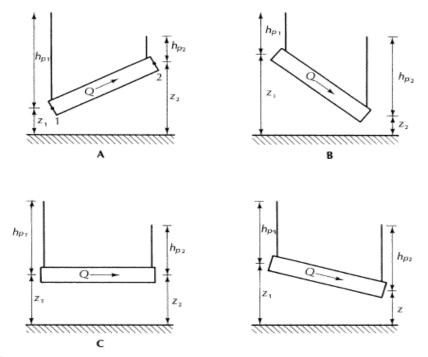
$$-\frac{h_a - h_b}{L} = -\frac{dh}{dl} = \Delta h$$

- Negative by convention; dimensionless

• Driving force for ground-water movement

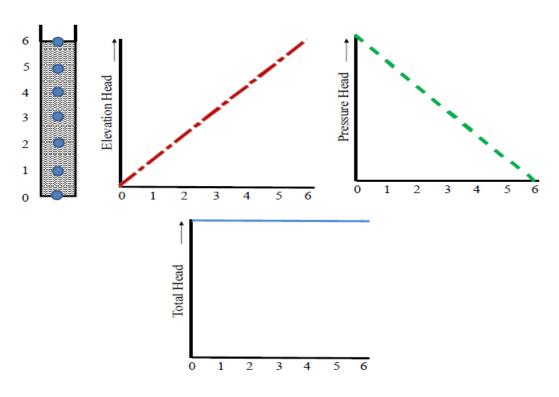
• The gradient defines the direction of groundwater flow from regions of high head to regions of lower head.

• Groundwater flows in the direction of the steepest gradient

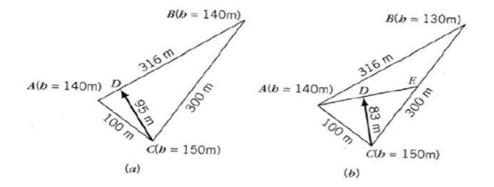


▲ FIGURE 5

Apparatus to demonstrate how changing the slope of a pipe packed with sand will change the components of elevation, z, and pressure, h_{pr} heads. The direction of flow, Q, is indicated by the arrow.







• Pick 3 points (wells or piezometers) without identical h values

• If 2 points (A and B) have the same h values, draw a line through the third point (C) and \bot to AB (with intercept D)

• Hydraulic gradient is iCD = (hC-hD)/CD

If h points are not equal

The 3-point problem (continued)

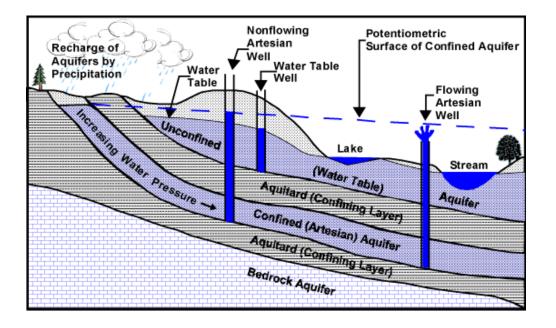
• If h values are different for all 3 points, connect each pair of points to form a triangle

- Define well C as having highest h and well B as having lowest h
- Find point on line BC (E) with h equal to h at point A

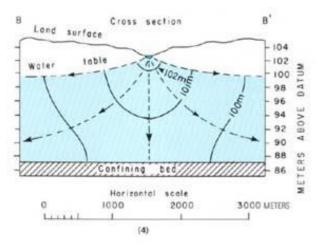
• Draw line AE, then draw line through C 1 to AE; intersection will be at point D

• Hydraulic gradient is iCD = (hC-hD)/CD

Mapping ground-water flow



- h varies in 3-D and in time
- Best to draw cross-section parallel to mean direction of ground-water flow
- Potentiometric surface = contour map of h in a single aquifer (traditionally a confined aquifer)



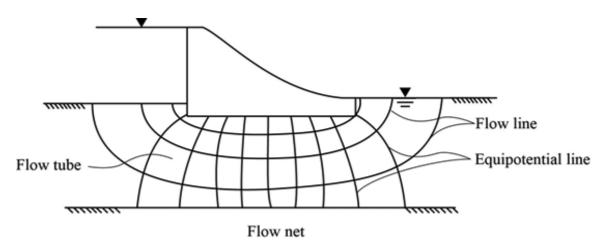
• Contouring h in an unconfined (surficial) aquifer gives a water-table map

