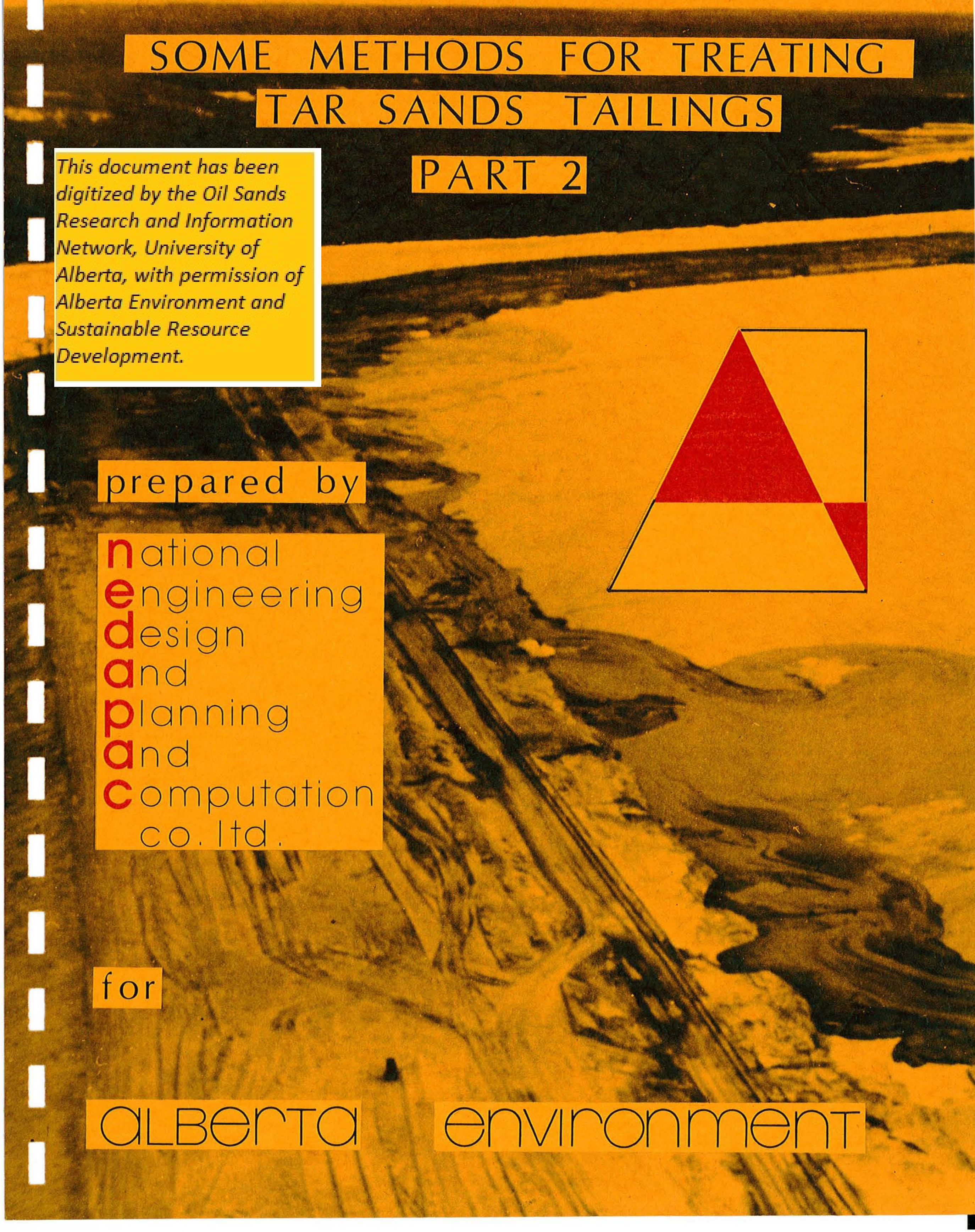

SOME METHODS FOR TREATING TAR SANDS TAILINGS

PART 2

prepared by

national
engineering
design
and
planning
and
computation
co. ltd.

for

alberta environment

SOME METHODS FOR TREATING TAR SANDS TAILINGS

PART II

THEORY OF CO_2 PROCESS

prepared by National
Engineering
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for ALBERTA ENVIRONMENT

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1. INTRODUCTION

This remaining part of the report deals with the theoretical aspects of the reactions between carbon dioxide and tailings.

From the experimental results described in Part 1 it can be stated that:

1) the CO_2 is the active reagent responsible for the complete and rapid separation of the sludge and
2) the separation rate depends on the pH of the mixture.

Two experiments were carried out to compare the influence of CO_2 and air on the sedimentation process. Two samples of tailings No. 4 (viz. 4 - 5 - A15 and 4 - 5 - 15) were separately placed into two glass beakers and heated to 50°C. The samples were stirred while being heated and their pH was adjusted to 5 with H_2SO_4 . Then air was introduced to sample 4 - 5 - A15 and CO_2 to sample 4 - 5 - 15. The residence time for both air and CO_2 was 15 minutes. The percentage of sediment (%S) was observed over a period of ten days. The results of these observations are shown in Table 1 and Graph 1 which show that a much higher percentage of sediment was obtained with CO_2 than with the air.

According to the results given in Part 1 (see pp 11 Figure 2 - 2, pp 17 Figure 2 - 5, pp 18 Figure 2 - 6) the fastest separation occured at about pH = 5 for both No. 3 and No. 4 tailings. (The separation at pH adjusted to less than 4 was very slow.) These results are in agreement with the findings of M. V. BAPTISTA and C. W. BOWMAN[1] which show that the highest rate for the separation of solids from tar sands slurries occurs at pH values between 4 and 8 . They did not use CO_2 . J. LEJA[2] also discusses the importance of pH but also the influence of bicarbonate and sulphate ions on the solidification of soap - like films in the upgrading of metal ores.

2. THEORY

The pH of the tailings on leaving the bitumen extractors is in the range 8.3 to 8.8 . In this pH range naphthenic acids exist in the tailings mixture as water soluble naphthenic salts R - COOM where M is mainly Na^+, K^+ but can be also Ca^{++}, Mg^{++} and other metal ions. The existence of these salts has been described by M. V. BAPTISTA and C. W. BOWMAN [1] and others. The presence of these salts has been confirmed by infrared spectrograph SG1 from untreated tailings No. 4 showing absorption at 1600 cm^{-1} which is typical for salts of organic acids.

Naphthenic salts dissociate in water according to the following manner:

$$(1) \qquad R - COO^-Na^+ \longrightarrow R - COO^- + Na^+$$

The existence of this dissociated soap - like salt gives the emulsion its stability. Introducing CO_2 to the mixture results in carbonic acid according to the equation:

$$(2) \qquad CO_2 + H_2O \rightleftharpoons H_2CO_3$$

Due to the dissociation of carbonic acid in aqueous solution:

$$(3) \qquad H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$(4) \qquad HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$$

the concentration of hydrogen ions increases and the pH of the solution decreases.

It is assumed that the reaction between dissociated naphthenic salts and carbonic acids is the most important reaction for breaking the emulsion:

$$(5) \qquad R - COO^- + Na^+ + H_2CO_3 \rightleftharpoons R - COOH + Na^+ + HCO_3^-$$

Naphthenic acid (R - COOH) which is formed by reaction (5) is insoluble in water and is carried with the hydrocarbons to the surface of the water. If the dissociation constant of naphthenic acid (Ka_{RCOOH}) is much higher than that of carbonic acid ($Ka_{H_2CO_3}$) then the concentration of $R - COO^-$ in the solution does not change. If $Ka_{RCOOH} < Ka_{H_2CO_3}$ then the equilibrium of reaction (5) goes to the right and the product of the reaction is R - COOH which dissociates according to:

$$(6) \qquad R - COOH \rightleftharpoons R - COO^- + H^+$$

and the dissociation constant of this reaction is as follows:

$$(7) \qquad Ka_{RCOOH} = \frac{\left[H^+\right]\left[R\text{-}COO^-\right]}{\left[R\text{-}COOH\right]} = K_a$$

The stability of the emulsion depends on the amount of $R - COO^-$ in the mixture. It is assumed that in the original untreated sample:

$$(8) \qquad \left[R - COO^-\right] + \left[R - COOH\right] = C$$

where C is a constant.

From (7):

$$(9) \qquad \left[R - COO^-\right] = \frac{K_a \left[R - COOH\right]}{\left[H^+\right]}$$

From (8):

$$(10) \qquad \left[R - COOH\right] = C - \left[R - COO^-\right]$$

Substitution to (9) gives:

$$(11) \qquad \left[R - COO^-\right] = \frac{K_a\left(C - \left[R - COO^-\right]\right)}{\left[H^+\right]}$$

Rearranging (11)

$$\left[H^+\right]\left[R - COO^-\right] = K_a\,C - K_a\left[R - COO^-\right]$$

$$\left[R - COO^-\right]\left(\left[H^+\right] + K_a\right) = K_a\,C$$

$$(12) \qquad \therefore \left[R - COO^-\right] = \frac{K_a\,C}{K_a + \left[H^+\right]}$$

since $pH = -\log\left[H^+\right]$,

$\therefore \quad \left[H^+\right] = 10^{-pH}$

$$(13) \qquad \left[R - COO^-\right] = \frac{K_a\,C}{K_a + 10^{-pH}}$$

if a) $pH \longrightarrow 0$ then $\left[R - COO^-\right] = \dfrac{K_a\,C}{K_a + 1} = x$

b) $pH \longrightarrow \infty$ then $\left[R - COO^-\right] = \dfrac{K_a\,C}{K_a} = y$

$$(14) \qquad y > x$$

From (14) it can be assumed that a) $\left[R - COO^-\right]$ is lowered on lowering the pH and b) $\left[R - COO^-\right]$ is increased on raising the pH .

3. DISCUSSION

1) The introduction of any reagent which does not increase the hydrogen ion concentration, $\left[H^+\right]$, cannot cause any change in the chemical equilibrium. In such a case the $\left[R - COO^-\right]$ would remain constant and since the existence of $R - COO^-$ in the sludge is necessary for the emulsion to remain stable the emulsion would not break.

2) It has been found that introduction of an acid, other than H_2CO_3, as the source of H^+ results in a certain percentage of sediment but that the rate of sedimentation is much lower than that obtained with CO_2 (see Table 1, Graph 1). Consideration was given to the study of J. LEJA[2] which referred to the ease of soap formation in the presence of alkyl sulphates but which did not fully explain this phenomenon.

3) Equations (12) and (13) are limited by the following conditions:

a) $\left[H^+\right]$ never approaches infinity nor does pH approach zero.

$$\therefore \left[R - COO^-\right] = \frac{K_a\ C}{K_a + \left[H^+\right]} \neq 0$$

$\therefore$ it is not possible to convert all the $R - COO^-$ to $R-COOH$,

$\therefore$ there will always be some salt in the sludge.

b) The concentration of $R - COO^-$ ions as in (12) and (13) is limited by the minimum pH attainable with CO_2, which is around 4. Graphs 2,3,4 and 5 show the pH change caused by CO_2 in an acidic solution, a basic solution and distilled water at two different temperatures. These results are in agreement with those of COTTON and WILKINSON[3], FISHER and PETERS[4], OLSON and YOULE[5], and others who discuss the strength of H_2CO_3 in solution. Carbonic acid is exceptional in that the directly measured first dissociation constant $K_1 = 4.47 \times 10^{-7}$, pK_1, 6.38, does not refer to the following process:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad \text{where } K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

Since CO_2 in solution is largely present as the more loosely hydrated species, CO_2 (aq), and only partly in the form H_2CO_3, then the following equilibrium is more appropriate:

$$CO_2\ (aq) + H_2O \rightleftharpoons H_2CO_3\ (aq)$$

In this case the pK_1 value is about 3.5 and a $K_1 = 3 \times 10^{-4}$ is obtained which indicates that a much stronger carbonic acid can be obtained than the previous value of $K_1 = 4.47 \times 10^{-7}$ indicates.

4. CALCULATION OF OPTIMUM pH FOR CO_2 TREATMENT

From Part 1 (viz. pp 18 Figure 2 - 6 and pp 21 Figure 2 - 8) it can be deduced that the highest sedimentation rate occurs when the initial pH is adjusted to about 5 before injecting CO_2 (pp 28 sample 4 - N - 15 and pp 21 4 - N - 5). The mathematical calculation (given below) of the rate of reaction:

$$(1) \qquad R-COO^- + H_2CO_3 \rightleftharpoons R-COOH + HCO_3^-$$

tends to support the experimental results.

Rate , R , of reaction (1) is:

$$(2) \qquad R = K\left[R - COO^-\right]\left[H_2CO_3\right]$$

Carbonic acid dissociates in aqueous solution as follows:

$$(3) \quad H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$(5) \quad K_2 = \frac{\left[H^+\right]\left[HCO_3^-\right]}{\left[H_2CO_3\right]}$$

where K_2 is the first dissociation constant for H_2CO_3

Naphthenic acid dissociates in aqueous solution as follows:

$$(4) \quad R - COOH \rightleftharpoons H^+ + R\text{-}COO^-$$

$$(6) \quad K_1 = \frac{\left[H^+\right]\left[R - COO^-\right]}{\left[R - COOH\right]}$$

where K_1 is the dissociation constant for naphthenic acid

The amount of undissociated and dissociated acids at the same pH and constant temperature should be constant:

$$(7) \quad \left[HCO_3^-\right] + \left[H_2CO_3\right] = b$$

$$(8) \quad \left[R - COO^-\right] + \left[R - COOH\right] = a$$

where b and a are constants.

