CHAPTER II
# LITERATURE REVIEW

2.1 Background

Chromium exists in several oxidation states (e.g., Cr^{3+} or Cr^{6+}), but only hexavalent (Cr^{6+}) and trivalent (Cr^{3+}) are biologically important. The hexavalent form is more toxic. However, long-term exposure to trivalent form can cause allergic skin reactions and cancer (Evangelou, 1998). Twenty five percent of the chromium used in the industry is in leather tanning and electroplating (25% of its use) which uses chromium pigments such as chrome yellow, chrome orange and chrome oxide green (Watts, 1997).

The removal of trivalent chromium (Cr^{3+}) can be made through the precipitation with metal hydroxides, such as magnesium hydroxide ($Mg(OH)_2$) and magnesium oxide (MgO) (Tongchai, 1995).
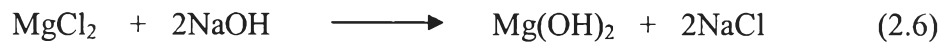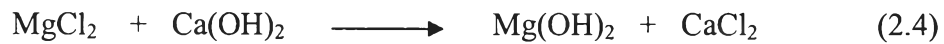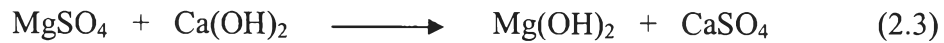
Seawater is a saturated salt solution, which contains sodium chloride, magnesium chloride, calcium chloride and water. Upon the addition of slaked lime ($Ca(OH)_2$) or caustic soda (NaOH) to the seawater and added to water or wastewater in the present of carbonate ions, will provide hydroxyl (OH^-), calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions, which are needed to raise the pH to the required level and to induce the chemical reactions that would produce calcium carbonate ($CaCO_3$) and magnesium hydroxide ($Mg(OH)_2$). Calcium carbonate has a point-of-zero charge (PZC) of approximately $8-9$, precipitates at pH values greater than 9.5, following the reaction. (Ayoub, 1999)

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_{3(s)} \qquad (2.1)$$
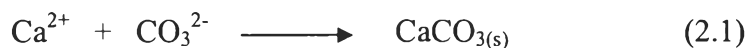
Similarly, $Mg(OH)_2$ (PZC of magnesium oxide (MgO) is approximately 12.4 precipitates at pH greater than 10.5, following the reaction.

$$Mg^{2+} + 2OH^- \longrightarrow Mg(OH)_{2(s)} \qquad (2.2)$$
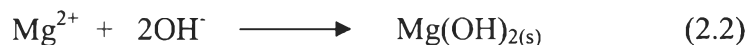
Having a relatively higher power of coagulation than $CaCO_3$, $Mg(OH)_2$ inevitably performs better in coagulating negative colloids and suspended particles. When alkalinized by either $Ca(OH)_2$ or $NaOH$, magnesium sulfate ($MgSO_4$) and magnesium chloride ($MgCl_2$) found in seawater will react to produce $Mg(OH)_2$, following the reaction.

$$MgSO_4 \;+\; Ca(OH)_2 \longrightarrow Mg(OH)_2 \;+\; CaSO_4 \qquad (2.3)$$

$$MgCl_2 \;+\; Ca(OH)_2 \longrightarrow Mg(OH)_2 \;+\; CaCl_2 \qquad (2.4)$$

$$MgSO_4 \;+\; 2NaOH \longrightarrow Mg(OH)_2 \;+\; NaSO_4 \qquad (2.5)$$

$$MgCl_2 \;+\; 2NaOH \longrightarrow Mg(OH)_2 \;+\; 2NaCl \qquad (2.6)$$

Similarly, Saline ground water (SGW) is an important and inexpensive source of magnesium and calcium. SGW is a saturated salt solution, which contains sodium chloride ($NaCl$), magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), calcium sulfate ($CaSO_4$) and water. Upon an addition of sodium hydroxide (or strong base) to the saline ground water, magnesium hydroxide ($Mg(OH)_2$) and calcium carbonate ($CaCO_3$), will precipitate. Magnesium hydroxide ($Mg(OH)_2$), calcium carbonate ($CaCO_3$), and sodium chloride produced from this reaction exist together but in two physical states; $Mg(OH)_2$ and $CaCO_3$ are formed as solid particles. An aqueous suspension containing solid particles is referred to as slurry. Gravity is used to separate the solids from the liquid in aqueous suspension $Mg(OH)_2$ and $CaCO_3$ are heavier than water.

2.2 Tanning process (http://www.epa.gov)

Leather tanning is the process of converting raw hides or skins into leather. Hides and skins have the ability to absorb tannic acid and other chemical substances that prevent them from decaying, make them resistant to wetting, and keep them supple and durable. The surface of hides and skins contains the hair and oil glands and is known as the grain side. The flesh side of the hide or skin is much thicker and softer. The three types of hides and skins most often used in leather manufacture are from cattle, sheep, and pigs. Tanning is essentially the reaction of collagen fibers in the hide with tannins, chromium, alum, or other chemical agents. The most common tanning agents used in Thailand are trivalent chromium and vegetable tannins extracted

from specific tree barks. Alum, syntans (man-made chemicals), formaldehyde, glutaraldehyde, and heavy oils are other tanning agents.

