CHAPTER IV

RESULTS AND DISCUSSION

This research studied the recovery of chromium from tanning wastewater by precipitation with the alkalinized saline groundwater. Saline groundwater was taken from different locations to compare the concentration of calcium, magnesium and Chloride. Then location with the highest concentration was selected to use in the study. Preparation of the white slurry which is mainly composed of $Mg(OH)_2$ and $CaCO_3$. The optimum pH for maximum precipitation as indicated by the volume of white slurry and the concentration of calcium and magnesium were determined by varying pH of groundwater samples. Precipitation of chromium was performed by adding the white slurry into tanning wastewater. The optimum dosage of white slurry was determined under the controlled pH ranges by Jar test. Chromium in the precipitated form of $Cr(OH)_3$ was recovered by adding H_2SO_4 to dissolve the chromium as $Cr_2(SO_4)_3$. Model scale test was performed by using optimum dosage of white slurry and H_2SO_4 obtained from laboratory scale tests.

The experimental result presented and discussed in this chapter cover the following topics: tanning wastewater characteristics, saline groundwater quality, preparation of white slurry of magnesium hydroxide and calcium carbonate by alkalinization, precipitation of chromium with the white slurry of magnesium hydroxide and calcium carbonate, recovery of chromium from chromium hydroxide precipitate and recovery of chromium in the model scale test.

4.1   Characteristics of tanning wastewater

The tanning industry is categorized into two types of tanning which are chrome and vegetable tanning. This research focused solely on chrome tanning. Therefore, chrome tanning wastewater was collected from the Khon Kaen Tanner Group Co., Ltd., who is a leading leather tanning cooperation which applies chrome tanning process, located in Phon District, Khon Kaen province. The basic survey of the tanning factory wastewater characteristic is shown in Figure 4.1-4.8. Chromium (III)

salt is the most widely used chemicals for tanning process with the hides. Therefore, about 30% of the chromium content remains in the wastewater (especially the spent tanning solution). Analysis of the tanning wastewater data is shown in Table 4.1.

Table 4.1 Analysis result of tanning wastewater taken from Khon Kaen Tanner Group Co.Ltd., Phon District, Khon Kaen Province.

Sampling date	pH	Cr (mg/l)	COD (mg/l)	Na (mg/l)	TS (mg/l)	SS (mg/l)	TDS (mg/l)	Cl⁻ (mg/l)
April 30, 2001	3.89	498	1,798	610	46,718	528	46,190	27,650
July 20, 2001	3.72	302	1,510	480	31,830	465	31,365	19,000
October 26, 2002	4.58	236	1,367	271	10,650	340	10,310	12,550
December 12, 2002	4.07	242	1,384	263	10,500	380	10,120	12,140

The wastewater sampling is collected from the discharging point of the chrome tanning drum. Trivalent chromium (Cr^{3+}) content from different sampling days were different. The difference is depending on the amount of tap water used for chrome washing. The content of Cr^{3+} was in the range of 236 to 498 mg/l. The pH value were not significantly different of these samples. NaCl used to prevent fermentation of skins would generate sodium and chloride in wastewater. They also varied, i.e., 263 to 610 mg/l and 12,140 to 27,650 for sodium and chloride, respectively. The amount of total dissolved solids, in relation with the ions content, show similar result which was varied from 10,120 to 46,190 mg/l. Total solids and suspended solids generated during the hair and epidermis elimination process, were varied in the range of 10,500 to 46,718 mg/l and 340 to 528 mg/l, respectively.
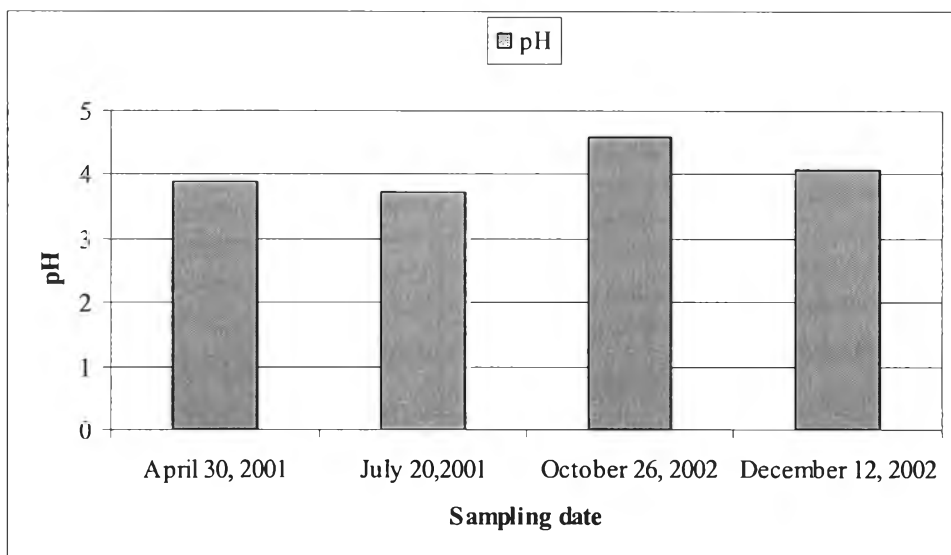
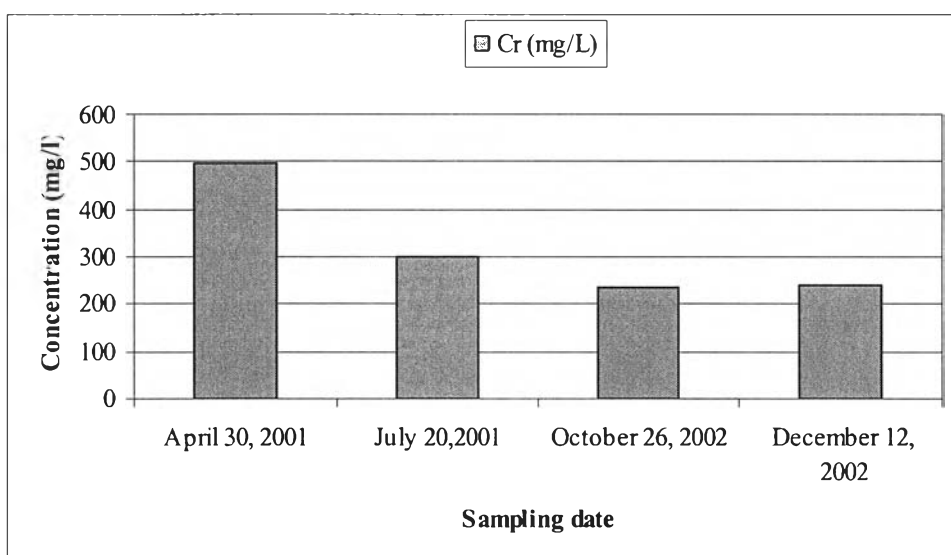**Figure 4.1** Analysis of pH of tanning wastewater.

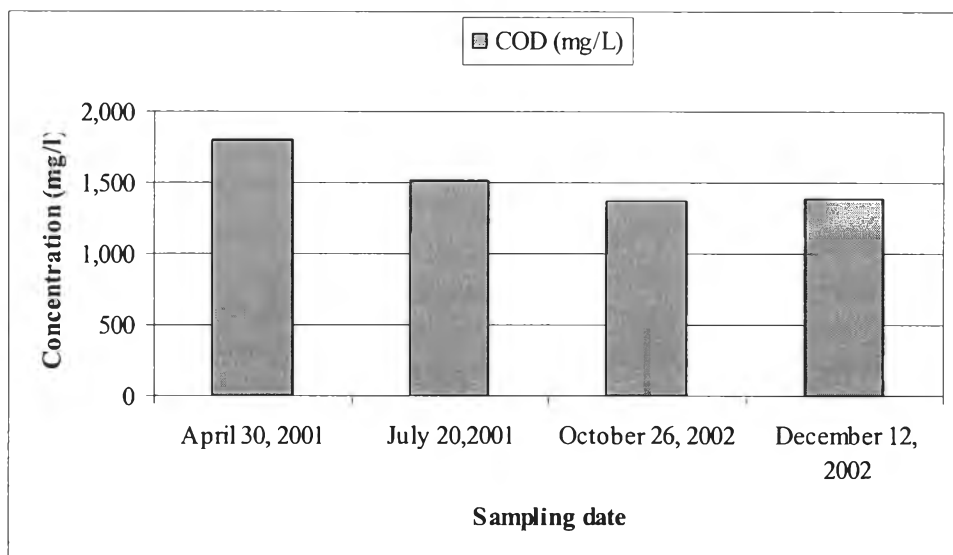**Figure 4.2** Analysis of Chromium content of tanning wastewater.

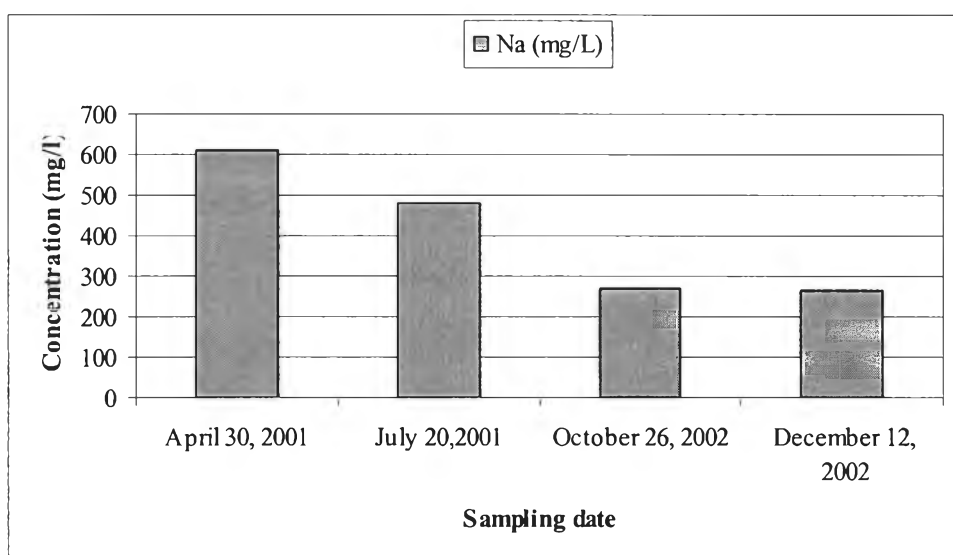**Figure 4.3** Analysis of COD content of tanning wastewater.
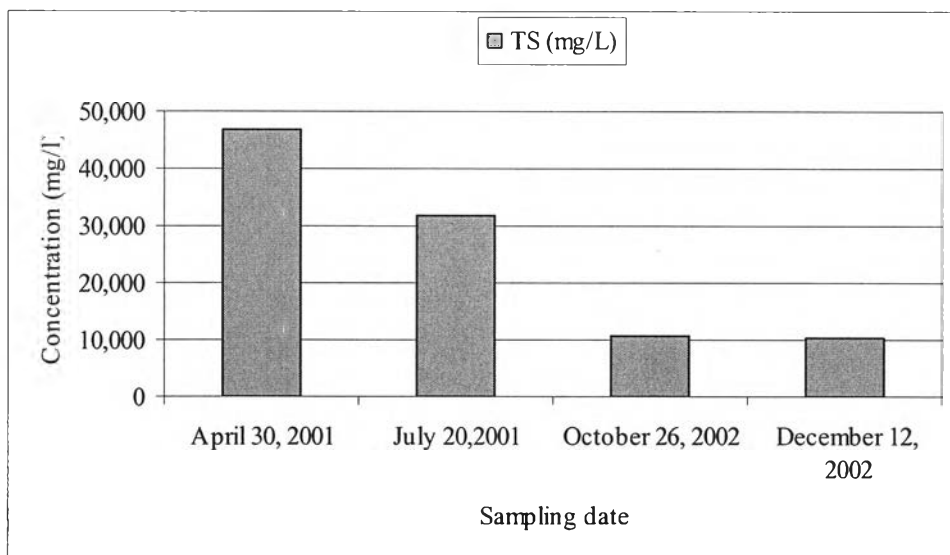

Figure 4.4 Analysis of Na content in tanning wastewater.

