CHAPTER V

RESULTS AND DISCUSSIONS

5.1 Characteristics of the Treated Effluents

Results of the experiments shown in Tables 5 and 6 indicated the possibility of using the ion exchange system for treating chrome wastewater. The chromium content in the treated water at 400 cu.dm.(200 BV) of effluent was ranging from as low as the trace amount to 0,18 mg/cu.dm.Cr VI. The pH of the composite trated water was rather low, ranging from 2.83 to 7.7. This could be explained by the fact that the breakthrough points of chloride and other anions occurred prior to that of dichromate ions. When the former group of ions combined with hydrogen, the reaction would end up with acids which tended to decrease the pH of the product water. However, the treated water could be either disposed of with minimum adverse effect to the environment, providing that neutralization was practiced prior to discharge, or directly recycled to the rinsing stage in the electroplating process. As a result, a close-circuit or non-waste system could be experienced.

In each experiment, the treated water volume at breakthrough point of the ion exchange cycle was ranging from 300 to 600 cu.dm.(150 to 300 BV/cycle) and it was found that the break-

Table 5 Heavy Metal Removal by Ion Exchange Process

Demineralization Flowrate = 16 BV/hour

Run No.	1	2	3	4	5	6	7	8
Date	2.2.78	9.2.78	18.2.78	23.2.78	1.3.78	9.3.78	15. 3.78 2	4.3.78
Regeneration Level,				Militari et e er zanyaren egelen e.	: 10 1-40 . 1007 Harrier 14. 17. 10 (40)	erina demine e decreta e decembra de	t de til desse i de la primer femologie	•
gm NaOH/cu.dm.Resin	349.20	222.18	105.57	72.74	162.50	284,63	162.50	162.50
meq./cu.cm.Resin	8.73	5.55	2.64	1.82	4.06	7.12	4.06	4.06
Regenerant NaOH Concn, % by wt.	15.0	10.0	5.0	3.5	7.5	12.5	7.5	7.4
Breakthrough Volume, cu.dm.	5 7 5	633	575	528	537	515	575	545
Influert pH	6.0	4.7	4.4	4.13	3.97	3.53	3.6	3.57
Cr VI	104	88	91	97	98	97.5	97	100
Zn			111/6/16	5			- A COM BUILDING	
Fe				0.	.02			
Cu				0.	.1			
Effluent pH	6.5	7.0	5.9	6.65	6.55	4.6	7.7	5.25
at 200BV Cr VI	tr	tr	tr	0.02		tr	tr	tr
(400 cu. Zn		VA.						
dm.) Fe				Ni:	1 7			
Cu								

Note: All values except pH are in mg/cu.dm.

tr = trace amount

Table 6 Heavy Metal Removal by Ion Exchange Process

Demineralization Flowrate = 16 BV/hour

Regeneration Level = 162.5 gm NaOH/cu.dm.Resin

= 4.06 meq./cu.cm.Resin

Run No.		9	10	11	12	13	14	15	16	17
Date	CALLED TO SELECT SECTION OF THE PARTY OF THE	13.6.78	22.6.78	29.6.78	6.7.78	13.7.78	19.7.78	27.7.78	7.8.78	14.8.78
Regenerant Concn, % k		3.5	5.0	10.0	12.5	15.0	7.5		7.5	
Breakthrou Volume, cu		443	405	392	386	321	411	392	367	380
	pH Cr VI	3•2 9 8	3.37 99	3.4 101	3.4 98	3.4 98	3.3 105	3.33 99	3.2 105	2.8 101
	Zn Fe Cu					5 0.02 0.1				
Effluent at 200 BV	pH Cr VI	4.8 tr	4.2 0.01	3.9 0.04	3.6 0.05	3.3 0.18	3.75 tr	3.33 0.04	3.2 0.03	2.83 0.02
(400 cu. dm.)	Zn Fe Cu		·			nil				

Note: All values except pH are in mg/cu.dm.

tr = trace amount

through volumes in the experiments No. 9 to No. 16 were less than those in the experiments No. 1 to No. 8. The breakthrough volumes in the experiments No. 1 to 8 and No. 9 to 17 ranged from 500 to 600 and 300 to 400 cu.dm./cycle. This could be explained that after the eighth experiment, the exhausted ion exchange resin beds were left standing in diluted chromic acid solution for nearly three months, Chromic acid is a strong oxidising agent. It may deteriorate the resin to some extent and, as a result, decrease the efficiencies of the resins. (1)

5.2 SBA Column Regeneration

The regeneration condition of the SAC column was kept constant throughout this investigation. Four cu.dm. of eight per cent by weight hydrochloric acid was used as the regenerant. With this method, the quality of the feed water from SAC column to SBA column would be the same in every cycle. On the contrary, different regeneration levels, contact times, regeneration flowrate and concentrations, of sodium hydroxide regenerant were used for the regeneration of SBA column such that their effects could be evaluated.

5.2.1 SBA Column Regeneration at Constant Regenerant Volume

The results of the experiments No. 1 to No. 6 are shown in Table 7. Four cu.dm. of sodium hydroxide regenerant was used while the regeneration flowrate was kept constant at the rate of 150 cu.cm./min.(4.5 BV/hr.) and variation of sodium hydroxide

Table 7 Characteristics of Eluted Sodium Dichromate and Reclaimed Chromic Acid at Various Sodium hydroxide Regenerant Concentrations

Run No.		1	2	3	4	5	6	7	8
Date		2.2.78	9.2.78	18.2.78	23.2.78	1.3.78	9.3.78	16.3.78	24.3.78
NaOH Concn	, % by wt.	15.0	10.0	5.0	3.5	7.5	12.5	7.5	7.5
Regenerati gm NaOH/cu meq./cu.cm	.dm.Resin	349.20 8.73	222.18 5.55	105.57	72.74 1.82	162.50 4.06	284.63 7.12	162.50 4.06	162.50 4.06
Regenerati cm.cm./m BV/hour	on Flowrate, in.	150 4.5	150 4.5	150 4.5	150 4.5	150 4.5	150 4.5	100 3.0	200 6.0
Contact ti	me, min.	26.7	26.7	26.7	26.7	26.7	26.7	40.0	20.0
Eluted Na ₂ Cr ₂ 7	Composite pH Peak Cr VI	13.77 23,300		13.40	11.80 9,094		7 13.70 2 23,360		3 13.5 3 18,67
2 2	Composite Cr VI Composite Na	6,030	5,532	4,313 16,813	•		4,89° 5 25,62		3 4,09 3 16,50
Reclaimed H ₂ Cr ₂ O ₇	Composite pH Peak Cr VI Composite Cr VI Composite Na Composite Acidit (CaCO ₂)	1.87 5,250 3,810	4,782	4,157 5 3,225 5 92.5	3,532 2,953 4.2	5,469 4,000 294.0	4,29° 3,11° 112,	7 4,438 0 3,438 5 350.6	B 3,95 B 2,86 O 115.

Note: All values except pH are in mg/cu.dm.