Although the title of this section is "Leather Tanning", the entire leathermaking process is considered here, not just the actual tanning step. "Leather tanning" is a general term for the numerous processing steps involved in converting animal hides or skins into finished leather. Production of leather by both vegetable tanning and chrome tanning is described below. Chrome tanning accounts for approximately 80 percent of Thailand tanning production. Figure 2 presents a general flow diagram for the leather tanning and finishing process. Trimming, soaking, fleshing, and unhairing, the first steps of the process, are referred to as the beamhouse operations. Bating, pickling, tanning, wringing, and splitting are referred to as tanyard processes. Finishing processes include conditioning, staking, dry milling, buffing, spray finishing, and plating.

2.2.1 Vegetable Tanning

Heavy leathers and sole leathers are produced by the vegetable tanning process, the oldest of any process to use in the leather tanning industry. The hides are first trimmed and soaked to remove salt and other solids and to restore moisture lost during curing. Following the soaking, the hides are fleshed to remove the excess tissue, to impart uniform thickness, and to remove muscles or fat adhering to the hide. Hides are then dehaired to ensure that the grain is clean and the hair follicles are free of hair roots. Liming is the most common method of hair removal, but thermal, oxidative, and chemical methods also exist. The normal procedure for liming is to use a series of pits or drums containing lime liquors (calcium hydroxide) and sharpening agents. Following liming, the hides are dehaired by scraping or by machine. Deliming is then performed to make the skins receptive to the vegetable tanning. Bating, an enzymatic action for the removal of unwanted hide components after liming, is performed to impart softness, stretch, and flexibility to the leather. Bating and deliming are usually performed together by placing the hides in an aqueous solution of an ammonium salt and proteolytic enzymes at 27^0 to 32^0C (80^0 to 90^0F). Pickling may also be performed by treating the hide with a brine solution and sulfuric acid to adjust the acidity for preservation or tanning. In the vegetable tanning process, the

concentration of the tanning materials starts out low and is gradually increased as the tannage proceeds. It usually takes 3 weeks for the tanning material to penetrate to the center of the hide. The skins or hides are then wrung and may be cropped or split; heavy hides may be retanned and scrubbed. For sole leather, the hides are commonly dipped in vats or drums containing sodium bicarbonate or sulfuric acid for bleaching and removal of surface tannins. Materials such as lignosulfate, corn sugar, oils, and specialty chemicals may be added to the leather. The leather is then set out to smooth and dry and may then undergo further finishing steps. However, a high percentage of vegetable-tanned leathers do not undergo retanning, coloring, fatliquoring, or finishing. Leather may be dried by any of five common methods. Air drying is the simplest method. The leather is hung or placed on racks and dried by the natural circulation of air around it. A toggling unit consists of a number of screens placed in a dryer that has controlled temperature and humidity. In a pasting unit, leathers are pasted on large sheets of plate glass, porcelain, or metal and sent through a tunnel dryer with several controlled temperature and humidity zones. In vacuum drying, the leather is spread out, grain down, on a smooth surface to which heat is applied. A vacuum hood is placed over the surface, and a vacuum is applied to aid in drying the leather. High-frequency drying involves the use of a high frequency electromagnetic field to dry the leather.

