

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Fluoride

2.1.1 Background

Fluoride is among the hazardous inorganic species that seriously threatens the aquatic environment. Fluoride is found naturally in rocks, seawater, surface water, and groundwater (Ndiaye et al., 2005). Different forms of fluoride are released into the environment naturally through the weathering and dissolution of minerals, in emissions from volcanoes, and in marine aerosols. Fluorides are also released into the environment via coal combustion, process waters, and waste from various industrial processes. Industrial processes that generate waste containing fluorides include steel manufacturing; primary aluminium and nickel production; phosphate ore processing; phosphate fertilizer production; glass, brick, and ceramic manufacturing; and glue and adhesive production (WHO, 2002).

2.1.2 Fluoride in Lamphun province

Lamphun province is located in Northern Thailand which is currently one of the areas where the groundwater contains high amounts of fluoride. Many local people in Lamphun province have been affected by dental and skeletal fluorosis. When the health effects of fluoride were made public, the local and central governments installed small-scale membrane filtration plants as community water systems (Matsui, 2007). These membrane plants are owned and operated by either public water utilities or the private sector.

Matsui (2007) investigated the groundwater quality of 133 wells for village waterworks in Lamphun province. The distribution fluoride concentration of 133 groundwater samples well is shown in Figure 2.1. The fluoride concentration on the map was classified into three levels, i.e., 0-0.5 mg/L, 0.5-1.5 mg/L, and 1.5-16.1 mg/L. In the north-eastern area of Muang district and Ban Thi district had a high fluoride concentration in the groundwater of up to 16.1 mg/L. In contrast, there were low fluoride concentrations in the groundwater in the areas of Pa Sang district and Mae Ta district.

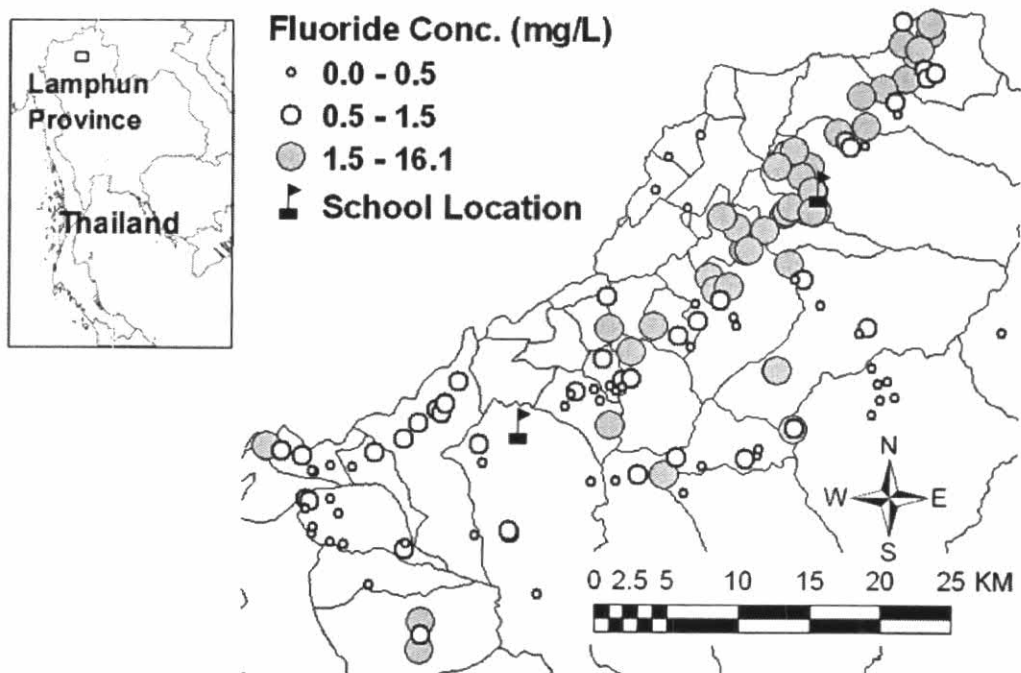


Figure 2.1 Fluoride concentrations in groundwater in Lamphun province
(Source: Takizawa, S. et al., 2008)

The membrane RO plants in Lamphun province were being operated without a recirculation system. They were run by the local community where the water production was relatively small. The filtered water was bottled and delivered to the households in this local community.

Table 2.1 The capacity of the membrane plants in Lamphun province and their specifications

Water production rate (m³/day)	Specification and operational conditions	Notes
1-5	<ul style="list-style-type: none"> - Polyamide composite - NaCl retention 99.4% @ 2000 mg/L, 1MPa, pH 7-8 - Module diameter: 4 inches - Operational pressure: 0.8-1.5 MPa - Permeate flux: 0.1-1.0 m³/m²/day - Recovery less than 30% per one bank module, 40-50% per two banks - Anti-scalant: citric acid for calcium carbonate scaling, sodium hydrosulfite for iron fouling 	<ul style="list-style-type: none"> - Delivery to 150-200 households - Supplied by bottle 1L or 20L capacity

(Source: Matsui, 2007)

The schematic diagram of a typical membrane plant is illustrated in Figure 2.2. Groundwater was pumped up to the receiving tank, which was connected to the pretreatment vessels and further on to the membrane modules. The pretreatment process consisted of a sand filtration tank (Sand Filter), a granular activated carbon adsorption tank (GAC Filter), and cation exchange reactor (CER Reactor). The Sand Filter was designed and operated for iron and manganese removal. The GAC Reactor was expected to reduce DOC in the groundwater. The CER Reactor was equipped basically with a strong acid cation exchange resin for Ca removal.

