Chemical interactions involving solids , gases , and water :

Sediments are the layers of relatively finely divided matter covering the bottoms of rivers, streams, lakes, reservoirs , estuaries, and oceans. Sediments typically consist of mixtures of fine-, medium-, and coarse-grained minerals, including clay ,silt, and sand, mixed with organic matter. They may vary in composition from pure mineral matter to predominantly organic matter. Sediments are repositories of a variety of biological, chemical, and pollutant detritus in bodies of water. Of particular concern is the transfer of chemical species from sediments into aquatic food chains via organisms that spend significant parts of their life cycles in contact with or living in sediments. Among the sediment-dwelling organisms are various kinds of shellfish (shrimp, crayfish, crab, clams) and a variety of worms, insects, amphipods, bivalves, and other smaller organisms that are of particular concern because they are located near the bottom of the food chain.

Formation of Sediments

Physical, chemical, and biological processes may all result in the deposition of sediments in the bottom regions of bodies of water. Sedimentary material may be simply carried into a body of water by erosion or through sloughing (caving in) of the shore. Thus, clay, sand, organic matter, and other materials may be washed into a lake and settle out as layers of sediment.

Sediments may be formed by simple precipitation reactions, several of which are discussed below. When a phosphate-rich wastewater enters a body of water containing a high concentration of calcium ion, the following reaction occurs to produce solid hydroxyapatite:

$$5Ca^{2+} + H_2O + 3HPO_4^{2-} \rightarrow Ca_5OH(PO_4)_3(s) + 4H^+$$

Calcium carbonate sediment may form when water rich in carbon dioxide and containing a high level of calcium as temporary hardness loses carbon dioxide to the atmosphere,

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3(s) + CO_2(g) + H_2O$$

or when the pH is raised by a photosynthetic reaction:

$$Ca^{2+} + 2HCO_3^- + h\nu \rightarrow \{CH_2O\} + CaCO_3(s) + O_2(g)$$

Oxidation of reduced forms of an element can result in its transformation to an insoluble species, such as occurs when iron(II) is oxidized to iron(III) to produce a precipitate of insoluble iron(III) hydroxide:

$$4Fe^{2+} + 10H_2O + O_2 \rightarrow 4Fe(OH)_3(s) + 8H^+$$
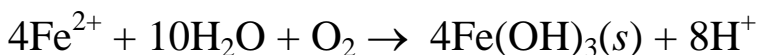
A decrease in pH can result in the production of an insoluble humic acid sediment from base-soluble organic humic substances in solution .

Biological activity is responsible for the formation of some aquatic sediments. Some bacterial species produce large quantities of iron(III) oxide as part of their energy-extracting mediation of the oxidation of iron(II) to iron(III). In anaerobic bottom regions of bodies of water, some bacteria use sulfate ion as an electron receptor,

$$SO_4^{2-} \rightarrow H_2S$$
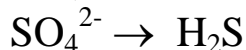
whereas other bacteria reduce iron(III) to iron(II):

$$Fe(OH)_3(s) \rightarrow Fe^{2+}$$
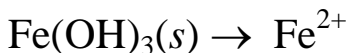
The net result is a precipitation reaction producing a black layer of iron(II) sulfide sediment:

$$Fe^{2+} + H_2S \rightarrow FeS(s) + 2H^+$$
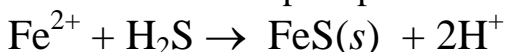
This frequently occurs during the winter, alternating with the production of calcium carbonate by-product from photosynthesis reaction during the summer.

