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Chang I. Fung

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A STUDY OF THE REMOVAL OF ALKYL BENZENE SULFONATE BY MEANS OF A COLUMN PACKED WITH SAND COATED WITH FERRIC OXIDE

by

CHANG I. FUNG - 1941

A

THESIS

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Aliss V. Martin (advisor) Wm R Carroll

Waggoner Sotiris G. Grigoropoulos

ABSTRACT

Iron, precipitated in the form of hydroxides on sand particles (-48 + 65 mesh) and stabilized by drying at 100°C for 10 hours, was utilized to remove alkyl benzene sulfonate (ABS) from aqueous solutions. Solutions containing a maximum of 5 mg/l ABS were passed through a glass column packed with treated sand. The ABS formed a complex with the iron precipitants which adhered to the sand particles.

Preliminary work, in which solutions containing 10 mg/l ABS were treated with various concentrations of $FeCl_2$ at the equivalence point (pH about 9.5), verified the fact that ABS could be removed by this type of treatment. The concentration of ABS was reduced from 10 mg/l to a limiting value of 4.5 mg/l by treating 100 ml of the ABS solution with 10 ml of 0.0071 N $FeCl_2$ solution under these conditions.

A glass column (1.5 inch inside diameter), filled to a depth of twelve inches with 516 gm sand treated in three runs with 10, 20, and 40 ml respectively of 0.0071 N $FeCl_2$ solution, was used to evaluate the adsorption of ABS. The quantity of ABS adsorbed from solutions of 5 mg/l ABS, flowing through the column at rates of 100 ml/hr, was proportional to the amount of iron precipitated (0.12 gm ABS/gm iron) on the sand. The removal of the ABS is attributed solely to the influence of the precipitated iron since there was no measurable effects with an untreated column.

The desorption of ABS with water was quantitative in the case of the sands treated with the quantities of iron less than 1.5×10^{-5} gm/gm sand. Approximately one-third of the ABS remained in the complexed form on the sand surface when 3×10^{-5} gm iron/gm sand was used to treat the sand.

The specific resistance (to flow) of the sand increased from 2.87 x 10^7 ft/lb, for the untreated sand, to 3.75 x 10^7 ft/lb, for sand treated with the maximum amount of iron. The specific resistance of the treated sand saturated with ABS was slightly greater than the treated sand free of ABS (3.89 x 10^7 ft/lb maximum).

The techniques utilized in this investigation can be used to evaluate other similar situations.

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I. INTRODUCTION

The pollution of surface waters by toxic materials, both natural and man-made, has been of interest for many years. The cumulative effects associated with the re-use of surface waters for both domestic and commercial purposes as well as related conditions which may develop in natural underground reservoirs is cause for concern at the present time.

The expansion of the synthetic detergent (syndet) market since the end of World War II, to the point where 90 per cent of the washing products used in the American home (over four billion pounds annually) are syndets, is representative of changes contributing to the problem of water treatment and re-use. This problem will become greater in the future(17).

Numerous instances of adverse effects of synthetic detergents on water and waste treatment processes have been observed and reported. The South District Filtration Plant in Chicago has carried out experiments on the quantitative evaluation of a method for removing detergents from water by chemical treatment(22).

Alkyl benzene sulfonate (referred to as ABS) has been one of the ingredients of most synthetic detergents on the market. While it has been recognized that ABS has a low acute oral toxicity, it has produced foaming when present in water to the extent of a few parts per million and has caused difficulty in the re-use of water because of this effect. (3)

The purpose of this investigation was to examine the ability of relatively small quantities of iron, precipitated upon the surface of river sand, to remove ABS at low concentrations from water. This situation resembles the conditions which exist in naturally occuring sands and other mineral deposits. Other objectives were to determine the effects of both the precipitated iron and the ABS upon the permeability of the sand and to examine the conditions under which the ABS could be desorbed from treated sands. The latter objectives may be related to the operation of sand filters.

Although bio-degradable detergents have nearly replaced ABS in household detergents, this study was made using ABS because a supply of ABS was readily available, the results from studies using this sample as well as other results found in the literature were available, and the results of this work would be expected to be similar to those for similar sulfonated materials which are frequently found in wastes.

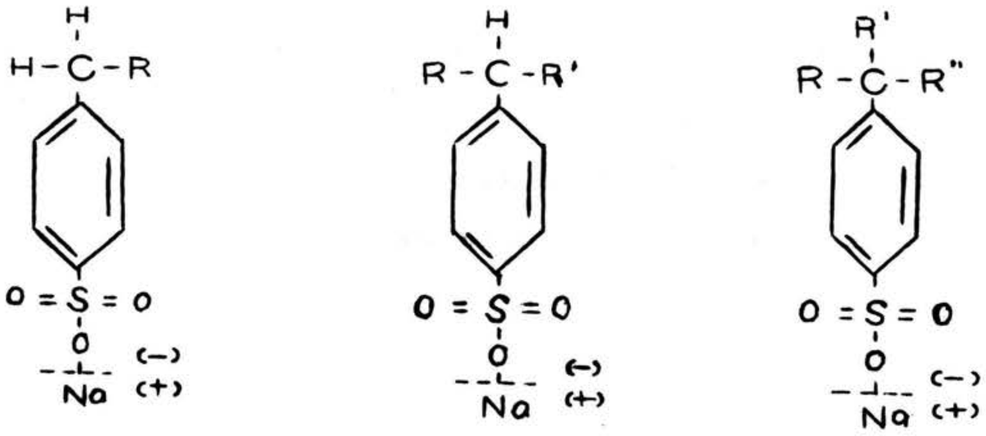
II. LITERATURE REVIEW

A literature search was made to review (1) the characteristics of detergents, (2) the problems related to the treatment of water containing synthetic detergents, (3) the effects of detergents upon equipment used in water treatment plants, and (4) the terminology characteristic to this type of work.

Synthetic Detergents. All synthetic detergents (syndets) contain an organic, surface-active agent (surfactant) which has the important qualities of wetting out, dispersing and emulsifying material characterized as dirt. Unlike soaps syndets are unaffected by salts of calcium and magnesium. This is the principal reason for their wide popularity. In addition to the surface-active material, household detergents may contain additional active compounds, generally called "builders", and typified by complex phosphates and silicates, as well as inert or filler materials. Products formulated to include builder compounds as well as the surface-active agent are known as all-purpose syndets. They are equivalent to soaps in their ability to remove dirt from soiled clothing(18).

