

CHAPTER II

LITERATURE REVIEWS

2.1 Chromium

Chromium is a *d*-block transition metal of Group VIB of the Periodic Table. It has an atomic number of 24 and an atomic weight of 51.996 (Rollinson, 1975).

Chromium has been used in alloy steels since about 1877, and chrome plating dates from about 1926. Chromium metal is grey and brittle and can be highly polished. It occurs in +3 and +6 oxidation states in the environment, though Cr (III) (Cr^{3+}) is the most stable; ionic radii are 0.052-0.053 nm for Cr^{6+} and 0.064 nm for Cr^{3+} (Rollinson, 1975). Table 2-1 shows some properties of chromium.

Table 2-1 Some nuclear properties of chromium

Property	Value
Atomic number (Z)	24
Atomic weight	51.996
Color	grey
Melting point (m.p.)	1903+10°C
Boiling point (b.p.)	2642°C

Source: The chemistry of chromium, molybdenum and tungsten, 1975

2.1.1 Usage

Chromium is produced from the ore chromites, which is mixed oxide with the general formula $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ but also variable amounts of Mg and Al. Of the 10^7 t of Cr produced annually, about 60-70% is used in alloys including stainless steel which contains Fe, Cr and Ni in varying proportions according to the properties required in the final product. Alloy steels contain 10-26% Cr. The refractory properties of Cr exploited in production of refractory bricks for lining furnaces and kilns, accounting for approximately 15% of the chromate ore used. About 15% is also used in the general chemical industries, e.g. chrome alum (Cr (III)) for tanning leather, pigments and wood preservatives (sodium dichromate) (McGrath and Smith ref. in Alloway, 1993). Major uses of Cr chemicals are shown in Table 2-2 about 4% is converted into chromic acid and used for electroplating as an oxidant.

Table 2-2 Some uses of chemicals containing Cr

Antifouling pigments	Emulsion hardeners	Metal finishing	Tanning
Antiknock compounds	Flexible printing	Metal primers	Textile preservatives
Catalysts	Fungicides	Mordant	Textile printing and dyeing
Ceramics	Gas absorbers	Phosphate coatings	Wash primers
Corrosion inhibitors	High-temperature batteries	Photosensitization	Wood preservatives
Drilling mud	Magnetic tapes	Pyrotechnics	
Electronics		Refractory	

Source: Alloway, 1993

2.1.2 Geochemical occurrence

Chromium is the seventh most abundant element on Earth, but 21st in abundance in the crystal rocks, with an average concentration of 100 mg/kg rock. Chromium is found in igneous rock where it readily substitutes for Fe which has an ionic radius of 0.067 nm, close to that of Cr (III). Mafic and ultramafic rocks are richest in Cr, containing up to 3400 mg/kg of Cr (Table 2-3).

Table 2-3 Concentrations of chromium in various types of rocks (mg/kg)

	Cr	
	Average	Range
Ultramafic igneous	1800	1000 – 3400
Basaltic igneous	220	40 – 600
Granitic igneous	20	2 – 90
Shale and clay	120	30 – 590
Black shale	100	26 – 1000
Limestone	10	-
Sandstone	35	-

Source: Alloway, 1993

2.1.3 Chromium behavior in the natural water

Chromium may exist in number of oxidation states, but the most stable and common forms are Cr (III) and Cr (VI). These have sharply contrasting chemical properties: Cr (VI) exists as an anion, it is more readily extracted from soil and sediment particles and is considered the more toxic form. Chromate is in pH-dependent equilibrium with other forms of Cr (VI) such as HCrO_4^- and dichromate ($\text{Cr}_2\text{O}_7^{2-}$), with CrO_4^{2-} the predominant form at $\text{pH} > 6$. Chromium (III) on the other hand, is much less mobile and adsorbs to particulates more strongly (McGrath and Smith ref. in Alloway, 1993). The solubility of Cr (III) decreases above pH 4, and above pH 5.5 complete precipitation occurs (Rai, 1987 ref. in Phannasawat and Chawanparid, 1993). Chromium (VI) is the more stable form in equilibrium with atmospheric oxygen. However, Cr (VI), with its high positive reduction potential, is a strongly oxidizing species, and in the presence of soil organic matter Cr (VI) is reduced to Cr (III). Figure 2-1 summarized about chromium transformation and distribution in natural water.