2.2.2 Chrome Tanning

Chrome-tanned leather tends to be softer and more pliable than vegetable-tanned leather, has higher thermal stability, is very stable in water, and takes less time to produce than vegetable-tanned leather. Almost all leather made from lighter-weight cattle hides and from the skin of sheep, lambs, goats, and pigs is chrome tanned. The first steps of the process (soaking, fleshing, liming/ dehairing, deliming, bating, and pickling) and the drying/ finishing steps are essentially the same as in vegetable tanning. However, in chrome tanning, the additional processes of retanning, dyeing, and fatliquoring are usually performed to produce usable leathers and a preliminary degreasing step may be necessary when using animal skins, such as sheepskin. Chrome tanning in the Thailand is performed using a one-bath process that is based on
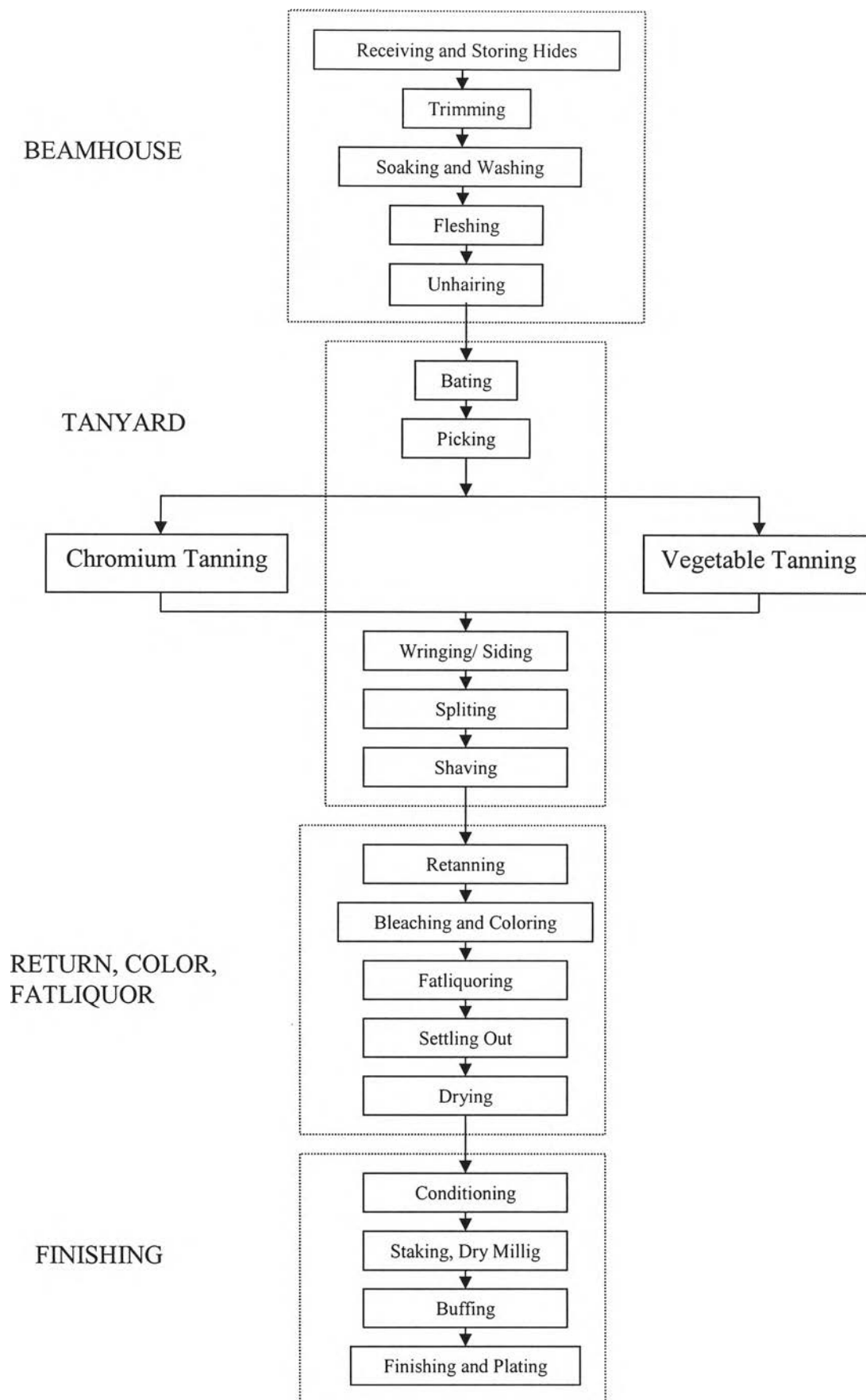
the reaction between the hide and a trivalent chromium salt, usually a chromium oxide (Cr_2O_3). In the typical one bath process, the hides are in a pickled state at a pH of 3 or lower, the chrome tanning materials are introduced, and the pH is raised. Following tanning, the chrome tanned leather is piled down, wrung, and graded for the thickness and quality, split into flesh and grain layers, and shaved to the desired thickness. The grain leathers from the shaving machine are then separated for retanning, dyeing, and fatliquoring. Leather that is not subject to scuffs and scratches can be dyed on the surface only. For other types of leather (i. e., shoe leather) the dye must penetrate further into the leather. Typical dyestuffs are aniline-based compounds that combine with the skin to form an insoluble compound. Fatliquoring is the process of introducing oil into the skin before the leather is dried to replace the natural oils lost in beamhouse and tanyard processes. Fatliquoring is usually performed in a drum using an oil emulsion at temperatures of about 60^0 to 66^0C (140^0 to 150^0F) for 30 to 40 minutes. After fatliquoring, the leather is wrung, set out, dried, and finished. The finishing process refers to all the steps that are carried out after drying.

Chrome tanning is popular because it takes a shorter period of time. However, by using chromium oxide (Cr_2O_3), this process releases Cr^{3+} into wastewater. Chrome tanning wastewater characteristics are shown in Table 2.1.

Table 2.1 Wastewater characteristics of chrome tanning.