Chromic Acid Reclamation Flowrate = 16 cu.dm./hour = 8 BV/hour.

concentration ranging from 3.5 to 15.0 per cent by weight was investigated. History curves of the SBA column regeneration as represented by the concentration of the hexavalent chromium in the eluted sodium dichromate solution are shown in Figure 9. Since the highest possible concentration of recovered dichromate was required, it was evident that the optimum concentration of sodium hydroxide regenerant was 7.5 per cent by weight. The peak values of chromium concentration in the eluted sodium dichromate solution rose from 9,094 to 22,422 mg./cu.dm.Cr VI (an increase of 147 per cent) as the concentration of sodium hydroxide regenerant was raised from 3.5 to 7.5 per cent, see Figure 10. Furthermore, the average chromium content in the whole composite sodium dichromate solution increased from 3,538 to 5,938 mg./cu.dm.Cr VI, when the concentration of regenerant was raised from 3.5 to 7.5 per cent respectively.

Beyond the optimum 7.5 per cent regenerant concentration, there was no clear distinction among the concentrations of chromic acid. An increase of the regenerant concentration from 7.5 to 15.0 per cent could only raise the peak value of dichromate from 22,422 to 23,300 mg./cu.dm.Cr VI, or a 0.04 per cent rise. In some case, as shown in Figure 10, both the peak and average values of the chromium content even declined. This was probably due to the high density of the concentrated sodium hydroxide solution. The specific gravity of SBA resin in chloride form was 1.09 while those of sodium hydroxide solution was reported to be 1.0869, 1.1089,

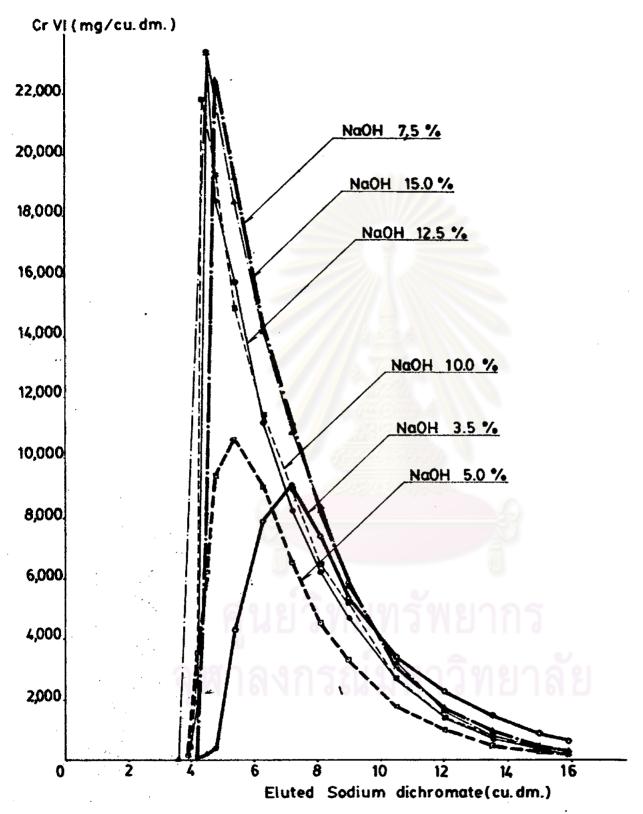


Fig. 9 History Curve of SBA Column Regeneration at 3.5 to 15 % by wt. NaOH Concentrations, Various Regeneration Levels

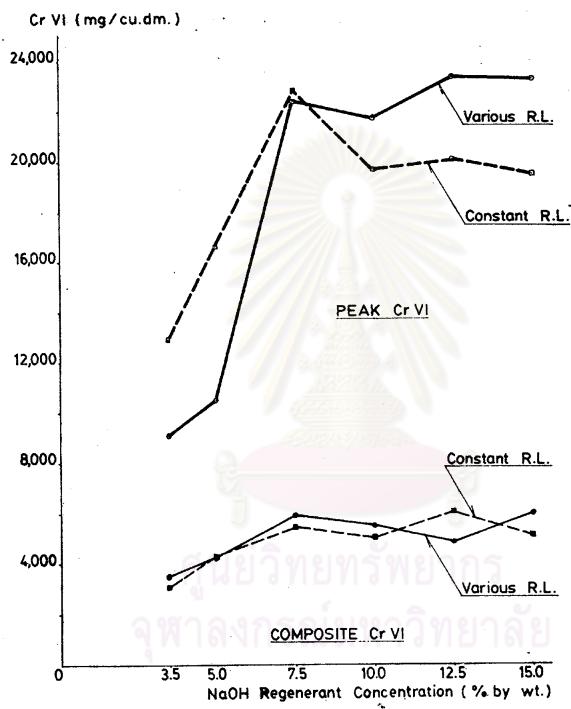


Fig. 10 Peak and Composite Cr VI in Na₂Cr₂O₇ at Various NaOH Regenerant Concentrations Comparing between Various Regeneration Levels & Constant Regeneration Level.

respectively (16). It was obvious that during the upflow regeneration of the SBA column, the resins could be pushed up and dispersed. The operating capacity of resin would, accordingly, decline (14) and it was therefore a waste to use any regenerant with concentration above the optimum 7.5 per cent.

of the SBA column also changed in this study and, hence, their impact on the concentrations of the eluted sodium dichromate solution might be anticipated. On the other hand, this effect would be insignificant because all regeneration levels were very high, ranging from 1.82 to 8.73 meq./cu.cm. of resin. They were in excess of the exchange capacity of the SBA resin which was theoritically 1.5 meq./cu.cm. of resin, see Table 4.

5.2.2 SBA Column Regeneration at Constant Regeneration Level

In the experiments No. 9 to No. 13, the sodium hydroxide solution of 3.5 to 15.0 per cent by weight concentration were used as regenerants at the regeneration level of 162.5 gm.NaOH/cu.dm. resin. This was the optimum regeneration level of SBA column obtained from the previous set of experiments. The regeneration flowrate was keept constant at 150 cu.cm./min.(4.5 BV/hr.). The results of the experiments are shown in Table 8. It can be seen that the maximum peak Cr VI value of 22,813 mg./cu.dm. Cr VI could be obtained from the SBA column regeneration with

Table 8 Characteristics of Eluted Sodium dichromate and Reclaimed Chromic Acid at Various Sodium hydroxide Regenerant Concentrations (Constant Regeneration Level = 162.5 gm NaOH/cu.dm. Resin)

Run No.		9	10	11	12	13	14	16
Date	ayayı ildə sərəyini ilə ili sərəyini ildə ərəkində ilə bəyakla azərbi sərəkində ildə ilə ilə ilə ilə ilə ilə i	13.6.78	22.6.78	29.6.78	6.7.78	13.7.78	19.7.78	7.8.78
NaOH Concn	, % by wt.	3.5	5.0	10.0	12.5	15.0	7.5	7.5
NaOH, Regen used, cu.d		8.94	6.16	2.93	2.28	1.86	4.0	4.0
Contact ti		59.60	41.07	19.53	15.20	12.40	26.67	26.67
Eluted Na ₂ Cr ₂ O ₇	Composite pH Peak Cr VI Composite Cr VI Composite Na Volume, cu.dm.	13.13 12,969 3,100 6,150 20.94	13.3 16,641 4,300 0,250 18.16	13.25 17,500 5,050 10,250 14.93	13.15 20,469 6,063 11,000 14.28	19,532 5,188	13.47 22,813 14,922 19,500 3.15	13,125° 26,000°
Reclaimed H ₂ Cr ₂ O ₇	Composite pH Peak Cr VI Composite Cr VI Composite Na Composite acidi (CaCO ₃)	248	1.83 4,225 3,188 340 8,459	1.65 4,800 3,750 250 10,070	1.7 5,625 4,300 525 10,876	3,875 775	10,547 7,688	1.4 6,875 300 18,781
	Volume, cu.dm.	13.87	12.27	11.20	10.67	11.20	8.00	8.00

Notes: All values except pH are in mg/cu-dm-

Chromic Reclamation Flowrate = 16 cu.dm./hour = 8 BV/hour.