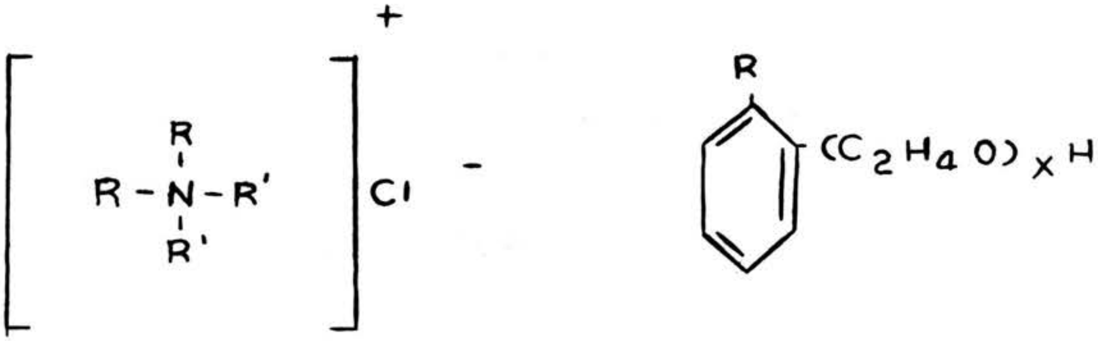
Figure 1 illustrates the method of classifying surfactants into anionic, cationic and nonionic types by their ionization characteristics in water. This figure also shows the three possible forms of the anionic alkyl benzene sulfonate (ABS).

Detergent Related Problems. The American Water Works Association (AWWA), in 1949, initiated a study of detergent related difficulties in water treatment. The results of a study made by an AWWA task Group E5.8 published in 1945(21) defines these problems with respect to quantities present and effective methods of treatment.



Primary Secondary Tertiary

Alkyl Benzene Sulfonates (Anionic)



Typical Cationic Typical Nonionic

FIGURE 1. Structural Formulae of Representative Surfactants (6)

The ORSANCO detergent subcommittee(11) has pointed out that the problems attributed to detergents in the presence of "builders", dispersed material from the laundering process, and other sewage products are different from those which may be postulated and studied using a detergent in pure water. For instance controlled laboratory experiments using sewage free water have shown that coagulation and sedimentation problems are not created by ABS concentrations below 5 mg/1. Sewage treatment equipment, however, is often affected adversely by these low concentrations(16). The water treatment plant at Osawatomie, Kansas, has reported a reduction in filter run time from 100 to 9 hr because of detergents in raw water(5). Laboratory results have shown that ABS concentrations as high as 40 to 50 mg/1 do not contribute to taste or odor. The above committee has stated that people with sensitive tastes can detect ABS at concentrations of 16 mg/1 or less. Various reports substantiate the fact that foaming becomes a problem when the ABS concentration exceeds 5 mg/1.

The Removal of Detergents from Water. The Chicago South District Filtration Plant(22) has evaluated the use of various chemical agents for the removal of ABS. The concentration of ABS was reduced from 20 mg/1 to less than 1 mg/1 by treatment with primary amine acetate (50 lb/$\overline{\text{m}}$ gal) and carbon (1000 lb/$\overline{\text{m}}$ gal). Ferrous sulphate and bentonite were capable of reducing the concentration from 20 mg/1 to 10 mg/1 when additive amounts were 200 lb/$\overline{\text{m}}$ gal and 100 lb/$\overline{\text{m}}$ gal, respectively. Tests were also made to determine the effects of sediment produced in alum and lime-iron water treatment, as well as the effects of various silicates, limestone in various forms and chlorine dioxide. They also showed that while the floc produced in the treatment could effect a pronounced decrease in filtration rates, very little of the decrease could be attributed to the presence of the ABS in the filter unless foaming was a problem.

Conrad(4) in a research study conducted at the Missouri School of Mines and Metallurgy, used different clays (Kentucky ball clay, Georgia Kaolin and Wyoming bentonite) to remove ABS from water. One gram of the clay was added to 300 milliliters of a solution containing 1.5 mg/l of ABS. The mixture was agitated and allowed to settle for 24 hours. The clear supernatant liquid was then removed and analyzed for ABS content. It was found that Kentucky ball clay and Georgia kaolin removed about 64 per cent of ABS, while the bentonite removed approximately 97 per cent.

Daboo(7) and Malik(10) investigated the foam fractionation method for removing ABS from water. They used a Fragergen Laboratories test type flotation machine to examine both raw river water and sewage effluent containing from 1 mg/l to 10 mg/l ABS. They found that between 72 per cent and 84 per cent of the ABS originally present was removed after two minutes operation by foam flotation. Up to 92 per cent of the ABS was removed after 12 to 14 minutes of continuous operation. The optimum range for the air flow rate was between 12 and 27 cubic feet per hour for this particular flotation cell when an inlet rate of 120 milliliters per minute of sewage plant effluent was used. They did not discuss the costs of power and maintenance required for this type of treatment.

Theory of Surface Effects. The problems which result from synthetic detergents in water were shown to be related to their surface active nature. The Double Layer Theory developed by Sern, et al(24) has been discussed extensively in textbooks on colloidal and surface chemistry. This theory recognizes that atoms on the surface of a solid are peculiar because they contribute to both the characteristics of the solids and of the solution surrounding it. Some solids are unaffected by the liquid surrounding them. Large particles of sand fall into this category. However, if the size of the sand particle is reduced by grinding or if a very fine sand product has been obtained by precipitation from the silicate, the surface may be very different. In general, electrostatic and physical forces which are specific for the atomic forms at the surface are used to explain surface effects. For instance, a very slight tendency for sand to hydrate coupled with the polar nature of the water molecule may explain a slightly negative electrostatic charge on the surface of relatively large sand particles. Metals such as iron may dissolve in aqueous solutions as simple cations or become a part of a polar complex, depending upon the presence of anions and the pH.

Sanford and Gates(13) in their discussion of surface effects accepted the fact that ABS exists in solution in an anionic form as illustrated in Figure 1. In their discussion they pointed out that the adsorption of anionic ABS on negatively charged sand surfaces is improbable. They have verified experimentally that ABS may be adsorbed by a positively charged surface such as that present on certain metals. Sanford and Gates(13) have also shown that as the surface of a sand is altered by the presence of an adhering floc, the voids within the bed are modified and the permeability of the sand is decreased.

Characteristics of Sand Filters - Permeability. The quantitative aspects of filtration has been discussed in numerous references. Foust and others(8) have considered the separation of relatively large amounts of solids from a liquid in the filtration process. The build-up of cake during filtration offers the major resistance to flow. Others have been interested in the use of filters to separate trace amounts of solids from large amounts of liquids as in the operation of sand filters in water clarification. Flow through natural "sands" has also been of interest. In the two latter cases the major resistance to flow in operational situations is the sand bed rather than the filtered solids. Attention is focused in this case upon the "openness" or permeability of the sand.