Parameter	Chrome tanning wastewater without additive		Chrome tanning wastewater with additive	
	Average (n = 9)	S.D.	Average (n = 8)	S.D.
pH	2.93	0.21	3.56	0.34
Conductivity (ms/cm.)	63.60	3.30	91.50	8.10
Redox, mV	342	38	247	26
Total Solids, mg/l	86,851	4,510	131,672	16,391
Total Volatile Solids, mg/l	12,771	1,730	35,727	28,936
Total Fixed Solids, mg/l	74,079	4,622	95,945	33,163
Total Dissolved Solids, mg/l	85,573	3,950	129,165	15,933
Total Suspended Solids, mg/l	1,277	806	2,507	1,731
Settle able Solids, mg/l	40	30	70	26
Acidity(Total), mg/l asCaCO$_3$	8,641	1,720	4,100	703
Chloride, mg/l	24,896	2,461	45,281	3,084
Calcium, mg/l	462	110	503	119
Ammonia Nitrogen, mg/l	447	202	811	259
COD, mg/l	4,028	530	5,499	1,406
Chromium (soluble), mg/l*	3,070	741	1,541	365
Chromium (Total), mg/l**	4,133	904	2,166	304

*Analyzed by titration method, ** Analyzed by colorimetric method (Tongchai, 1995).

```
┌─────────────────────────────────────────┐
│        ┌──────────────────────────┐      │
│        │ Receiving and Storing Hides │    │
│        └──────────────────────────┘      │
│                    ↓                      │
│            ┌──────────────┐               │
BEAMHOUSE   │   Trimming   │               │
│            └──────────────┘               │
│                    ↓                      │
│        ┌──────────────────────┐           │
│        │  Soaking and Washing │           │
│        └──────────────────────┘           │
│                    ↓                      │
│            ┌──────────────┐               │
│            │   Fleshing   │               │
│            └──────────────┘               │
│                    ↓                      │
│            ┌──────────────┐               │
│            │  Unhairing   │               │
│            └──────────────┘               │
└─────────────────────────────────────────┘
```


Figure 2.1 Process of Tanning.

2.3 Chemical of Chromium

Chromium has atomic weight of 52.00, boiling point at 2482^0C and melting point ,of 1890^0C, and is a transition metal (VI B) that has various valence oxidation numbers from zero (metal form) to six. But in natural water, only Cr^{3+} and Cr^{6+} are found. Cr^{6+} is more toxic than Cr^{3+}, but only Cr^{3+} could be precipitated. In order to treat Cr^{6+} in water and wastewater, there are reduce Cr^{6+} to Cr^{3+}, and then add hydroxide compound to precipitate $Cr(OH)_3$. The precipitation of Cr^{3+} can occur at pH 8 – 9; beyond this range, Cr^{3+} will dissolve back into the solution again (Figure 2).
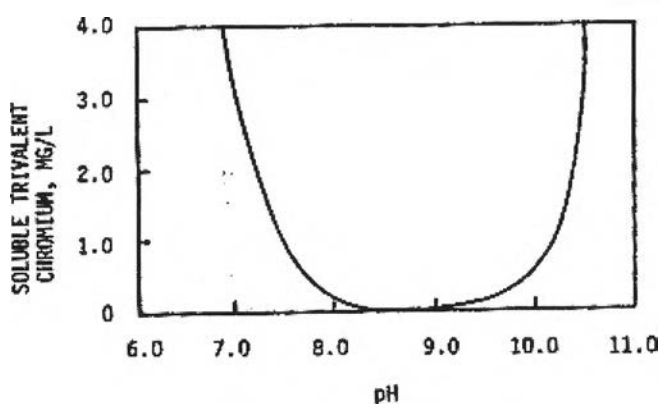
Figure 2.2 Chromium hydroxide solubility (Palmer, 1988).

The precipitation of $Cr(OH)_3$ depend on pH which relates with hydroxide content. The following reaction express relationship between the solubility of $Cr(OH)_3$ and pH ,at 25^0c.

Table 2.2 Equilibrium constant of a amphoteric trivalent chromium (Stumm, 1996).

Reaction	$\log K$ ($I = 0$)	$\log K$ ($I = 0.01$)
$Cr(OH)_{3(s)} = Cr^{3+} + 3OH^-$	-30.0	-29.4
$Cr^{3+} + OH^- = CrOH^{2+}$	10.0	9.8
$Cr^{3+} + 2OH^- = Cr(OH)_2^+$	18.3	17.9
$Cr^{3+} + 3OH^- = Cr(OH)_{3(aq)}$	24.0	23.7
$Cr^{3+} + 4OH^- = Cr(OH)_4^-$	28.6	28.1
$Cr^{3+} + 4OH^- = Cr_3(OH)_4^{5+}$	47.8	47.5
$H^+ + OH^- = H_2O$	14.0	13.91

Table 2.3 Principal aqueous species of environmentally important metal ions. (Vanloon, 2000).