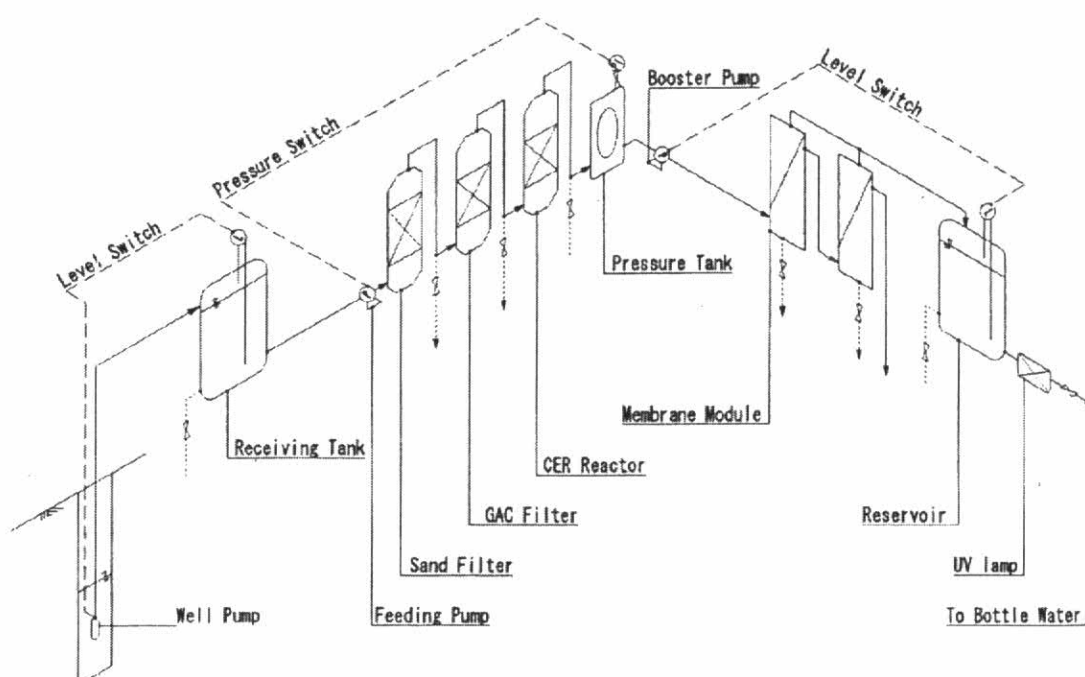


Figure 2.2 Diagram of typical membrane plant

2.1.3 Health effects of fluoride

Fluoride affects both the teeth and bones. The ingestion of excess fluoride can cause dental fluorosis and skeletal fluorosis. Fluoride concentrations in drinking water and the possible health effects are summarized in Table 2.2.

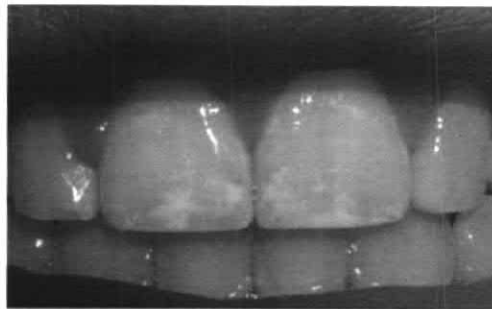
Table 2.2 Fluoride concentrations in drinking water and the possible health effects

Concentration of fluoride (mg/L)	Possible health effects
Less than 0.5	Dental cavities may occur
0.5 – 1.5	No adverse health effect; cavities decrease
Greater than 1.5	Mottling of teeth and dental fluorosis may occur
Greater than 3.0	Association with skeletal fluorosis at higher concentrations

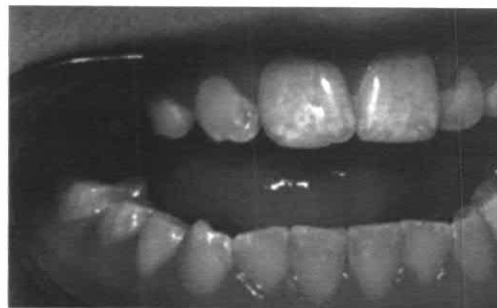
(Source: Guidelines for Drinking Water Quality. 1996. WHO, Geneva)

2.1.3.1 Dental Fluorosis

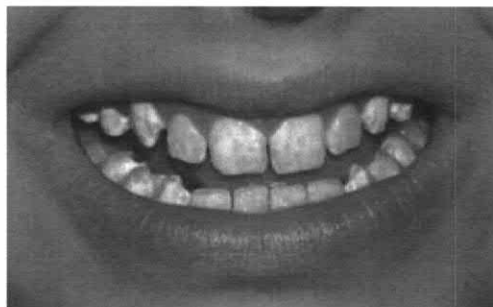
Dental fluorosis occurs because of the excessive intake of fluoride through naturally occurring fluoride in water, water fluoridation, toothpaste and/or other sources. Figure 2.3 shows examples of dental fluorosis. The damage in tooth development from the overexposure to fluoride occurs between the ages of 6 months to 5 years. Teeth are generally composed of hydroxyapatite and carbonated hydroxyapatite; when fluoride is present, fluorapatite is created. Excessive fluoride can cause the yellowing of teeth, white spots, and the pitting or mottling of enamel. Consequently, the teeth become unsightly. Fluorosis cannot occur once the tooth has erupted into the oral cavity. At this point, fluorapatite is beneficial because it is more resistant to dissolution by acids (i.e., demineralization) (Wikipedia, 2008).



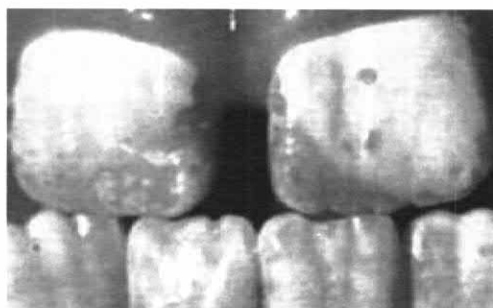
(a) Very Mild/ Mild Fluorosis



(b) Mild Fluorosis



(c) Severe Fluorosis



(d) Severe Fluorosis

Figure 2.3 Dental fluorosis

2.1.3.2 Skeletal Fluorosis

Skeletal fluorosis is a health-related effect of excessive fluoride accumulation in bones leading to changes in bone structure that make them extremely weak and brittle. The early stages of skeletal fluorosis are characterized by increased bone mass, which is detectable by X-ray. If very high fluoride intake persists over many years, joint pain and stiffness may result from the skeletal changes. The most severe form of skeletal fluorosis is known as "crippling skeletal fluorosis," which may result in ligament calcification, immobility, muscle wasting, and neurological problems related to spinal cord compression (Greenfacts, 2007). The examples of skeletal fluorosis were shown in Figures 2.4 and Figure 2.5.