Values of Composite Na₂Cr₂O₇ for Recovery

7.5 per cent sodium hydroxide regenerant. The peak Cr VI value increased from 12,969 to 22,813 mg./cu.dm. Cr VI (an increase of 76 per cent) as the concentration of sodium hydroxide was raised from 3.5 to 7.5 per cent and decreased from 22,813 to 19,532 mg./cu.dm. Cr VI as the concentration of sodium hydroxide was increased from 7.5 to 15.0 per cent. (See Figures 10 and 11)

5.2.3 SBA Column Regeneration at Different Regeneration Levels

Figures 12 to 17 show the history curves of SBA column regeneration with same concentration of sodium hydroxide solution but at different regeneration levels. The results show that higher peak Cr VI values could be obtained by using higher regeneration level. This is because more quantity and volume of sodium hydroxide regenerant was used with longer contact time and the ions could exchange more completely.

5.2.4 SBA Column Regeneration at Different Regeneration Flowrate

once the optimum regenerant concentration had been determined, different regeneration flowrate were studied. Figure 18 shows the history curves of SBA column regeneration at 100, 150 and 200 cu.cm./min.(3.0, 4.5 and 6.0 BV/hr.) and the results of the experiment are shown in Table 7. From the results and history curves, it can be seen that the SBA column regeneration at 150 cu.cm./min. was the most effective.

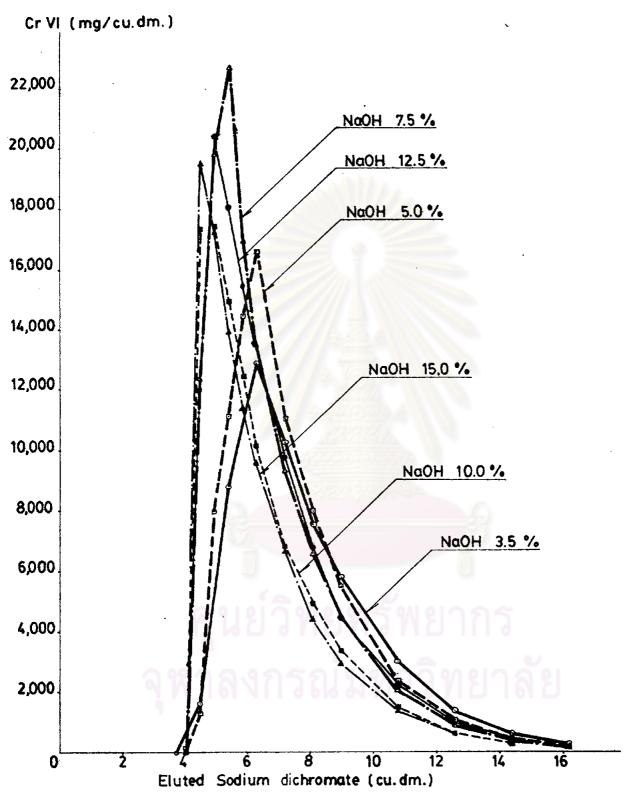


Fig. 11 History Curve of SBA Column Regeneration at 3.5 to 15 % by wt. NaOH Concentrations (Regeneration Level 162.5 gm NaOH/cu.dm.Resin)

