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CHEMICAL EXFOLIATED VERMICULITE FOR REMOVAL OF PHOSPHATE FROM WASTEWATERS

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CHEMICALLY EXFOLIATED VERMICULITE FOR REMOVAL OF PHOSPHATE FROM WASTEWATERS

by

Jacob Block

W. R. Grace & Company
Clarksville, Maryland 21029

for the

FEDERAL WATER QUALITY ADMINISTRATION

DEPARTMENT OF THE INTERIOR

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ABSTRACT

Many aluminum-vermiculites were prepared and tested for phosphate removal. The maximum capacity obtained was 10 mg PO_4/gram of treated vermiculite. The highest phosphate capacities were obtained with materials prepared at relatively low pH (3.0) and dilute aluminum solutions (0.1-0.05M), materials prepared at higher pH values (3.8) and more concentrated aluminum solutions (0.33M) had lower phosphate capacities. Experimental results have shown hydroxylated aluminum vermiculite is inactive towards phosphate ion, and that our original concept of hydroxyl ion replacement was not valid. The mole ratio of phosphate adsorbed to exchanged aluminum seemed to approach 0.33, or an exchange capacity of 13.7 mg PO_4/gm. The highest experimental capacity obtained was 12.2 mg/gm for a Li-expanded Poole vermiculite.

Various regeneration schemes were attempted, the most successful being one in which a dilute sulfuric acid solution containing a small amount of $Al_2(SO_4)_3$ was used as the regenerant. The addition of the $Al_2(SO_4)_3$ prevented the loss of aluminum from the vermiculite.

No significant differences in capacity were found between thermally and chemically exfoliated vermiculite. In addition, an aluminum vermiculite prepared directly from a vermiculite ore without prior exfoliation had a capacity of 7.3 mg PO_4/gm (compared to about 9 mg/gm for exfoliated material).

Vermiculites containing cations other than Al were also prepared. These included Fe(III), Fe(II), La(III), and Cu(II). None, however, appeared more promising than Al-vermiculite.

The adsorption isotherm of aluminum-vermiculite was obtained, and the data were found to fit both the Langmuir and Freundlich plots. However, adsorption at phosphate concentrations of around 25 ppm was extremely low ($\sim$ 0.4 mg/gm), and for this reason work on this project was terminated.

TABLE OF CONTENTS

	Page No.
FOREWORD	ii
ABSTRACT	v
STATEMENT OF THE PROBLEM	vi
RECOMMENDATIONS	vii
INTRODUCTION	1
EXPERIMENTAL WORK	3
Chemicals	3
Equipment	3
Analytical	3
Exchange Capacity Determination	3
Exfoliation	3
Chemical	3
Thermal	4
Preparation of Al-Vermiculite	4
Determination of Phosphate Capacities	4
Batch Method	4
Column Method	5
Regeneration	5
Batch Method	5
Column Method	5
Adsorption Isotherm	5
RESULTS AND DISCUSSION	6
Vermiculite Ore Characterization	6
Exfoliation	7
Preparation and Phosphate Capacity of Aluminum Vermiculite	7
Use of Cations other than Al	11

TABLE OF CONTENTS (cont'd)

	Page No.
Regeneration	12
NH_4OH	12
HCl	13
Various Salts	14
$Al_2(SO_4)_3 + H_2SO_4$	15
Working Capacity of Al-Vermiculite	15
Economic Evaluation	17
REFERENCES	21
APPENDIX A - Economic Evaluation	A-1
APPENDIX B - Assumption and Data for Calculations	B-1
APPENDIX C - System Design	C-1
APPENDIX D - Capital Cost Estimate	D-1
APPENDIX E - Cost Estimate of Phosphate Removal from Wastewater	E-1
APPENDIX F - Breakdown of Total Capital Requirements	F-1

STATEMENT OF THE PROBLEM

The primary objective of the work described herein was to prepare a chemically treated vermiculite with a high phosphate capacity that could be economically regenerated. Our original concept was to replace the exchangeable cations in an expanded vermiculite with hydroxylated aluminum ions. Phosphate removal could then be achieved by exchange with the hydroxyl groups, resulting in the aluminum being bonded to the vermiculite and phosphate. Regeneration was to be attempted with an alkali such as ammonia, which would replace the phosphate groups with hydroxyls.

RECOMMENDATIONS

In studies on the use of activated alumina to remove phosphate from wastewater, Yee[1] used NaOH as the regenerant and observed an 8% alumina loss per cycle. Neufeld and Thodos[2] found that an activation step with nitric acid is needed before recycle. In the current work on aluminum-vermiculite we found that a dilute sulfuric acid solution containing a small quantity of $Al_2(SO_4)_3$ served simultaneously as a good regenerant and "activator." We recommend that this regenerant be applied to activated alumina to achieve a lower raw material cost, decreased alumina losses and a highly active alumina.

We feel that the idea of producing a selective inorganic anion exchanger has some merit. The replacement of the exchangeable cations in vermiculite with aluminum does not seem to be the answer, however. A better approach might be the direct synthesis of an inorganic anion exchanger, rather than trying to convert a cation exchanger into an anion exchanger.

INTRODUCTION

Phosphates occur in municipal effluents mainly from human wastes and synthetic detergents. The phosphates used in detergents are sodium tripolyphosphate and tetrasodium pyrophosphate. However, these condensed phosphates break down to ortho-phosphates in sewage, and it can be assumed that after 24 hours at 23°C most of the condensed phosphates are in the ortho form.[3] Phosphates are a problem because they create a nutrient imbalance in natural waters which leads to algae blooms (growths) and eutrophication.

Phosphate presently is removed with lime, iron salts and alum. These treatments, however, are not selective for phosphate and result in large quantities of sludge. In addition, highly alkaline effluents are produced in the lime treatment, and high sulfate or chloride effluents in the other treatments.

Adsorption methods for phosphate removal include the use of ion exchange resins and activated alumina [1,2]. The resins, however, suffer from the disadvantage of being non-selective for phosphate, whereas activated alumina tends to show losses of 8-10% per cycle.

Our objective was to develop a selective anion exchanger for phosphate by chemically treating vermiculite to convert it from a cation exchanger to an anion exchanger.

The mineral is a layer silicate, consisting of thin aluminosilicate platelets held together by hydrated, exchangeable cations (Ca and Mg). When vermiculite ore is passed through a hot furnace, the water of hydration associated with the exchangeable cations is converted to steam. As a result, the ore exfoliates, i.e., the platelets are separated by expansion of the steam. Thermally exfoliated vermiculite is sold commercially as an insulation material.

Thermal exfoliation ruptures the chemical bonds which hold the platelets together and also partially decreases the available surface area. In addition, some of the mobile cations become "fixed" to the surface.

On the other hand, vermiculite can be exfoliated chemically without the use of excessive temperature. Simple cation exchange of the exchangeable divalent cations with monovalent cations followed by hydration with H_2O, will readily separate the platelets. On chemical exfoliation, platelet size and integrity is retained, maximum surface area is developed and, most importantly for our current purposes, the calcium and magnesium ions are still exchangeable.

At present, no chemically exfoliated vermiculite is marketed commercially; however, the process of chemical exfoliation is inherently simple and lends itself to being performed on tonnage scale.

Cation exchange capacity of thermally exfoliated vermiculites ranges from 30 to 70 meq/100 gm. Upon chemical exfoliation, this capacity can be raised as high as 130 meq/100 gm.

Anion exchange capacities for vermiculites are very low, never being more than 30-40 meq/100 gm. It is apparent that the anion exchange capacity of vermiculite is much too low to be considered for removal of phosphate from wastewaters. On the other hand, we developed a concept by which the higher cation exchange capacity of chemically exfoliated vermiculite may be converted to phosphate anion exchange capacity, and this phosphate anion exchange capacity can, at the same time, be greater than the original cation exchange capacity.

Our concept was based on the replacement of the exchangeable cations with hydroxylated aluminum ions such as $Al(OH)^{+2}$ and $Al(OH)_2^{+}$. We reasoned that the aluminum ions would be firmly held by the vermiculite while the hydroxyl groups would be exchangeable with phosphate, thus converting the cation exchange capacity to an even greater anion exchange capacity.

EXPERIMENTAL WORK

CHEMICALS

All chemicals were reagent grade. Vermiculite was obtained from the Zonolite Division of W. R. Grace & Co. and consisted of three types, a South Carolina blend, a Libby-Montana ore, and a Poole vermiculite from South Carolina. The first two vermiculites are normally used to form packaging materials, while the latter exfoliates poorly but has a high exchange capacity.

EQUIPMENT

All colorimetric measurements were made with a Bausch and Lomb Spectronic 20 spectrophotometer. A Beckman zeromatic pH meter was used for pH measurements, and for some sodium ion determinations.

ANALYTICAL METHODS

Phosphate was determined colorimetrically with ammonium molybdate and 1-amino-2-naphthol-4-sulfonic acid as the colorimetric reagents.

Aluminum and iron were determined colorimetrically with aluminon and o-phenanthroline, respectively.

Calcium and magnesium determinations were made by EDTA titration, using either Murexide or Eriochrome Black T as indicators.

Potassium was determined by flame photometry, and sodium either by flame or with a sodium ion electrode.

EXCHANGE CAPACITY DETERMINATION

Vermiculite exchange capacities were determined by reacting 25 grams of previously washed and air dried vermiculite with one liter of 3.5M NaCl at 80°C for at least 18 hours. The amount of Ca, Mg and K released was then determined.

EXFOLIATIONS

Chemical

Four different reagents for chemical exfoliation were tried: NaCl, LiCl, H_2O_2 and H_2SO_4. (Exfoliation is needed to facilitate the ion exchange

reactions of vermiculite). The exfoliation is caused by the hydration of the sodium, lithium or sulfuric acid. The peroxide-induced expansion is a result of a catalytic decomposition of the peroxide which causes the vermiculite platelets to separate.