Figure 2.4 Example of skeletal fluorosis in Lamphun province, Thailand

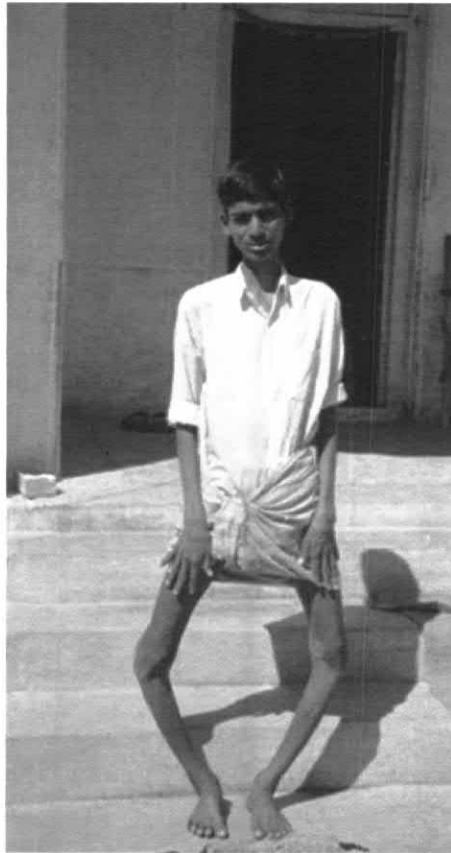


Figure 2.5 Skeletal fluorosis in India

2.2 Membrane Technology

2.2.1 Background

Membranes can be categorized into four types by the differential pressures on both sides of the membrane and the pore size of the membrane. There are microfiltration membranes (MF membranes), ultrafiltration membranes (UF membranes), nanofiltration membranes (NF membranes), and reverse osmosis membranes (RO membranes) (Metcalf and Eddy, 2003). A comparison of the five membranes is shown in Table 2.3.

Table 2.3 Comparing the five membranes: ULPRO, RO, NF, UF, and MF

	Ultra Low Pressure Reverse Osmosis	Reverse Osmosis	Nanofiltration	Ultrafiltration	Microfiltration
Membrane	Asymmetrical	Asymmetrical	Asymmetrical	Asymmetrical	Asymmetrical Symmetrical
Pore size	< 0.001 μm	< 0.002 μm	< 0.002 μm	0.2 - 0.02 μm	4 – 0.02 μm
Rejection	LMWC, Monovalent ions	HMWC, LMWC Glucose, Amino acids	HMWC, Polyvalent neg. ions	Macro molecules, Polysaccharides	Particles, Clay
Membrane material	Crosslinked Aromatic Polyamide, Thin film composite	Cellulose acetate, Thin film composite	Cellulose acetate, Thin film composite	Ceramic, Polysulfone, PVDF, Thin film composite	Ceramic, Polysulfone PVDF
Operating pressure	0.1-0.5 MPa	1.5-15 MPa	0.5-3.5 MPa	0.1-1 MPa	< 0.2 MPa
Method	Dead-end filtration Cross-flow filtration	Dead-end filtration Cross-flow filtration	Dead-end filtration Cross-flow filtration	Dead-end filtration Cross-flow filtration	Dead-end filtration Cross-flow filtration

(Source: Jørgen Wagner, 2001)

HMWC = High Molecular Weight Component, LMWC = Low Molecular Weight Component

PVDF = Polyvinylidenedifluoride

2.2.2 Membrane transport theory

Many mechanistic and mathematical models have been proposed to describe reverse osmosis membranes.

2.2.2.1 Irreversible thermodynamic model

The irreversible thermodynamic model has been used to describe the transportation of solute through a membrane. This model considers the membrane as a “block box”; it means that membrane structure and membrane properties are not taken into account (Dickson, 1988; Williams, M. E., 2003). Irreversible thermodynamics models assume the membrane is not far from equilibrium and so fluxes can be described by phenomenological relationships (Jonsson, 1980; Soltanieh and Gill, 1981; Dickson, 1988; van den Berg and Smolders, 1992).

Kedem and Katchalsky (1971) provided the equations for water flux based on membrane area (J_v) and the solute flux based on membrane area (J_i) in Equation (2-1) and Equation (2-2), respectively.

$$J_v = L_p(\Delta p - \sigma \Delta \pi) \quad (2-1)$$

$$J_i = \omega \Delta \pi + (1 - \sigma) \bar{C}_i J_v \quad (2-2)$$

where L_p = pure water permeability, σ = reflection coefficient, ω = solute permeability, and \bar{C}_i = logarithmic mean solute concentration.

2.2.2.2 Solution diffusion model

The solution-diffusion model was proposed by Lonsdale et al. (1995). This model is based on diffusion of the solute and solvent through the membrane. Differences in the solubilities and diffusivities of the solute and solvent in the membrane phase are important in this model since these strongly influence fluxes through the membrane (Williams, M. E., 2003).

