# WATER QUALITY ASSESSMENT AND MANAGEMENT

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## INTRODUCTION

Hydrosphere is the term used to define all water bearing units of the earth. It is difficult to understand the occurrence and movement of water within subsurface. The physical and chemical characters of water vary within all the components of hydrologic cycle. Rainwater gets contaminated due to atmospheric pollution. Depending on soil characteristics, the infiltrated rain water gets contaminated. Aquifer is the term used to the litho units or set of litho units that store water within the available openings and yield water whenever recovered through wells. Openings are due to structural disturbance in case of consolidated formations. They are due to the space between grains in case of unconsolidated and semi consolidated rocks. The alteration of rocks gives an opportunity to minerals to interact with the water that is available within subsurface. More the contact time between water and minerals more the leaching. This process of leaching of minerals into water changes the chemical characters of groundwater. The mineralogical characters of rocks their intensity of weathering control the characters of the water. In the present articles the characters of groundwater in rocks viz; granitic rocks, basaltic rocks, schistose rocks, sandstones, limestones, quartzites and laterites are discussed. In addition to this the groundwater characters with respect to aquifers close to sea coast, hydraulic gradient, conjunctive use of surface water and groundwater, dilution of groundwater within the aquifer and agricultural practice and groundwater quality are also discussed.

Water occurs in three forms viz, vapors, liquid and solid. Hydrologic cycle is the term used to explain all forms of water hydrosphere is the term used to define all water baring or possessing units of the earth. The different components of hydrologic cycle are evaporation, precipitation, surface runoff and infiltration.

It is simple to mitigate the surface water, but it is difficult to understand the occurrence and movement of water within subsurface because it is not visible to necked eyes. Even it is difficult to know its perfect occurrence and movement and quality characters of subsurface water are discussed.

## GENERAL CHARACTERS OF WATER

Water is made up to two important elements viz, hydrogen and oxygen. These two together constitute 99.99% of water. Thus, chemically water mean "$H_2O$. The 0.01% constituents control the water quality. The constituents that are present in water other than 'H' and 'O' are Ca, Mg, Na, $HCO_3$, Cl and $SO_4$ as major ones. The secondary ones are Fc, K, $CO_3$ $NO_3$, I while Al, As, Ba, BR, Co, Cr, I, GE, Zn, Pb, Mn, Ni are minor ones and Be, Bi, Ce, Ga, An, Ag, Sn, Y, Zr are tracers. The physical characters like color, odor, turbidity are also important in defining the water quality.

## WATER QUALITY AND HYDROLOGIC CYCLE

The water from surface water bodies gets vaporized to atmosphere due to solar radiations leaving behind the salts. The vaporized part of water contains 'H' and 'O'. This is converted into clouds and later returns to earth in the form of rains or snowfall. This is "precipitation". This process is similar to that of distillation. Thus, precipitated water should be pure form of water. Due to atmospheric pollution these days, the rain water gets contaminated with many constituents before it reaches the earth surface. Once the precipitated water reaches the earth's surface it starts flowing. In this process of the movement from one place to other the flowing water dissolves soluble components and carries insoluble components in suspended form. This converts the water into contaminated one. Depending on soils physical and chemical characters, the infiltrated rain water gets contaminated or changes its chemical and physical characters.

## OCCURRENCCE AND CHARACTERS OF GROUNDWATER IN HARD ROCK AREAS

The infiltrated rainwater gets into subsurface and it is stored in the openings available in the rock formations. "Aquifer" is the term used to the litho units or set of litho units that store water within the available openings and infield water whenever recovered through wells.

The continuous precipitation or rains helps in more infiltration. The infiltration depends on soil characters (both physical and chemical) and number and concentration of openings in the rock units. The sandy soil helps faster infiltration than clayey soil. Depending upon the soluble constituents in soil the infiltered water changes its quality. More number of openings help to store large quantity of water in rock formations. The quantity of water that could be stored subsurface within the rocks or a set of rock formations depend on openings available. The intensity and density of openings play an important role. The openings in rocks mean the space between the particles in case of unconsolidated and semi consolidated rocks. In case of consolidated (Hard) rocks the openings mean the factures, joints, shear zones and fault planes. All these together can

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be called as "openings" in hard rocks or consolidated rocks. Such openings are normally created by earth movement's structural disturbances and organic activities. Such openings in hard rocks are called as "secondary openings" because they have developed after the formation of rocks.