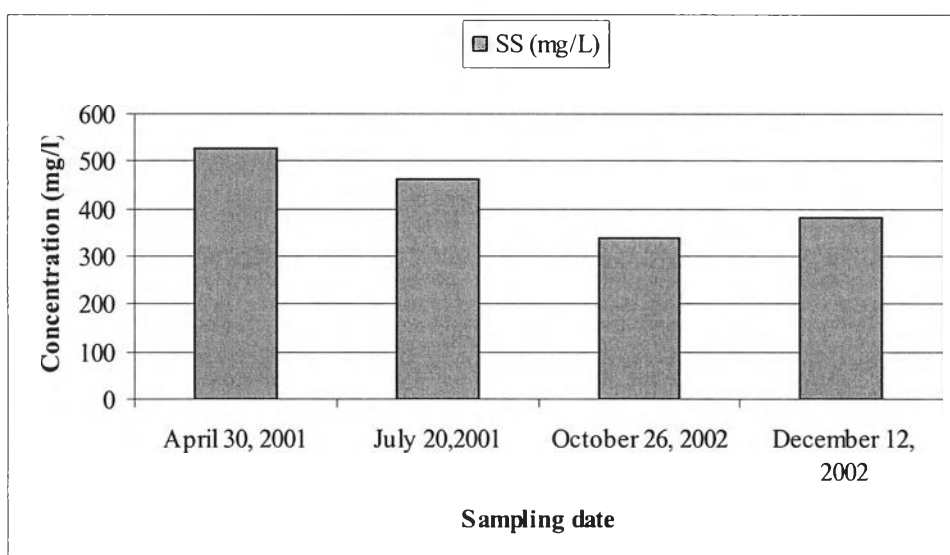**Figure 4.5** Analysis of TS content in tanning wastewater.

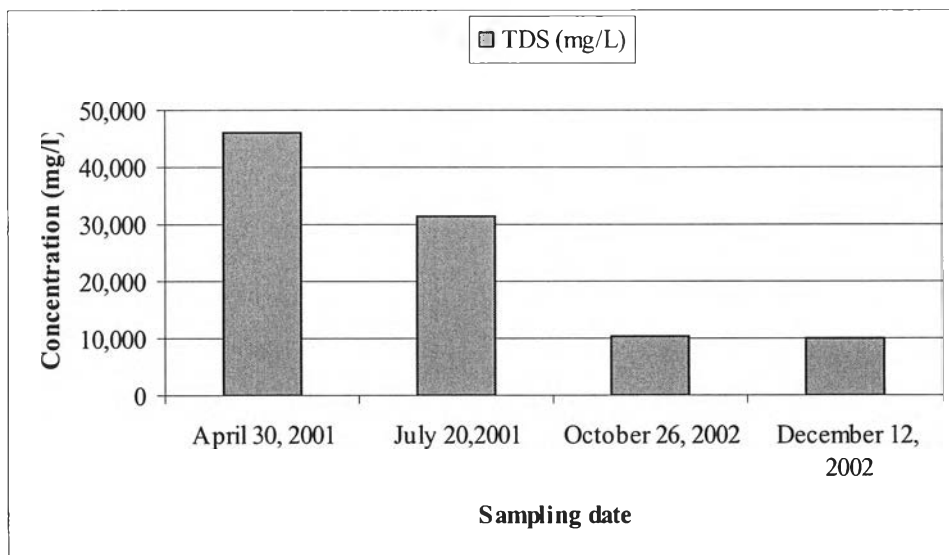**Figure 4.6** Analysis of SS content in tanning wastewater.

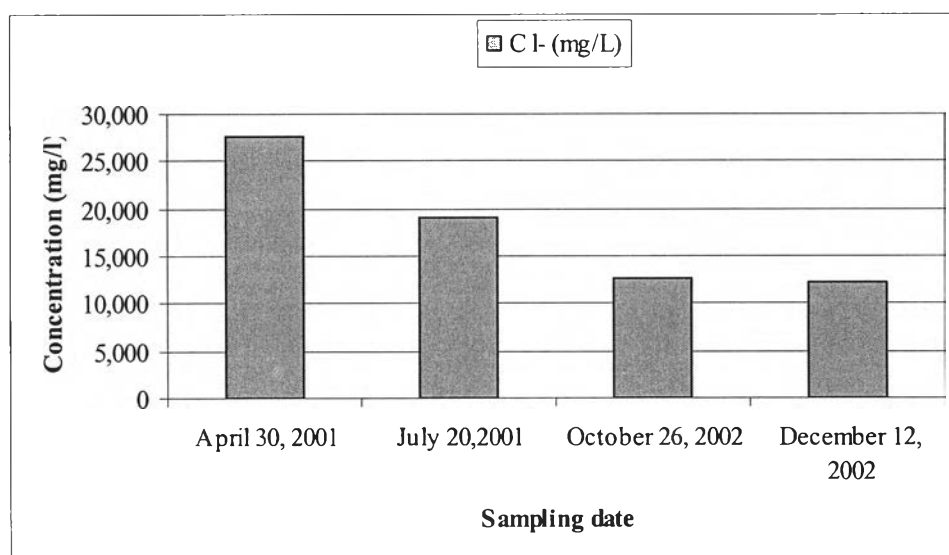**Figure 4.7** Analysis of TDS content of tanning wastewater.

Figure 4.8 Analysis of Cl⁻ content in tanning wastewater.

4.2 Saline Groundwater

Saline groundwater is an important and inexpensive source of magnesium and calcium. It is a saturated salt solution which contains sodium chloride, magnesium chloride, calcium chloride and water. Magnesium and calcium can be precipitated as magnesium hydroxide and calcium carbonate that can act as coagulant for chromium precipitation.

4.2.1 Saline groundwater quality

Saline groundwater was taken from four different locations which are Bandung District, Udon Thani Province, Phon District, Khon Kaen Province, Nongsung District, Nakonratsima Province Muang District, Mahasarakam Province. The samples were also collected in dry and rainy season to compare calcium and magnesium content and to select suitable saline groundwater site for precipitation of white slurry of $CaCO_3$ and $Mg(OH)_2$. The optimum saline groundwater was indicated by the volume of white slurry and the concentration of calcium and magnesium The samples of saline groundwater were analyzed for pH, Ca, Mg, Na, Cl, acidity and alkalinity according to the standard method (Ann, 1992) at the chemical laboratory of Environmental Engineering Department, Khon Kaen University. The results of the analysis are presented in Table 4.2.

Table 4.2 Analysis result of pH, Ca, Mg, Na, Cl, Acidity and Alkalinity of saline groundwater samples taken from different sources and time.

Sampling Site	Sampling date	pH	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	Cl⁻ (mg/l)	Acidity (mg/l as CaCO₃)	Alkalinity (mg/l as CaCO₃)
1. Bandung District, Udon-thani Province	July 25, 2001	7.10	4,435	2,200	901,854	1,550,000	< 4	846
	October 3, 2001	7.00	4,500	2,500	876,352	1,570,000	< 4	782
	December 3, 2001	6.98	7,500	2,500	983,666	2,270,000	< 4	802
	March 5, 2002	7.10	6,435	2,200	951,000	1,830,000	< 4	790
	March 30, 2002	7.00	7,500	2,200	986,200	2,280,000	< 4	814
	October 20, 2002	7.18	3,950	2,180	899,000	1,450,000	< 4	768
	September 2,2002	7.21	3,690	2,010	892,760	1,410,000	< 4	796
2. Phon District, Khon Kaen Province	March 12, 2002	6.97	462	217	200	1,300	< 4	514
	April 8, 2002	6.68	418	181	176	1,344	< 4	486
3. Nonsung Distric Nakhonratsima Province	March 17, 2002	7.66	5,421	195	495	396,000	300	2,200
	April 21, 2002	6.92	6,100	298	600	427,000	240	2,350
4. Muang, District Mahasarakam Province	March 24, 2002	6.74	304	66	986	4,300	< 4	602
	April 29, 2002	6.89	262	54	930	4,210	< 4	584

4.2.2 Selected groundwater source

Comparing calcium and magnesium content from four locations at the same time of sampling (in dry season), it was found that concentration of calcium and magnesium taken from Bandung District, Udon Thani Province was the highest which is shown in Figure 4.9 and 4.10 respectively.
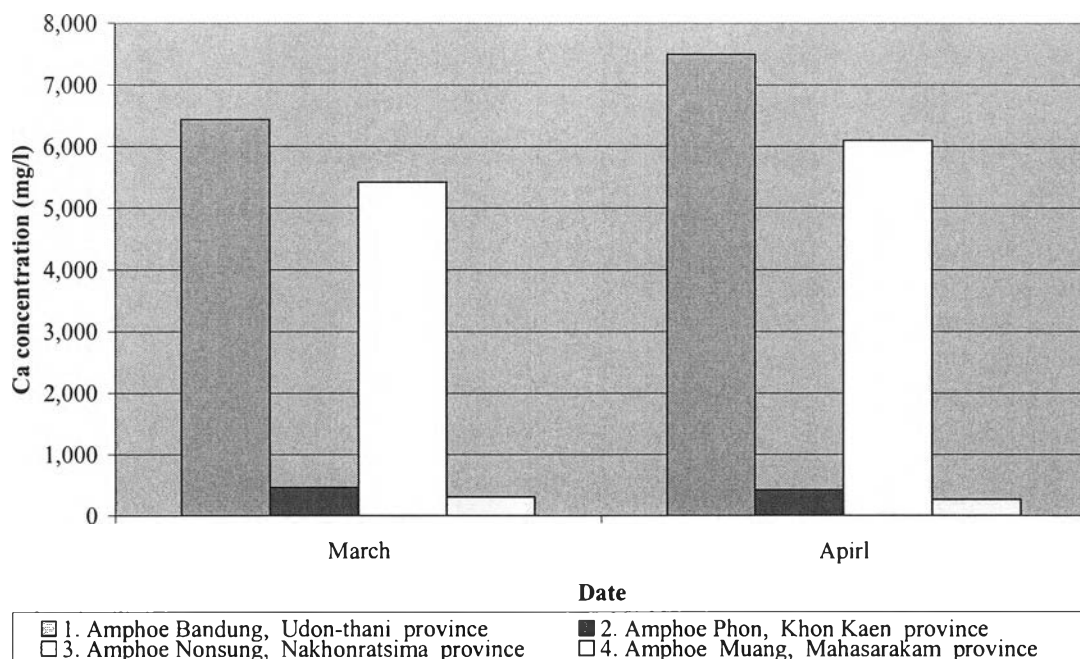
Figure 4.9 Concentrations of Ca in saline groundwater from four locations in dry season.
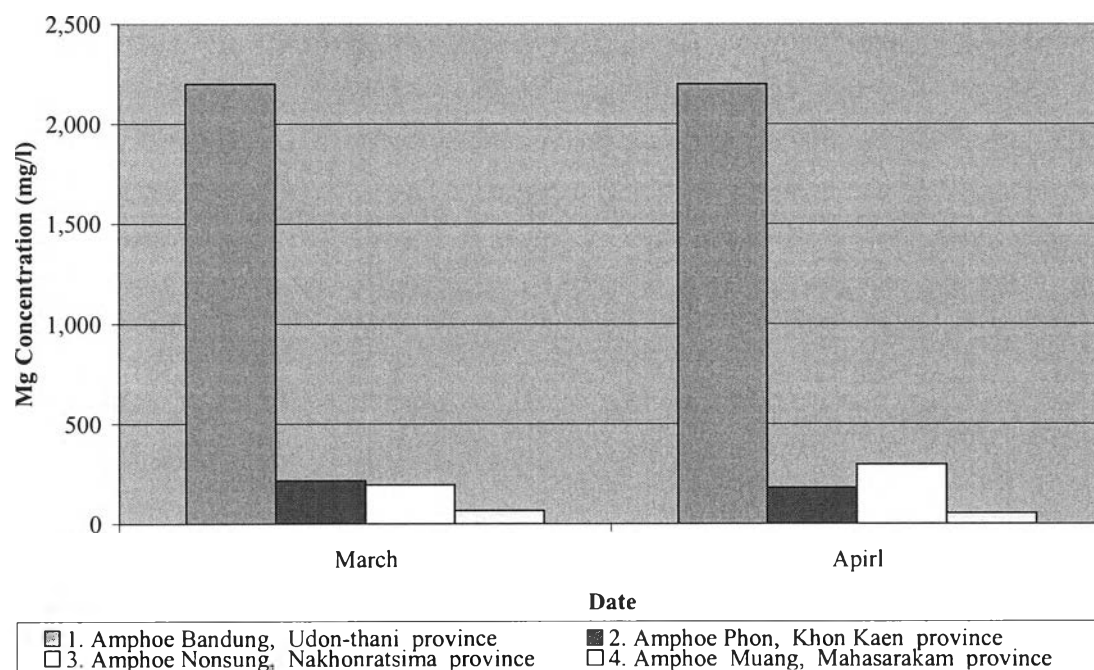