From (5) and (7) :

$$(9) \quad K_2 = \frac{\left(b - \left[H_2CO_3\right]\right)\left[H^+\right]}{\left[H_2CO_3\right]}$$

$$\therefore \left[H_2CO_3\right] K_2 = b\left[H^+\right] - \left[H^+\right]\left[H_2CO_3\right]$$

$$\text{or} \quad (11) \quad \left[H_2CO_3\right] = \frac{b\left[H^+\right]}{K_2 + \left[H^+\right]}$$

From (6) and (8) :

$$(10) \quad K_1 = \frac{\left[H^+\right]\left[R\text{-}COO^-\right]}{a - \left[R\text{-}COO^-\right]}$$

$$\therefore K_1 a - K_1\left[R\text{-}COO^-\right] = \left[H^+\right]\left[R\text{-}COO^-\right]$$

$$\text{or} \quad (12) \quad \left[R\text{-}COO^-\right] = \frac{K_1 a}{\left[H^+\right] + K_1}$$

Substituting (11) and (12) into (2) :

$$(13) \quad R = K \frac{a\, b\, K_1 \left[H^+\right]}{\left(K_1 + \left[H^+\right]\right)\left(K_2 + \left[H^+\right]\right)}$$

where K, a, b, K_1 and K_2 are constants.

Let $k = K\,a\,b$

$$\therefore (14) \qquad R = k \frac{K_1 \left[H^+\right]}{\left(K_1 + \left[H^+\right]\right)\left(K_2 + \left[H^+\right]\right)}$$

$$\therefore R \longrightarrow 0 \quad \text{as} \quad H^+ \longrightarrow 0$$

$$\text{and} \quad \therefore R \longrightarrow 0 \quad \text{as} \quad H^+ \longrightarrow \infty$$

From (14) :

$$(15) \qquad \frac{R}{a\,b\,K} = \frac{K_1 \left[H^+\right]}{\left(K_1 + \left[H^+\right]\right)\left(K_2 + \left[H^+\right]\right)}$$

See APPENDIX I for practical examples.

5. INFRARED SPECTRA

Infrared spectra were obtained for solid samples (using KBr pellets) of untreated tailings No. 4 (SG 1), for the sediment resulting from treating tailings No. 4 with CO_2 and for the extracted bitumen from the surface of tailings No. 4 during CO_2 treatment. (SG 2 and SG 3 respectively). SG 3 shows a very strong absorption of aliphatic hydrocarbons (2840 - 2950 cm^{-1} for $-CH_2$ and $-CH_3$ groups) . However, SG 1 and SG 2 show strong absorptions for carboxylate salts (1400 - 1450 cm^{-1} and 1580 - 1620 cm^{-1}) and inorganic salts at 1000 - 1100 cm^{-1}. Although not quantitative, this spectra support our preliminary measurements of oil recovery during CO_2 treatment which we estimate to be at least 50% of the bitumen found in the tailings. The peaks at 3400 cm^{-1} to 3700 cm^{-1} belong to the hydroxyl group which indicates the presence of H_2O and possibly $-COOH$ although the typical carboxyl absorption of organic acids at 1700 cm^{-1} might not show because of shielding by the broad peak of carboxylic salts.

Samples of tailings No. 3 and No. 4 both untreated and treated with CO_2 were extracted with carbon tetrachloride and carbon disulphide. Infrared examination of the extracts showed the presence of carboxylic acids and salts (1700 cm^{-1}, 1600 cm^{-1}) and aliphatic hydrocarbons (2840 - 2950 cm^{-1}). There was no evidence of aromatics. Similar spectra were obtained by M. V. BAPTISTA and C. V. BOWMAN[1]. In the case of untreated samples of tailings No. 3 and No. 4 the peak for carboxylic groups (1700 cm^{-1}) shows splitting in CS_2 solution (SG 6, SG 7 and SG 8). This splitting did not occur in CCl_4 solution. The absorption for carboxylic acids (1700 cm^{-1}) in treated samples (SG 9 thru SG 13) was stronger than the carboxylate salts absorption (1600 cm^{-1}). This difference was less pronounced in the spectra for untreated samples (SG 6, SG 7 and SG 8). The difference in the size of both peaks is clearly seen in the spectra of those samples extracted with CS_2 (SG 7 compared to SG 9 , SG 10 and SG 11). The relative size of the $-COOH$ peak to the $-COO^-$ peak is shown on each spectrograph. This indicates an increase in naphthenic acid concentration due to CO_2 treatment as shown in equation (5) pg 3 .

The spectrum for recovered bitumen (SG 14) shows a much higher proportion of aliphatic hydrocarbons compared to acids. The 1460 cm^{-1} peaks (asymetric $-CH_3$ bend and $-CH_2$ scissoring) were compared to the $-COOH$ absorption at 1700 cm^{-1} in spectra SG 12, SG 13, and SG 14 . The results of these comparisons agree with those of spectra SG 3 and SG 5 .

The spectra SG 4 and SG 5 show the relative amounts of hydrocarbons in the sediment (SG 4) and in the extracted bitumen from the same sample during the CO_2 treatment. The hydrocarbons in these samples were dissolved in equal volumes of carbon tetrachloride.

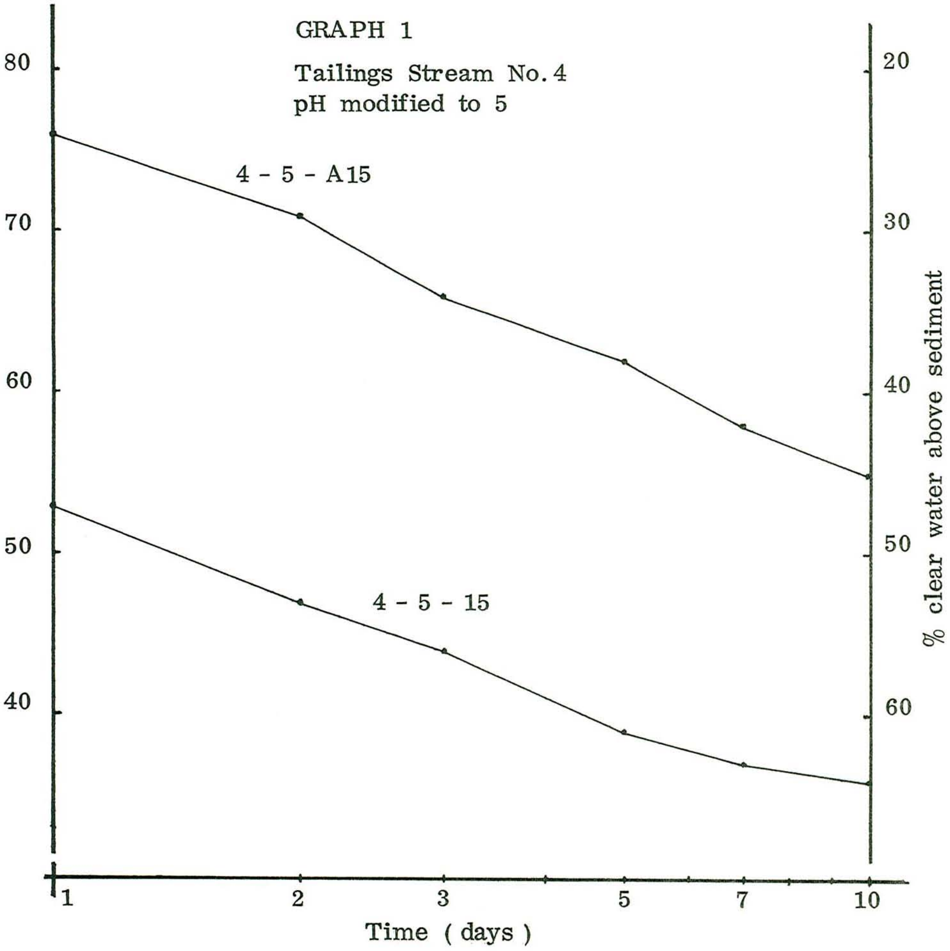
6. CONCLUSIONS AND RECOMMENDATIONS

i An attempt was made to explain chemically and mathematicaly the influence of carbon dioxide on the separation of tar sands tailings.

ii The mathematical derivation of the optimum pH (around 5) to obtain the highest reaction rate is presented. From the chemical point of view the phenomena of the special position of H_2CO_3 is not fully understood and further research is suggested.

iii Preliminary experiments for additional bitumen recovery from tar sands tailings were succesfull and it is recommended to carry on further research to determine the highest possible rate of bitumen recovery.

The presented work was done in very short period of time and additional time is required to continue in this research.



