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A STUDY OF THE EQUILIBRIA BETWEEN BENTONITE AND THE VARIOUS REPLACING AGENTS IN ALCOHOLIC AND WATER SOLUTIONS

A Thesis

Presented to

The Committee on Graduate Work

Utah State Agricultural College

In partial Fulfillment

of the requirements for the Degree

Master of science in the school of

Agriculture

Department of Agronomy and

Soils

By

Joel E. Fletcher

May 1937

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The Author Wishes to Express

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A Study of the Equilibria between Bentonite and the Various Replacing Agents in Alcoholic and Water Solutions

J. E. Fletcher

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Investigators in soils have long recognized the importance of the colloidal fraction of soil, and also the almost inseparable problem of replaceable bases. It is generally accepted that the replaceable base fraction of a colloid controls to a large degree the physical properties exhibited by it. Volumes of work have been written on the problem of controlling the reactions of this fraction and on studies of the properties exhibited by it when it is saturated with various cations. Each worker has proceeded in his own individual way or followed the example set by some previous worker with specific modifications.

The chief methods of determining what cations are in the colloid may be briefly classified as follows: leaching with a salt solution, electrodialysis by the cell method, electrodialysis by the funnel method, migration method, titration method, and electrofilteration. These methods are followed up by numerous methods of analysis for each particular cation. In the outlining of these methods by their authors, they gave few data concerning the reasons for the use of each method except its ease of analysis.

Very little work has been carried on systematically to determine the equilibria between various cations and the colloids. Vanselow (1) investigated the equilibria of Na-K, NH_4-Ca, and found noted histeresis which he attributed to the crystaline structure of the colloid. However, he gave no results where in the equilibria were carried out in any solutions other than water, or where any sparingly soluble salts were present to alter the natural results.

Numerous authors have given some data on replacing power and absolute velocity of the cations and the colloids, and a few have compared the two. For example, Wilson (3) has given the replacing power of a few cations as: $K > Ca > Na$ and Wheeting (2) has given the absolute velocities as: $H > NH_4 > K > Ca > Mg > Na$. On comparison, these two prove to be in the same order.

Magistad and Burgess (4): Fieger, Gray and Reed (12): Wheeting (2): Godlin (5): Bray and Willhite (6): Aiyar (7): Puri (8): Solgado (9): Kelley and Chapman (10): Peterson (11): and others have given a good introduction to equilibria studies by their investigations of the ions in their final state. Few papers have been published giving the effects of using a number of cations on the same sample to test other than qualitatively the equilibria

The author has undertaken to find a few quantitative relations in both alcoholic and water solutions by the following methods: Samples of bentonite

--bentonite was chosen in this study because it was the most available material high in replacement bases--were taken and saturated with various cations after the method suggested by Peterson (11). From these samples two 15 gm portions of calcium saturated, sodium saturated and potassium saturated bentonite were chosen and placed in 500 cc. flat bottom flasks. To each was added a measured volume of solution of the replacing agent. The mixture was shaken periodically throughout the day and then allowed to settle over night. The supernatent liquid was then syphoned off and analyzed, and the operation repeated. Not measuring the volume syphoned off makes the individual syphonings slightly variable, but it does not alter the accuracy of the final result. Using repeated treatments in the flasks enables one to find how fast each cation is being replaced by each other cation. The following salts and concentrations were used to get quantitative results: NaCl 0.1N,* 0.5N, 0.1N in 50% and 95% alcohol, KCl, 0.1N, 0.5N, 0.1N in 50% alcohol, $CaCl_2$; 0.1N, 0.1N in 50% and 95% alcohol, Cu $(NO_3)_2$, 0.1N in H_2O, 50% alcohol and 95% alcohol and, NH_4Ac; 1N 0.1N and 0.5N, in H_2O and 0.1N in 50% and 95% alcohol. In making the solutions used for replacing, the author used Bakers C.P. Analyzed reagents throughout and in the case of ammonium acetate, both neutralized and unneutralized salts were used. The analysis for the individual cations was carried out briefly as follows: calcium by the gravimetric ammonium oxalate method, potassium by the butyl alcohol perchlorate method, and sodium by the zinc uranyl acetate method recommended by Barber and Kolthoff (13) modified by Williams (14). Alcoholic solutions were mixed to 50% and 95% by means of their specific gravity.

