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The Effect of Various Concentrations of Alkali with the Adsorption of Calcium Ions onto Oleic Acid

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The Effect of Various Concentrations
of Alkali

With the Adsorption of Calcium Ions
onto Oleic Acid

by .

Thomas J. Mc Alpine

A Thesis submitted to the Faculty
of the Department of Paper Science
and Engineering in partial
fulfillment of the
Degree of Bachelor of Science

Western Michigan University

Kalamazoo, Michigan

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The author wishes to express his appreciation to Mr. David K. DeKam, Georgia-Pacific Corporation, who produced the opportunities and first-hand experience so that this thesis could be compiled. Unexpressible appreciations to my wife and son for enduring the hardships most experience when a family sees so little of their husband and father.

Abstract

The purpose of this thesis was to find an optimum condition for the formation of the precipitated calcium soaps. The system investigated included the range of alkali addition of 0 to 1.2 pounds per one hundred gallons (#/100 gal.). A direct relationship between the adsorption of calcium and the added alkali showed an increasing adsorption with an increasing alkali concentration to a maximum of 145 parts per million calcium ion adsorbed to 833.7 ppm oleic acid when .225 (#/100 gal.) is applied. It shows that any higher concentration of an alkali will level out the maximum calcium adsorption to approximately 140 ppm.

It was also found that the alkali demand was an increasing function and eventually leveled out at a maximum concentration.

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HISTORICAL BACKGROUND

Since the beginning of papermaking history, the recycle of paper wastes eliminated high pulp usages. "Since early in the 20th century, wastepaper has been used to produce low grade pulp in the production of jute liner, bogus liners, and folding or chipboard grades of paper."¹ A demand for cleaner pulp from wastepaper aroused the paper industry in the early 1950's. Hence this demand resulted in new inventions, techniques and system innovations.

The major operations developed contained basic steps for operational efficiency: 1) pulping; 2) cleaning; 3) washing; 4) brightening. The major systems are listed as the following:

- A) Lancaster washers; B) Pressure washers; C) Vacuum washers;
- D) Sidehill washers; E) Flotation cells.

A) Lancaster washers

This process forms a mat on the surface of a revolving cylinder by the control of a differential head. The stock is pressed to eight to ten percent consistency. It is costly and space consuming and relies on control of freeness and differential head for maximum efficiency.²

B) Pressure washers

This process is not considered an efficient washing method but it is mostly used in recovery of heat and chemicals.

A screw raises the stock in a confined perforated tube forcing the water to pass through perforations and the thickened stock remains. "In the pressure induced type, the stock is subjected to the pressure of a reducing cross-sectional area, allowing the stock to be dewatered to a fifteen to twenty-five percent consistency."³

C) Vacuum washers

A drum is immersed in the stock slurry and a vacuum is applied to the submerged portion of the drum. This causes the fibers to deposit on the outer surface as the drum passes through the slurry. The stock is dewatered between twelve to seventeen percent consistency.⁴

D) Sidehill washers

This process is crude compared to other types of washers. The stock enters the headbox at two to two and one half percent. It flows onto an inclined wire mesh screen allowing the free water to drain through the wire. The stock collects at a discharge box at three to seven percent consistency.

E) Flotation cells

This process is becoming very popular in its early growth. The main function of cleaning is by means of chemically and mechanically floating the contaminants from the system. The previous cleaning operations were mostly dewatering

units; this process is completely different. The flotation cell consists of a tank provided with a feed, an overflow for froth removal, and a discharge pipe for passing the stock into the next cell in the flotation line. A mechanical agitator provides violent agitation and creates a partial vacuum that causes air to enter into the rotating member. The air combines with the flow of stock to which flotation aids have been added in the form of small bubbles.

The theory of flotation was discovered in 1903 by Alcide Froment. He patented it noting that gas liberated from an acid solution containing sulfides or carbonates picked up particles of sulfide minerals. Later, Salman, Picard and Lalot showed that air would serve as the bouyant medium. Pierre Hines of Portland, Oregon in the mid 1930's applied this process to the de-inking of paper. J.W. Jelkes, then of Denver Equipment Company, started the first de-inking installation in 1950.⁵

De-inking by the flotation process is most commonly used in Europe and Japan. It has been a special process in the United States but it has developed an expanding interest in the past few years. It has a direct advantage over de-inking by washing--low fiber losses (7-10% instead of 30%) and low water consumption (4800 gallons per ton instead of 30,000 to 43,000 gallons per ton).⁶ Dr. Gartemann claims that "a prerequisite

for the physical process of selective flotation is differing wettability of the components to be separated in a complex e.g. a liquid/solid system."⁷ This system contains fibers, fillers and ink particles in an aqueous solution. The purpose of flotation is to bring the ink to the surface while leaving the fiber and filler in solution. This can be achieved because the ink particles have a poorer wettability than the fibrous material.

To get a selective process for removing ink particles by flotation, a flotation aid is usually added to the pulper. In a simple form, it could be representative of soft soaps. Normally, a flotation aid would be characterized as a long chain of molecules containing hydrophilic (water-loving) and/or hydrophobic groups (water-hating). The hydrophilic group acts as frothers and reduces the surface tension while the hydrophobic groups react with the hardness--calcium and magnesium ions--forming precipitated flaky calcium soaps. These sticky substances act as collectors. A collector has an important function of attracting the separated ink particles and the finely dispersed air bubbles.⁸

The frothers are utilized to maintain a reduced surface tension so that the floating calcium soaps can break and remain on the surface.

Many forms of flotation aids are utilized but the best-known exponents, according to Dr. Ortner, "are the soaps, the alkali salts of fatty acids, substances with a long chain of molecules containing the hydrophobic end--the fatty acid component with a negative charge--and a functional group-hydrophilic with a positive charge."⁹ Figure 1 is a schematic representation of the chemical arrangement of the functional groups once the ions are attracted in the alkali solution.

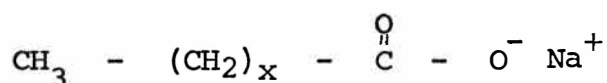
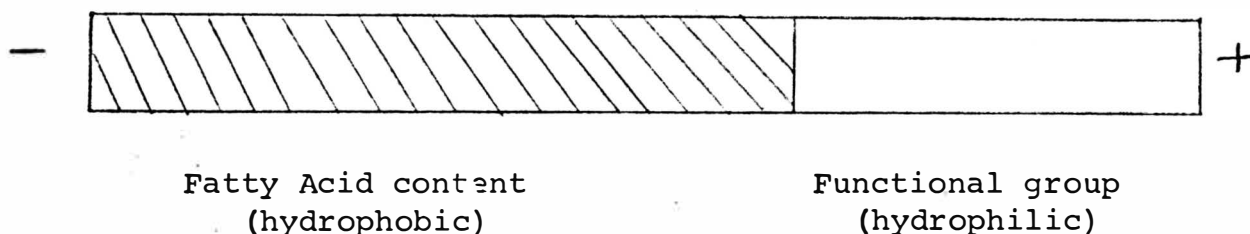


Figure 1 (Schematic representation of fatty acid soaps)¹⁰

The best results have shown in the past lab studies that a flotation aid consists of predominantly unsaturated fatty acids soaps with a ten to twenty percent long-chain saturated fatty acid soap.¹¹ According to G. Beckstein, "fatty acids mixtures can contain up to forty percent linoleic acid without significantly reducing the effectiveness compared to oleic acid."¹² Certain studies also reveal that upon exceeding optimum concentration, a loss in effectiveness is encountered.

Chemically speaking, these soaps are dispersed in spherical clusters called micelles, each of which may contain hundreds of soap molecules. Each soap molecule has a polar end--- COO^-Na^+ ---and a non-polar end---the twelve to eighteen carbon chain. Since the soaps have the two different characteristics, they are said to be amphipathics--a polar and non-polar end, each of which are big enough for each to display its own solubility behavior. In terms of the rule of thumb "like dissolves like", each non-polar end seeks a non-polar environment--the non-polar ends of other soap molecules resulting in the huddling in the center of the micelle. The polar end projects outward into the polar solvent, water. "Negatively charged carboxylate groups stud the surface of the micelle, and it is surrounded by an ionic atmosphere. Repulsion between similar charges keeps the micelles dispersed."¹³

The non-polar ends of soap molecules dissolve in the oil droplet, leaving the carboxylate ends projecting into the surrounding water layer. Repulsion between similar charges keeps the oil droplets from coalescing; a stable emulsion of oil and water forms, and can be removed from the surface.¹⁴

These salts of carboxylate acid are crystalline non-volatile solids made up of positive and negative ions. The strong electrostatic forces holding the ions in the crystal lattice can be

overcome only by heating to a high temperature or by a very polar solvent.¹⁵ These carboxylate acid salts are classified as oleates. Figure 2 represents a froth flotation mode for optimum flotation.