Under such conditions, a layered bottom sediment is produced composed of alternate layers of black FeS and white $CaCO_3$ as shown in Figure 1
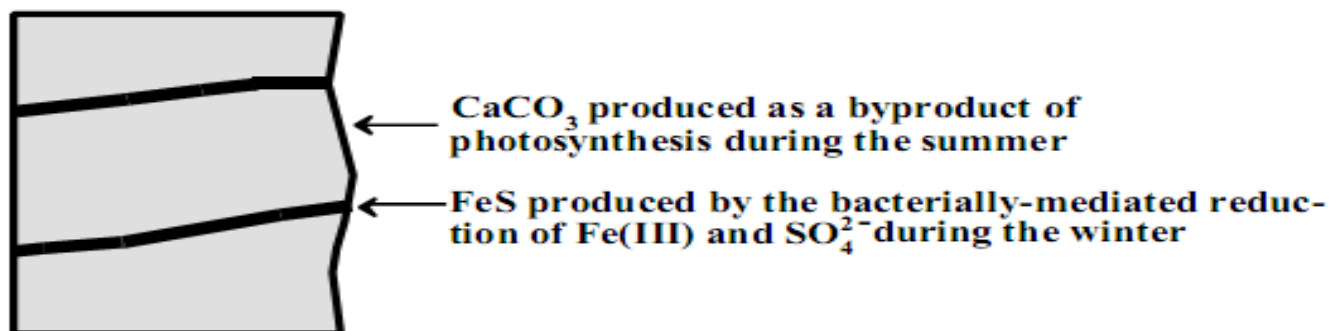

Figure (1) :Alternate layers of FeS and $CaCO_3$ in a lake sediment. This phenomenon has been observed in Lake Zürich in Switzerland.

The preceding are only a few examples of reactions that result in the formation of bottom sediments in bodies of water. Eventually these sediments may become covered and form sedimentary minerals.

Solubility of Solids

Generally, the solubility of a solid in water is of concern when the solid is slightly soluble, often having such a low solubility that it is called "insoluble."

The solubility of lead carbonate was considered . This salt can introduce toxic lead ion into water by reactions such as:

$$PbCO_3(s) \longleftrightarrow Pb^{2+} + CO_3^{2-}$$
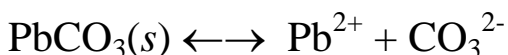
The solubility of an ionic solid can be performed on barium sulfate, which dissolves according to the reaction.

$$BaSO_4(s) \longleftrightarrow Ba^{2+} + SO_4^{2-}$$
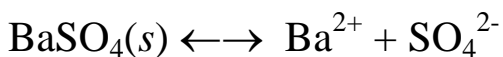
Colloidal particles in water

Many minerals, some organic pollutants, proteinaceous materials, some algae, and some bacteria are suspended in water as very small particles. Such particles, which have some characteristics of both species in solution and larger particles in suspension, which range in diameter from about 0.001 micrometer (μm) to about 1μm, and which scatter white light, are classified as **colloidal particles**. The characteristic light-scattering phenomenon of colloids results from their being the same order of size as the wavelength of light and is called the **Tyndall effect**.

Occurrence of Colloids in Water

Colloids composed of a variety of organic substances (including humic substances), inorganic materials (especially clays), and pollutants occur in natural water and wastewater. These substances have a number of effects, including effects on organisms and pollutant transport. The characterization of colloidal materials in water is obviously very important, and a variety of means are used to isolate and characterize these materials. The two most widely used methods are filtration and centrifugation.

Kinds of Colloidal Particles

Colloids may be classified as *hydrophilic colloids*, *hydrophobic colloids*, or *association colloids*. These three classes are briefly summarized below.

Hydrophilic colloids generally consist of macromolecules, such as proteins and synthetic polymers , that are characterized by strong interaction with water resulting in spontaneous formation of colloids when they are placed in water. In a sense, hydrophilic colloids are solutions of very large molecules or ions. Suspensions of hydrophilic colloids are less affected by the addition of salts to water than are suspensions of hydrophobic colloids.

Hydrophobic colloids interact to a lesser extent with water and are stable because of their positive or negative electrical charges as shown in Figure 2 The charged surface of the colloidal particle and the **counter-ions** that surround it compose an **electrical double layer**, which causes the particles to repel each other.
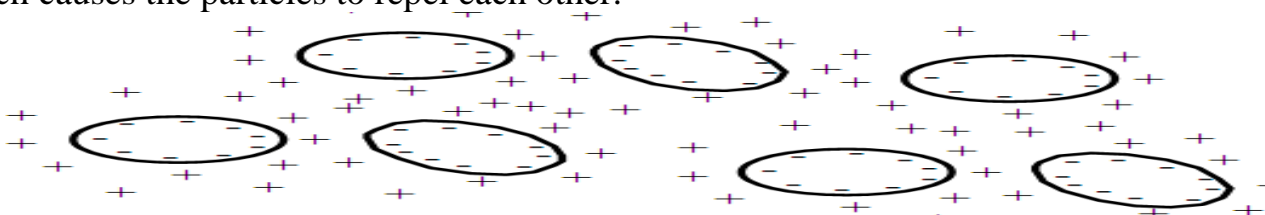