GRAPH 1

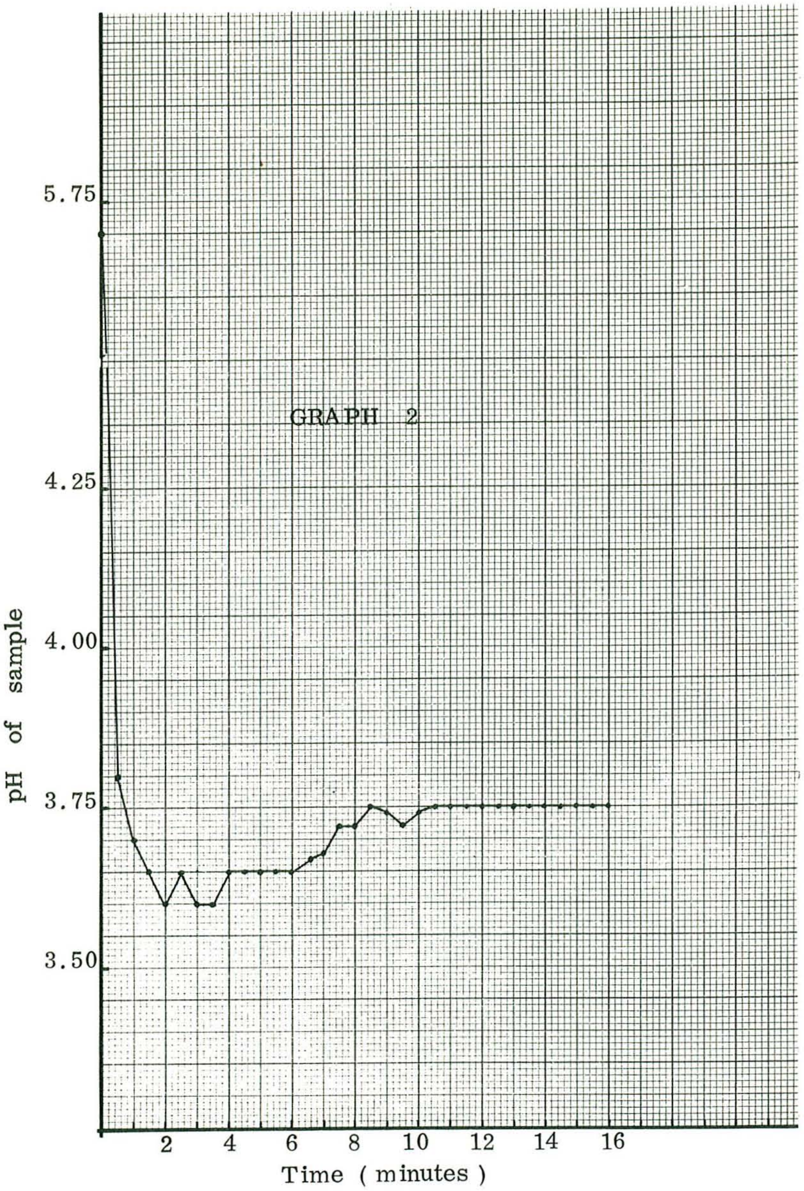
Tailings Stream No. 4
pH modified to 5

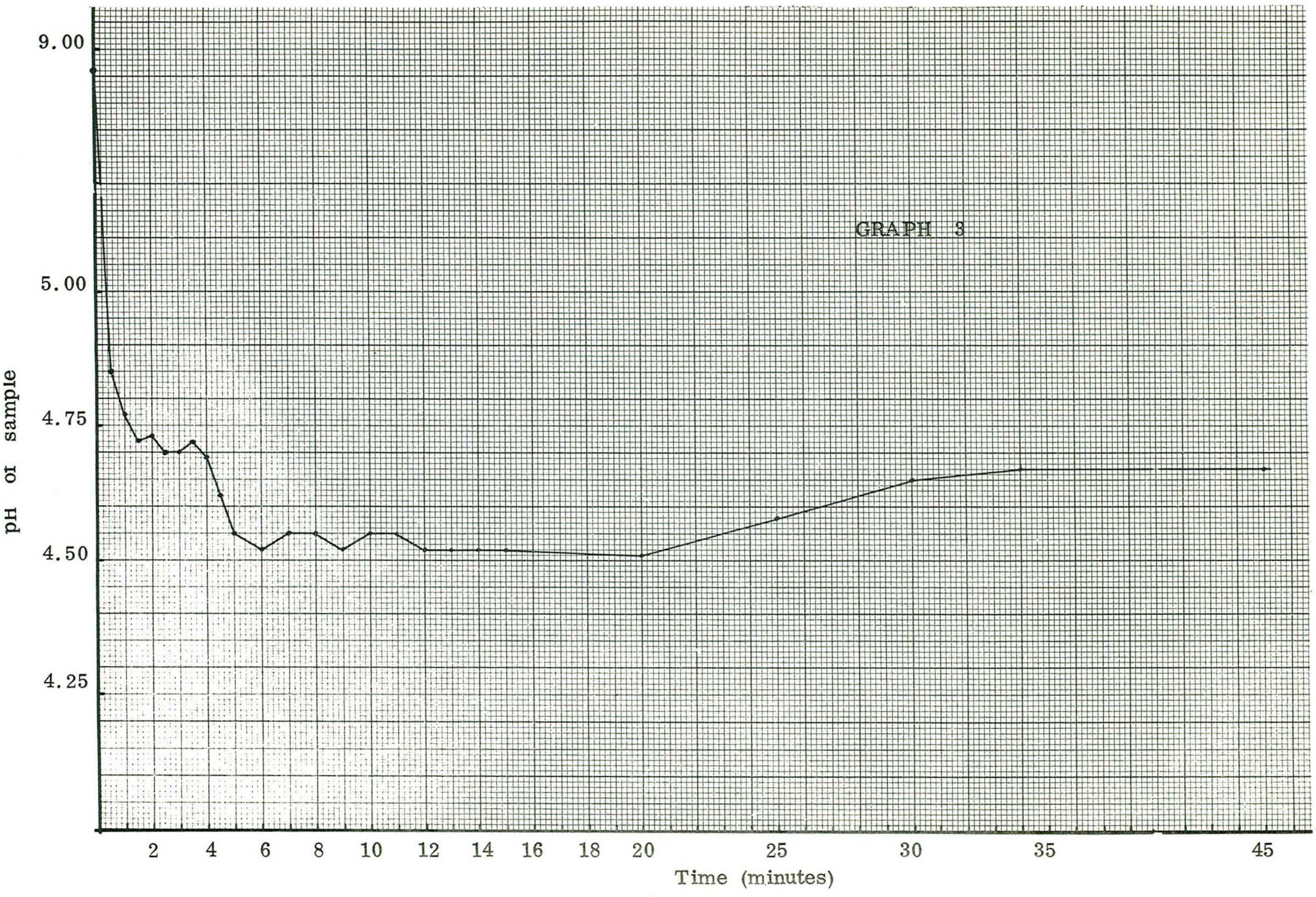
TABLE 1

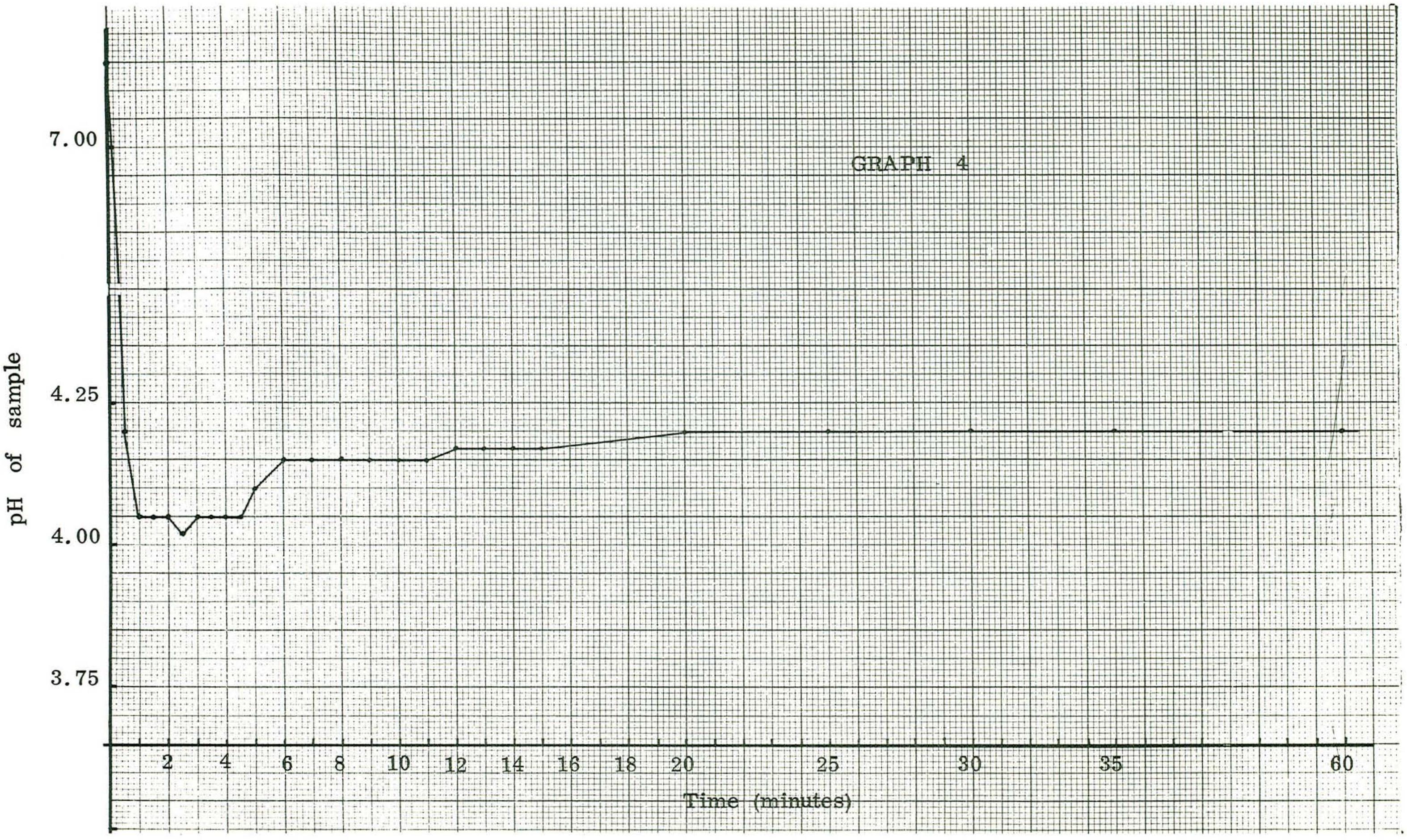
Sample	4 - 5 - 15	4 - 5 A15
Initial pH	8.3	8.3
Modified pH	5.0	5.0
CO_2	15 min.	---
Air	---	15 min.
Temperature	50°C	50°C

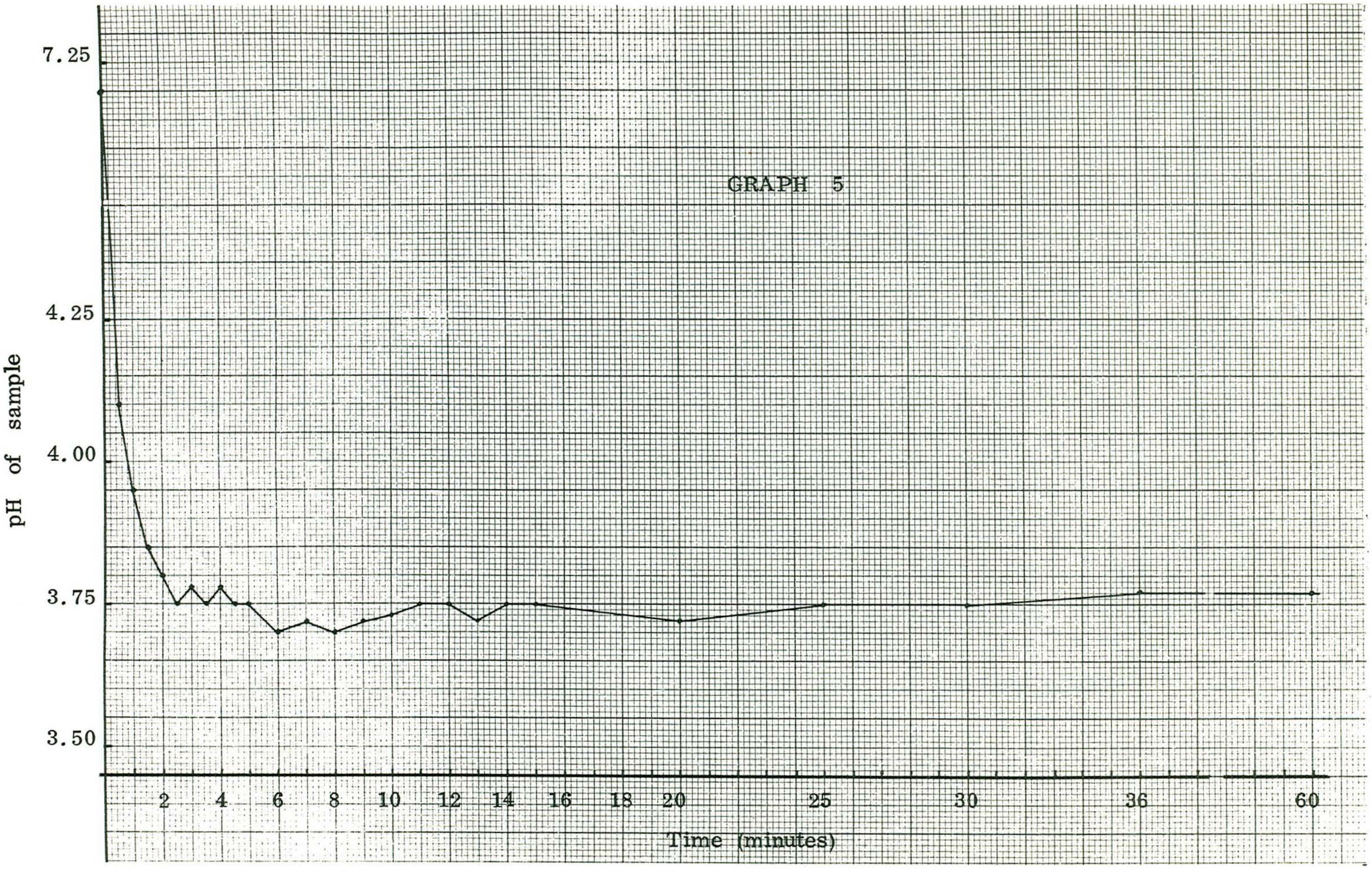
SEDIMENTATION TEST

Time	%S	%S
0	100	100
1 day	53	76
2 days	47	71
3 days	44	66
5 days	39	62
7 days	37	58
10 days	36	55


GRAPH 2

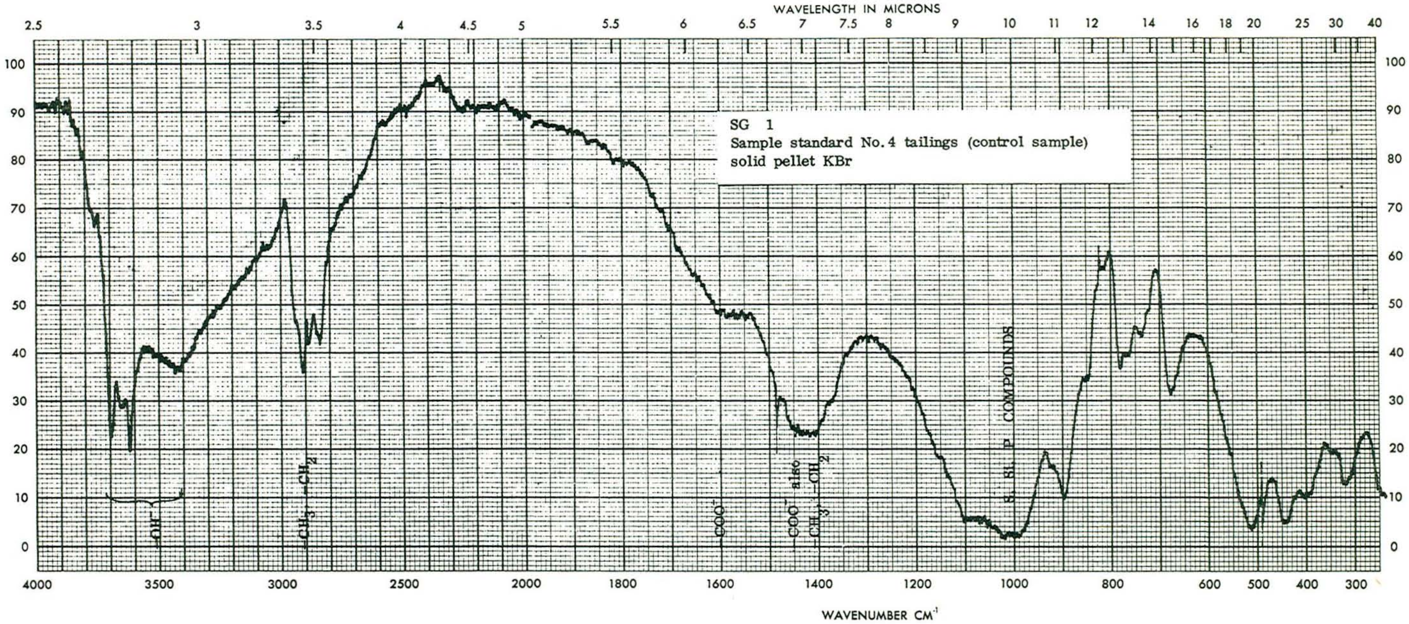

GRAPH 3
9.00
5.00
4.75
4.50
4.25
pH of sample
2
4
6
8
10
12
14
16
18
20
25
30
35
45
Time (minutes)