The first group noted that liquid flow is directly proportional to the available pressure drop through the cake and inversely proportional to the resistance in the cake. The following are representative forms of the Carman-Kozeny(8) equation for laminar flow used to characterize these conditions:

$$\frac{1}{A}\frac{dV}{dt} = \frac{\epsilon^3}{5\, S_o^2\, (1 - \epsilon)^2}\, \frac{g_c}{\mu}\, \frac{(-\Delta p)}{(L + L_e)} \tag{1}$$

if $\frac{1}{A}\frac{dV}{dt}$ is defined as V_s and $\frac{5\, S_o^2\, (1 - \epsilon)^2}{\epsilon^3}$ as α, then

$$V_s = \frac{1}{\alpha}\, \frac{g_c}{\mu}\, \frac{(-\Delta p)}{(L + L_e)} \tag{2}$$

This expression is recognized as the Darcy equation for viscous flow of an incompressible fluid through a fixed bed. When the specific resistance (α') is used

$$V_s = \frac{1}{\alpha' (1 - \epsilon) \rho_s}\, \frac{g_c}{\mu}\, \frac{(-\Delta p)}{(L + L_e)} \tag{3}$$

where:

dV/dt = the filtration rate, that is, the volume of filtrate passing through the bed per unit time, ft^3/sec

A = filtration area, ft^2

V_s = superficial velocity of fluid (based on total cross sectional area), ft/sec

g_c = dimensional constant, 32.17 $(lb/lb_f)(ft/sec^2)$

ϵ = bed porosity, fraction of total volume that is void, dimensionless

$-\Delta p$ = pressure drop across the packed bed, lb_f/ft^2

μ = fluid viscosity, lb/ft sec

S_o = specific surface area of particle, ft^2/ft^3 of solid volume

L = height of bed, ft

L_e = height of bed equivalent to resistances other than the sand, ft

α = viscous resistance coefficient, ft^{-2} also $(\text{permeability})^{-1}$

α' = specific bed resistance, ft/lb

ρ_s = solid particle density, lb/ft^3 sand

If the units of the various terms are expressed in the metric system units of permeability $(1/\alpha)$ are darcies. The differential form applies equally well to the constant rate process. Equations 1 and 2 show that the permeability is related to both the fraction of voids and total surface of sand particles in the filter. The literature shows that permeability decreases with increased pressure for compressible sands or cakes. Sands which are uniform in size have permeabilities which are greater than denser aggregate type mixtures. Many test procedures have been developed based upon this type of reproducible information:

Equation 2 is rearranged to show:

$$\frac{dt}{dV} = \alpha \frac{\mu}{g_c(-\Delta p)\ A} (L + L_e) \qquad (4)$$

This form indicates that a plot of the inverse of the flow rate through the filter bed (dt/dV) is proportional to the filter depth (L) if the head of water ($-\Delta p$), filter area (A) and temperature and composition of the liquid (effect on μ) remain constant and if the sand is incompressible (α constant). α is constant at low pressures. This form also serves as a basis for a discussion of methods used to evaluate permeability shown by Foust(8).

The American Foundryman's Association(1) has been instrumental in the development of a formula, similar to equations 2 and 4, to evaluate a permeability index, K, defined as follows:

$$V_s = K \frac{H\ A}{L} \qquad (5)$$

where:

H = the pressure drop through the sand bed, psf.

All of the terms with the exception of K are measured directly. This method assumes that a linear relationship exists between the depth of filter bed and the inverse of the flow rate. Expressed in units consistent with equations 2 and 3,

$$K = \frac{g_c}{\alpha\mu} = \frac{g_c}{\alpha'(1 - \epsilon)\ \rho_s\ \mu} \qquad (6)$$

<u>Methods of Analysis for ABS</u>. Two principal methods of analysis have

been used to quantitatively determine ABS in sewage and raw river water. The infrared method of analysis has been developed by a subcommittee on analytical methods of the Association of American Soap and Glycerine Producers Inc.(12). This is the most precise method developed to date but it is also more complicated and time consuming. The method utilized carbon as an adsorbent from which the ABS can be recovered quantitatively and analyzed by a spectrophotometric technique.

The methylene blue method has been used extensively to analyze for ABS content. This method is based upon the solubility of a blue colored salt in chloroform. The methylene blue and ABS are both water soluble but insoluble in chloroform. These facts are illustrated in Figure 2. The unknown sample is treated with methylene blue and extracted with chloroform in a standard manner. The spectrophotometric adsorption of the chloroform solution of unknown concentration is then determined at 652 mμ and the results compared with calibration curves obtained from known concentrations analyzed using the same technique(19). The spectrophotometric equipment necessary for the methylene blue method is less expensive than that used in the infrared method.