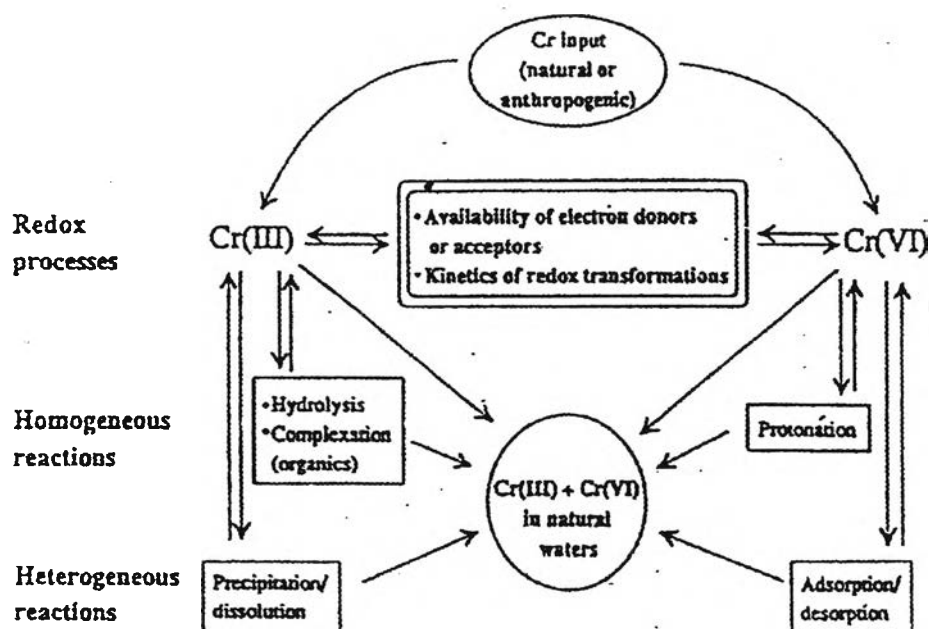


Figure 2-1 Aqueous geochemistry of chromium

(Richard, 1991 ref. in Phannasawat and Chawanparid, 1993).

2.1.4 Biological aspects

Chromium is essential to life. A deficiency (in rats and monkeys) has been shown to impair glucose tolerance, decrease glycogen reserve, and inhibit the utilization of amino acids. It has also been found that inclusion of chromium in the diet of humans sometimes, but not always, improves glucose tolerance. Certain chromium (III) compounds enhance the action of insulin (Mertz, 1969 ref. in Rollinson, 1975).

On the other hand, chromate and dichromate are severe irritants to the skin and mucous membranes, so workers who handle large amount of these materials must be protected against dusts and mists. Continued breathing of the dusts finally leads to serious ulceration and perforation of the nasal septum. Contact of cuts or abrasions with chromate may lead to serious ulceration. Even on normal skin, dermatitis frequently results. Cases of lung cancer have been observed in plants where chromates are manufactured (Mertz, 1969 ref. in Rollinson, 1975).

2.2 Tanning industry

Tanning is defined as the preservation of hides or skin by use of a chemical that (1) makes them immune to bacterial attack; (2) raises the shrinkage temperature; and (3) prevents the collagen fibers from sticking together on drying, so that the material remains porous, soft and flexible. Vegetable tanning is used mostly for sole and heavy-duty leathers. The chief vegetable tannins are water extracts of special types of wood or bark, especially quebracho and wattle. The main active constituent is tannic acid. The tannins penetrate the skin or hides after long periods of soaking, during which the molecular aggregates of the tannin form cross-links between the polypeptide chains of the skin protein; hydrogen bonding is an important factor (Lewis, 1997).

In mineral or chrome tanning, the sulfates of chromium, aluminium, and zirconium are used (the last two for white leather); here the reaction is of a coordination nature between the carboxyl groups of the skin collagen and the metal atom. Syntans are also used; these are sulfonated phenol or naphthols condense with formaldehyde. Condensation products other than phenol having strong hydrogen-bonding power have been developed. Tanning by any method is time-consuming and exacting process, requiring careful control of pH, temperature, humidity, and concentration factors. (Lewis, 1997)

The leather industry uses a wide range of chemicals which may subsequently appear in liquid, sludge or solid waste arising from various tanning processes such as cleaning, chemical surface treatment and dyeing (Rahman, 1997).

Leather is tanned animal hide or skin free of hair and subcutaneous tissue. Tanning is a durable preservation of perishable biological material. The transformation of hides and skins into leather, which contains the original fibrous structure, involves the removal of a great part of hide substances like hair, soluble proteins, epidermis, fat, flesh, blood, etc., by mechanical and chemical processes. To facilitate this works, to save time and water and to confer desired characteristics to the end product, a multitude of chemicals are employed. The combination of excess chemicals and their transformation products, residues of the hide substances dissolved or suspended in water compose the different effluents, solid wastes and by-products of the leather production (Rahman, 1997).

One ton of raw hides yield an average of 0.2 ton leather, up to 0.6 ton solid wastes and by-products about 50 cubic meter effluents. Figure 2-2 gives an overview.