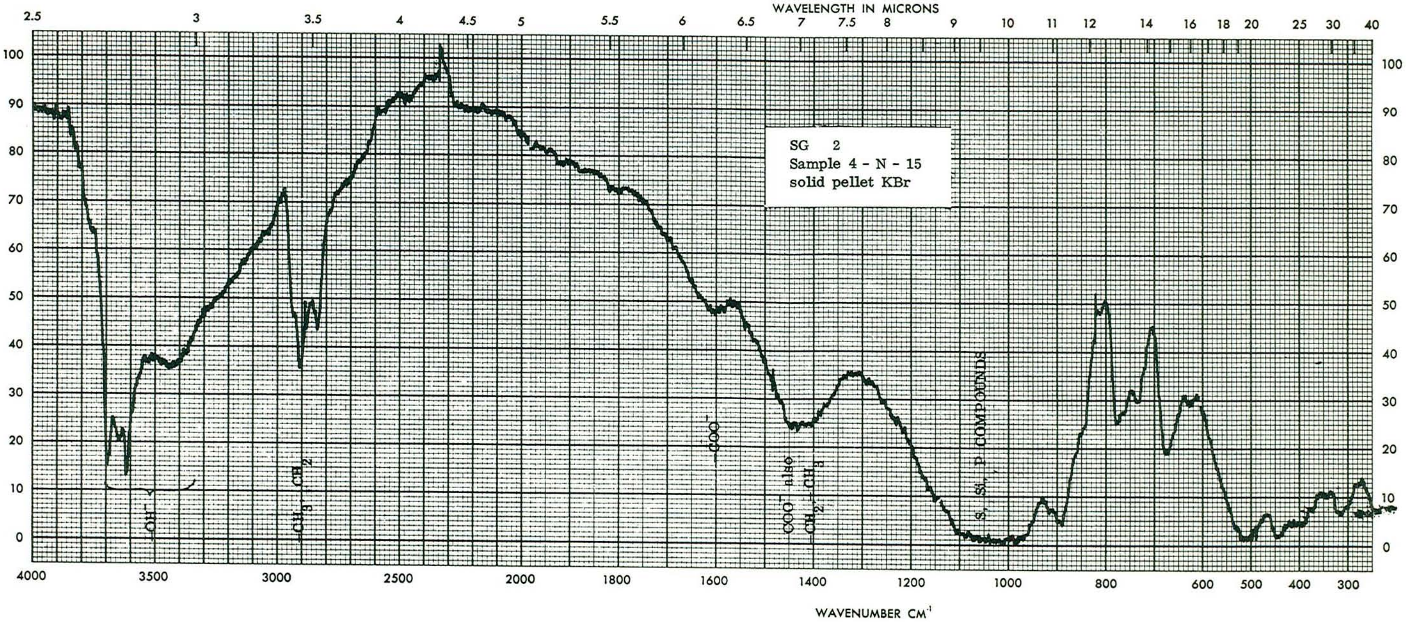

GRAPH 4
7.00
4.25
4.00
3.75
pH of sample
2
4
6
8
10
12
14
16
18
20
25
30
35
60
Time (minutes)



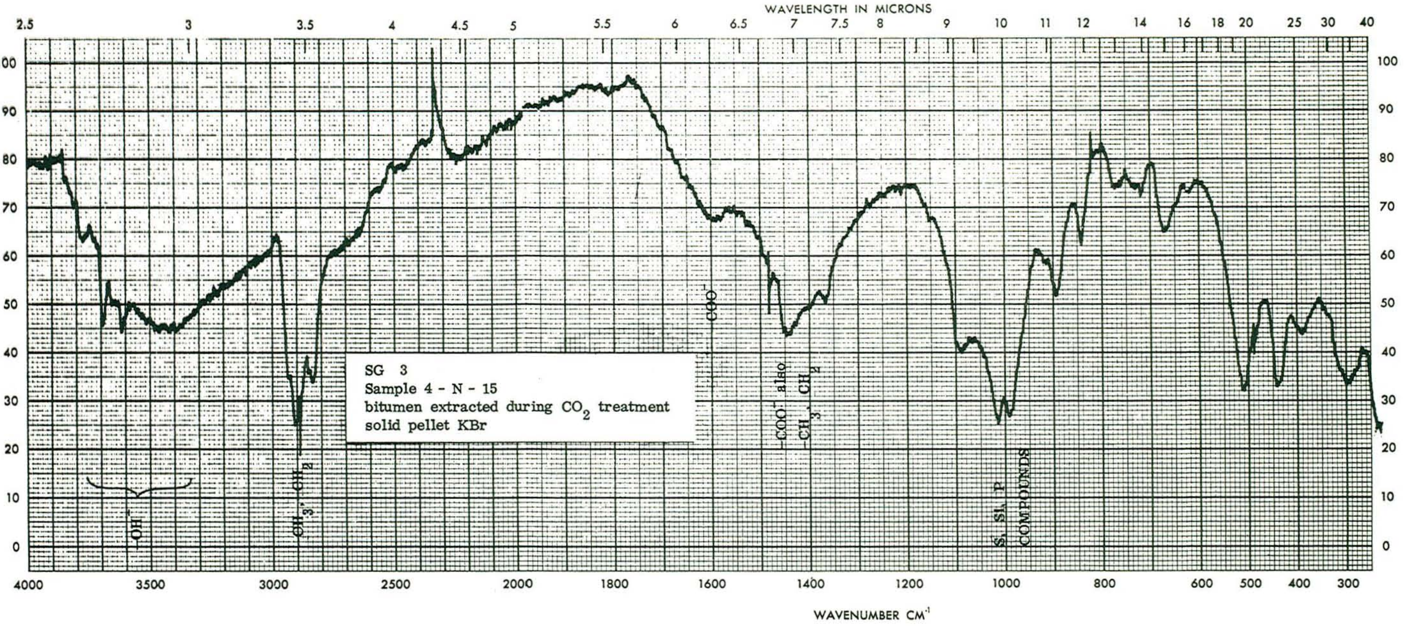
GRAPH 5

7.25
4.25
4.00
3.75
3.50
pH of sample
2
4
6
8
10
12
14
16
18
20
25
30
36
60
Time (minutes)

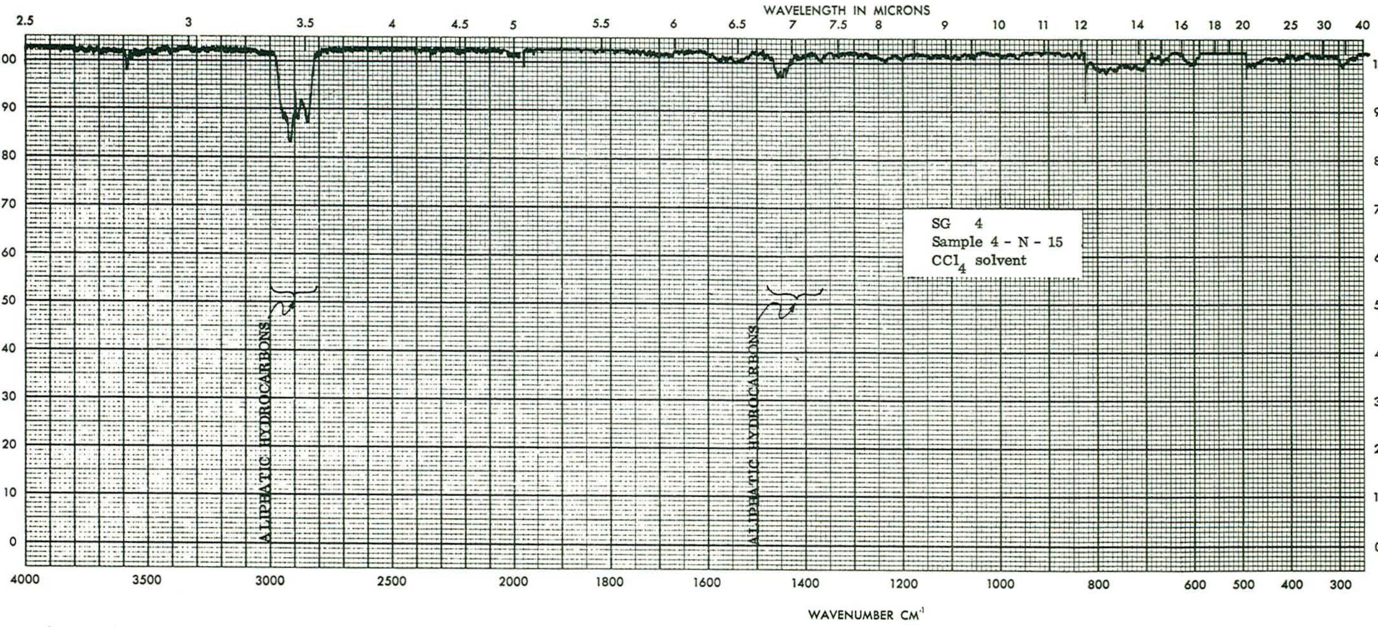

WAVELENGTH IN MICRONS
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
7.5
8
9
10
11
12
14
16
18
20
25
30
40
100
90
80
70
60
50
40
30
20
10
0
SG 1
Sample standard No. 4 tailings (control sample)
solid pellet KBr
-OH
-CH$_3$ -CH$_2$
COO$^-$
COO$^-$ also -CH$_3$, -CH$_2$
S, Si, P COMPOUNDS
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
500
400
300
WAVENUMBER CM^{-1}