Figure 4.10 Concentration of Mg in saline groundwater from four locations in dry season.

From Figures 4.9 and 4.10, it could be concluded that saline groundwater from Bandung District, Udon Thani gave the highest amount of white slurry of

$CaCO_3$ and $Mg(OH)_2$. When compared with other sources in the same period. Although the sample were taken in different seasons, dry and rainy season, the content of calcium and magnesium showed satisfactory result for precipitation of white slurry of $CaCO_3$ and $Mg(OH)_2$. So this groundwater site was selected for the next step of the experiment.

4.2.3 Groundwater quality of different seasons

Quality of groundwater, collected from Bandung Subdistrict, with respect to the collection time is shown in Table 4.2 and Figure 4.11-4.16.
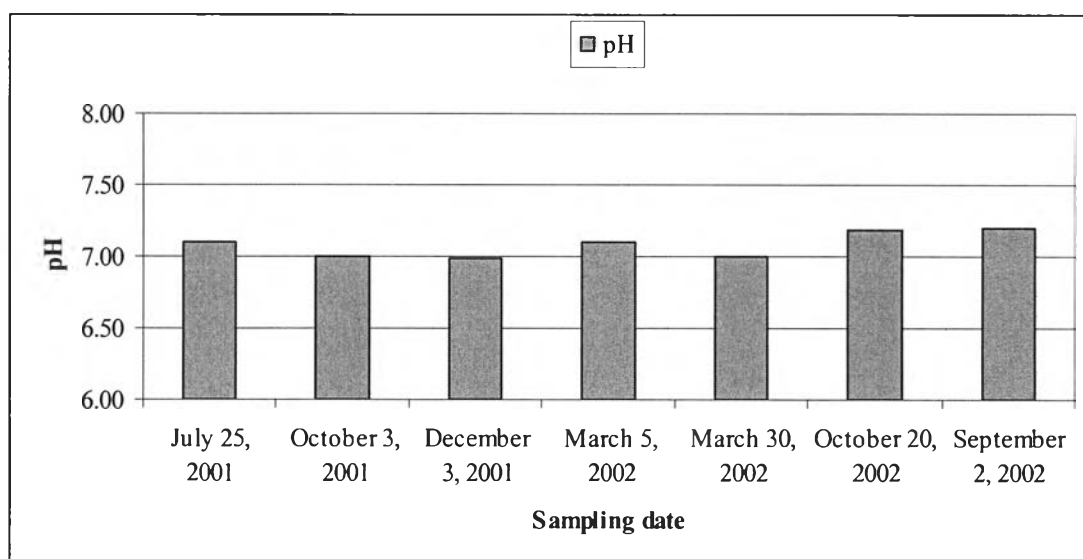

Figure 4.11 pH of saline groundwater at different seasons.

Figure 4.11 shows that there is no significant variation of the pH value between dray and rainy seasons, i.e. about 6.98 –7.21.
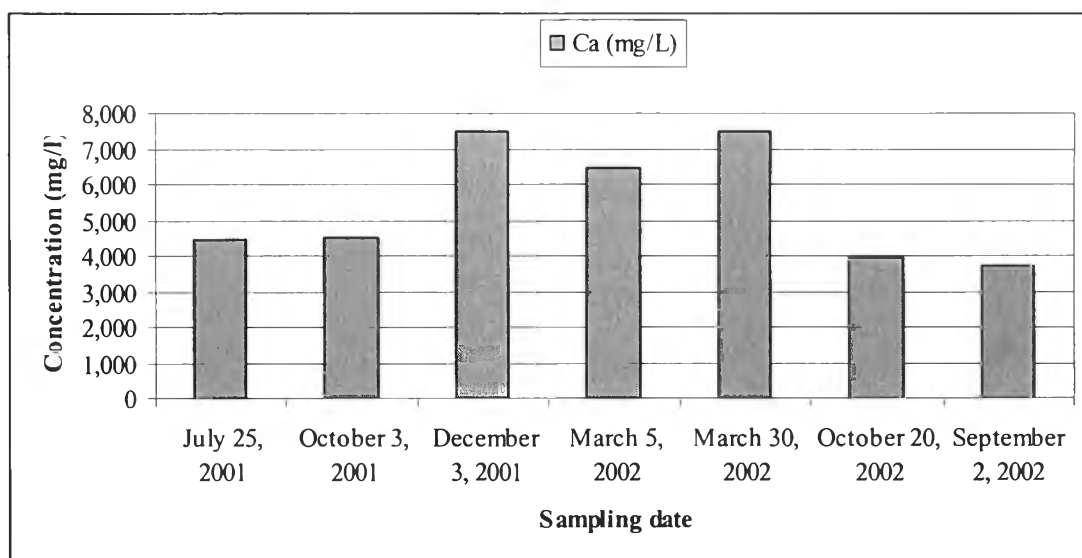
Figure 4.12 Ca content of saline groundwater at different seasons.

It could be concluded (Figure 4.12) that calcium concentration depends on the season. Dry season which is from December to March, yielded the highest amount of calcium (7,500 mg/l) while rainy season, July to September, showed decreasing in the calcium content. (3,690 mg/l)
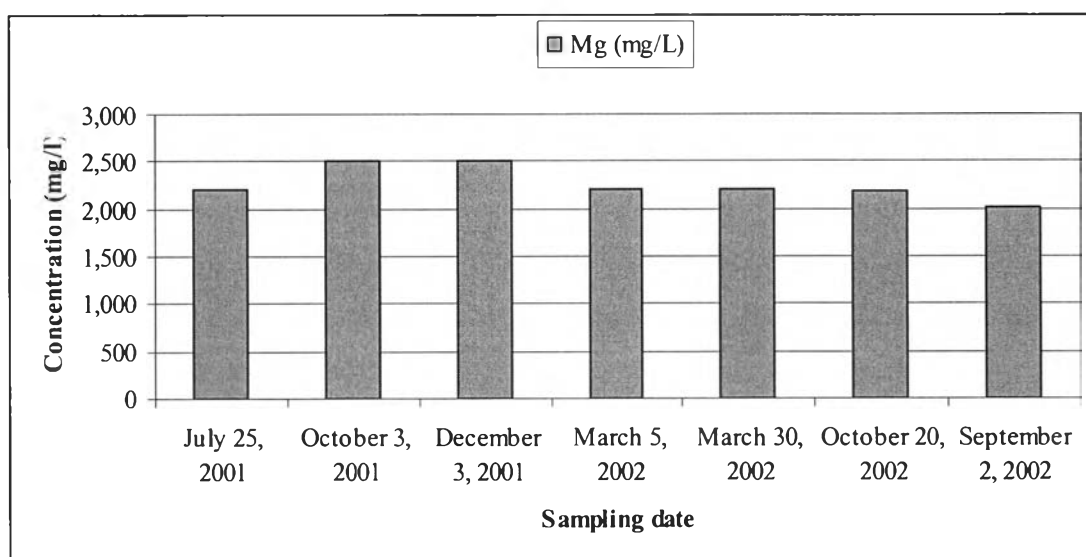

Figure 4.13 Mg content of saline groundwater at different seasons.

