CHAPTER 1

INTRODUCTION

Human normally takes fluoride from food, water and the fluoride containing products. The presence of fluoride in the body possesses effects pros and cons, for example, the fluoride intake in the suitable level can create a good dental health and protection from tooth decay; while as fluoride is ingested in excessive amounts, it can cause dental fluorosis and bone damage.

The poisonous problem of fluoride or the problem of high fluoride in drinking water more over standard. The World Health Organization accord the populations drinking water containing fluoride at a concentration 1 mg F/liter or more [1]. Several areas in the north of Thailand have high fluoride content in the source of water which punctures ground water for consumption and effective the poison to the peoples live in these areas [2]. The communities remedy the high fluoride content in water by using technology for improvement of water i.e. Reverse Osmosis (RO) system, this system can eliminate fluoride in water therefore the water are used for consumption but in this process has the waste water which have high fluoride content was released from the process into environment especially once it is released into the soil. The amount of high fluoride in soil from waste water in RO process can affected poison for living around there and return to ground water again. Therefore, analysis of fluoride distribution in soil at the installation points of RO drinking water vending machines in high fluoride accumulation areas.

1.1 Fluoride in the environment

1.1.1 Fluoride in soil

Fluorine naturally occurs at about 0.06-0.09% of the earth's crust. In rock and soil, fluorine may occur in various forms of minerals, such as fluorspar, cryolite, apatite, mica, topaz and tourmaline. Each mineral has commercial importance, such as rock phosphate is used for the production of fertilizers and cryolite is used for the production of aluminium [3]. The availability of free fluoride ion in the soil is governed by the natural solubility of fluoride compounds, the acidity of the soil, the presence of other minerals or chemical compounds, and the amount of water present. The fluoride content of the soil is usually relatively low in high mountain areas. The erosion of the mountains causes the fluoride to be removed and transferred to a lower place or to the sea or rivers. Therefore, it is constantly deprived from their original content [1].

1.1.2 Fluoride in water

The fluoride content in all kind of water is present in varying concentrations. Sea water contains fluoride at level of 0.8-1.4 mg/kg. The fluoride content of water in the lakes, rivers, or artesian wells is generally below 0.5 mg/kg, but in some areas the concentrations may be as high as 95 mg/kg. For water that have been trapped in sediments since their deposition and thermal waters associated with volcanoes and epithermal mineral deposits usually have fluoride levels of 3-6 mg/kg [1].

1.1.3 Fluoride in air

The amount of fluoride in the air arise from both natural sources and human activity. The natural sources of fluoride in the Earth's atmosphere are gases emitted in the areas of volcanic activity, the dust from soil and sea water droplets. The fluoride distribution in the air usually comes from human activity, it is emitted from industrial waste, aluminum industry, steel production plants, superphosphate plants, coal-burning power plants, brickworks, glassworks, and oil refineries. In many of these industries, exposures in the order of magnitude of 1 mg/m^3 may occur [1, 4].

In some factories, the amount of fluoride content in the air can reach up to the levels of 1.4 mg of F^- per m^3 and in the neighborhood of such factories the levels of 0.2 mg of F^- per m^3 air may be attained. The fluoride concentration of 0.5-3.8 µg of F^- per m^3 of the air samples used to be found in an industrial city in the Federal Republic of Germany during 1965 and 1966 [1].

1.2 Fluoride ingestion by man

1.2.1 Fluoride in solid food

The content of fluoride in foods is of utmost significance, the combined ingestion of fluorine containing water, fluoridated dentifrices, and high fluoride foods may be either a useful or a harmful nutritional practice. Care needs to be exercised in avoiding the constant use of high fluoride foods or the ingestion of fluoride from sources not proved important to dental health [5].

Human can receive fluoride through consumption of different kinds of food, for example plants, either vegetables or fruits, which have fluoride contents in the order of 0.1-0.4 mg/kg, the fluoride content in meat is mediocre (0.2-1.0 mg/kg), whereas fish products such as salmon and sardines may sometime have fluoride content up to 40 mg/kg. In recent study, there are great individual variations in the daily intake of fluoride from solid foods, figures ranging from 0.2 up to 3.4 mg per day per person have been reported [1].

1.2.2 Fluoride in drinks

Fluoride content in drinking water is normally found to be the largest single contribution to the daily fluoride intake. The fluoride intake from water depend the fluoride concentration in the water, the age of person, climatic conditions, and dietary habits [6].