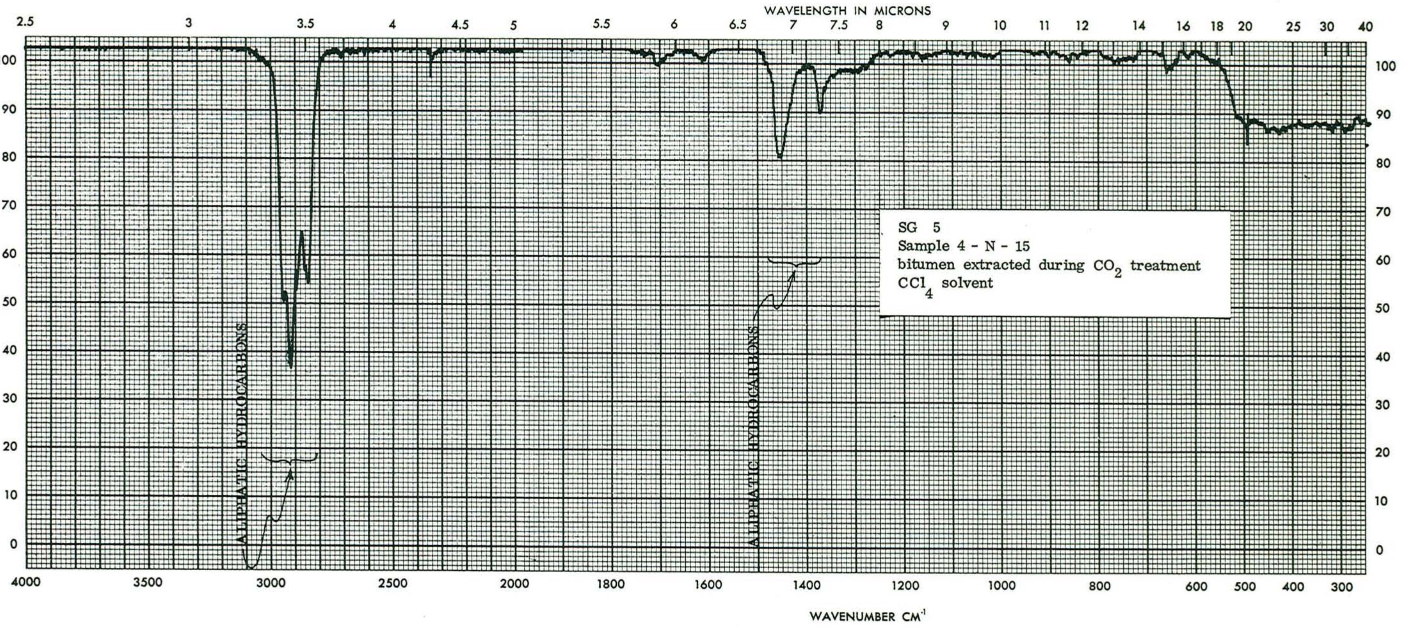
SG 2
Sample 4 - N - 15
solid pellet KBr



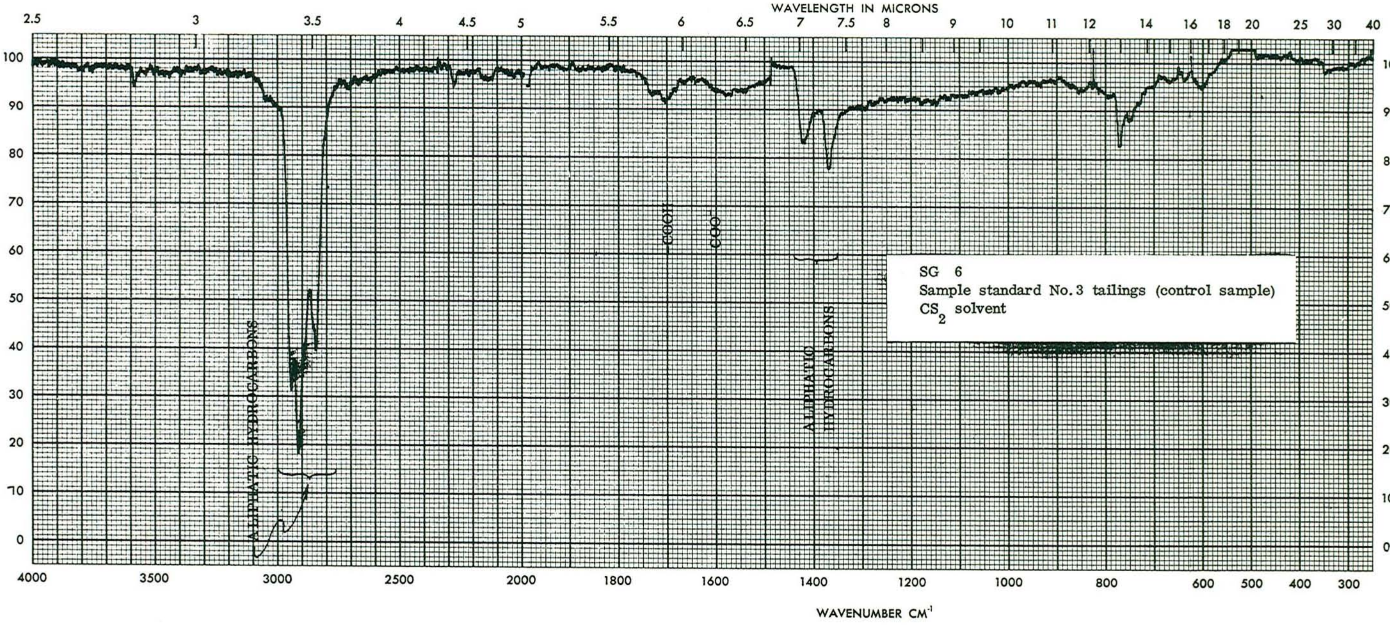
SG 3
Sample 4 - N - 15
bitumen extracted during CO_2 treatment
solid pellet KBr



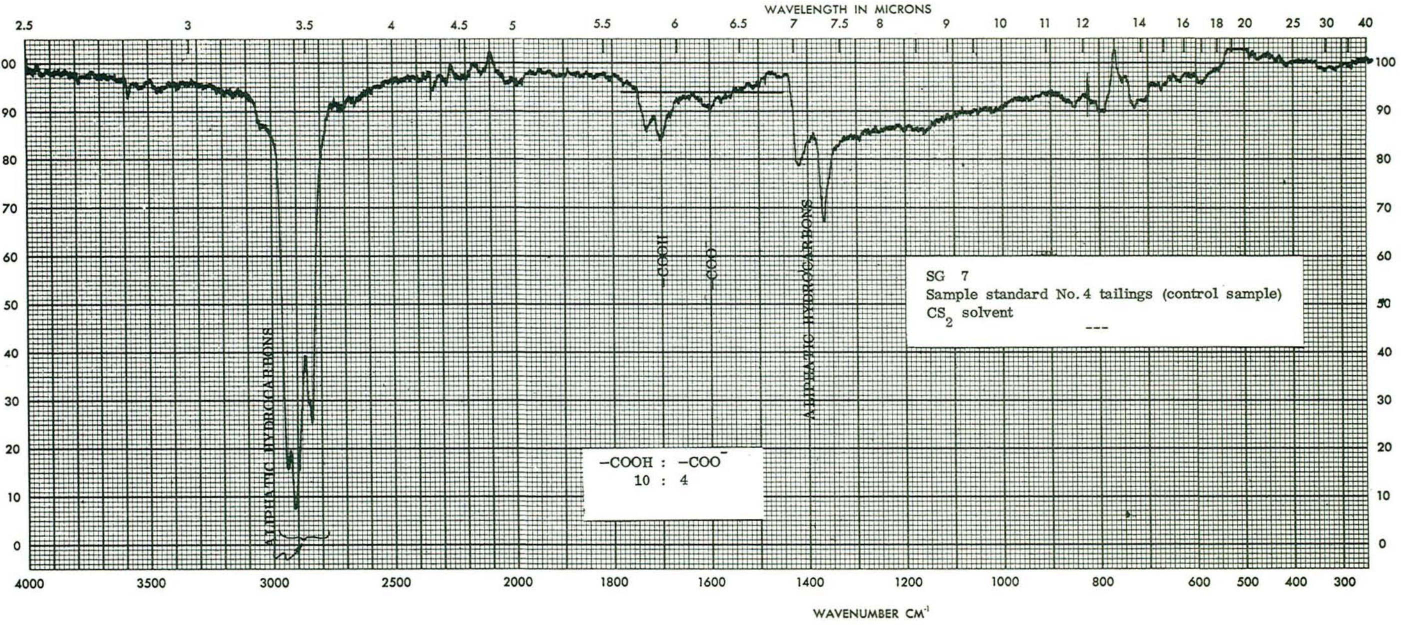
SG 4
Sample 4 - N - 15
CCl_4 solvent



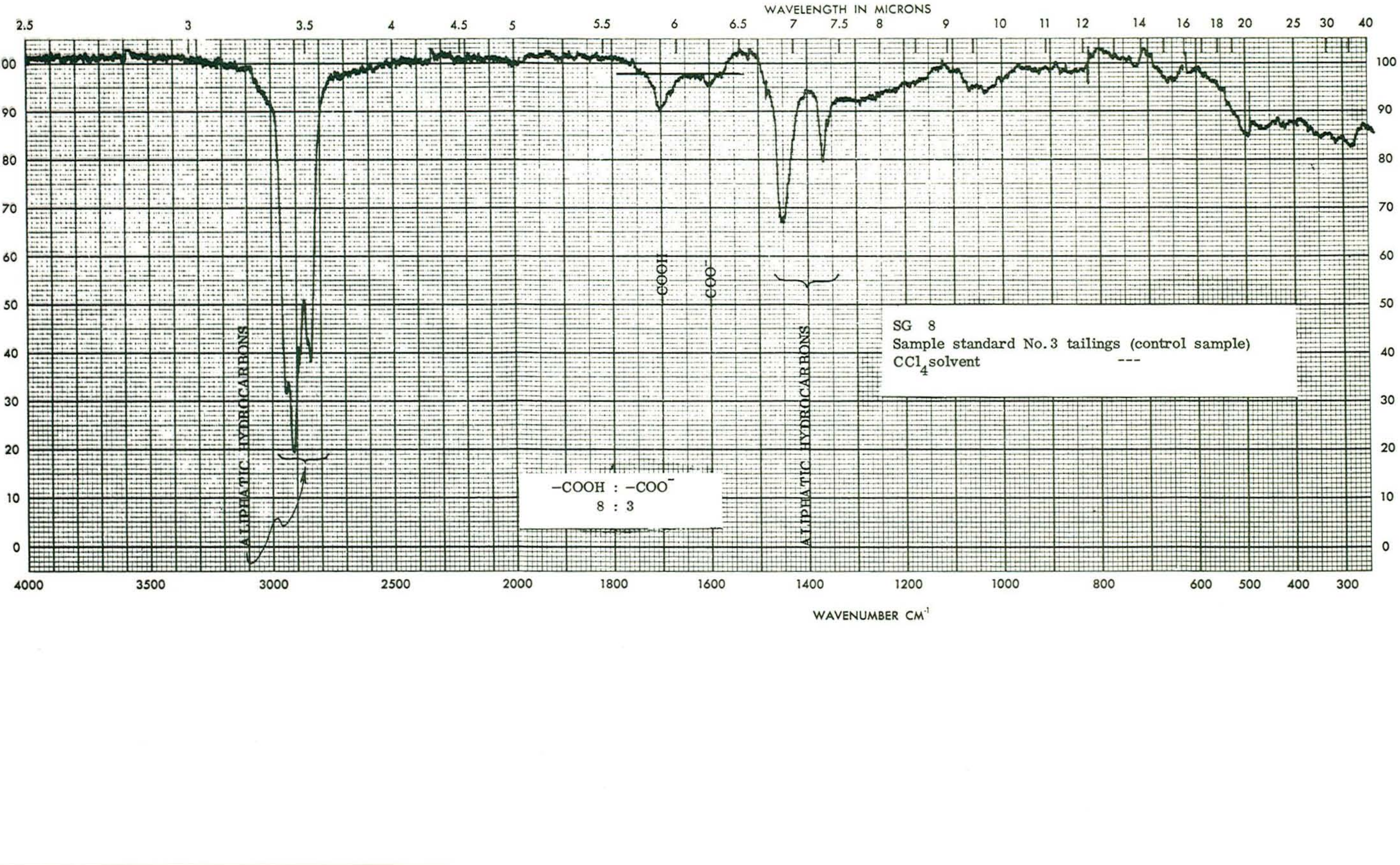
SG 5
Sample 4 - N - 15
bitumen extracted during CO_2 treatment
CCl_4 solvent



SG 6
Sample standard No. 3 tailings (control sample)
CS_2 solvent

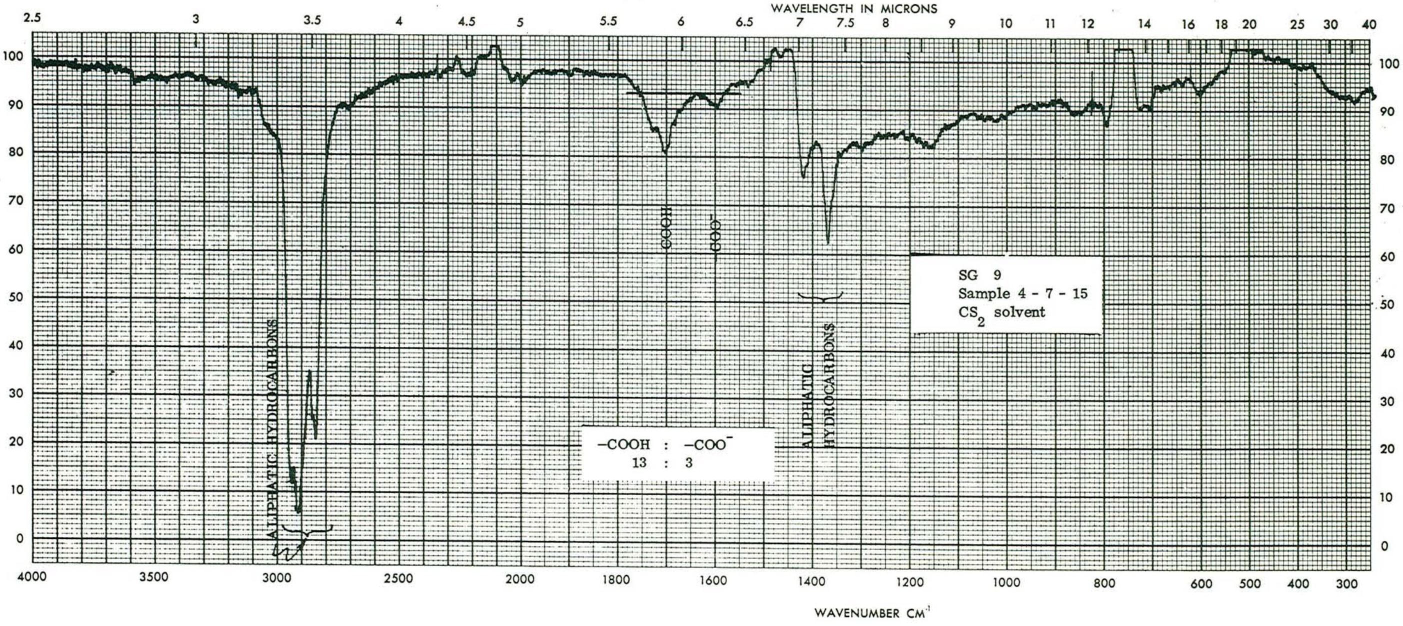

WAVELENGTH IN MICRONS
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
7.5
8
9
10
11
12
14
16
18
20
25
30
40
100
90
80
70
60
50
40
30
20
10
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
500
400
300
WAVENUMBER CM⁻¹
ALIPHATIC HYDROCARBONS
-COOH
-COO
ALIPHATIC HYDROCARBONS
SG 7
Sample standard No. 4 tailings (control sample)
CS2 solvent