NaCl - 1.0 kg of ore was placed in a 4-liter beaker. Then 2.0 liters of 20% NaCl solution were added. The beaker was covered and heated overnight at 80°C. The solution was decanted and the vermiculite was water-washed until the filtrate was negative to an $AgNO_3$ test. The vermiculite was then left in 2.0 liters of distilled water overnight, filtered and air-dried.

This procedure was later modified by substitution of a 6M NaCl solution followed by a boiling water treatment.

LiCl - Same as the original NaCl procedure except that 15% LiCl was used. The material was difficult to filter and was left as a slurry.

H_2SO_4 - 1.0 kg of ore was treated with one liter of concentrated H_2SO_4 for 16 hours. The acid was decanted and the vermiculite was water-washed until negative to $BaCl_2$. The material was then allowed to stand overnight in distilled water, then filtered and air-dried.

Thermal

Portions of vermiculite ore (75 grams each) were put in a porcelain dish and placed in a furnace, at a preset temperature, for 45 minutes.

PREPARATION OF AL-VERMICULITES

Fifty grams of exfoliated vermiculite were treated with one liter of $Al(NO_3)_3$ solution at the desired concentration and pH. In order to avoid the addition of foreign ions, pH adjustments were made either by the addition of HNO_3 or by the addition of Amberlite IR 45 ion exchange resin (a weak base in the hydroxyl form). After the desired pH was reached, the resin was filtered off. The vermiculite and the aluminum solution was stirred for a minimum of 18 hours. The vermiculite was then filtered, washed and air-dried. The filtrates were gravimetrically analyzed for Al.

The vermiculites containing other cations were prepared in a similar manner.

DETERMINATION OF PHOSPHATE CAPACITIES

Batch Method

A stock pH 7 sodium phosphate solution was prepared by dissolving 280 gm of sodium hydrogen phosphate ($Na_2HPO_4 \cdot 7\ H_2O$) and 50 gm of sodium dihydrogen

phosphate ($NaH_2PO_4 \cdot H_2O$) in water and diluting to 4-liters. (Total phosphate concentration is 0.37 moles/liter). To determine PO_4 capacity, 100 ml of this solution was added to 5 grams of Al-vermiculite and the mixture was stirred for a minimum of 18 hours. The vermiculite was then filtered, washed and air-dried. A one-gram sample was then treated with 100 ml of a 2% NaOH solution for 18 hours, and the resultant liquid was analyzed for phosphate. (The 2% NaOH treatment was checked for complete phosphate removal by analyzing the filtrate for phosphate and good agreement was obtained).

Column Method

Four grams of vermiculite were placed in a 25 ml burette over a glass-wool plug. A phosphate solution, previously boiled to remove CO_2 and fitted with an Ascarite plug, was then passed through the column at the desired flow rate. The effluent was analyzed for phosphate.

REGENERATION

Batch Method

A quantity of vermiculite containing a known amount of phosphate was weighed into a flask. A measured amount of regenerant was then added, and the mixture was placed in a shaker for 18 hours. The vermiculite was then filtered and washed. The filtrate was analyzed for phosphate and aluminum after first being brought to volume.

Column Method

The vermiculite containing a known amount of phosphate was placed in a 25 ml burette over a glass-wool plug. The regenerant was passed through the column at a controlled rate, and the effluent was analyzed for phosphate and aluminum as in the batch method.

ADSORPTION ISOTHERM

Samples of sodium phosphate solution (20 ml), each of a different phosphate concentration, were added to one-gram samples of Al-vermiculite. The mixtures were placed in a shaker for 18 hours. The vermiculite was then filtered, washed and air-dried. Both solids and liquids were then analyzed for phosphate.

RESULTS AND DISCUSSION

VERMICULITE ORE CHARACTERIZATION

The following properties of the vermiculite ores were determined: ion exchange capacity, exchangeable cations, elemental composition (by emission spectroscopy), interlayer spacing (by x-ray diffraction), surface area, and particle size distribution. The results are summarized in Table I.

X-ray diffraction patterns of the ores revealed that the South Carolina ore was a typical vermiculite having a d spacing of 14.3 Å. The Libby-Montana ore also showed the same spacing, but an impurity of a three-layer structure mica was also present. The Poole ore diffraction pattern was one of a different type of vermiculite having a d spacing of 13.4 Å.

The surface area (by nitrogen adsorption) of all three ores was less than 1 m^2/gm.

The mesh size of the South Carolina and the Poole ores was -8 + 30 (No. 3 size) and the Libby ore was -4 + 16 (No. 2 size). Originally we planned to work with all No. 2 ores, but these were not available from the South Carolina mill.

TABLE I

Vermiculite Ore Characterization

A. Exchangeable Cations and Exchange Capacity (meq/100 gm)

Ore	Ca	Mg	K	Na	Total
Libby	26	20	10	0.4	56
South Carolina	22	27	10	0.4	59
Poole	3	110	6	0.7	120

B. Differences in Ores Found by Emission Spectroscopy (%)

Element	Libby	South Carolina	Poole
Ba	0.1-1	0.1-1	0.01-0.1
B	0.01-0.1	0.01-0.1	n.d.*
Ca	0.1-1	1-5	0.01-0.1
Na	0.1-1	0.1-1	n.d.*
Ti	1-5	1-5	0.1-1

* None detected

The following elements were detected, but had the same value for each ore: Al(1-5%), Cr(0.1-1%), Fe(1-5%), Mg (> 5%), Mn (0.1-1%), Ni (0.01-0.1%), Si (> 5%) and V(0.01-0.1%).

EXFOLIATION

The sulfuric acid exfoliation resulted in partial decomposition of the Libby and the Poole vermiculites as evidenced by 30-40% weight losses and large amounts of iron in the acid phase. The volume change after expansion, however, was between 90-100% (measured by comparing the volumes of 10-gram samples of the ore and the expanded material). Because of the obvious attack of the vermiculite in two cases and the difficulties involved in handling concentrated H_2SO_4, work with this material was discontinued.

The LiCl expansion resulted in a product that was so highly hydrated it could not be filtered. It was extremely slimey and remained suspended in the aqueous phase. Because of these unfavorable properties, plus the relatively high cost of LiCl, work with Li-expanded material was also halted.

The H_2O_2 reaction resulted in excellent expansion for the Libby ore (> 200%) but only fair expansion for the other two ores (40% for the South Carolina and 25% for the Poole).

The expansion with 3.4M NaCl was less than 20% in all cases. However, further tests with 6M NaCl (nearly saturated solution) followed by a boiling water treatment, resulted in expansions of 25, 60 and 65% for the Poole, Libby and South Carolina ores, respectively. This material was used in subsequent experiments with Al solutions.

PREPARATION AND PHOSPHATE CAPACITY OF ALUMINUM VERMICULITE

The results of Al-vermiculite preparation and phosphate capacity are summarized in Table II.

From the sodium values in Table II, it can be concluded that complete exchange occurred in the Poole and South Carolina vermiculites, but not in the Libby. Also, it should be noted that the relationship of the average charge on the exchanging Al ion (obtained by dividing mmoles of Na released by the mmoles of Al adsorbed) with pH, i.e., at pH 3.0, 3.5 and 3.8 the charge is approximately 3.0, 2.6 and 2.1, respectively. This means that at the lower pH values, we are exchanging mostly with hydrated Al^{+3}, whereas at the higher pH values, we have a hydroxylated species such as $Al(OH)^{+2}$ (or a mixture of Al^{+3} and $Al(OH)_2^+$).

This is confirmed by the pH decrease after the high pH exchange reactions which can be expected if the hydrolysis product is removed from solution, i.e.,

TABLE II

Phosphate Removal with Al-Vermiculite

Aluminum Exchange							Phosphate Adsorption	
Vermiculite	ml $Al(NO_3)_3$ Solution	pH Initial	pH Final	mm Al Adsorbed/ 100 gm	mmoles Na Released/100 gm	Effective* Charge on Al	mg PO_4/gm	(mmoles PO_4/ mmoles Al)
A. 0.05M $Al(NO_3)_3$								
25 gm Poole	1000	3.29	3.20	46.7	119	2.5	7.8	0.18
25 gm Poole	1000	3.79	3.41	48.9	114	2.3	4.9	0.11
B. 0.1M $Al(NO_3)_3$								
50 gm Poole	1000	2.82	3.05	43.3	132	3.0	8.2	0.20
50 gm Poole	1000	3.05	3.18	42.0	127	3.0	7.2	0.18
50 gm Poole	1000	3.25	3.10	47.5	130	2.7	7.4	0.16
50 gm Poole	1000	3.55	3.12	49.7	130	2.6	---	---
50 gm Poole	1000	3.81	3.22	62.8	126	2.1	6.0	0.10
50 gm Poole	50	3.22	3.71	9.6	26.2	2.7	2.6	0.28
50 gm Poole	100	3.22	3.70	18.4	55.8	3.0	3.2	0.18
50 gm Poole	150	3.22	3.52	25.2	81.4	3.2	4.7	0.19
50 gm S.C.	1000	3.22	3.14	21.2	59.2	2.8	1.8	0.09
50 gm S.C.	1000	3.48	3.38	21.6	62.0	2.8	---	---
50 gm S.C.	1000	3.75	3.69	25.1	59.2	2.4	2.0	0.08
50 gm Libby	1000	3.19	3.21	14.5	36.0	2.6	1.7	0.12
50 gm Libby	1000	3.50	3.51	13.8	36.0	2.7	---	---
50 gm Libby	1000	3.80	3.76	18.0	38.4	2.1	2.2	0.13
C. 0.333M $Al(NO_3)_3$								
50 gm Poole	500	3.19	---	49.1	127	2.6	4.7	0.10
50 gm Poole	500	3.49	---	57.3	117	2.0	4.3	0.08
50 gm Poole	500	3.79	---	57.0	103	1.8	4.8	0.09

* mmoles Na released/mmoles Al adsorbed

$$Al^{+3} + H_2O \rightleftarrows Al(OH)^{+2} + H^+,$$

removal of $Al(OH)^{+2}$ would lower the pH. Thus, the Al-vermiculite prepared at the higher pH values should have a greater number of hydroxyl groups.