Similar to calcium, the magnesium content was also directly related to the season. Dry season gave the highest magnesium concentration (2,500 mg/l) whereas rainy season yielded the lower magnesium concentration. (2,010 mg/l)
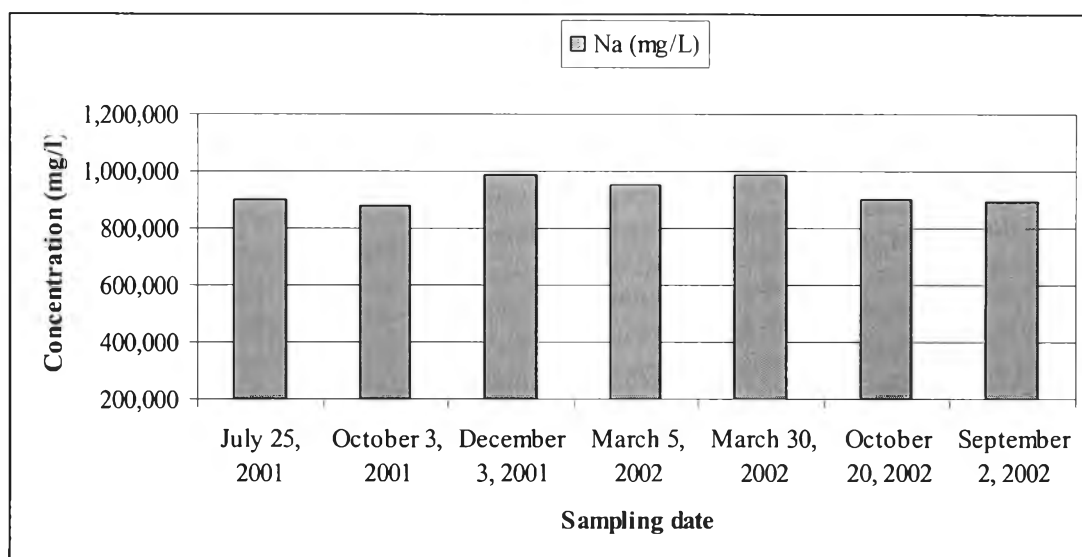
Figure 4.14 Na content of saline groundwater at different seasons.
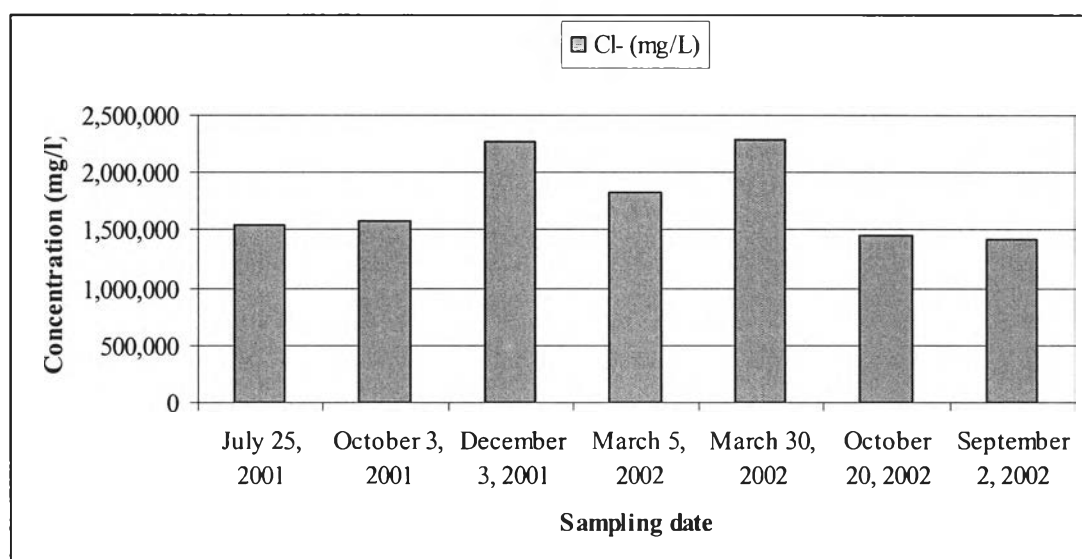

Figure 4.15 Cl content of saline groundwater at different seasons.

From figure 4.14 and 4.15, it can be stated that sodium and chloride concentration is also directly related to the season similar to that of calcium and magnesium. Dry season gave the highest amount of chloride (2,280,000 mg/l), while the rainy season gave lower concentration. (1,410,000 mg/l)
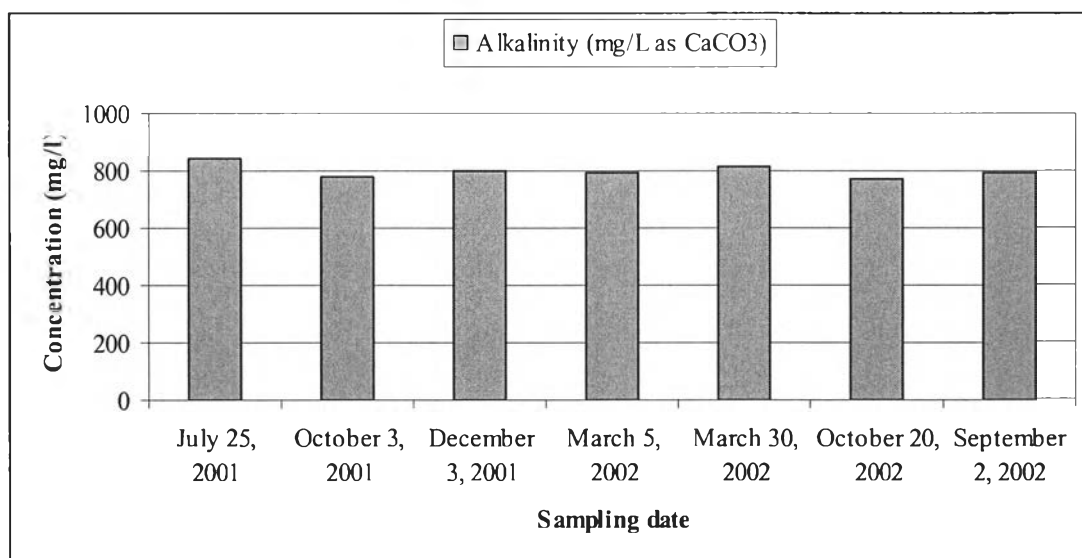
Figure 4.16 Alkalinity of saline groundwater at different seasons.

Unlike the other quality, alkalinity does not varied with the season. Both rainy and dry seasons gave the likely constant value, approximately 800 mg/l as $CaCO_3$

4.3 Precipitation of $CaCO_3$ and $Mg(OH)_2$ slurry

Precipitation of $CaCO_3$ and $Mg(OH)_2$ white slurry from the saline groundwater, collected from Bandung Subdistrict, samples by alkalinizing with NaOH. Determination of the optimum pH level was performed, of which the experimental results are presented as follows.

4.3.1 Optimum pH

The laboratory experiment was divided into two steps; the first step was performed by using all saline groundwater samples from four locations for precipitation of $CaCO_3$ and $Mg(OH)_2$ to determine the suitable saline groundwater source. Ca and Mg content in each saline groundwater samlpes were compared under the optimum pH. The second step was to take the selected saline groundwater site twice a month for four months covering the dry and rainy seasons to compare the effect of season to Ca and Mg content. Saline groundwater contains sodium chloride, magnesium chloride, calcium chloride and water. Upon an addition of sodium hydroxide to the analyzed saline groundwater for varying pH, $CaCO_3$ and $Mg(OH)_2$ were obtained in white slurry form (referred to Equations 2.1 and 2.2 of Chapter 2). The optimum pH had to be in the range of 12-13.5. The pH for precipitation is

approximately 12.5. Results of this experiment are shown in Table 4.3-4.9 and Figure 4.17-4.23.

Table 4.3 $CaCO_3$ and $Mg(OH)_2$ precipitation of saline groundwater: July 25, 2001.

NaOH (g)	pH	concentration (mg/l)	
		Ca	Mg
2.04	10.05	8,800	4,300
3.06	12.03	21,000	23,000
5.08	12.39	40,000	24,000
7.05	12.61	41,000	24,100
10.16	12.92	46,000	24,500
15.06	13.05	48,000	25,000

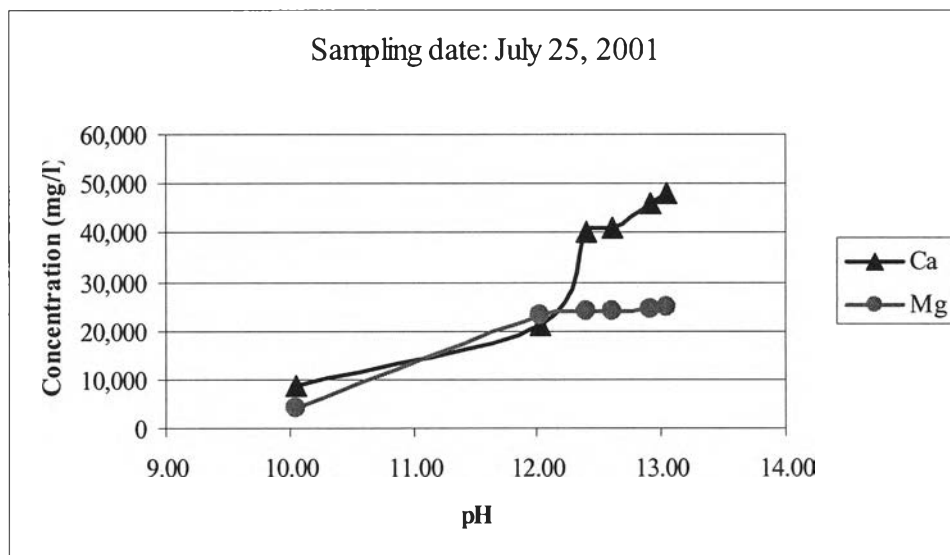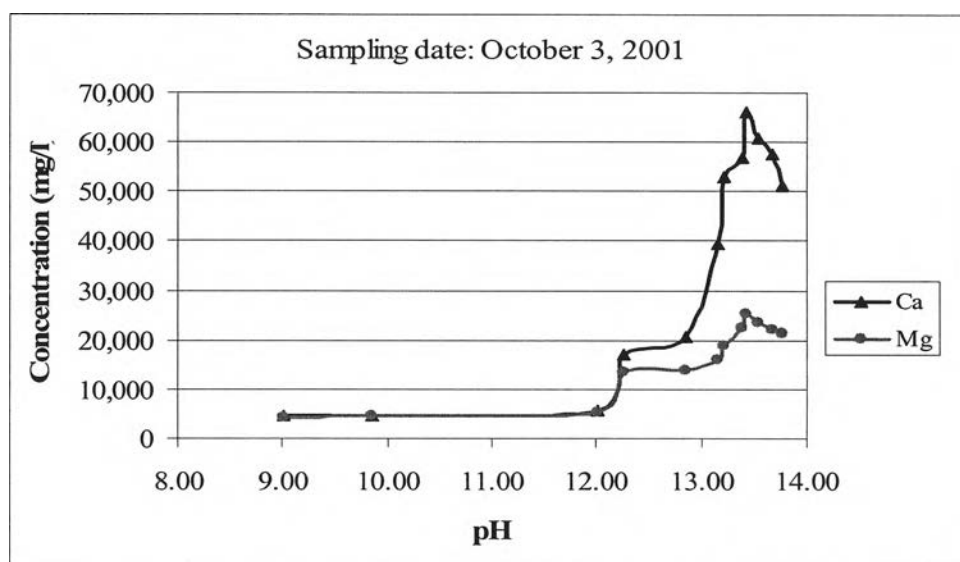**Figure 4.17** Optimum pH for precipitation of Ca & Mg: July 25, 2001.

NaOH in solid form was added into the selected saline groundwater to adjust the pH level which raised up 10-13. Then, the $CaCO_3$ and $Mg(OH)_2$ slurry and supernatant were taken to analyze calcium and magnesium concentration. Then, the comparison of calcium and magnesium content was performed in respect to each pH value.

**Table 4.4** $CaCO_3$ and $Mg(OH)_2$ precipitation of saline groundwater: October3, 2001.

NaOH (g)	pH	concentration (mg/l)	
		Ca	Mg
2.04	9.02	4,500	4,100
3.06	9.85	4,720	4,720
5.08	12.02	5,550	5,300
7.05	12.27	17,200	13,400
10.16	12.86	20,600	14,000
15.06	13.16	39,600	16,000
20.01	13.21	53,000	19,000
25.07	13.38	57,000	22,500
30.02	13.42	66,000	25,200
35.08	13.55	60,600	23,400
40.12	13.67	57,600	22,000
45.27	13.78	51,000	21,200

Figure 4.18 Optimum pH for precipitation of Ca & Mg: October 3, 2001.

From the result shown in Table 4.3 indicated that pH 13.0 gave the highest content of calcium and magnesium. To clarify the actual optimum pH, the experimental test was performed by using dedicated pH range (pH 9.02-13.78). The result revealed that pH raised up leading to the increasing of calcium and magnesium amount until at pH 13.42 where the highest amount was recorded, then the concentration started to decrease at pH 13.55, 13.67 and 13.78 respectively. It should be noted that with the very little pH change (from pH 13.0 to 13.42), the amount of calcium and magnesium at pH 13.42 were increased in the range of 2.5 to 3.0 times of the amount occurred at pH 13.0.