The consumption of water increases with age, assessing estimated the daily fluoride intake of children aged 1-12 years from water containing 1 ppm fluoride. Adolph assessed the daily water requirement as equal to 1 ml per calorie of energy in the daily diet [7].

For examples of fluoride content in liquid such as The fluoride concentration in cow's milk is report to be 0.02-0.05 mg/L, the tea infusion itself will have a fluoride concentration of 0.5-1.5 mg/L, human breast milk has fluoride content less than 0.02 mg/L [1].

1.2.3 Fluoride in pharmaceutical products for caries prevention

Fluoride in the pharmaceutical products normally presents in either organic or inorganic form. Products such as sodium fluoride tablets or combined fluoride and vitamin pills are used for caries prevention. The tablets contain 0.025, or 0.50, or 1.00 mg of F^-. For those in the forms of solutions and gels for treatment, the concentrations range from 0.25 to 24.0 g of F^- per litre or per kg [1].

1.2.4 Fluoride intake from the air

Inorganic fluorides are present in the environment in considerable amount in the forms of dusts, gaseous compounds, and particulates[4]. Airborne fluoride exists in gaseous and particulate forms emitted from both natural and anthropogenic sources. The gaseous fluorides include hydrogen fluoride, carbon tetrafluoride, hexafluoroethane and silicon tetrafluoride. Particulate fluoride include cryolite, chiolite, calcium fluoride, aluminium fluoride and sodium fluoride [8].

For some locations near heavily industrial sources, of the level of fluoride in air can be found to be from 0.5 to 3.8$\mu g/m^3$[4]. While the fluoride level of 0.05 to 1.89 $\mu g/m^3$ can be found in the areas of non-industrial sources. The source of fluoride from the air such as heavy dust pollution from special industrial plants, airborne fluorides can be the main contributor to the occurrence of dental fluorosis or skeletal fluorosis [1, 4, 8].

1.3 Toxic effects of fluoride

1.3.1 Dental fluorosis

Dental fluorosis is the condition occurring as a result from excessive fluoride intake during the period of tooth development. This may result in defective tooth formation. Generally, from birth to 6-8 years of age, tooth starts developing dental enamel and dentine that will associate the fluoride into the structures. However, if excessive fluoride is incorporated during this period, the appearance of small white areas or brown spots in the enamel will be observed [8].

1.3.2 Skeleton fluorosis

Skeleton fluorosis is the condition observed after long term intake of fluoride at high level that causes fluoride to be incorporated into bone. The incorporation of fluoride into the bone may increase the stability of the crystal lattice and make the bone less soluble.

The fluoride concentration in the bone of individuals in the preclinical and crippling states of skeletal fluorosis may be between 3500 and 5500 mg/kg bone and greater than 8400 mg/kg bone, respectively [8].

1.3.3 Other effects

Considerable evidence has been presented indicating that fluoride exposure does not represent any carcinogenic or teratogenic hazard, and no effect on mortality patterns has been detected. However, exposure to high levels of fluoride occurs in connection with the use of fluorine-containing anaesthetic agents, in particular methoxyflurane. These exposures have given rise to water-losing nephritis. A number of other toxic effects and specific health problems have been suggested and studied during recent years. However, the claim that fluoride played any role in these problems has never been substantiated [4].

1.4 Methods for removing fluoride in drinking water

Defluoridation of drinking water is the only practicable option to overcome the problem of excessive fluoride in drinking water, where alternate source is not available. The most common methods for the defluridation of water are precipitation,

ion exchange, adsorption and other methods such as electrodialysis and reverse osmosis [9, 10].

1.4.1 Precipitation

Precipitation is a chemical means that can be used for fluoride removal. It is a technique of adding some precipitating agents to precipitate out the fluoride in water. The precipitation will occur when the fluoride is in contact with those precipitating chemicals. There are many materials that can be used as precipitating agents, most of them are cation such as aluminium, magnesium and calcium. A lot of studies have been reported on the use of alum and lime. In the 70 s, a co-precipitation technique, the so called ‘‘Nalgonda technique’’, was introduced to the Indian population for fluoride removal from drinking water. Hydroxy and phosphate group can be added in order to adjust the pH condition of the water and to act as coprecipitating agent, thus cause the complex formation resulting in the precipitation of fluoride.

Although precipitation is an economical and a robust technique in the removal of fluoride from water, the technique has been found to suffer from excessive sludge generation and dewatering such sludge has proven to be difficult since the solid size and content are extremely small and low, respectively; instability of the sludge under adverse environmental conditions has too been reported and in most cases, achieving the maximum contaminant level has been found to be difficult. Considering the fact that chemical handling of this technique may not be popular with many uneducated groups. In line with the above disadvantages, this technique has not been very attractive to many end users [9, 11].