The groundwater in hard rock terrains normally occurs under water table or unconfined conditions. In case of same sedimentary or volcanic rocks like basalts the groundwater occur under unconfined and confined conditions. In case of many consolidated rock the openings are available from surface to deep into the crust. These serve as conduits to transmit and store water. This movement either vertical or horizontal is possible till the openings discontinue. In case of flow basalts the intratrappean formation can store water. The openings by wait of fracturing and joints in intertrappeans is under "confined" or "semi confined" conditions, when on either side a compact basalt occur. Similarly the groundwater in highly fractured limestones or quartzites or sandstones which are founded by impervious shale or day formations on either side acts as "confined" or "Semi confined" aquifer conditions.

## MINERALS IN ROCK FORMATIONS AND THEIR IMPACT ON WATER QUALITY

The quality of subsurface water or groundwater generally depends on the characters of minerals available in the rock formations. The disintegration is the physical breakdown of rocks and minerals. These do not get dissolved into surrounding groundwater immediately or easily. The total time of contact of disintegrated minerals and water cause chemical alteration of minerals. Such chemically altered minerals easily dissolve into the groundwater causing chemical change in the groundwater causing chemical change in the quality. This process of altering of minerals in rocks and their dissolution into water is a continuous process till the water is in circulation within the subsurface. At this point of time it is very important to know the characters of the minerals and their chemical composition. Owing under normal geological conditions the flow direction of groundwater is parallel to the topography of the region. The direction of movement of subsurface is known as "hydraulic gradient". The movement of subsurface water is very slow when compared to the movement of surface water or streams. The groundwater flow rate is a few centimeters per day. In gravelly formations it is 15cms.day. The river flow is 20 to 50 cm/s. Therefore, the availability of groundwater for recovery from subsurface to the characters of minerals the chemical characters of the groundwater are controlled.

The table below lists the minerals and constituents that could be leached into water from weathered rocks.

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| Constituents | Minerels |
|---|---|
| Calcium: (Ca) | Plagioclase, pyroxenes, amphibolites, calcite, aragonite, dolomite, anhydrite, gypsum, apatite, wollastonite, fluorite, etc. |
| Magnesium: (Mg) | Olivine, biotite, hornblende, augite, calcite, dolomite, serpentine, tale, diopside, tremolite. etc. |
| Sodium: (Na) | Plagioclase, clay minerals, nepheline, sodalite, stilbite, glucophane etc |
| Potassium: (K) | Orthoclase, microcline, biolytic, Lucite etc. |
| Chloride: (Cl) | Sodalite, micas, horhblende, chlorite, apatite. |
| Sulphate: (SO₄) | Pyrite, gypsum, barite. |
| Bicarbonate: and Carbonate | atmospheric carbondioxide, some evaporates, seawater intrusion |

## CASE STUDIES

In the foregoing pages, the groundwater quality variation in different rocks is discussed.

All acidic igneous plutonic rocks are considered as `Granite rocks'. The groundwater available in unaltered granite rocks is normally of good quality. The total dissolved solids in the water is less than 500 mg/l. When these rocks are altered and minerals like plagioclase, orthoclase micas etc. decompose, the decomposed minerals easily dissolve in water depending upon the contact time between water and minerals. The total dissolved solids in such groundwater ranges from 3000 to 8000 mg/l. The groundwater occurs under unconfined conditions.

The table below shows the chemical analyses of less weathered granite rocks and highly weathered granites rock.

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| Type of Rocks | Ca | Mg | Na | K | Hco₃ | Co₃ | Cl | So₄ | TDS | TH | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Unaltered Granite | 30 | 08 | 200 | 01 | 348 | - | 42 | 11 | 419 | 144 | 7.4 |
| Weather Granite | 202 | 16 | 590 | 05 | 234 | 24 | 130 | 411 | 4288 | 144 | 7.9 |

## 2. Basaltic Rocks

The ground water in fractured basalts are more softer than the amygdaloidal basalts because the amygdaloidal basalts contain minerals like zeolites and calcites. These minerals are more susceptible for easy dissolution in groundwater. The groundwater occurs under unconfined, semi-confined and confined conditions.