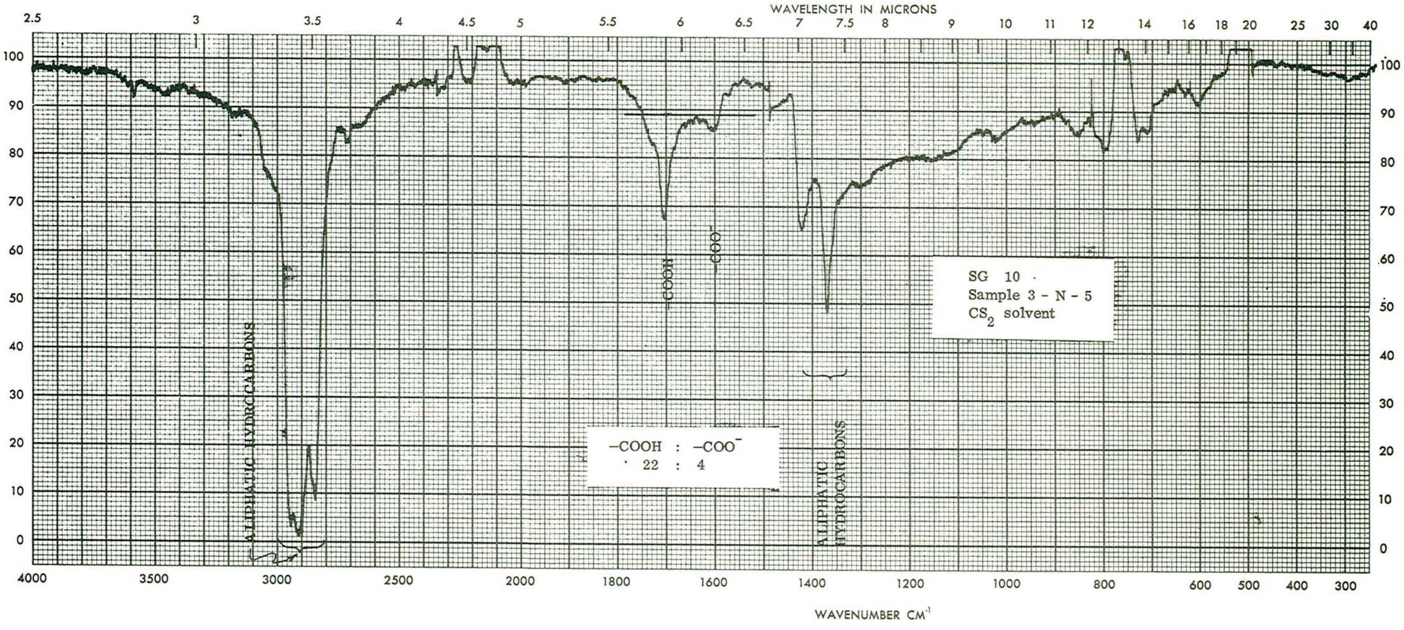
-COOH : -COO⁻
10 : 4



$-COOH : -COO^-$
8 : 3

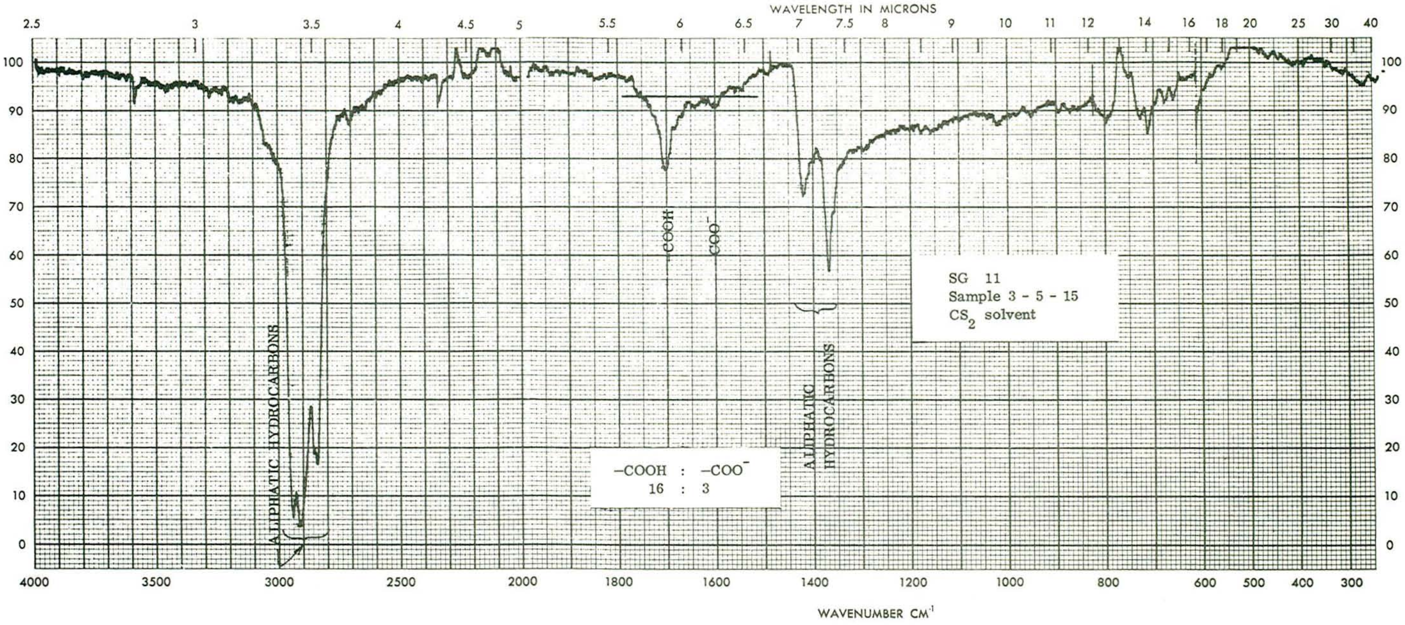
SG 8
Sample standard No. 3 tailings (control sample)
CCl_4 solvent ---


WAVELENGTH IN MICRONS
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
7.5
8
9
10
11
12
14
16
18
20
25
30
40
100
90
80
70
60
50
40
30
20
10
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
500
400
300
WAVENUMBER CM⁻¹
ALIPHATIC HYDROCARBONS
COOH
COO⁻
ALIPHATIC HYDROCARBONS
–COOH : –COO⁻
13 : 3
SG 9
Sample 4 - 7 - 15
CS₂ solvent



SG 10
Sample 3 - N - 5
CS_2 solvent

–COOH : –COO⁻
22 : 4


WAVELENGTH IN MICRONS
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3.5
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4.5
5
5.5
6
6.5
7
7.5
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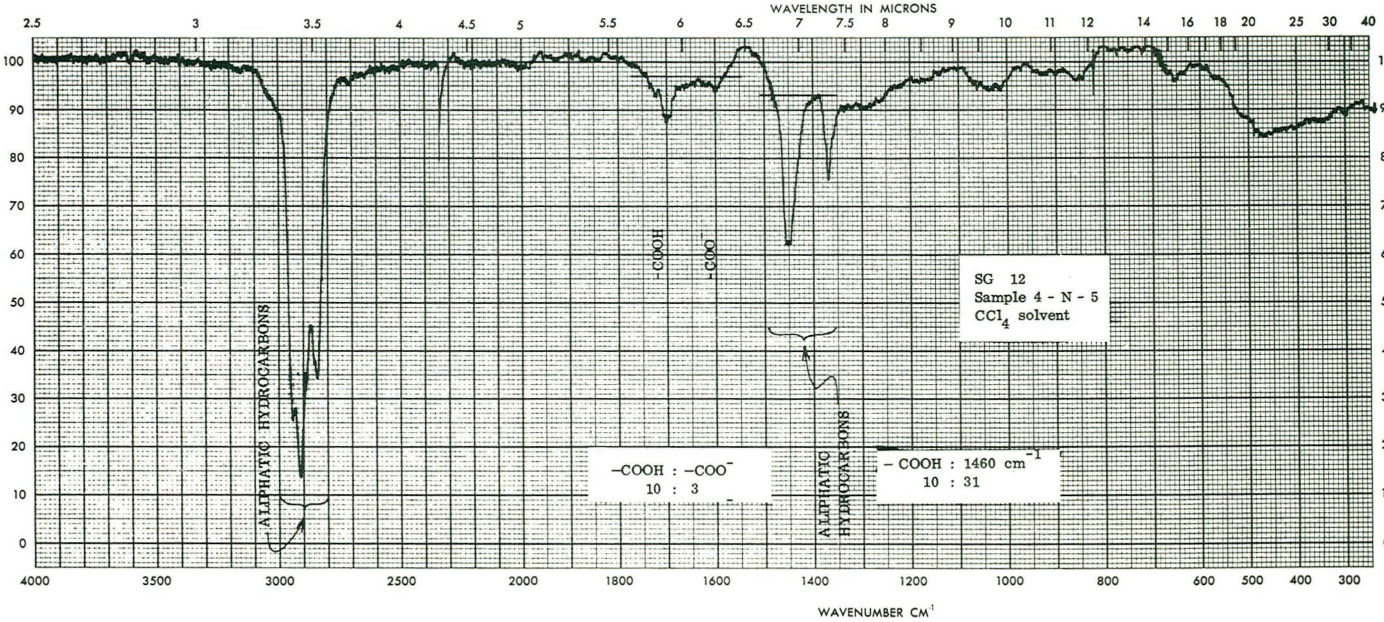
10
11
12
14
16
18
20
25
30
40
100
90
80
70
60
50
40
30
20
10
0
ALIPHATIC HYDROCARBONS
–COOH
COO$^-$
ALIPHATIC HYDROCARBONS
SG 11
Sample 3 - 5 - 15
CS$_2$ solvent
–COOH : –COO$^-$
16 : 3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
500
400
300
WAVENUMBER CM^{-1}


WAVELENGTH IN MICRONS
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5.5
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6.5
7
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9
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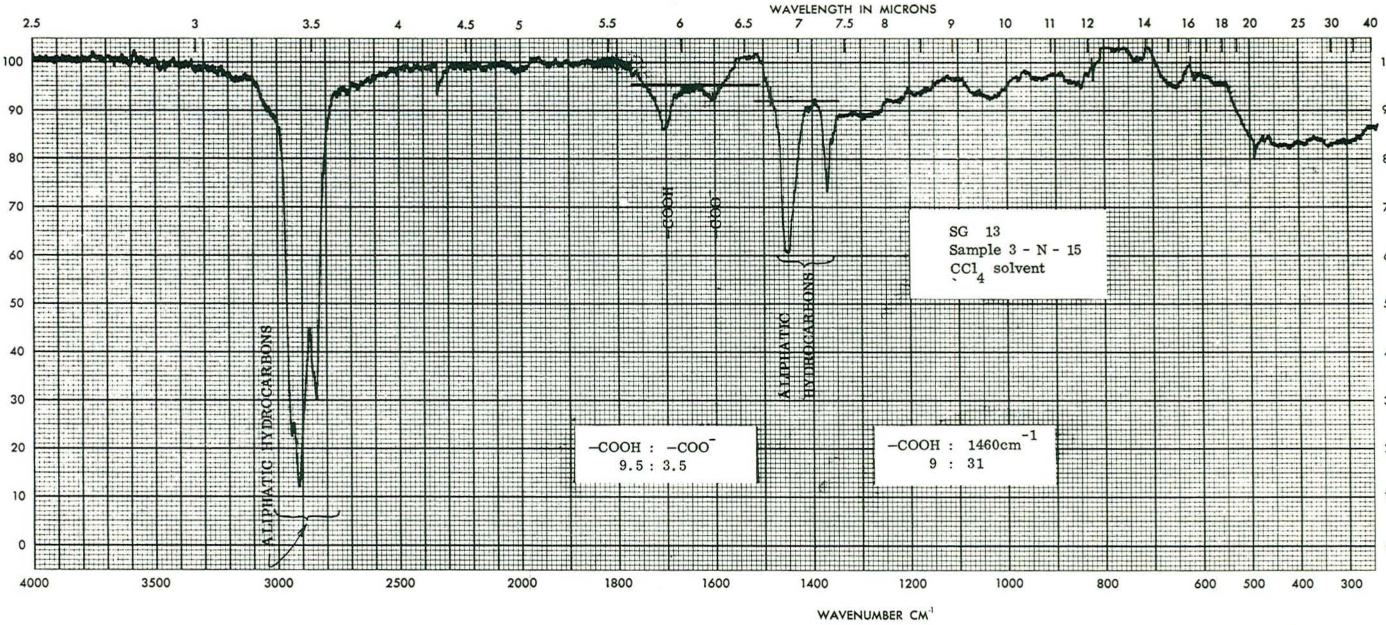
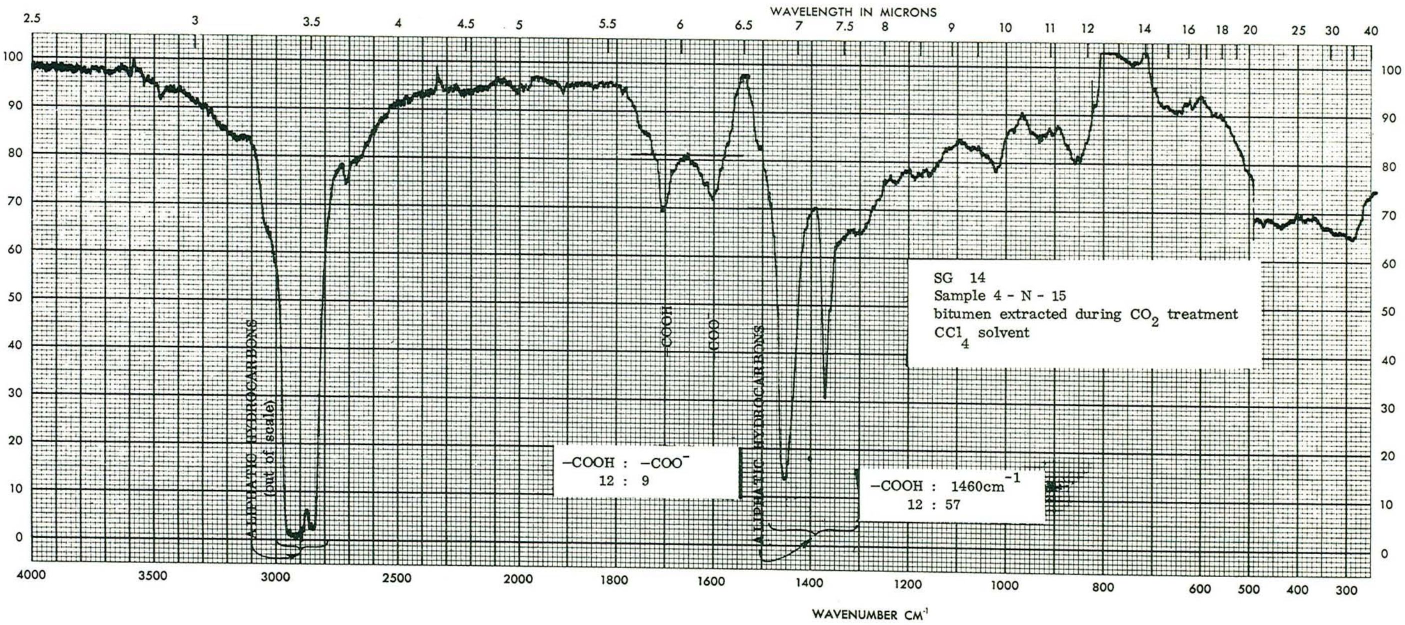
11
12
14
16
18
20
25
30
40
100
90
80
70
60
50
40
30
20
10
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
500
400
300
WAVENUMBER CM^{-1}
ALIPHATIC HYDROCARBONS
-COOH
-COO^{-}
ALIPHATIC HYDROCARBONS
SG 12
Sample 4 - N - 5
CCl_4 solvent
–COOH : –COO^{-}
10 : 3
– COOH : 1460 cm^{-1}
10 : 31


