CHAPTER 1

INTRODUCTION

Man has a need for water as an essential nutrient that is in common with other forms of life. Water is required for wide variety of functions including regulation of the body temperature, as a solvent, and as a vehicle in the transportation of the nutrients and of waste products to vascular system and through inter- and intra-cellular spaces. The need for water is a continuing process and the body's stores must be maintained and replenished at appropriate intervals.

Of the waters available to man personal needs, it may be regarded as certain that none is pure in the strict sense of the word. All will contain a variety of substances, either in suspension or in solution, in greater or lesser amount. Calcium, magnesium, sodium, potassium, manganese, sulfate, chloride, and wide variety of other substances may be found in most water in varying concentration. Fluoride will be found also in most, if not in all, potable water. It is consequently almost universally available for ingestion by man from this source.

1.1 Fluoride and defluoridation method

1.1.1 Occurrence in groundwater [1, 2, 3]

Most groundwater has low or acceptable concentrations of fluoride (<1.5mg/l). However, some large groundwater provinces have significant concentration, which cause prominent health problems. Most of high fluoride provinces occur in the developing world, largely because of lack of suitable infrastructure for treatment.

The dominant controls on fluoride build-up in water are:

i) geology

ii) contact times with fluoride minerals

iii) groundwater chemical composition

iv) climate

Fluoride in water derives mainly from dissolution of natural mineral in the rocks and soils with water interacts. The most common fluoride bearing minerals are fluorite, apatite and micas. Fluoride problems therefore tend to occur where the element is most abundant in the host rocks. Groundwater from crystalline rocks, especially granites are particularly susceptible to fluoride build-up because they often contain abundant fluoride-bearing mineral. Reaction times with mineral are also important. High fluoride concentrations can be build-up in groundwater, which have long residence times in the host aquifers. Deeper groundwaters from dug wells are almost likely to contain high concentration of fluoride. High-fluoride concentrations are also a feature of arid climate conditions. Fluoride build-up is less pronounced in the humid tropics because of high rainfall inputs and their diluting effect on groundwater chemical composition.

1.1.2 Fluoride toxicity [4, 5, 6]

Fluoride has been found to have a significant mitigating effect against dental caries and it is accepted that some fluoride presence in drinking water is beneficial. Optimal concentrations are 1 mg/l. However, chronic ingestion of concentrations much greater than 1.5mg/l (WHO guideline value) is linked with development of dental fluorosis, in extreme cases, skeletal fluorosis. High doses have also been linked to cancer. Fluorosis has a result from the consumption of to high level of fluoride and affects many parts of the human body. It has direct impact on hard tissue at first. The effect on dental tissue is mottled enamel or dental fluorosis that is classified by several degrees of tooth discoloration and surface destruction that show in Figure 1.1. Fluorotoxicosis can cause not only physical problem such as malnutrition especially in children as they do not have a healthy tooth structure to tear and grind food but also psychological problem due to bad looking teeth. The bony effect is calcium deposits on bony surface and interruption of calcification during bone formation causing bone deformities, osteosclerosis and loss of bone strength. Osteosclerosis of the joints can reduce movement and if it occurs at nerve foramen it can cause nerve depression with motor and sensory dysfuntion. In addition, fluoride has an effect on kidneys, muscular and nervous system and there are also some report about the relationship between erythrocyte abnormalities and serum fluoride in patients whose fluoride intake is high. Health impacts from long-term use of fluoride-bearing water have been summarized as:

< 0.5 mg/l	dental caries
0.5 – 1.5 mg/l	promotes dental health
1.5 – 4 mg/l	dental fluorosis
>4 mg/l	dental, skelatal fluorosis
>10 mg/l	crippling fluorosis

The basis for each classification of dental fluorosis was as follow:

1. Normal – The enamel is translucent, smooth and presents a glossy appearance.
2. Questionable – The enamel discloses aberrations from the translucency of

normal enamel, ranging from a few white flecks to occasional white spots. This classification is utilized in those instances where a definite diagnosis of the mildest from of fluorosis is not warranted and a classification of “normal” not justified.

3. Very mild – Small, opaque, paper-white area are seen scattered irregularly over the tooth but not involving as much as approximately 25 % of the tooth surface.
4. Mild – The white opaque areas in the enamel of the teeth are more extensive but do not involve as much as 50% of the tooth.
5. Moderate – All enamel surface of the teeth are affected, and surfaces subject to attrition show marked wear. Brown stain is frequency a disfiguring feature.
6. Severe – All enamel surfaces are affected and hypoplasia is so marked that the general form of the tooth may be affected. Brown stains are widespread and teeth often present a corroded-link appearance.

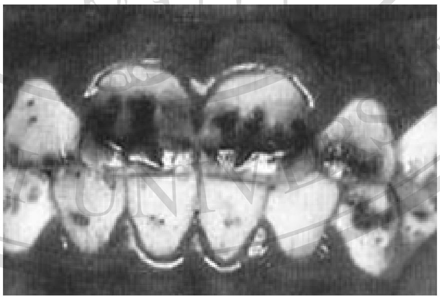

Figure 1.1 Dental fluorosis

Fluorosis is a serious problem in Thailand, especially in the northern and western part. People become ill from drinking underground water containing excessive fluoride. Bone and dental fluorosis are the main problem from excessive fluoride intake in Thailand.