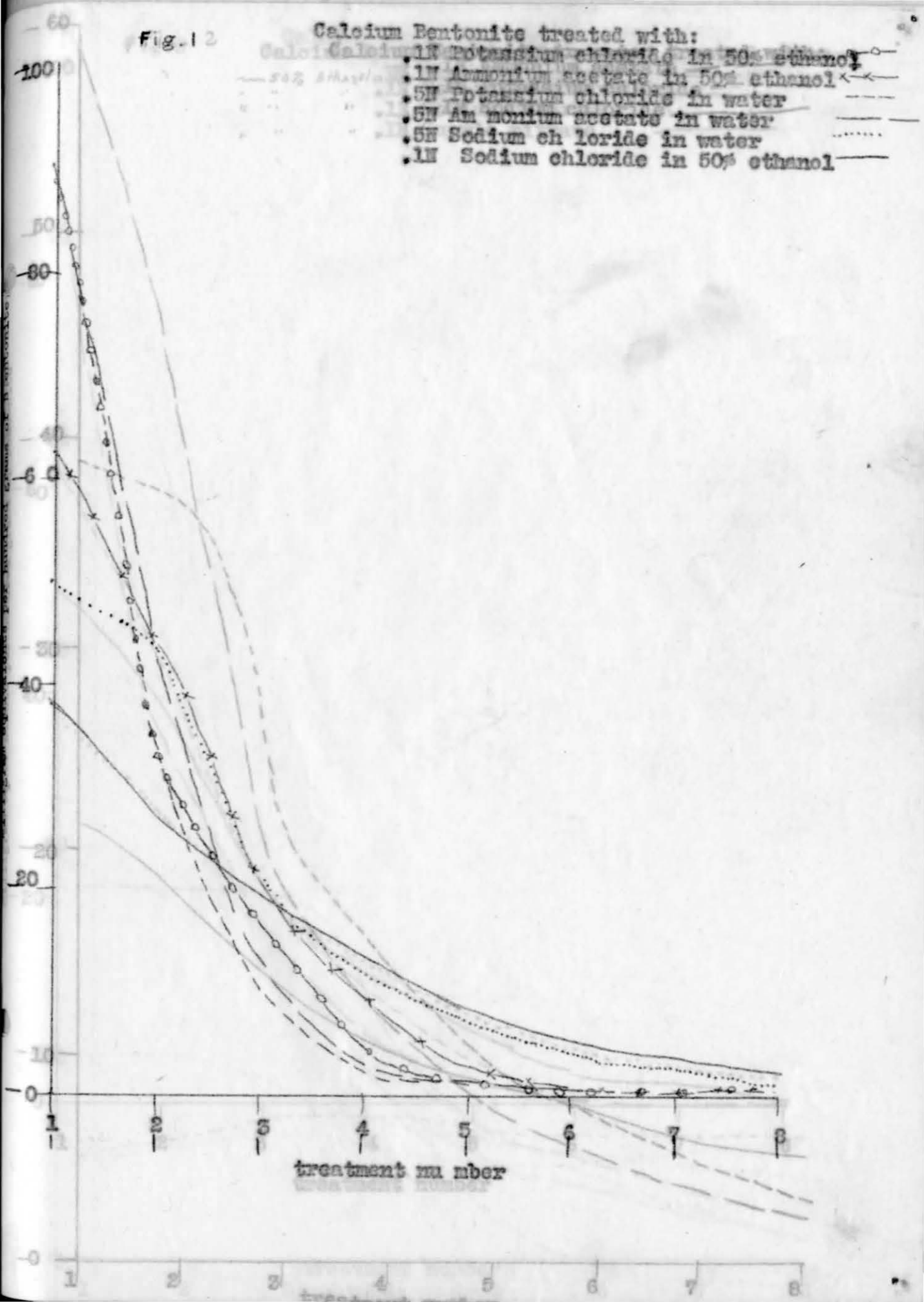
It was found that in water, the replacing ~~order~~ power of the cations used were: on calcium bentonite; $NH_4 > K > Na$, on potassium bentonite; $NH_4 > Ca > Cu > Na$, and on sodium bentonite; $K > NH_4 > Ca > Cu$. In 50% alcohol they were: on a calcium bentonite; $K > NH_4 > Cu > Na$; on potassium bentonite; $NH_4 > Cu > Ca > Na$; and on sodium bentonite; $K > NH_4 > Cu > Ca$. In 95% alcohol they were: on calcium bentonite; $K > Cu > NH_4 > Na$, on potassium bentonite; $Cu > NH_4 > Na > Ca$; on sodium bentonite; $K > Cu > NH_4 > Ca$. Some of these relationships are shown quantitatively by Figs. 1 - 10.

Fig. 1 was made by taking the total solution syphoned off from one treatment of 150 cc. and finding the milligram equivalents of calcium it contains and plotting this value against the treatment numbers. For example, 15 gm. of calcium bentonite is placed in a flask and 150 cc. of salt solution is added. This is shaken periodically throughout the day and allowed to stand over night. In the morning, the supernatent liquid is syphoned off and analyzed. This is called one treatment and the number of milligram equivalents of calcium found in it is plotted against the treatment number which in this case is one.

The figure shows a comparison of three salts (ammonium acetate, sodium chloride and potassium chloride) in 0.1N solution of 50% alcohol with three salts (ammonium acetate, potassium chloride, and sodium chloride) in 0.5N solution of water. It will be observed that the curves for the 0.1N KCl in alcohol and the 0.5N KCl or 0.5N NH_4 Ac in water lie almost directly over

* Unless otherwise stated salts are in water solution.

Fig. 12


Calcium Bentonite treated with:
.1N Potassium chloride in 50% ethanol
.1N Ammonium acetate in 50% ethanol
.5N Potassium chloride in water
.5N Am monium acetate in water
.5N Sodium ch loride in water
.1N Sodium chloride in 50% ethanol
100
80
60
40
20
0
1
2
3
4
5
6
7
8
treatment nu mber