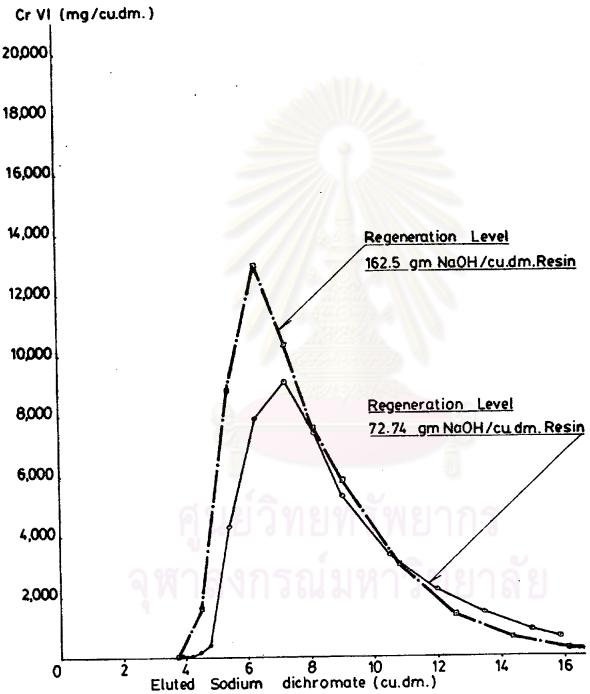


Fig. 12 History Curve of SBA Column Regeneration at 3.5 % NaOH Concentration

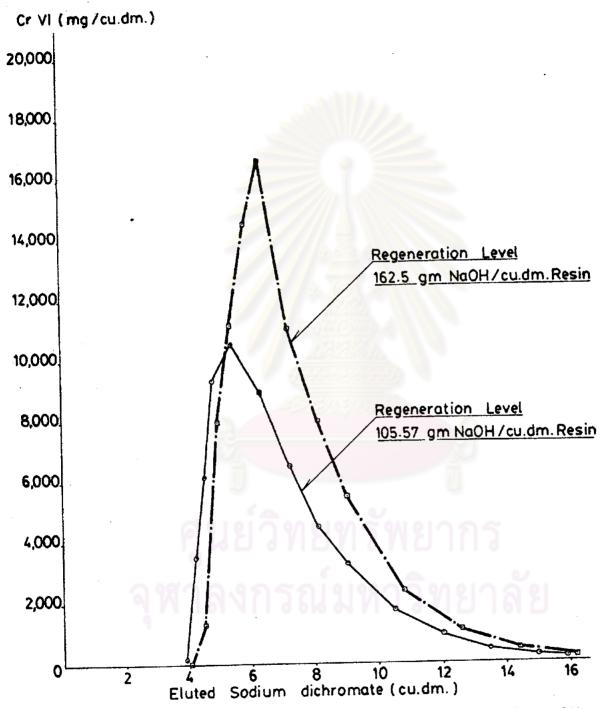


Fig.13 History Curve of SBA Column Regeneration at 5.0 % NaOH Concentration

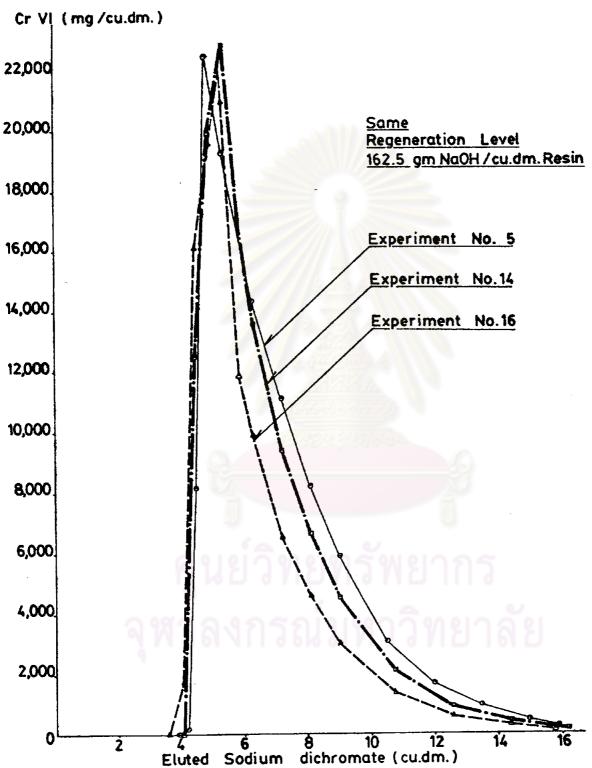


Fig.14 History Curve of SBA Column Regeneration at 7.5 % NaOH Concentration

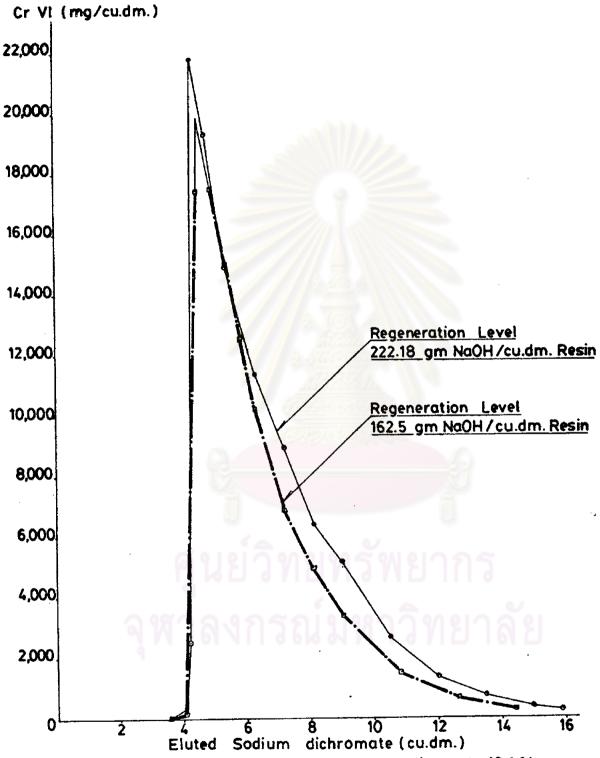


Fig.15 History Curve of SBA Column Regeneration at 10.0 % NaOH Concentration

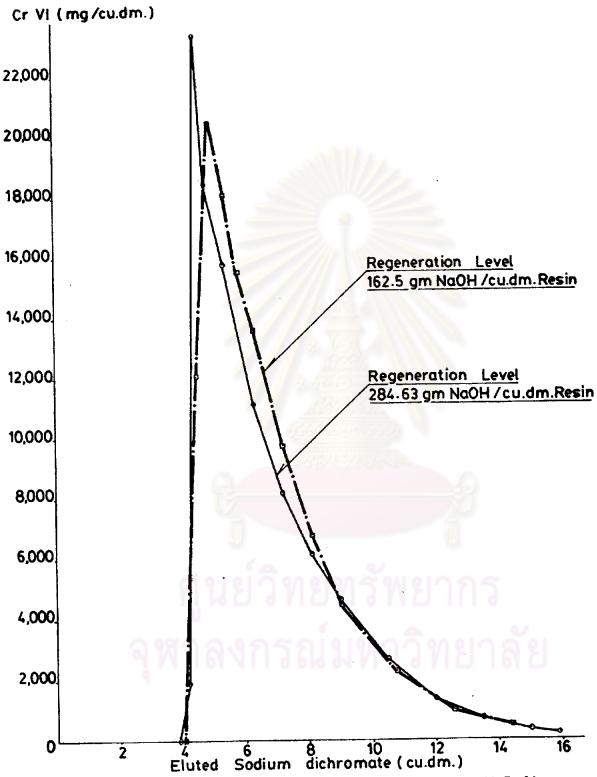


Fig.16 History Curve of SBA Column Regeneration at 12.5 % NaOH Concentration

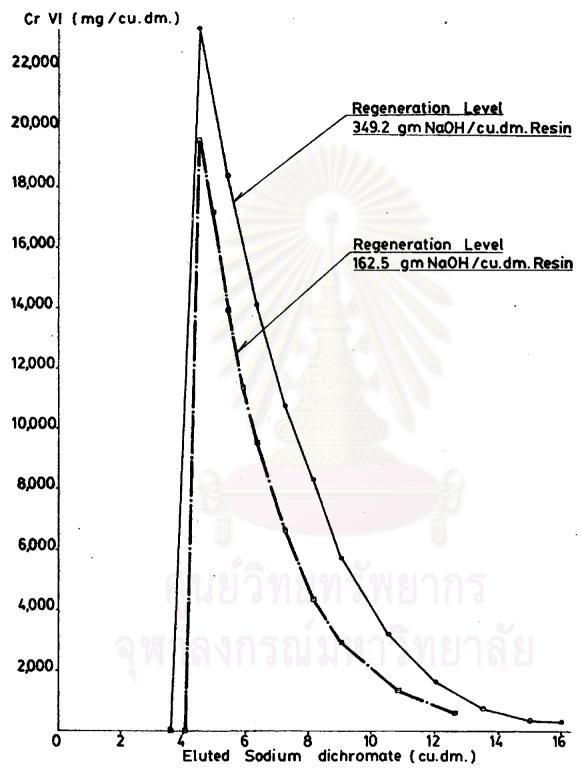


Fig.17 History Curve of SBA Column Regeneration at 15 % NaOH Concentration

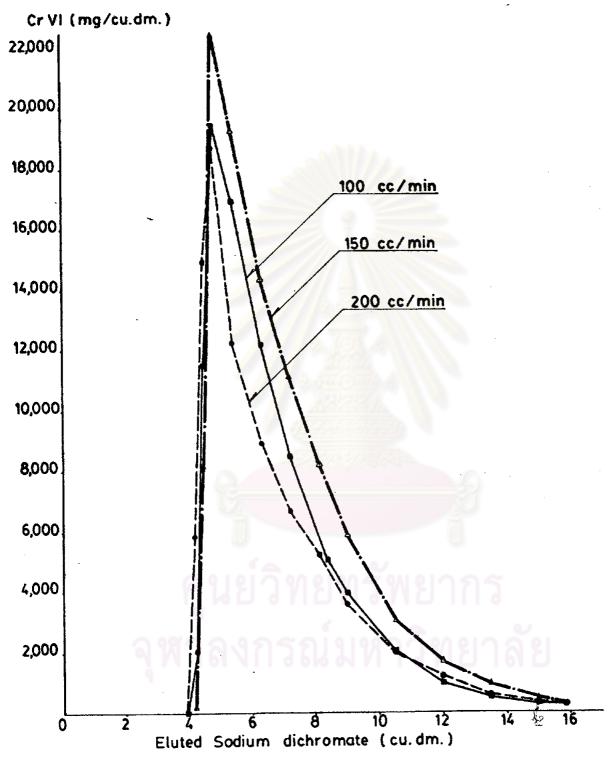


Fig.18 History Curve of SBA Column Regeneration at Different Regeneration Flow Rate.