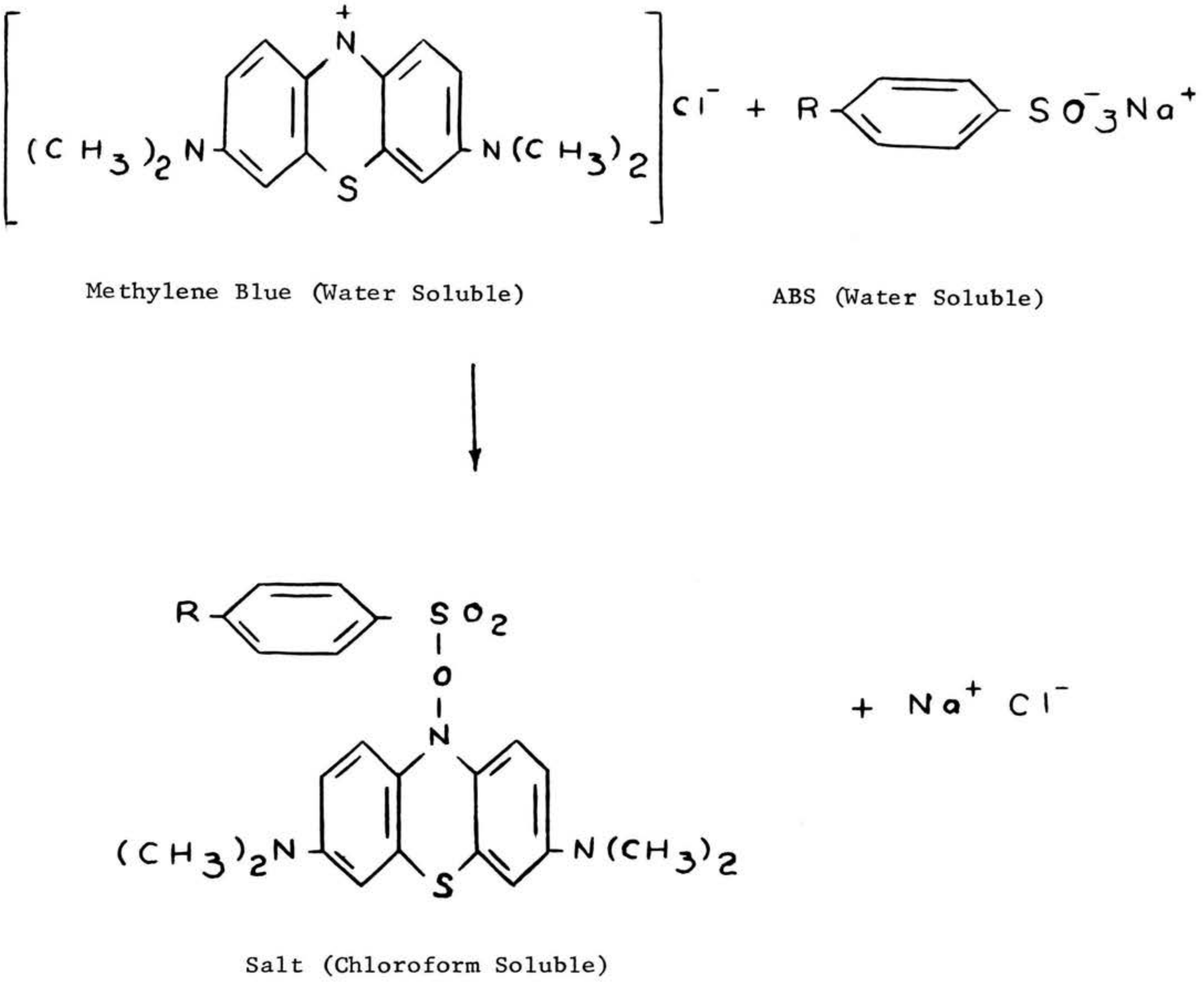


FIGURE 2. The Methylene Blue-ABS Complex(19)

III. EXPERIMENTAL

This section presents the experimental and analytical procedures, the materials and equipment used, the data obtained and results calculated.

Purpose of Investigation. Small quantities of iron, when precipitated on sand, may have an effect on the removal of ABS from water when the ABS is present at low concentrations. The purpose of this investigation was to study this effect in a treated sand filter.

Plan of Experimentation. Preliminary work (such as a study of the effect of pH upon the hydrolysis and oxidation of $FeCl_2$ in water) was undertaken to determine the conditions which would be most desirable to complex ABS with soluble forms of iron. The initial work included the preparation of stable solutions, the calibration necessary for the ABS analysis, and the preparation of iron treated sand which would give reproducible results. The performance of the treated filter was then studied to determine its effectiveness in the removal of ABS from solution and the effect of the iron, precipitated upon the sand particles, as well as the ABS, upon the permeability of the sand. A final study was made to determine the conditions of reversibility for the adsorption process.

Materials. Materials used during the investigation were as follows:

Chloroform. (Fisher Scientific Co., Fair Lawn, N. Y.) Reagent grade chloroform was used to extract the ABS-methylene blue complex from aqueous solutions. These solutions were used to determine the ABS concentration.

Ferrous Chloride. ($FeCl_2$ $4H_2O$) (Baker's. Blue-green, monoclinic)

Ferrous chloride was used to prepare the treated sand and the hydrolysed complexing solutions. The impurities in the ferrous chloride were shown as follows:

PO_4^{-3}	0.001%	Substance not ppt by NH_4OH	0.015%
SO_4^{-2}	-----		
Al^{+3}	-----	Zn^{+2}	0.003
Mn^{+2}	-----	Cu^{+2}	0.005

Alkyl Benzene Sulfonate. (Association of American Soap and Detergent Producers, Inc., 295 Madison Ave., New York 17, N. Y.) This material was used to prepare standard solutions of ABS in distilled water. The composition was given as:

Lot 3; June 1961; pH 11.0; Equivalent weight 348

ABS	54.8%
$NaSO_4$	40.3
Free Oil	0.5
NaOH	1.3
$NaCO_3$	0.7
H_2O	2.6
	100.2%

Distilled Water. Double distilled. (Physical Chemistry Laboratory, Department of Chemistry, University of Missouri at Rolla, Rolla, Mo.) The water was free of materials which would affect its use in the spectrophotometric analysis where a wavelength of 652 mμ was used.

Sand. (Meramec river run, Powell Lumber Company, Rolla, Mo.) It was screened to -48 + 65 mesh, washed free of "fines" and used as a "filter" media.

Diphenylamine. (Baker's reagent grade) Diphenylamine was used as an indicator (0.2% solution) in the analysis of iron chloride solutions.

Potassium Dichromate. Baker's reagent grade. The standardized (0.1 N) solution was used to determine ferrous chloride concentrations.

Apparatus. The principal piece of equipment was a sand filled glass column equipped to maintain a constant head. Figure 3 shows this column as connected to the feed system and the receiver assembly.

The Sand Column. The filter was assembled within a 1.5 inch inside diameter pyrex glass column, 53 inches in height. First a rubber ring, approximately 1/8 inch thick, was inserted into the bottom of the column. A 3.5 mesh galvanized screen was inserted above the rubber ring. The materials which made up the filter bed were then added to the column. Since it was used in a vertical position, the screen and rubber ring supported the bed. The bed was constructed by first adding distinct layers of 1/2 inch Raschig rings, 3/16 inch glass beads, and -14 + 20 mesh sand in that order. The depth of the supporting materials was approximately 3 inches. Washed sand (-48 + 65 mesh) was then added to depths of 6, 12, 18, 24 or 30 inches. The depth of the filter sand was measured to within ± 0.1 inches. The assembled column was clamped in a rigid vertical position with a conventional iron stand arrangement.

The Feed System. A five liter glass bottle served as the feed reservoir which supplied feed to a constant-head reservoir. The latter was placed on a wooden platform approximately one-half foot above the feed point into the column. Flow from the reservoir to the constant head device was controlled by a pinch clamp and a very small amount of overflow was maintained during the run. The primary flow control, out of the constant head device, was adjusted to maintain a predetermined position of the liquid level within the column.