Table 4.5 CaCO$_3$ and Mg(OH)$_2$ precipitation saline groundwater: December 3, 2001.

NaOH (g)	pH	concentration (mg/l)	
		Ca	Mg
2.04	9.02	4,500	4,100
3.06	9.85	4,720	4,720
5.08	12.02	5,550	5,300
7.05	12.27	17,200	13,400
10.16	12.86	20,600	14,000
15.06	13.16	39,600	16,000
20.01	13.21	53,000	19,000
25.07	13.38	57,000	22,500
30.15	13.52	64,320	23,200
34.28	13.74	59,000	21,980
39.97	13.93	56,400	21,000
45.38	14.02	50,140	20,120
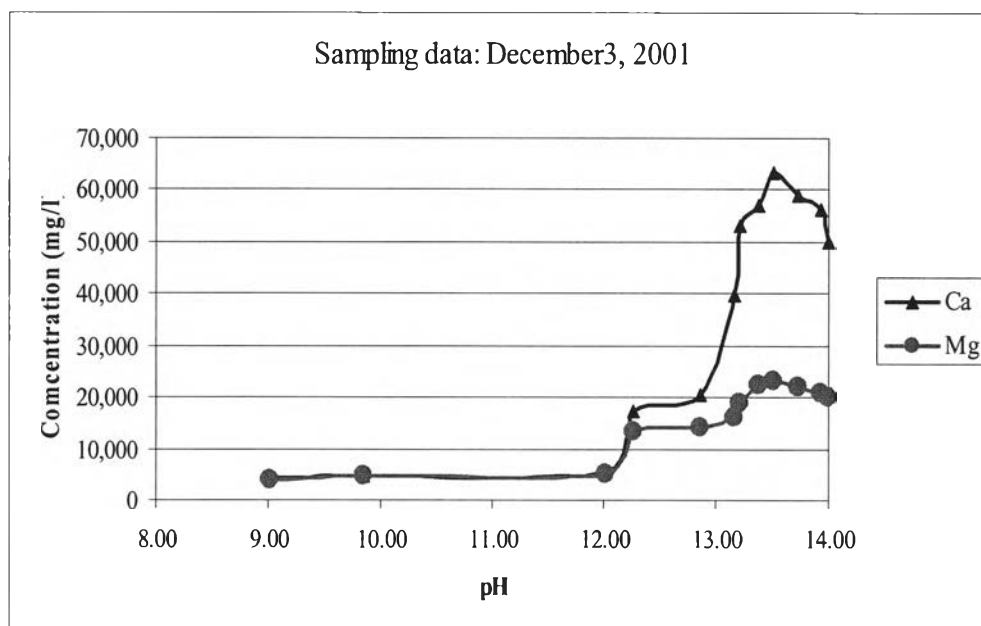
Figure 4.19 Optimum pH for precipitation of Ca & Mg: December 3, 2001.

Test results from the saline groundwater samples collected in December 2001, shown similar trend to the samples taken in July 2001 and October 2001.

The process for separation of magnesium and calcium from saline groundwater which contains sodium chloride, magnesium chloride, calcium chloride and water included agitating groundwater with addition of flocculating agent, sodium hydroxide, which can precipitate Mg^{2+} and Ca^{2+} as $Mg(OH)_2$ and $CaCO_3$, respectively. The chemical reaction is written in chapter 2.

Magnesium hydroxide, calcium carbonate, and sodium chloride produced from the reaction exist together but in two physical states; magnesium hydroxide and calcium carbonate are formed as solid particles while sodium chloride is dissolved in the liquid or water phase. An aqueous suspension containing solid particles is referred to as slurry. Gravity is used to separate the solids from the liquid in the aqueous suspension since magnesium hydroxide and calcium carbonate are heavier than water. After allowing the precipitate to settle for six hours, the supernatant was drained out and white slurry was collected to analyzed the calcium and magnesium content which the results indicate that calcium and magnesium content taken from Amphoe Bandung saline groundwater sample yielded the highest amount of calcium and magnesium content in range of 48,000-66,000 and 22,500-25,200 mg/l, respectively compared with other sources. It could be concluded that Amphoe Bandung saline groundwater source is best for the next step of the experiment.

The second step was to collect groundwater samples at Amphoe Bandung, Udonthani twice a month for 4 months covering dry and rainy season in order to compare the calcium and magnesium content relative to each season. The results are shown in Table 4.6-4.9 and Figure 4.20-4.23.

In dry season, Ca and Mg concentration under optimum pH range of 13.38-13.40 was in the range of 76,000-80,000 mg/l and 32,800-35,000 mg/l respectively. While calcium and magnesium concentration under optimum pH ranges of 13.42-13.51 was in the range of 29,500-30,450 mg/l and 17,000-18,000 mg/l respectively. It indicated that more calcium and magnesium content were found in dry season than rainy season. Therefore season has affect on the concentration of calcium and magnesium in saline groungwater.

Table 4.6 Ca & Mg concentration white slurry of saline groundwater: March 5, 2002.

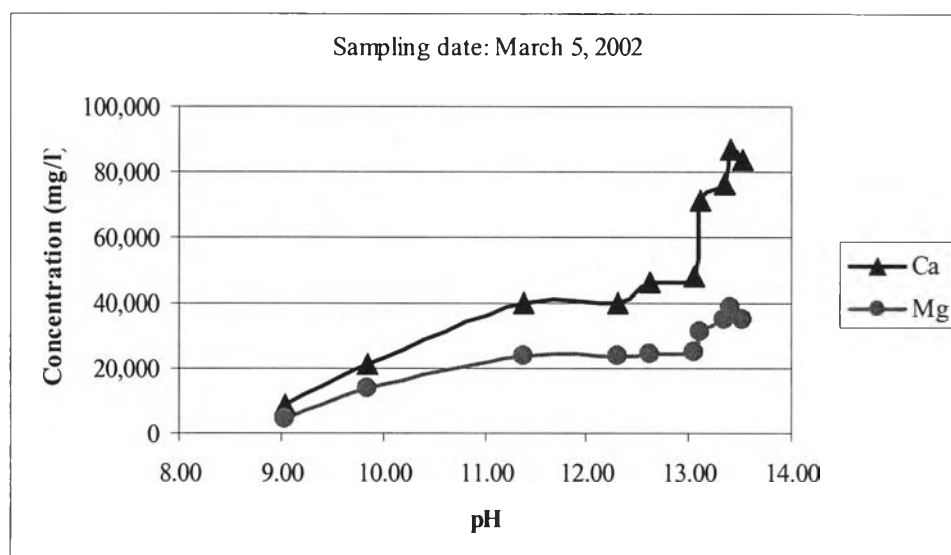| NaOH (g)	pH	concentration (mg/l)	
		Ca	Mg
2.04	9.04	8,800	4,300
3.06	9.85	21,000	14,000
5.08	11.39	40,000	24,000
7.05	12.31	40,000	24,000
10.16	12.62	46,000	24,500
15.06	13.05	48,000	25,000
20.01	13.12	71,000	31,000
25.07	13.35	76,000	35,000
30.02	13.40	87,000	38,500
35.08	13.53	84,000	35,200

Figure 4.20 Optimum pH for precipitation of Ca & Mg: March 5, 2002.

This sample was taken in dry season to study the calcium and magnesium content which occur from precipitation by NaOH. At pH 13.40 yields the highest amount of calcium (87,000 mg/l) and magnesium (38,500 mg/l).

Table 4.7 Ca & Mg concentration of white slurry saline groundwater: March 30, 2002.

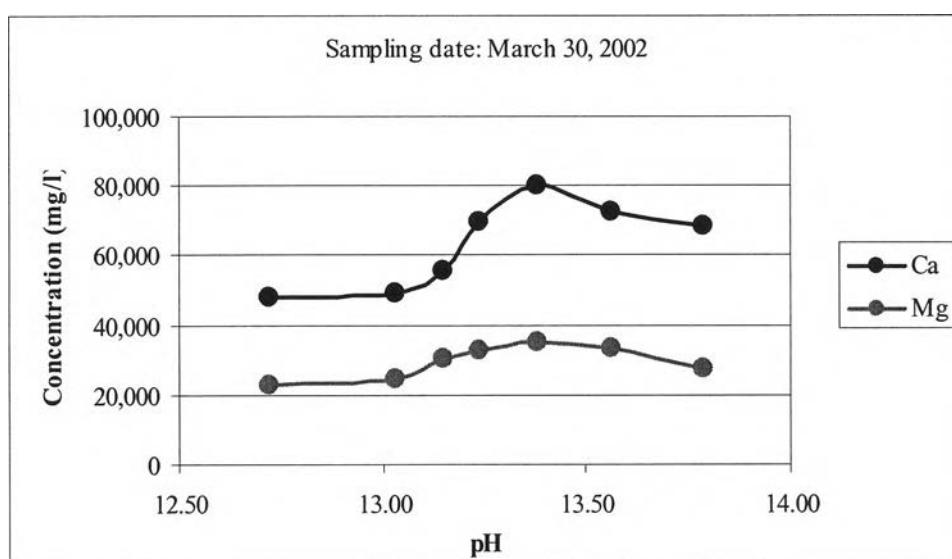| NaOH (g)	pH	concentration (mg/l)	
		Ca	Mg
10.08	12.72	48,000	22,800
15.01	13.03	49,300	24,500
20.18	13.15	55,500	30,500
25.00	13.24	69,300	32,800
30.12	13.38	80,000	35,000
35.02	13.56	72,500	33,200
40.01	13.79	68,300	27,700

Figure 4.21 Optimum pH for precipitation of Ca & Mg: March 30, 2002.

On March 30, 2002 the sample was taken again to confirm the former result. This result gave the same trend; at pH 13.38 yields the best value that precipitate the highest amount of calcium and magnesium.

Table 4.8 Ca & Mg concentration of white slurry saline groundwater: October 20, 2002.

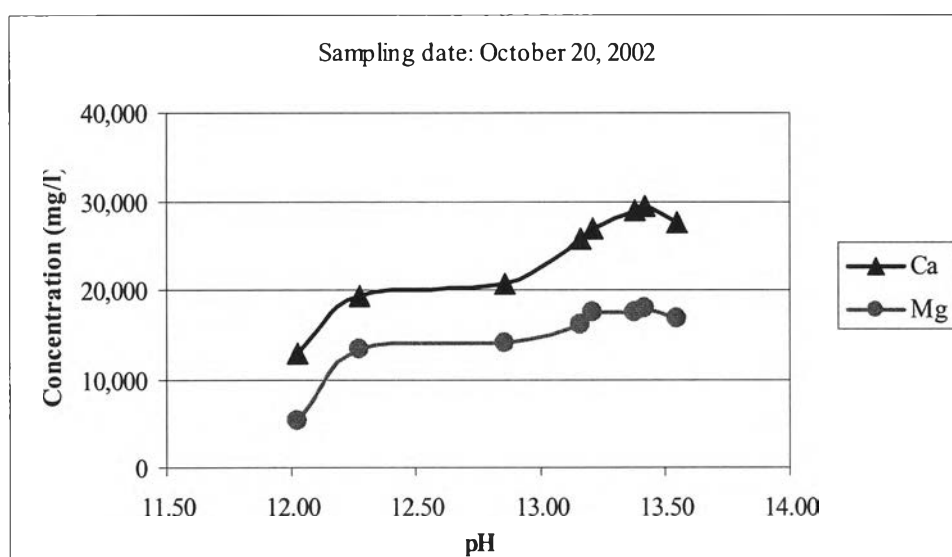| NaOH (g)	pH	concentration (mg/l)	
		Ca	Mg
5.08	12.02	12,840	5,300
7.05	12.27	19,200	13,400
10.16	12.86	20,600	14,000
15.06	13.16	25,700	16,000
20.01	13.21	26,800	17,400
25.07	13.38	28,950	17,500
30.02	13.42	29,500	18,000
35.08	13.55	27,600	16,800

Figure 4.22 Optimum pH for precipitation of Ca & Mg: October 20, 2002.