1.1.3 Removal methods for fluoride from drinking water [7, 8, 9, 10]

The process for removal of fluoride is generally termed as defluoridation. Numerous methods have been described employing various materials for the fluoride removal since 1930s. Base on nature of process, the defluoridation can be grouped under the following categories

i) Precipitation
ii) Adsorption or ion-exchange
iii) Other methods such as electrodialysis and reverse osmosis

1.1.3.1 Precipitation

Fluoride elimination from water by precipitation is a technique of adding some precipitating agent to fluoride water. After fluoride is in contact with those chemicals, precipitation occurs. There are many materials that can be used but most of them are element or molecules that have the positive charge such as aluminium, magnesium and calcium. Hydroxy and phosphate group can be added in order to adjust water pH condition and to be co-precipitating agent, then the complex formation or precipitation will occur. Various chemicals and other informations of precipitation process are illustrated in Table1.1.

Table 1.1 The precipitation method for defluoridation

Chemical	**Capacity /dose**	**Working pH**	**Interference**	**Advantages**	**Disadvantages**	**Relative cost**
Alum	150 mg/mgF	Non-specific	-	Established process	Sludge produced, treated water is acidic, residual Al present	Med-high
Lime	30 mg/mgF	Non-specific	-	Established process	Sludge produced, treated water is alkaline	Med-high
Alum +lime (Nalgonda)	150 mg alum+ 7mg lime /mgF	Non-specific Optimum 6.5	-	Low-tech, established process	Sludge produced, high chemical dose, residual Al present	Med-high

1.1.3.2 Ion exchange and adsorption

Magnesite, zeolite, alkali soil, acidic clay, activated carbon, bone char etc. are among the numerous material which have been studied and confirmed to be able to adsorb fluoride from water. The common of these adsorbents is their content of metal lattice hydroxy - groups which can be exchanged with fluoride:

Ion-exchange of a metal compound M:

$$\text{M-OH (s)} \quad + \quad F^- \quad \longrightarrow \quad \text{M-F (s)} \quad + \quad OH^- \qquad (1.1)$$

Several materials and other informations of adsorption process are shown in Table 1.2.

Table 1.2 The adsorption/ ion exchange method for defluoridation

adsorbent	Capacity /dose	Working pH	Interference	Advantages	Disadvantages	Relative cost
Activated carbon	Variable	<3	Many	--	Large pH change before and after treatment	High
Plant carbon	300 mgF/ kg	7	-	Locally available	Requires socking in potassium hydroxide	Low-med
Zeolites	100 mgF/ kg	Non-specific	-	-	Poor capacity	High
Clay pot	80 mgF/ kg	Non-specific	-	Locally available	Low capacity, slow	Low
Activated alumina	1200 g F/m^3	5.5	Alkalinity	Effective, well established	Need train operators, chemical not always available	Med
Bone	900 gF/m^3	>7	Arsenic	Locally available	May give taste; degenerate, not universally accepted	Low
Bone char	1000 gF/m^3	>7	Arsenic	Locally available, high capacity	Not universally accepted	Low

1.1.3.3 Other methods

Other techniques that can be used in the defluoridation of water are electrodialysis and reverse osmosis (RO). Electrodialysis and reverse osmosis are effective in reducing fluoride. Electrodialysis method is similar to RO in that they are membrane process but electrodialysis used direct current to electrically charge ions to be transferred through the membrane under low pressure instead of forcing water through the membrane under high pressure. Some of information of these methods are illustrated in Table1.3.

Table 1.3 The other methods used for removing fluoride ion

Removal method	**Capacity /dose**	**Working pH**	**Interference**	**Advantages**	**Disadvantages**	**Relative cost**
Electro dialysis	High	Non-specific	Turbidity	Can remove other ions, use for high salinity	Skill operators, high cost, not much use	Very high
Reverse osmosis	High	Non-specific	Turbidity	Can remove other ions, use for high salinity	Skill operators, high cost	Very high

1.2 Adsorption [11, 12]

Adsorption is a means of neutralizing or satisfying the force of attraction that exists at a surface. These forces at the surface of solid or a liquid are merely extensions of the forces within the body of the material. At the surface, the average number of neighboring atoms or molecules is only half as great as underneath the surface. Thus, there is unbalance of forces at the surface, and marked attraction of the surface toward atom in its environment.

There is also a greater attraction of surface atoms toward neighboring atom in the liquid or solid. This results in stronger bonds between surface atom and closer distances as compared with atoms underneath the surface. This tendency for the atoms to compress gives rise to surface tension. The unfilled forces at the surface can be satisfied by adsorption of atom or molecule of another species. This reduces the attraction of the surface atoms or molecules of solid or liquid toward its neighbors of the same kind, and reduces the surface tension. Thus, adsorption is always accompanied by a decrease in surface tension. The process of adsorption continues until the free surface energy of the system, due to the imbalance of surface forces, has reach a minimum value.