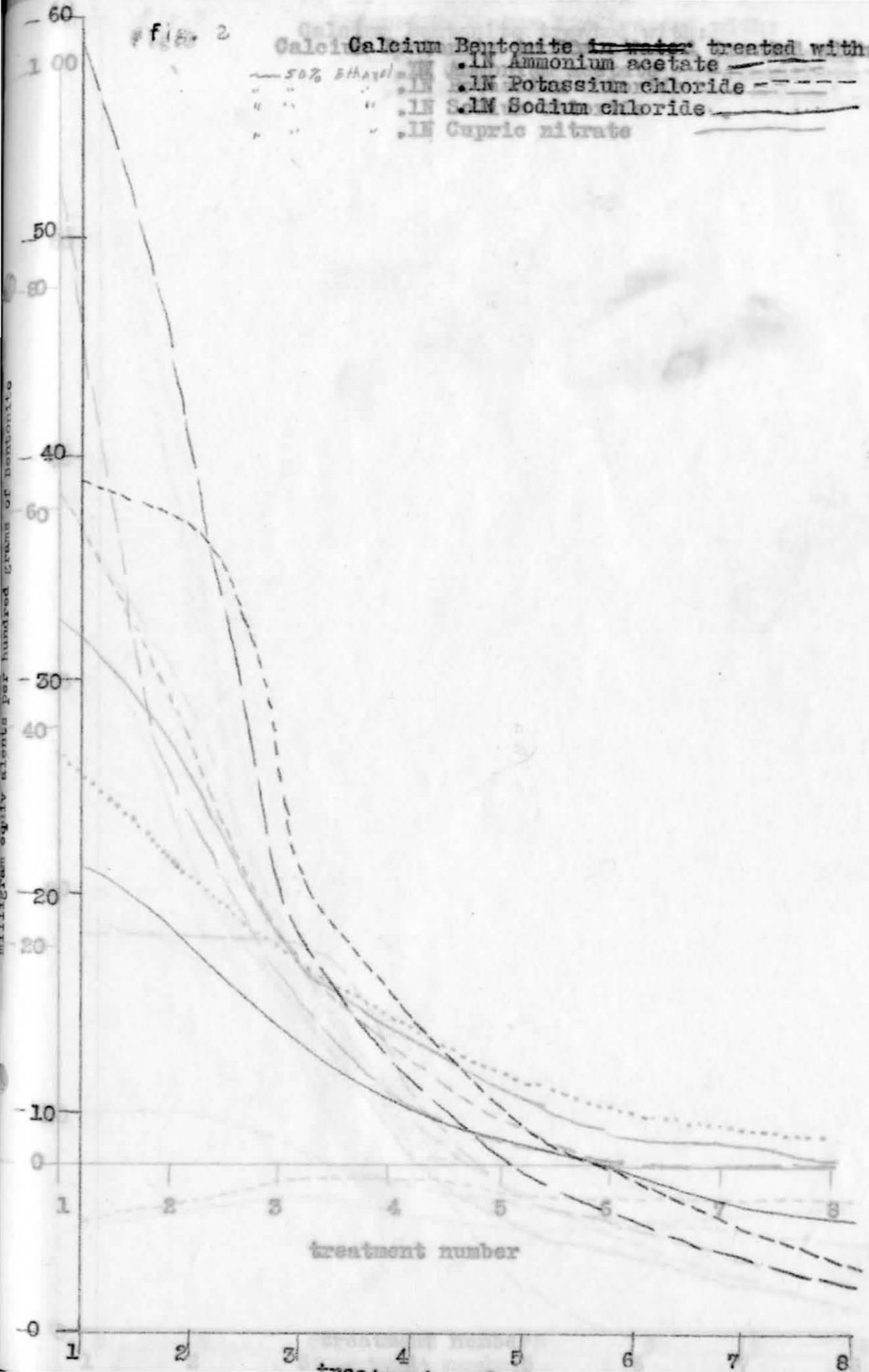


Fig. 2
Calcium Bentonite ~~in water~~ treated with:
.1N Ammonium acetate
.1N Potassium chloride
.1M Sodium chloride
50% Ethanol .1N
.1N
.1N Cupric nitrate
60
100
50
80
40
60
30
40
20
20
10
0
0
1
2
3
4
5
6
7
8
treatment number

Fig. 3

Calcium Bentonite ~~in 50% ethanol~~ treated with:

50% Ethanol .1N Ammonium acetate

" " " .1N Potassium chloride

" " " .1N Sodium chloride

" " " .1N Cupric nitrate

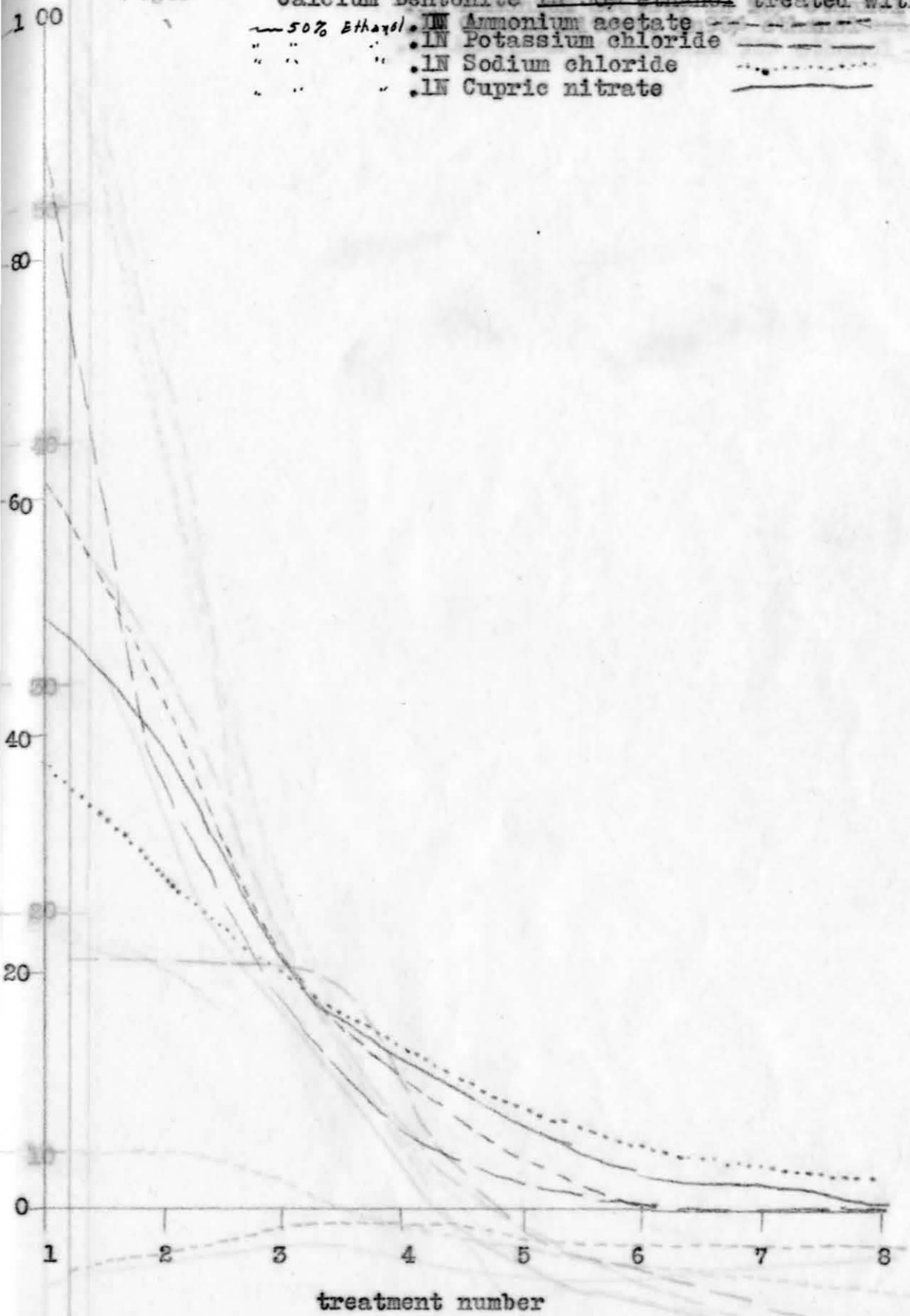
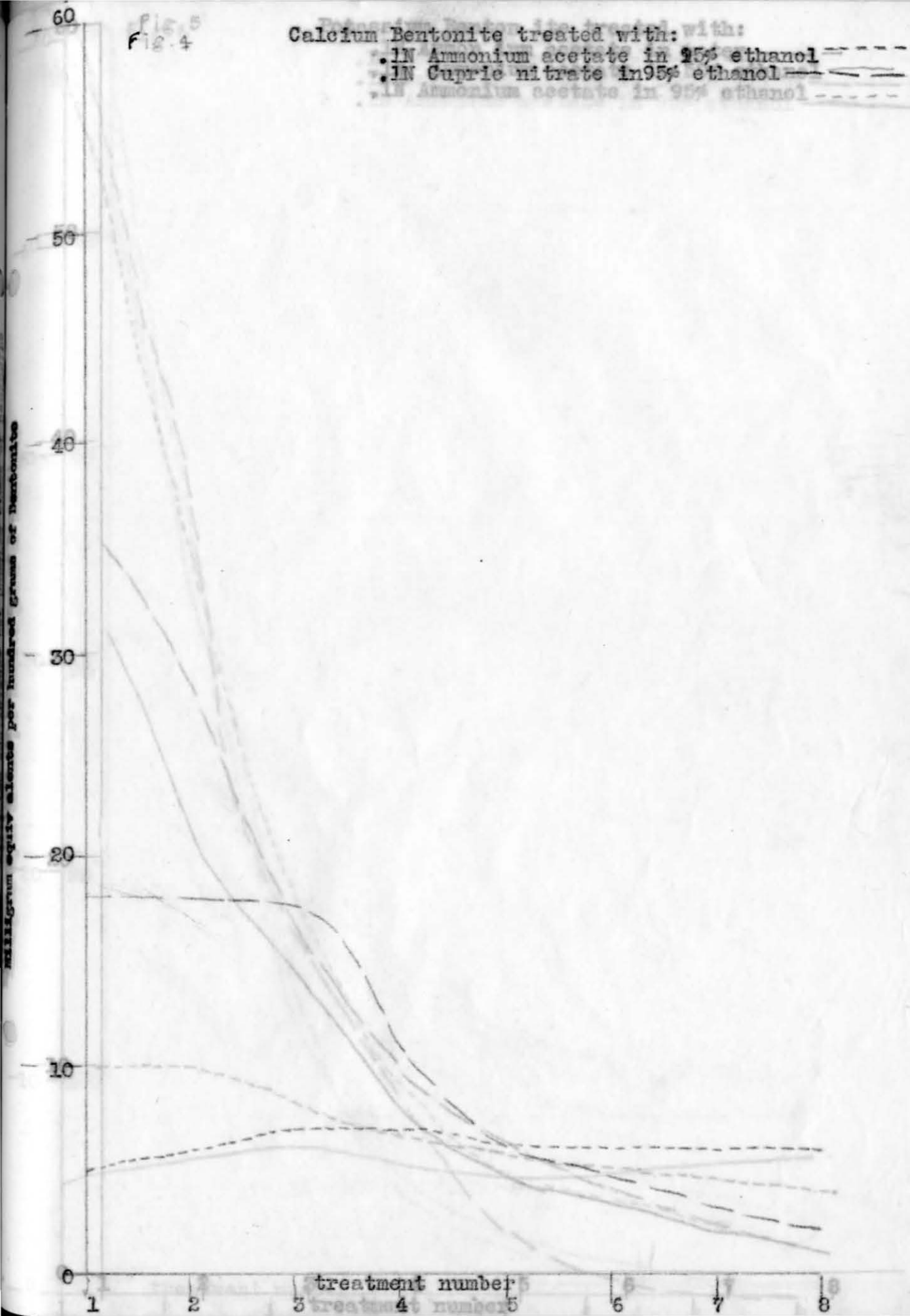