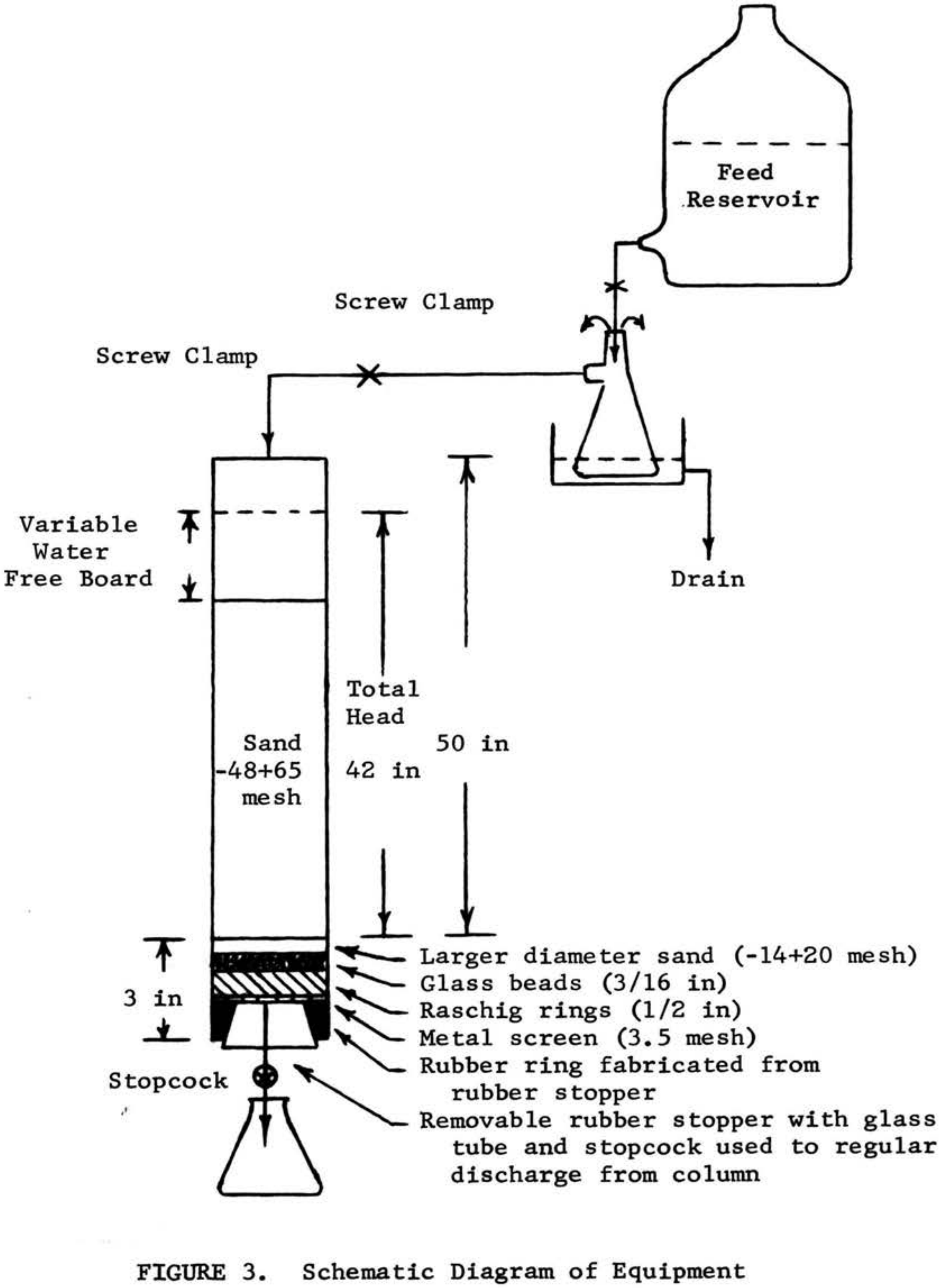


FIGURE 3. Schematic Diagram of Equipment

The Receiver Assembly. Two types of flow were utilized in this work: (1) An unrestricted flow to determine permeabilities, and (2) restricted flow to determine ABS adsorption properties of the sand. The bottom of the column was sealed with a rubber stopper-glass tube-stopcock arrangement to adjust the restricted flow rate. In both cases the solution was collected in an Erlenmeyer flask. Volumetric flow rates were measured with a precision of ± 5%.

Spectrophotometer. Beckman, Model B. Equipped with two Corex rectangular cells, 1 cm x 1 cm x 4 cm. Manufactured by Beckman Division, Beckman Scientific Instruments Inc., Fullerton, California. The spectrophotometer was used to determine the absorbancies of both known and unknown concentrations of ABS in chloroform.

pH Meter. Model No. 7664, equipped with standard electrodes, manufactured by Leads and Northrup Co., 4901 Station Ave., Philadelphia 44, Pennsylvania. This instrument was used to determine the equivalence points for various reactions. This data was necessary for the development of standardized procedures which would give reproducible results.

Burette. 10 ml, 50 ml pyrex, scalor divisions 0.01 ml. The Burette was used to standardize iron samples and to determine the equivalence point of iron samples.

Pipette. 1, 10, 25 and 50 ml pipette, precision within 2 drops or approximately 0.1 ml. The pipette was used to prepare solutions of known concentration by dilution.

Preliminary Experimental Work. This work consisted of (1) the preparation of standard solutions of ABS, (2) the construction of a calibration curve to be used in the methylene blue procedure for the analysis of ABS, (3) the preparation of a standard solution of $FeCl_2$, (4) the study of conditions under which the Fe-ABS complex could be formed, (5) the treatment of sand with $FeCl_2$, and (6) the verification of the stability of the treated sand in the adsorption column.

Preparation of the Standard ABS Solution. A stock solution with a concentration of 500 mg/l was prepared by transferring 1.8245 gm ABS to a 2000 ml glass stoppered volumetric flask. A second stock solution with a concentration of 100 mg/l was prepared by diluting 50 ml of the first to 250 ml. One, 2.5, 5, 7.5 and 10 ml of the 100 mg/l stock were diluted to 100 ml to prepare 1, 2.5, 5, 7.5 and 10 mg/l solutions. All of these were stored in glass-stoppered volumetric flasks.

Preparation of Calibration Curves. The methylene blue method of analysis was used to determine the spectrophotometric adsorbance of the solutions in the low concentration ranges listed above. The details of this method are given in Appendix A. Concentrations, as mg/l in the chloroform extract, are plotted as a function of the absorbance in Figure 4. Table I lists the data used to determine this plot and indicates the variation between the data and a straight-line correlation assumed for the data. Twenty milliliters of the aqueous phase were used in all of the analyses in this investigation.