At low pH values, Al^{+3} is removed, and the pH should increase due to decreased hydrolysis. This is confirmed by the results at initial pH of 2.8 and 3.0.

The amount of phosphate adsorbed is surprisingly low, and is inconsistent with our idea of hydroxyl group replacement. In fact, better phosphate removal is obtained with Al-vermiculites prepared at low pH and dilute aluminum solutions, conditions which result in a high concentration of unhydrolyzed Al^{+3} ions. This leads to the conclusion that hydroxyl groups on the aluminum are "inactive" towards phosphate.

Further evidence of this can be seen from the following: we have observed that some of the aluminum on vermiculite is readily exchangeable with Na, while the remainder is not. According to the literature[4], unhydrolyzed Al is readily exchangeable, whereas the hydrolyzed Al is firmly held. We therefore reacted some pH 3.8 Al-Poole vermiculite with 1M NaCl solution in order to leave only hydroxyl aluminum on the vermiculite. The resultant vermiculite was then reacted with phosphate as in previous experiments. The results, summarized in Table III show a decrease in PO_4/Al ratio, indicating a lower phosphate adsorption with hydroxy-aluminum.

TABLE III

Preparation of, and Reaction with, Hydroxy-Al Vermiculite

pH_i	pH_f	(mg Al/gm) (Initial)	(mg Al/gm) (Removed)	(mg Al/gm) (Remaining)	mg PO_4/gm	(Moles PO_4/ Moles Al)
~ 7.0	3.30	17.0	4.5	12.5	2.2	0.05*

* Initial ratio was 0.10

The original phosphate capacity of the above-mentioned vermiculite was 6.0 mg PO_4/gm. We can then assume that 6.0-2.2 or 3.8 mg of PO_4 were originally adsorbed by 4.5 mg of Al (the unhydrolzyed aluminum), for a mole ratio of 0.24. In the experiment with partially exchanged vermiculite we obtained a mole ratio of 0.28 (Table II) and the mole ratio obtained with the Li-expanded vermiculite described in the following paragraphs was ~ 0.29. These mole ratios seem to be approaching a maximum of 0.33, i.e., one mole of adsorbed phosphate for every three moles of adsorbed aluminum. If we then assume a maximum ratio of 0.33 and an exchange capacity of 130 meq/100 gm, the maximum phosphate capacity attainable is 13.7 mg/gm.

Other experiments were carried out with highly expanded vermiculites to determine if greater interplatelet distances would improve phosphate adsorption. In one experiment, a H_2O_2 expanded Libby ore (vol. 210% greater than ore) was treated with 0.1M $Al(NO_3)_3$ at pH 3.10. The phosphate capacity of this material was 2.3 mg PO_4/gm, compared to 1.7 mg/gm for an equivalent Na-expanded vermiculite (volume 60% greater than the ore), a 35% increase in capacity.

In another experiment, a Li-expanded Poole vermiculite (as a slurry) was treated with 0.1M $Al(NO_3)_3$ solution at pH 3.15. (The Li-expanded vermiculites are highly expanded and cannot be filtered). The resultant Al-vermiculite was then reacted with PO_4 according to our standard procedure, and the capacity was 12.2 mg/gm (compared to 7.4 mg/gm for an equivalent Na-expanded material), a 65% increase in capacity. Thus both the peroxide and Li-expanded vermiculite showed significant increases in phosphate adsorption, the latter value approaching the predicted value of 13.7 mg/gm mentioned above.

Still other experiments were carried out with thermally expanded vermiculites. It is known that heating vermiculite ores to about 900°C will result in expansion of the ore into the well-known, highly exfoliated commercial packing material. However, the high temperature also causes a loss in ion exchange capacity of the vermiculite. In our experiments, we hoped to expand the vermiculite at lower temperatures thereby obtaining significant expansion but at a minimum loss in exchange capacity. The results are summarized in Table IV.

TABLE IV

Preparation and Adsorption - Thermally Exfoliated Vermiculite

Exfoliation Temperature, °C	Volume of 10 gm (cc)	Ca and Mg Released (meq/100 gm)	Phosphate Adsorbed (mg/gm)
25	10.0	85	7.3
200	10.0	95	7.4
250	10.0	109	6.7
300	10.0	113	7.8
350	10.5	109	8.9
400	11.0	105	8.9
450	13.5	101	8.3
500	15.5	96	8.6
600	24	79	4.8
700	26	30	< 4

As expected, vermiculite expansion increases with temperature. However, the exchange capacity first increases with temperature as the platelets expand, and then decreases at high temperatures as the mobile cations become fixed to the surface. Phosphate adsorption on the other hand, nearly follows the exchange capacity, and is at about the same level as the sodium expanded vermiculites.

In efforts to improve phosphate adsorption the following experiments were carried out:

(1) Reaction with 0.1M $Al(NO_3)_3$ at 60^oC

Na-expanded Poole vermiculite was reacted with 0.1M $Al(NO_3)_3$ solution at 60^oC instead of room temperature. All other conditions were identical to previous experiments. The results show no significant change over previous experiments, i.e., capacity = 7.4 mg/gm.

(2) Reaction with PO_4 for 70 hours

In order to be certain that PO_4 removal was complete, a sample of pH 3.2 Al-Poole vermiculite was reacted with phosphate solution for 70 hours instead of the usual 18 hours. The phosphate adsorption was 8.3 mg/gm, compared to 7.4 found previously, only slightly higher than the 16 hour test results we are now using.

(3) Use of Powdered Vermiculite

A sample of pH 3.2 treated Al-vermiculite was ground to a fine powder and then reacted with the standard phosphate solution. The phosphate capacity was 6.8 mg/gm (compared to 7.4), showing that an increase in external surface area is not significant, and that internal surface area may be more important.

(4) Use of a Mixed Al-Fe Vermiculite

A mixed Al-Fe(III) vermiculite was prepared by reacting Na-expanded Poole vermiculite with a 0.1M mixed nitrate solution containing 80% Al and 20% Fe. The mixed vermiculite was then reacted with phosphate solution and its capacity was 6.7 mg/gm, about the same as Al and Fe vermiculites (see below).

USE OF CATIONS OTHER THAN Al

The following cations were exchanged with Na-expanded Poole vermiculite in a manner similar to Al: Fe(III), La(III), Ca(II), Cu(II), Fe(II). These vermiculites were then tested for PO_4 adsorption. The results, summarized in Table V, show no significant improvement over the Al-vermiculite results.

TABLE V

The Use of Cations Other than Al

Cation	pH_i	pH_f	mmoles M/ 100 gm Vm	mmoles Na Released/ 100 gm	Avg. Chg. on M	mg PO_4/ gm Vm	mmoles PO_4/ mmoles M
Fe(III)	1.75	1.79	47.6	127	2.7	5.9	0.13
Fe(III)	2.10	2.02	50.6	127	2.5	6.4	0.13
La(III)	2.98	3.69	---	127	---	4.2	---
Ca(II)	5.31	5.21	47.9	117	---	3.0	0.07
Cu(II)	4.32	3.74	---	127	---	9.4*	---
Fe(II)	3.45	3.12	---	---	---	5.6	---

* PO_4 removal may be due to the formation of $Cu_3(PO_4)_2$.

M represents metal

Vm represents vermiculite

In the copper experiment, a blue precipitate was found in the flask after reaction of the copper vermiculite and phosphate, indicating removal of copper from the vermiculite followed by precipitation. A precipitate was also observed with Ca-vermiculite. However, no precipitates were observed with the trivalent cations, confirming that these ions are held much more strongly than the divalent cations.

REGENERATION

Several regeneration schemes were attempted by both batch and column techniques.

NH_4OH

Batch experiments with various concentrations of ammonia solutions and phosphate-containing vermiculite were set up. The results are summarized in Table VI.

TABLE VI

Batch Regeneration with NH_4OH

Vm* Taken (gm)	NH_4OH Conc. (M)	ml	Initial PO_4 (mg/gm)	PO_4 Removed (mg/gm)	Initial Al** (mg/gm)	Al Removed (mg/gm)
5.00	1.5	100	4.9	4.7	11.7	2.8
5.00	0.75	100	4.9	4.7	11.7	2.3
5.00	0.50	100	4.9	4.7	11.7	2.2
1.00	0.45	20	4.9	4.8	11.7	1.7
1.00	0.375	20	4.9	5.1	11.7	1.7
1.00	0.30	20	4.9	4.7	11.7	1.3
1.00	0.15	20	4.9	3.2	11.7	0.6
1.00	0.075	20	4.9	0.7	11.7	---

* Vermiculite
** Exchangeable Aluminum

It is apparent that phosphate can be removed from vermiculite with ammonia; however, an appreciable quantity of aluminum is also lost.

Some of the vermiculite that had been ammonia treated was recycled with our standard phosphate solution. One sample had been treated with 0.5M and the other with 0.3M NH_4OH. The recycle phosphate capacity was 1.2 and 1.4 mg/gm respectively, indicating that the ammonia treatment had left the vermiculite fairly inert to phosphate. This can be explained by the lost aluminum, and the probable conversion of the aluminum groups to hydroxy-aluminums.

Column regeneration with dilute ammonia solution was also tried, but these results appeared to be no more promising than the batch results, so all work with NH_3 regeneration was terminated.