Fig. 4


Calcium Bentonite treated with:
.1N Ammonium acetate in 25% ethanol
.1N Cupric nitrate in95% ethanol
60
50
40
30
20
10
0
Milligram equivalents per hundred grams of Bentonite
treatment number
1
2
3
4
5
6
7
8

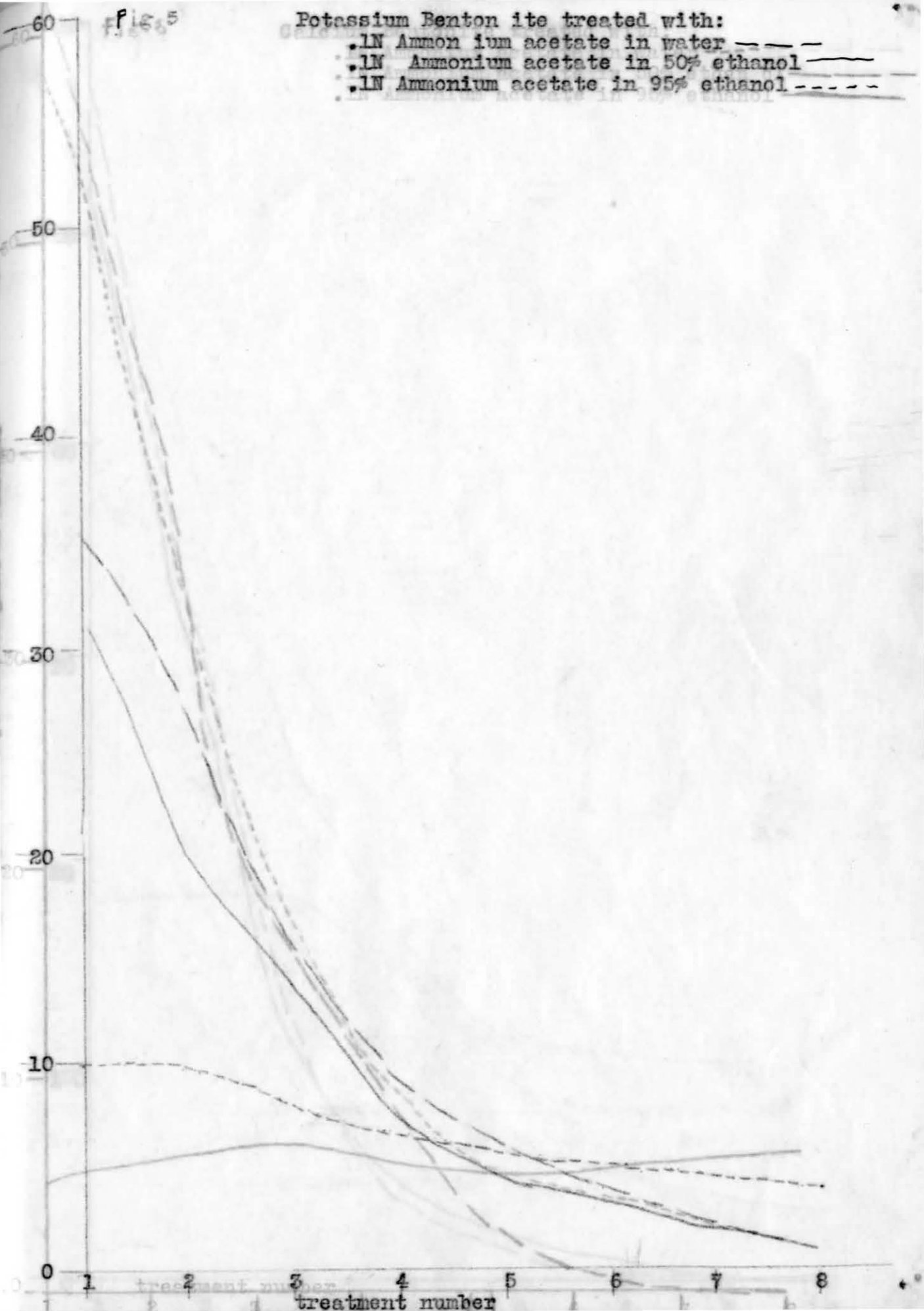


Fig. 5
Potassium Benton ite treated with:
.1N Ammon ium acetate in water
.1N Ammonium acetate in 50% ethanol
.1N Ammonium acetate in 95% ethanol
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
treatment number