1.2.1 Physical adsorption and chemisorption [13, 14, 15]

All adsorption processes, whether physical or chemical in character, are accompanied by decrease in a free surface-energy. Physical adsorption frequently referred to as van der Waals adsorption, occurs where there are relatively weak adhesional forces between adsorbate and adsorbent. The heat evolved when a gas is physically adsorbed is usually similar to the heat of liquefaction of the gas. On the other hand, chemical adsorption arises from the actual formation of a chemical bond with the surface. The heat evolved is the same of the order as those liberated in chemical reaction, from about 10 to 100 kcal per mole. Physical adsorption occurs rapidly and is readily reversible. Chemisorption is irreversible or reversible with great difficulty. Physical adsorption also differs from chemical adsorption in that the former requires little of any activation energy. With chemisorption, the activation energy can be very considerable.

The difference between physical and chemical adsorptions is illustrated in Table 1.4. [16]

Table 1.4 The properties of physical and chemical adsorptions

Physical Adsorption	Chemical adsorption
Enthalpy of adsorption less than about 40 kJ/mol	Enthalpy of adsorption greater than about 80 kJ/mol
Adsorption appreciable only at temperatures below the boiling point of the adsorption	Adsorption occur at high temperature
Incremental increase in amount adsorbed increase with each incremental increase in pressure of adsorbed	Incremental increase in amount adsorbed decrease with each incremental increase in pressure of adsorbed
Amount of adsorption on surface a function more of adsorbate than adsorbent	Amount of adsorption characteristic of both adsorbate and adsorbent
No appreciable activation energy involved in adsorption process	Activation energy may be involved in adsorption process
Multilayer adsorption occur	Adsorption lead to monolayer, at most

1.2.2 Classification of adsorption isotherm [13, 16]

Adsorption is most generally described in terms of isotherms that show the relationship between pressure of the adsorbate gas and amount of gas adsorbed at a constant temperature. Three phenomena may be involved in physical adsorption: monolayer adsorption, multilayer adsorption, and condensation in capillary or pore. The contour of a complete isotherm, from zero pressure to the saturation pressure. Brunauer, Emmett and Teller have distinguished five types of contour involving physical adsorption as shown in Figure 1.2

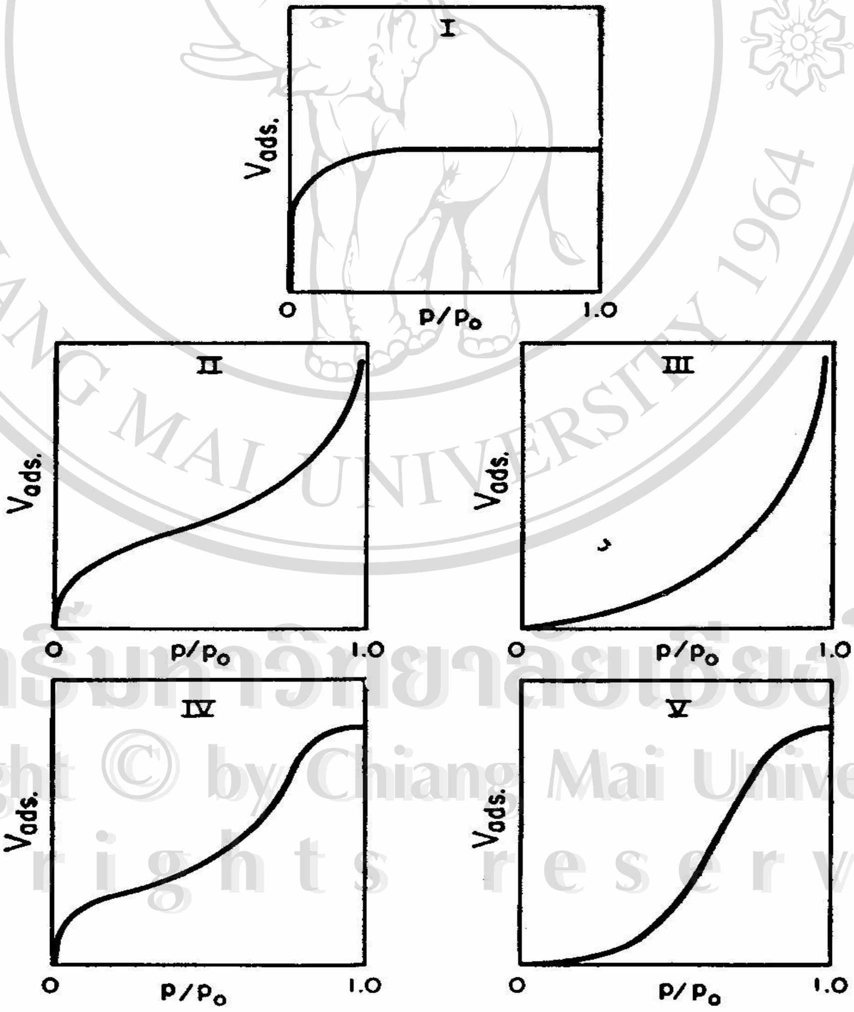

Figure 1.2 Five types of adsorption isotherms

Type I approximates monomolecular adsorption and is frequently referred to as Langmuir type. This type of curve is obtained by low temperature adsorption of oxygen or nitrogen on certain charcoals and silica xerogels, because a monolayer saturates the surface or fills the pores. Chemisorption phenomena frequently produce this curve.