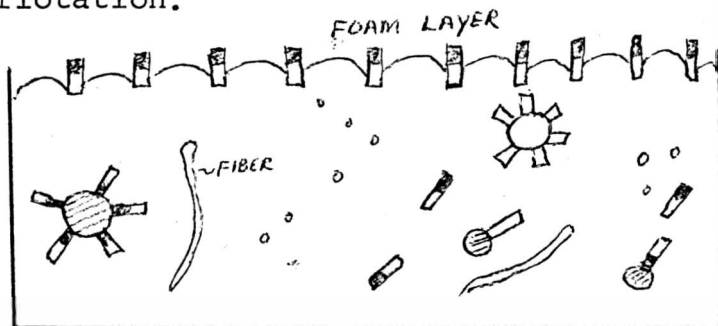


Fig. 2
(Flotation mode of flotation aids)¹⁶

Other important parameters lie in parallel areas of the flotation aids that improve its functional capabilities: consistency, the size of the air bubble, and ink particle size.

The stock consistency is important because the elevation in consistency would show that the transport of the solid particle adhering to air bubbles would slow down to such an extent that they cannot rise to the surface. This theorizes along with Stokes law:

$$f = 6\pi\eta rv$$

where f is the frictional force opposing its motion

η is the viscosity of the suspension

r is the radius of the particle

v is its velocity.

From this law and the fact of increasing viscosity with increasing consistency, velocity of the particle when under a constant

frictional opposing force decreases. A consistency that might be too low would increase the shrinkage--overall fiber and filler losses-- by fiber flotation. An optimum range suggested by flotation experts is .8 to 1.0 percent.

A good flotation bubble must be small and must not join other air bubbles until it gets on top of the slurry.¹⁷ To maintain optimum conditions, "frothers" are utilized. "Frothers" are chemicals that ionize to a very small extent in water. One ion must be hydroxyl (OH)⁻, as bubbles in water have their surface composed in part from these hydroxyl ions.¹⁸ The hydroxyl ions become one of the chemical members of the bubble surface. According to J.W. Jelks, "the carbon hydrogen chain that goes with this hydroxyl ion will follow the bubble and in effect give a 'fuzzy bubble'. This 'fuzz' around the bubble makes it remain a sphere as well as keeping it from uniting with other bubbles until it gets to the top of the slurry."¹⁹ A collector--the oleates--is used to attach itself to the ink and also to the fuzzy portion of the air bubble.

For effective flotation of the particle, the total upward pull of the meniscus on the vertical sides of the particle must balance its apparent weight.²⁰ "Theory shows that the vertical force applied to such a particle is given by $\gamma_{a/w} \cos \theta$ (perimeter of the particle) = $V(dp-dw)g$, where $\gamma_{a/w}$ is the surface tension of the particle; dp and dw are the densities

of the particle and water phase, respectively; g is the gravitational constant; θ is the contact angle of the water phase; V is the volume of the particle."²¹

The relationship between the surface tension of the water phase $\gamma_{a/w}$ and the contact angle θ it makes with the vertical sides of the particle is given by $\gamma_{a/w} \cos \theta = F_{s/a} - F_{s/w}$ where $F_{s/a}$ and $F_{s/w}$ are the Helmholtz free energies of the solid-air and solid-water interfaces, respectively.²² Since the value of $F_{s/a}$ is usually so great for minerals, the value of $\cos \theta$ must also be great, resulting in a small θ . Therefore, pure water would wet the solid mineral particle completely, and flotation would not occur. Consequently, the described flotation aids are added--"collector oils"--which adsorb on the particle surface, reducing $F_{s/a}$ to such an extent that θ increases. Normal cases show a θ value to have a typical minimum requirement of fifty to seventy-five degrees. This may be achieved by as little as five percent surface coverage of the adsorbed "collector oil".

Vanderhoff expressed the maximum size of an ink film for a cylindrical particle of diameter D and height H as:

$$D \times H = \gamma_{a/w} \cos \theta / (dp - dw)g$$

Substituting the following values in the equation:

$$\gamma_{a/w} = 50 \text{ dynes/cm (the minimum value for flotation of } 50^\circ \text{ for } \theta)$$

$(dp-dw) = 0.2 \text{ g/cm}^3$ (corresponding to an ink film density of 1.2)

Therefore, $D \times H = 0.66 \text{ cm}^2$. Jointly he assumes that the height equals the diameter of 0.8 cm.

The following figure represents the diagram of interfacial phenomena:

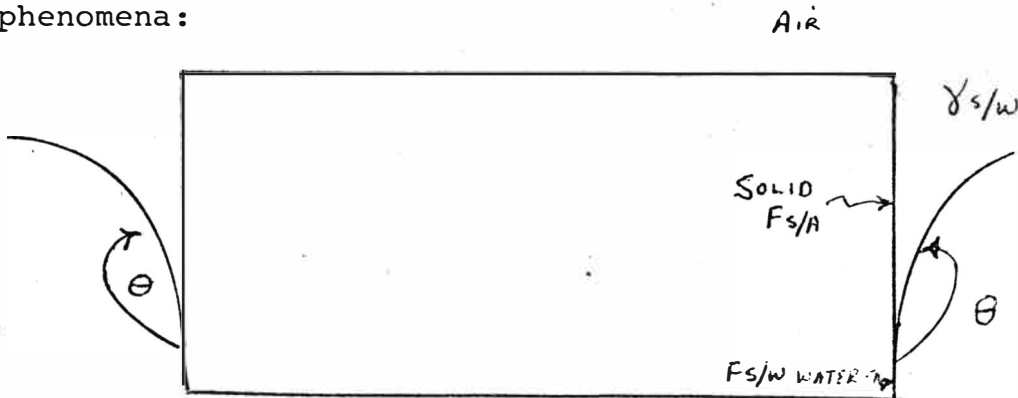


Fig. 3
(Schematic representation of flotation of a cylindrical particle)²⁴

It is these areas that enhance the profitability of flotation secondary recovery. The calcium soaps are not just formed when in contact with the fatty acid. There is a certain alkali demand needed to create the functionalability for calcium soaps. It is the purpose of this report to determine the optimum alkali conditions needed to create the largest quantity of calcium soaps.

Experimental Objective and Design

Since the era of flotation de-inking is relatively new, many characteristic features have not yet been determined. Many parallel areas have been determined using the Langelier Saturation Index--the measurement of conditions to determine the precipitation of Calcium Carbonate, commonly called scale. These conditions are prompted by the elevation of pH. From this theory, it is the objective of this thesis to find an optimum alkali concentration that will pull the maximum calcium ion out of solution for adsorption on the fatty acid.

The alkali adjustments are made with 1.0 normal sodium hydroxide. The calcium content is held at a constant value--range of 180-200 ppm. The oleic acid was selected for the fatty acid group. Dar-Chem 210, manufactured by Darling Chemical Company, was the selected oleic acid. It too was added at a constant volume--two milliliters, which is equivalent to a 833.7 ppm addition rate to the final solution.

Experimental Procedure

Distilled water was used as a base carrier medium at a given constant volume of 2,000 milliliters. Twenty-five milliliters of a given calcium chloride solution was added while the desired amount of alkali was added with 1 normal sodium hydroxide. Two (2) fifty (50) milliliter samples were pipetted from the 2,000 milliliter sample to determine the initial calcium ion content and the initial total alkali. The calcium content was determined by titration with Hercules hardness titrant using a Hercules calcium indicator. The total alkali was determined by titration with .1 normal sulfuric acid and using cresol red (pH range 7.2-8.8) as an indicator. The water was placed in a circulation tube, which was designed by myself, and circulated with a small laboratory centrifugal pump for fifteen minutes. (See Figure I, Appendix A.) Alkali and calcium content were determined after the fifteen minute period.