Fig. 6

Calcium Bentonite treated with:
- .1N Ammonium acetate in water
- .1N Ammonium acetate in 50% ethan ol
- .1N Ammonium acetate in 95% ethanol

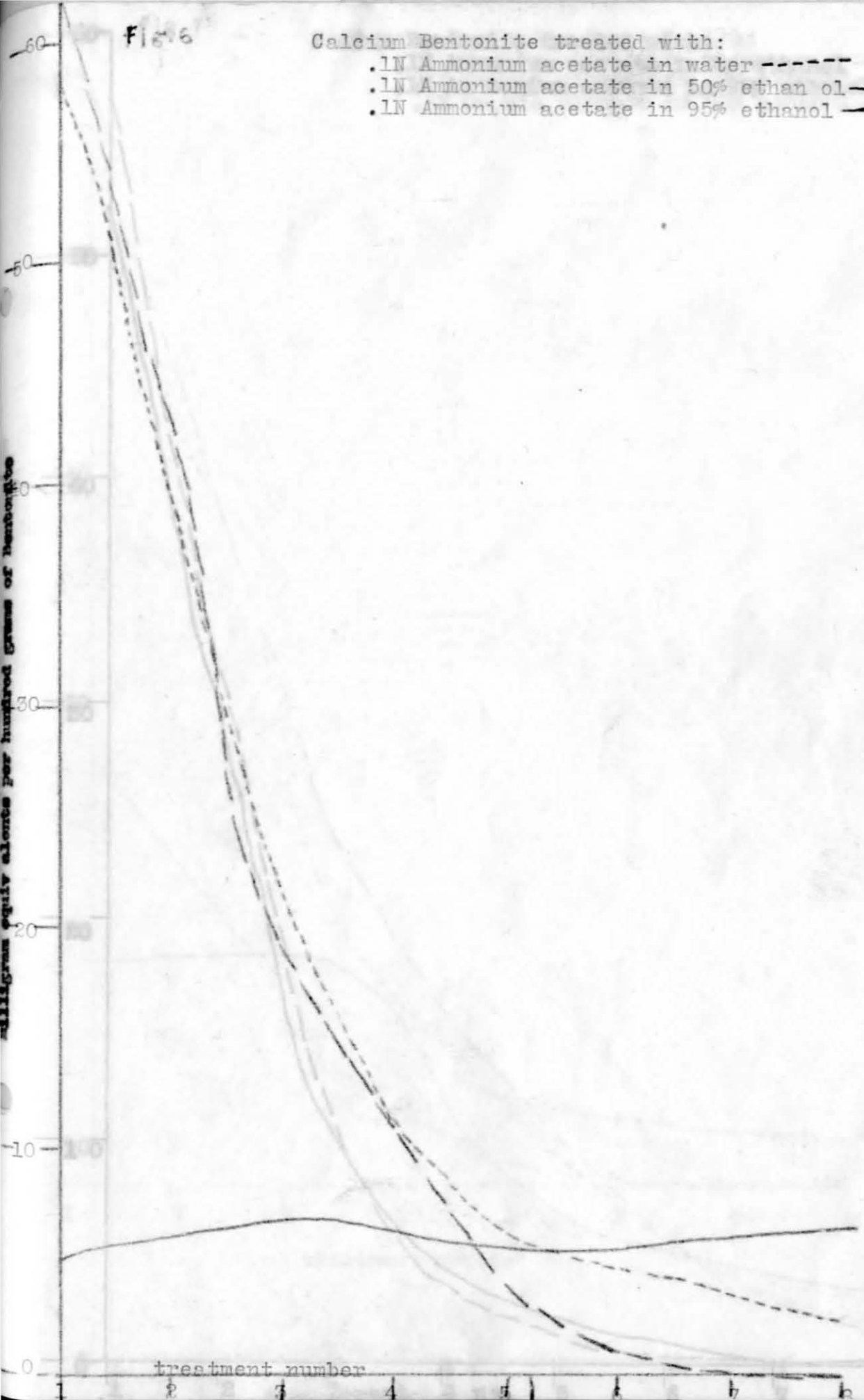
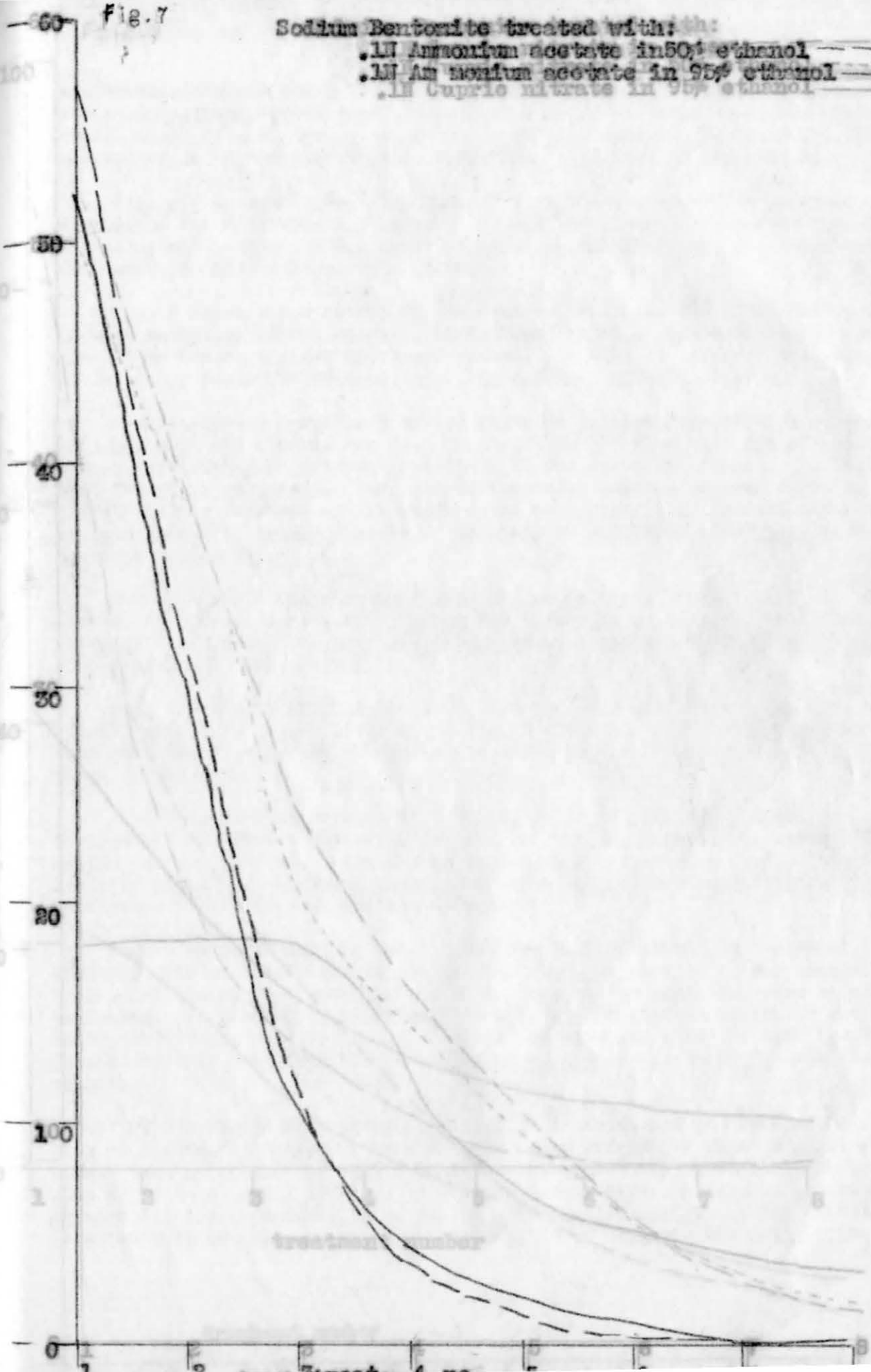