WAVELENGTH IN MICRONS
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
7.5
8
9
10
11
12
14
16
18
20
25
30
40
100
90
80
70
60
50
40
30
20
10
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
500
400
300
WAVENUMBER CM⁻¹
ALIPHATIC HYDROCARBONS
-COOH
-COO-
ALIPHATIC HYDROCARBONS
SG 13
Sample 3 - N - 15
CCl4 solvent
-COOH : -COO-
9.5 : 3.5
-COOH : 1460cm-1
9 : 31



SG 14
Sample 4 - N - 15
bitumen extracted during CO_2 treatment
CCl_4 solvent

$-COOH : -COO^-$
12 : 9

$-COOH : 1460 cm^{-1}$
12 : 57

7. LITERATURE

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4 R. B. FISHER and D. G. PETERS : " Quantitative Chemical Analysis ", third edition, pp 302 - 303 .

5 A. R. OLSON, P. V. YOULE : " The Strength Of Carbonic Acid. The Rate Of Reaction Of Carbon Dioxide With Water And Hydroxyl Ion ", J. Am. Chem. Soc. 62, 1027 (1940) .

APPENDIX I

CALCULATION OF OPTIMUM pH FOR CO_2 TREATMENT

PRACTICAL EXAMPLES

CALCULATION OF OPTIMUM pH FOR CO_2 TREATMENT

Solutions of equation

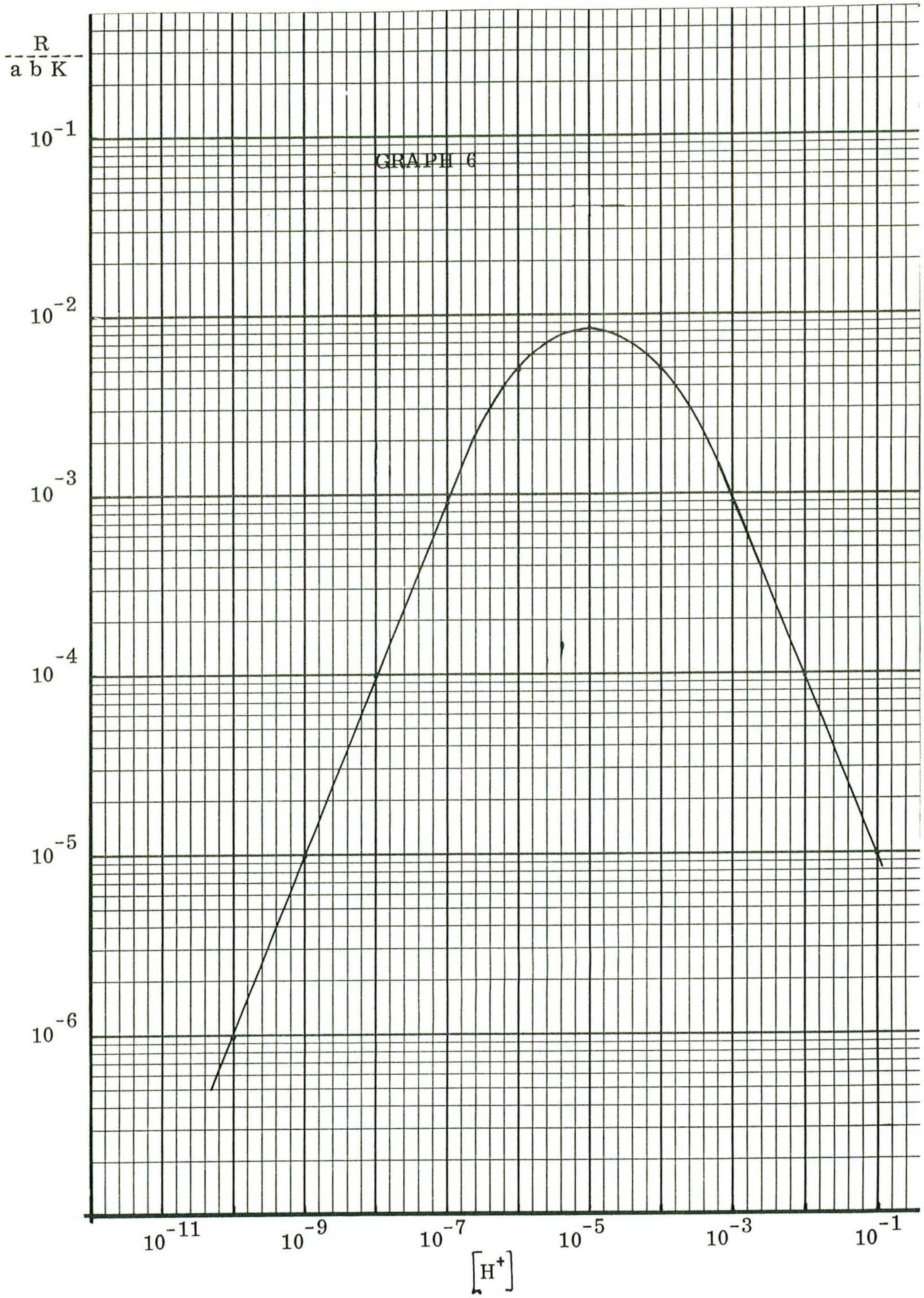
$$(15) \qquad \frac{R}{a\,b\,K} = \frac{K_1\,[H^+]}{\left(K_1 + [H^+]\right)\left(K_2 + [H^+]\right)}$$

are shown in Tables 2, 3, 4 and 5. Tables 2 and 3 are for a dissociation constant of carbonic acid, K_2, in the vicinity of 10^{-4}. Table 2 is for a dissociation constant of naphthenic acid, K_1, of 10^{-6} and Table 3 is for a K_1 of 10^{-4}. Tables 4 and 5 are for a K_2 of 10^{-7}. Table 4 is for a K_1 of 10^{-4} and Table 5 for a K_1 of 10^{-6}.

The tabulated results are plotted on Graphs 6, 7, 8 and 9. On all the graphs the maxima occur in the pH range 4 to 6.5, which agrees with the experimental results (i.e. the fastest reaction rate was in the sample whose initial pH was adjusted to 5). Graph 10 shows the relationship between optimum pH and the dissociation constant of naphthenic acid, K_1, (specific values: 10^{-4}, 10^{-5} and 10^{-6}) at values for the dissociation constant of carbonic acid, K_2, of 10^{-7} and 10^{-4}.

TABLE 2

$[H^+]$	$\frac{R}{a\ b\ K}$ for $K_1 = 10^{-6}$, $K_2 = 10^{-4}$
10^{-1}	9.9899100×10^{-6}
10^{-2}	9.9000000×10^{-5}
10^{-3}	9.0818271×10^{-4}
10^{-4}	4.9504950×10^{-3}
10^{-5}	8.2644627×10^{-3}
10^{-6}	4.9504950×10^{-3}
10^{-7}	9.0818271×10^{-4}
10^{-8}	9.9000000×10^{-5}
10^{-9}	9.9899100×10^{-6}
10^{-10}	9.9989900×10^{-7}



GRAPH 6

TABLE 3

$\left[H^+\right]$	$\frac{R}{a\,b\,K}$ for $K_1 = K_2 = 10^{-4}$
10^{-1}	9.9800298×10^{-4}
10^{-2}	9.8029603×10^{-3}
10^{-3}	8.2644627×10^{-2}
10^{-4}	2.5000000×10^{-1}
10^{-5}	8.2644627×10^{-2}
10^{-6}	9.8029603×10^{-3}
10^{-7}	9.9800298×10^{-4}
10^{-8}	9.9980001×10^{-5}
10^{-9}	9.9998000×10^{-6}
10^{-10}	9.9999800×10^{-7}
10^{-11}	9.9999980×10^{-8}