Element	pH = 4.00		pH = 7.00		pH = 10.00	
	oxidizing environment	reducing environment	oxidizing environment	reducing environment	oxidizing environment	reducing environment
Sodium	Na^+	Na^+	Na^+	Na^+	Na^+	Na^+
Magnesium	Mg^{2+}	Mg^{2+}	Mg^{2+}	Mg^{2+}	Mg^{2+}	Mg^{2+}
Calcium	Ca^{2+}	Ca^{2+}	Ca^{2+}	Ca^{2+}	Ca^{2+}	Ca^{2+}
Chromium	HCr^{4-}	$CrOH^{2-}$	HCr^{4-}	$CrOH^{2+}$	CrO_4^{2-}	$Cr(OH)_4^-$

From the above table can seen that trivalent chromium can form various soluble compounds depending on pH value and redox reaction. Chromium is a amphoteric element. At lower pH, $CrOH^{2-}$ and HCr^{4-} are formed and act as a lewis base, donating electron pair to form coordinate covalent. Adding hydroxide ion can form a complex until reach a higher point more than K_{sp} value trivalent chromium forming neutral compound ,$Cr(OH)_3$, which precipitation can be occur. Similarly, fig 2.2 shown that pH range 8.5 – 9.0 have the lowest soluble chromium. However, adding excess hydroxide $Cr(OH)_4^-$ begins to form and act as a lewis acid.

However, if $Mg(OH)_2$ presents in the system, will be aiding in coagulation $Cr(OH)_4^-$. Due to $Mg(OH)_2$ has a lower solubility than $Ca(OH)_2$ and $NaOH$. (refered table 2.3). Adding $Mg(OH)_2$ should be precipitated Cr^{3+} by hydroxide ion, but excess $Mg(OH)_2$ has no completely dissociation so some part of the compound stay in $Mg(OH)_2$ form. $Cr(OH)_4^-$ occuring from excess OH^- ion would be coagulated by $Mg(OH)_2$. This resulted in decreased Cr^{3+} ion in the wastewater, and gave a higher percent removal than $NaOH$.

2.4 Chrome tanning precipitation and recovery

Chromium oxide (Cr_2O_3) called tanning chromium is green in color and reacts with water producing acidic aqueous. Usually, it was treated by chemical precipitation process. Adding basic precipitants such as carbonate, sulfide or hydroxide have been suitable treatment because the process is simple and give a high percent removal.

The basic precipitant is well-known for the chemical treatment such as NaOH, $CaCO_3$ or $Mg(OH)_2$. $CaCO_3$ are one of the popular precipitating , but it mainly compose of calcium which precipitation occur giving a high sludge volume.

Adding hydroxide ion like $Mg(OH)_2$ or MgO will precipitate Cr^{3+} and form chromium hydroxide as shown in Equation 2.7 (Boehnke, 2000).

$$Cr^{3+}_{(aq)} + 3(OH)^-_{(aq)} \longrightarrow 2Cr(OH)_{3(s)} \tag{2.7}$$
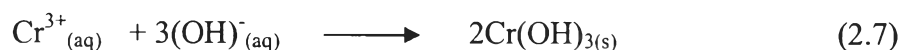
For example hydroxide ion is NaOH. NaOH has a higher solubility (referred table 2.3) in aqueous system it nearly complete dissociation into Na^+ and OH^- form. Thus, adding NaOH into chrome tanning wastewater should be occur $Cr(OH)_3$ and then $Cr(OH)_4^-$, from OH^- ion which dissolve into the wastewater again.

Moreover, the basic precipitants gave very dense precipitates of $Cr(OH)_3$ which settled very quickly than $Ca(OH)_2$ and NaOH. Because hydroxide ion came from $Ca(OH)_2$ and $Mg(OH)_2$ compound that gave sludge density higher than NaOH compound as shown in table 2.4.

Table 2.4 Comparison of hydroxide reagent properties.

Property	$Ca(OH)_2$	NaOH	$Mg(OH)_2$
Molecular weight	74.1	40.0	58.3
Hydroxide content (%)	45.9	42.5	58.3
Solubility (g/100ml H_2O)	0.185[a]	41.0[a]	0.0009[b]
Reactive pH maximum	12.5	14	9.0
Solid content of sludge (%)[f]	35.0	30.0	55.0
Sludge density (lb/ft$_3$)	85.0	80.0	100-110
Filtration time (hr)	7 – 9	7 – 8	1.5-2.0
Sludge volume (yd$_3$/10000lb)	12.5g	15.0	6.4

a temperature = 0^0C, b temperature = 0^0C, f sludge from a plate-and-frame filter press, g consists of metal hydroxide and gypsum, (Palmer, 1988)

Langerwerf et al. (1977) studied the concentration of trivalent Cr in wastewater from the tannery was reduced to less than 5 mg/L by addition of MgO as a precipitant at a concentration of 8.8 g, which increased the basicity of the effluent 1% for each 1 kg of Cr_2O_3 present, and a pH 8-9. MgO addition gave high sedimentation rates, 0.25 m/h, and the precipitated $Cr(OH)_3$ obtained was easily reused in the tanning process. Other precipitants which were effective but required additions of 15.0-33.0 g to increase basicity 1% and higher pH, were NaOH, $Ca(OH)_2$, Na_2CO_3, $NaHCO_3$, $CaCO_3$, and basic Mg carbonate.