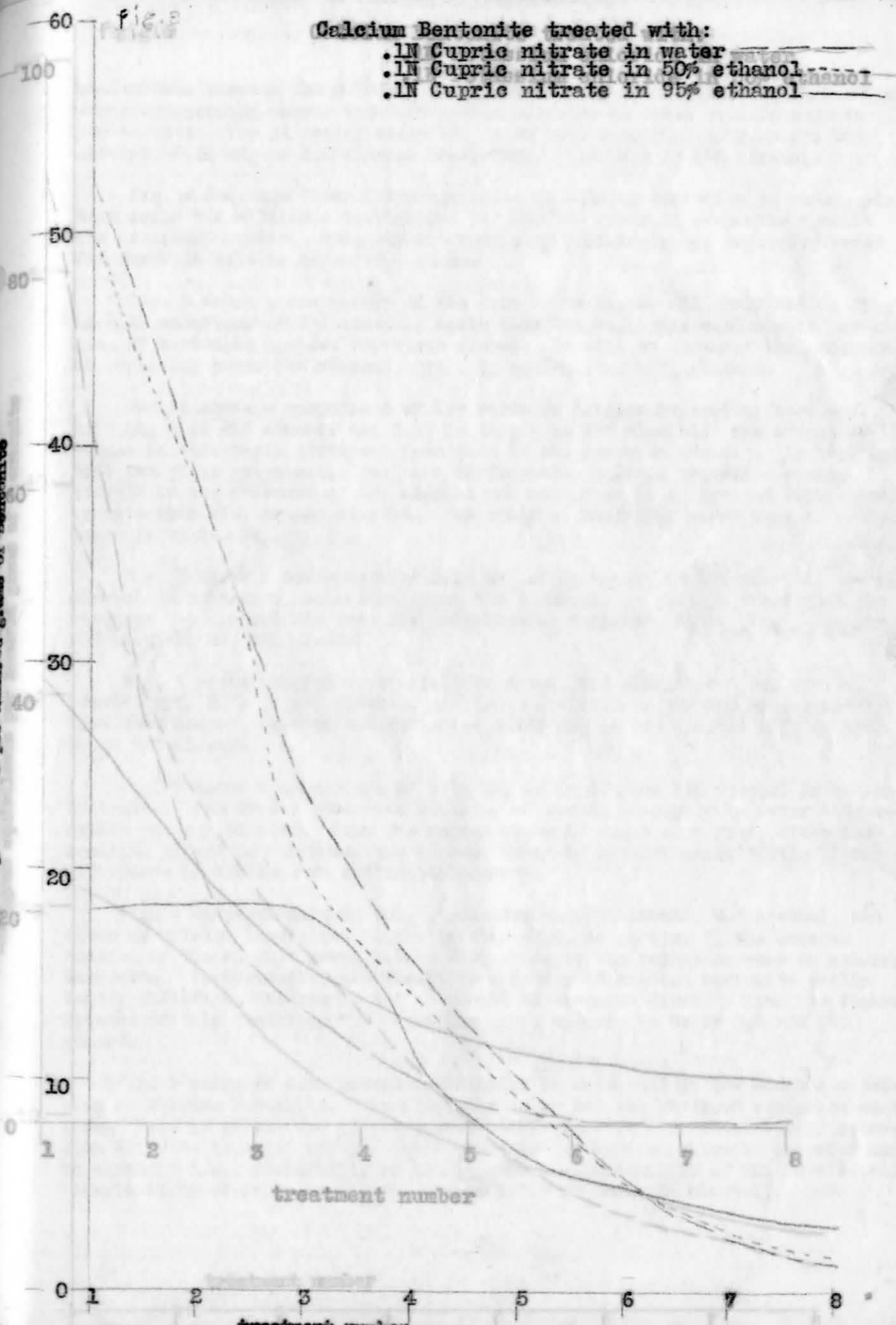
Fig. 7

Sodium Bentonite treated with:

.1M Ammonium acetate in50% ethanol

.1M Ammonium acetate in 95% ethanol




Calcium Bentonite treated with:
.1N Cupric nitrate in water
.1N Cupric nitrate in 50% ethanol
.1N Cupric nitrate in 95% ethanol
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
treatment number