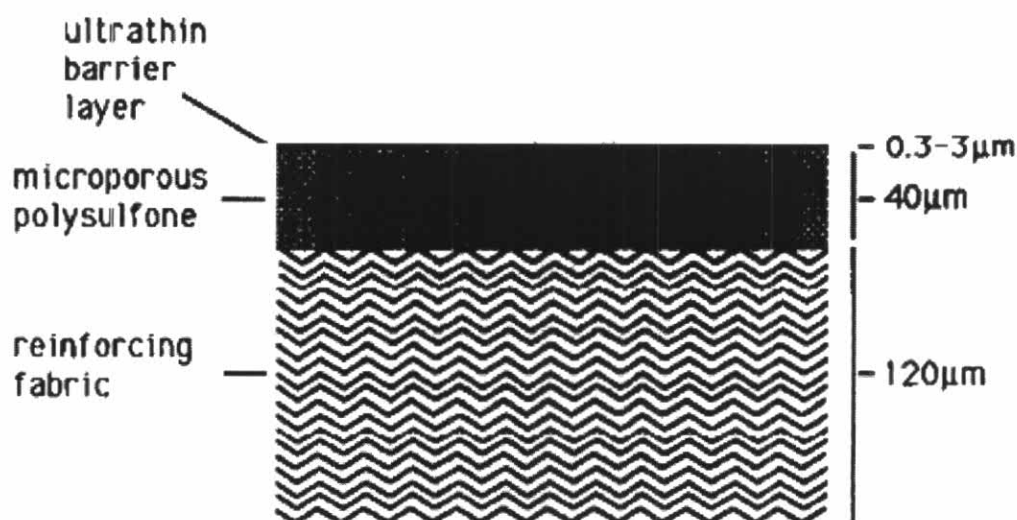
2.2.2.3 Charged membrane model

The charged RO membrane theory is used to predict ionic solute separations. These models account for electrostatic effects as well as for the diffusive and/or convective flow in order to describe solute separation. Donnan equilibrium models assume that a dynamic equilibrium is established when a charged membrane is placed in a salt solution (Bhattacharyya and Cheng, 1986; Bhattacharyya and Williams, 1992c). The counter-ion of the solution, opposite in charge to the fixed membrane charge (typically carboxylic or sulfonic groups), is present in the membrane at a higher concentration than that of the co-ion (same charge as the fixed membrane charge) because of electrostatic attraction and repulsion effects. This creates a Donnan potential which prevents the diffusive exchange of the counter-ion and co-ion between the solution and membrane phase. When a pressure driving force is applied to force water through the charged membrane, the effect of the Donnan potential is to repel the co-ion from the membrane; since electroneutrality must be maintained in the solution phase; the counter-ion is also rejected, resulting in ionic solute separation (Williams, M. E., 2003).

2.2.3 Ultra Low Pressure Reverse Osmosis (ULPRO) membrane

The ULPRO membrane can be operated at very low pressures. Most of ultra low pressure reverse osmosis (ULPRO) membranes are thin film composite membranes. The active membrane surface layer usually consists of negatively charged sulphone or carboxyl groups (Ozaki, H. et al. 2002).

Petersen (1993) concluded that a composite reverse osmosis membrane may be defined as a bilayer film formed by a two-step process. Such a membrane typically consists of a thick porous nonselective layer formed in the first process step, which is subsequently overcoated with an ultra thin barrier layer on its top surface in a second process step. A cross-section of a thin film composite membrane is shown in Figure 2.6.



(Source: Petersen, 1993)

Figure 2.6 Cross-section of thin film composite membrane

A base layer of a woven or a non-woven fabric is overcoated with a layer of an anisotropic microporous polymer (usually polysulfone). The surface of the microporous support is coated with an ultrathin veneer of polymeric composition, which provides the controlling properties such as semipermeability (Petersen, 1993).

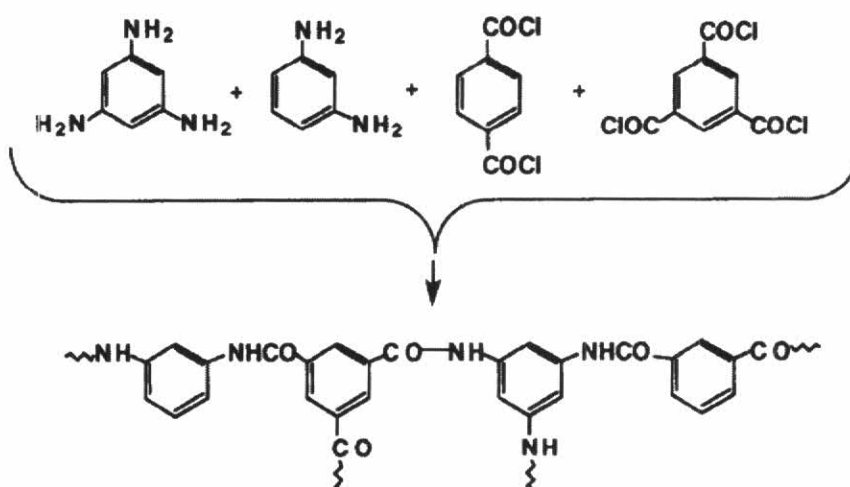
Petersen reported that the composite membrane approach has some key advantages relative to the asymmetric membrane approach. In a thin film composite membrane, each individual layer can be optimized for its particular function, i.e. the thin barrier layer can be optimized for the desired combination of solvent flux and solute rejection, while the porous support layer can be optimized for maximum strength and compression resistance combined with minimum resistance to permeate flow. Additionally, a vast variety of chemical compositions can be formed into thin barrier layers, including both linear and crosslinked polymers, whereas the asymmetric membrane formation process is quite limited to linear soluble polymers.

Wongrueng et al. (2006) studied fluoride removal in groundwater using an ULPRO membrane (UTC-70) and a nanofiltration membrane (UTC-60). Groundwater came from selected sites in a fluorotic area, namely the Pra Too Khong Bottled Drinking Water Plant (site A) and the San Pa Hiang Membrane Plant (site B). Site A produced that a fluoride concentration in the range of 12.05-16.98 mg/L, while site B produced a fluoride concentration in the range of 2.84-3.12 mg/L. Using UTC-

70 at 0.5 MPa and natural pH produced a 97% fluoride rejection in groundwater from site B and a 98% fluoride rejection in groundwater from site A.