Procedure for Determination of Calcium in Water

1. Pipette 50 milliliters of sample into a 250 milliliter Erlenmeyer flask.
2. Add one dropper (about 0.5 ml.) of calcium buffer

solution and stir.*

3. Add calcium indicator powder while stirring the sample until color develops. If calcium is present, the solution will turn pink or red.
4. Titrate immediately with 0.02 normal hardness titrating solution (EDTA) with stirring. The color change will be from red to blue. The end point is taken when the last trace of reddish color disappears.
5. Calculate and record the results as calcium hardness (mg/liter CaCO_3).

milliliters titration $\times 20 = \text{mg/l hardness}$

*(Note: The buffer solution incorporates materials which prevent interference by heavy metals and magnesium.)

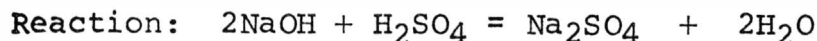
Procedure for Total Alkali Determination

1. Pipette fifty (50) milliliters of sample into a 250 milliliter Erlenmeyer flask.
2. Add 8-10 drops of cresol red indicator; a blue to purple color indicates the presence of alkali--the appearance of a yellow color indicates the absence of alkali.
3. Titrate with 0.1 normal sulfuric acid (H_2SO_4) to a straw yellow end-point.

4. Calculate and record the results as pounds of alkali per one hundred gallons (#/100 gal.).

$$\begin{aligned} (\#/100 \text{ gal.}) &= 0.1 (\text{norm. H}_2\text{SO}_4) \times 40 (\text{equiv. wt. NaOH}) \times \text{ml.'s H}_2\text{SO}_4 \times 0.834 / \\ &\quad 50 \text{ cc (sample size)} \end{aligned}$$

$$= .06675 \times \text{ml.'s .1 N H}_2\text{SO}_4$$



Procedure for Operation of Circulation Tube

1. Place 2,000 milliliters of distilled water in a 4,000 milliliter beaker. (Note: Distilled water has a hardness of 0.00 ppm.)
2. Add 25 milliliters of calcium chloride solution (Note: 10 grams of Dow-Flake--80% calcium chloride--per 1,000 milliliters of water)
3. Add various concentrations of 1 normal sodium hydroxide.
4. Withdraw two (2) fifty (50) milliliter samples and place in 250 milliliter Erlenmeyer flasks for titration of initial calcium and alkali concentrations.
5. Place the remainder of the sample in the circulation tube.
6. Turn on the centrifugal pump.
7. Open the air valve.

8. Place two (2) milliliters of oleic acid (Dar-Chem 210) by pipette into the air valve.
9. Run the centrifugal pump for fifteen (15) minutes to insure the fatty acid emulsifies completely.
10. Shut the air valve.
11. Turn the pump off.
12. Withdraw 150 milliliters of sample from the circulation tube after the 15 minute period from the top outlet.
13. Titrate two (2) fifty (50) milliliter samples for final total alkali and calcium concentrations.
14. Record:
 - (a) Total alkali applied (#/100 gal.)
 - (b) Final alkali (#/100 gal.)
 - (c) Consumed alkali (#/100 gal.)
 - (d) Natural log (ln) alkali applied
 - (e) Total initial calcium concentration (ppm)
 - (f) Total final calcium concentration (ppm)
 - (g) Calcium consumed (ppm)
 - (h) Ratio of oleic acid applied (ppm) to the calcium consumed (ppm)
 - (i) ln of step (h)
 - (j) Percent calcium consumed
 - (k) Percent alkali consumed

Discussion of Data

The data is tabulated in Tables I, II, III, IV in Appendix B. The Data was collected by randomly changing the alkali concentration so that there was no biased testing results. Tables I and II represent that portion of the data that correlates with calcium adsorption and alkali consumption, respectively. The data is listed in the order that the samples were tested; therefore, each line number in Table I has a comparative line number in Table II. Table III is a collection of randomly selected data from Tables I and II so that positive trends could be identified. Table IV is a collection of data that represents adsorption characteristics at 130° F. From this data, the corresponding graphs were drawn.

Discussion of Graphs

Figures 2 through 8, Appendix A, represent the randomly collected data in graphical form. The tabulated data was plotted showing the effect alkali has on the adsorption of calcium ions onto the oleic acid. All other variables were kept constant--temperature, Ca^{++} ion content, and oleic acid strength.

Figure 2 represents the adsorption of calcium ions onto the oleic acid with just a small change in alkali concentration. It appears to have similar characteristics to the Freudlich and Langmuir isotherms--each are exponential functions representing monolayer adsorption.

Figure 3 represents the effect of percent calcium ion adsorbed with a changing alkali concentration. It is a carry-over of Figure 2 in that it shows the fraction of calcium adsorbed to that which was applied.

Figure 4 represents the change in the ratio of the concentration of oleic acid applied (833.7 ppm) to that of calcium ion adsorbed by changing the applied alkali concentration. All other variables were kept constant.

Figure 5 represents the natural log functions of Figure 4. Since Figure 4 represents an assymtote type curve, the linear relationship in Figure 5 was expected to be two linear

intersecting at a maximum adsorption.

Figure 6 represents the relationship between the amount of alkali consumed when adsorption takes place and the alkali application is changed.

Figure 7 represents the relationship between the percent calcium ion adsorbed with the percent alkali consumed.

Figure 8 represents the relationship between the calcium ion adsorbed with the actual alkali consumed. It has a linear relationship.

Discussion of Results

The experimental work shows that sodium hydroxide has a direct relationship in the formation of calcium soaps. Figure 2, Appendix A, relates the concept of an exponential increase in calcium adsorption to a peaking concentration of approximately 130 ppm at a maximum alkali addition of .3#/100 gal. (360 ppm) of which only a certain percentage of alkali was actually consumed. Figure 6, Appendix A, is a good example of the alkali rate of consumption. The efficiency of the sodium ion is seen to increase at a level less than .4#/100 gal. (480 ppm) and within an optimum range of .1-.2#/100 gal. (120-240 ppm). This relates to the application of alkali to the adsorption of the calcium ions in Figure 8, Appendix A, expressing a relationship with a linear line with a slope of 989.3 and an intercept of 19.4 ppm. This identifies the estimated concentration of alkali needed to force the adsorption of calcium ions into calcium soaps. When the linear slope-intercept equation ($y = mx + b$) is used, the value of the maximum alkali demand for adsorption of 200 ppm calcium ion can be determined as .1825#/100 gal. (219 ppm). According to Figure 5, Appendix A, the adsorption phenomena creates a double linear line intersecting at the optimum conditional point when the natural log is taken on the data plotted in Figure 4, Appendix A. By visual inspection of the inter-

section, the optimum range for efficient adsorption is between -1.7 and -1.6. These values correlate to .1827#/100 gal. (219.2 ppm) and .2019#/100 gal. (242 ppm) respectively. Consequently, the optimum alkali addition would fall within these limits. Similar results are then compared to the calculated concentration of .1825#/100 gal. (219 ppm) obtained previously. It appears from these two lines on Figure 5, Appendix A, the optimum condition for calcium soap formation would fall between those two factors (.1825-.2019#/100 gal.).

Further strengthening evidence of this correlation is the fact that the thickest calcium soap layer was produced in the region of .18 to .22#/100 gal. (216-264 ppm) applied alkali. Beyond that region, a flat, oily substance floated in the circulation tube (Figure 1, Appendix A). This interprets Figure 5, Appendix A, explaining the portion of the curve beyond the minimum peak; where higher alkali concentrations were applied, fewer calcium soaps were being formed.

Table III, Appendix B, shows the direct relationship between the actual alkali consumption with calcium ion adsorption. Table III is composed of randomly selected data points from Tables I and II. It appears to be conclusive that a close relationship exists between the amount of alkali consumed and the amount of calcium ion being adsorbed onto the oleic acid. From this data, the mean of the ratio of the

alkali consumption to the calcium ion adsorbed becomes 1.016 with a standard deviation of 0.158. Table III also shows a trend of calcium ions increasing their adsorption with increasing concentrations of applied alkali. Although the alkali concentration applied in a range of .03#/100 gal. (36 ppm) to .8338#/100 gal. (1,000 ppm), the calcium ion was adsorbed onto oleic acid to the degree of the alkali consumption--the more alkali consumed allowed more calcium ions to adsorb onto oleic acid.