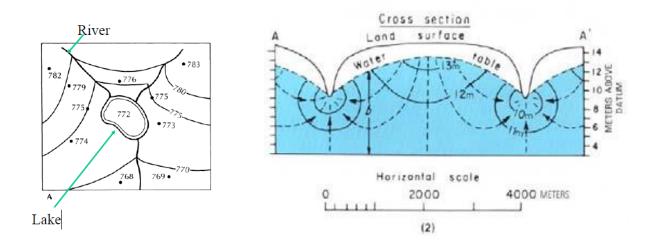
• If vertical flow in the mapped area is negligible, directions of lateral flow can be inferred.

Potentiometric Surface

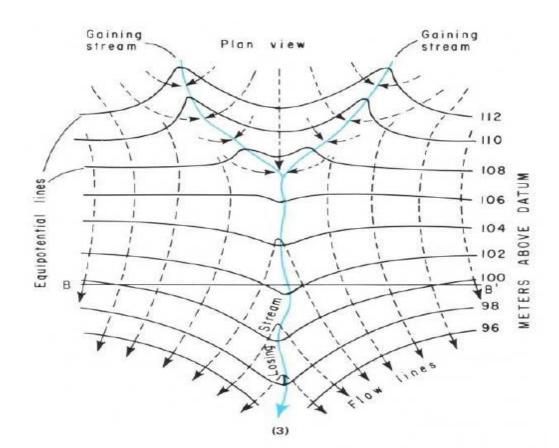
- A potentiometric map should be for a single aquifer;
- Assume flow in the aquifer is horizontal
- Equipotential can't cross other equipotential
- For surface-water bodies (large lakes, streams, etc.), the shoreline is constant-head boundary (an equipotential line)
- Relatively **impermeable stratigraphic** contacts represent no-flow boundaries (parallel to flow lines)

Equipotential Lines The points along the equipotential line will have the **equal head**, which causes the flow. If we place the piezometer at different points along an equipotential line, the water level will be same. This is the line present in the flow net, and also called as drop line. The equipotential line will not meet another equipotential line.

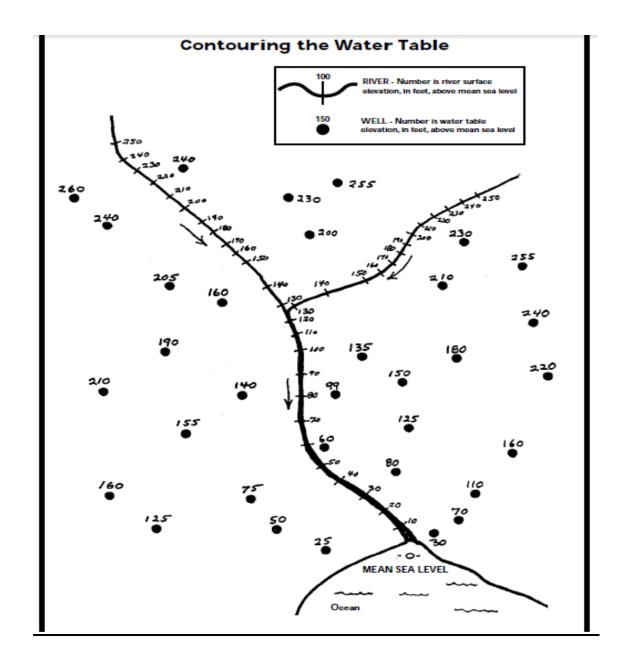




Water-table map (Plane view)



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<u>References:</u>

Fetter, C.W., 2018. Applied hydrogeology. Waveland Press.

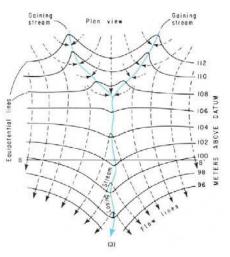
Lecture (7)

Flow Net

Flow lines (streamlines): flow path of a water particle

Equipotential lines: contours of equal heads

Streamlines *end* at extraction wells, drains, and gaining streams, and they *start* from injection wells and losing streams.



In natural groundwater systems, streamlines

often begin and end at the water table in area of groundwater recharge and discharge, respectively.