Langerwerf et al. (1978) studied in the precipitation of Cr(III) from tannery effluents the best results were obtained with MgO. The basic precipitants gave very dense precipitates of Cr hydroxide (approximate 10% Cr_2O_3 on wet weight) which settled very quickly (approximate 250 mm/h). The purified and clear effluent contained less than 5 mg Cr/L in the presence of formats and phosphates, and had a relatively low pH (8-9). The reuse of the precipitation Cr did not cause any problem as far as tanning and the quality of the leather were concerned.

Tomaselli et al. (1981) studied the recovery of Cr from tanning wastewater by precipitation with MgO and the direct use of the resulting hydroxide in the successive tanning cycle is acceptable with respect to the leather behavior on drying and its required content of Cr and fats. The use of MgO as precipitate agents for Cr decreases the time required to obtain a compact hydroxide precipitate which eliminates the filtration required in case of Na_2CO_3 and NaOH as precipitate agents. The optimum tanning time for leathers was 20 hr which was necessary to complete the redissolution of the hydroxide and to complete the recovery of Cr from the preceding cycle. The use of MgO as precipitate agent required a lower content of an alkalizing agent due to the presence of hydroxides during the tanning process which decreased the salt content in the wastewaters.

Hrnjic et al. (1985) studied KOH gave optimum results in precipitation of Cr^{3+} from wastewater from chrome tanning of sheepskins and cattle hides. Results obtained in precipitation with NH_4OH and $Ca(OH)_2$ were less satisfactory. The recovered precipitation $Cr(OH)_3$ can be used in chrome tanning of fur. The effectiveness of the precipitants was evaluated from

sedimentation curves on 50-100 mL samples of tannery effluent in the lab.

Suleimanov et al. (1985) studied wastewaters from leather manufacture contains extremely high concentration of Cr which can effectively be removed by precipitation with NaOH as $Cr(OH)_3$, filtration, and treatment with H_2SO_4 to produce $Cr(OH)SO_4$, which is suitable for reuse. Such wastewaters can also be treated using high-S2- wastewaters to precipitate Cr as $Cr_2(SO_4)_3$ (also suitable for reuse), however such process is accompanied by the release of high concentration of H_2S into the environment.

Khavroshin et al. (1987) studied Cr-containing precipitate (mainly Cr hydroxide) was obtained from spent tanning solution by using a 10% Na_2CO_3 solution as the precipitate agent, followed by dewatering of the precipitate on a filter press. Less satisfactory dewatering results were obtained when NH_3 and $Ca(OH)_2$ solution were used as the precipitate agents.

Azeez et al. (1990) studied Cr was recovered from spent chrome tanning liquors by precipitation as Cr hydroxide followed by conversion to basic Cr sulfate by the addition of H_2SO_4. The basicity of the Cr sulfate was 33.3%, which is the same as for the usual chrome tanning material, and this could be recycled in the chrome tanning process. The maximum amount of Cr hydroxide recovered was mainly pH-dependent, and the temperature and kind of alkali used had little effect. The maximum recovery of basic Cr sulfate was 25%.

Wood et al. (1992) studied the removal of chromium aqueous. The results showed that MgO can immediately form precipitate using less quantity than lime. The pH of chrome tanning affects the precipitation as shown in Table 2.5.

Table 2.5 Laboratory studies of the reaction between magnesium and commercially spent chrome tan liquors.

Initial Chrome content (g Cr_2O_3/litre)	pH of Spent tan liquor	MgO added (g/litre)	pH after settling overnight	Sludge volume (%)	Residual Chrome concentration (mg/Cr/litre)
12.0 + syntan	3.9	3.0	9.0	10	10
14.5 + syntan	3.8	4.2	9.0	15	28
11.6 + formate	2.8	5.1	7.6	12	99
3.3	3.4	2.7	8.7	19	71
12.2	3.2	9.4	9.1	32	12
3.8	3.3	2.6	8.8	9	16
3.7 + Al +syntan	3.6	3.0	8.8	10	8
38	3.8	13.7	7.9	25	96
3.7 + formate	4.0	4.0	9.4	16	27

Tongchai et al. (1995) studied chrome recovery from tanning wastewater was studied in field conditions using a real-sized pilot plant. The tested wastewaters were from the tanning process both without and with tanning additive, whereas the precipitated chemicals of interest were MgO and Na_2CO_3. The precipitation with MgO followed by 1-h sedimentation was the best solution. The optimal dosages were 2 and 4 times that of stoichiometric requirement for conditions without and additives. By redissolving the sludge with 1:1 sulfuric acid and maintaining the pH at 2.5-2.8, the Cr recovery was 97.6 and 88.6%, respectively. Another alternative of using Na_2CO_3 as the precipitant was not promising because of its high chemical cost and excessive sludge-setting period (15-20). The MgO precipitation scenario to be able to pay back economically within 3 years for the without-additive waste stream whereas that of with-additive wastewater was not worth the investment. This is because the with-additive discharge contains low Cr whereas it requires high chemical dosages.