Since the calcium ion adsorption is limited to the consumption of the alkali, the adsorption rate of calcium ions onto oleic acid becomes a function of the applied alkali concentration.

Figure 2, Appendix A, concurs the limited adsorption rate of calcium ions onto oleic acid by showing the rapid increase of adsorption with low alkali concentrations until the maximum point is reached (.18#/100 gal.); consequently, it tends to slow down to a constant adsorption rate.

Table IV, Appendix B, expresses a relationship between the alkali applied and the adsorbed calcium ion at 130° F. The ratio of alkali consumed to the calcium ion adsorbed is slightly lower than the ratio calculated for the data in Table III, Appendix B. The ratio was approximately .97 with a standard deviation of 0.1. The ratio range for the 130° F adsorption

is comparable to the 80° F adsorption ratio--(.87-1.07) compared to (.86-1.17) respectively. Since the data in Figure 4 Appendix A, is a fraction of what data is needed for accurate analysis, the data points were not included in any of the graphs. However, an approximated slope and intercept were calculated using this data; 817.0 and 45.5 respectively. When the maximum dosage rate at 130° F was calculated for maximum adsorption, it was found to be .189#/100 gal. (226.8 ppm) compared to the .183#/100 gal. (219.6 ppm) for the 80° F adsorption curve. From these figures, it is apparent that the same alkali demand is necessary for each temperature. The important factor is that they have different y-intercepts and slightly different slopes, which indicates a shift of the curve to a higher level and not quite parallel to the 80° F adsorption curve represented in Figure 8, Appendix A.

Since the calcium ion content was kept constant, Figure 7, Appendix A, shows that as the percent alkali consumed decreases, the percent calcium ion adsorbed remains relatively constant at a mean of 73.0% level with a standard deviation of 7.90%. The relative scatter has increased the error factors.

Experimental Error

Since the circulation time of the solution was only five minutes, the infinite adsorption point was not reached. Consequently, a great deal of scatter was seen in the plotted data points. Reproducible data was not investigated because of the lack of laboratory time, but individual random tests were conducted at narrow differing concentrations to eliminate any bias testing. The calcium soaps are tacky substances that adhere to plastic. Cleaning the circulation tube was mandatory, but complete cleaning became impossible. Consequently, some residual calcium soaps could have carried over into the subsequent tests. It is believed that this did not affect the over-all accuracy. The titrations were done with appropriate testing techniques to eliminate any added error. Over-all, the experimental procedures were outlined to eliminate the noticeable error.

Conclusions

From the collected data, it has become known that the calcium ion depends on the sodium ion for adsorption onto oleic acid. There exists a 1:1 ratio between the amount of alkali consumed and the amount of calcium adsorbed onto oleic acid. There also is evidence that this ratio is a linear relationship that will allow a maximum theoretical adsorption of 200 ppm calcium ion onto oleic acid by applying .18#/100 gal. of alkali. Evidence also shows that the adsorption of calcium ions onto oleic acid increases slightly when increasing the reaction temperature to 130° F. The figures in Appendix A concur the theoretical assumptions of monolayer adsorption presented by Freudlich and Langmuir. Finally, calcium ions adsorb onto oleic acid only when influenced by alkali presence; otherwise, no apparent loss of calcium ions is noticed.