Figure (2):. Representation of negatively charged hydrophobic colloidal particles surrounded in solution by positively charged counter-ions, forming an electrical double layer. (Colloidal particles suspended in water may have either a negative or positive charge.)

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Hydrophobic colloids are usually caused to settle from suspension by the addition of salts. Examples of hydrophobic colloids are clay particles , petroleum droplets, and very small gold particles.

Association colloids consist of special aggregates of ions and molecules called **micelles**. To understand how this occurs, consider sodium stearate, a typical soap with the structural formula shown below:
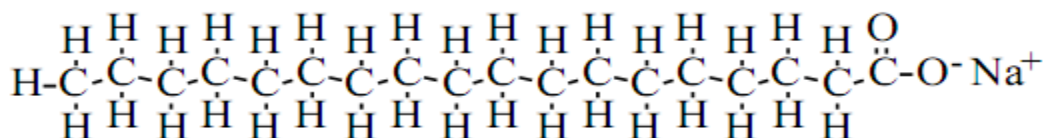
The stearate ion has both a hydrophilic $-CO_2^-$ head and a long organophilic tail,$CH_3(CH_2)_{16}-$. As a result, stearate anions in water tend to form clusters consisting of as many as 100 anions clustered together with their hydrocarbon "tails" on the inside of a spherical colloidal particle and their ionic "heads" on the surface in contact with water and with Na^+ counter ions. This results in the formation of micelles as illustrated in Figure 3. **Micelles can be visualized as droplets of oil about 3-4 nanometers (nm) in diameter and covered with ions or polar groups**.
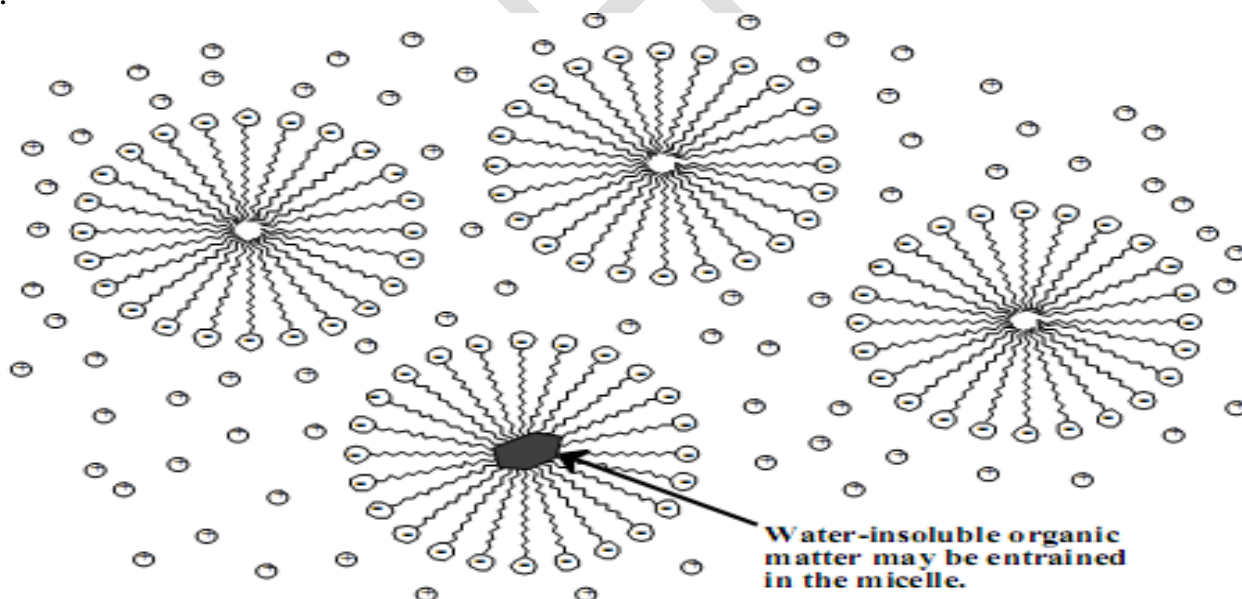
Figure(3): Representation of colloidal soap micelle particles.