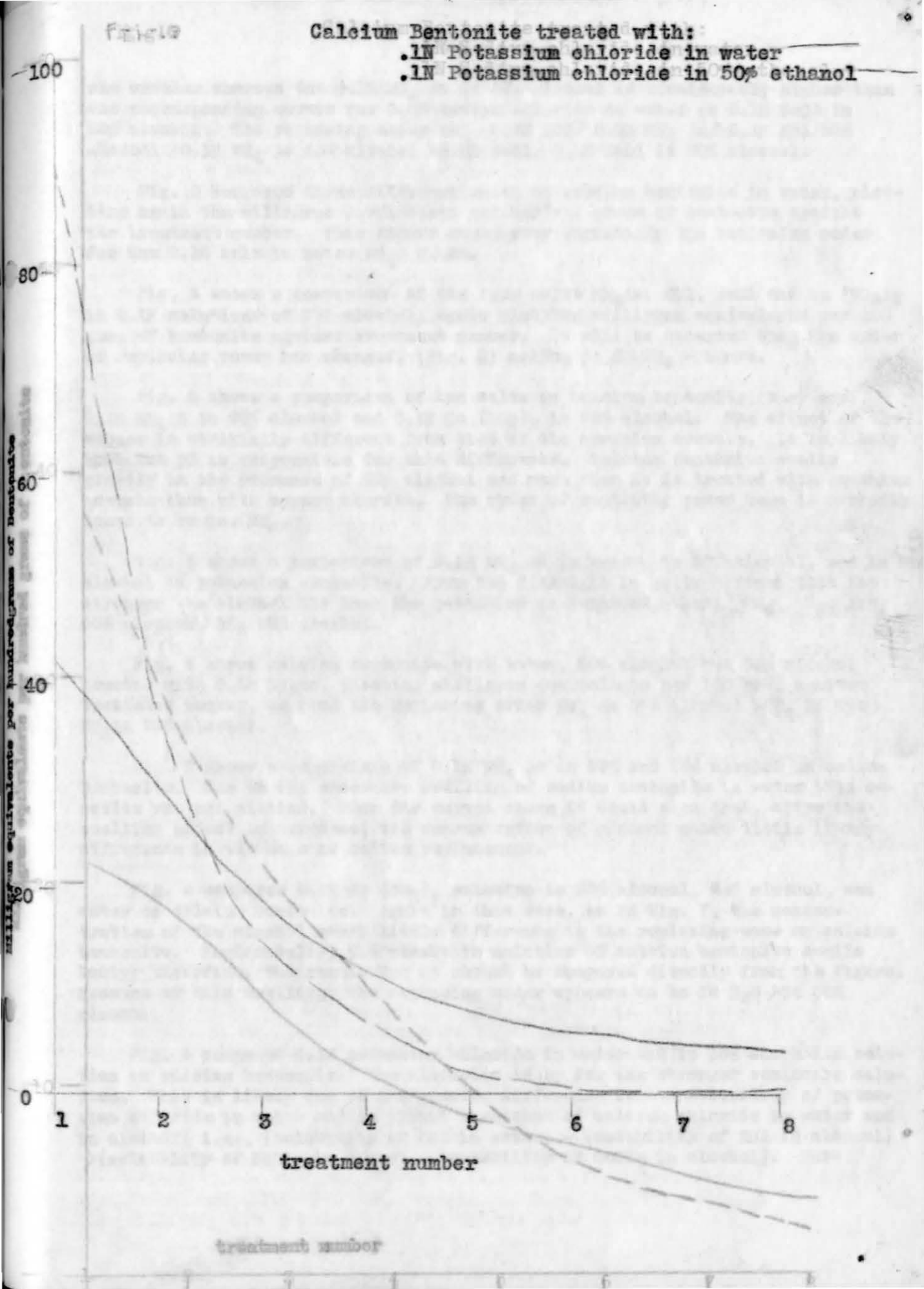
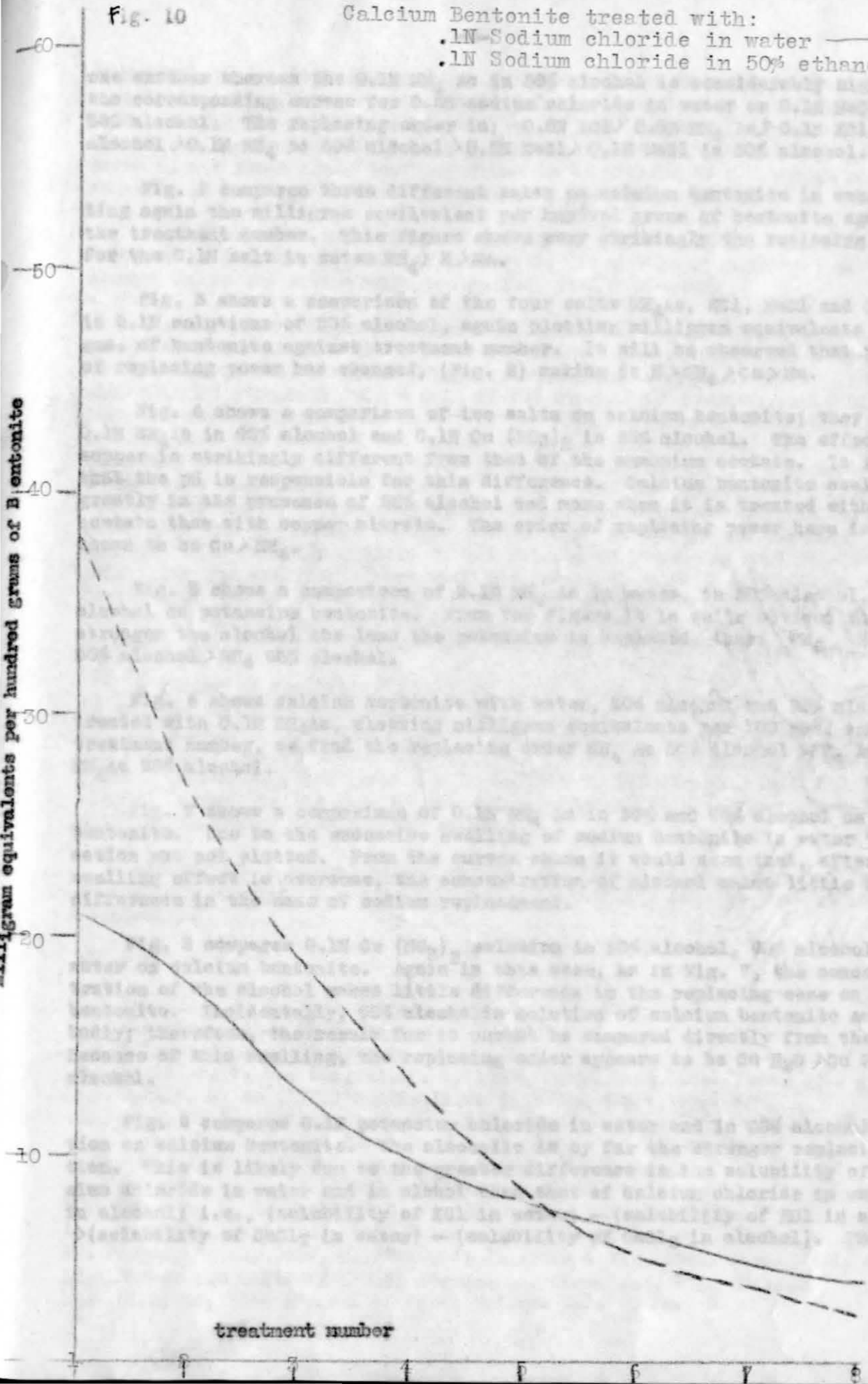