1.4.2 Ion exchange

Ion-exchange resins are most commonly used in water treatment processes to soften the water supply by exchanging sodium ions for ‘‘hardness’’ ions including calcium and magnesium. Ion-exchange filters exchange the major ions present in the water, removing fluoride and negative charge in water. Selective fluoride removal can be performed using the calcium form of DOWEX G-26 (H) strong acid cation exchange resin. The calcium forms an insoluble complex with the fluoride in water with low to high salt concentrations. Soluble anions such as sulfate, arsenic, selenium and nitrate and TDS can compete with fluoride and can affect the run length. Thus, if the systems contain high levels of suspended solid and precipitated iron that can cause clogging of the IE bed, then pre-treatment may be required.

This process can be applied to either concentrated or dilute solution, and they are capable of providing complete removal of the fluoride ion under proper conditions. The economics are generally more favorable when the processes are used to treat dilute solutions to achieve low residual fluoride concentrations. Thus, they are commonly used to defluoridate drinking water supplies or dilute fluoride-bearing wastewaters [9, 11, 12].

1.4.3 Adsorption

Adsorption in water treatment is a robust technique for removing water-soluble ions, especially when these ions exist in water at low concentrations. Coincidentally, fluoride ions exist in some ground waters at low concentrations, which are above the permissible limits. The principle behind this technique is that a fluoride is transported by diffusion from the bulk phase to the solid surface where it is bound at the surface or interface between two phases by either chemical or physical forces. Numerous investigations have focused on surface adsorption as a means of removing fluoride from water. As a result of these studies various water treatment plants using treatment media such as activated alumina or bone char have been constructed and are in use in several countries. The fluoride removing efficiency of activated alumina gets affected by hardness and surface loading (the ratio of total fluoride concentration to activated alumina dosage). Chloride does not affect the defluoridation capacity of activated alumina. The process is pH specific, so pH of the solution should be between 5.0 and 6.0 because at pH > 7, silicate and hydroxide become stronger competitor of the fluoride ions for exchange sites on activated alumina and at pH less than 5, activated alumina gets dissolved in acidic environment leading to loss of adsorbing media. The process is highly selective but it has low adsorption capacity, poor physical integrity, requires acidification and pretreatment and its effectiveness for fluoride removal reduces after each regeneration [10, 11].

1.4.4 Membrane techniques

Although various conventional techniques of water purification described earlier are being used at present to solve the problem of groundwater pollution, none of them is user-friendly and cost-effective technique due to some or the other limitation and has either no or very long pay back period. As the quality of drinking water sources gets worse, the methods of water treatment or the traditional water treatment systems need to be modernized. In the recent years, RO membrane process has emerged as a preferred alternative to provide safe drinking water without posing the problems associated with other conventional methods. RO is a physical process in which the contaminants are removed by applying pressure on the feed water to direct it through a semipermeable membrane. The process is the reverse of natural osmosis as a result of the applied pressure to the concentrated side of the membrane, which overcomes the natural osmotic pressure. RO membrane rejects ions based on size and electrical charge. The factors influencing the membrane selection are cost, recovery, rejection, raw water characteristics and pretreatment [10, 11].

1.5 Potentiometry

1.5.1 Principles of potentiometric measurements

Potentiometric methods in analytical chemistry are based on the relationship between the potentials of electrochemical cells and the concentrations or activities of the chemical species in the cells [12]. The composition of a sample is obtained through the potential appearing between two electrodes [8], a reference electrode, which maintains a constant potential, and an indicator electrode, which responds to the sample composition, the potentials relate the activities of the chemical species in the cell or concentration of the ion in the solution follow Nernst equation [13].

1.5.2 The Nernst Equation

Potentiometry is suitable for the analysis of substances for which electrochemical equilibrium is established at a suitable indicator electrode at zero current. According to the Nernst equation [9], it is used for all calculations of half-cell potential where the half-cell reaction is at equilibrium. Such half-cell reactions are termed electrochemically reversible. For the generalized half-cell reaction, which is written as a reduction in the form [13]:

$$\text{Ox} \quad + \quad \text{ne}^- \quad \rightleftharpoons \quad \text{Red} \qquad 1$$