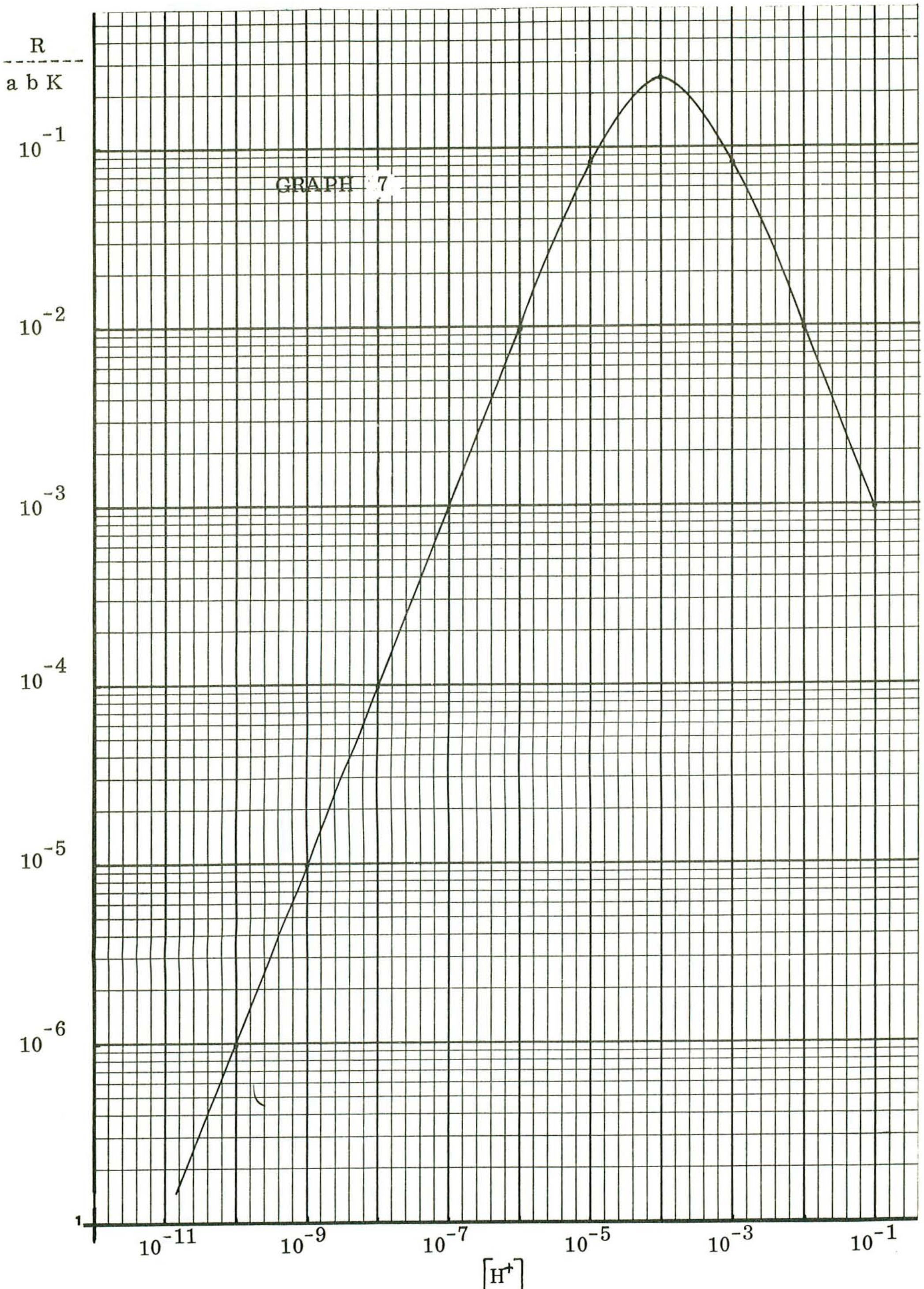
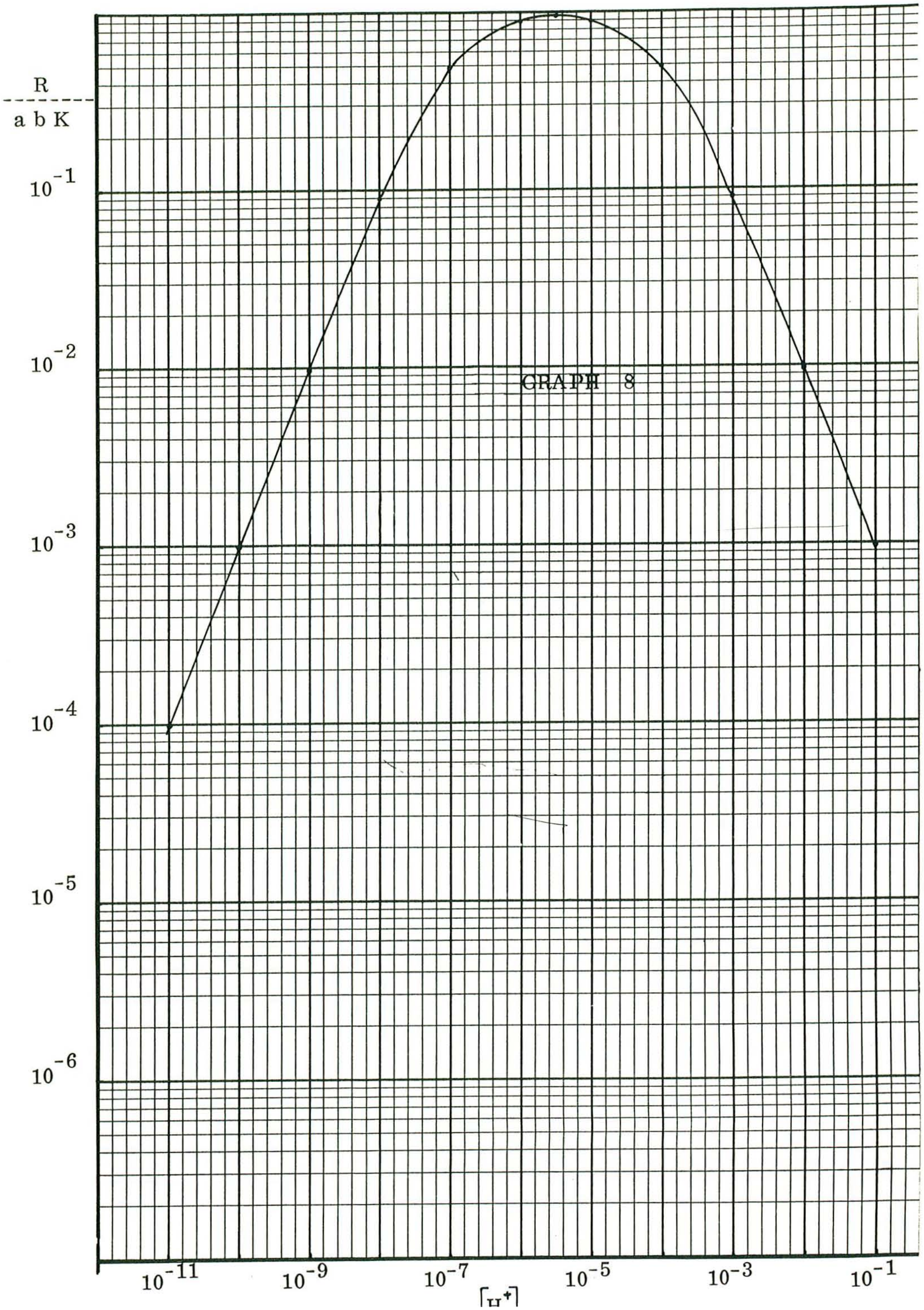

GRAPH 7

TABLE 4

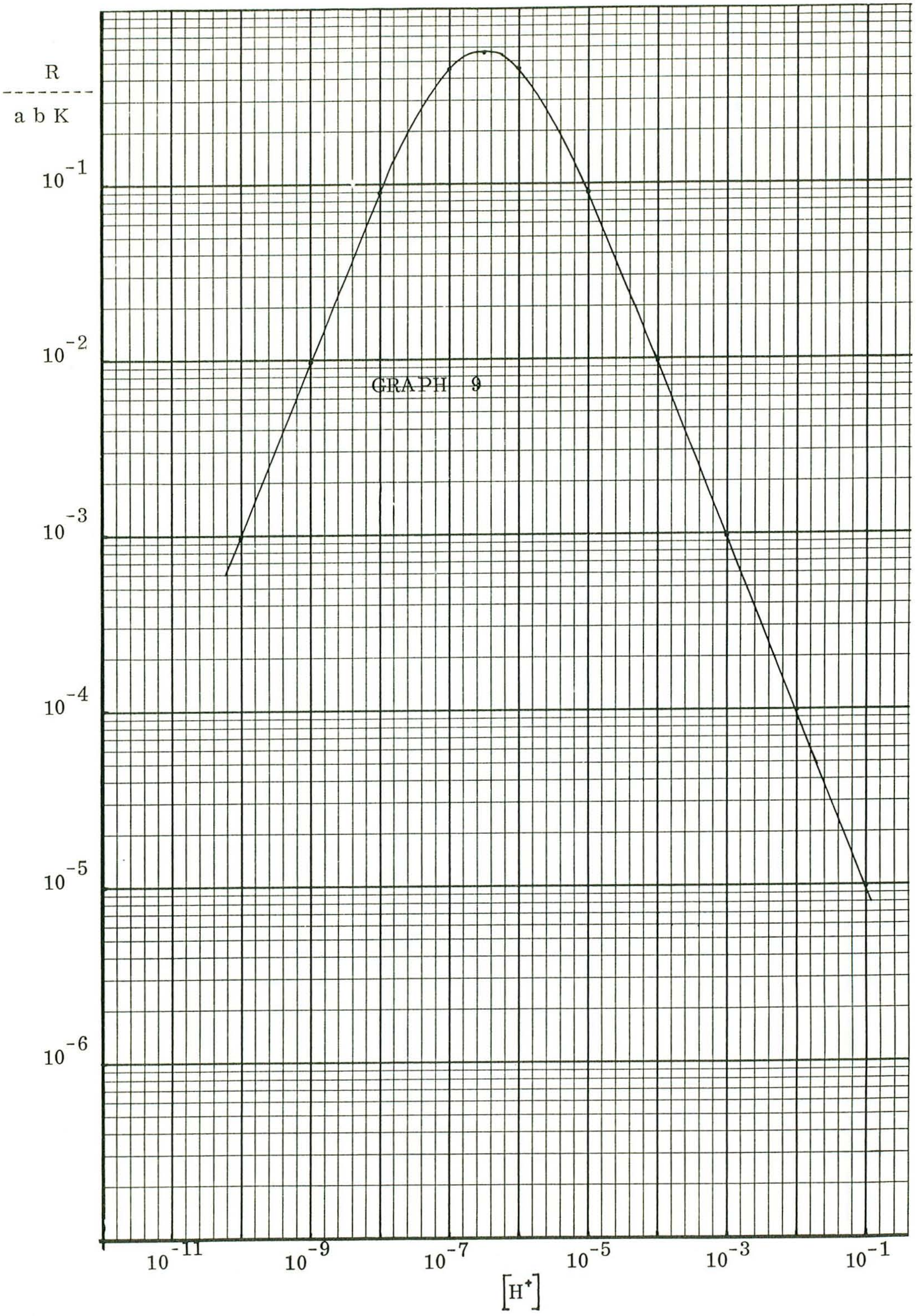
$[H^+]$	$\frac{R}{a\,b\,K}$ for $K_1 = 10^{-4}$, $K_2 = 10^{-7}$
10^{-1}	9.9899999×10^{-4}
10^{-2}	9.9008909×10^{-3}
10^{-3}	9.0900000×10^{-2}
10^{-4}	4.9950049×10^{-1}
10^{-5}	9.0009000×10^{-1}
$10^{-5.5}$	9.3963281×10^{-1}
10^{-6}	9.0009000×10^{-1}
10^{-7}	4.9950049×10^{-1}
10^{-8}	9.0900000×10^{-2}
10^{-9}	9.9008909×10^{-3}
10^{-10}	9.9899999×10^{-4}
10^{-11}	9.9989991×10^{-5}

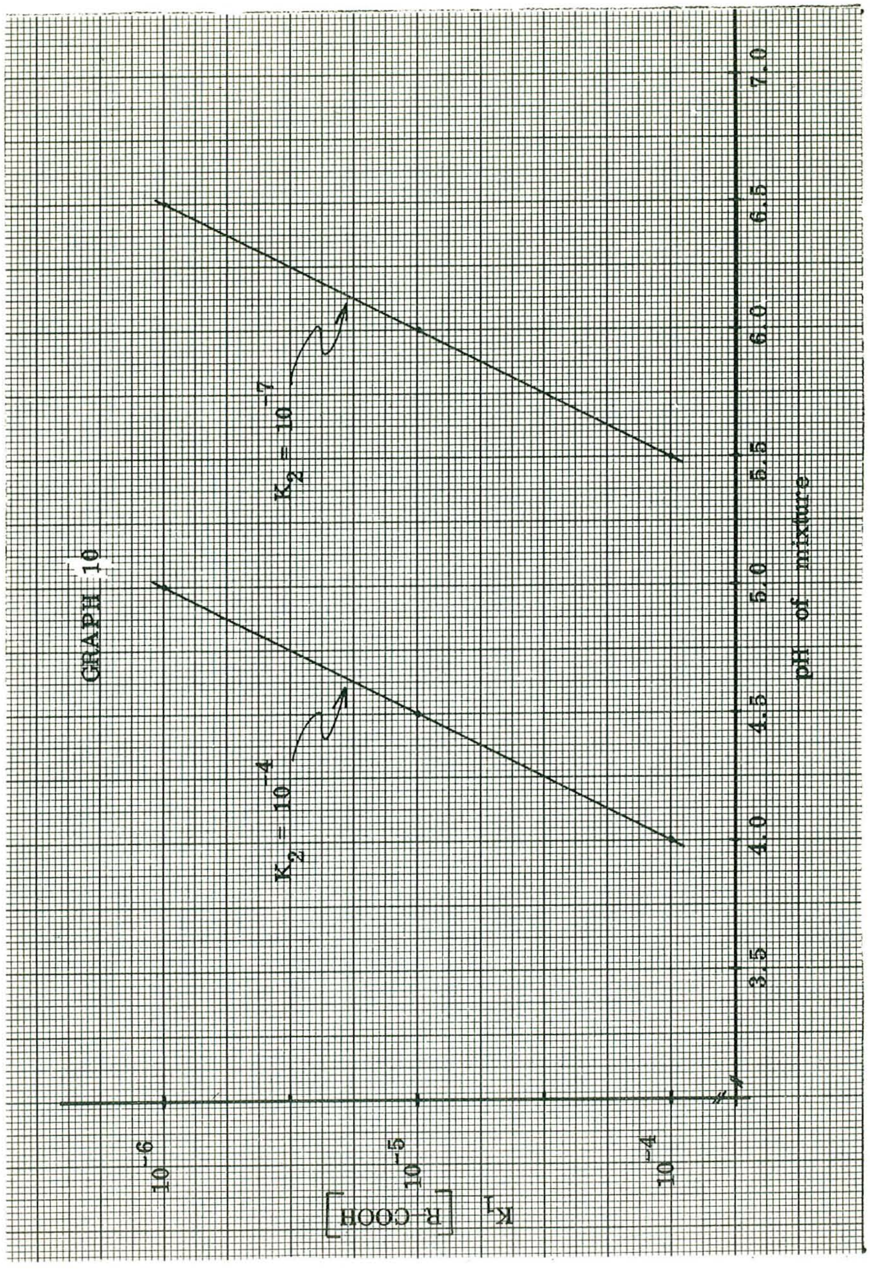


GRAPH 8

TABLE 5

$\left[H^{+}\right]$	$\frac{R}{a\,b\,K}$ for $K_1 = 10^{-6}$, $K_2 = 10^{-7}$
10^{-1}	9.9998900×10^{-6}
10^{-2}	9.9980000×10^{-5}
10^{-3}	9.9890109×10^{-4}
10^{-4}	9.8910989×10^{-3}
10^{-5}	9.0009000×10^{-2}
10^{-6}	4.5454545×10^{-1}
$10^{-6.5}$	5.7721541×10^{-1}
10^{-7}	4.5454545×10^{-1}
10^{-8}	9.0009000×10^{-2}
10^{-9}	9.8910989×10^{-3}
10^{-10}	9.9890109×10^{-4}


GRAPH 9



GRAPH 10

$K_2 = 10^{-4}$
$K_2 = 10^{-7}$
$K_1 \left[\text{R-COOH}\right]$
10^{-6}
10^{-5}
10^{-4}
pH of mixture
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0