HCl

In order to avoid formation of hydroxy-aluminum groups, regeneration was tried with HCl. The results of preliminary batch experiments are summarized in Table VII.

TABLE VII

Batch Regeneration with HCl

Vm* Taken (gm)	HCl Conc. (M)	ml	Initial PO_4 (mg/gm)	PO_4 Removed (mg/gm)	Initial** Al (mg/gm)	Al Removed (mg/gm)
1.00	0.032	20	4.9	3.2	11.7	1.1
1.00	0.020	20	4.9	1.9	11.7	---
1.00	0.010	20	4.9	0.9	11.7	---
1.00	0.002	20	4.9	0.5	11.7	---

* Vermiculite
** Exchangeable Aluminum

It is apparent from these results that either larger quantities or more concentrated HCl will be needed to obtain sufficient phosphate removal. Also, the loss of aluminum will be a problem.

Column regeneration was tried with 0.032, 0.05 and 0.08M HCl, and the results showed again that more concentrated HCl would be required and that appreciable Al was being lost.

Various Salts

To avoid extreme acidity (or alkalinity), and consequently the loss of aluminum, batch experiments were set up with a variety of salts. Our aim was to remove phosphate by replacement with the salt anion. The results are summarized in Table VIII.

TABLE VIII

Regeneration with Various Salts

Salt Added	Conc.* (M)	ml	pH	gm Vm	Initial PO_4 (mg/gm)	PO_4 Removed (mg/gm)
NaCl	1.0	100	5.7	1.00	5.8	0.3
$NaHCO_3$	1.0	100	8.0	1.00	5.8	0.9
$AlCl_3$	0.33	100	3.0	1.00	5.8	1.5
Na_2SO_4	1.0	100	8.4	1.00	5.8	0.6
$Al_2(SO_4)_3$	0.33	100	2.9	1.00	5.8	3.2

* All 1M in anion concentration.

The most promising of the salts was $Al_2(SO_4)_3$, and this may be due in part to the low pH. However, the sulfate salts were all more promising than the corresponding chlorides, probably because of complexing between sulfate and aluminum. A possible advantage of using an aluminum salt for regeneration would be the prevention of aluminum losses by the vermiculite.

The experiment with $Al_2(SO_4)_3$ regeneration was repeated at lower pH values. (H_2SO_4 was used for pH adjustment). These results, summarized in Table IX, show improved phosphate removal at lower pH.

TABLE IX

Batch Regeneration with $Al_2(SO_4)_3$

Vm Taken (gm)	pH	Initial PO_4 (mg/gm)	PO_4 Removed (mg/gm)
1.00	2.5	5.8	4.2
1.00	2.0	5.8	5.2
1.00	1.5	5.8	5.4

The vermiculite sample that had been treated at pH 1.5 was water-washed and recycled with our pH 7 phosphate solution. Its capacity was 8.1 mg/gm, which agrees with previous values for an Al-vermiculite. This test showed that $Al_2(SO_4)_3$ treated vermiculite can be recycled for further phosphate removal.

$Al_2(SO_4)_3 + H_2SO_4$

Experiments were first tried with H_2SO_4 alone. As with HCl, these tests showed significant loss of aluminum from the vermiculite. Column experiments were then set up with solutions of $Al_2(SO_4)_3$ plus H_2SO_4 as the regenerant. The phosphate-containing vermiculite was placed in a 25-ml burette. Flow rates were controlled with fine control metering valves. The effluent was collected in 5-ml portions and each was analyzed for PO_4. After passage of the final portion of regenerant, the vermiculite was water-washed, air-dried and tested for phosphate removal by our standard test using pH 7 phosphate solution.

The results, summarized in Table X, show that a pH of about 0.9 is needed for complete regeneration. In addition, the material can be recycled for further phosphate removal. In fact, the recycle capacity is greater than the initial capacity. This result is not yet fully understood, but our experiments show that it is not due to insufficient removal of excess aluminum. The increase seems to be a result of either the low pH or the presence of $SO_4^{=}$ rather than NO_3^-.

WORKING CAPACITY OF Al-VERMICULITE

Up to this point, all PO_4 capacities were determined by a batch procedure using relatively concentrated PO_4 solutions. It was therefore necessary to determine the actual working capacity of Al-vermiculite with dilute PO_4 solutions in a column operation.

A column containing 4 grams of Al-vermiculite was prepared, and a 23.6 ppm PO_4 solution at pH 7 was passed through at a rate of 0.76 cc/min. The effluent was collected and analyzed for phosphate. The results showed that only 26.7% of the phosphate was removed from the first 100 ml of effluent, and 16.9% from the second 100 ml. The run was stopped, and the column washed with H_2SO_4-$Al_2(SO_4)_3$ regenerant. The dilute phosphate solution was again passed through the column, but only 14.4% of the phosphate was removed from the first 100 ml of effluent.

To be certain that the problem was not one of bicarbonate competition, the solution was boiled to remove CO_2. The cooled solution was passed through a fresh column, and PO_4 removal from the first 100 ml of effluent was 33.2%, just slightly better than the previous run.

TABLE X

Column Regeneration with H_2SO_4 - $Al_2(SO_4)_3$

Conc. H_2SO_4 (ml/100)	$Al_2(SO_4)_3 \cdot 18\ H_2O$ (gm/100)	pH	Vm* (gm)	Bed Ht. (cm)	Bed Vol. (cc)	Flow Rate (cc/min)	Initial PO_4(mg)	Total PO_4 Removed (mg)	Total Vol. Regenerant (cc)	PO_4 Adsorbed on Recycle (mg/gm)
0.96	0.833	0.7	4.0	7.7	4.7	0.3	21.8	21.9	60	9.7
0.86	0.833	0.75	4.0	7.8	4.7	0.3	21.8	22.3	60	9.6
0.80	0.833	0.8	4.0	7.8	4.7	0.3	21.8	22.0	60	9.5
0.66	0.833	0.9	4.0	7.8	4.7	0.15	21.8	21.4	50	10.3
0.58	0.416	0.9	4.0	7.7	4.7	0.15	21.8	20.8**	50	8.5
0.57	0.208	0.9	4.0	7.7	4.7	0.15	21.8	20.9	50	8.4
0.53	0.416	0.95	4.0	7.8	4.7	0.15	21.8	21.1	50	9.0

* Vermiculite
** Initial flow rate for first 15 cc was about 0.23 ml/min, and is probably the cause of this low value

Batch experiments were set up to determine the phosphate capacity of Al-vermiculite in dilute solution. A one-gram sample of Al-vermiculite was reacted with 500 ml of the 25 ppm PO_4 solution for 16 hours. The phosphate capacity was 0.4 mg/gm, indicating that the problem in the column experiments was one of low capacity at low phosphate concentrations. The experiment was repeated at 100°C, and no improvement in capacity was obtained, showing that the problem was not one of slow kinetics.

Finally, an adsorption isotherm was obtained by reacting one-gram samples of Al-vermiculite with a series of phosphate solutions. The results, plotted in Figure 1, show a typical adsorption isotherm, which results in a straight line when plotted as 1/c vs 1/x (Langmuir[5] - Figure 2) or log c vs log x (Freundlich[6] - Figure 3), where c = solution concentration and x = solid concentration. Unfortunately, the adsorption at low concentrations drops off very sharply, i.e., the equilibrium constant for the reaction:

$$\text{Al-Vm} + PO_4^{-3} \rightleftarrows \text{Al-Vm-}PO_4$$

is relatively low, and the material is therefore impractical as a PO_4 adsorbent.

ECONOMIC EVALUATION

During the course of the investigation, a cost estimate was made of a phosphate removal process using Al-vermiculite. The evaluation was made on the following initial parameters which were thought to be applicable at that time:

- A PO_4 capacity of 10 mg/gm
- An attrition rate of 3% per cycle
- Ammonia regeneration requiring 47 moles of NH_3 per one mole of PO_4

It later became apparent that the material could not be regenerated with ammonia. However, the use of H_2SO_4 plus $Al_2(SO_4)_3$, might be more economical.

The cost estimate, plus an earlier one made prior to the study are included in Appendices A and E.