The potential is given by the generalized form of the Nernst equation

$$E = E^0 - \frac{RT}{nF}\ln\frac{a_{red}}{a_{ox}} = E^0 - \frac{RT}{nF}\ln\frac{\text{Red}}{\text{Ox}} = E^0 - \frac{2.303\,RT}{nF}\log\frac{\text{Red}}{\text{Ox}} \qquad 2$$

where E^0 = standard electrode potential in volts

R = molar gas constant (8.314 J/K-mol)

T = absolute temperature in Kelvin

Red or a_{red} = activity of the reduced form

Ox or a_{ox} = activity of the oxidized form

If numerical values are inserted for the constants and the temperature is 25 ^{o}C, the Nernst equation becomes

$$E = E^0 - \frac{0.05916}{n}\log\frac{a_{red}}{a_{ox}} \qquad 3$$

Pure phases have unit activity, solvents containing very large quantities of dissolved solutes are generally assumed also to have unit activity. The partial of gases and the molarities of uncharged solutes are use for the activities in equation 3, when they appear in half-reaction. The molarities of charged solutes differ too much from the activities to be rigorously in equation 3 directly. The activity and the concentration are related by

$$a = f_i C_i \qquad 4$$

where a = activity

f_i = activity coefficient of ion “ i “

C_i = concentration of ionic species “ i “

The Nernst equation 2 can be written as follows when the component of the half-cell reaction are solutes :

$$E = E^0 - \frac{RT}{nF} \ln \frac{f_{red}\,[Re\ d]}{f_{ox}\,[Ox]} = E^0 - \frac{RT}{nF} \ln \frac{f_{red}}{f_{ox}} - \frac{RT}{nF} \ln \frac{[Re\ d]}{[Ox]} = E^{o'} - \frac{RT}{nF} \ln \frac{[Re\ d]}{[Ox]} \qquad 5$$

Where E^0 = formal electrode potential

The formal potential, which is somewhat like a standard potential under given set of experiment conditions. It can be measured directly as long as the half-cell reaction is reversible.

The departure of activity from concentration for charge species is a function of ionic strength, I, of the solution:

$$I = \frac{1}{2} C_i Z_i^2 \qquad 6$$

Where C_i = concentration of ionic species " i "

Z_i = charge on that ion

The activity coefficient, f_i , can be estimated from the ionic strength using equation developed through Debye-Huckel theory. Various relationships have been derived depending on whether ions are considered point charges in solution or are assigned certain radii for their hydrate spheres. For solution of higher ionic strength, the form is

$$\log f_i = \frac{0.5 Z_i^2 I^{1/2}}{1 + I^{1/2}} \qquad 7$$

The point-charge approximation, an assumption that ions do not interact in solution ($I < 0.01$), and a solvent of water at 25 ^{0}C, Debye-Huckel limiting law can be used to estimate f_i :

$$-\log f_i = 0.5 Z_i^2 I^{1/2} \qquad 8$$

The note that only as I approaches zero (the experimentally unreachable “infinite dilution” point) is Debye-Huckel theory rigorous, the estimates worsen as the ionic strength increases [3, 13].

1.5.3 Electrodes of potentiometry

The important equipment required for potentiometric measurements includes an indicator electrode and a reference electrode

1. Reference electrode is a half-cell having a known electrode potential, E_{ref}, that remains constant at constant temperature and completely insensitive to the composition of the analyte solution.

2. Indicator electrode has a potential, E_{ind}, that depends on the activity of an analyte [14].

1.5.4 Reference Electrodes

The reference electrode is performed as an anode of electrochemical cell and be the secondary electrode used in analytical potentiometry. The popular electrode is the saturated calomel electrode (SCE) used to be widely used, but today the silver-silver chloride electrode is the most popular.

The secondary reference electrode is the metal electrode of the second kind (The electrode of metal, immersed in the solution that is saturated with salt of metal). The electrode is immersed in the solution as same as the indicator electrode. This kind of electrode does not required salt bridge because the composition of secondary electrode which the terminal side of electrode connects between the analyte solution and the solution in tube of the electrode, therefore there is not salt bridge. The calomel electrode and the silver-silver chloride electrode contain the solution saturated with KCl. These electrodes are normally denoted as the following representation [11,14]

The calomel electrode: Hg / Hg_2Cl_2(satd.), Cl (xM)

The silver-silver chloride electrode: Ag/AgCl (satd.), KCl (satd.)

1.5.5 Indicator Electrodes

An ideal indicator electrode must have a character of giving response rapidly and reproducibly to changes in the concentration of an analyte ion (or group of analyte ions). Potentiometric indicator electrodes are classified as follows [3].