5.3 Results of Chromic Acid Recovery

Tables 7 and 8 also illustrates the characteristics of the composite chromic acid recovered from the last SAC column while Figures 19 to 22 show the elution patterns of the chromic acid reclaimed. In every operation cycle, the concentrations of the chromic acid were found to be less than those of the feed sodium dichromate solution. (See Figures 23 a and 23 b.) For example, in Figure 23 b, the concentrations of the composite chromic acid were 4,000 and 2,953 mg./cu.dm. Cr VI when the concentrations of feed sodium dichromate solution were 5,938 and 3,538 mg./cu.cm. Cr VI at the regenerant concentration of 7.5 and 3.5 per cent, respectively. This phenomenon was due to the dilution effect of the rinse water still remaining in the column after each regeneration cycle. However, as it is shown in Figures 19 to 22, the peak values of the reclaimed chromic acid approached those of the feed sodium dichromate solution as the exchanges proceeded. The concentrations of the chromic acid appeared to reach their plateaus at about 8 cu.dm. or 4 bed volumes of effluents. The peak chromic contents, for instance, were as high as 4,157 and 4,782 mg./cu.dm. Cr VI when the feed chromium concentrations were 4,313 and 5,532 mg./cu.dm. Cr VI, respectively. (See Table 7.)

Based on the experience gained from this phenomenon, it could be suggested that larger recovery column be used. By so-doing, many recovery cycles would be possible for each regenera-

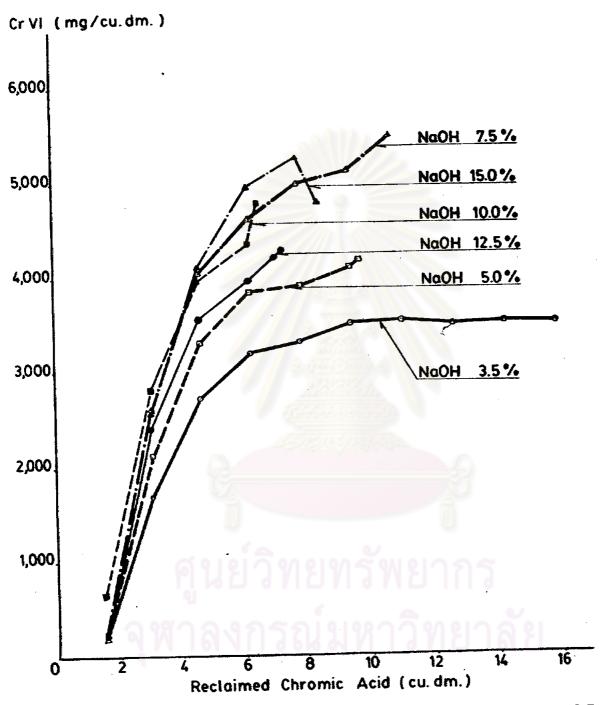


Fig.19 Chromic Acid Reclamation from Na₂Cr₂O₇ Solutions at 3.5 to 15 % by wt. NaOH Regenerant Concentrations (Various Regeneration Levels)

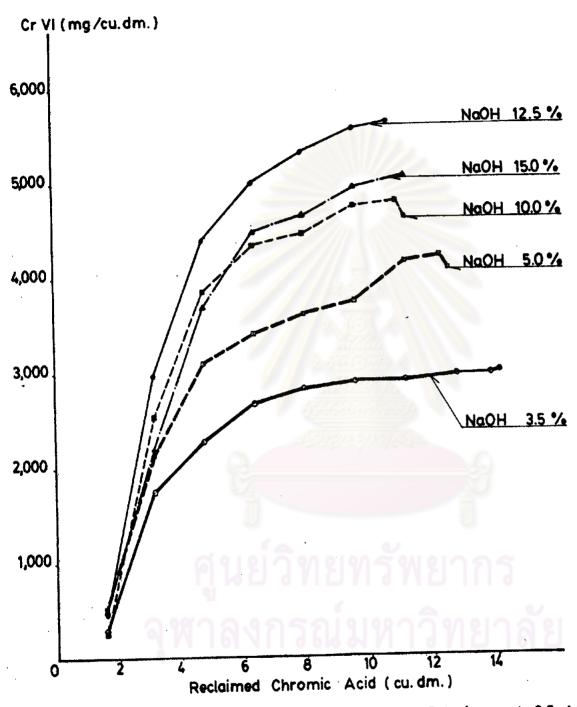


Fig.20 Chromic Acid Reclamation from Na₂Cr₂O₇ Solutions at 3.5 to 15 % by wt. NaOH Regenerant Concentrations (Constant Regeneration Level = 162.5 gm NaOH/cu.dm. Resin)

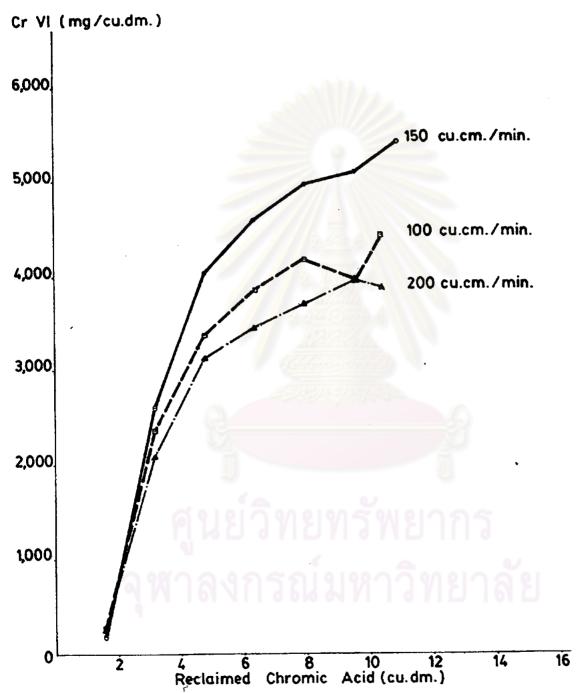


Fig.21 Reclaimed Chromic Acid at Different Regeneration Flowrates of SBA Column

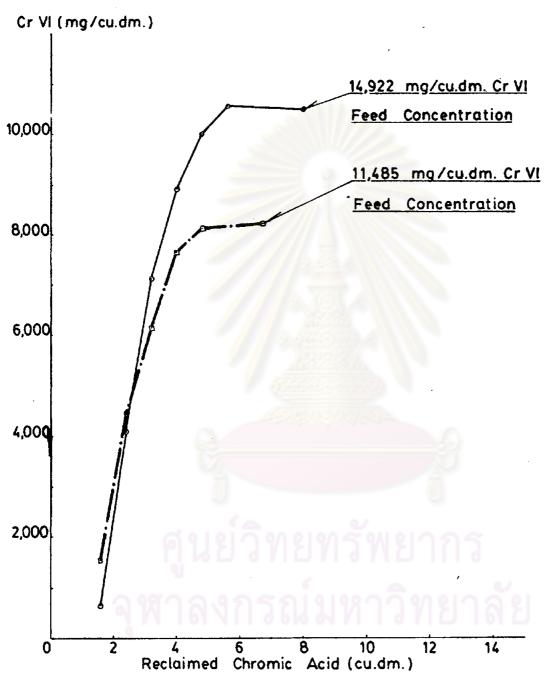


Fig.22 Chromic Acid Reclamation from Concentrated $Na_2Cr_2O_7$ Solutions

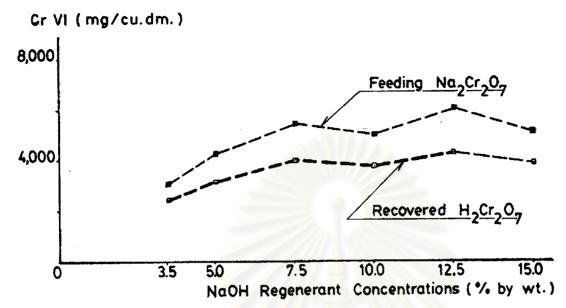


Fig. 23a Cr VI Concentrations Comparing between Feeding Na₂Cr₂O₇ and Reclaimed H₂Cr₂O₇ Solutions at Constant Regeneration Level 162.5 gm NaOH/cu.dm. Resin