Flow net in isotropic and homogeneous media

Two-dimensional steady state flow in homogeneous and isotropic media:

Assumptions:

- 1. The aquifer is homogeneous and isotropic
- 2. The aquifer is fully saturated
- 3. The flow is steady state, i.e. no change in the flow field with time
- 4. Flow is laminar
- 5. All boundary conditions are known

Construct a Flow Net

Basic Rules:

1. Streamlines are perpendicular to equipotential lines;

2. Same quantity of groundwater flows between two adjacent pair of flow lines;

3. Drop in hydraulic head between two adjacent equipotential lines is the same.

Boundary Conditions:

No-flow boundary: Adjacent flow lines are parallel to the boundary;

Equipotential lines are perpendicular to the boundary

Constant head boundary: Flow lines are perpendicular to the boundary;

Adjacent equipotential lines are parallel to the boundary

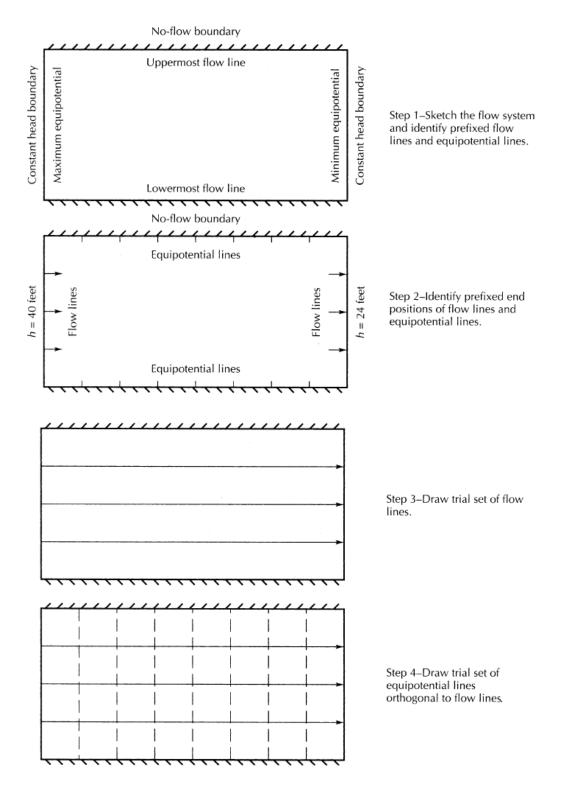
Water-table boundary: is a streamline when there is no recharge or ET.

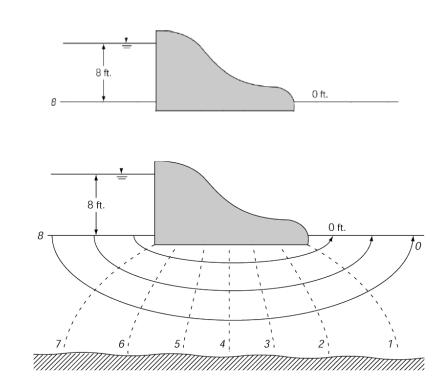
When there is a recharge, the water table is neither a flow line nor an equipotential line.

Steps:

- 1: Sketch the flow system, including boundary conditions
- 2: Identify prefixed flow lines and equipotential lines
- 3: Draw a set of flow lines
- 4: Draw a set of equipotential lines

A Simple Flow Net



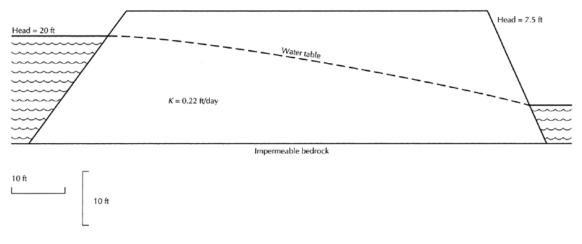


Flow Net under an Impervious dam

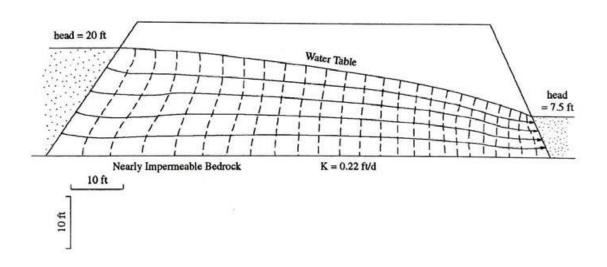
Flow net exercise

Draw a flow net for seepage through the earthen dam shown in figure below.