Pathe et al. (1996) studied the Cr removal and recovery from chrome tanning wastewater, and the economics of the process are described. The

optimum mixing time for maximum Cr removal was 20 seconds rapid mixing at 100 rpm and 15 minutes slow mixing at 10 rpm followed, by sludge settling for 90 minutes. At pH 8, approximate 99.7% Cr removal was achieved with a optimum lime dose of 3,500 mg/L. Sludge with a Cr content of 280-300 mg/L was produced, the lime-treated wastewater contains 30 mg/L Cr and is suitable for biological treatment. The Cr recovery from sludge was achieved by dissolution with H_2SO_4 at pH 3 resulting in approximately 78% yield in relation to wastewater content. The Cr recovery is profitable only if wastewater contains more than 800 mg/L as initial concentration.

Fabiani et al. (1997) studied chromium (III) salts are the most widely used chemical for tanning processes, but only 60% of the total chromium salt reacts with the hides. Therefore, approximately 40% of the chromium amount remains in the solid and liquid wastes (space spent tanning solution). The presence of chromium (III) and salts in the sludge of both the wastewater biological treatment plants or the chemical plants for recycling spent tanning liquors, represents an inconvenience for the safe reuse of these sludge and a cost forming factor for their disposal. Among the several proposed methods for chromium recovery, lime or sodium hydroxide precipitation and filter-pressing of the chromium hydroxide is the usual way to recover chromium salts from spent process solution or from leaching solution of residues of hides. However, usually the chromium salts quality must be improved for their reuse in tanning processes. The integration of membranes in the treatment process for chromium recovery reduces the environmental impact, favors the reuse of both the protein residue and the biological plant sludge, reduces the consumption of chemical and decreases the costs of waste disposal.

Siddiqui et al. (1998) studied Chromium from spent chrome tanning liquor was precipitated in trivalent form by using MgO and NaOH. The process was optimized by studying the effect of temperature, alkali dose, and initial chromium concentration on chromium removal efficiency. The cost benefit analysis for a tannery processing 500 hides per days was carried out and the pay back period was found to be about 2 year.

Sreeram et al. (1999) studied the nature of alkali used for the precipitation of chromic hydroxide has been found to have profound influence on its settling behavior. The settled volume of chromic hydroxide produced

using NaOH, Na$_2$CO$_3$, Ca(OH)$_2$ and MgO has been found to vary from 72 to 8%. Similar variations have been observed in their particle size distribution. The mode of addition of alkali has been found to influence the settled volume of chromic hydroxide, with slow addition of alkali producing the most compact chromic hydroxide sludge. A pH of 8.5-9.0 has been found to be ideal for effective settling of chromic hydroxide using MgO as the precipitate agent. Precipitation of chromic hydroxide using NaOH, Na$_2$CO$_3$ and MgO has been found to leave 3.8, 3.6 and 1.4 mg/L respond of Cr(III) in the supernatant. Calcium hydroxide on the other hand was found to leave only 0.08 mg/L of Cr(III) in the supernatant. Scanning electron micrographs of the dried chromic hydroxide show that the morphol. of dry chromic hydroxide is influenced by the alkali used to produce the chromic hydroxide.

Farre Benejam et al. (2000) studied a two-stage alkalinization hydroxide precipitation method was developed for removal and recovery of chromium from tanning wastewater using a mixture of NaOH and small amounts of MgO as nucleating agent, with recycle of precipitate. The temperature of the first reactor is adjusted to 60°c while the second reactor does not require external heating; the total reactor residence time is more than 3 hr at pH > 7, preferably 7.5. The use of MgO leads to dense precipitates slow addition of MgO to the chromium solution allows for better control of precipitate formation and solubilization, resulting in a substrate that contains large amount of Cr that can be separated easily for recovery. The chromium recovery facility is designed for continuous operation and is fully automated; the process is adequate for chromium concentration of 1,500-5,000 mg/L in wastewater, for a less than 2 mg/L content in effluent. The Cr(OH)$_3$ recovered is suitable for recycling into the tanning process. The installation eliminates the need for treatment of chrome-contaminating wastewater by conventional methods, and the subsequent problems of treatment and disposal of contaminated sludges.