Colloid Stability

The stability of colloids is a prime consideration in determining their behavior. It is involved in important aquatic chemical phenomena including the formation of sediments, dispersion and agglomeration of bacterial cells, and dispersion and removal of pollutants (such as crude oil from an oil spill).

The two main phenomena contributing to the stabilization of colloids are **hydration** and **surface charge**. The layer of water on the surface of hydrated colloidal particles prevents contact, which would result in the formation of larger units. A surface charge on colloidal particles may prevent aggregation, since like-charged particles repel each other. The surface charge is frequently pH dependent; around pH 7 most colloidal particles in natural waters are negatively charged . Negatively charged aquatic colloids include algal cells, bacterial cells, proteins , and colloidal petroleum droplets.

One of the three major ways in which a particle may acquire a surface charge is by **chemical reaction at the particle surface**. This phenomenon, which frequently involves hydrogen ion and is pH-dependent, is typical of hydroxides and oxides and is illustrated for manganese dioxide, MnO_2, in Figure 4
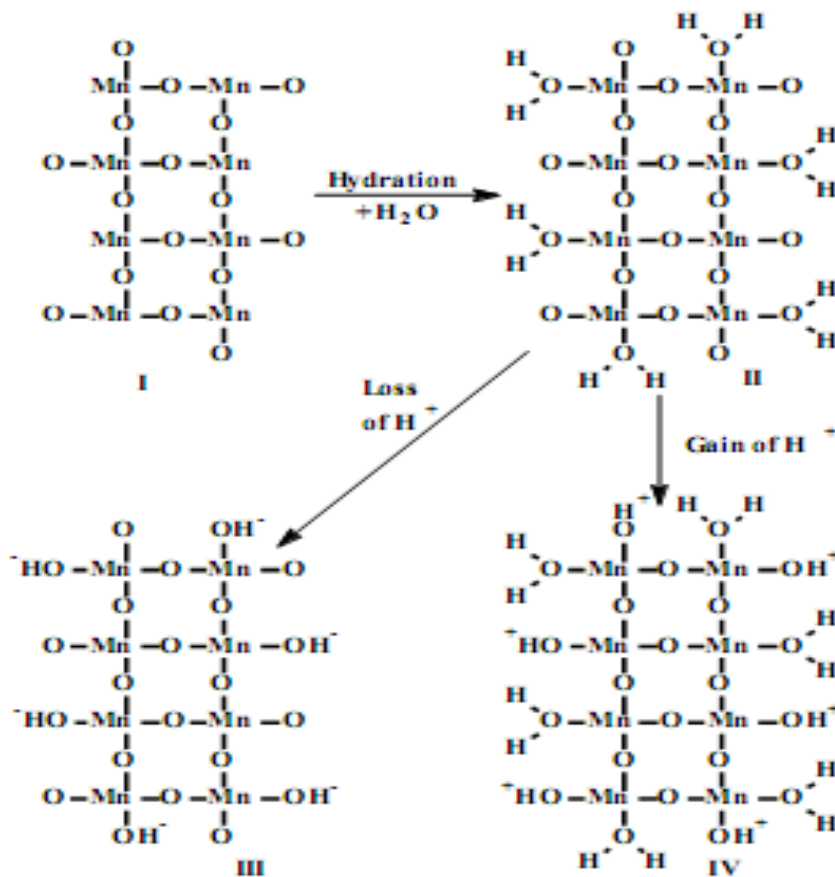

Figure (4): Acquisition of surface charge by colloidal MnO_2 in water. Anhydrous MnO_2 (I) has two O atoms per Mn atom . Suspended in water as a colloid, it binds to water molecules to form hydrated MnO_2 (II). Loss of H^+ from the bound H_2O yields a negatively charged colloidal particle (III). Gain of H+ by surface O atoms yields a positively charged particle (IV).