Type II is the most frequently encountered adsorption isotherm and is referred to as the sigmoid or S-shape isotherm. The first portion of the curve up to relative pressure corresponds to monolayer. This is followed by a multilayer region.

Type IV is similar to Type II, except in that portion of the isotherm approaching 1.0 relative pressure. The sharp approach to the line corresponding to the saturation pressure indicates a limited pore volume, because the diameter if the pores is only a small multiple of the diameter of the adsorbate molecules. This contour is common for many kinds of porous substrates.

Type III and Type V occur only when the forces of monolayer adsorption are small. They are rarely encountered. A limited pore volume distinguishes the type V isotherm, as compared with Type III.

1.2.3 Isotherm equations [16, 17, 18]

1.2.3.1 Langmuir adsorption isotherm

The adsorption equation was developed by Langmuir in 1916. Langmuir equation was one of the first and most important equation based on theory. Langmuir postulated that adsorption occurred as a monolayer film on over the surface of adsorbent, and derived adsorption isotherm results from investigation of the equilibrium that is set up between the gas phase and the partially formed monolayer.

When the gas is at a pressure P, Thus, S_0 represents the fraction of surface that is bare and S_1 , the fraction of surface covered by monolayer of adsorbed molecules. The equilibrium state can be interpreted in terms of dynamic equilibrium that results from an equal rate of desorption of the adsorbed material and rate of the condensation of the gas phase molecule. The rate of adsorption is proportional to the pressure of the gas and the fraction of the surface that is available,

$$\frac{dS_1}{dt} = k_1 P S_0 = k_1 P (1 - S_1) \qquad (1.2)$$

The rate at which molecules leave the surface is proportional to the fraction of the surface that is covered,

$$-\frac{dS_1}{dt} = k_2 S_1 \qquad (1.3)$$

At equilibrium, the rates of adsorption and desorption are equal.

$$S_1 = \frac{k_1 P}{k_2 + K_1 P} \qquad (1.4)$$

Many simplified assumptions were made in the derivation of this adsorption isotherm. Thus, it was assumed that the heat of adsorption is independent of fraction of the surface that is covered and that only elastic collision –monolayer- occurs on the covered surface. While Langmuir's equation fits experiment data in only a limited number of cases, it is important in the further development of the theory.

1.2.3.2 The Fruendlich adsorption isotherm

The variation of adsorption with pressure can often be represented (especially at moderately low pressure) by

$$v = kP^{1/n} \tag{1.5}$$

where k and n are constant, n usually > 1

This adsorption equation was originally proposed on purely empirical basis. Although not considered here it can be derived theoretically, however, the volume of gas adsorbed is not depicted as approaching a limiting value as in single Langmiur equation.

1.2.3.3 The BET equation for multimolecular adsorption

Because the forces acting in physical adsorption are similar to those operating in liquefaction, physical adsorption is not limited to a monolayer, but can continue until a multilayer of liquid cover sorbent surface. The theory of Brunauer, Emmett and Teller is an extension of Langmuir treatment to allow for multilayer adsorption on non-porous solid surface. The BET equation is again derived by balancing the rates of evaporation and consideration for the various adsorbed molecular layers, and is based on simplifying assumption that characteristic heat of adsorption applied to the first monolayer, while the heat of liquefaction of the vapour in question applied to adsorption in the second and subsequent molecular layer. The equation is usually written in the form:

$$\frac{p}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{(c-1)p}{V_m c P_0} \qquad (1.6)$$

The main purpose of BET equation is to describe type II isotherms. In addition, it reduces the Langmuir equation at low pressure. The isotherm equation which almost frequently used are summarize in Table 1.5.[16]

Table 1.5 Various types of isotherm equations

Name of isotherm	Equation	Adsorption type
Langmuir	$\frac{V}{V_m} = S = \frac{bP}{1+bP}$	Physical adsorption and chemisorption
Freundlich	$V = kP^{1/n}$	Physical adsorption and chemisorption
Slykin- Frumkin or Temkin	$\frac{V}{V_0} = S = \frac{1}{a}\ln C_0 P$	Chemisorption
Beunauer- Emmett-Teller,BET	$\frac{p}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{(c-1)p}{V_m c P_0}$	Physical adsorption(multilayer)

Where V is total volume of gas adsorbed

V_m is volume of gas adsorbed when the entire adsorbent surface is covered with a complete monolayer

S is fraction of the surface which occur as monomolecular adsorption at pressure P

P_0 is saturation pressure

b, n, C_0 and a are constant values

1.3 Potentiometry [19, 20, 21]

Potentiometric methods in analytical chemistry are based on the relationship between the potential of electrochemical cells and the concentration or activities of the chemical species in the cell. Applications of potentiometry generally involve use of an electrochemical cell composed of a reference electrode, which maintains a constant potential, and indicator electrode, which responds to the sample composition. A salt bridge is often used to prevent mixing of the sample and the reference solution to minimize the liquid junction potential.