The table below shows the chemical analyses of basalt and vermicular basalt.

| | Ca | Mg | Na | K | Hco₃ | Co₃ | Cl | So₄ | TDS | TH | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Basalt | 55 | 04 | 204 | 02 | 192 | - | 100 | 16 | 240 | 156 | 7.38 |
| Vesicular Basalt | 96 | 14 | 50 | 02 | 273 | - | 90 | 227 | 3900 | 224 | 7.20 |

## 3. Schistose Rocks

There are varieties of schistose rocks from simple chlorite schist's (low metamorphic rock) to granulites (high grade metamorphic rock). Their chemical composition and mineralogy vary widely. Depending on this and contact time with water the chemical character of groundwater vary. The groundwater occurs under unconfined conditions.

## 4. Sandstone, Quartzites and Limestone's

There are variations in chemical characters of groundwater in all these rocks. The groundwater is mostly softer within quartzites and sandstones when compared to those within limestones. Quartz is the major component in quartiles and sandstones, which do not easily alter but only disintegrate and its dissolution in water is little. The calcite and dolomite in limestone readily dissolves in water causing water quality variation particularly with respect to hardness and TDS.

The table below shows the chemical analyses of schistose rock that gets dissolved in water very early and alters the quality of water. The groundwater occurs under unconfined and semi unconfined conditions.

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| | Ca | Mg | Na | K | HCO₃ | Co₃ | Cl | SO₄ | TDS | TH | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Schist | 255 | 154 | 25 | 15 | 172 | - | 72 | 16 | 400 | 215 | 7.2 |

The table below shows the chemical analyses of sandstone and limestone.

| | Ca | Mg | Na | K | HCO₃ | CO₃ | Cl | SO₄ | TDS | TH | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sandstone | 82 | 38 | 07 | - | 250 | 26 | 43 | 62 | 128 | 320 | 7.6 |
| Limestone | 178 | 125 | 110 | - | 288 | 82 | 606 | 62 | 2680 | 392 | 8.1 |

## 5. Laterites

The laterites are secondary rocks formed by the alteration of original rock through the process of residual concentration in semiarid climatic conditions. The laterites are iron rich with less quantity of aluminous material. The soluble constituents are transported during their formation. Thus, there will be no soluble constituents available in laterites that can get into water. Therefore, the quality of water in lateritic terrain are normally good. The groundwater occurs in unconfined conditions.

The Table below shows the chemical analyses of laterite.

| | Ca | Mg | Na | K | Hco₃ | Co₃ | Cl | So₄ | TDS | TH | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Laterite | 30 | 03 | 03 | - | 120 | - | 21 | 04 | 237 | 90 | 7.6 |

## Coastal Aquifers

In case of aquifers close to coast usually groundwater occurs under unconfined conditions. Due to excess withdrawal of fresh water, the subsurface movement of seawater into the coastal aquifers causes salinization of these aquifers. `Sea water intrusion' is the term used. These, the coastal aquifer are contaminated by sea water intrusion. The table below shows change in the values of total dissolved solids in coastal aquifers. The groundwater lose to sea coast have higher total dissolved solids value when compared to those inland.

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| 1 | 2 | 3 |
| --- | --- | --- |
| One kms. Away From coast | Two kms. Away from coast | Three kms. Away from coast |
| 1. 1450 (2266) | 1230 (1922) | 580 (781) |
| 2. 599 (937) | 558 (872) | 444 (694) |
| 3. 1787 (1143) | 281 (180) | 225 (144) |

EC values mmhos/cm;values in brackets are TDS in mg/l

## 7. Hydraulic gradient and groundwater quality

The subsurface movement of water is urn ally from the area of recharge to the area of discharge. In the area of recharge infiltration is more and in the area of discharge either artificial with drawl is more or natural discharge is possible. During the movement of groundwater from the place of recharge to the place of discharge the quality of water changes depending upon lithologic characters (natural) and also due to anthropogenic activities. The table below shows the change in hydrogeochamical faces of water from the area of recharge to the area of discharge in basin.