Appendix A

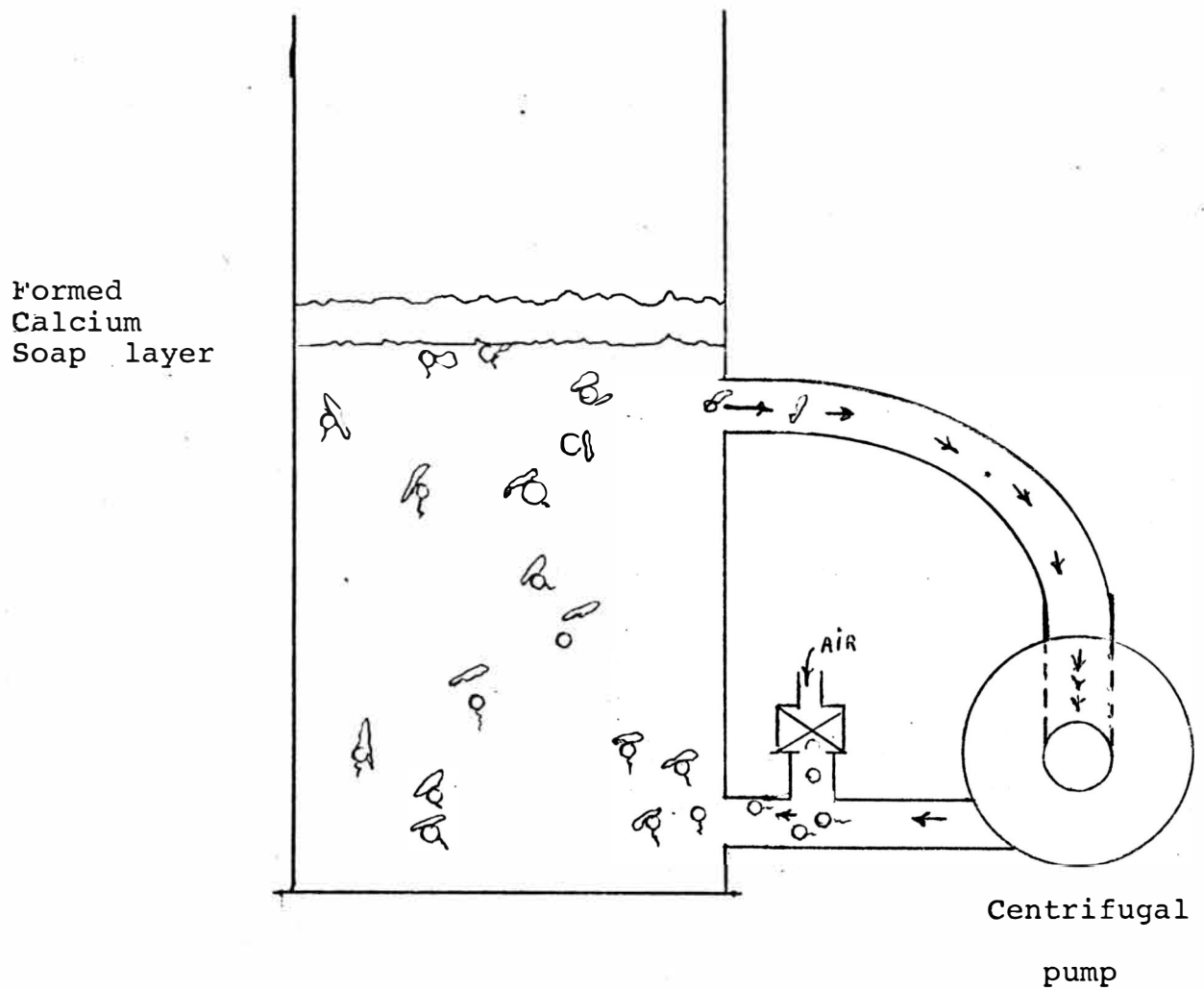


Figure 1
Circulation Tube

Figure 2
Calcium Ion Adsorbed
Vs.
Concentration of Alkali

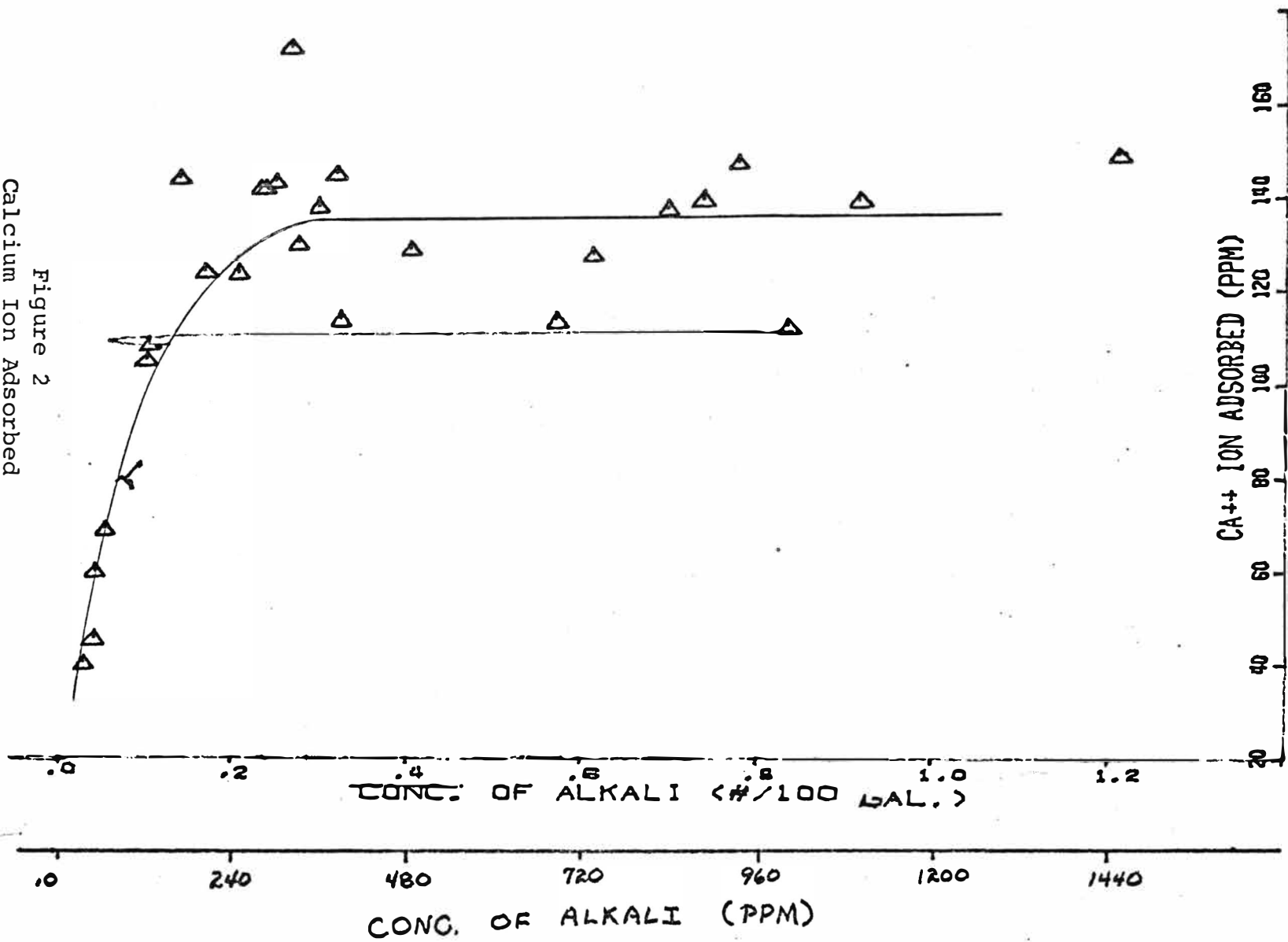
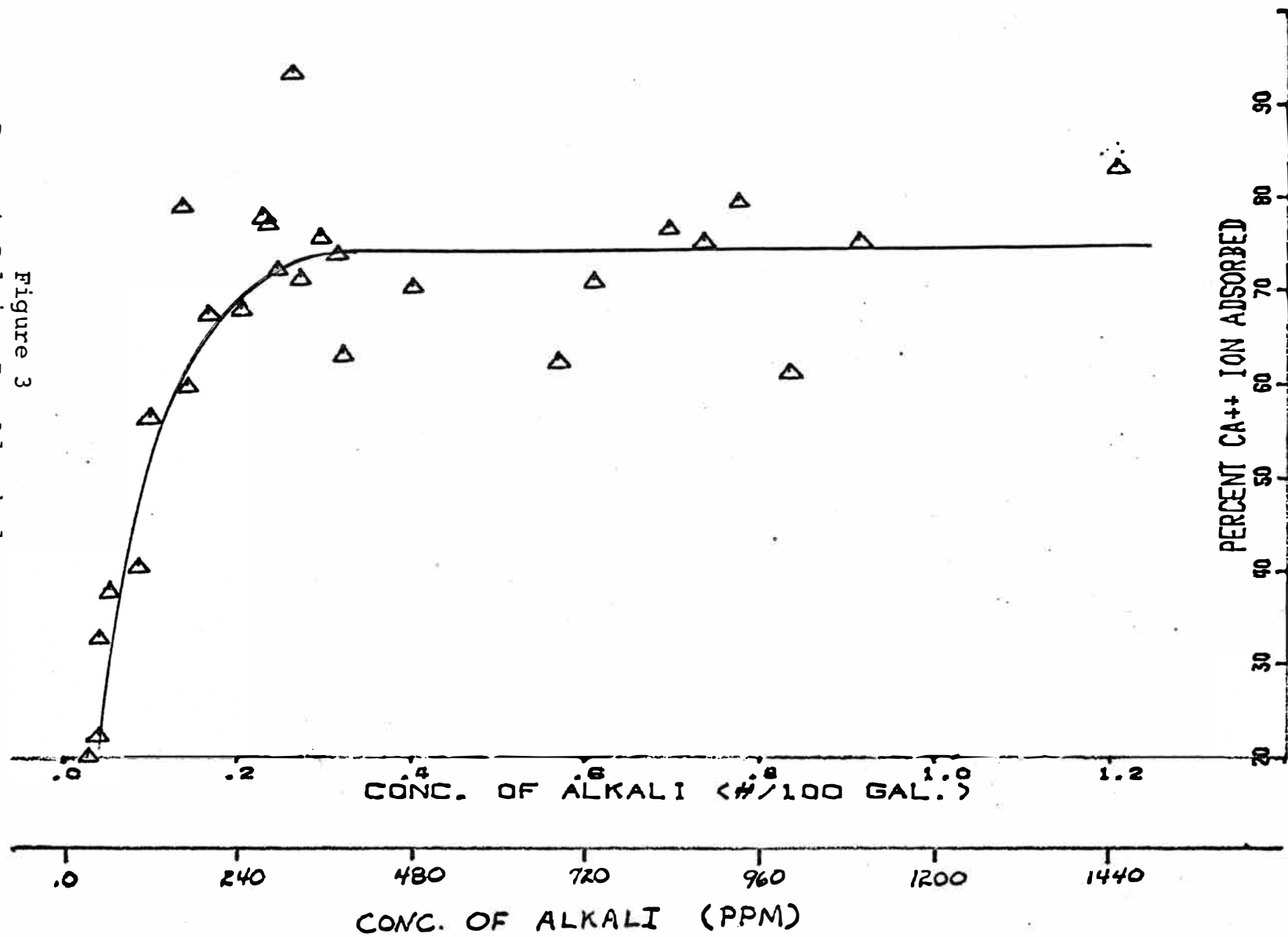
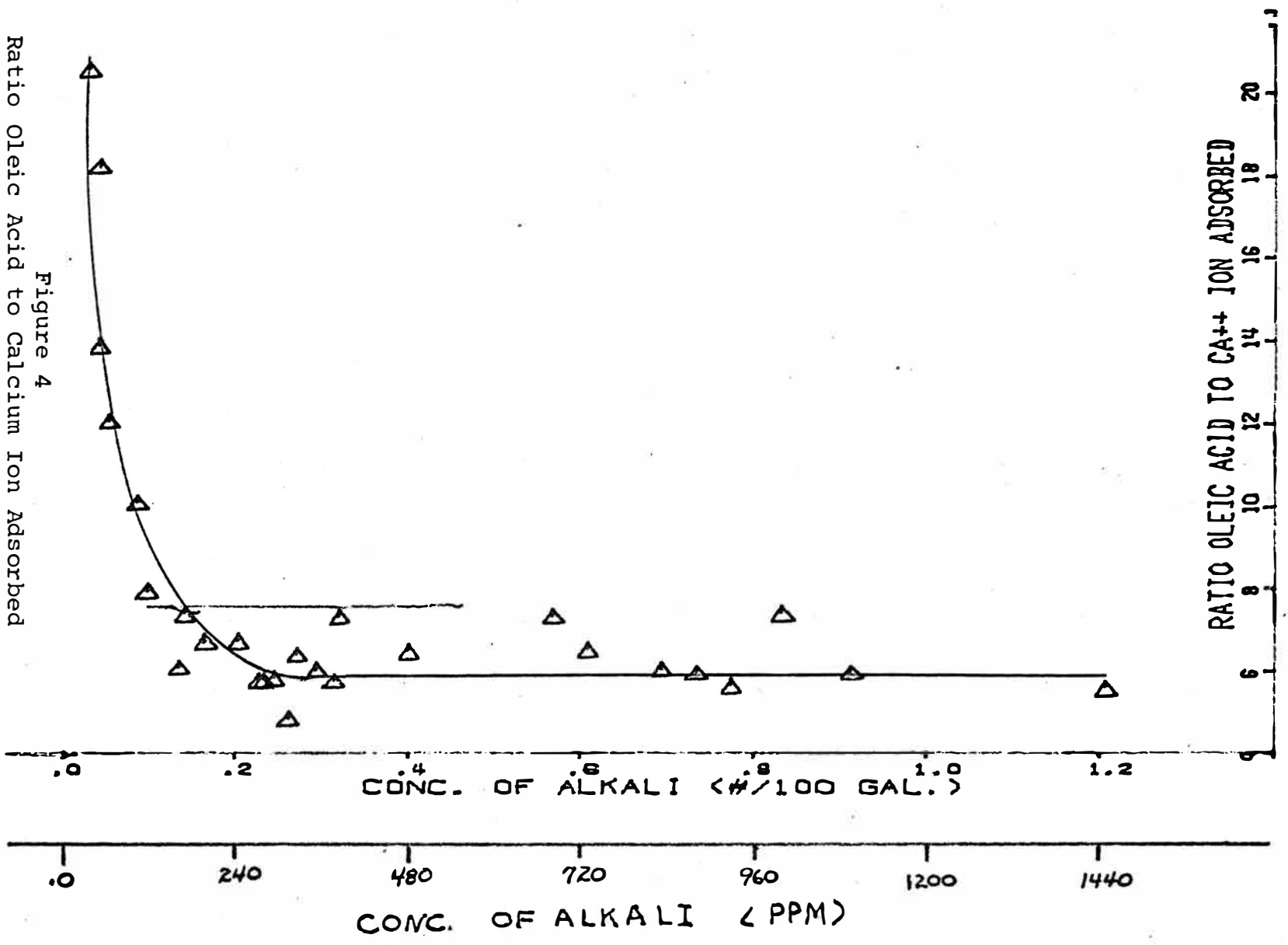