1.3.1 The Nernst equation

All electrochemical cells are considered to be a combination of two half cells, one for the reduction reaction and one for oxidation reaction .To have current flow in any electrochemical system both oxidation and reduction reaction must occur. Any half-cell reaction can be written as either an oxidation or reduction by convention, that is

$$\mathbf{Ox + ne^- \rightleftharpoons Red} \qquad (1.7)$$

Ox = general symbol for the oxidized form of the balanced half-reaction

Red = general symbol for the reduced form of the balanced half-reaction

n = number of electron involved in the half-reaction

The potential is given by the generalized form the Nernst equation

$$E = E^0 - \frac{RT}{nF}\ln\frac{a_{red}}{a_{ox}} = E^0 - \frac{RT}{nF}\ln\frac{Red}{Ox} = E^0 - \frac{2.303RT}{nF}\log\frac{Red}{Ox} \qquad (1.8)$$

where E^0 = standard electrode potential in volts

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

T = absolute temperature in Kelvins

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

$$E = E^0 - \frac{0.05916}{n}\log\frac{a_{red}}{a_{ox}} \qquad (1.9)$$

Pure phases have unit activity, solvent containing even every large quantities of dissolved solutes are generally assumed also to have unit activity .The partial of gases and the molarities of uncharged solutes are used for the activities in equation 1.6, when they appear in half-reaction. The molarities of charged solutes differ too much from the activities to be rigorously used in equation 1.8 directly. The activity and the concentration are related by

$$a = f_i C_i \qquad (1.10)$$

Where a = activity

f_i = activity coefficient of ion " i "

C_i = concentration of ionic species " i "

The Nernst equation 1.5 can be written as follows when the component of the half-cell reaction are solutes :

$$E = E^0 - \frac{RT}{nF}\ln\frac{f_{red}[Red]}{f_{ox}[Ox]} = E^0 - \frac{RT}{nF}\ln\frac{f_{red}}{f_{ox}} - \frac{RT}{nF}\ln\frac{[Red]}{[Ox]} = E^{o'} - \frac{RT}{nF}\ln\frac{[Red]}{[Ox]} \qquad (1.11)$$

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:

$$I = \frac{1}{2} C_i Z_i^2 \qquad (1.12)$$

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 develop with Debye Huckel theory. With 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 :

$$-\log f_i = 0.5Z_i^2 I^{1/2} \qquad (1.13)$$

For solution of higher ionic strength, the form

$$\log f_i = \frac{0.5Z_i^2 I^{1/2}}{1 + I^{1/2}} \qquad (1.14)$$

The higher charge on an ion leads to lower activity coefficient and higher ionic strengths cause a greater departure of the formal potential from standard potential. In fact, one method of estimating standard potentials is to measure $E^{0'}$ as a function of $I^{1/2}$ and extrapolate to $I = 0$

1.3.2 Indicator Electrode ; Solid-State Crystalline and Pressed-Pellet Electrode

Solid-state crystalline and press-pellet electrode are ion-selective electrodes in which the membrane is a solid crystalline material. The most important example of this electrode is the fluoride electrode, with a single europium-doped LaF_3 crystal as the sensor, that only fluoride ion can migrate through the lattice. The LaF_3 crystal sealed into the end of rigid cylinder electrode body. Internal electrolyte solution typically NaF and NaCl, and an internal reference electrode.(Figure1.3) At room temperature, LaF_3 is a pure fluoride ion conductor, free from interference. Virtually the only interference encountered with the electrode are at low pH, where the fluoride ion form HF (*$pK_a=3$*) and at pH values greater than about 8. The most interference is hydroxide ion, which is responsible for the concentration about 0.1 (F^-:OH^-). The other significant interference is that the halide for the concentration about 0.001 (F^-: X^-)

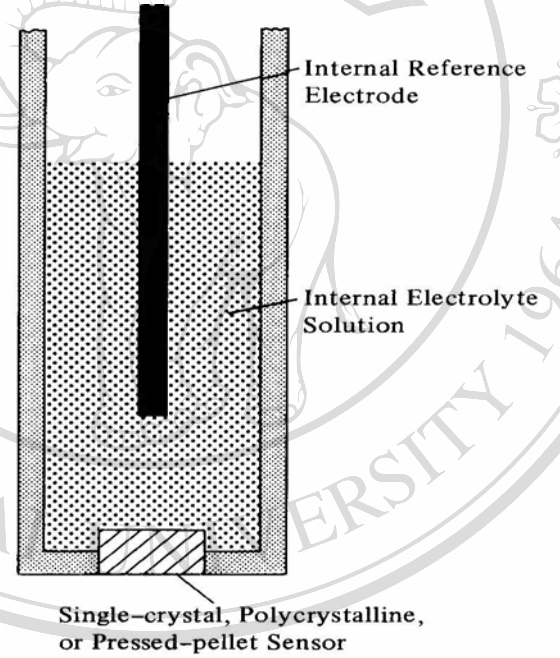

Figure 1.3 Crystal-sensor ion selective electrode

1.3.3 Reference electrode

The reference electrode used in analytical potentiometry must have a potential that is unchanged by the passage of the small amount of current. Ideally, the reference electrode is of known and constant potential. The cell potential of the overall system can be expressed as

$$E_{cell} = E_{constant} + E_{ind} \qquad (1.15)$$

where E_{ind} = potential (varying with the solution composition) of the indicator electrode

1.3.3.1 Calomel Electrode

The calomel electrode (Figure 1.4) is the most widely used reference for general electrochemical measurements. This electrode consists of mercury, mercurous chloride (calomel) and chloride-ion solution

$$Hg / Hg_2Cl_2(satd.), Cl^-(xM)$$

The half-cell reaction is

$$Hg_2Cl_2 + 2e^- \rightleftharpoons Hg + 2Cl^- \quad E^0 = 0.268\ V \qquad (1.16)$$

The potential is governed by the activity of the chloride ion (x). The most common type of this electrode is the saturated calomel electrode (SCE), in which solution is saturated with KCl. It is easily made and maintained, and its potential is highly reproducible. A grate variety of commercial calomel electrodes are available.