Preparation of the $FeCl_2$ Solution. A stock solution was prepared by dissolving 1.9883 gm $FeCl_2$ $4H_2O$ in 1000 ml distilled water. The solution was filtered into a 2 liter amber glass stoppered bottle and stored overnight. The light yellow solution was then standardized by means of the potassium dichromate method, described by Kolthoff and Becher(9), using diphenylamine as an indicator. The 0.0071 N filtered stock remained clear during this investigation. The solution was stored in a darkened desk when not being used. Swirling the container, after storage for several days, did not indicate precipitate at any time.

Study of Fe-ABS Complexing. A series of observations were made to discover conditions under which the complex could be formed.

Various quantities of the $FeCl_2$ standardized solutions (0.0071 N) were mixed with 100 ml of 10 mg/l ABS solution. The mixtures were thoroughly shaken, allowed to stand overnight, centrifuged to remove any precipitate, and analysed by the methylene blue method. There was a slight decrease in the ABS concentration.

Sodium hydroxide (0.483 N) was used to increase the pH of the $FeCl_2$ stock solution in steps from approximately 2.0 to 4.6 and 9. The procedure outlined above was used to study the effect on the ABS concentrations. Treatment with $FeCl_2$ solution at a pH of 9 gave a decrease in ABS concentration. For this case the reproducibility was poor, however.

Further study indicated that a $FeCl_2$ stock with a pH of 12 could be used to decrease the ABS concentration from 10 mg/l and 5 mg/l to 4.46 mg/l and 2.48 mg/l respectively. The effect of $FeCl_2$ concentration is indicated in Figure 5. Table II lists the original data from which Figure 5 was obtained. The pH of the solution from which the ABS had been removed was about 12.

Procedure Used to Treat Sand with $FeCl_2$. River run sand (-48 + 65 mesh), free of fine particles of sand and silt, was used to prepare the treated sand. Microscopic examination verified the fact that the sand was "clean". This also showed that the principal particle dimensions were within the range shown by the sample size. The shape of

TABLE I

Data for Calibration Curve Used with the Methylene Blue Method

ABS Concentration in $CHCl_3$ mg/100 ml	Absorbance Observed	Absorbance Calculated	Absorbance Difference	Percentage Deviation
0.00	0.000	-0.001	-0.001	--
0.02	0.054	0.041	-0.013	-24.10
0.05	0.097	0.104	0.007	7.22
0.10	0.205	0.210	0.005	2.42
0.15	0.296	0.315	0.019	6.42
0.20	0.438	0.421	-0.017	-3.88

Average Deviation ± 5.0 per cent; neglecting the first reading

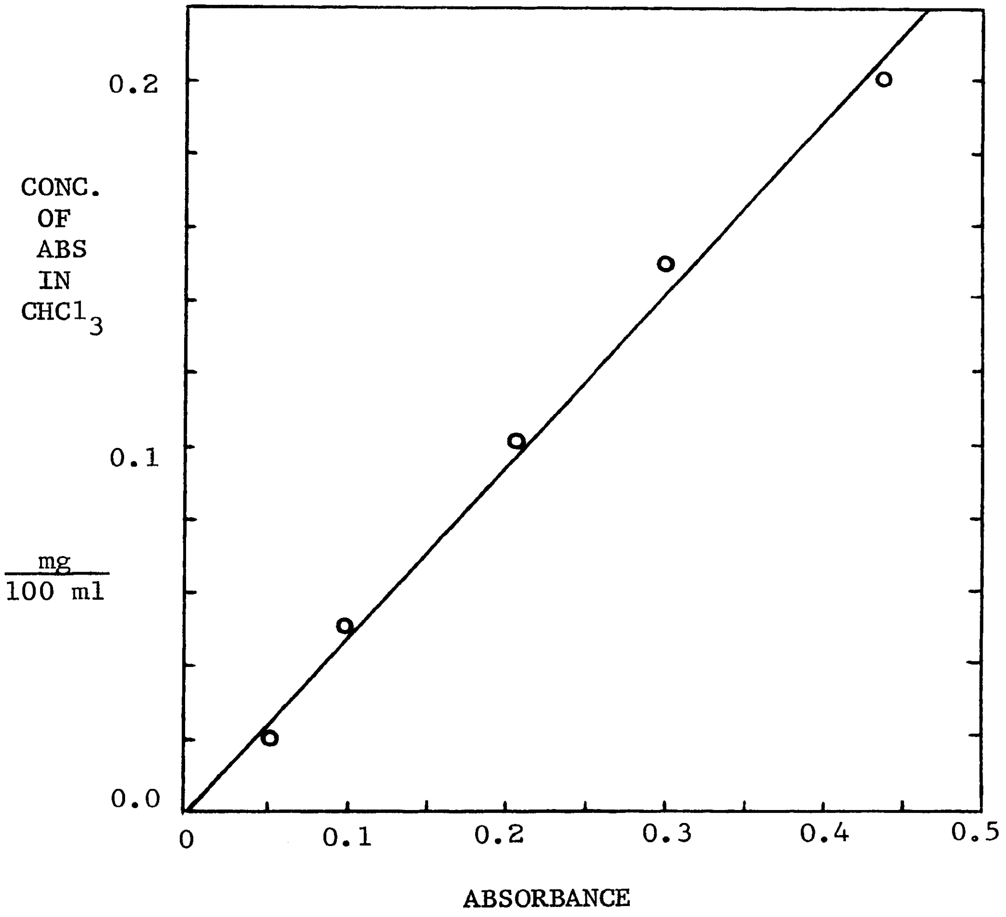


FIGURE 4. Calibration Curve for ABS Analysis

individual particles lay between that of a sphere and a cube.

Ten, 20 and 40 ml respectively of the 0.0071 N $FeCl_2$ were diluted to 60 ml with distilled water. To this a sufficient 0.483 N NaOH was added to increase the pH to 12. The resulting solution was transferred immediately to 516.9 gm sand in a one gallon tinned cylindrical metal container. The moist mixture was stirred vigorously for approximately 15 minutes. The resulting uniform mixture was then stabilized by heating in a drying oven at 100°C for 10 hours. The dried mixture was inspected after approximately three hours. In all cases the walls of the container remained bright upon rotation. The $FeCl_2$ treatment gave a distinct reddish color to the sand.

<u>Determination of the Stability of the Treated Sand</u>. The sand column was prepared with treated sand as described for restricted flow under Procedures. With the discharge closed, the sand was soaked with distilled water for approximately two hours. The discharge cock was then opened and the bed was washed with distilled water. The wash water was collected until the discharge was free of iron. The upper surface was kept covered with water during the wash period. The column was stored for short intervals (at the end of the wash run, and between the adsorption and permeability runs) with water covering the sand surface so that the sand remained wet until the experimentation was completed.