1.5.5.1 Electrodes of the First Kind The electrode of metal M, immersed in a solution of its cation M^{n+}, shows a potential given by:

$$E = E^0 + \frac{RT}{nF} \ln a\left(M^{n+}\right) = E^{0'} + \frac{RT}{nF} \ln \left[M^{n+}\right] \qquad 9$$

The potential is determined by the reaction $M^{n+} + ne^- \rightleftharpoons M$ and the electrode material M is involved in it. The electrodes of this type are called electrodes of the first kind. In principle, these electrodes can indicate the metal ion activities (or concentrations). However, only a few metal ion/metal electrodes work satisfactorily as potentiometric indicator electrodes. An Ag+/Ag electrode is an example of such electrodes. The potential, determined by reaction $Ag^+ + e^- \rightleftharpoons Ag$, is

$$E = E^0 + \frac{RT}{nF} \ln a\left(Ag^+\right) = E^{0'} + \frac{RT}{nF} \ln \left[Ag^+\right] \qquad 10$$

1.5.5.2 Electrodes of the Second Kind A typical example is a silver–silver chloride electrode [$Cl^{-}(aq)|AgCl(s)|Ag$]. To prepare the electrode, a silver wire is coated with AgCl and dipped into a solution containing chloride ions. Its potential is primarily determined by the reaction $Ag^{+} + e^{-} \rightleftharpoons Ag$, and thus by Eq. (10). However, because of the relation $K_{sp}(AgCl) = a(Ag^{+})a(Cl^{-})$, the potential is determined by the activity of the chloride ion:

$$\begin{aligned} E &= E^{0}\left(\frac{Ag^{+}}{Ag}\right) + 0.0592\ \log K_{sp} - 0.0592\ \log a\left(Cl^{-}\right) \\ &= E^{0}\left(\frac{AgCl}{Ag}\right) - 0.0592\ \log a\left(Cl^{-}\right) \qquad [25\ ^{o}C] \qquad 11 \end{aligned}$$

where $E^{0}(AgCl/Ag)$ is the standard potential of the silver-silver chloride electrode. The silver-silver chloride electrode is an indicator electrode for chloride ion activity (or concentration). However, more importantly, the silver-silver chloride electrode in saturated (or 3.5 M) KCl is the most popular reference electrode .

1.5.5.3 Ion-Selective Electrodes Ion-selective electrodes (ISEs) are usually electrochemical half-cells, consisting of an ion-selective membrane, an internal filling solution, and an internal reference electrode :

$$\text{External reference electrode} \;|\; \text{sample solution} \;|\; \underbrace{\text{ion-selective membrane} \;|\; \text{internal solution} \;|\; \text{internal reference electrode}}_{\text{ion-selective electrode}}$$

They are classified by membrane materials into glass membrane electrodes, crystalline (or solid-state) membrane electrodes, and liquid membrane electrodes. Liquid membrane electrodes are further classified into liquid ion-exchange membrane electrodes and neutral carrier-based liquid membrane electrodes. Some examples are shown in Fig. 1.1 and Table 1 If the membrane is sensitive to ion i of charge z_i and the activities of i in the sample and internal solutions are equal to a_1(i) and a_2(i), respectively, the membrane potential, E_m, which is developed across the membrane, is

$$E_m = \left(\frac{RT}{z_i F}\right) \ln \frac{a_1(i)}{a_2(i)}$$

In the ISE, a_2(i) is kept constant. If we express the potential of the ISE by E_{ISE}, that of the external reference electrode by E_{ref}, and the liquid junction potential between the sample solution and the external reference electrode by E_j, the emf of cell is given by

$$E_m = E_{ISE} - E_{ref} + E_j$$

If E_j is negligible or constant, E can be expressed by

$$E = E' + \frac{RT}{z_i F} \ln a_1(i)$$

E’ is a constant which depends on the cell configuration.

If the ISE is sensitive to ion i and other ion(s) j, the EMF of the cell is represented by the Nicolsky-Eisenman equation:

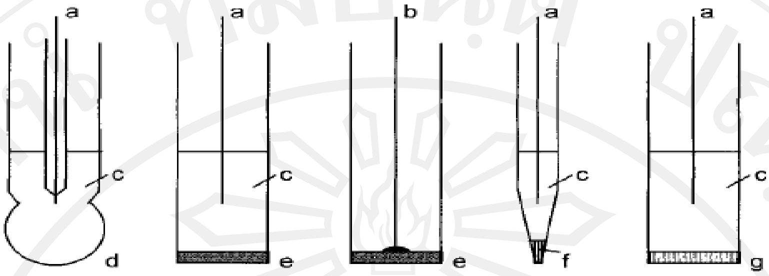

Fig. 1.1 Various types of ion-selective electrodes: (a) internal reference electrode; (b) silver wire for direct contact to the membrane; (c) internal solution; (d) glass membrane; (e) solid-state membrane; (f) ion exchanger filled at the tip of capillary; (g) ion exchanger incorporated in PVC membrane [15].