| Faces in the area of recharge above 700 mts. msl. | Faces in the between 700 – 600mts. msl. | Faces in the area of discharge below 600 mts. msl. |
| --- | --- | --- |
| Ca + Mg – Na + K | Ca + Mg – Na + K | Na + K – Ca + Mg |
| Na + K  - Ca  + Mg | Na + K  - Ca + Mg | Na + K |
| $HCO_3$ - Cl + $SO_4$ | $Hco_3$ - Cl + $SO_4$ | Cl + $SO_4$ - $HCO_3$ |
| Cl + $SO_4$ - $HCO_3$ | Cl + $SO_4$ - $HCO_3$ | Cl + $SO_4$ |

## 8. Conjunctive use of surface water and groundwater

Highly saline groundwaters are reported from some areas. In such cases it is advised to use both fresh surface water and subsurface water together. Such use of both surface as well as subsurface water is called as `Conjunctive use of water'. This

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method helps in minimal use of surface water and use of salute water. If this is not followed the water table in such areas will raise and the area will be converted into a water logged area or marshy land. The table below shows the change in the content of total dissolved solids when it is mixed with fresh water in different propositions.

| Original EC value | 4 time dilution | 6 time dilution | 8 time dilution |
|---|---|---|---|
| 9768 (15262) | 5348 (8336) | 3165 (4945) | 1746 (2728) |
| 5566 (8697) | 1746 (2728) | 1201 (1876) | 982 (1534) |
| 5130 (8015) | 1528 (2387) | 1091 (1704) | 873 (1364) |
| 4911 (7673) | 1473 (2301) | 1037 (1620) | --- |
| 3874 (6053) | 1146 (1790) | 819 (1280) | --- |

*Values in Brackets are TDS.*

## 9. In-situ dilution of groundwater

The saline groundwater can be diluted by artificially recharge. The artificial recharge methods include construction of barriers to streams, percolation pits etc. These structures help in infiltration of fresh surface water into ground. Such infiltrated fresh water dilutes the saline groundwater. This is called "Fluoride" content of groundwater before monsoon and after monsoon. The 'F' content is comparatively lesser in the groundwater samples of post monsoon.

| 'F' content Pre monsoon | 'F' Content Post monsoon |
|---|---|
| 3.34 | 2.73 |
| 2.16 | 1.16 |
| 3.30 | 1.57 |
| 2.30 | 1.64 |
| 4.25 | 3.78 |
| 4.05 | 2.93 |
| 5.80 | 3.42 |
| 1.64 | 0.52 |
| 5.26 | 3.02 |
| 3.42 | 1.75 |

## 10. Agricultural practice and Groundwater quality

In order to get good yield of crops farmers use excess quantity of chemical fertilizers. In addition to this large quantity of water is fed to crops. The crops absorb the required quantity of the fertilizers and the excess ones are left in soil. Along with these unabsorbed chemicals the water fed to agricultural land in filters and contaminates groundwater. This contaminated groundwater is again used for the crops in the same area or field. This circulation of water is called `irrigation return flow of water'. Such reuse of used water is harmful to crops and human. To avoid such contamination of groundwater, required quantity of water and measured quantity of fertilizers should be practiced.

## Environmental Geochemistry

**Definitions** (from Faure, 1991, *Environmental Geochemistry*)

*Geochemistry* is the science of learning to understand why some stones are "good" and how they form. (In this context, "good" is relative to resource extraction, so it primarily concerns ores.). *Environmental geochemistry* grows out of the need to understand why some stones went "bad".

*Why we care about bad stones:*

Bad rocks affect water consumption and water quality: drinking water, human health, animals, soils, etc.

They do economic damage, including resource damage.

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## Minerals

Mineral is the basic contributor of natural colour, taste and odour. This depend basically on the mineralogical composition of the rocks. Metals and metalloids present in the native ores and minerals move through the hydrosphere. In between time spent in solution, these elements tend to occur in authigenic or allogenic form such as oxide, hydroxide, sulfate, carbonate, and phosphate minerals. (Authigenic = formed in place; allogenic = formed elsewhere.)

## Acid-Base Reactions

In aqueous systems, the Brönsted-Lowry definition of an acid as a hydrogen-ion donor is usually sufficient. A base then is a hydrogen-ion acceptor — $OH^-$, $NH_3$, etc. In aqueous systems, a base ends up liberating a hydroxide ion, either directly or indirectly. The Lewis definition is more general: an acid is an electron-pair acceptor, and a base is an electron-pair donor.