The quantity of wash collected varied from one to two liters. In all cases, the wash water draining from the column at the end of the wash period was free of iron when tested with potassium dichromate - diphenylamine as outlined in Appendix B.

The total amount of iron washed from the column was calculated

TABLE II

The Removal of ABS from Water at a pH of 12 by Treatment with Ferrous Chloride

$FeCl_2$ added to 100 ml ABS solution ml	Volume Analyzed ml	Mean Absorbance at 652 mμ	ABS Remaining mg/l	ABS Remaining %	ABS Removed %
Run number 1, 5 ppm ABS Original concentration, 68°F					
0	--	--	5.00	--	--
1	20	0.115	2.80	56.0	44.0
3	20	0.105	2.50	50.0	50.0
5	20	0.103	2.48	49.6	50.4
Run number 2, 10 ppm ABS Original concentration, 72°F					
0	--	--	10.00	--	--
1	20	0.208	4.95	49.5	50.5
3	20	0.190	4.50	45.0	55.0
5	20	0.185	4.45	44.5	55.5
8	20	0.185	4.45	44.5	55.5
10	20	0.186	4.46	44.6	55.4

Ferrous Chloride: 0.0071 N solution

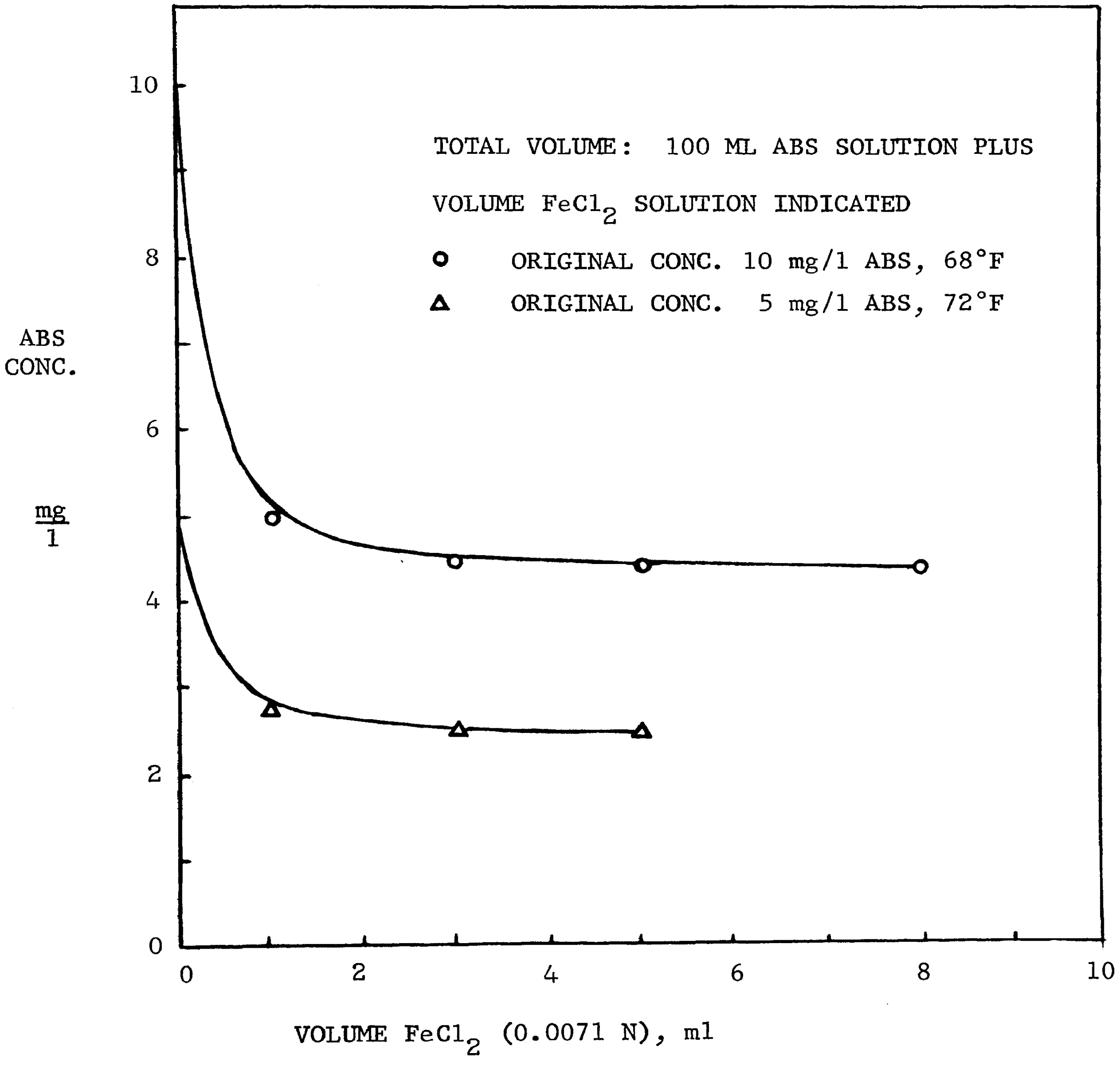


FIGURE 5. The Removal of ABS from Water at a pH of 12 by Treatment with Ferrous Chloride

from the analysis of the wash water. Although some iron was washed from the prepared sand, the quantities were small and within the experimental limitations characteristic at very low concentration measurements. The quantities of ferrous chloride solution used to prepare the sand served as a basis for the calculation of the concentration of the iron in the sand.

Experimental Procedures. The performance of the treated sand filter is discussed in this section.

ABS Adsorption by $FeCl_2$ Treated Sand Column. The washed treated sand columns described on page 22 were first used to determine the permeability of the treated sand. This procedure is described on page 29. The 12 inch columns were then used to study the capacity of the treated sand to remove ABS from solution.

The assembly used was that shown in Figure 3 and described on page 16 for restricted flow. The run was initiated with the discharge stopcock closed and the upper surface of the sand column covered with distilled water to a depth of approximately 1/16 inch. The ABS solution (5 mg/l in distilled water) was then added to the column, in a manner such that the sand would not be disturbed, until the total head was 42 inches. (The depth of solution above the 12 inches sand bed was 30 inches.)

The flow into and out of the column was 100 ml/hr (2.2 gal/hr-ft^2) so that the total head remained constant. The flow rate was checked and maintained constant (within 3% variation limits) during the run.

Preliminary work showed that approximately 125 ml distilled water was necessary to fill the voids in the sand column, to provide for the volume of water above the sand column necessary to insure wetness of sand surface, and to fill the void space in the retainer section at the base of the column. This volume was used as a basis for the analysis of the treated water leaving the column.