Table 1 Examples of ion-selective electrodes (ISEs) for aqueous solutions

Type of ISE	Ions	Membrane material	Type of ISE	Ions	Membrane material
Glass Membrane electrodes	H^+	Na_2O-CaO-SiO_2 Li_2O-Cs_2O-La_2O_3-SiO^2	Liquid membrane electrode	Cl^-	Dimethyldistearylammonium/Cl^-
	Na^+	Na_2O-Al_2O_3-SiO_2		ClO_4^-	1,10-phenanthroline Fe(II)/ClO_4
	K^+	Na_2O-Al_2O_3-SiO_2		Ca^{2+}	Didecylphosphate/Ca^{2+}
Solid membrane Electrodes	F^-	LaF_3		Bivalent cation (M^{2+})	Didecylphosphate/M^{2+}
	Cl^-	AgCl; AgCl-Ag_2S		K^+	Valinomycin/K^+
	Br^-	AgBr; AgBr-Ag_2S		Alkali metal ions (M^+)	Crown ether/M^+
	I^-	AgI; AgI-Ag_2S	Gas-sensing electrode	CO_2	H^+ glass electrode/ $NaHCO_3$/GPM[1)]
	CN^-	AgI		NH_3	H^+ glass membrane/ NH_4Cl/GPM[1)]
	S^{2-}	Ag_2S		SO_2	H^+ glass electrode/ $NaHSO_3$/GPM[1)]
	Cu^{2+}	CuS-Ag_2S	Enzyme electrode	Urea	NH_4^+ glass electrode/ urease-membrane
	Cd^{2+}	CdS-Ag_2S			
	Pb^{2+}	PbS-Ag_2S			

1) GPM = gas-permeable membrane

$$E = E' + \frac{RT}{z_i F} \ln \left\{ a_1(i) + \sum_{j \neq i} K_{ij}^{pot} a_1(j) \right\}$$

Where K_{ij}^{pot} is the selectivity coefficient [23]. If $K_{ij}^{pot} >> 1$, the ISE is much more sensitive to ion i than to ion j. The most popular ISE is a pH glass electrode. However, a great number of ISEs have been developed and widely used in such fields as clinical and environmental analyses [15].

1.6 Soil

Soil is a natural material covering loosely on the earth surface. Soil is composed of particles of broken rock, minerals and organic matters mixed together by participately assembling as follows.

a. Mineral matter, this is normally present in the form of small particles of mineral and rock which are disintegrated by chemical, physical and biochemical processes.

b. Organic matter**,** the part that from result the decay or disintegration of plant and animal to constitute as part of the soil.

c. Water, water in soil can be found in the cavity between soil particles.

d. Air**,** the air is also in between soil particles, those mostly found gases are nitrogen, oxygen and carbon dioxide.

The soil components, appropriate for agricultural purposes, generally contain 45% of minerals, 5% of organic matters, 25% of water and 25% of the air (Figure 1.4).

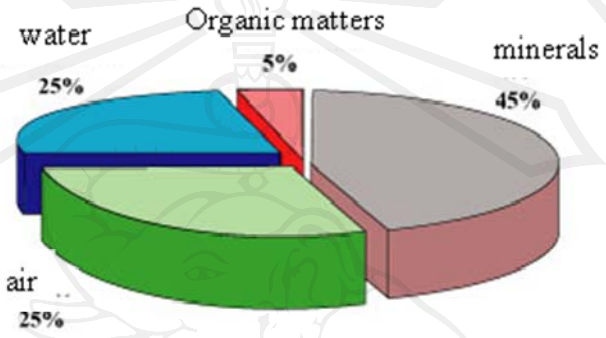

Fig. 1.2 The components of the soil [16]

1.6.1 Soil Forming Materials

The soil that originated from the eroding rock generally have minerals that contain in the rock. There are two important soil forming materials i.e. the inorganic matters which are rocks and minerals such as feldspar, quartz and mica, and organic matters.