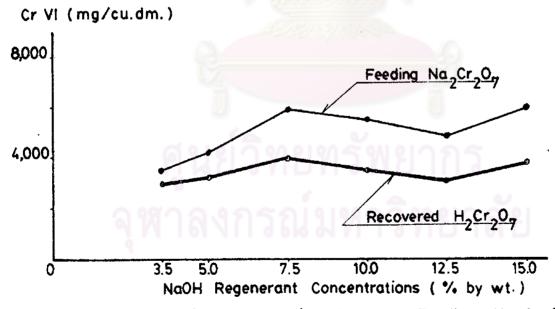


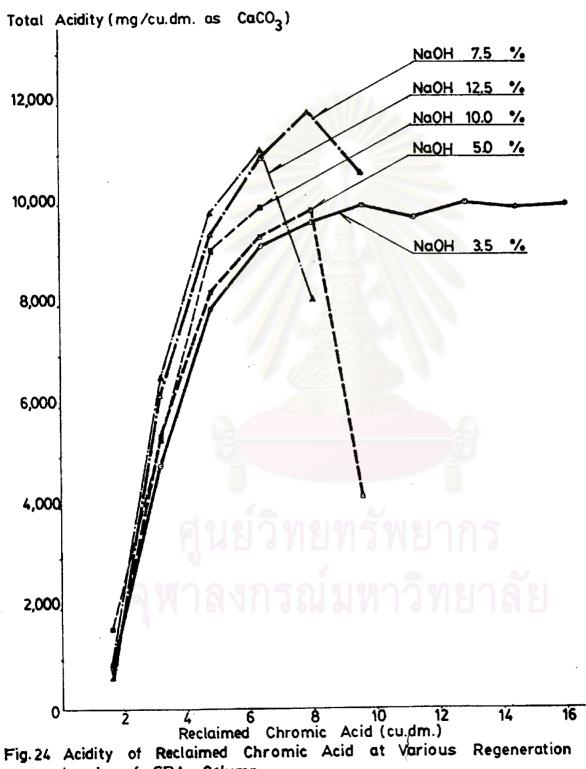
Fig. 23b Cr VI Concentrations Comparing between Feeding Na $_2$ Cr $_2$ O $_7$ and Reclaimed H $_2$ Cr $_2$ O $_7$ Solutions at Various Regeneration Levels

tion cycle of the SAC recovery bed. As a result, the dilution effect of the remaining rinse water for every cycle would be eliminated. Only the first recovery cycle would be affected, resulting in higher concentration of reclaimed chromic acid.

Figures 24, 25 and 26 show the elution patterns of acidity of chromic acid, while Figure 27 shows the relation between Cr VI concentration and acidity of chromic acid. It was found that the acidity of recovered chromic acid was ranging between 5,898 to 10,876 mg./cu.dm. as CaCO₃. (Also see Tables 7 and 8.) The value of acidity depended on Cr VI value, when Cr VI value of chromic acid was high, the acidity would be subsequently high but the acidity would be suddenly dropped when the breakthrough of SAC resin in recovery column was reached.

5.4 Sodium Content in Eluted Sodium dichromate and Recovered Chromic Acid Solutions

tion in composite samples of eluted sodium dichromate and recovered chromic acid. From the results in Table 7, it can be seen that when the SBA column was regenerated with higher regeneration level, i.e., more quantity of sodium hydroxide was used for the regeneration, higher concentration of sodium in eluted sodium dichromate solution would be obtained. Table 8 shows the results obtained from the SBA column regeneration at constant regeneration level of 162.5 gm. NaOH/cu.dm. resin, i.e., same quantity of sodium



Levels of SBA Column

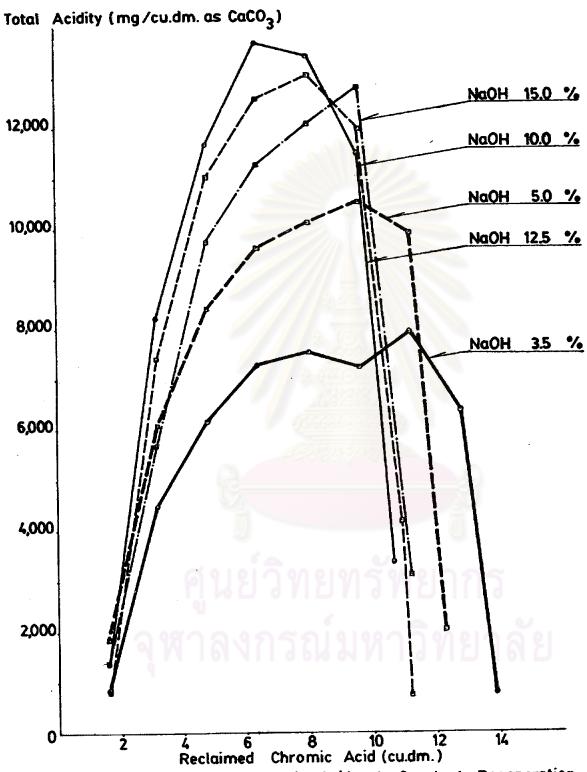


Fig. 25 Acidity of Reclaimed Chromic Acid at Constant Regeneration Level of SBA Column (162.5 gm NaOH/cu.dm.Resin)

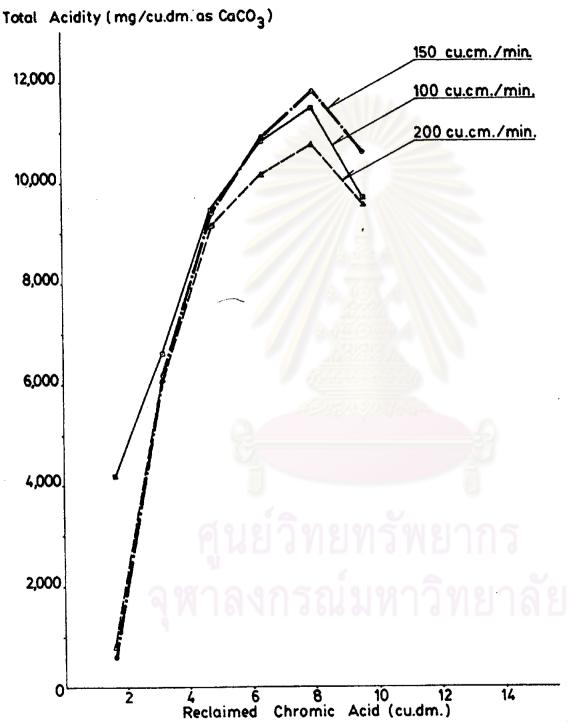


Fig. 26. Acidity of Reclaimed Chromic Acid at Different Regeneration Flowrate of SBA Column