## A. Dissolution-Precipitation

Examples: $NaCl\ (s) \longrightarrow Na^+\ (aq) + Cl^-\ (aq)$

$CaCO_3\ (s) \longrightarrow Ca^{2+}\ (aq) + CO_3^{2-}\ (aq)$

The equilibria governing these reactions are described by solubility products, $K_{sp}$.

Examples: $HCl \longrightarrow H^+ + Cl^-$

$CO_3^{2-} + H_2O \longrightarrow HCO_3^- + OH^-$

$HCO_3^- + H_2O \longrightarrow H_2CO_3 + OH^-$

"Carbonic acid" or "$H_2CO_3$", is a shorthand term for hydrated carbon dioxide. The $H_2CO_3$ molecule does exist under certain circumstances (in the gas phase), but the structure of the actual carbonic acid (hydrated $CO_2$) is more complicated, probably involving multiple water molecules.
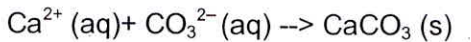
## B. Combinations of (A) and (B)

Example: $Ca^{2+} + HCO_3^- \longrightarrow CaCO_3 + H^+$

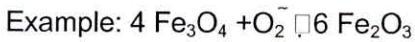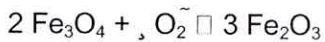This is a combination of a dissolution-precipitation and an acid-base one.

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$HCO_3^-$ (aq)--> $H^+$ (aq) + $CO_3^{2-}$ (aq)

and

$Ca^{2+}$ (aq)+ $CO_3^{2-}$ (aq) --> $CaCO_3$ (s)
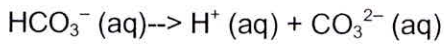
## C. Oxidation-Reduction (Redox) Reactions

Example: $4\ Fe_3O_4 + O_2 \rightarrow 6\ Fe_2O_3$
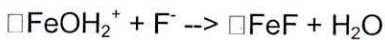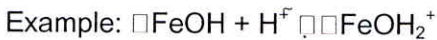
or

$2\ Fe_3O_4 +\ O_2 \rightarrow 3\ Fe_2O_3$

## D. Surface Reactions

These are reactions, usually involving solutes, that take place on a surface and involve surface sites of a mineral crystal.(The symbol≡represents three horizontal lines, the typical representation of attachment to a surface binding site.)

Example: ≡$FeOH + H^+ \rightarrow$ ≡$FeOH_2^+$

≡$FeOH_2^+ + F^- \rightarrow$ ≡$FeF + H_2O$

Here at a hydroxide group on the surface of an iron oxyhydroxide is protonated, after which a fluoride ion displaces the water.

Acid-base reactions are important in ground water because of their influence on pH and the ion chemistry. pH is a master variable controlling chemical systems.  It is defined as the negative logarithm of the hydrogen ion activity and describes whether a solution is acidic, neutral or basic Hydrogen ion activity is represented here as so that In solution, hydrogen ion exists as a proton associated with a molecule of water Thus, we can express hydrogen ion activity as writing the hydrogen activity as differentiates between a proton (a hydrogen atom that has lost an electron, and a hydrogen ion in solution.

## Alkalinity

The pH determines the distribution of carbonate species.  In actual ground water systems, the situation is more complex.  The pH and carbonate speciation are interdependent, a function of not only the ionization equilibria for the carbonate species

and water but also strong bases added through the dissolution of carbonate and silicate minerals.

Water is an excellent solvent, it dissolves gases, liquids, and solids in the subsurface. Dissolution, more than any other process is responsible for the large solute loading to ground water. Other processes like gas ex-solution, volatilization, and mineral precipitation remove mass from water.

## Gas Solution and Ex-solution

Gas solution and ex-solution can transfer significant quantities of mass between soil gases and ground water. Commonly, we model these processes using equilibrium concepts based on Henry's law. This mass law equation relates the concentration of dissolved gas in solution to the partial pressure of the same gas in an atmosphere in contact with the solution. Henry's law strictly speaking does not apply to gases such as that react in solution. However, in the case of so little of the reacts that Henry's law approximates the distribution of gas between the two phases.