The former process (loss of H+ ion) predominates for metal oxides. As an illustration of pH-dependent charge on colloidal particle surfaces, consider the effects of pH on the surface charge of hydrated manganese oxide, represented by the chemical formula $MnO_2(H_2O)(s)$. In a relatively acidic medium, the reaction

$$MnO_2(H_2O)(s) + H^+ \rightarrow MnO_2(H_3O)^+(s)$$
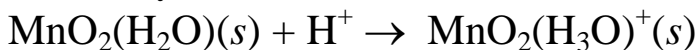
may occur on the surface giving the particle a net positive charge. In a more basic medium, hydrogen ion may be lost from the hydrated oxide surface to yield negatively charged particles:

$$MnO_2(H_2O)(s) \rightarrow MnO_2(OH)^-(s) + H^+$$

At some intermediate pH value, called the **zero point of charge (ZPC)**, colloidal particles of a given hydroxide will have a net charge of zero, which favors aggregation of particles and precipitation of a bulk solid:

Number of $MnO_2(H_3O)^+$ sites = Number of $MnO_2(OH)^-$ sites
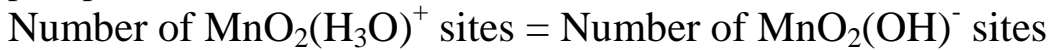
Individual cells of microorganisms that behave as colloidal particles have a charge that is pH-dependent. The charge is acquired through the loss and gain of H^+ ion by carboxyl and amino groups on the cell surface:

$^+H_3N(+$ cell$)CO_2H$ $^+H_3N($neutral cell$)CO_2^-$ $H_2N(-$ cell$)CO_2^-$

     low pH   intermediate pH   high pH
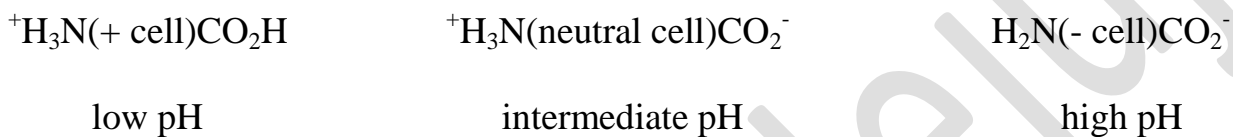
Ion absorption is a second way in which colloidal particles become charged.
This phenomenon involves attachment of ions onto the colloidal particle surface by means other than conventional covalent bonding , including hydrogen bonding and London (Van der Waal) interactions.

Ion replacement is a third way in which a colloidal particle may gain a net charge; for example, replacement of some of the Si(IV) with Al(III) in the basic SiO_2 chemical unit in the crystalline lattice of some clay minerals as shown in Equation

$$[SiO_2] + Al(III) \rightarrow [AlO_2^-] + Si(IV)$$

yields sites with a net negative charge. Similarly, replacement of Al(III) by a divalent metal ion such as Mg(II) in the clay crystalline lattice produces a net negative charge.

General Questions

Q1: Describe the reactions that result in the formation of bottom sediments in bodies of water.
Q2: How can the sediments salt introduce toxic lead ion into water column?
Q3: What is the kinds of colloidal particles in rivers ?
Q4: Match the sedimentary mineral on the left with its conditions of formation on the right:
    2 (a) FeS(s)   (1) May be formed when an aerobic water is exposed to O .
    4 (b) $Ca_5OH(PO_4)_3$ (2) May be formed when aerobic water becomes anaerobic.
    1 (c) $Fe(OH)_3$ (3) Photosynthesis by-product.
    3 (d) $CaCO_3$ (4) May be formed when wastewater containing a particular kind of contaminant
                           flows into a body of very hard water.

Q5: What is thought to be the mechanism by which bacterial cells aggregate?