Figure 3
Percent Calcium Ion Adsorbed
Vs.
Concentration of Alkali





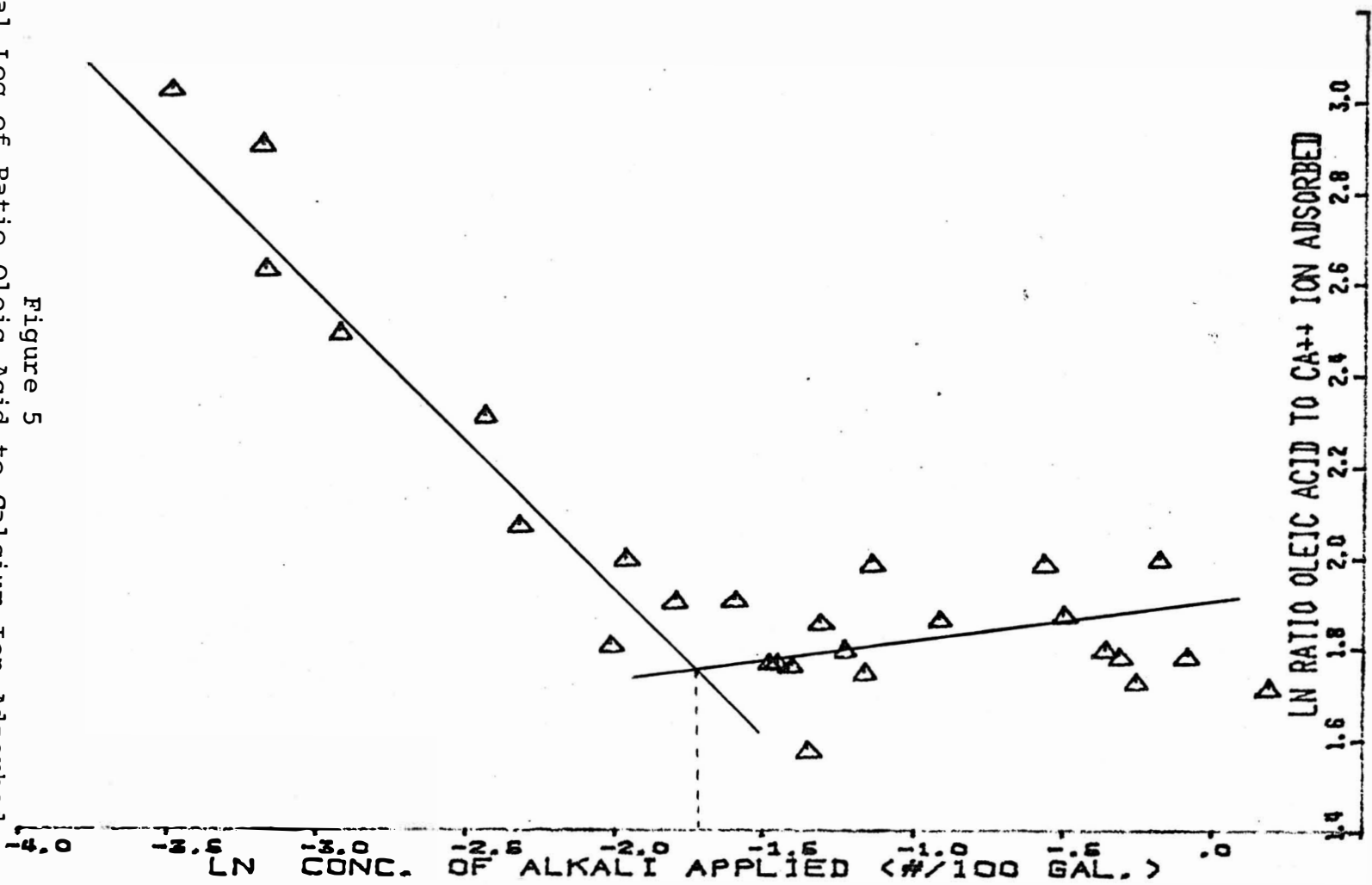
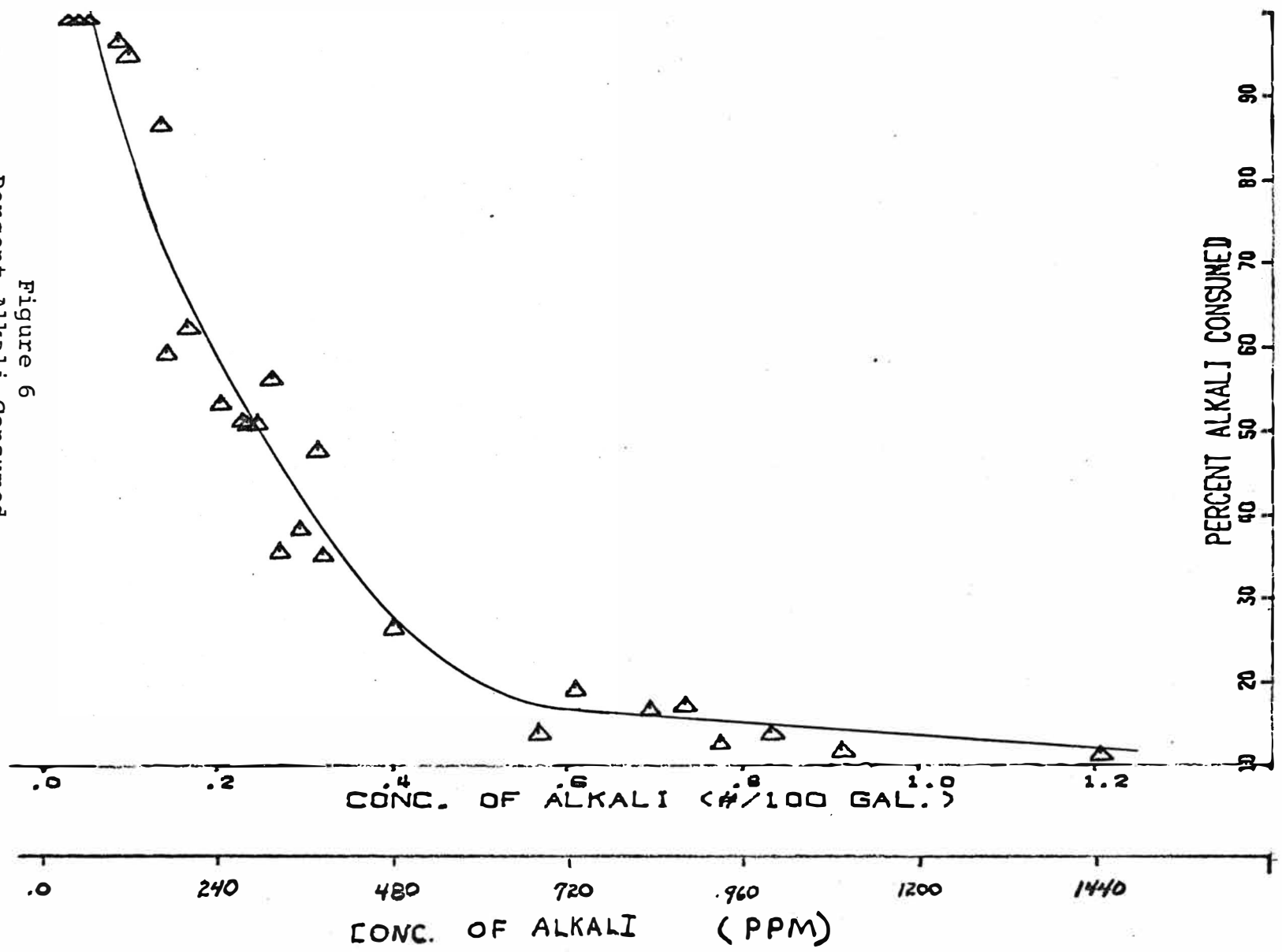