## Volatilization

Volatilization is a process of liquid or solid phase evaporation that occurs when contaminants present either as non-aqueous phase liquids or dissolved water in contact of a gas phase. This situation commonly arises with organic contaminants in the saturated and unsaturated zones during the sampling and analysis of volatile compounds. The process itself is controlled by the vapor pressure of the organic solute or solvent. The vapor pressure of a liquid or solid is the pressure of the gas in equilibrium with respect to the liquid or solid at a given temperature. Vapor pressure represents a compound' tendency to evaporate and is essentially the solubility of an organic solvent in a gas. At equilibrium, Raoult's law describes the equilibrium partial pressure of a volatile organic in the atmosphere above an ideal solvent (like benzene)

## Dissolution and Precipitation of Solids

Of all the processes that influence solute transport, the dissolution and precipitation of solids are two of the most important in terms of their control on ground water chemistry. Extremely large quantities of mass can be transferred under some conditions between the ground water and solid mineral phases. For example, recharge derives almost its entire solute load through the dissolution of minerals along flow paths. Mineral precipitation removes much of the metal present in a low-pH contaminant plume as dispersion and other processes increase the pH of the ground water. These examples show how ground water proceeds toward chemical equilibrium with respect to various

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minerals under saturation in the case of evolving natural ground water and from super saturation in the case of metal transport.

## Solid Solubility

The solubility of a solid reflects the extent to which the reactant (solid) or products (ions and/or secondary minerals) are favored in a dissolution precipitation reaction. In many reactions where the activity of the reacting solid is equal to one, a comparison of the relative size of the equilibrium constant provides an indication of the solid solubility in pure water. Minerals in the carbonate and the silicate and aluminum silicate groups have a small but significant solubility.

## Complexation Reactions

A complex is an ion that forms by combining simpler cations, anions, and sometimes molecules. As interest developed in modeling the chemistry of aqueous systems, hydrogeologists became aware of the importance of complexation reactions in determining the saturation state of ground water. However, because complexation reactions are most significant in reasonably saline ground water, the hydrogeological literature does not treat this topic extensively. With the explosion of knowledge in contamination reaction has changed for example, complexation facilitates the transport of potentially toxic metals such as cadmium, chromium, copper, lead, uranium, or plutonium. Such reactions also influence some types of surface reactions.

## C. Oxygenation State

This is a description of the amount of oxygen and other oxidizing agents (electron acceptors) present.

When you poke around in wet ground or in stream sediments, you generally find one of two situations: either you find black or grey, stinky mud, or you find non-stinky mud that is brown, reddish, or orange. In the former case there may be a lot of hydrogen sulfide; in the latter, there is probably some dissolved oxygen in the pore spaces.

The 3 types of geochemical environments you may find are called

1. *Oxic*, which means there is abundant oxygen in solution. This produces red, orange, or brown, clean-smelling mud. The color is from the presence of Fe(III) oxides or oxyhydroxides.
2. *Suboxic*, meaning there is a little free dissolved oxygen, usually less than 5% of saturation.

3. *Anoxic,* meaning there is no measurable oxygen. Anoxic environments are often characterized by black or grey, stinking mud.

In an anoxic situation the redox state is usually reduced (low $E_h$). This is not always true, though; in the absence of organic matter or some other reducing agent the redox state may be "perched" at high $E_h$ even though there is no free oxygen.

## D. Conductivity

This is the ability of a medium to conduct electricity. It correlates well with the total dissolved solids concentration. It sometimes correlates well with the dissolved concentration of a given element in a system. (Example: Kesterson Reservoir in California is the site of serious selenium contamination. When there was water in the lake, conductivity correlated well with dissolved Se.) In any case, it is a quick and easy, rough measurement to estimate TDS.

## Chemical Phases and Species

*Definition:* A chemical *species* is a form taken by an element in or out of solution.

There are two main phases that can hold contaminants: *particulate* and *solute.* Within these phases can be found various species.

How does one define the boundaries between "particulate" and "solute"?

Consider the range of particle sizes in water.

Cobbles ~$10^5$ □ m, Sand ~$10^3$ □ m, Clays, bacteria ~ 1 □ m, Virus molecules ~ $10^{-1}$ to $10^{-2}$ □ m, "Colloids" ~$10^{-1}$ to $10^{-3}$ □ m

Ions in solution ~ $10^{-3}$ □ m and less

The definition generally used is strictly operational: *If it is <0.45 □ m, it is a solute.*

## Geochemical Classification

The geochemical environment is based on pH and $E_h$ (or pe). It is characterized by the $E_h$-pH diagram, which is based on activities of $H^+$ and $e^-$. Thus it is constructed from thermodynamic data. It predicts partitioning of phases and mineralogical separation.