The disadvantage of the SCE is that its potential varies strongly with temperature, owing to the change in solubility of KCl. The SCE can be used only at the temperature lower than 80 ° C.

1.3.3.2 Silver/Silver Chloride Electrode

A silver/silver chloride reference electrode (Figure 1.5) is prepared by plating a layer of silver chloride onto a metallic silver wire or sheet. The electrode is immersed in a chloride solution (usually KCl) of known concentration, which is also saturated with AgCl. The half-cell constructed may be represented as

$$\text{Ag/AgCl (satd.), Cl}^- \text{ (xM)}$$

For which the half-reaction is

$$\text{AgCl} + e^- \rightleftharpoons \text{Ag} + \text{Cl}^- \quad E^0 = +0.2223\ \text{V} \quad (1.17)$$

The potential is governed by the chloride ion activity. Commercial silver/ silver chloride electrodes are available in a variety of styles and sizes. They are often used as internal reference electrodes in glass pH and other ion-selective electrodes. This electrode is also sufficiently stable for use at temperature up to about 275 ° C, making it an appropriate alternative to calomel electrode at elevated temperatures.

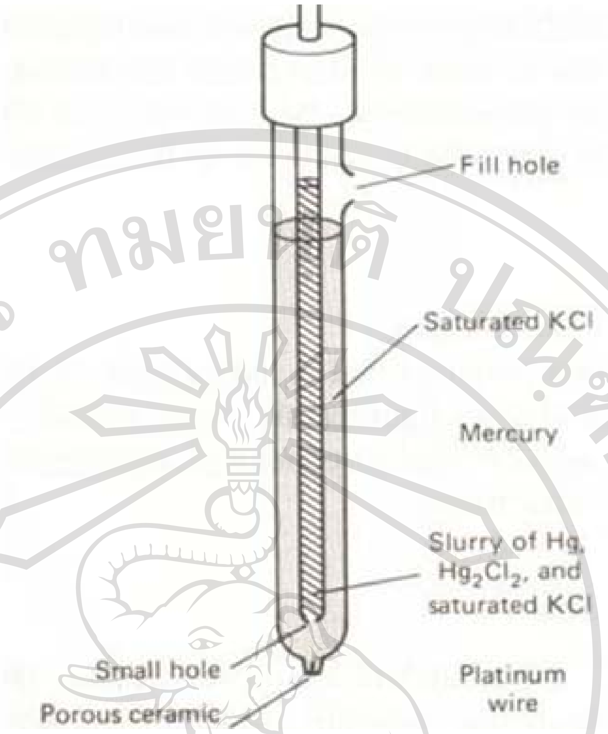

Figure 1.4 Calomel electrode[19]

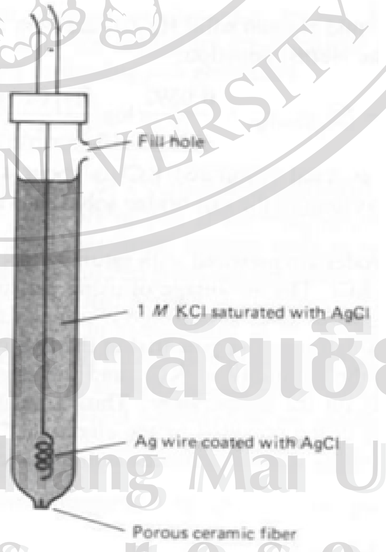

Figure 1.5. Silver/ Silver chloride electrode[21]

1.4 Firebrick [22-25]

Firebricks are in almost every part of construction, and the construction industry plays a very important role in development. The firebrick producers may be divided into two groups, the large and small-scale. The large firms use more advance technology and produce better quality firebrick than small-scale producers do. Most of large firms produce many types of firebricks including severe-weathering bricks (outdoor brick) and non-weathering bricks use for indoor construction. Whereas, small-scale firms produce only non-weathering bricks. Most of small-scale producers are farmers who cultivate rice or other agricultural products.

The difference between firebricks made by large firms and small-scale firms is that bricks made by the large firm are quality bricks since clay and water are mixed and compressed into forms by machine. While small-scale firms produces by hand, and simply put mixed clay into molds without any pressure to compress the bricks. The price of hand-made bricks is cheaper than made by machine.

1.4.1 Raw materials used in the production.

The four most important raw materials used in the production of firebrick are clay, water, rice husks and wood. Water is used to soften dry clay before pressing it through the mold. Rice husk and/or wood are used in the burning process. Firebricks vary considerably in chemical compositions, generally in the percentage of alumina silica and iron. Clays from different sources contain difference components are shown in Table 1.6.