Groundwater sample was taken in rainy season to compare the content of Ca and Mg with that of the dry season. The result showed that calcium and magnesium content were lower than the concentration of the dry season. The content of Ca and Mg in $CaCO_3$ and $Mg(OH)_2$ slurry was 2.5-3 times less in the dry season at the same pH.

Table 4.9 Ca & Mg concentration of white slurry saline groundwater: September 2, 2002.

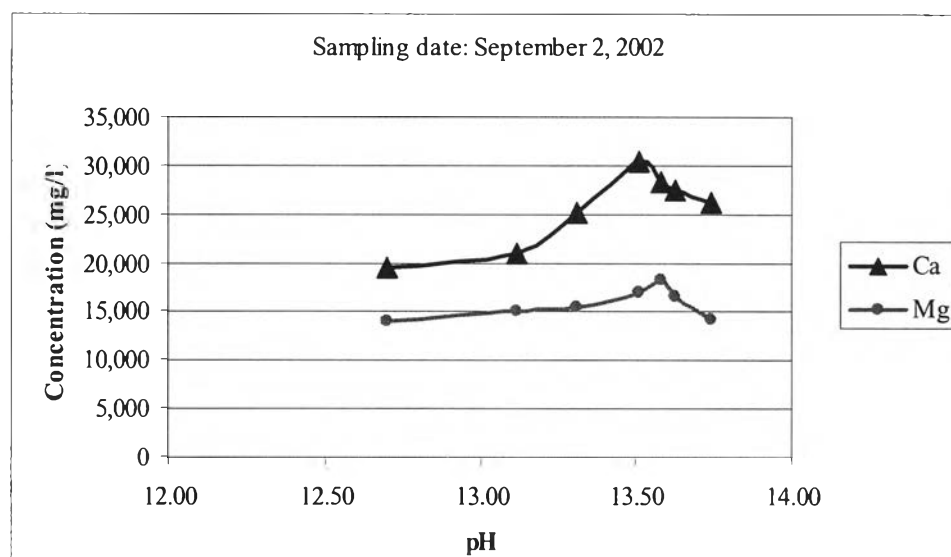| NaOH (g)	pH	concentration (mg/L)	
		Ca	Mg
10.08	12.7	19,400	14,000
15.01	13.12	21,000	15,000
20.18	13.31	25,200	15,500
25.20	13.51	30,450	17,000
30.02	13.58	28,350	18,300
35.19	13.63	27,500	16,500
40.01	13.74	26,300	14,300

Figure 4.23 Optimum pH for precipitation of Ca & Mg: September 2, 2002.

The sample was taken again on September 2002 to confirm the result in rainy season. At pH 13.51 was the best value that occur the highest calcium and magnesium amount. Similarly on October 20, 2002 the test showed that amount the is also 2.5-3 times less than the dry season at the same pH. This confirmed that the Ca and Mg content have a direct relationship with respect to the season.

4.4 Precipitation of Chromium Tanning Wastewater with White Slurry.

Precipitation of chromium was performed by adding white slurry of $CaCO_3$ and $Mg(OH)_2$, prepared from alkalinization at the optimum pH of saline groundwater (pH 13.38 to 13.56), into the tanning wastewater (pH 3.7 to 4.6). Cr^{3+} will be precipitated as $Cr(OH)_3$ in pH ranges between 8.5-9.0 based on literature reviews. The experiments of Jar test were used for determination of the optimum dosage of the white slurry in the pH range of 7.5 to 9.8. The optimum dosage was indicated by the removal efficiency of chromium, which are presented in Table 4.10-4.13 and Figures 4.24 - 4.27.

Analyses of supenatant is also presented in Table 4.14. It obviously showed that except pH and chromium, other contents including COD, solids, sodium and chloride were not removed through this precipitation.

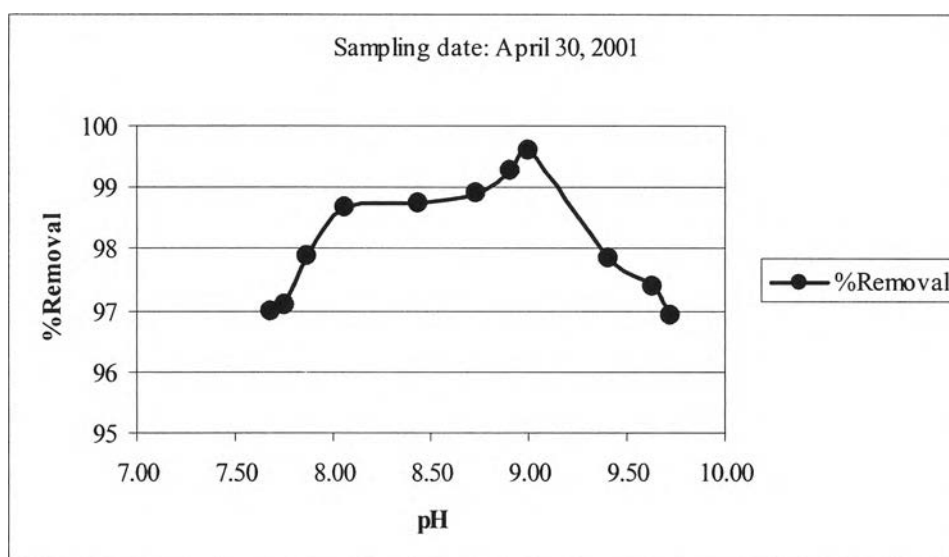**Table 4.10** Chromium removal efficiencies by $Mg(OH)_2$ & $CaCO_3$: July 20,2001.

Initial chromium (mg/l)	Ca(OH)$_2$& Mg(OH)$_2$ dose (ml)	pH	chromium (mg/l)	% Removal
498	10	7.52	7.25	98.54
	11	7.67	7.21	98.55
	12	8.20	5.39	98.92
	13	8.43	3.25	99.35
	14	8.87	3.12	99.37
	15	8.90	3.05	99.39
	16	8.97	2.78	99.44
	17	9.07	2.30	99.54
	18	9.18	8.10	98.37
	19	9.21	8.30	98.33
	20	9.34	9.76	98.04
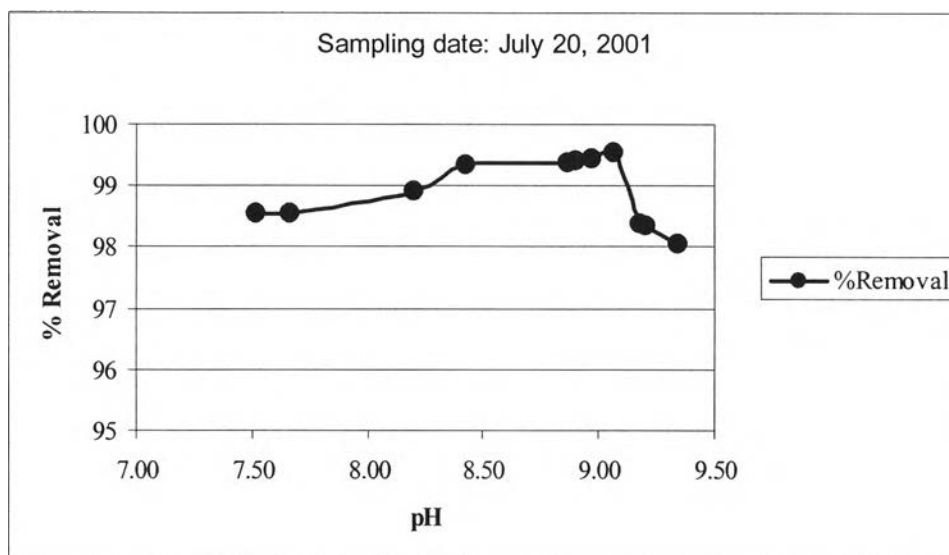
Figure 4.24 Optimum pH for Cr removal: July 20,2001.

The white slurry of $CaCO_3$ and $Mg(OH)_2$ was added to adjust pH from 7.52 to 9.34 of the tanning wastewater which contained 498 mg/l of chromium. Table 4.10 shows that in the pH range of 7.52 to 9.34, 98.04-99.54% of chromium could be removed whereas the maximum removal was at pH 9.07.

Table 4.11 Chromium removal efficiencies by Mg(OH)2 & $CaCO_3$: April 30, 2001.

Initial chromium (mg/l)	$Ca(OH)_2$&$Mg(OH)_2$ dose (ml)	pH	chromium (mg/l)	%Removal
236	10	7.68	7.12	96.98
	11	7.75	6.89	97.08
	12	7.87	5.01	97.88
	13	8.06	3.15	98.67
	14	8.44	2.98	98.74
	15	8.73	2.54	98.92
	16	8.91	1.73	99.27
	17	9.00	0.95	99.60
	18	9.41	5.11	97.84
	19	9.63	6.13	97.40
	20	9.72	7.28	96.92

Figure 4.25 Optimum pH for Cr removal: April 30, 2001.

For other testes with the wastewater taken on April 2001, October 2002 and December 2002, similar results were obtained as shown in Table 4.11 – 4.1 and Figures 4.25 – 4.27. The optimum pH was about 9.0 and the chromium removal was about 99.0%. However, the Cr concentration of the supernatant (remaining chromium) was still higher(0.93-2.30 mg/l at 99.5% removal) than the effluent standard (0.05 mg/l).

Table 4.12 Chromium removal efficiencies by Mg(OH)2 & CaCO$_3$: October 26, 2002.

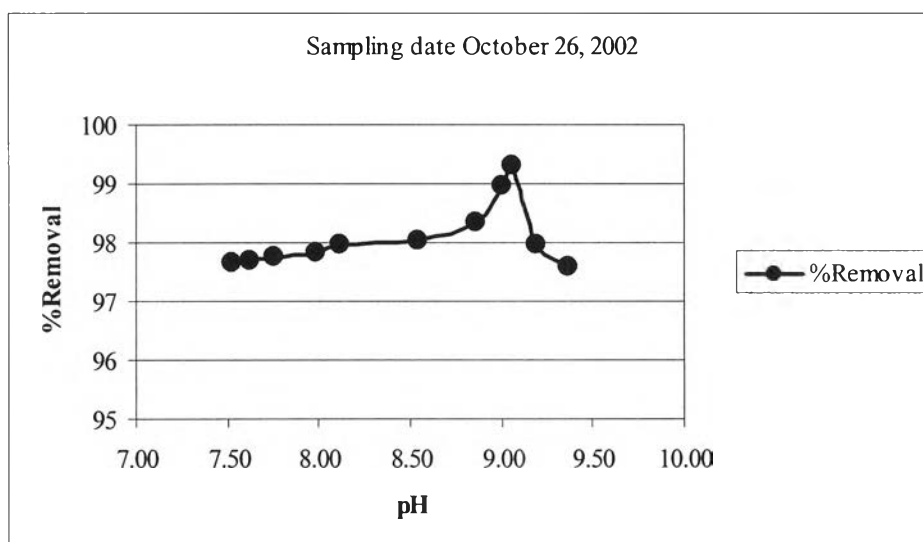| Initial chromium (mg/l)	Ca(OH)$_2$&Mg(OH)$_2$ dose (ml)	pH	chromium (mg/l)	% Removal
302	10	7.53	7.10	97.65
	11	7.62	7.02	97.68
	12	7.76	6.75	97.76
	13	7.98	6.53	97.84
	14	8.12	6.13	97.97
	15	8.54	5.93	98.04
	16	8.86	4.98	98.35
	17	9.00	3.10	98.97
	18	9.06	2.06	99.32
	19	9.19	6.10	97.98
	20	9.37	7.35	97.57

Figure 4.26 Optimum pH for Cr removal: October 26, 2002.