See the example diagram below. Note that the transition from species 1 to species 2 is strictly pH-controlled, while the transition from species 3 to species 4 is strictly $E_h$-controlled. Both pH and Eh influence the transition between species 2 and 4.
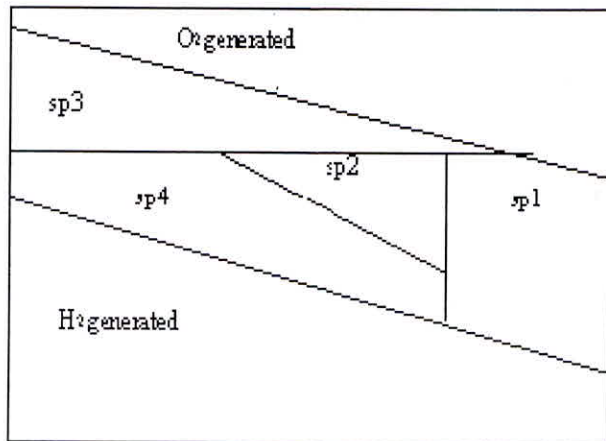


The $O_2$ and $H_2$ lines define the redox region in which water is stable.

The boundaries are equilibrium conditions. A given diagram is valid

- at equilibrium, and
- at the specific conditions of T, P, and concentration.

## Berner's Classification of Geochemical Environments

Berner starts by noting that there are two things we can measure easily down to about 1 ☐☐☐ dissolved oxygen and hydrogen sulfide. These two species are very useful because:
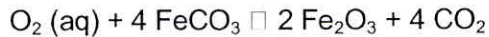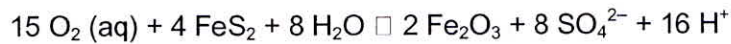
- They are very strongly tied to redox reactions.
- Their concentrations have very major effects on organisms.
- They exert a major amount of control on the formation of authigenic minerals.
- They cannot coexist.
- Bacteria divide neatly into *aerobes* (killed by $H_2S$) and *anaerobes* (killed by oxygen). (Note: under this classification, *facultative anaerobes* are considered to be aerobes.)

Berner's scheme:

- If dissolved oxygen is > 0.5% of saturation (~1 $\mu$M), the environment is *oxic*.
- If dissolved oxygen is < 0.5% of saturation, it is *anoxic*.

For an anoxic environment, if sulfide species are > 1 $\mu$M, it is *sulfidic*. If sulfide species are < 1 $\mu$M, it is *postoxic* or *methanic*.
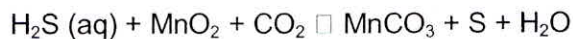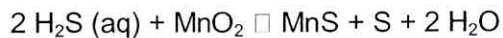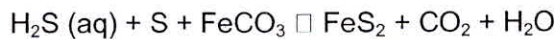
**For an oxic environment,**

$15\ O_2\ (aq) + 4\ FeS_2 + 8\ H_2O \rightarrow 2\ Fe_2O_3 + 8\ SO_4^{2-} + 16\ H^+$

$O_2\ (aq) + 4\ FeCO_3 \rightarrow 2\ Fe_2O_3 + 4\ CO_2$

$O_2\ (aq) + MnS \rightarrow MnO_2 + S$

**In other words, oxygen + sulfides $\rightarrow$ $CO_2$, $SO_4^{2-}$, and metal oxides.**

**For an anoxic-sulfidic environment,**

$3\ H_2S\ (aq) + S + Fe_2O_3 \rightarrow 2\ FeS_2 + 3\ H_2O$

(Note the complexity of this redox reaction! S starts out in 2 different redox states.)