Assume there is no recharge or ET across the water table.

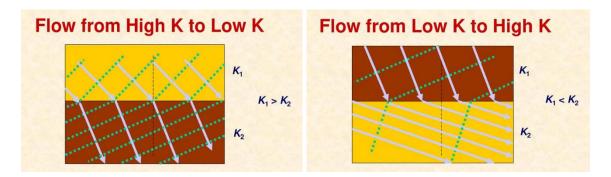


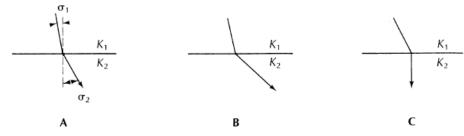
Water Hydraulics



Refraction of flow lines

When water passes from one stratum to another stratum with a different hydraulic conductivity, the direction of the flow path will change.

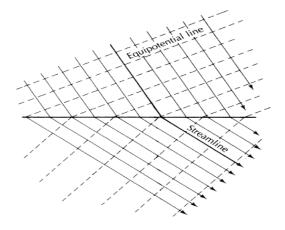




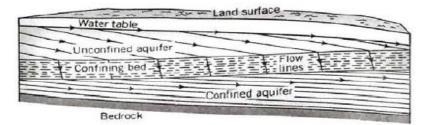
▲ FIGURE 14

A. Refraction of a flowline crossing a conductivity boundary. B. Refracted flowline going from a region of low to high conductivity. C. Refracted flowline going from a region of high to low conductivity.

► FIGURE 15 A flow net with flow crossing a conductivity boundary showing refraction of flowlines and equipotential lines. The hydraulic conductivity above the boundary is less than that below the boundary.



Flow net in heterogeneous media



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References:

Fetter, C.W., 2018. Applied hydrogeology. Waveland Press.

Dr. Saadi Sattar Shahadha

Lecture (8)

Overview of Water Chemistry

- Natural water always contain at least small amount of dissolved gases and solids.
- For most water uses, chemical properties of water are as important as water quantity.
- Solute, solvent, solution, aqueous solution
- ✓ When one substance dissolves into another, a **solution** is formed.
- ✓ A solution is a homogeneous mixture consisting of a solute dissolved into a solvent.
- \checkmark The **solute** is the substance that is being dissolved,
- ✓ The **solvent** is the dissolving medium.
- ✓ An aqueous solution is a solution in which water is the solvent. A NaCl solution is an aqueous solution.
- \checkmark A **non-aqueous** solution is a solution in which water is **not** the solvent.
- Common units: mg/L and mol/L

Rocks and minerals dissolve in water to form ions

Cation: positively charged ion; Anion: negatively charged ion

Salt: $NaCl = Na^+ + Cl^-$

Calcite: $CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$

Carbon Dioxide: $CO_2 + H_2O = H^+ + HCO_3^-$

Some solids or gases dissolve as nonionic (uncharged)

Oxygen: $O_{2(gas)} = O_{2(aqueous)}$ Silica: $SiO_{2(solid)} + 2H_2O = H_4SiO_{4(aqueous)}$



Major Ions in Groundwater

 Major solutes (typically > 1 mg/L each; attribute to 90% of the total dissolved solids):

Ca2+, Na+, K+, Mg2+, HCO3-, SO42-, Cl-, Si (as H4SiO40)

 Common Minor solutes (typically 0.01 – 10 mg/L): Fe²⁺, Sr²⁺, NO₃⁻, F⁻, O₂

Charge balance: CBE% =
$$\frac{\sum z \times m_{cation} - \sum |z| \times m_{anion}}{\sum z \times m_{cation} + \sum |z| \times m_{anion}}$$

z: charge of an ion m_{cation} : concentration of cation in mol/L m_{anion} : concentration of anion in mol/L

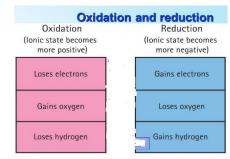
Other Typical Chemical Parameters

- Other chemical parameters:
- pH
- TDS (total dissolved solids)

- E_h (oxidation-reduction potential; indicator of oxic conditions)