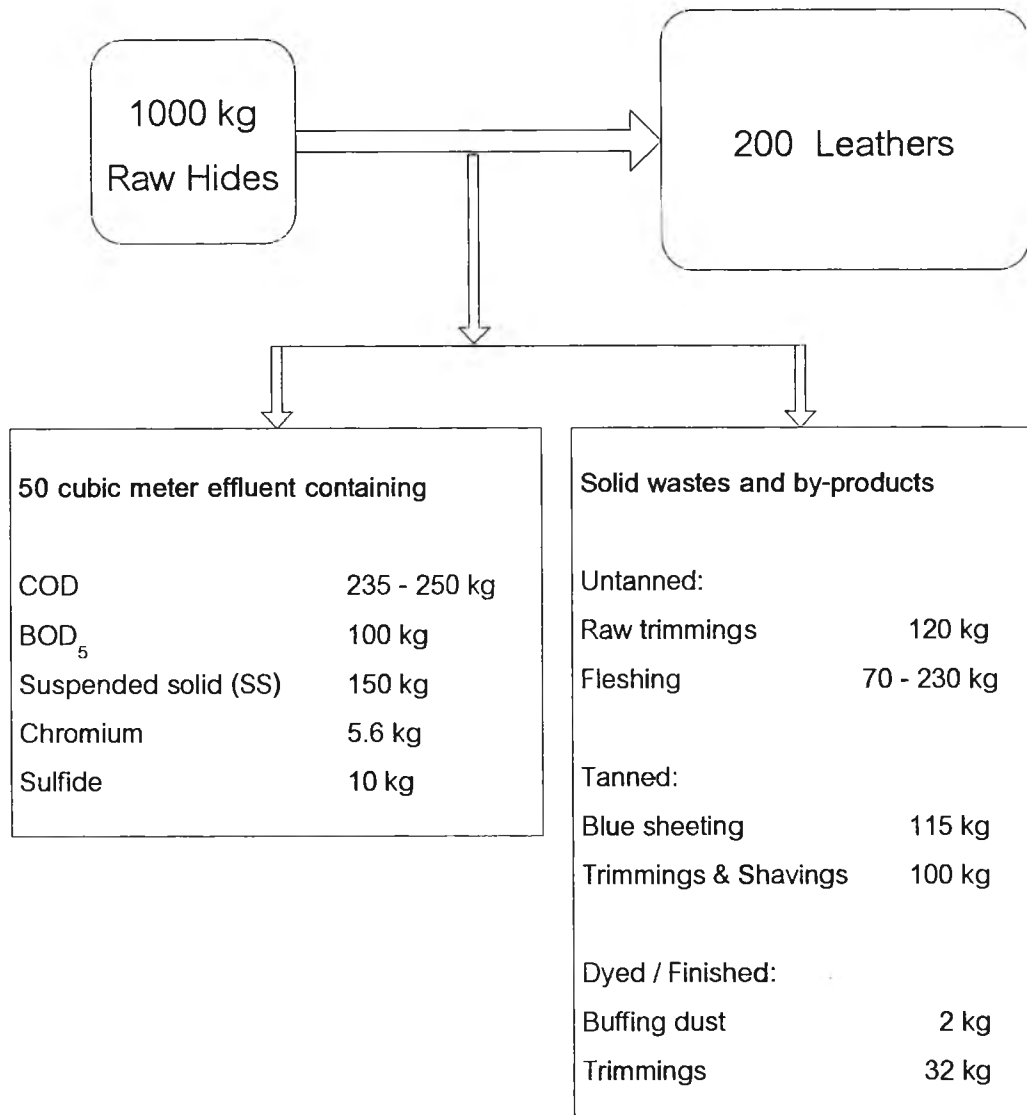


Figure 2-2 Solid and liquid waste produced during leather processing

(Adapted from Rahman, 1997)

Due to the variety of recipes used by tanneries an exact mass balance must be calculated for each plant in particular. Figure 2-3 shows the processes of leather production.