2.2.4 Specification of the UTC-70 membrane

Petersen (1993) reported that UTC-70 was developed by the Toray Corporation of Japan and was the basis of their SU-700 series of spiral element products. This membrane contains an aromatic polyamide barrier layer consisting of the product of a blend of diamine (1,3-benzenediamine) and the triamine (which appears to be 1,3,5-benzenetriamine). The triacyl halide is apparently trimesoyl chloride, and the diacyl halide, terephthaloyl chloride. The probable chemistry of the UTC-70 membrane is shown in Figure 2.7.



(Source: Toray Industries)

Figure 2.7 The probable chemistry of the UTC-70 membrane

Some specifications of the UTC-70 membrane reported by Kurihara in 2003 are provided in Table 2.4.

Table 2.4 Specifications of the UTC-70 membrane

	UTC-70 membrane
Material	Crosslinked Aromatic Polyamide
Structure	Thin film composite membrane
Rejection	Low MW Organic materials, Monovalent ions
MWCO	MW ~ 60 ^a
Mechanism	Electric repulsion Solution diffusion Molecular interaction
Pore size	< 1 nm

(Source: Kurihara, Toray Company, 2003)

^a Yashinari, 1999

2.2.5 Osmotic pressure

Osmosis is the movement of a solvent through a semi-permeable membrane from the more dilute solution side to the more concentrated solution side (C.N. Sawyer et al., 2003). Osmotic pressure (π) is the excess pressure that needs to be applied to the solution to produce equilibrium of both sides.

Van't Hoff Equation can be use to determine of the osmotic pressure in a single salt solution, which can be calculated as follows:

$$\pi = i \cdot z \cdot nRT \quad (2-3)$$

where i = the permeation factor, z = the sum of the valency of the electrolyte, n = the salt concentration (mol/kg), R = the universal gas constants, and T = the temperature ($^{\circ}\text{K}$)

2.2.6 Concentration Polarization

Concentration polarization is an undesirable phenomenon. It can cause precipitation or the formation of a gel layer on the membrane surface when a solute concentration exceeds its saturation limit. The concentration polarization effect causes the solute concentration on a membrane surface to be higher than the concentration in the bulk solution (Sutzkover, I. et al., 2000). Figure 2.8 shows the concentration profile of a solute in a concentration polarization model.

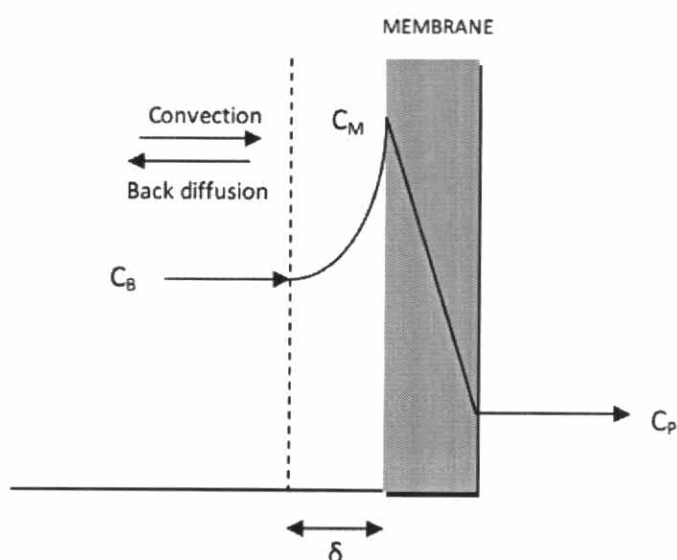


Figure 2.8 Concentration profile of a solute in a concentration polarization model

Solutes are carried to the membrane by the bulk motion of fluid (convection). As water permeates through the membrane, the rejected solutes are left behind to accumulate at the membrane surface. The rejected solutes diffuse away from the membrane surface due to the resulting concentration gradient (bulk diffusion) (Bader, M.S.H., 2006).

The negative effects of concentration polarization are as follows:

- Decreases in water flux due to increased osmotic pressure at the membrane wall
- Increases in solute flux through the membrane because of increased concentration gradient across the membrane

- Precipitation of the solute if the surface concentration exceeds its solubility limit, leading to membrane scaling or particle fouling and reduced water flux

- Changes in membrane separation properties

- Enhanced fouling by particulate or colloidal materials in the feed which block the membrane surface and reduce water flux

According to the thin-film model, the solute concentration on a membrane surface can be estimated by the following equation:

$$(J_v)_{solute} = k \ln \left(\frac{C_M - C_P}{C_B - C_P} \right) \quad (2-4)$$

where $k = (D/\delta)$ = the mass transfer coefficient, D = the diffusion coefficient, δ = the thickness of the boundary layer, $(J_v)_{solute}$ = the permeate flux of the solute solution, C_M = the solute concentration on the membrane surface, C_P = the solute concentration in the permeate solution, and C_B = the solute concentration in the bulk solution.

Sutzkover, I. et al. studied a simple technique for determining the mass transfer coefficient and the concentration polarization level in a reverse osmosis (RO) system. This technique is based on an evaluation of the permeate flux decline induced by the additional of a salt solution to an initially salt free water feed. The mass transfer coefficient is given by

$$k = \frac{(J_v)_{solute}}{\ln \left\{ \frac{\Delta P}{\pi_B - \pi_P} \cdot \left[1 - \frac{(J_v)_{solute}}{(J_v)_{H_2O}} \right] \right\}} \quad (2-5)$$

where $(J_v)_{H_2O}$ = the permeate flux of pure water, ΔP = the transmembrane pressure, π_B = the osmotic pressure of the bulk solution, and π_P = the osmotic pressure of the permeate solution.