- EC (specific conductance, or electrical conductivity; rough measure of total dissolved solids)

 \bullet pH, EC, $E_h,$ dissolved $O_2,$ and temperature (T) are typically determined in the field



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Reversible and Irreversible Reactions

Chemical reactions are either reversible (e.g. NaCl dissolution) or irreversible (e.g., radioactive decay)

A reversible reaction (Both reactions are occurring simultaneously):

NaCl \rightarrow Na⁺ + Cl⁻

 $Na^+ + Cl^- \rightarrow NaCl$

Law of Mass Action

Consider a generic reaction

 $cC + dD \leftarrow \Rightarrow xX + yY$

Equilibrium constant *K*:

 $K = \frac{[\mathbf{X}]^{x}[\mathbf{Y}]^{y}}{[\mathbf{C}]^{c}[\mathbf{D}]^{d}}$

• Concentration of a pure liquid or solid is defined as **1** [] represents concentration

Concentration vs. Activity

 $a = \gamma m$

a: chemical activity; γ : activity coefficient (close to 1 in dilute solutions and decreases as salinity increases); *m*: concentration

Ion Activity Product:

$$IAP = \frac{[X]^{x}[Y]^{y}}{[C]^{c}[D]^{d}}$$

[] represents chemical activity

*(In groundwater chemistry, we commonly assume concentration = activity)

Saturation Index

$$SI = \log \frac{IAP}{K_{sp}}$$

IAP: Ion Activity Product from measured data

 K_{sp} : equilibrium constant of a soluble mineral.

For dissolution of a solid:

SI < 0: the solution is undersaturated with respect to the solid.

The solution will dissolve the solid if the solid presents.

SI = 0: the solution is in equilibrium with the solid.

SI > 0: the solution is supersaturated with respect to the solid.

The solid may precipitate if the right conditions are met.

Acid-base reactions

- Involve H⁺ transfer in aqueous phase or between solution and solid
- Recall $pH = -log(H^+)$
- pH is acidic if < 7, neutral if = 7, and basic if > 7
- pH of ground water is typically 4 to 8.5
- pH is commonly (but not exclusively) regulated by carbonate equilibria

Dissociation of water: $H_2O = H^+ + OH$

Carbonate Equilibrium

One of the most important geochemical reactions: calcium carbonate, water and CO₂.

- 1. Dissolution of CO_2 to form carbonic acid $CO_2 + H_2O = H_2CO_3$
- 2. Dissolution of carbonic acid to form bicarbonate

 $H_2CO_3 = H^+ + HCO_3^-$

3. Dissolution of bicarbonate to form carbonate

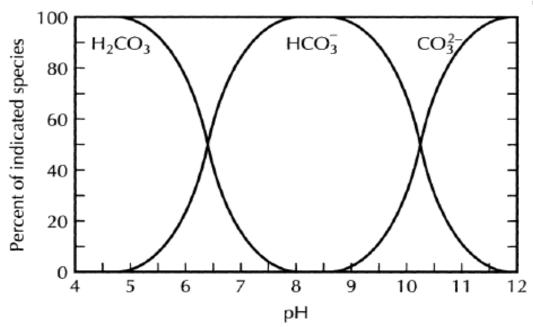
 $HCO_3^- = H^+ + CO_3^{2-}$

4. Dissolution of calcium carbonate

 $CaCO_3 = Ca^+ + CO_3^{2-}$

Carbonate Equilibrium

Distribution of carbon species vs. pH at 20 °C



Ion exchange

• Cation exchange involves desorption of one type of cation accompanied by adsorption of another.

- Example: Ca^{2+} + Na-clay = $2Na^+$ + Ca-clay

- Clays tend to have greater affinity for divalent cations.
- Cation exchangeability: $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$

Cation Exchange Capacity (CEC)

CEC: the quantity of cations bounded to the mineral surface, which are available for exchange with ions in solution.

- Soils with a higher clay fraction tend to have a higher CEC.
- Organic matter has a very high CEC.

• Sandy soils rely heavily on the high CEC of organic matter for the retention of nutrients in the topsoil.

• In groundwater remediation, CEC is used an indicator for a soil to attenuate pollutants with exchangeable ions.

<u>References:</u>

Fetter, C.W., 2018. Applied hydrogeology. Waveland Press.