Figure 5
Natural Log of Ratio Oleic Acid to Calcium Ion Adsorbed
Vs.
The Natural Log of Concentration of Alkali

Figure 6
Percent Alkali Consumed
Vs.
Concentration of Alkali



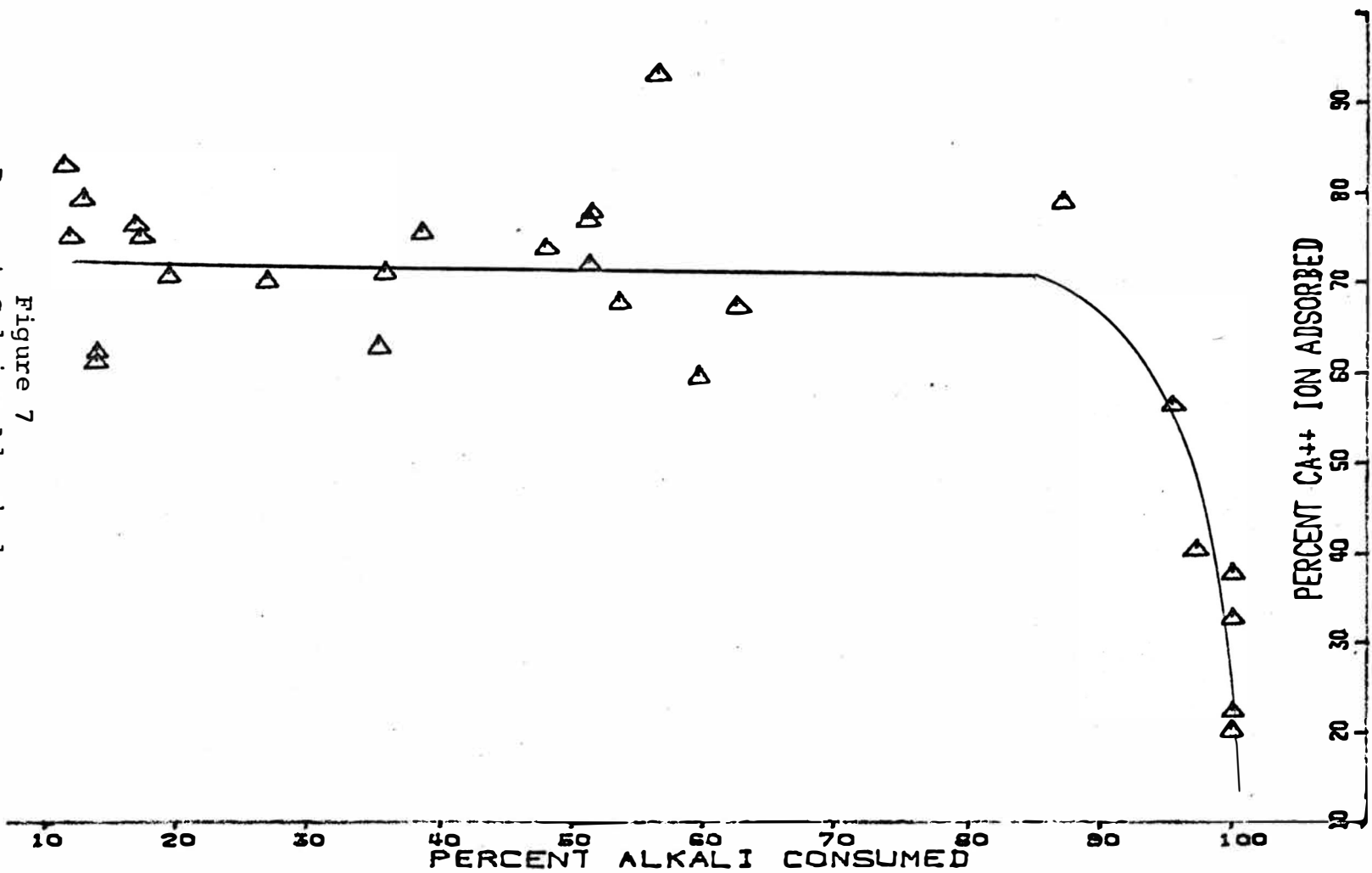
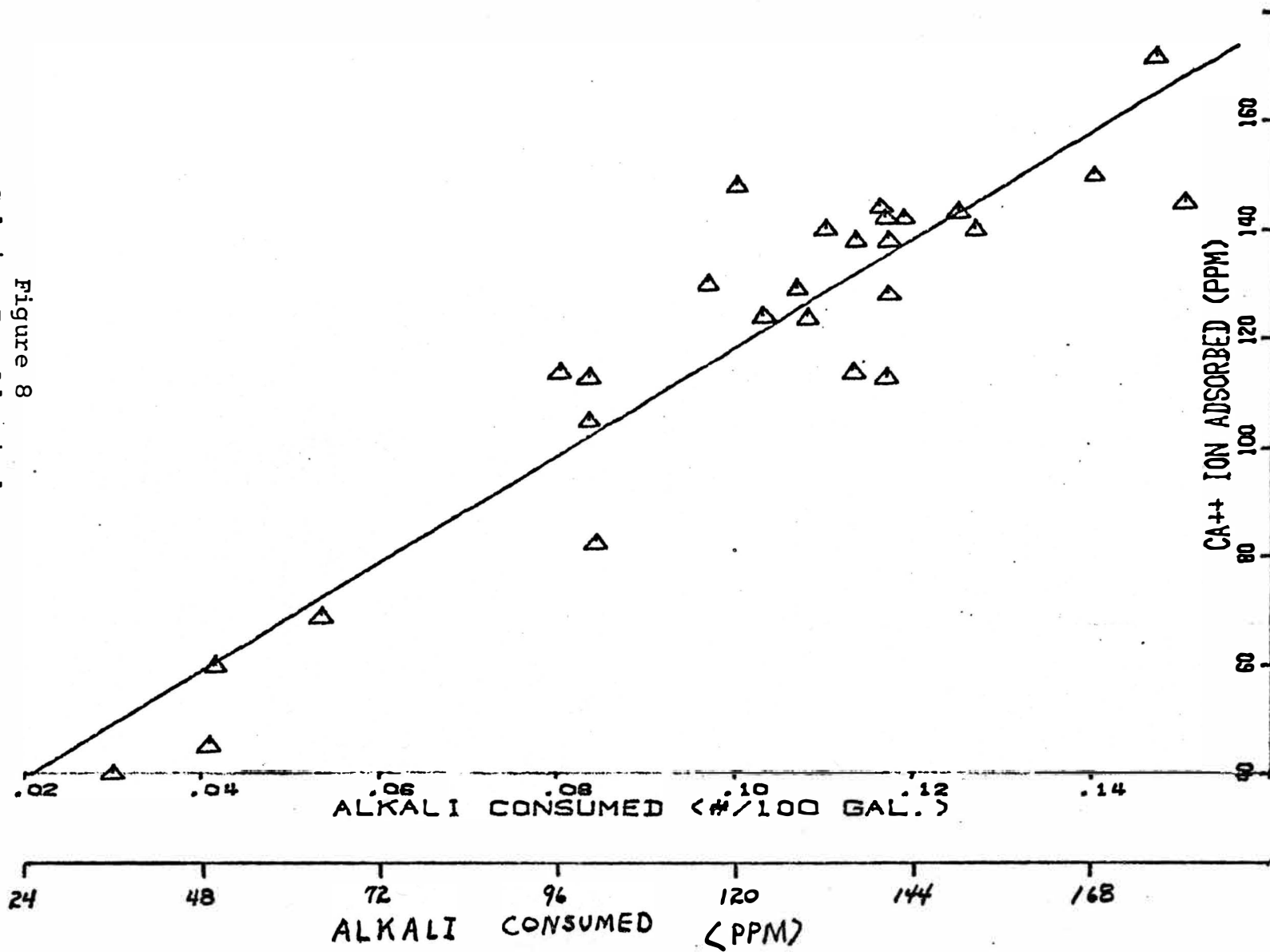