1.6.1.1 Minerals The minerals are natural occurring solid, classified in two types.

a. Primary minerals, that is a cooled mineral crystallized directly from the magma such as mica, feldspar and quartz. These minerals can be found in the earth crust.

b. Secondary minerals this kind of mineral is a result from the erosion of low durable primary mineral. The eroded products normally reprecipitated recrystallized.

Clay silicate mineral and iron oxide are examples of this mineral type.

The most abundant mineral found in the earth crusts is the minerals that exist extensively which can be categorized as:

Quartz (SiO_2) The pure quart mineral is colorless and transparent. In the crystalline form, it has a characteristic of being hexagon. The abundant of quartz mineral is second to the feldspar group, this mineral is a major component of the sandstone type sedimentary rock. It is very durable to disintegration. Soil that contain this type of mineral are classified as sandy soil which can let water very well.

Feldspar ($XAlSi_3O_8$) The feldspar is a aluminosilicate compound of potassium, sodium, and calcium. The feldspar mineral has dark white or turbid white color and abound most in all mineral assembled rock. However this mineral presents in a small quantity in soil because it can be easily decomposed through chemical process by reacting with carbonic acid (carbon dioxide in water) to become clay.

Mica This mineral is a complex form of alumono silicate compound containing potassium , magnesium and iron as major constituents. Mica can be mostly found in granite or mica schist.

Calcite ($CaCO_3$) Calcite is a mineral having carbonate compounds as a main composition and it is a major component of soft rock (lime stone) and metamorphic rock (marble). The calcite is a most abundant and important in carbonate class minerals. It is normally existent as crystal with different shapes and its color is white or clear white.

1.6.2 Factors influencing soil formation

Soil can always be changed under the influences of climate, organisms, parent materials, topography and time. These factors cause the changes differently as follows.

a. Climate This includes heat, rain, snow, wind, sunlight, other environmental impacts which cause erosion and disintegration of the original matters.

b. **Organisms** Plants and animals living in or on the soil, water content and the plant nutrients do have some effects to soil origination. Organisms living in the soil will normally help digest crumble waste matters and move materials along soil profile, this includes plant and animal remains. The resulting organic matters will make soil fertile.

c. Parent materials Soil quality is dependent on the parent materials, such as parent rock, organic materials, original soil surface or the layers of sedimentary rock that occurred through drifting by water , wind , glacier, volcano, or the materials that move from the slope areas**.**

d. Topography The climate may post some effects to the soil depends on soil topography such as soil at the foothills contains more moisture than soil in the slope area.

e. Time The development of soil layers always increases as the time goes by.

1.6.3 Soil texture

Soil texture is represented by the physical compositions of the soil including grain size or the coarseness of inorganic particles. The particles composed in the soil can be classified through grain size as follows,

a. sand, this type of particle has the biggest size.

b. silt, the silt particle is about the middle size.

c. clay, the smallest particle size belongs to the clay particles.

1.6.4 Textural classification

Generally soil consists of three types of particles with different sizes as mentioned above, this includes sand, silt and clay. The types of soil depends on the particle sizes of mixing sediment such as, the sandy soil which has the coarse particle because having, a large-sized particle composition. Thus it has spaces for water to permeate quickly. Whereas, clay has a fine-grained texture which composes with small particles that packs very tightly, not having much spaces for water permeation. But loam which composes of middle particle size such as silt, is suitable for growing plant because water can be easily drained and the moisture can be kept in the soil very well.

Geologists have divided soil into 12 types by a proportional distribution of soil particles such as sandy soils consist of 80% sand, 10% silt and 10% clay and loamy soils consist of 40% sand, 40% silt and 20% clay, but clay soils consist of 20% sand, 20% silt and 60% clay.

The classification of soil helps understand the soil properties, for example the ability of water retaining and energy transference which is applicable to agriculture and engineering [16], etc.

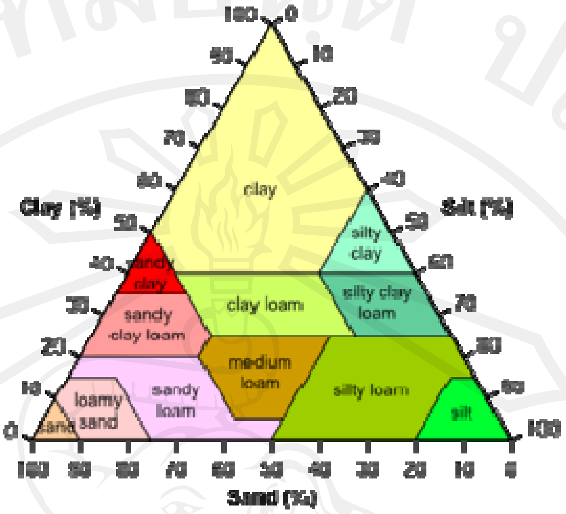

Fig. 1.3 Soil types by clay, silt and sand composition [16]

1.7 Literature reviews

Literature reviews involve initially the finding of optimum conditions for fluoride extraction which is very important in determining the amounts of fluoride. So the following literature reviews will focus on the soil sample pretreatments and some fluoride distribution profiles in various surroundings.