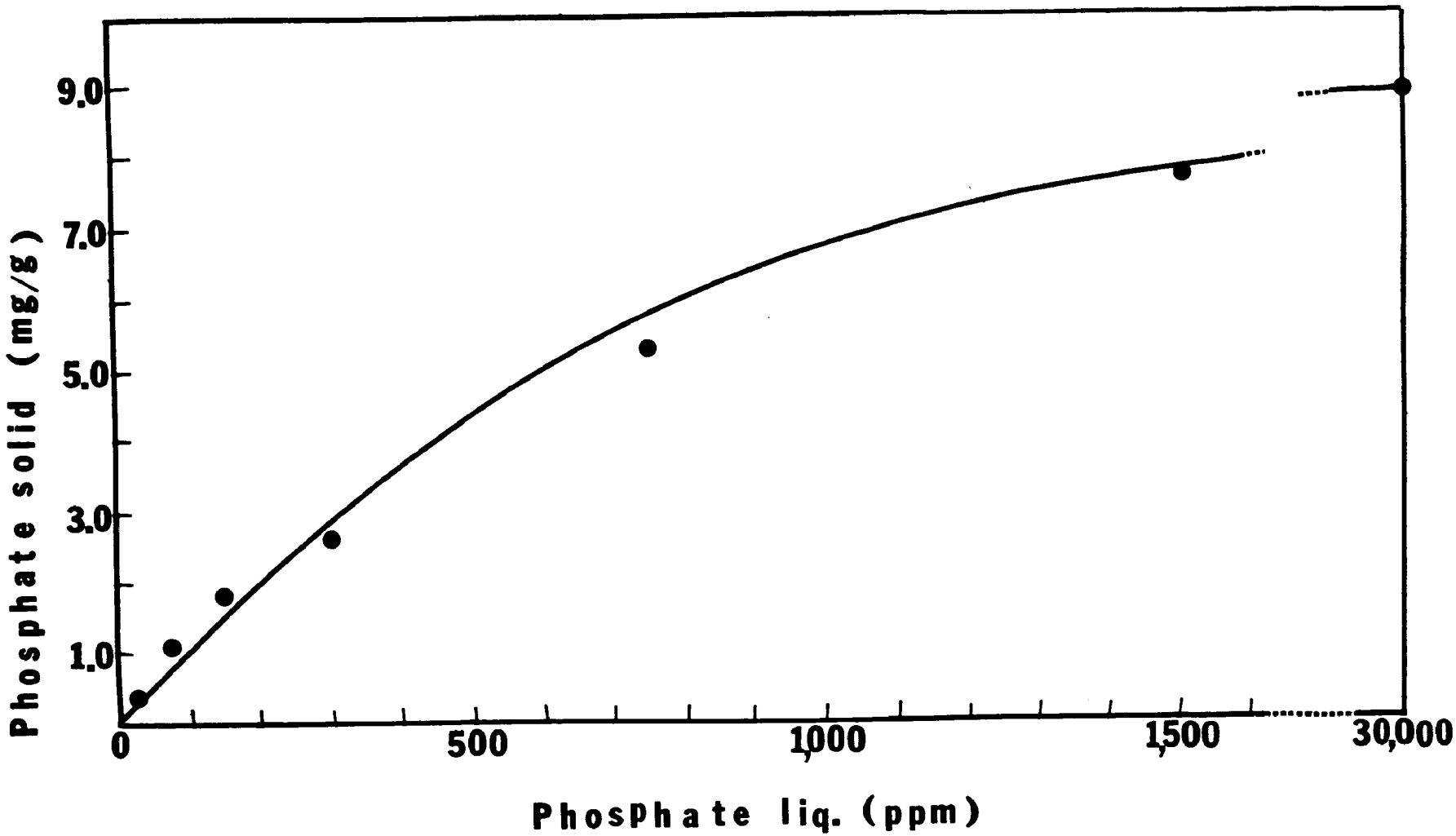

Figure 1

Adsorption Isotherm, Al-Vermiculite + PO_4

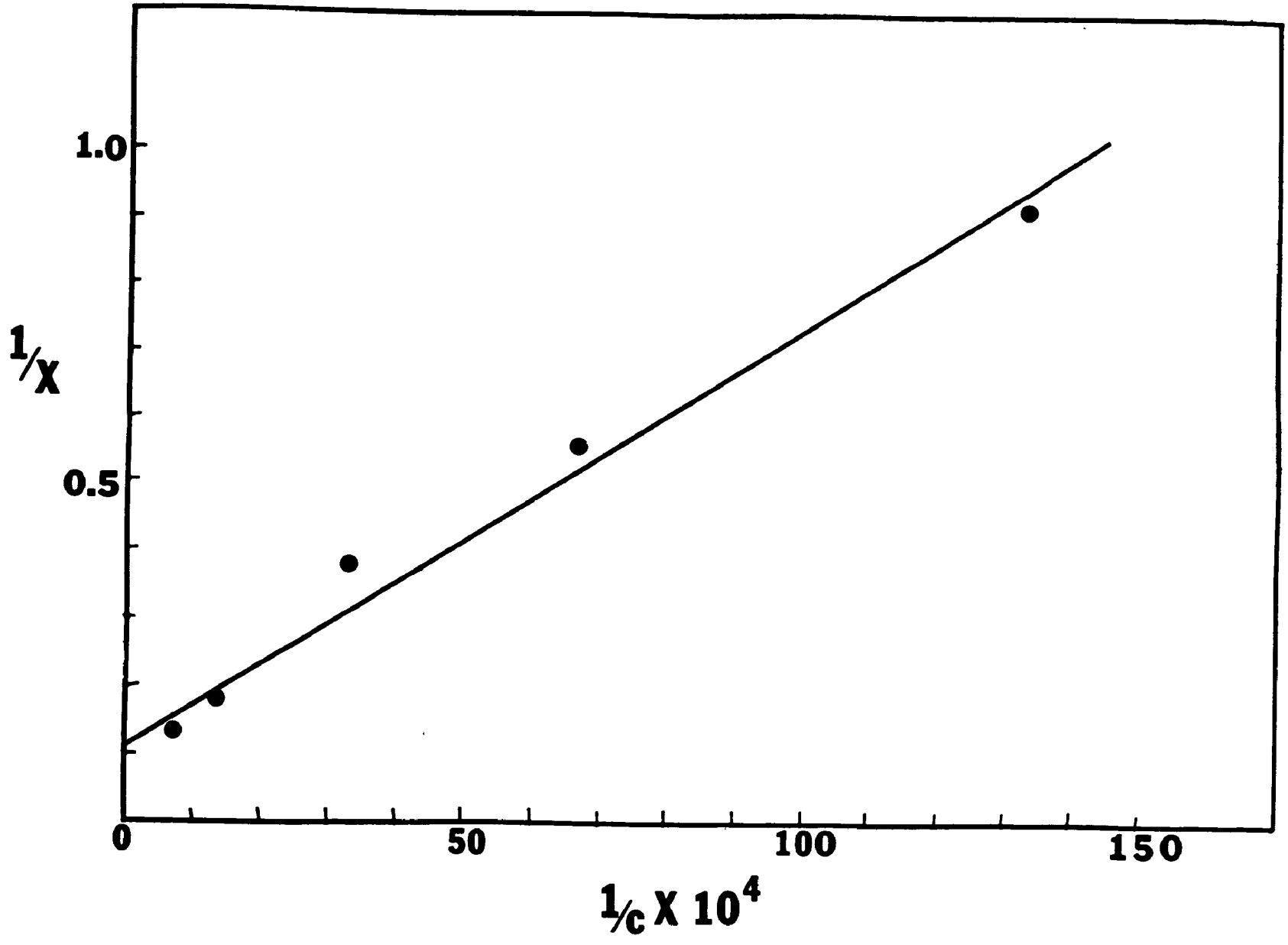

Figure 2

Langmuir Plot

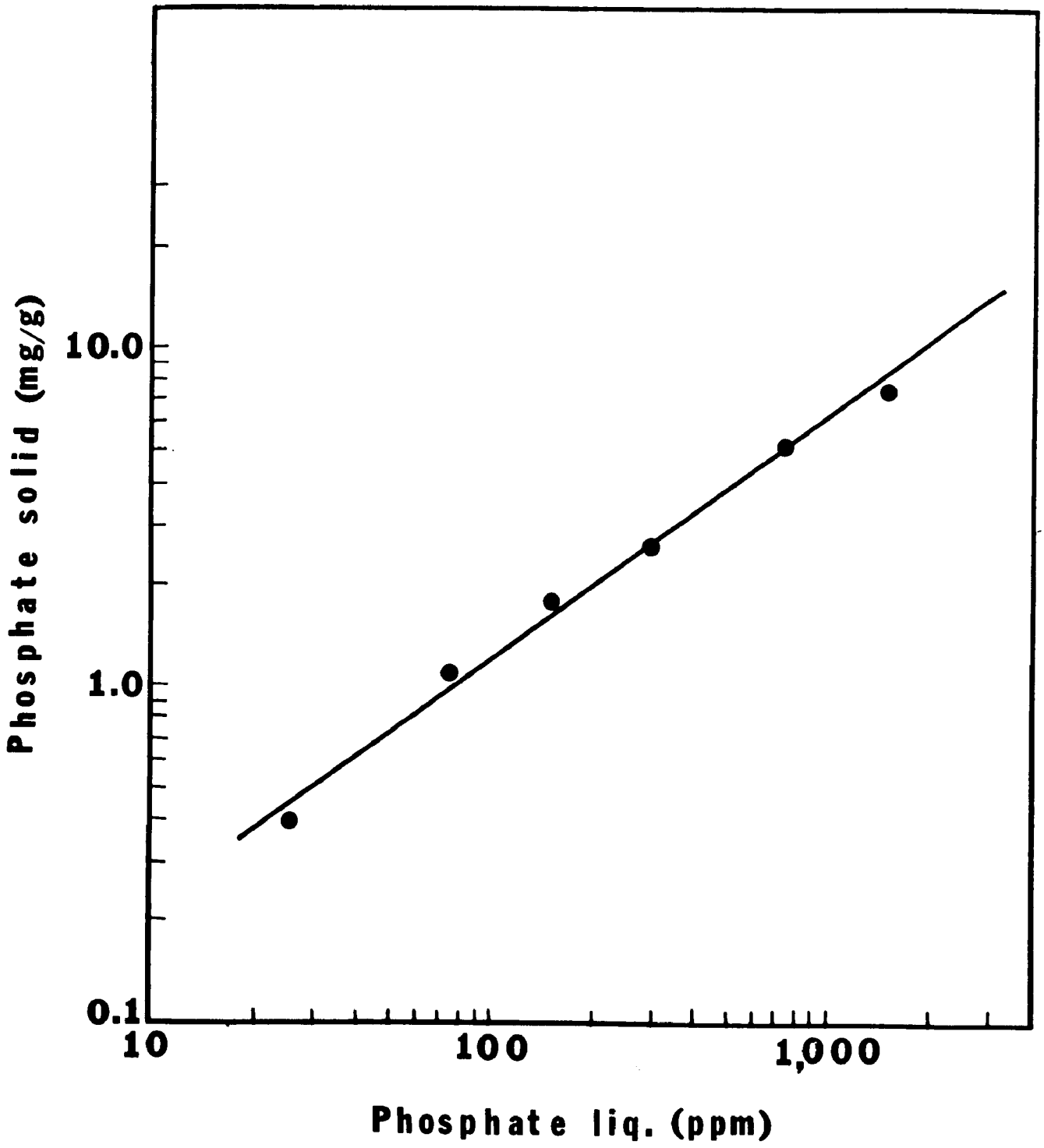

Figure 3

Freundlich Plot

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APPENDIX A - ECONOMIC EVALUATIONS

COST ESTIMATE - PO_4 REMOVAL WITH VERMICULITE 6/11/69

by R. J. Bettacchi

SUMMARY

You have requested a revision in the cost estimate for phosphate removal from waste water using an aluminum treated vermiculite.