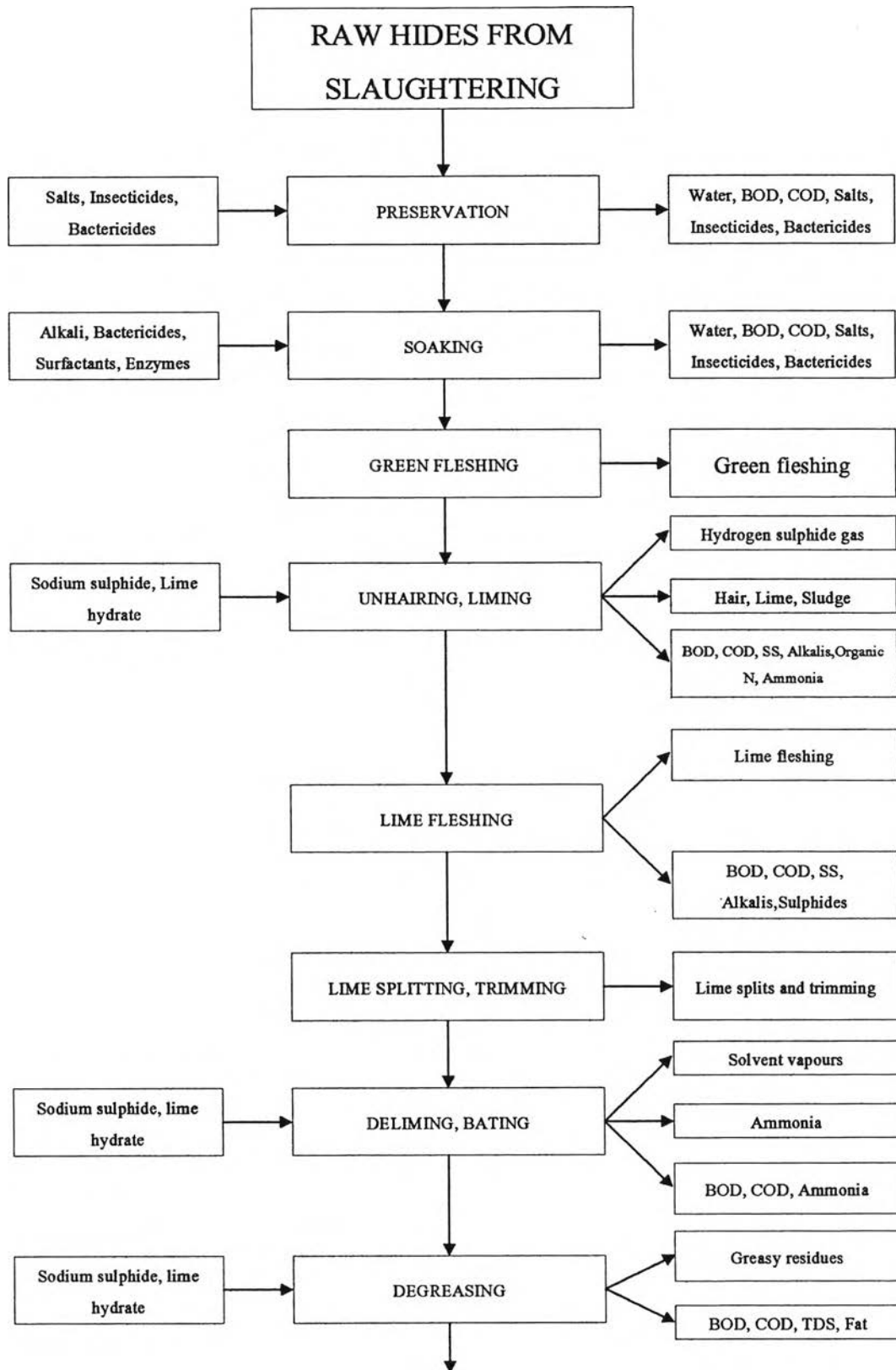


Figure 2-3 Process flow of leather production

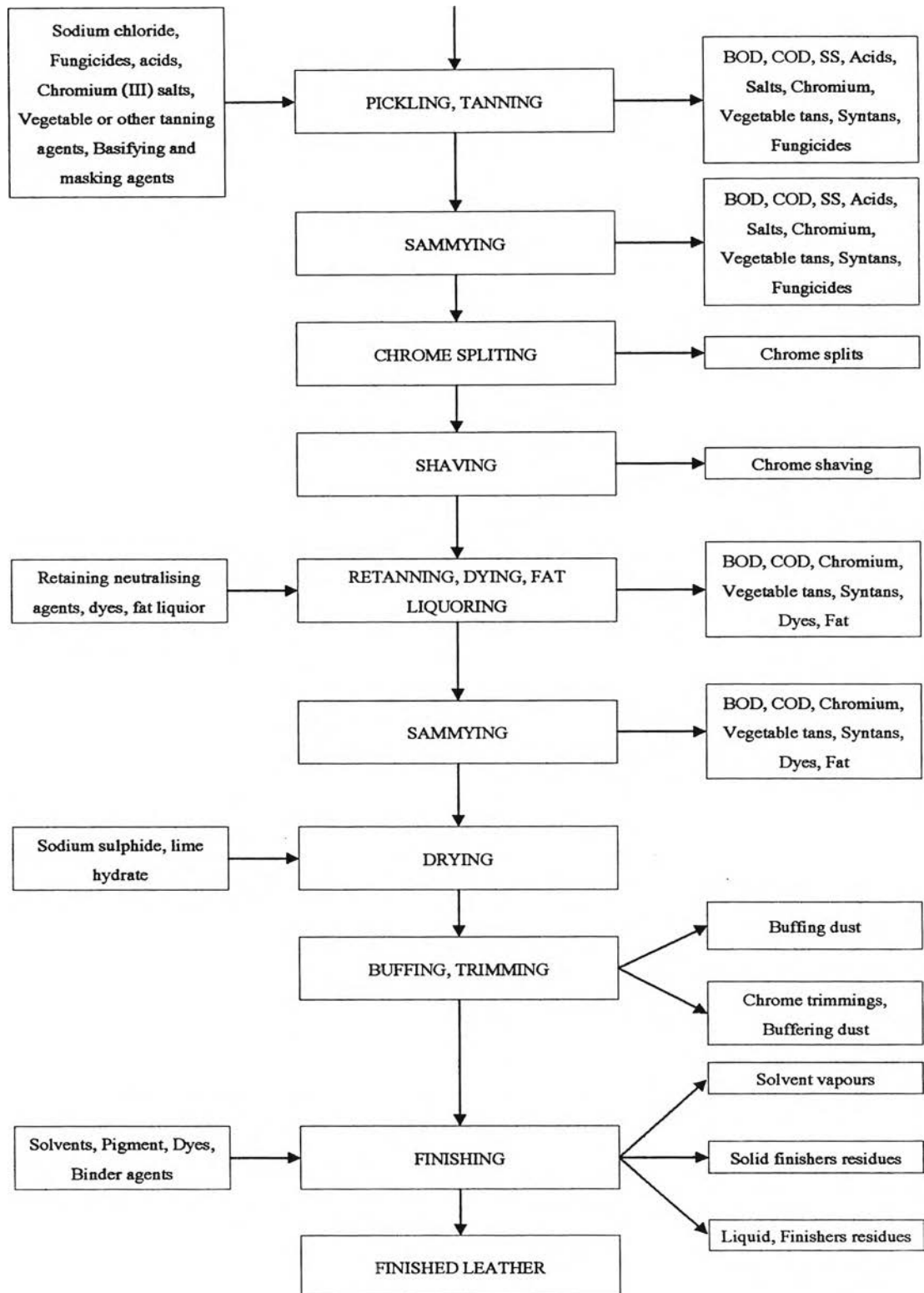


Figure 2-3 Process flow of leather production (cont.) (Adapted from Rahman, 1997)

2.3 Constructed wetland systems

Wetlands are defined as land in which the water table is above or at the ground surface level for a sufficient length of time to maintain saturated soil conditions and the growth of micro-organisms and related vegetations. Natural wetlands have been used for wastewater treatment and polishing but they have some operational limitations due to difficulties in hydraulic control and potential interference of the wastewater constituents on wildlife habitat and ecosystems (Poh-eng and Polprasert, 1996).