$H_2S\ (aq) + S + FeCO_3 \rightarrow FeS_2 + CO_2 + H_2O$

$2\ H_2S\ (aq) + MnO_2 \rightarrow MnS + S + 2\ H_2O$

$H_2S\ (aq) + MnO_2 + CO_2 \rightarrow MnCO_3 + S + H_2O$

**$H_2S$ + oxides $\rightarrow$ sulfides $\rightarrow$ carbonates**

Consider a water-sediment interface (see diagram on board), say at pH 7. If there is not much sulfur present, then $Fe^{2+}$ predominates at low $E_h$ (which is to say, a little way down into the sediments). If there are free $Fe^{2+}$ and $Mn^{2+}$ in the pore water, then the system is anoxic.
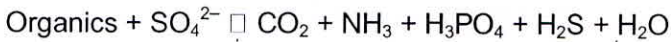
What drives their reactions?

"Organic matter" is approximately $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)_1$.

In oxic environments,

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Organics + $O_2$ $\square$ $H_2O$ + $CO_2$ + $HNO_3$ + $H_3PO_4$.
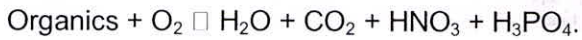
(This is aerobic respiration as microbes do it.)

In sulfidic environments, we see sulfate as the oxidizing agent:

Organics + $SO_4^{2-}$ $\square$ $CO_2$ + $NH_3$ + $H_3PO_4$ + $H_2S$ + $H_2O$

Typically,

$Fe^{2+}$ + $H_2S$ $\square$ FeS + 2 $H^+$,

followed by

FeS +S $\square$ $FeS_2$

For iron, pyrite is the stable form. For other metals, one or another sulfide will form.

The iron came from the reduction of iron (III). We showed hematite reduction above, to simplify things. Actually, iron oxyhydroxides are more commonly the candidates for reduction.

2 FeOOH + $H_2S$ $\square$ S + 2 $Fe^{2+}$ + 4 $OH^-$

For all this to happen, it is necessary to have

- enough S (usually present),
- enough bacteria (never a problem), and
- enough organic matter (food for the bacteria).

### *Anoxic Non-Sulfidic Environments*

*1. Low Organics (= Postoxic)*

When oxygen is exhausted, microbes turn to other energy sources: first Mn (IV), then nitrate, then Fe (III).

Organics (low) + $MnO_2$ + $H^+$ $\square$ $Mn^{2+}$ + $CO_2$ +$H_3PO_4$ + $N_2$ (or $NH_3$)

Organics (low) + $NO_3^-$ $\square$ $CO_2$ + $H_3PO_4$ + $N_2$ (or $NH_3$)

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Organics (low) + Fe (III) $\square$ $CO_2$ + $H_3PO_4$ + $Fe^{2+}$ + $N_2$ (etc.)

Since organics are low, the oxidizing species may never be used up, and sulfate reduction does not get started.

## 2. Low Sulfur, High Organics (Methanic)

Sulfur was low to begin with or was exhausted, and there are plenty of organics left. This is typical of some freshwater systems such as marshes. Once oxygen, Mn (IV), nitrate, Fe (III), and sulfate are gone, fermentation and carbon dioxide reduction set in. Some species also reduce water!

Organics $\square$ $CO_2$ + $CH_4$ + $NH_3$ + $H_3PO_4$ + $H_2O$ + $H_2$

Carbohydrates + $H_2O$ $\square$ formic acid + $H_2$

4 $H_2$ + $CO_2$ $CH_4$ + 2 $H_2O$

*Remarks*

The basic idea of this topic is to provide preliminary information on the hydrogeological cycle and the porosity and permeability of porous material. These concepts are important when we deal with fluid, energy and mass transport in porous media. Scientific developments in recent years, in the area of Environmental geochemistry include analytical and modeling approaches that permit us to determine the actual form of an element in the water being studied. This section will serve a diversity of interest, including those of geologists, practicing hydrogeologists and engineers, geochemists, and geophysicists interested in fluid dynamics.

## Conclusions

The above discussion reveals that the major cause for the change in the chemical characters of groundwater within different rocks depend on the mineralogical characters of rock formations where the groundwater is stored and recovered. This is to say that the chemical characters of water depends on the natural environment where the groundwater is associated. The interference of man has played a major role in altering the chemical nature of groundwater and contaminate it. The anthropogenic activities on the surface of the earth has changed the surface as well as the groundwater quality. These activities include rural and urban liquid and solid waste disposals, industrial effluents and effluents and unhealthy agricultural practices.

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Thus, it is challenging to study groundwater quality characterization in hard rocks when compared to those of semi consolidated and consolidated rock units.

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