In the solution-diffusion flow model, it was assumed that solute flow through membrane was a diffusion controlled and the solvent flow through a membrane was pressure controlled. The permeate flux of a solute solution, $(J_v)_{solute}$, and solute flux, J_i , through a membrane is given by

$$(J_v)_{solute} = k_w [\Delta P - (\pi_M - \pi_P)] \quad (2-6)$$

$$J_i = k_i (C_M - C_P) \quad (2-7)$$

where k_w = the water permeability of the membrane, k_i = the solute mass transfer coefficient through the membrane, and π_M = the osmotic pressure on the membrane surface.

The solute intrinsic rejection (R_{int}) of a membrane is defined by the following equation:

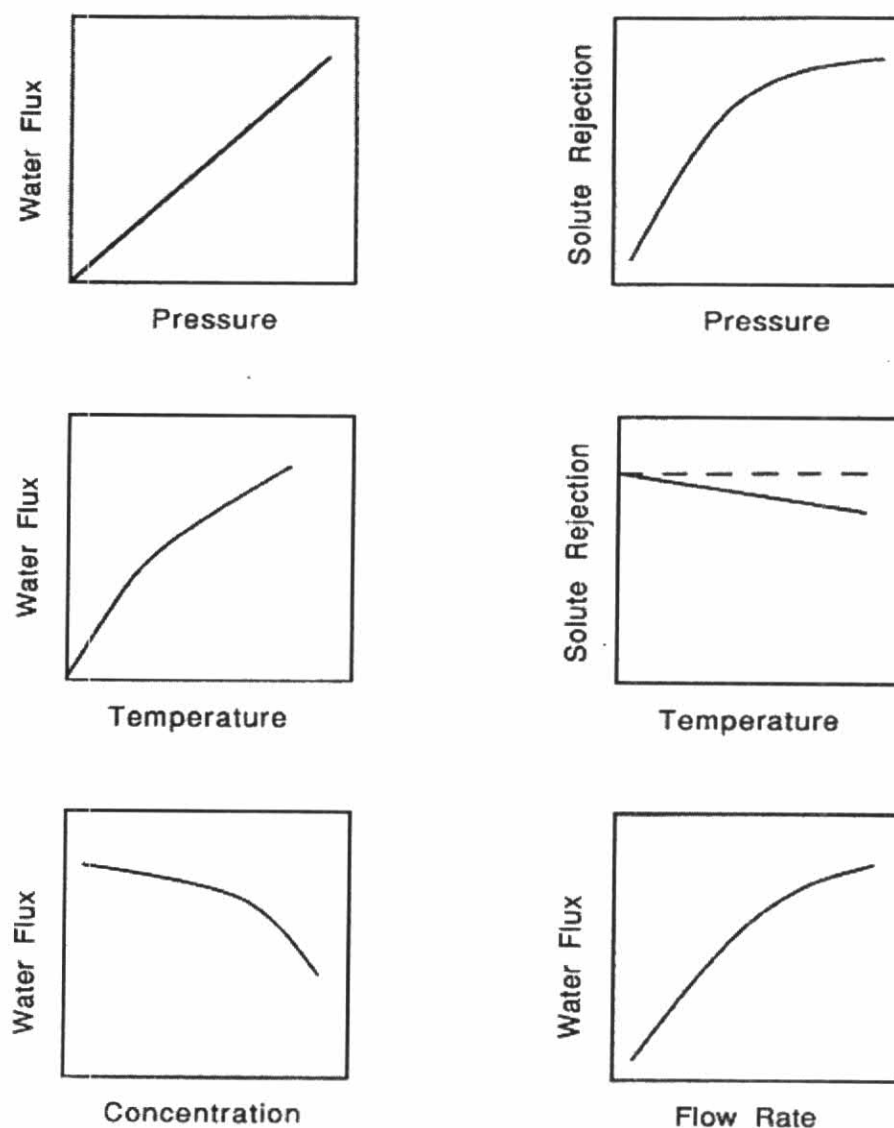
$$R_{int} = 1 - \frac{C_P}{C_M} \quad (2-8)$$

Consequently, the intrinsic rejection is higher than the observed rejection if concentration polarization is taken into consideration for membrane rejection. In a practical membrane process, the degree of solute rejection is applied by the observed rejection (R_{obs}), which is the concentration ratio between the concentration of the bulk solution and the concentration of the permeate solution (Matsui, Y., 2007).

$$R_{obs} = 1 - \frac{C_P}{C_B} \quad (2-9)$$

2.2.7 Effects of operating variables on RO separations

In membrane separation processes, some of the many factors affecting their performances include feed water variables such as temperature, pH, solute concentration, and pretreatment facilities; membrane system variables such as membrane type, membrane module, and module arrangement; and operating condition variables such as feed flow rate, operating pressure, operating time, and water recovery (Bhattacharyya et al., 1992; Williams, M. E., 2003). The effects of variables on RO separations are shown in Figure 2.9.



(Source: Williams, M. E., 2003)
Figure 2.9 Effects of variables on RO separations

Water flux increases linearly with applied pressure. Water flux also increases with temperature, since the water diffusivity in a membrane increases, and the water viscosity in a membrane decreases with temperature. The increase in water flux can be described by an Arrhenius temperature dependence of the water permeability constant or by the change in water viscosity (Sourirajan and Matsuura, 1985; Dickson, 1988; Mehdizadeh et al., 1989; Mehdizadeh and Dickson, 1991). Also, water flux is greater at higher feed flow rates since this minimizes concentration polarization (Williams, M. E., 2003).

Water flux decreases with increasing feed solute concentration since the higher concentrations result in larger osmotic pressures and a smaller driving force across the membrane. Water flux can also gradually decrease over the operating time because of compaction (mechanical compression) or other physical or chemical changes in the membrane structure (Bhattacharyya et al., 1992 and Williams, M. E., 2003).

It was found that solute rejection usually increases with pressure since water flux through the membrane increases while solute flux is essentially unchanged when pressure is increased; however, rejection of some organics with strong solute-membrane interactions decreases with pressure (Bhattacharyya and Williams, 1992c).