Table 4.13 Chromium removal efficiencies by Mg(OH)2 & CaCO₃: December 12, 2002.

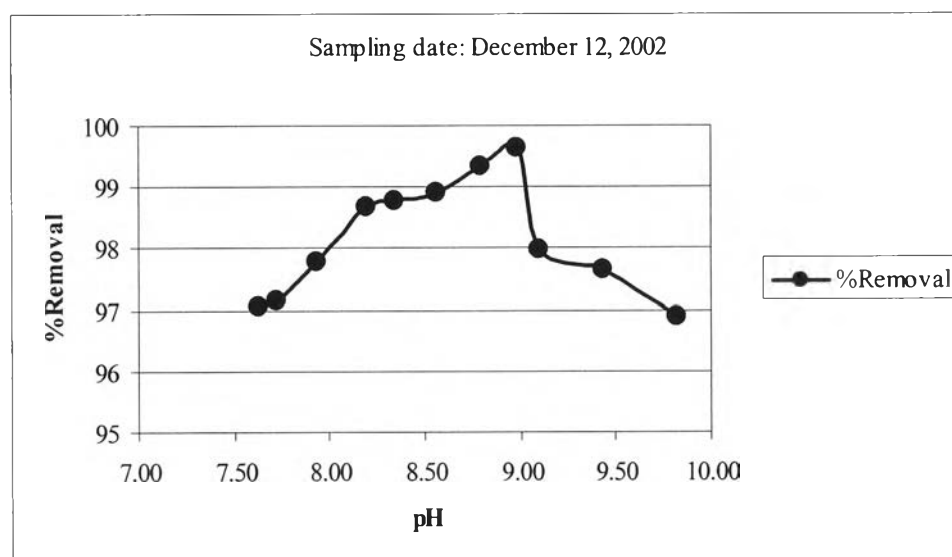| Initial chromium (mg/l)	Ca(OH)₂&Mg(OH)₂ dose (ml)	pH	chromium (mg/l)	%Removal
242	10	7.63	7.14	97.05
	11	7.72	6.92	97.14
	12	7.93	5.35	97.79
	13	8.20	3.21	98.67
	14	8.34	3.00	98.76
	15	8.56	2.67	98.90
	16	8.79	1.62	99.33
	17	8.98	0.93	99.62
	18	9.10	4.88	97.98
	19	9.43	5.67	97.66
	20	9.82	7.52	96.89

Figure 4.27 Optimum pH for Cr removal: December 12, 2002.

Table 4.14 Analyses of supernatant after precipitating by Mg(OH)$_2$ & CaCO$_3$ various sampling date.

Sampling Date	Initial Cr (mg/l)	Eff. Cr (mg/l)	pH	COD (mg/l)	TS (mg/l)	SS (mg/l)	TDS (mg/l)
July 20,2001	498	17	9.07	1,186	36,770	110	36,660
April 30, 2001	236	17	9.07	1,186	36,770	110	36,660
October 26, 2002	302	2.06	9.06	1,100	39,265	145	39,120
December 12, 2002	242	0.93	8.98	637.1	17,390	100	17,290

In conclusion, the white slurry obtained at optimum pH was added into the tanning wastewater at any concentration of chromium to precipitate chromium. The optimum pH for chromium precipitation by adding white slurry was in the range of 8.0-9.0. The average chromium removal efficiency was 99.45 %. Moreover, the chromium hydroxide precipitate generated by the white slurry of CaCO$_3$ and Mg(OH)$_2$ was packed, thus resulted in less sludge volume. The mechanism of chromium precipitation taken place by chromium react with hydroxide that raised by magnesium hydroxide. In the mean time magnesium hydroxide itself and calcium carbonate act as the coagulant that enhance coagulation of chromium hydroxide.

4.5   Recovery of Chromium from Cr(OH)$_3$ Precipitate

Chromium in the precipitation form of Cr(OH)$_3$ can be recovered by adding H$_2$SO$_4$ to dissolve chromium as Cr$_2$(SO$_4$)$_3$, which can be reused again in the tanning process. Cr(OH)$_3$ precipitation was analyzed for chromium before adding H$_2$SO$_4$ which is used to decrease the pH level to the range of 1.6 -2.8. Supernatant was analyzed for pH and total chromium.

The recovery was according to the chemical reaction shown in equation 4.1. (Tongchai, 1995)

$$2Cr(OH)_{3(s)} + 3H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 6H_2O \qquad (4.1)$$

The recover results are presented in Table 4.15 and Figures 4.28 - 4.31. At any concentration of chromium in the precipitate, the highest recovery was obtained at pH 2.0. However, the recovery could be gained in the range of 53.47-63.33%. The recovery efficiency was varied likely with the concentration of chromium precipitate. At the optimum pH (pH 2.0), the recovery efficiency of 53.47%, 53.09%, 57.73% and 63.33% were for the chromium of precipitate of 242, 236, 302 and 498 mg/l, respectively.

Table 4.15 Recovery of Chromium from $Cr(OH)_3$ Precipitate various in sampling date.

| Sampling Date	Initial Cr (mg/L)	Precipitation Cr (mg/g)	pH	Cr (mg/g)	% Recovery
July 20,2001	498	86.53	1.60	51.50	59.52
			1.80	52.20	60.33
			2.00	54.80	63.33
			2.20	46.75	54.03
			2.40	44.32	51.22
			2.60	42.99	49.68
April 30, 2001	236	28.29	1.60	14.1	49.84
			1.80	14.23	50.30
			2.00	15.02	53.09
			2.20	13.89	49.10
			2.40	10.39	36.73
			2.60	9.12	32.24
October 26, 2002	302	65.82	1.60	37.20	56.52
			1.80	37.65	57.20
			2.00	38.00	57.73
			2.20	37.51	56.99
			2.40	33.78	51.32
			2.60	31.65	48.09
December 12, 2002	242	30.15	1.60	15.28	50.68
			1.80	15.73	52.17
			2.00	16.12	53.47
			2.20	14.13	46.87
			2.40	12.38	41.06
			2.60	11.48	38.08
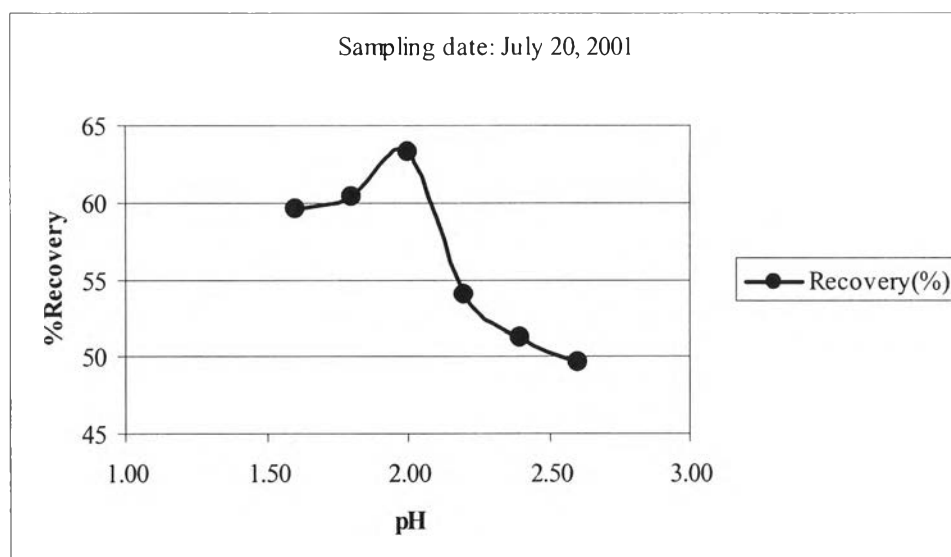
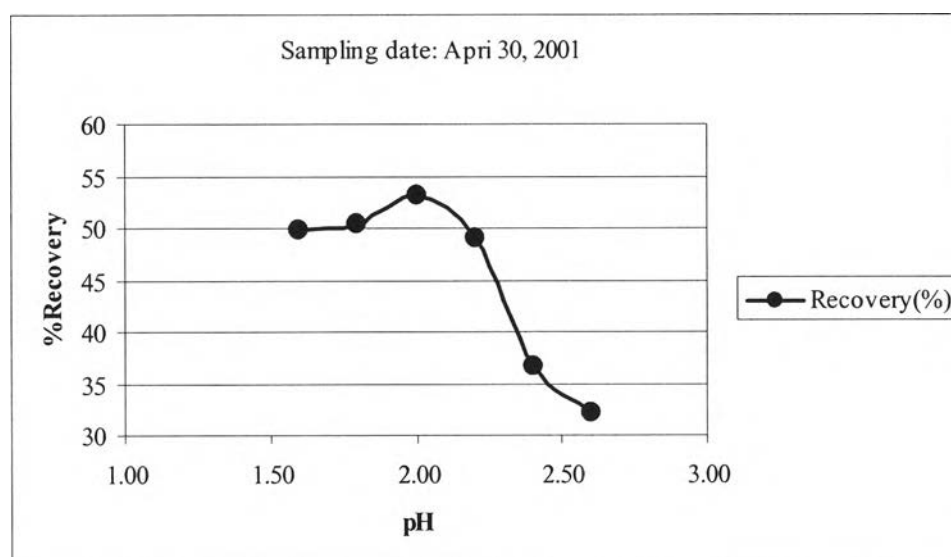**Figure 4.28** Optimum pH for Cr recovery: July 20, 2001.

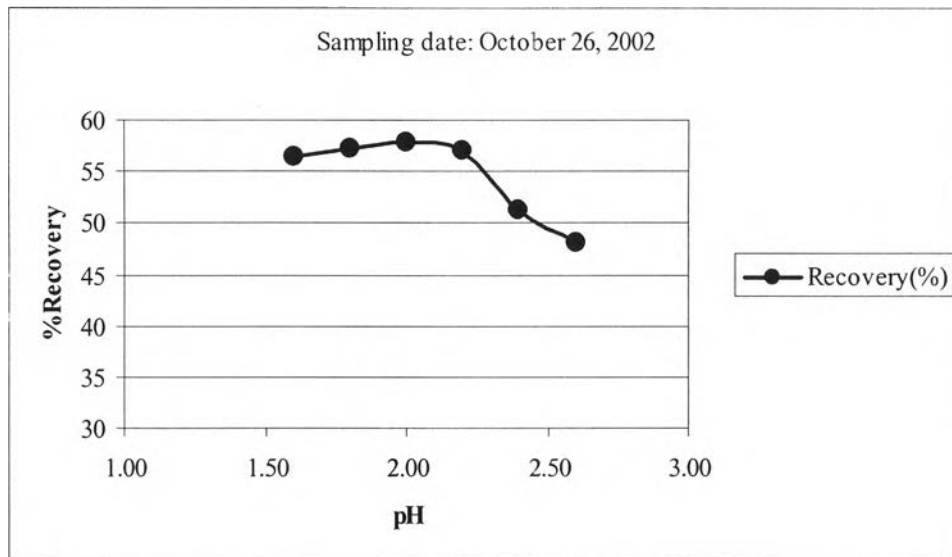**Figure 4.29** Optimum pH for Cr recovery: April 30, 2001.