Ali et al. (2000) studied a leather tanning system combining both vegetable tannins and chromium (semi-chrome process) is indispensable for certain types of leathers. However, the effluent generated from such a process presents a problem of separation chromium from vegetable tannins, as the latter tend to precipitate along with chromium. Environmental legislations on the releasing of chromium into various water bodies demands its recovery and

reuse at every possible stage. This investigation describes the development suitable methods for separation of vegetable tannins followed by recovery of chromium. The best oxidizing agent for vegetable tanning was H_2O_2. Oxidation of the components was followed by precipitation of chromium hydroxide using NaOH.

Bojanowska (2002) discussed on Cr recovery from chromic wastewater neutralization sludge. Cr (III) hydroxide was the main component of this sludge. Recovery was based on a process of transforming chromium (III) hydroxide to Cr^{6+}. This method includes precipitation and dissolution of chromium (III) hydroxide, oxidation of Cr^{3+} to Cr^{6+}, solvent extraction., and re-extraction of Cr^{6+}. Cr recovery yields for each procedural stage was 92-99%. Overall, Cr recovery was approximately 99%.

2.5 Precipitation of magnesium hydroxide and calcium hydroxide from saline groundwater

Pribicevic Svetozar and Stancic Boydan (1970) Factor affecting the precipitation rate of $CaCO_3$ and $Mg(OH)_3$ slurry in a brine were Ca^{2+} and Mg^{2+} concentration, temperature, addition of flocculating agents, etc. The optimum $Ca^{2+} : Mg^{2+}$ weight ratio is 0.8:0.2. The fastest precipitation is obtained if the brine before treatment with NaOH and $NaCO_3$ contains approximate 1.0 gram Ca^{2+} and Mg^{2+} per a liter. The precipitation rate is directly proportional to temperature, and the presence of flocculating agents is also beneficial. All the experiments were carried out in a brine saturated with a mixture of NaOH and $NaCO_3$.

Gancy Alan B. and Kaminski Chester J (1977) studied the strontium, calcium and magnesium impurities are precipited from a raw sodium chloride solution by adding $NaCO_3$ and NaOH separating the precipited $SrCO_3$, $CaCO_3$ and $Mg(OH)_2$ and feeding back to fresh raw sodium chloride solution 25-1000% (based on the amount of strontium, calcium and magnesium new raw solution) of the precipited separating. Significantly more strontium, calcium and magnesium are removed when 300% excess of the sludge is fed back to fresh raw solution.

Lee John M. and Bauman William C. (1983) studied the alkaline earth metal ions, e.g. magnesium ions and/or calcium ions are removed from alkali

metal brine, e.g. sodium chloride, by using a particulate, macroporous, anion exchange resin in-situ reaction product of polymeric, amorphous, hydrous zirconium oxide and a source of phosphate ions, e.g. H_3PO_4.

Khodorkovskaya S. I. et al. (1986) studied the original brine solution is pretreated with milk of lime and then with $(NH_4)_2 CO_3$ and allowed to stand. In order to increase the rate of setting, the $(NH_4)_2 CO_3$ treatment is carried out by setting, the purified brine with NH_3 and CO_2 until the concentration of $(NH_4)_2 CO_3$ in the reaction mixture become 0.7-2.4 g/L. In one embodiment, the saturation is carried out until the carbonate concentration becomes 144.1-187.4 g/L and the NH_4OH concentration 21.0-66.6 g/L.

Man and Yuankang (1991) studied the process includes agitating magnesium ion-concentration sodium chloride solution at moderate strength, using recycled slurry as crystal seeds, and alkali (NaOH or $Ca(OH)_2$) as precipitating agent for precipitation of magnesium ions as $Mg(OH)_2$, adding flocculating agent, and removing magnesium concentration residue by settlement to obtain purified sodium chloride solution concentration that yeilds magnesium less than 1 ppm. Operating condition of the $Mg(OH)_2$ precipitation step is as follow: slurry temperature 15-65 ^0c, $Mg(OH)_2$ concentration in slurry is 20– 40 g/L, and pH 9.2 – 11.2 (stabilized within pH 10.2 by adjustment). The method for the separation of magnesium from groundwater of which the major component is sodium chloride. The process includes agitating saline groundwater with addition of flocculating agent [NaOH or $Ca(OH)_2$], which can precipitate Mg^{2+} as $Mg(OH)_2$. The result found that $Mg(OH)_2$ concentration in slurry is 20,000 – 40,000 mg/l .

Shevchenko T.V. et al. (2002) studied the method comprises using a reaction product of polyacrylamide and an alkali metal hydroxide (e.g. NaOH) as a flocculants and polypropylene glycol monobutyl either as a flotation agent. The method decreases the amount of the polyacrylamide flocculants and provides a higher degree of purification of the solution and lower expenses at a further filtration stage to feeding it into electrolyzers for production of Cl_2, H_2 and NaOH. The method is suitable for removing of calcium and magnesium salts from the sodium chloride solution.