Constructed or artificial wetlands, that represent an emerging ecotechnological treatment system, are designed to overcome the disadvantages of natural wetland systems, but possess the positive attributes of a natural wetland. A constructed wetland is anticipated to perform better than a natural wetland of equal area as a bottom is usually graded and the hydraulic regime in the system is controlled. Process reliability is also improved because the vegetation and other major components of constructed wetlands can be managed as required. Constructed wetlands can be created from existing marshlands or built at any place including on lands with limited alternative uses. The emergent aquatic plants most commonly planted in constructed wetlands are cattails (*Typha*), common reeds (*Phragmites*), bulrushes (*Scirpus*) and sedges (*Carex*)

In general, natural treatment systems can be constructed and operated at a lower cost than conventional systems. Among the aquatic treatment systems, constructed wetlands have a greater potential in wastewater treatment because they can tolerate higher organic loading rate and shorter hydraulic retention time with improved effluent characteristics (Table 2-4). Consequently, land area requirement for constructed wetlands have the capability of treating more than one type of pollutants such as BOD, total nitrogen and suspended solids simultaneously to some satisfactory levels. This can rarely be achieved by other aquatic systems (Poh-eng and Polprasert, 1996).

Table 2-4 Comparison of design features and expected performance among the aquatic treatment systems

Systems	Treatment goals	Typical criteria				Effluent characteristics		
		Climate needs	HRT days	Depth m	OLR kg/ha.d	BOD mg/l	TN mg/l	TSS mg/l
Oxidation pond	Secondary	Warm	10 – 40	1 – 1.5	40 – 120	20 – 40	-	80 – 140
Facultative pond	Secondary	None	25 – 180	1.5 – 2.5	22 – 67	30 – 40	-	40 - 100
Aerated pond partially mixed	Secondary, polishing pond	None	7 – 20	2 – 6	50 – 200	30 – 40	-	30 - 60
Storage and controlled discharge pond	Secondary, storage, polishing	None	100 – 200	3 – 5	-	10 - 30	-	10 - 40
Hyacinth pond	Secondary	Warm	30 – 50	< 1.5	< 30	< 30	-	< 30
Hyacinth pond	AWT, with secondary input	Warm	> 6	< 1	< 50	< 10	< 5	< 10
Natural marsh	Polishing, AWT, with secondary input	None	14	0.2 – 1	< 4	5 - 10	5 - 10	5 - 15
Constructed wetland (FWS)	Secondary, or AWT	None	5 – 10	0.1 – 0.3	100 – 110	5 – 10	5 - 10	5 - 10
Constructed wetland (SF)	Secondary, or AWT	None	5 - 10	-	80 - 120	5 - 40	5 - 20	5 - 20

Note: AWT is Advance Wastewater Treatment

2.3.1 Types of constructed wetlands

Constructed wetlands are classified into only two types in general: namely, free water surface systems (FWS) and subsurface flow systems (SF).

1) Free water surface systems (FWS)

This system (Fig.2-4) mimics natural marshlands. It has a natural or constructed clay layer or impervious liner made of geotechnical material as bottom to prevent seepage. Above the impervious layer is the soil or other suitable medium to support the growth of emergent plants. Wastewater, at a relatively shallow depth, flows horizontally over the soil surface. The configuration of the system, which is usually in the form of long narrow channel, the shallow water depth, low flow velocity and presence of plant stalks, as well as litter, provide the necessary conditions for near plug-flow hydraulic pattern.

2) Subsurface flow systems (SF)

This system has is also variously known as Vegetated Submerged Bed (VSB); Root Zone System; Rock Reed Filter; or Microbial Rock Filter. The SF wetlands basically consist of the same components as the FWS systems, but the wastewater is confined to the substratum. The media supporting plant growth normally consist of soil, sand, gravels and rocks in that order downwards to provide better bed porosity (Fig.2-5). The flow format of wastewater can be up flow, down flow or horizontal flow with the more commonly encountered SF wetlands belonging to the horizontal type. Most systems have been designed with 1 % slope or slightly higher.

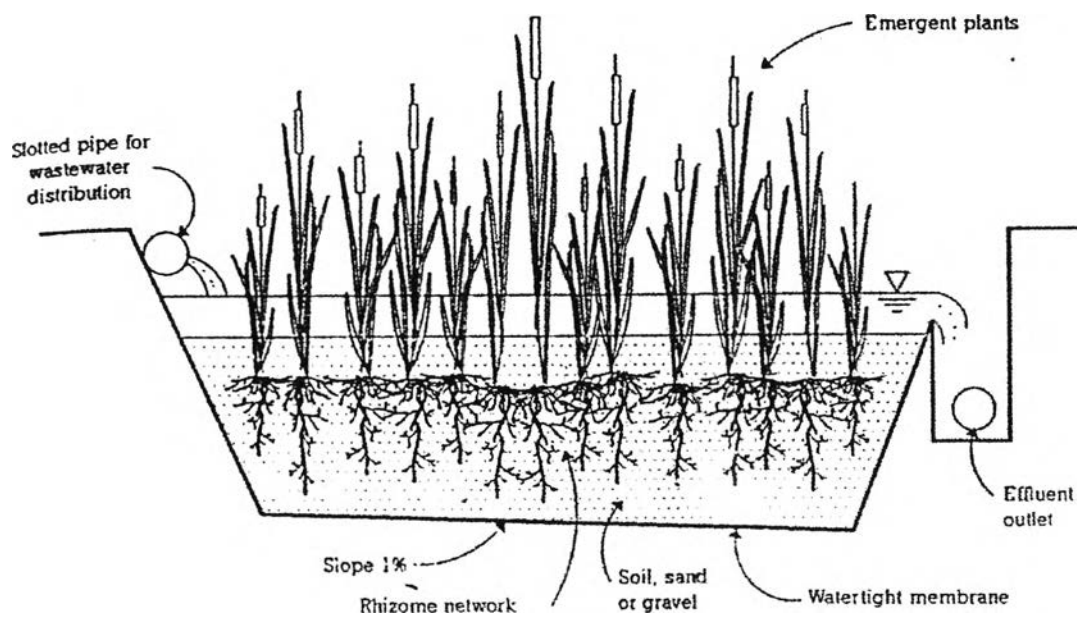


Figure 2-4 Free water Surface wetland system (FWS)