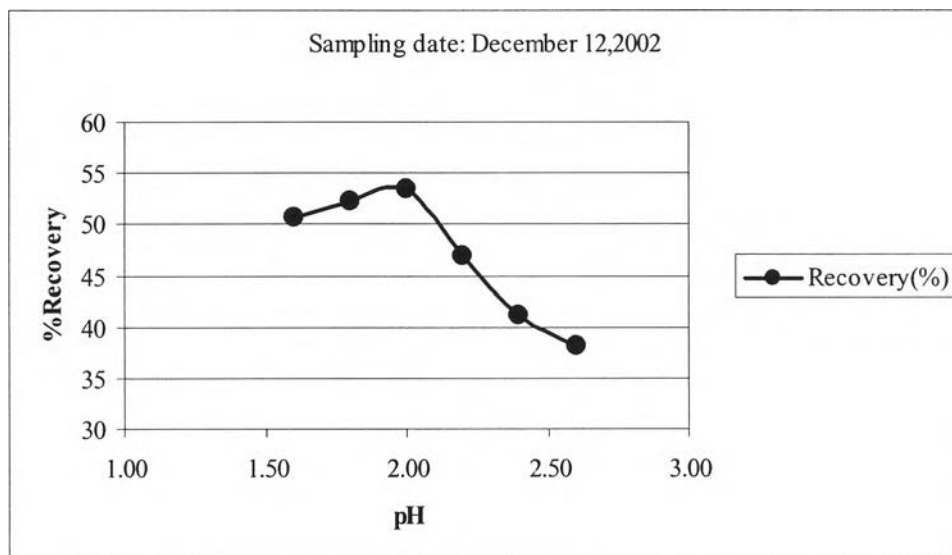**Figure 4.30** Optimum pH for Cr recovery: October 26, 2002.

Figure 4.31 Optimum pH for Cr recovery: December 12, 2002.

4.6 Model Scale Test

The reactor was filled up with six liters of tanning wastewater. Then the optimum dosage of the mixture of $Mg(OH)_2$ and $CaCO_3$, white slurry obtained from Jar test was added to the reactor for precipitation of $Cr(OH)_3$ for the pH ranges of 8.5-9.0. The recovery of chromium was carried out by adding H_2SO_4 to reach the optimum pH at 2.0. Analyses parameters included initial total Cr of wastewater, total

Cr of $Cr(OH)_3$ precipitate, and total Cr of the recovery solution are shown in Table 4.16. The optimum pH for Cr removal are presented in Figures 4.32-4.35.

Table 4.16 Chromium Removal by $Mg(OH)_2$ & $CaCO_3$ in model scale test various in sampling date and initial concentration.

| Sampling Date	Initial chromium (mg/L)	Ca(OH)₂ & Mg(OH)₂ dose (mL)	pH	Chromium (mg/L)	% Removal
July 20, 2001	498	208	8.14	10.23	97.95
		230	8.53	4.67	99.06
		248	8.83	7.01	98.59
		265	9.16	11.68	97.65
April 30, 2001	236	105	8.10	5.33	97.74
		128	8.57	2.64	98.88
		135	8.94	1.42	99.40
		150	9.42	5.89	97.50
October 26, 2002	302	155	8.02	7.46	97.53
		185	8.48	4.33	98.57
		200	9.10	2.71	99.10
		226	9.52	5.01	98.34
December 12, 2002	242	110	8.22	5.74	97.63
		145	8.65	2.79	98.85
		162	9.04	1.63	99.33
		185	9.71	6.42	97.35
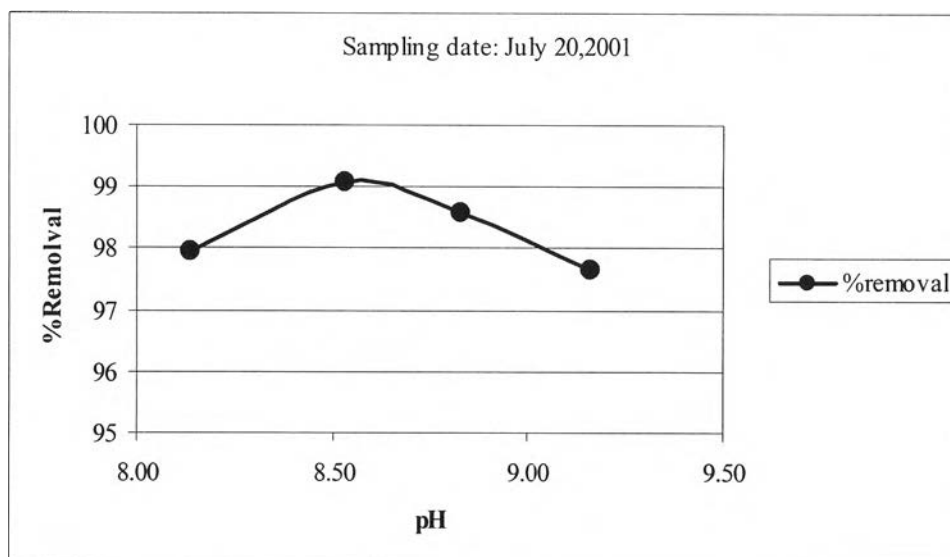
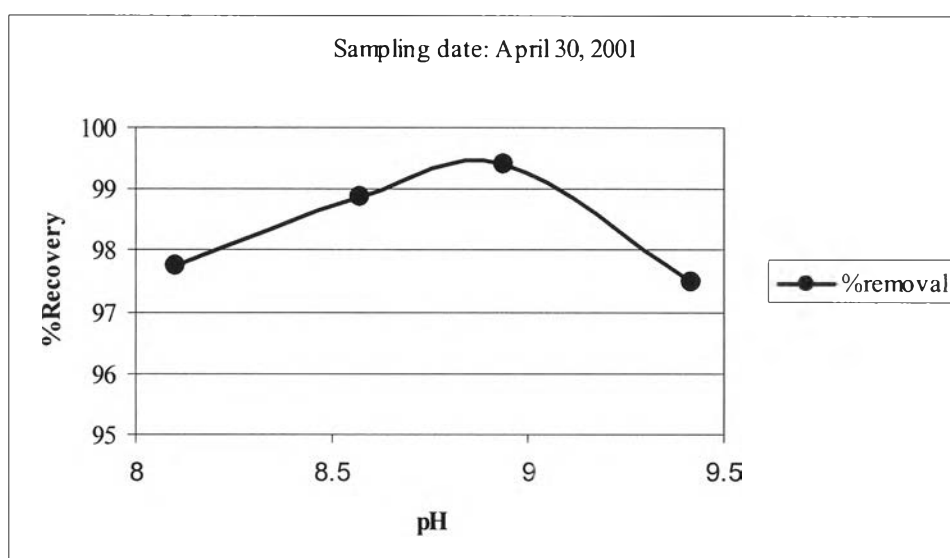**Figure 4.32** Optimum pH for Cr removal: July 20, 2001.

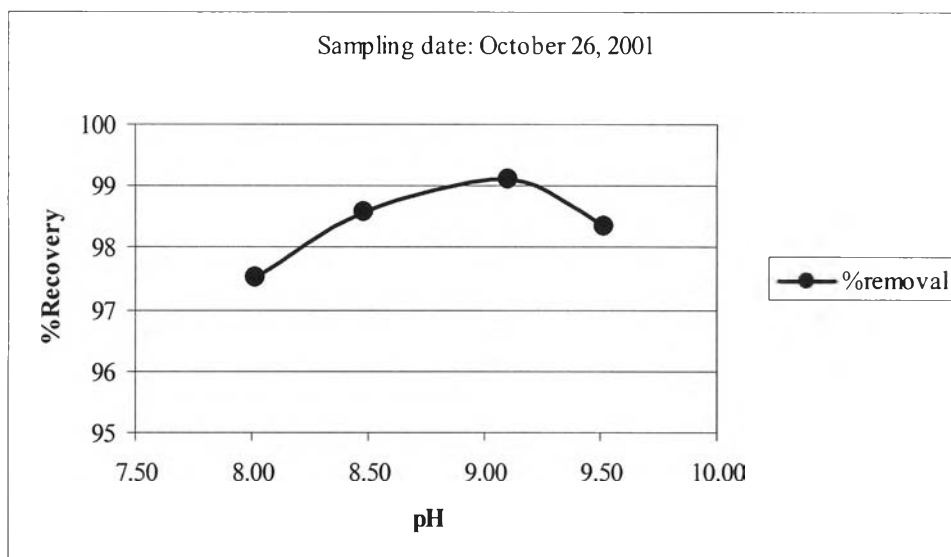**Figure 4.33** Optimum pH for Cr removal: April 30, 2001.

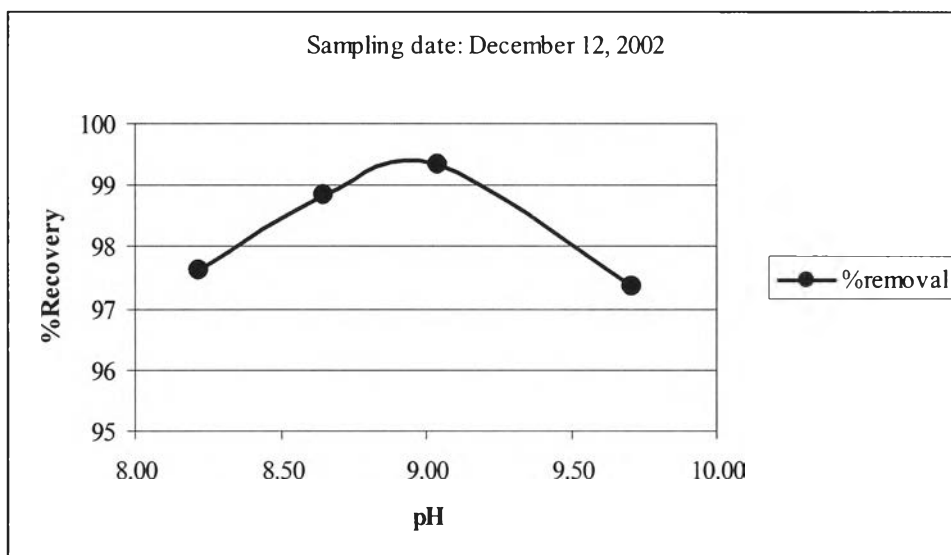**Figure 4.34** Optimum pH for Cr removal: October 26, 2002.

Figure 4.35 Optimum pH for Cr removal: July 20, 2001.

Similarly to the jar test results, the removal efficiency was found to be 97.35-99.40%. However, the concentration of chromium in the effluent was in the range of 1.42 to 11.68 mg/l which is sitll higher than the industrial effluent standard of 0.05 mg/l. Therefore, it is suggested that additional steps of chromium removal is needed.