Table 1.6 The components of clay used for making firebrick in some countries

Country	% by weight		
	Fe_2O_3	SiO_2	Al_2O_3
Thailand	29.5	47.3	10.2
India	29.5	43.3	12.0
Kenya	25.3	11.4	14.6

1.4.2 The process of production

The process in the production of bricks may be divided into 3 steps.

1. The preparation of the clay.

The preparation of the clay is to mix the clay which is ready for forming. Before mixing the clay, the producers usually put hard, dry clay in water for about one day and mix it in the next day. Small-firms use workers to mix the clay by hand, but large firms mix clay by mixing machine.

2. The forming and drying of raw brick.

Small-firms use simple wooden mold for forming bricks by hand on the ground, and make them up with a knife, whereas, large firms use a machine to do it. Raw clay bricks are commonly stored in sheds for drying; these are open at the side and cover on the top. Usually it takes about four to five days for drying.

3. The firing of the bricks in kiln and removing brick from the kiln.

When the raw bricks are dried naturally, the bricks are placed in the kiln for firing. The producers have to supply fuel until the bricks are through fired; they are removed from the kiln when they are cool. This step takes about a week.

1.4.3 Physical properties of firebrick [26]

The physical property requirements in most specifications are compressive strength, water adsorption and saturation coefficient. These properties must be determined in accordance with ASTM C 67. The minimum compressive strength, maximum water adsorption and maximum saturation coefficient are used in combination to predict the durability of the unit in use. The physical property requirements for each standard are listed in Table 1.7.

Table 1.7 Standard properties of firebrick

ASTM standard	Minimum. compressive strength (psi)	Maximum water absorption (%)	Maximum saturation coefficient
C62 SW	3000	17.0	0.78
C216SW	3000	17.0	0.78
C902SX	8000	-	0.78
C32 SS	8000	6.0	-

1.5 Fluoride level in natural water in Thailand [27]

The human organism is exposed to fluoride in number of ways. Water is the predominant source of natural fluoride. Data from over country survey of natural drinking water sources showed that people in Northern and Western area of Thailand had more chance to expose to high fluoride (above optimum level) than other parts of the country. There are 429 sources of natural drinking water, which contain fluoride level higher than 0.6 mg/l and about 1% of the natural source contain more than 2 mg/l. Areas where the fluoride content can be found in natural drinking water are shown in Figure 1.5.

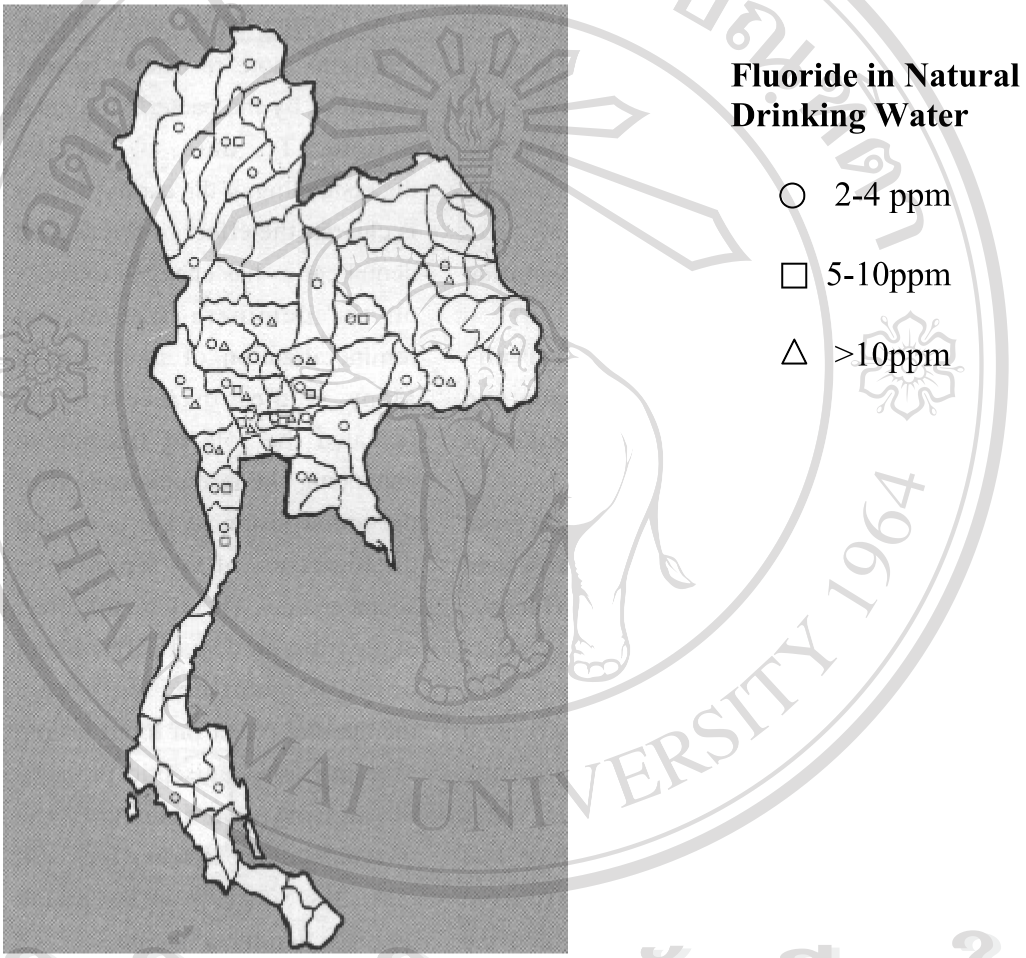

Figure 1.6. Illustration of provinces which fluoride contents in natural drinking water were found > 2 mg/l (1995)