(Poh-eng and Polprasert, 1996)

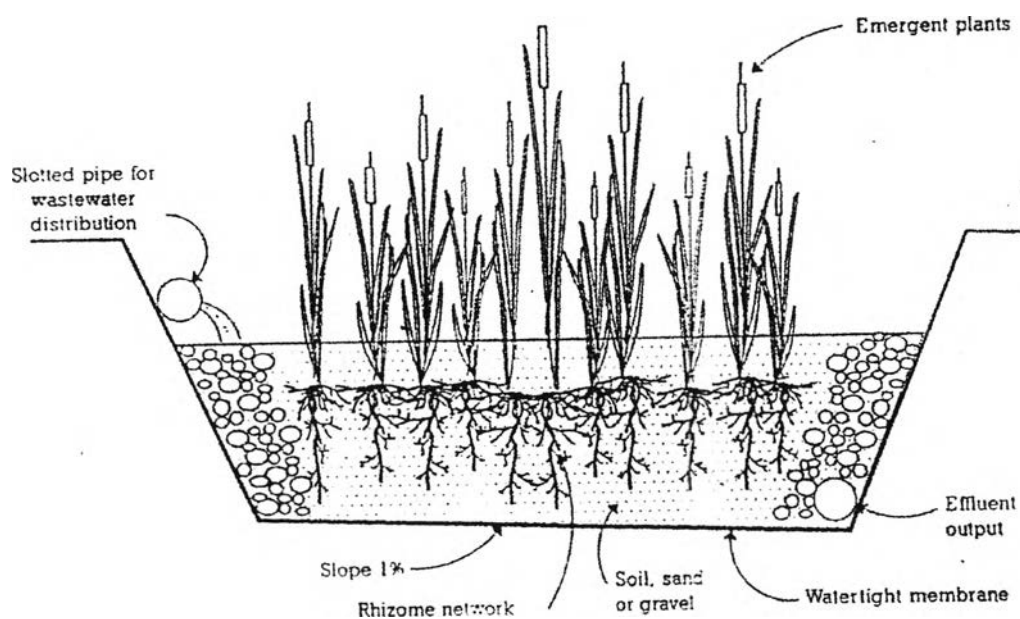


Figure 2-5 Subsurface flow wetland system (SF)

(Poh-eng and Polprasert, 1996)

When the wastewater flows through the media, it is being purified through contact with the surfaces of the media and the root zone of the plants. The subsurface zone is generally anoxic but the plants can transfer excess oxygen to the root system thus creating aerobic micro-sites adjacent to the roots and rhizomes. There is also a thin aerobic zone in the substratum adjacent to the air-soil interface.

2.3.2 Wetland components

The major system components having some influence in the treatment process in wetlands are the vegetation, media, bacteria and animal, but only the first two can be selected for optimum wetland design.

1) Vegetations

Many types of aquatic plants have been used in wetland systems designed for wastewater treatment but the plants most commonly used in constructed wetlands include cattails, reeds, rushes, bulrushes and sedges. All these plants are ubiquitous and tolerate freezing conditions. In terms of species suitability, reeds and bulrushes are normally selected for SF systems because deeper rhizome penetration allows for the utilization of deeper beds.

For FWS wetlands, the water depth in the systems is one of the important factors for the selection and maintenance of wetland vegetation. Cattails grow well in water depths over 0.15 m. Bulrushes can tolerate water depths of 0.05 m. - 0.25 m. whereas reeds are poor competitors in shallow waters. The above factors notwithstanding, it is important to stress that the species dominating in the local area should preferably be selected for both SF and FWS Wetlands to ensure successful establishment and maintenance over time.

2) Media

Wetland vegetations can propagate in many different soils and in gravel. The void spaces in the soil or other media serve as the flow channels for the SF wetlands during which treatment is provided by microorganisms attached to the roots, rhizomes and the adjacent soil or media surfaces. Very often gravel beds are used because they can handle higher hydraulic loading rate with less susceptibility to media clogging than soil beds. The type of media for FWS systems is not crucial but a media depth above the impervious barrier that is at least equal to the maximum root penetration is recommended.

2.3.3 Treatment process mechanisms

1) Solids removal

Settleable solids are removed easily via gravity sedimentation as wetland systems generally have long hydraulic retention times. Nonsettling/colloidal solids are removed via mechanisms which include: straining (if sand media is used); sedimentation and biodegradation (as a result of bacterial growth); and collisions (inertial and Brownian) with an adsorption (van der Waals forces) of other solids (plants, soil, sand and gravel media etc.). For gravel media which forms an important component in a subsurface flow wetland system, Sapkota and Bavor (1994) suggested that the suspended solids removal is primarily by sedimentation and biodegradation similar to what is occurring within a trickling filter.

In short, the kinds of removal mechanism at work are very dependent on the sizes and nature of solids present in the wastewater and the types of filter media used. In all cases, wetland vegetation has a negligible role to play in solids removal.