Loganathan *et al*. [17] studied the fluoride accumulation in pasture forages and soils following long-term applications of phosphorus fertilizers. Fluoride analysis of soil was carried out by a NaOH fusion method, the soil was fused with NaOH inside a muffle furnace at 600 °C for half an hour. The finding showed that the total fluoride concentration of the surface soil (0-75 mm depth) increased up to 217-454 mg kg^{-1} with phosphorus fertilizer application. One-third to two-third of fluoride applied in fertilizers resided in the top 75 mm soil depth. Pasture forage accumulation of fluoride was low, and therefore, fluoride intake by grazing animals through pasture consumption was expected to be much lower than fluoride intake by soil ingestion.

Xie *et al*. [18] investigated the distribution characteristics of fluoride in the soil profiles of the abandoned tea plantation in Hong Kong. The deionized distilled water, hydrochloric acid and ammonium acetate were extractants, shaken for 30 min at 20 °C for extracting fluoride from the soil samples. The water-soluble F contents ranged from 1.41 to 3.45 mg/kg in A layers (0±3 cm), 1.20 to 1.91 mg/kg in B layers (3-x cm) and 1.00 to 1.67 mg/kg in C layers (beneath x cm). The accumulation of fluoride along the soil profile followed the order of A layer>B layer>C layer. The accumulation of fluoride in the surface soil (A layer, 0±3 cm) was due to the biological accumulation of fluoride by tea plants and the release of fluoride into the surface soil from fallen leaves/litter upon decomposition.

Xie *et al*. [19] studied the fluoride emission from soils at high temperature related to the brick-making process. For total F analysis, direct determination of total fluoride in samples was made using a NaOH fusion method, the sample was then placed in a muffle furnace at 600 °C for 30 min. The results obtained in this study indicated that fluoride emission as gaseous HF and SiF_4 related to the firing temperature, total soil fluoride content, soil composition and calcium compounds added to the soils. Marked increases of the average fluoride emission rate from 57.2% to 85.4% of total fluoride in the soils were noticed as the heating temperature was increased from 700 to 1100 °C. It was found that the major proportion (over 50%) of the total soil fluoride was emitted from soils at approximately 800 °C. The amount of fluoride released into the atmosphere when heating depended on the total fluoride contents in the soils.

Franzaring *et al*. [20] performed an environmental monitoring study in the vicinity of a HF producing plant in Germany. The monitoring of fluoride emissions was done through the analyses of precipitation, dust, plant and soil samples. The fluoride was extracted with distilled water and stirred for 1 hr for mobile fluoride, but an alkali fusion was used for total fluoride determination. The result showed that the fluoride concentrations in the upper soil (0-30 cm) were well above the concentration level in the lower soil (> 30 cm). Maximum F concentrations were found to be 3243 and 1655 ppm in the topsoil and subsoil, respectively. The significant pollution gradient with high fluoride content in plant samples were close to the value detected at the emission source.

Zhu *et al*. [21] studied the total fluoride profile in Guangdong soils, relating to its spatial distribution and vertical variation. The total soil fluoride determination was obtained using the alkaline fusion. The soil sample was placed inside a muffle furnace and fused at 600 °C for half an hour. The soil fluoride contents followed an approximately log normal distribution. Although the soil fluoride geometric mean concentration of 407 mg/kg is lower than that of China, its content varied from 87 to 2860 mg/kg. An upper baseline concentration of 688 mg/kg was estimated for surface soils. In A-, B-, and C-horizon soil fluoride spatial distribution presented similar patterns that high fluoride concentration mainly located in limestone, purple shale, and sandshale areas, indicated that soil fluoride spatial distribution was primarily dependent on the regional bedrock properties rather than anthropogenic inputs.

1.8 **Research Objectives**

1 To find the optimum extraction condition, including the types of extractant, extraction time, temperature and the appropriate conditions for soil sample preparation.

2 To study the fluoride distribution profile in the soils at the installation points of RO drinking water vending machines.