A base case was established based on the information in the original estimate (DeCicco 2/28/68). The data and assumptions for the base case are appended (Appendix B). Using these data and assumptions, the cost of treating 1000 gallons of water (25 ppm PO_4 influent - 2.5 ppm effluent) was determined and the results were analyzed to determine the important variables.

The results of the analysis (Basis: 1,000 gallons of water treated) are listed below:

- For the base case the cost to remove the phosphate is 14¢/thousand gallon.

- Nearly 75% of the cost is contributed by the raw materials (vermiculite make up 30%, ammonia regenerant 45%).

- The cost of the vermiculite make up is determined by -

  1. The assumed percentage loss per cycle,

  2. the capacity of the vermiculite,

  3. the price of the vermiculite.

- The regenerant cost is the most critical variable and this cost is dependent upon -

  1. The lbs/ft^3 of NH_3 required to regenerate,

  2. the capacity of the adsorber.

- The other operating costs and the fixed capital investment are dependent on -

  1. The vermiculite bed depth,

  2. the volumetric flow rate through the bed (GPM/ft^3).

- All raw material costs are directly proportional to the amount of PO_4 removed.

We can conclude from these results that if further work is to be done on this project, it must be directed towards determining -

1. The operational capacity of the vermiculite,

2. the operational regeneration level,

3. an accurate estimate of the vermiculite loss per cycle.

DISCUSSION

Capital Cost

In order to determine the cost of removing phosphate from wastewater, with an aluminum treated vermiculite, a treatment system was designed based on the data and assumptions in Appendix B. The design calculations are shown in Appendix C and indicate that the system (under base case conditions) will require nine columns, each 11 ft diameter with a bed depth of 5 ft of vermiculite. The columns will operate in a 15-hour cycle (11 to exhaust and 4 to regenerate) with an average flow of 2.44 GPM/ft^3.

The capital was estimated for this system and is summarized in Appendix D. The capital estimate is dependent on the assumptions of volumetric flow rate and bed depth as shown in the following Table A-1.

TABLE A-1

Capital Cost ($M)

Bed Depth (Ft)	Flow Rate (GPM/Ft^3) 1.73	2.44	4.1
2	908	685	492
4	688	534	361
6	604	470	340

Although the capital estimate will vary between 340 and 900 $M, these variables are not critical as the operating cost is relatively unchanged with these fluctuations.

Operating Cost

Based on the information known about vermiculite and on the assumptions in Appendix B, an operating cost summary was calculated for the base case and is shown in Table A-2. As the results in this table show, the greatest cost is contributed by the raw material components with the ammonia regenerant contributing about 45% of the cost and the vermiculite make up contributing 30%. Examination will show that a 100% increase in the fixed capital would result in only a 7.5% increase in the operating cost.

TABLE A-2

Operating Cost Summary Base Case

Direct Operating Cost		¢/Thousand Gal.
Raw Materials		10.3
Vermiculite make up	4.1	
Ammonia @ 4¢/lb. delivered	6.2	
Direct Labor	1 man-shift/12 units @ 4 shifts/day $30/day	0.9
Indirect Labor	40% D.L.	0.4
Maintenance	1% of Capital	0.2
Utilities	1¢/kwh, 7430 kwh	0.7
Supplies		0.1
	TOTAL DIRECT OPERATING COST	12.6
Overhead Operating Cost		
G & A	30% of D.L.	0.3
Debt Service (Amortize @ 5% for 25 years)		1.1
Taxes and Insurance	2% of Capital	0.4
	TOTAL OVERHEAD COST	1.8
TOTAL OPERATING COST		14.4

SENSITIVITY ANALYSES

Sensitivity analyses were performed to determine what assumptions and variables affected the raw material cost. The cost of the vermiculite make up is summarized in Figure A-1. Examination of this figure shows that the cost of the vermiculite make up is highly sensitive to the capacity of the vermiculite and to the assumption of what the loss/cycle will be. The cost is less sensitive to the price of vermiculite (over the range of prices the operating cost varies 2¢/thousand gal.).

A second sensitivity analysis was performed to show the effect of the regeneration level (which is the largest cost component) on the cost. This is shown in Figure A-2. As this figure shows, the regeneration cost is dependent on the NH_3 usage per cycle and on the capacity of the vermiculite.

GENERAL

The most critical variable in the system is the capacity of the vermiculite. Both raw material cost components are inversely proportional to the capacity. Since the regeneration costs and the vermiculite make up costs are calculated per cycle, and since the volume of water treated per cycle is dependent on the capacity, the cost/thousand gallons is dependent on the capacity. This is important since the Base Case capacity is the total capacity of the vermiculite which may be greater than the column or operational capacity.