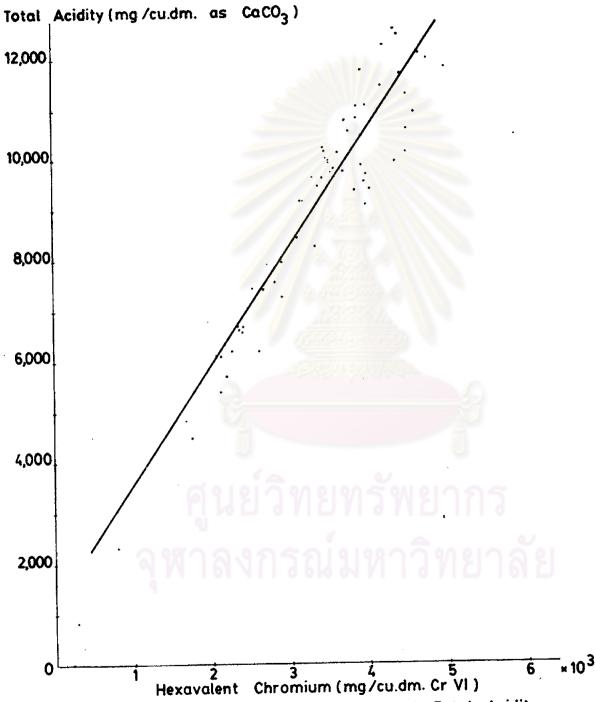


Fig. 27 Relation between Cr VI Concentration and Total Acidity of Reclaimed Chromic Acid

hydroxide regenerant was used in each cycle. It was found that the concentration of sodium in eluted sodium dichromate obtained from low sodium hydroxide regenerant concentration was lower than the one obtained from the higher regenerant concentration. This could be explained by the fact that the volumes of sodium hydroxide regenerant at lower concentrations must be larger than those of higher concentrations. As a result, the total volumes of the eluted sodium dichromate solution, obtained from the regeneration at low concentration of sodium hydroxide, would be also larger than those, obtained at higher concentration of regenerants. As the quantity of sodium hydroxide for regeneration was constant, the concentrations of sodium increased as the volume of the sodium dichromate solution decreased.

In the recovery column, the H-type SAC resin was used as ion exchangers so that sodium dichromate would be exchanged to become chromic acid. However, the H-type SAC resins have certain capacity to exchange their H⁺ ions with Na⁺ and also with other cations in the feed solution. In case of the chromic acid recovery, if the competing sodium concentration in the other forms of sodium salt was low, the column could recover relatively more chromic acid before its breakthrough capacity was reached and vise versa.

The elution patterns of sodium content of chromic acid are shown in Figures 28, 29 and 30. It is shown that there would be a sudden rise of sodium concentration as the SAC revovery

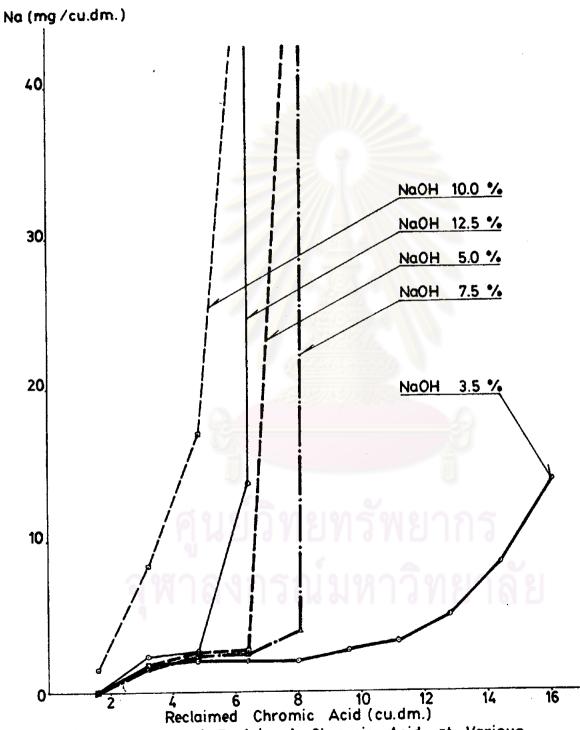


Fig. 28 Sodium Content of Reclaimed Chromic Acid at Various Regeneration Levels of SBA Column

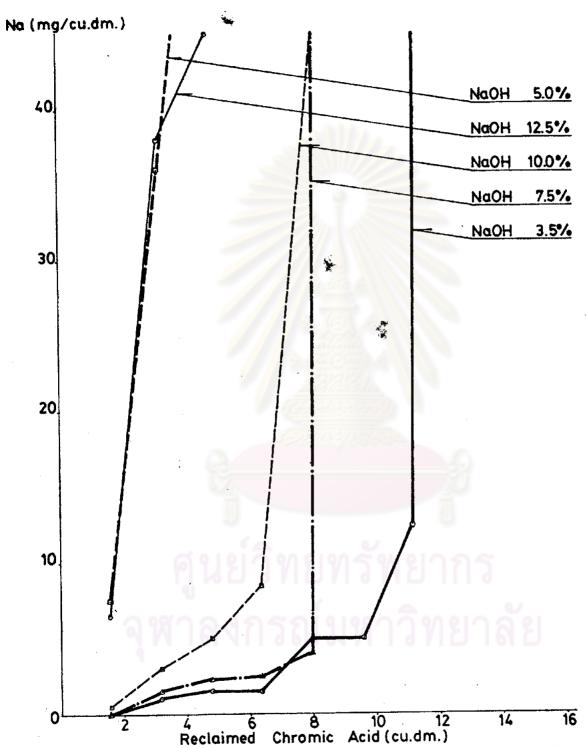


Fig. 29 Sodium Content of Reclaimed Chromic Acid at Constant Regeneration Level of SBA Column (162.5 gm NaOH/cu.dm. Resin)

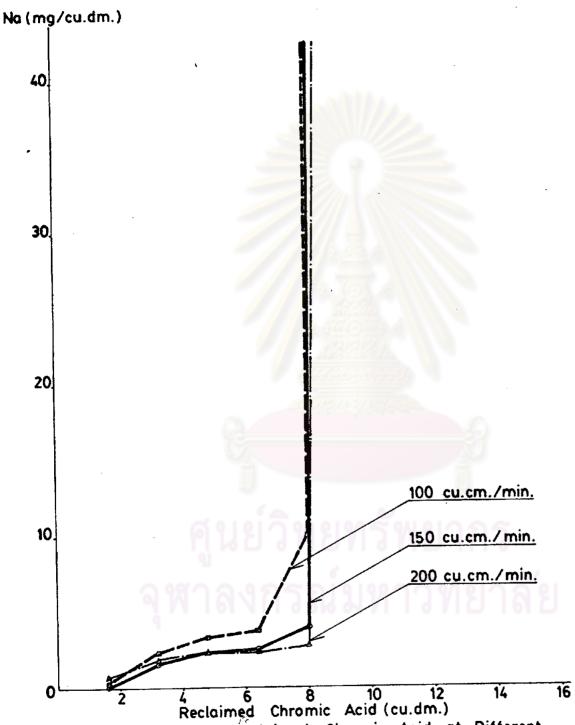


Fig. 30 Sodium Content of Reclaimed Chromic Acid at Different Regeneration Flowrate of SBA Column

column reached its breakthrough point.