2) Heavy metals removal

When dissolved metals entered a wetland ecosystem, possible removal mechanisms include:

- Precipitation as insoluble metal hydroxides in the aerobic zone and metal sulfides in the anaerobic zone of the substratum,
- Adsorption onto precipitates of iron and manganese oxyhydroxides in the aerobic zone,
- Complexation or chelation with dead plant materials and soil media, and
- Uptake into roots, rhizomes and leaves of wetland vegetations.

Research efforts thus far have not been able to identify the dominant removal mechanism among those listed above, but it is generally agreed that vegetative uptake of metals accounts for only a small part of the total metal input (Gersberg et al., 1984; Reed et al., 1988; Wildemann and Laudon, 1989; Dunbabin and Bawmer, 1992 ref. in Poh-eng and Polprasert, 1996). Nonetheless, wetland plants can influence metals removal and storage indirectly through their effects on hydrology, sediment chemistry and microbial activity. Since the substratum is the major sink for metals, the maximum capacity for metals retention eventually will be reached. Ultimate removal of heavy metals from wetland systems will be by dredging the substratum for proper disposal.

2.3.4 General design procedures

The principal process variables for constructed wetland systems include organic loading rate (OLR), hydraulic loading rate (HLR), hydraulic retention time (HRT) and water depth (for FWS systems only). Recommended ranges for design are given in Table 2-5.

Table 2-5 Summaries of design guidelines for constructed wetlands

Design parameter	Unit	Type of system		Source (ref. in Poh-eng and Polprasert, 1996)
		FWS	SF	
Organic loading rate (as BOD loading rate)	kg/ha.day	< 110	< 133	Reed et al. (1988)
		< 112	< 133	USEPA (1988)
		100-110	80 – 120	WPCF (1990)
		< 67	< 67	Metcalf and Eddy (1991)
		< 80	< 75	Crites (1994)
		< 100	< 100	Reed and Brown (1995)
hydraulic loading rate	cm/day	2.5 – 5	6 - 8	WPCF (1990)
		1.4 – 4.7	1.4 – 4.7	Metcalf and Eddy (1991)
		0.7 – 6	-	Crites (1994)
Hydraulic retention time	days	5 – 10	5 – 10	WPCF (1990)
		4 – 15	4 – 15	Metcalf and Eddy (1991)
		5 – 14	2 – 7	Crites (1994)
Water depth	m	Cattails > 0.15	NA	USEPA (1988)
		Reeds > 1.5		
		Bulrushes 0.0075 – 0.25		
		< 0.5	NA	WPCF (1990)
		0.09 – 0.6	NA	Metcalf and Eddy (1991)
		0.1 – 0.5	NA	Crites (1994)

Note: NA – Not applicable

1) Organic Loading Rate (OLR)

Organic loading rate, normally expressed as $\text{kg} / (\text{m}^2 \cdot \text{day})$, is defined as the mass of applied organic material, usually characterized by BOD, per unit surface area of the system per unit time. Although this process variable has no direct relevance to the design of wetland systems for the treatment of nutrients and other non-BOD pollutants, it is used as a check to ensure prevalence of aerobic conditions in the system which is important for wastewater treatment, mosquito and odor control. The maximum OLR is estimated based upon: (1) the oxygen transfer rate for the wetland vegetations which is assumed to be $20 \text{ g} / (\text{m}^2 \cdot \text{d})$; (2) the oxygen requirement which is equal to 1.5 times the organic loading; and (3) a factor of (2) (Reed et al., 1988 ref. in Poh-eng and Polprasert, 1996) (see equation 2-1).

$$\text{OLR} = \frac{\text{BOD}_5}{A \times t} \quad (2-1)$$

Where

- OLR = organic loading rate, ($\text{kg} / (\text{m}^2 \cdot \text{day})$)
- BOD_5 = biochemical oxygen demand during 5 days
- A = surface area, (m^2)
- t = hydraulic retention times, (days)

2) Hydraulic loading rate (HLR)

Hydraulic loading rate also known as surface hydraulic rate refer to the volume of wastewater applied to the system per unit surface area per day. The units commonly used are $\text{m}^3 / (\text{m}^2 \cdot \text{day})$, mm / day or cm / day . When establishing the HLR, the site-specific conditions of weather, soil conditions (e.g. permeability) and types of vegetation must be considered (see equation 2-2).

$$\text{HLR} = \frac{Q}{A} \quad (2-2)$$

Where HLR = hydraulic loading rate, ($m^3 / (m^2 \cdot day)$)

Q = average flow, ($m^3 d^{-1}$)

A = surface area, (m^2)

3) Hydraulic retention time (HRT)

In a constructed wetland system, the HRT is one of the major factors affecting the treatment performance. In general a too long HRT can result in stagnant anaerobic conditions whereas shorter HRTs do not provide sufficient time for the degradation of pollutants. Estimating the HRT in wetland systems can be difficult due to several reasons, including existence of large dead spaces because of variation in topology, plant growth, solids sedimentation and short-circuiting; and evapotranspiration in and ice formation (see equation 2-3).

$$HRT = V/Q \quad (2-3)$$

Where HRT = hydraulic retention time, (day)

V = active volume of the wetland cell, (m^3)

Q = average flow, ($m^3 d^{-1}$)

4) Water depth (H)

This particular process variable is of relevance to FWS wetlands only. The water level and the duration of flooding in the FWS wetland system can be important factors for the selection and maintenance of wetland vegetation. Initial establishment of emergent plants may require shallow water depth of 0.15 m after which depth should be increased to 0.3 m-0.6 m (Gearheart, 1992 ref. in Poh-eng and Polprasert, 1996). Optimum depth for selected vegetation determines the designed water depth (see equation 2-3).

$$h = H - G \quad (2-4)$$

Where h = depth of water in wetland cell, (m)

H = level of water, (m)

G = level of wetland soil bed, (m)

5) Flow rate (Q)

A constructed wetlands system is designed to use one or more of three types of flow pattern, i.e. plug flow, step feed, or recirculation. Plug flow is once through flow down the cell length. It requires minimal piping, energy use, operation, and maintenance (Steiner and Freeman, 1989 ref. in Poh-eng and Polprasert, 1996).