2.3 Membrane Fouling

2.3.1 Background

One of the major problems in the membrane filtration process is membrane fouling. Membrane fouling is referred to as a flux decline of a membrane filter caused by the accumulation of certain constituents in the feed water on the surface of the membrane or in the membrane matrix (Liu, C. et al., 1998).

According to the type of fouling materials, fouling can be categorized into four types: inorganic fouling/scaling, particles/colloids fouling, microbial fouling, and organic fouling (Liu, C. et al., 1998).

2.3.1.1 Inorganic fouling/scaling

Inorganic fouling or scaling is caused by the accumulation of inorganic precipitates, such as metal hydroxides and scales on the membrane surface or within the pore structure. Precipitates are formed when the concentrations of chemical species exceed their saturation concentrations. Scaling is a major concern for reverse osmosis (RO) and nanofiltration (NF).

2.3.1.2 Particles/colloids fouling

The particles and colloids are referred to as biologically inert particles and colloids that are inorganic in nature; they originate from the weathering of rocks. During the filtration process, particles and colloids retained by a membrane will form a cake layer on the membrane surface.

2.3.1.3 Microbial fouling

Microbial fouling results from the formation of biofilms on membrane surfaces. Once the bacteria attach to the membrane, they start to multiply and produce extracellular polymeric substances (EPSs) that form a viscous, slimy, and hydrated gel.

2.3.1.4 Organic fouling

Organic fouling is profound in membrane filtration with source water containing relatively high natural organic matter (NOM). Surface water typically contains higher NOM than groundwater.

2.3.2 Silica fouling

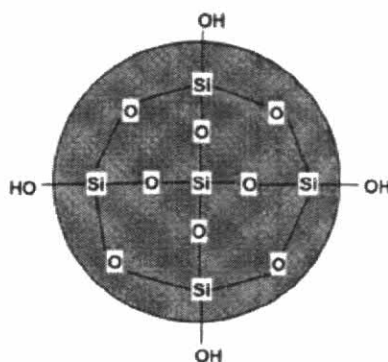
Silica (SiO_2)_n is widely found in the environment. It is a noncombustible colorless to white in color, tasteless crystal. Silica occurs naturally in amorphous and crystalline forms (Sahachaiyunta, P., et al., 2002). Alexalder et al. found that amorphous silica, a general term for any silica lacking crystal structure, has a solubility of 100-140 ppm SiO_2 at 25°C.

Silica fouling has been described as a major unsolved problem in desalination units (Sheikholeslami, R., and Tan, S., 1999). The deleterious effects are reductions in process equipment efficiency due to high-pressure drops, damage to

membranes, unsteady-state operations as well as increases in energy losses and the overall cost (Sahachaiyunta, P. et al., 2002). Silica can be separated into three categories depending on its size: dissolved silica or reactive silica ($< 0.001 \mu\text{m}$), colloidal silica ($0.001 - 1 \mu\text{m}$), and particulate silica ($> 1 \mu\text{m}$), respectively.

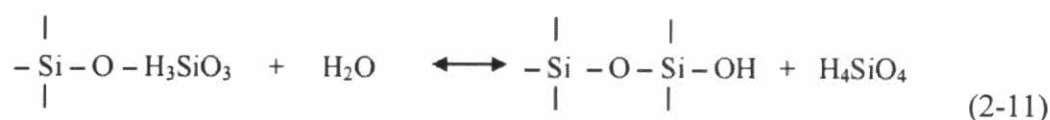
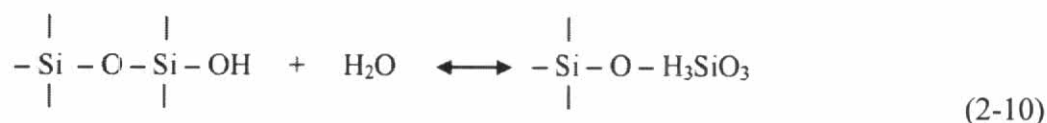
Reactive silica, also known as “dissolved silica,” is a silicon dioxide dissolved in water that creates a compound known as monosilicic acid (H_4SiO_2). Colloidal silica is widely thought to be either a silicon that has polymerized with multiple units of silicon dioxide or a silicon that has formed loose bonds with organic compounds or with other complex inorganic compounds. Particulate silica is larger in size and mostly comprised of sand or suspended solids in water.

The silica $(\text{SiO}_2)_n$ structure is shown in Figure 2.10. Thus, the molecules of silica represented by the formula SiO_2 is polymeric form, and is more accurately represented by the formula of $(\text{SiO}_2)_n$ where n is infinite in number, allowing for extensions in term of amorphous and crystalline forms of silica (R. Y. Ning et al., 2002).



(Source: K.D. Demadis et al., 2005)
Figure 2.10 Silica $(\text{SiO}_2)_n$ structure

The dissolution process of silica in water occurs when silicon-oxygen bonds (Si-O-Si) are hydrolyzed. Fleming (1986) proposed that a mechanism for the dissolution of silica included 2 steps. Firstly, water molecule will adsorb on the hydroxylated silica surface as shown in Equation (2-10). Then, the water-adsorbed silica form will further react with another water molecule to form monosilicic acid (H_4SiO_4) as given in Equation (2-11).



The reversible reaction of monomer aqueous silica with SiO_2 polymorphs is commonly written as (Sjoberg, 1996):



There are two relevant categories of fouling, namely precipitation fouling and particulate fouling. Precipitation fouling occurs when monomeric silica polymerizes at the membrane surface, also called scaling or polymerized silica fouling. On the other hand, particulate fouling involves the accumulation of colloids that are formed initially in bulk solution and deposited subsequently on the membrane surface (Sahachaiyanta, P. et al., 2002).

The groundwater quality of Lamphun province from 133 wells was investigated (Matsui, 2007). It was found that the average SiO_2 concentration in the groundwater was 28 mg/L. The SiO_2 concentration was not being removed by the pretreatment process. Membrane fouling with SiO_2 would not be a critical factor in a short period of time but the membranes may gradually become attached in the long run.