Calcium Bentonite treated with:
.1N Potassium chloride in water
.1N Potassium chloride in 50% ethanol
100
80
60
40
20
0
1
2
3
4
5
6
7
8
treatment number

Fig. 10

Calcium Bentonite treated with:
.1N Sodium chloride in water ———
.1N Sodium chloride in 50% ethanol — —



one another whereas the 0.1N NH_4 Ac in 50% alcohol is considerably higher than the corresponding curves for 0.5N sodium chloride in water or 0.1N NaCl in 50% alcohol. The replacing order is: 0.5N KCl > 0.5N NH_4 Ac > 0.1N KCl 50% alcohol > 0.1N NH_4 Ac 50% alcohol > 0.5N NaCl > 0.1N NaCl in 50% alcohol.

Fig. 2 compares three different salts on calcium bentonite in water, plotting again the milligram equivalent per hundred grams of bentonite against the treatment number. This figure shows very strikingly the replacing order for the 0.1N salt in water NH_4 > K > Na.

Fig. 3 shows a comparison of the four salts NH_4Ac, KCl, NaCl and Cu $(NO_3)_2$ in 0.1N solutions of 50% alcohol, again plotting milligram equivalents per 100 gms. of bentonite against treatment number. It will be observed that the order of replacing power has changed, (Fig. 2) making it K > NH_4 > Cu > Na.

Fig. 4 shows a comparison of two salts on calcium bentonite; they are: 0.1N NH_4Ac in 95% alcohol and 0.1N Cu $(NO_3)_2$ in 95% alcohol. The effect of the copper is strikingly different from that of the ammonium acetate. It is likely that the pH is responsible for this difference. Calcium bentonite swells greatly in the presence of 95% alcohol and more when it is treated with ammonium acetate than with copper nitrate. The order of replacing power here is markedly shown to be Cu > NH_4.

Fig. 5 shows a comparison of 0.1N NH_4 Ac in water, in 50% alcohol, and in 95% alcohol on potassium bentonite. From the figure it is quite obvious that the stronger the alcohol the less the potassium is replaced, thus: NH_4 H_2O > NH_4 50% alcohol > NH_4 95% alcohol.

Fig. 6 shows calcium bentonite with water, 50% alcohol and 95% alcohol treated with 0.1N NH_4Ac, plotting milligram equivalents per 100 gms. against treatment number, we find the replacing order NH_4 Ac 50% alcohol > NH_4 Ac H_2O > NH_4Ac 95% alcohol.

Fig. 7 shows a comparison of 0.1N NH_4 Ac in 50% and 95% alcohol on sodium bentonite. Due to the excessive swelling of sodium bentonite in water this reaction was not plotted. From the curves shown it would seem that, after the swelling effect is overcome, the concentration of alcohol makes little if any difference in the ease of sodium replacement.

Fig. 8 compares 0.1N Cu $(NO_3)_2$ solution in 50% alcohol, 95% alcohol, and water on calcium bentonite. Again in this case, as in Fig. 7, the concentration of the alcohol makes little difference in the replacing ease on calcium bentonite. Incidentally, 95% alcoholic solution of calcium bentonite swells badly; therefore, the result for it cannot be compared directly from the figure. Because of this swelling, the replacing order appears to be Cu H_2O > Cu 50% alcohol.

Fig. 9 compares 0.1N potassium chloride in water and in 50% alcoholic solution on calcium bentonite. The alcoholic is by far the stronger replacing solution. This is likely due to the greater difference in the solubility of potassium chloride in water and in alchol than that of calcium chloride in water and in alcohol; i.e., (solubility of KCl in water) - (solubility of KCl in alcohol) > (solubility of $CaCl_2$ in water) - (solubility of $CaCl_2$ in alcohol). This

difference in solubilities in water and alcohol and consequent strength as a replacing agent has been used in formulating a method of determining replaceable calcium in calcareous and, to a lesser degree, in gypsum soils. Due to the insolubility of KCl in 95% alcohol, the 0.1N KCl in 95% alcohol curve is not shown since the method had to be altered to get enough potassium chloride in each successive treatment and, therefore, could not be compared.

Fig. 10 shows a comparison of the curves from 0.1N NaCl and 0.1N sodium chloride in 50% ethanol on calcium bentonite. From this it appears that 50% alcohol makes the cation more active than it is in water.

A study of the figures suggests that alcohol has an effect on the equilibria of bentonite and the various replacing salts varying with its concentration and on the relation of their solubilities to one another. It appears also that as a general rule a salt in 50% ethanol is a better replacing agent than the corresponding salt in water, and that a replacing salt which is less soluble than the salts of the cation which is being replaced is a stronger replacing salt. For example, 0.1N potassium chloride in 50% ethanol combines these (both solubility and activity effect) with the result that it is uncommonly strong as a replacing agent. Sometimes these two effects work against each other and the result is that the stronger of the two is dominating. For example, 0.4N ammonium acetate in 50% ethanol on potassium bentonite combines solubility and activity effect with the result that the solubility effect predominates. Due to the swelling of calcium bentonite in 95% ethanol, the results in this system will require further study before any comparisons can be made. The swelling in this case rivals that of sodium bentonite in water.

A number of equilibria have been tried and the replacing order of elements in various solutions was found to be: On calcium bentonite K 50% alcohol > NH_4 50% alcohol > NH_4 H_2O > Cu H_2O > Cu 50% alcohol > K H_2O > Na 50% alcohol > Na H_2O > Cu 95% alcohol > Na 95% alcohol. In the case of bentonites other than calcium bentonites, the order may be written Ca 50% alcohol > Ca H_2O > Ca 95% alcohol, except in the case of potassium bentonite in which any alcoholic solution is weaker than a water solution.

Alcohol has a marked effect on the equilibrium relationships of one ion to another, especially where it is one of solubility such as that of potassium compounds.

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