Figure 7
Percent Calcium Adsorbed
Vs.
Percent Alkali Consumed

Figure 8
Calcium Ion Adsorbed
Vs.
Alkali Consumed



APPENDIX B

Table I
Calcium Data Table

Sample No.	Alkali Applied (#/100 Gal.) (X)	Ca ⁺⁺ Ion Applied (ppm) (B)	Ca ⁺⁺ Ion Remain (ppm)	Ca ⁺⁺ Ion Adsorbed (ppm) (A)	(Y)**	ln (Y)	(A/B)***
1	.140	189	76	113	7.378	1.998	59.8
2	.0867	204	121.4	82.6	10.093	2.312	40.5
3	.0407	201.6	156	45.6	18.280	2.906	22.6
4	.2435	198.2	55	143.2	5.820	1.762	72.3
5	.3135	196.0	51.0	145	5.750	1.749	74.0
6	.0300	198.0	157.6	40.4	20.636	3.027	20.4
7	.8338	184.0	71.0	113	7.378	1.998	61.4
8	.2014	182.0	58.2	123.8	6.734	1.907	68.0
9	.2268	182.0	40.0	142	5.781	1.770	78.0
10	.2321	184.0	42.0	142	5.781	1.770	77.2
11	.0534	182.0	113.0	69.0	12.083	2.492	37.9
12	.0975	186.0	81.0	105	7.940	2.072	56.5
13	.1334	182.0	38.0	144	6.103	1.809	79.1
14	.1647	184.0	60.0	124	6.723	1.906	67.4
15	.0414	182.0	122.0	60.0	13.895	2.632	32.9
16	.2601	184.0	12.0	172.0	4.847	1.578	93.5
17	.2701	182.0	52.0	130	6.413	1.858	71.4
18	.2935	182.0	44.0	138	6.041	1.799	75.8
19	.3200	180.0	66.0	114	7.313	1.990	63.3
20	.4002	183.0	54.0	129	6.463	1.866	70.5
21	.5670	182.0	68.0	114	7.313	1.990	62.6
22	.7337	186.0	46.0	140	5.955	1.784	75.3
23	.7740	186.0	38.0	148	5.630	1.729	79.6
24	.9140	186.0	46.0	140	5.950	1.784	75.3
25	.6940	180.0	42.0	138	6.040	1.798	76.7
26	.6070	180.0	52.0	128	6.510	1.874	71.1
27	1.2070	180.0	30.0	150	5.558	1.715	83.3

**Note: (Y) = ratio of oleic acid to calcium ion adsorbed

***Note: (A/B) = % calcium adsorbed per applied calcium

APPENDIX B

Table II
Alkali Data Table

Sample No.	Alkali Applied (#/100 Gal.) (X)	Alkali Unused (#/100 Gal.)	Alkali Consumed (#/100 Gal.)	Percent Alkali Consumed	ln (X)
1	.140	.0567	.0833	59.5	-1.966
2	.0867	.0025	.0842	97.1	-2.445
3	.0407	.0000	.0407	100	-3.202
4	.2435	.1187	.1248	51.3	-1.413
5	.3135	.1632	.1503	48.0	-1.160
6	.0300	.0000	.0300	100	-3.506
7	.8338	.7170	.1168	14.0	-.1819
8	.2014	.0934	.1080	53.6	-1.602
9	.2268	.1101	.1167	51.5	-1.484
10	.2321	.1134	.1187	51.2	-1.461
11	.0534	.0000	.0534	100	-2.931
12	.0975	.0140	.0835	95.4	-2.328
13	.1334	.0173	.1161	87.0	-2.014
14	.1647	.0616	.1031	62.6	-1.803
15	.0414	.0000	.0414	100	-3.186
16	.2601	.1131	.1470	56.5	-1.347
17	.2701	.1734	.0967	35.8	-1.309
18	.2935	.1801	.1134	38.6	-1.226
19	.3200	.2068	.1132	35.4	-1.139
20	.4002	.2935	.1068	26.7	-.9157
21	.5670	.4869	.0801	14.1	-.5675
22	.7337	.6070	.1267	17.3	-.3097
23	.7740	.6740	.1000	12.9	-.2560
24	.9140	.8040	.1100	12.0	-.0902
25	.6940	.5770	.1170	16.9	-.3650
26	.6070	.4800	.1170	19.3	-.5000
27	1.2070	1.067	.140	11.6	+.1880

APPENDIX B

Table III
Alkali Demand for Calcium Adsorption at 80°F

Alkali Applied		Alkali Consumed		Calcium	Ratio Alkali
<u>(#/100 Gal.)</u>	<u>(PPM)</u>	<u>(#/100 Gal.)</u>	<u>(PPM)</u>	<u>Adsorbed</u>	<u>Consumed to</u>
				<u>(PPM)</u>	<u>Ca++ Adsorbed</u>
.0300	36	.0300	36	40.4	.891
.0414	49.7	.0414	49.7	60.4	.823
.0534	64	.0534	64	69.0	.929
.0867	104	.0842	101	82.6	1.220
.0975	117	.0835	100.2	105	.954
.2268	272	.1167	140	142	.986
.3200	384	.1132	135.8	114	1.190
.7337	880	.1267	142	140	1.086
.7740	928	.1000	120	148	.811
.8338	1000	.1168	140	113	1.240

APPENDIX B

Table IV
Alkali Demand for Calcium Adsorption at 130⁰F

Alkali Applied		Alkali Consumed		Calcium	Ratio Alkali
(#/100 Gal.)	(PPM)	(#/100 Gal.)	(PPM)	Adsorbed	Consumed to
				(PPM)	Ca++ Adsorbed
.0667	80	.0660	79	74	1.070
.0800	96	.0700	84	101	.832
.2065	248	.1040	125	133	.938
.2403	288	.1184	142	147	.966
.3140	377	.1272	153	144	1.070

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