The average flow through the wetland system can be calculated by the equation:

$$Q = LWdn / t \quad (2-5)$$

Where Q = the average flow through the wetland system, ($m^3 d^{-1}$)

L = length of the wetland cell, (m)

W = width of the wetland cell, (m)

d = depth of water in wetland cell, (m)

n = porosity, or the space available for water to flow through the wetland (0.75 for FWS system)

t = hydraulic retention times, (days)

2.4 *Colocasia esculenta* (L.) Schott

Colocasia esculenta (L.) Schott is in Family Araceae, Genus *Colocasia* (L.) Schott., commonly known as elephant ear. This perennial herb with tuberous rhizomes has thick succulent stems usually from 0.5 – 1.2 m tall, but occasionally reaches a height of over 2 m under ideal conditions. Its large stiff leaves, 40 – 90 cm long, are thick in texture, ovate with a cordate base, and always peltate. The inflorescence is much shorter than the petioles with staminate flowers occupying the upper three quarters and pistillate flowers the lower quarter section of a short cylindrical crowded spadix (Figure 2-6). The pale yellow spathe is ovate-lanceolate shaped usually with enrolling margins. The fruit of elephant ear is an oblong berry containing numerous viable seeds. Reproduction also occurs by the production of stolons (Sripen, 2000 and Aquatic Plant Research and Control Florida Department of Natural resources, 1979).

Colocasia esculenta (L.) Schott grow well at either high or low altitudes, in swamps, marshes, and other muddy soil shallow water areas. Optimum growth occurs in hot, humid areas. This large shore plant grows in marginal areas of reservoirs (Aquatic Plant Research and Control Florida Department of Natural resources, 1979).

A native of the Pacific Islands, elephant ear is found throughout the tropical and subtropical regions of the world. It is frequently sold as an ornamental or house plant because of its large leaves. However, this plant can become a problem along some fresh water marshes and streams by shading out native vegetation due to its prolific growth (Aquatic Plant Research and Control Florida Department of Natural resources, 1979).

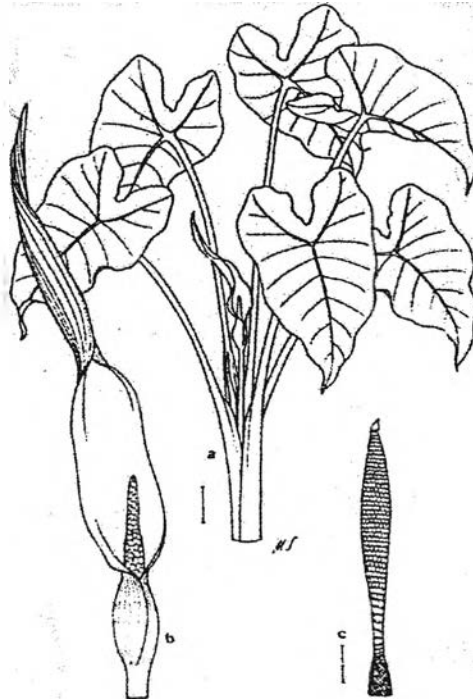


Figure 2-6 *Colocasia esculenta* (L.) Schott: a) habit b) inflorescence c) fruit

(Aquatic Plant Research and Control Florida Department of Natural resources, 1979)

For this study, two botanical types of *Colocasia esculenta* (L.) Schott which are identified with petiole color, green and violet, as shown in Figure 2-7



a)



b)

Figure 2-7 *Colocasia esculenta* (L.) Schott: a) green petiole b) violet petiole

2.5 Related research documents

Janice, Makos and Duane (1995) studied about chemistry of Cr(VI) in a constructed wetland which found that the feasibility of the use of constructed wetlands to treat acidic wastes containing hexavalent chromium is successfully demonstrated on a laboratory scale. Cr (VI) removal is highly dependent upon the organic content of the wetland matrix.

Polprasert, Dan and Thayalakumaran (1996) studied in the topic "application of constructed wetlands to treat some toxic wastewaters under tropical conditions". They found that the constructed wetland units could remove more than 99% of the applied chromium.

Kananidhinan (1996) studied about the efficiency of constructed wetlands for removing chromium from electroplating wastewaters by using four emergent plants, i.e. *Cyperus corymbosus*, *Typha angustifolia*, *Phragmites australis*, and *Eleocharis dulcis* which found that chromium could be removed from wastewater on pilot-scale more than 96%, especially *Cyperus sp.* could removed chromium at 98.21%.

Jampanil (2000) studied about the efficiency of arsenic removal from soil by *Colocasia esculenta* (L.) Schott which found that the efficiency of both *C. esculenta* was not different and they could survive under arsenic concentration ranged from 0-150 mg As/kg.