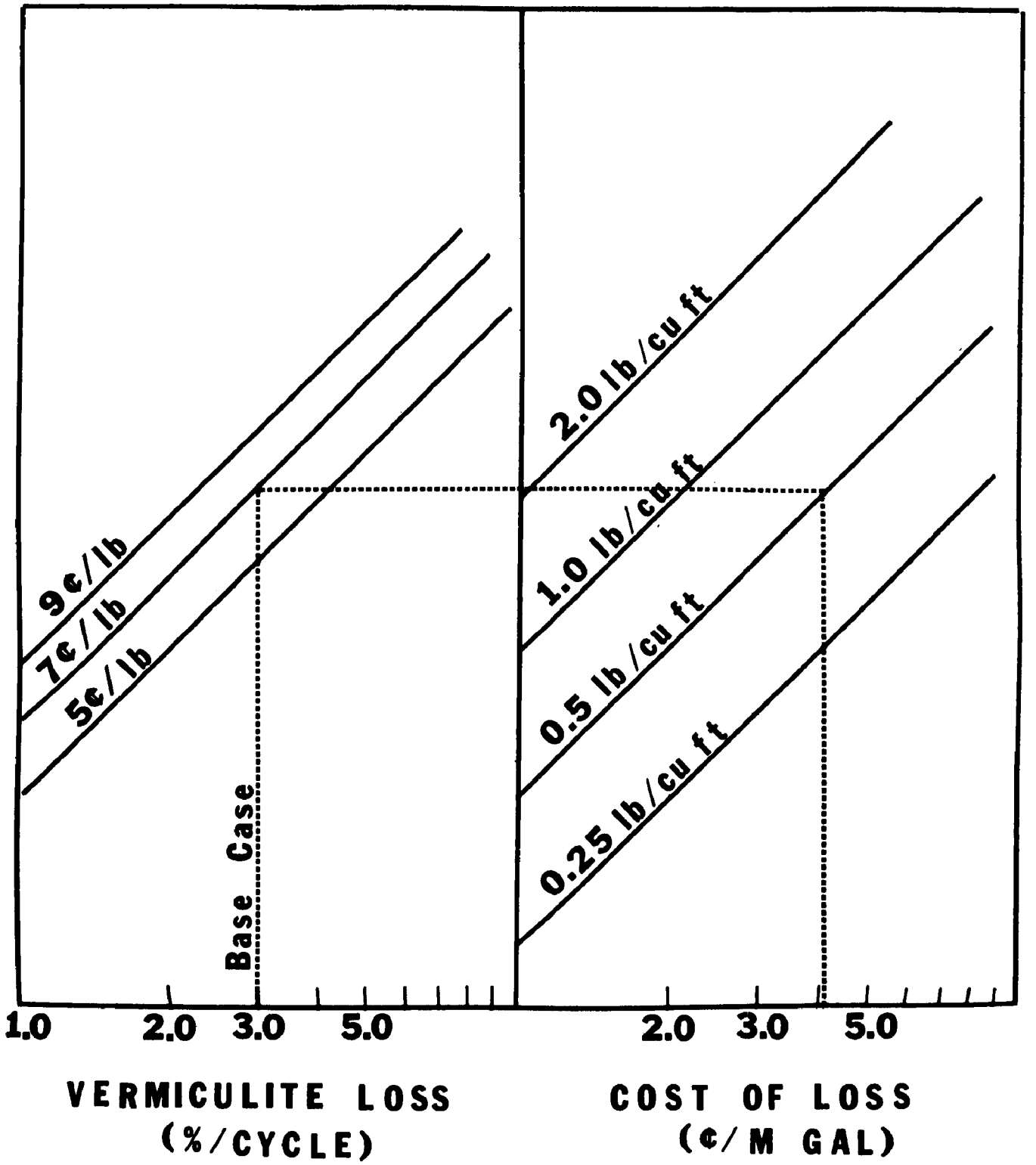

Figure A-1
Cost of Vermiculite Make-up

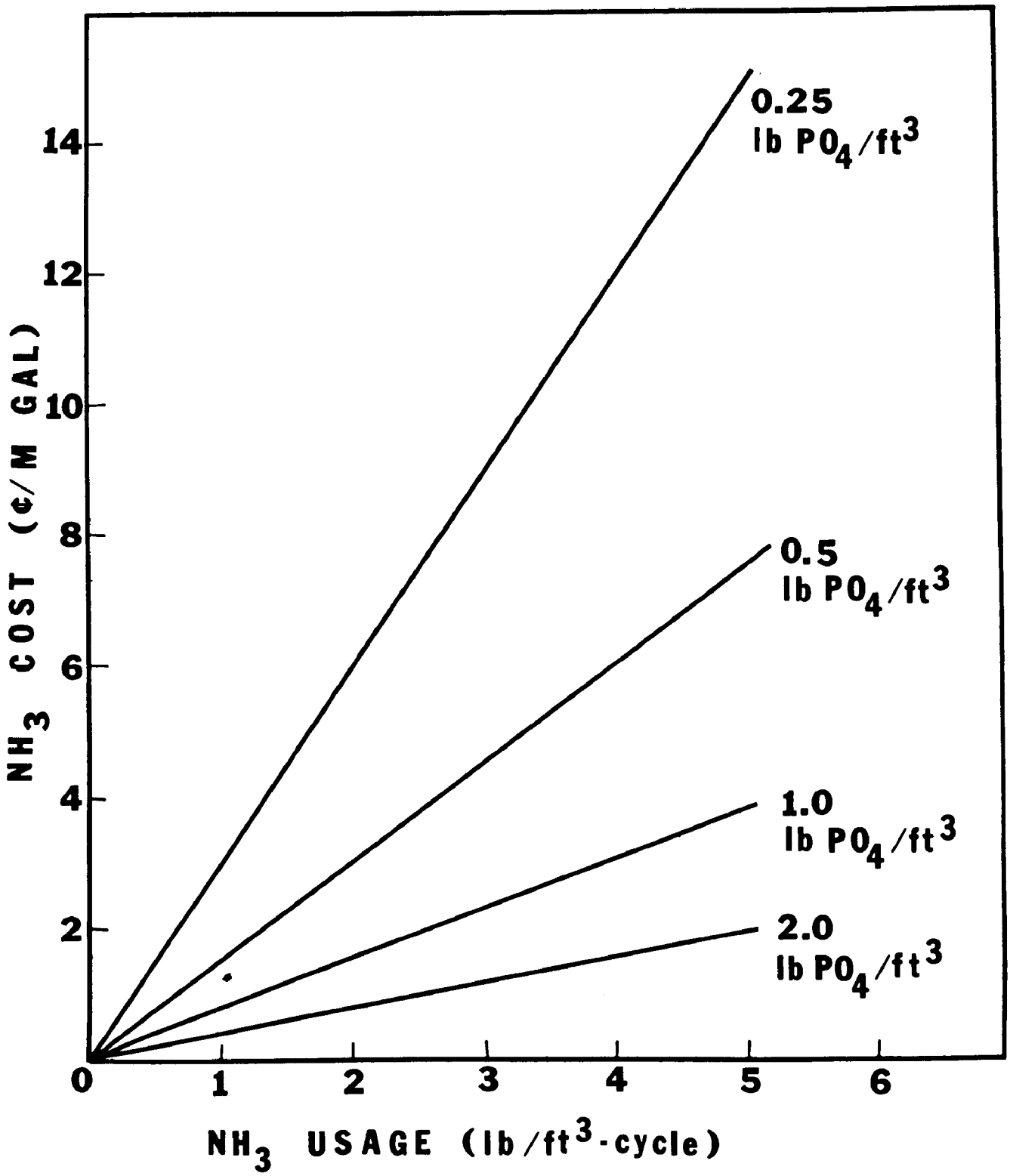

Figure A-2
Cost of Regeneration

APPENDIX B

Assumptions and Data for Calculations

A. Plant Information (Original Estimate)

1.	Capacity	10MM GPD
2.	PO_4 Influent	25 ppm
3.	PO_4 Effluent	2.5 ppm

B. Vermiculite Information (Your Memo of 5/27/69)

1.	Density	0.83 gm/cc
2.	Capacity	0.5 $\#PO_4/ft^3$
3.	Regeneration Level	4.15 $\#NH_3/ft^3$

C. Design Assumptions

1.	Regeneration Time	4 hrs
2.	Tower Diameter	11 ft

D. Assumed Variables

Variable	Range	Base Case
1. Attrition Rate	0-5% per cycle	3% per cycle
2. Vermiculite Price	5-9¢/lb	7¢/lb
3. Bed Depth	2-6 ft	4 ft
4. Volumetric Flow Rate	1.5 - 5.0 GPM/ft^3	2.44 GPM/ft^3

E. Rationale or Source for Assumed Variables

1. Attrition Rate - our conversation 6/6/69.
2. Price - based on DeCicco's memo of 2/28/68 giving price @ 8.7¢/lb and assumptions that a different method of manufacture could lower the price.
3. Bed Depth - based on knowledge that almost all ion exchange beds are in range of 2-6 ft with most at 4 ft. Depth is determined by pressure drop and kinetic considerations.
4. Flow Rate - our conversation of 6/6/69.

APPENDIX C

System Design

Flow Rate = 10^7 GPD = 6950 GPM

Volume of Vermiculite

$$= 6950 \text{ GPM} \div 2 \text{ GPM/ft}^3 = 3475 \text{ ft}^3$$

Volume per Tower

$$= \left(\frac{11 \text{ ft diameter}}{4}\right)^2 \times \pi \times 4 \text{ ft deep} = 390 \text{ ft}^3\text{/tower}$$

No. of Towers

$$= 3475 \text{ ft}^3 \div 390 \text{ ft}^3\text{/tower} = 9$$

Flow Rate per Tower

$$= 6950 \text{ GPM} \div 9 \text{ towers} = 773 \text{ GPM/tower}$$

PO_4 Removal per Tower - hr

$$= 773 \text{ GPM/tower} \times 60 \text{ min/hr} \times 8.34 \text{ lb/gal} \times 22.5 \text{ lbs}/10^6 \text{ lb} = \frac{8.7 \text{ lb } PO_4}{\text{tower - hr}}$$

PO_4 Removal per Tower-Cycle

$$= 0.5 \text{ lb/ft}^3 \times 390 \text{ ft}^3 = 195 \text{ lbs/tower cycle}$$

Cycle Time

$$= 195 \text{ lbs/cycle} \div 13 \text{ lbs/hr} = 15 \text{ hrs/cycle}$$

Flow Rate

$$= 2 \text{ GPM/ft}^3 \times \frac{15 \text{ hrs}}{(15-4 \text{ hrs})} = 2.44 \text{ GPM ft}^3$$

APPENDIX D

Capital Cost Estimate

Vermiculite Towers, 9 @ $27,000 (Chem. Engr. 12/6/65) 390 ft^3 tower, rubber lined carbon steel	$243,000
Blowdown Tank for Regenerant Effluent 95M gal, 5 days storage	23,200
Water Feed Pumps, 4 @ $3500 2,000 GPM, iron and bronze	14,000
Motors for Water Pumps, 4 @ $2800 100 HP enclosed	11,200
Transfer Pump 400 GPM Iron and bronze	900
Motor for Pump, 15 HP	900
Total Installed Equipment Cost (IEC)	$293,000
Instrumentation - (Chem. Engr. 12/6/65)	77,000
Piping - 5% of IEC	14,700
Electrical - 5% of IEC	14,700
Service Facilities and Buildings, 10% of IEC	29,300
Total Physical Cost	$428,900
Engineering and Construction, 10% TPC	42,900
Direct Plant Cost	$471,800
Contingency, 10% of DPC	47,200
Fixed Capital	$519,000
Vermiculite Charge 3475 ft^3 @ $3.64/$ft^3$	12,600
Total Fixed Capital	$531,600
Working Capital, 4% Fixed	20,000
Total Capital	$551,600

APPENDIX E

Cost Estimate of Phosphate Removal from Wastewater with an Aluminum Treated Vermiculite 2/28/68

by Robert DeCicco

I. Summary and Conclusions

The cost of a phosphate removal process utilizing aluminum treated vermiculite as the exchange resin has been estimated. The purpose of the estimate was to provide research guidance by establishing the economics of a "speculative" water treating system and to identify the factors controlling the economics of the system. The results of the cost estimate may be summarized as follows:

Step 1 - Conversion of vermiculite ore to aluminum vermiculite

Production	-	4,000 lb/day
Total Operating Cost	-	8.7¢/lb
Capital Investment	-	$99,600

Fixed	-	$93,600
Working	-	6,000

Step 2 - Treatment of water with aluminum vermiculite to remove phosphate and regeneration of vermiculite with ammonia.

Plant Capacity	-	10MM gal/day
Total Operating Cost	-	10.7¢/M gallons
Capital Investment	-	$910,000

Fixed	-	$880,000
Working	-	30,000

The following major conclusions were drawn from the analysis:

A. Ore Processing

1. With the exception of direct labor, the raw material cost of the vermiculite ore is the major cost component of the ore processing step. This is primarily the result of the assumed 25% ore loss. The high direct labor cost (¢/lb basis) is due to the relatively low production volume and long retention times which require two-shifts-per-day operation.

2. The large volume of water necessary for washout of the $Al_2(SO_4)_3$ and NaCl (2.4 gal/lb vermiculite for each step) requires the reaction vessel be of sizeable proportions. Reduction of the water requirement would reduce the volume of the vessel and thereby lower the fixed capital. Also, the wash water effluent (~ 20,000 gal/day) may be a disposal problem in itself if it cannot be discharged into the river. Should be be the case, an evaporator system would be needed to purify the water such that it can be either recycled or dumped.

B. Water Treatment and Vermiculite Regeneration

1. The cost of make-up vermiculite accounts for 30% of the total operating cost. The vermiculite loss is a function of the following three interdependent variables:

a. Flow rate of water per unit volume of vermiculite.

This variable determines the volume of vermiculite charged to all towers - V_t.

b. Exchange capacity of vermiculite. This variable determines the number of cycles per day - C_d.

c. Vermiculite loss per cycle - L_c.

The loss per day is then: $L_d = V_t \times C_d \times L_c$ (ft^3 vermiculite). Cost of make-up vermiculite: $C_d = L_d \times$ Unit Cost ($/day).