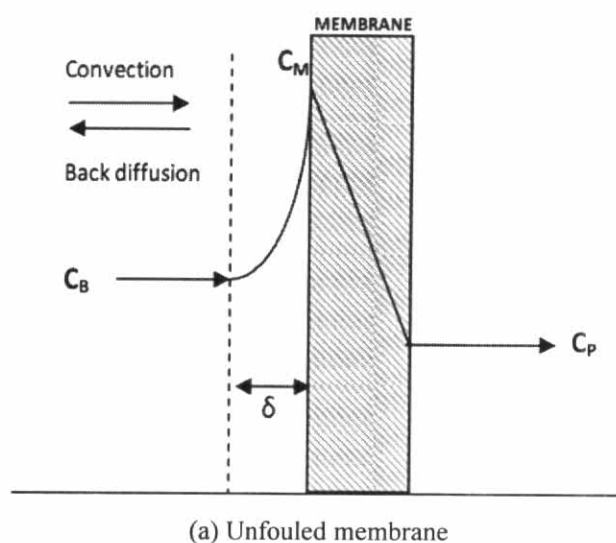
Matsui et al. (2007) observed the effects of fouling on membrane operation and fluoride rejection. CaF_2 , CaCO_3 , and SiO_2 are considered to be the causes of membrane fouling. A 2-level, 3-factor experimental design was arranged by taking fluoride, CaCO_3 , and SiO_2 concentrations as the factors. SiO_2 in feed water caused the maximum flux decline among the 3 factors. It was found that despite the SiO_2 concentration being below the saturation concentration in the feed bulk water, SiO_2 became saturated on the membrane surface. The gel layer formed by monosilicic silica was found to be densely polymerized with low permeability. Despite membrane

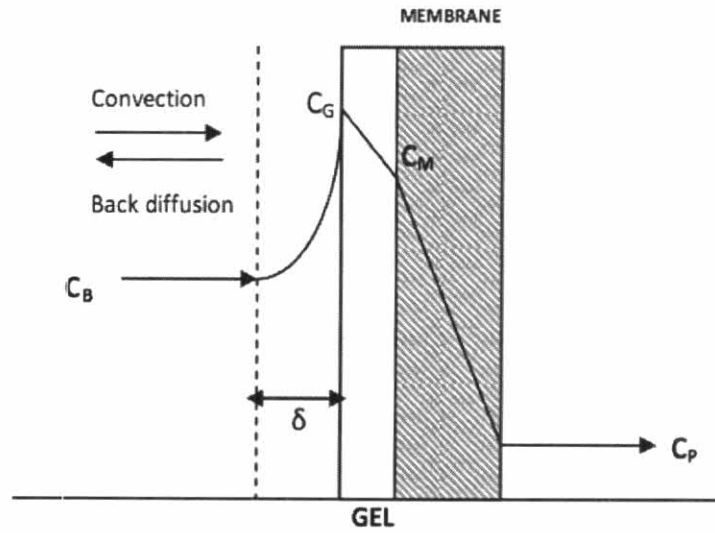
fouling due to CaF_2 , CaCO_3 , and SiO_2 , fluoride removal by the membrane was maintained as high as it was on a virgin membrane.

Koo et al. (2001) studied silica fouling and the membrane cleaning of reverse osmosis membranes. It was found that increasing the concentration of calcium and magnesium enhanced the polymerization of silica. The presence of calcium and magnesium in low concentrations did not help catalyze silica polymerization. But the presence of calcium and magnesium in higher concentrations did help catalyze silica polymerization. At silica concentrations greater than 300 ppm, polymerization took place even in the absence of calcium and magnesium. Moreover, carbonate was found to have a greater effect on silica polymerization than chloride. It was found that carbonate ions promoted silica polymerization more than chloride ions. In addition, the cleaning of membranes by using distilled water did not restore the membrane fluxes properly.

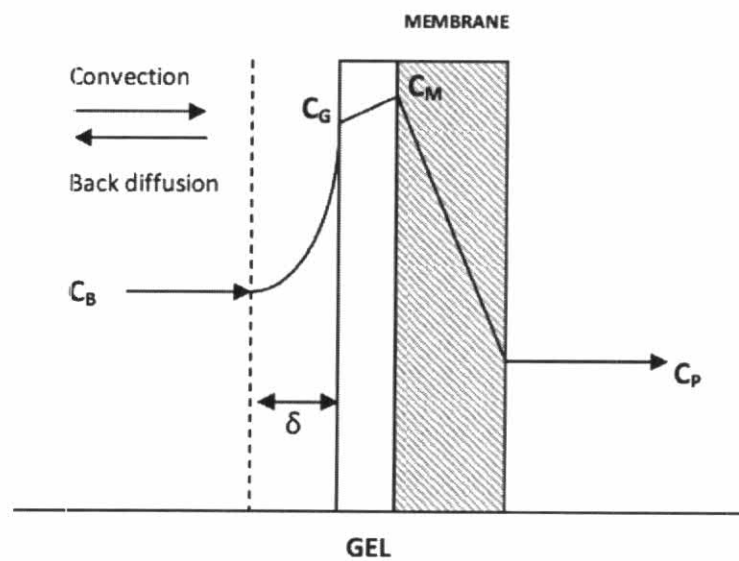
Sahachaiyunta reported that the type and extent of silica fouling depends on the condition of the system such as the silica concentration, pH of feed solution, temperature, and presence of other species.

A schematic profile of fluoride concentrations in the bulk solution, gel layer, membrane surface, and permeate water of an unfouled membrane, a membrane with a polymerized fouled layer (dense-gel layer), and a membrane with a colloidal fouled layer (loose-gel layer) are shown in Figure 2.11.





(b) Polymerized fouled layer (dense-gel layer)



(c) Colloidal fouled layer (loose-gel layer)

Figure 2.11 A schematic profile of fluoride concentrations in the bulk solution, gel layer, membrane surface, and permeate water