5.5 Some Experiments on SBA Column Regeneration and Chromic Acid Recovery

In the experimental cycles No. 14, 15, 16 and 17, the concentrated and diluted portions of eluted sodium dichromate solution were separated. The concentrated portion was passed through the SAC recovery column for recovery while the diluted portion was used as the pre-regenerant prior to the conventional regeneration by the sodium hydroxide solution. It was found that the results of regeneration as shown in Table 9 and presented by the history curves of regeneration in Figures 31 and 32 were not much disturbed. In cycle No. 17, 4.5 cu.dm. Cr VI concentration sodium dichromate solution was used as the regenerant prior to 4.0 cu.dm. of 7.5 per cent sodium hydroxide solution. The peak and composite Cr VI values were found to be 20,704 and 7,250 mg./ cu.dm. Cr VI, respectively. Eventhough the obtained peak value was lower than that obtained from the regeneration with pure 7.5 per cent sodium hydroxide, the composite Cr VI value was higher. (Also see Tables 7 and 8.) On the other hand, in cycle No. 14, sodium dichromate solution of 14,922 mg./cu.dm. Cr VI concentration was fed to the recovery column. The recovered chromic acid was found to be 7,688 mg./cu.dm. Cr VI with the peak Cr VI value of 10,547 mg./cu.dm. Cr VI while the acidity was 19,435 mg./cu.dm. as CaCO2.

Table 9 Characteristics of Eluted Sodium Dichromate

Reclaimed chromic Acid

Run No.		15	17
Date		27 .7.7 8	14.8.78
Regenerar	nt Na ₂ Cr ₂ O ₇		
	/cu.dm.Cr VI	2,200 8.5	2,525 4.5
Regenerar		7.5	7.5
Concn, % Volume, c		4	4
	ime, min.	83.3	56.7
	Composite pH	13,23	13.5
$Na_2Cr_2O_7$	Peak Cr VI Composite Cr VI	20,750 4,594	20,704 7,250
Composite Recovery	Na ₂ Cr ₂ O ₇ for	•19 3391	7,230
•	Composite Cr VI	4,594	11,485
	Composite Na Volume, cu.dm.	9,750 20,5	32,500 2.7
Reclaimed	Composite pH	1.8	1.47
H2Cr2O7	Peak Cr VI	4,463	8,219
	Composite Cr VI	3,500	6,344
	Composite Na Composite Acidity	200	150
	(CaCO ₃)	. 9,813	15,055
	Volume, cu.dm.	11.7	6.7

Note: All values are in mg/cu.dm. except pH and volume

Chromic Acid Reclamation Flowrate = 16 cu.dm./hour

= 8 BV/hour

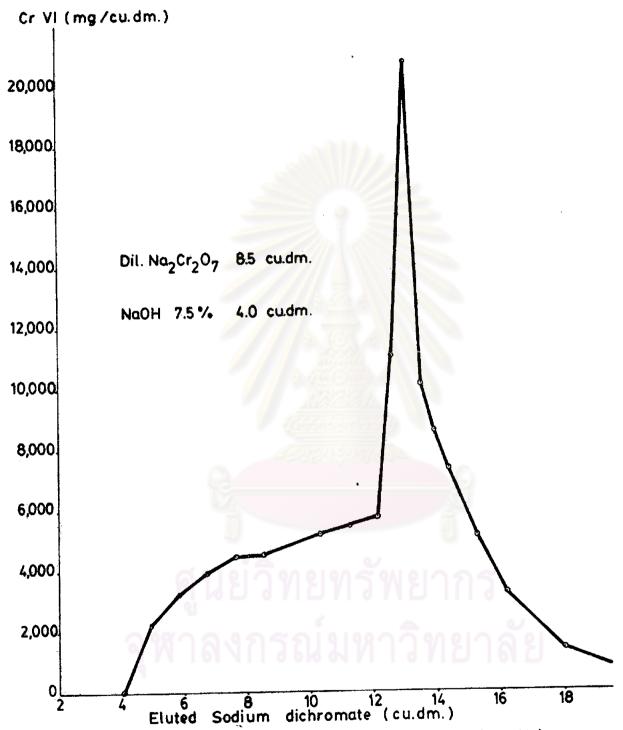


Fig. 31 History Curve of SBA Column Regeneration Using Dilute Eluted Na₂Cr₂O₇ from Previous Run Following by NaOH 7.5 % by wt. Concentration

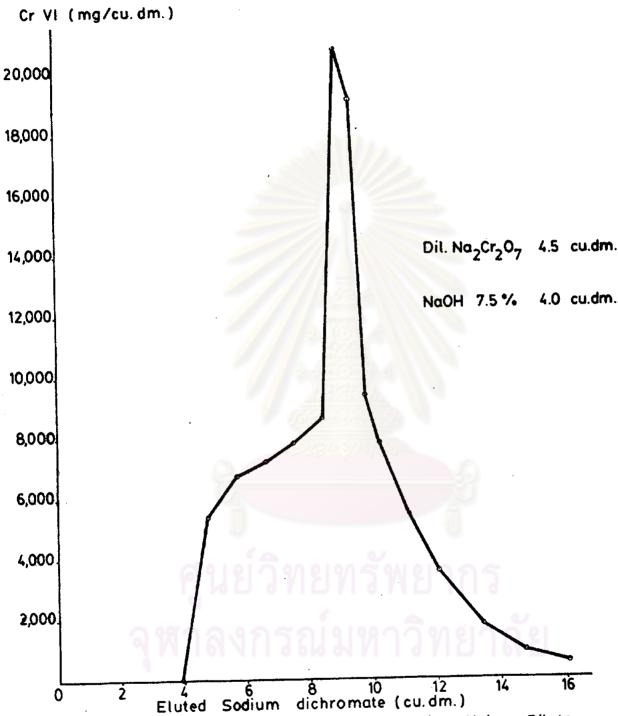


Fig. 32 History Curve of SBA Column Regeneration Using Dilute Eluted Na₂Cr₂O₇ from Previous Run Following by NaOH 7.5 % by wt. Concentration

The obtained data had shown the possibility to recover chromic acid of high concentration by separating and passing only the concentrated portion of eluted sodium dichromate through the SAC recovery column. The diluted portion of sodium dichromate solution would then be used as SBA column pre-regenerant prior to the sodium hydroxide solution with least adverse effects to the SBA column regeneration.

5.6 The Use of the Recovered Chromic Acid in Electroplating Process

The highest concentration of the recovered chromic acid obtained from this research was 7,688 mg./cu.dm. Cr VI. This concentration, however, was not high enough to be directly recycled to the electroplating process which normally required 130,000 to 200,000 mg./cu.dm. Cr VI (3,5). Nevertheless, the reclaimed chromic acid could be further evaporated at less expense to the required concentration; and consequently, could be used as the chromic acid bath in the electroplating process. This would provide some economic benefits in terms of lowering the energy and the capital costs of the concentration process.