These relationships point out the need for better establishing the physical and chemical properties of the system. An error in any one of the variables will lead to erroneous conclusions regarding the make-up vermiculite cost.

2. For the system considered, the controlling variable for both the vermiculite loss and process design is the flow rate of water per unit volume of vermiculite (1.17 gpm/ft^3). Although this value is not unreasonable, it is somewhat low from information available in the literature. If the flow rate could be increased without adversely affecting the exchange capacity or loss per cycle, the following would result:

- Reduction in volume of vermiculite charged. This, in turn, would reduce both the vermiculite loss and the fixed capital as smaller towers could be used.

- Increase the flow rate per tower cross sectional area and thereby reduce the number of towers required.

3. The vermiculite exchange capacity determines the number of days per cycle, where a cycle is defined as the time for regeneration plus the time for adsorption. To determine the number of towers required, it is

necessary to know either the time for regeneration or the time for adsorption. This analysis assumed the cycle time was divided equally between the two steps. Consequently, for every adsorption tower there must be a tower for regeneration.* As the cost of the towers represent the most significant part of the fixed capital, the cycle time split must be determined if a more accurate cost estimate is desired.

4. The by-products of ammonia formed during regeneration of the vermiculite may have some resale value. No value has been considered in this analysis.

The process specifications upon which the cost estimate was based are provided in Section II of this report. The detailed economics are shown in Section III. A breakdown of fixed capital investment for both ore processing and water treatment-regeneration is provided in Appendix F.

II. Process Specifications - 10MM GPD Wastewater Treatment for Phosphate Removal

A. Ore Processing

Ore Processing Loss - 25%

NaCl Treatment (20% solution) - 9.2 lb NaCl/100 lb ore

$Al_2(SO_4)_3$ Treatment (16.7% solution) - 20 lb $Al_2(SO_4)_3$/100 lb vermiculite

Washout of NaCl - 240 gal/100 lb vermiculite

Washout of $Al_2(SO_4)_3$ - 240 gal/100 lb vermiculite

Retention Time - 3 hours mixing for each step

Temperature - ambient for each step

B. Phosphate Adsorption and Regeneration of Vermiculite

$[PO_4^{-3}]$ in influent water - 25 ppm

$[PO_4^{-3}]$ in effluent water - 2.5 ppm

Exchange capacity of vermiculite - 4.15 lb PO_4/ft^3- cycle

Bulk density of vermiculite - 1.33 g/cc

Water Flow Rate/volume of vermiculite - 1.17 gpm/ft^3

Water Flow Rate/$\bar{x}$ sectional area of towers - 11.7 gpm/ft^2

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* The second tower would be used for absorption of phosphate while the charge in the first tower is regenerated.

Vermiculite Bed Height/Tower	10 ft
Tower Diameter	10 ft
Total Volume of Vermiculite Charged	11,870 ft^3
Volume of Vermiculite/Tower	742 ft^3
Number of Towers	16
Cycles/Day/Tower	13.2 days
Cycle Time/Tower	13.2 days
Adsorption and Draining - 6.6 days	
Regeneration and Wash - 6.6 days	
Vermiculite Loss/Cycle	5%
Vermiculite Loss/Tower/Day	0.38%
Total Vermiculite Loss/Day	45.1 ft^3
Vermiculite Turnover	263 days
Water/Vermiculite Contact Time	6.4 minutes
Volume of Vermiculite Regenerated/Day	899 ft^3

Ammonia Regenerate Required (3% solution) - 4.15 lb NH_3/ft^3 vermiculite

Wash Water Required - 100 gal/ft^3 vermiculite

III. Detailed Economics

A. Ore Processing - Operating Cost for 4M lb/day Production of Vermiculite

Direct Operating Cost	¢/lb Vermiculite
Raw Materials	2.1

Ore @ 0.8¢/lb f.o.b. - 1.06¢/lb verm.
NaCl @ 1.25¢/lb delivered - 0.15¢/lb verm.
$Al_2(SO_4)_3$ @ 3.81¢/lb delivered - 0.76¢/lb verm.
Water at 25¢/M gallons - 0.14¢/lb verm.

Direct Labor - 4 men/day @ $30/man-day	3.0	
Payroll Extras - 15% of Direct Labor	0.5	
Maintenance - 5% of Direct Capital/Year	0.3	
Utilities - 1790 kwh @ 1¢ kwh	0.4	
Supplies - 50% of Maintenance	0.2	
Ore Freight - 0.5¢/lb ore	0.7	
Total Direct Operating Cost		7.2

Overhead Operating Cost

General and Administrative Expense - 30%		
Direct Labor	0.9	
Debt Service (Amortization of Direct Capital @ 4-1/2% over 25 years)	0.4	
Taxes and Insurance - 2% of Direct Capital/yr	0.1	
Interest on Working Capital @ 4-1/2%/yr	0.1	
Total Overhead Operating Cost		1.5
Total Operating Cost		8.7¢/lb verm.

Direct Capital - $93,000

Working Capital- 6,000
Total Capital - $99,000

B. Water Treatment and Vermiculite Regeneration - 10MM GPD Direct Operating Cost

Direct Operating Cost		¢/Thousand Gallons
Raw Materials		
Vermiculite Make-up, 45.1 $\frac{ft^3}{day}$ @ $7.18/ft^3	- 3.2¢/M gal	
Ammonia at 4¢/lb delivered	- 1.4¢/M gal	4.9
Water at 25¢/M gal	-0.3¢M gal	
Direct Labor - 6 men/day @$30/man-day		1.8

Payroll Extras - 15% of Direct Labor	0.3	
Maintenance - 1% of Direct Capital/Year	0.2	
Utilities - 7430 kwh @ 1¢/kwh	0.7	
Supplies - 50% of Maintenance	0.1	
Total Direct Operating Cost		8.0

Overhead Operating Cost

General and Administrative Expense - 30% of Direct Labor	0.5	
Debt Service (Amortization of Direct Capital @ 4-1/2% over 25 years)	1.6	
Taxes and Insurance - 2% of Direct Capital/yr	0.5	
Interest on Working Capital @ 4-1/2%/yr	0.1	
Total Overhead Operating Cost		2.7
Total Operating Cost		10.7

Direct Capital - $880,000

Working Capital - 30,000

Total Capital - $910,000

APPENDIX F

Breakdown of Total Capital Requirements

A. Ore Processing - Design Capacity = 5M lb/day of Vermiculite

Item	Installed Equipment Cost
Conveyor for Vermiculite Ore - 24" belt x 50' L	$8,800
Water Pump - 400 GPM, Iron and Bronze	1,120
Motor for Water Pump - 15 HP Enclosed	950
Vermiculite Slurry Pump (Transfer of Vermiculite to Storage) 30 GPM, Iron and Bronze	600
Motor for Slurry Pump - 5 HP Enclosed	360
Vermiculite Slurry Pump (Transfer of Vermiculite to Towers) 30 GPM, Iron and Bronze	600
Motor for Slurry Pump - 5 HP Enclosed	360
Reaction and Wash Vessel - 12M gal, agitated, carbon steel	16,000
Storage Vessel for Vermiculite - 2M gal for two days storage, agitated, carbon steel	7,000
Total IEC	$35,790
Delivery of Equipment - 2% of Purchased Equipment Cost	570
Total IEC Delivered	$36,360
Instrumentation - 18% of IEC	6,550
Piping - 35% of IEC	12,730
Electrical - 20% of IEC	7,270
Service Facilities and Buildings - 40% of IEC	14,440
Total Physical Cost	$77,350
Engineering and Construction - 10% TPC	7,740
Direct Plant Cost	$85,090

Item (cont'd)	Installed Equipment Cost	
Contingency - 10% of DPC	8,510	
Total Direct Fixed Capital		$93,600
Working Capital		
Raw Material Inventory - 30 days @ RMC + Freight	$3,360	
Work-in-Process Inventory - 1 day @ Direct Operating Cost	290	
Finished Vermiculite - 2 days @ Total Operating Cost	690	
Cash - Payroll for one week	1,220	
Total	$5,560	
Say		6,000
Total Capital Investment		$99,600*

* Contains no provision for land site.

B. Water Treatment and Vermiculite Regeneration - 10MM GPD

Item	Installed Equipment Cost
Vermiculite Towers, 16 required @ $29,500	
742 ft^3 bed volume, rubber lined carbon steel	$472,000
Blowdown Tank for Regenerate Effluent	
95M gal for 5 days storage, carbon steel	23,200
Water Feed Pumps, 4 pumps required @ $3,500	
2,000 GPM, Iron and Bronze	14,000
Motors for Water Pumps - 4 required @ $2,800	
100 HP Enclosed	11,200
Transfer Pump for Regenerate Effluent	
400 GPM Iron and Bronze	900
Motor for Transfer Pump, 15 HP Enclosed	950
Total IEC	$522,250
Delivery of Equipment - 2% of Purchased Equipment Cost	8,350
Total IEC Delivered	$530,600
Instrumentation - 5% of IEC	26,500
Piping - 5% of IEC	26,500
Electrical - 5% of IEC	26,500
Service Facilities and Buildings - 10% IEC	53,000
Total Physical Cost	$663,100
Engineering and Construction - 10% of TPC	66,300
Direct Plant Cost	$729,400

Item (cont'd)	Installed Equipment Cost	
Contingency - 10% of DPC	$72,900	
Total Fixed Capital		$802,000
Vermiculite Charge - 11,870 ft^3 @ $7.18 ft^3	85,230	
Total Direct Fixed Capital		$887,530
Say		$880,000
Working Capital		30,000
Total Capital Investment		$910,000*

* Contains no provision for land site.

* U.S. GOVERNMENT PRINTING OFFICE : 1970 O - 405-130