A village, Ban Sankayom,[28] in northern Thailand is surveyed with respect to fluoride in water sources and the use of water. About 40% of the village wells contain high fluoride concentrations, between 1.5 and 10.3 mg/l. The village uses many sources of drinking water for daily consumption: one dug well for every household, rainwater, bottled water and two dug wells are in use- one at the school and one for the water distribution system in the village. The Figure 1.7 shows the distribution of fluoride concentration in Ban Sankayom. This picture confirms previous data from1995

Figure1.7. Distribution of fluoride concentration in mg/l in dugwells in Ban Sankayom. Dotted line is pipes water distribution system. Shaded areas has uniform fluoride concentration, while isolate high concentration are encircled (1999)

1.6 Literature review

There are many researches dealing with defluoridation which use many adsorbents similar to firebrick.

Moges *et.al.* [29] studied on the adsorption of fluoride ions onto fired clay pot. It was found that the maximum efficiency of the adsorbent for defluoridating 1-2 liters of water was found to be 200 mg fluoride kg^{-1} adsorbent. The adsorbent at the amount of 120-240 g can reduce 5-20 mg/l fluoride in 1 liter of water to less than 1.5 mg/l.

Zevenbergen *et.al.* [30] used the local Kenya soil (Ando soil) as a fluoride adsorbent. Ando soils are relatively young soil derived from volcanic ash, which in part has weathered to high active aluminium and high porosity. Ando soil can remove 5450 mg fluoride kg^{-1} adsorbent.

Hauge *et.al.* [31] studied the fluoride binding capacity of clay and clay ware, especially the effect of temperature on the fluoride binding process. It was found that the rate and capacity of fluoride binding in the clay ware varied with the fired temperature. Clay fired at 600 ^{o}C was the most effective. Temperature over 700 ^{o}C caused a decline in fluoride binding. And pottery fired at 900 ^{0}C and above seemed unable to remove fluoride from water. Pots fired at 500 ^{0}C or less cracked in water.

The fluoride binding capacity of ordinary potters clay was investigated by Bardsen and Bjorvatn[32] fired at 600 ^{0}C. Fluoride solution at concentrations ranging from 12.5-1600 mg/l was added to the fired clay. It was found that with the initial concentration 1600 mg/l, fired clay can remove 4.6 mgF/g fired clay.

Padmasiri[33] used broken pieces of freshly burnt brick of size 15-20 mm which is readily available in village packed in PVC pipe with 225mm diameters. 25

domestic defluoridators were distributed to households having fluoride rich water in their wells in the villages. For fluoride content of 3.0 mg/l with a withdrawing capacity mentioned at 15 liters/day, the fluoridated water could be kept below a fluoride content of 1.0 mg/l in this filter unit. The filter unit could be used for more than 5 years if handled carefully and change the filter medium at the correct time.

Defluoridation using bone char was studied by Fangsrikhum.[34] The study was started with fluoride adsorption behavior on bone char. Many factors were studied including temperature, pH, size of bone char and interfering ions. It was found that the particle sizes had slight effect on the adsorption of fluoride. The effect of temperature was studied and found to be endothermic with maximum amounts of fluoride adsorbed per gram on the first layer of bone char surface at 25, 35 and 45°C were 21.1, 22.4 and 25.7 μmol, respectively. The optimum pH for the adsorption was between 7.00-7.50. The bone char can defluoridate water sample from 10.8 and 13.0 mgF/l to 4.40 and 4.10 mgF/l respectively.

Watanesk and Watanesk[35] studied sorption behavior of fluoride on activated carbon and bone char. The experiment for sorption was determined by varying the pH in the range of 3-9. Both activated carbon and bone char seem to exhibit sorption behavior which is independent of pH within the range of 3-8. The removal capacity of activated carbon and bone char were 0.1 and 0.4 mg g^{-1}adsorbent respectively.

Wang and Reardon[36] used soil from Xinzhou, China as a sorbent for defluoridation of high fluoride drinking water. The soil is composed of quartz, feldspar, illite and goethite, with iron (III) oxide of 6.75%. Batch and column experiments were done in order to characterize the fluoride removal properties and develop an optimum activation and regeneration procedure. The activation and regeneration can be done by acid-base rinsing procedure. Based on the result of the batch test, the fluoride uptake occurs quickly, within 1.5 hours. From the column test, it was found that the soil's sorption capacity is 150 μg/g.

1.7 Aims of the work

1. To study the adsorption behavior and isotherm of fluoride by using firebrick as adsorbent.
2. To study the operating parameters for column operation in reducing fluoride content in water
3. To apply the method for using at a household level.