The treated water leaving the column was collected until the ABS was no longer being removed. Treated samples (20 ml) were analyzed by the methylene blue method (Appendix A) at various volumetric intervals to determine the effectiveness of the column in the removal of ABS from the water.

Data and Results from the Study of ABS Removal by $FeCl_2$ Treated Sand. The results of this work is shown in Table III and Figure 6. These results show the concentration of ABS in the effluent from the sand columns as a function of the volume of treated effluent. Three correlations show the effect of variations in the amount of iron (0.00396 to 0.1584 gm) used to treat a given quantity of sand (516.9 gm).

Results obtained with untreated sand verified the fact that within experimental limitations an insignificant amount of ABS was removed by untreated sand.

Desorption of ABS from the ABS Saturated Treated Sand Column. The 12 inch treated sand columns, saturated with ABS, were used in this study. The assembly was the same as that used in the removal of ABS from aqueous solutions. The procedure was very similar.

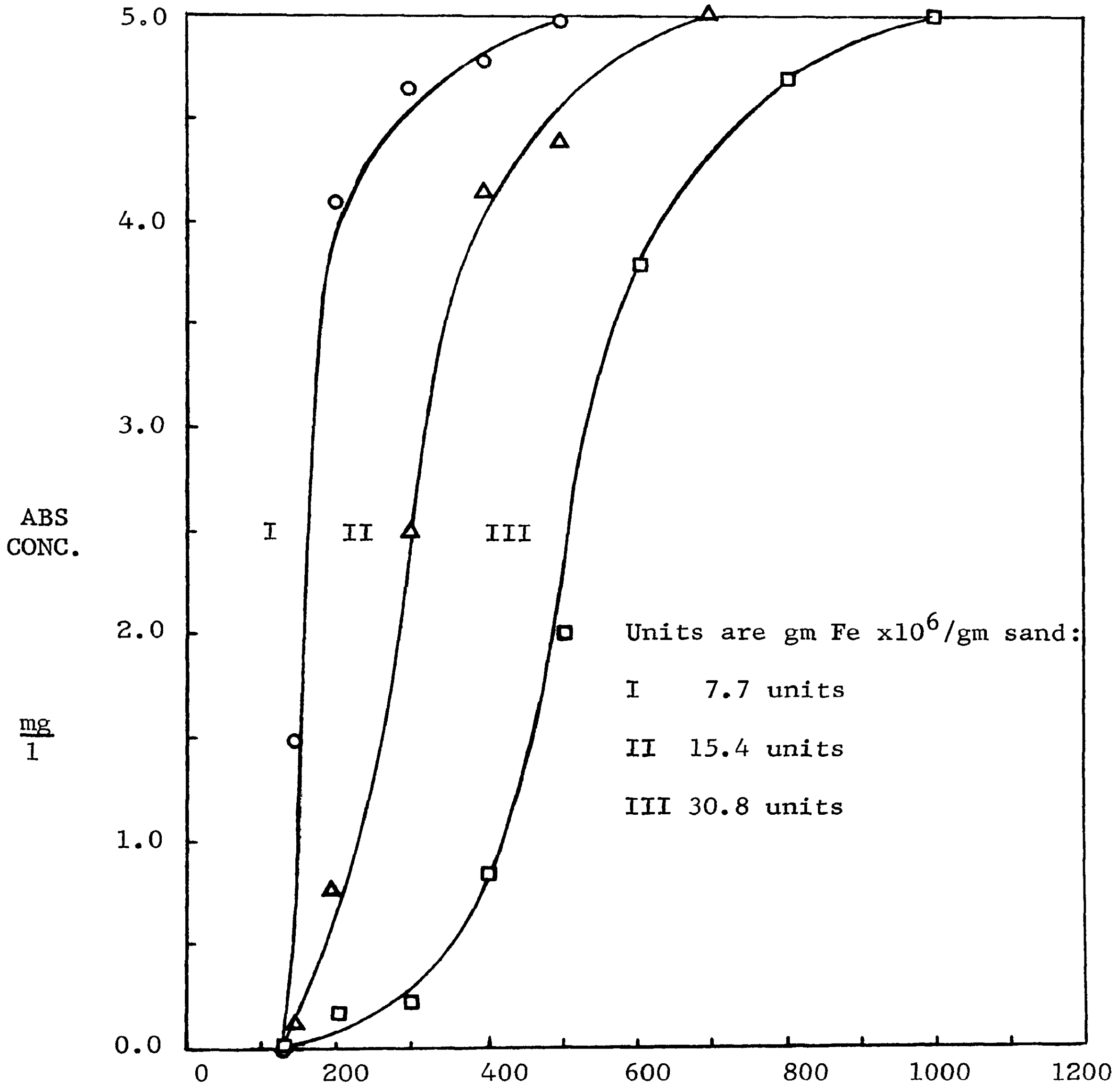
A run was initiated with the discharge stopcock closed and the upper surface of the sand column covered (1/16 inch) with the solution containing 5 mg/l ABS. Distilled water was added to the column to give a total head of 42 inches and a flow rate of 100 ml/hr.

TABLE III

The Removal of ABS by a Column of Sand Coated with Iron Oxide

Total Volume of Discharge ml	Volume Analyzed ml	Mean Absorbance at 652 mμ	ABS Remaining in Effluent mg/l
Untreated sand			
100	20	--	--
125	20	0.221	5.00
150	20	0.221	5.00
200	20	0.221	5.00
7.7 x 10^{-6} gm Fe/gm sand			
100	20	--	--
125	20	0.000	0.00
150	20	0.063	1.50
200	20	0.172	4.10
300	20	0.195	4.65
400	20	0.201	4.80
500	20	0.219	4.98
15.4 x 10^{-6} gm Fe/gm sand			
100	20	--	--
125	20	0.000	0.00
150	20	0.003	0.10
200	20	0.031	2.75
300	20	0.105	2.50
400	20	0.175	4.15
500	20	0.185	4.40
700	20	0.222	5.01
30.8 x 10^{-6} gm Fe/gm sand			
100	20	--	--
125	20	0.000	0.00
200	20	0.005	0.15
300	20	0.006	0.16
400	20	0.033	0.80
500	20	0.084	2.00
600	20	0.156	3.75
800	20	0.196	4.70
1000	20	0.221	5.00

Original concentration of solution: 5 ppm ABS
Average flow rate: 100 ml/hr
Total head: 42 inches water



VOLUME OF EFFLUENT FROM COLUMN, ml

FIGURE 6. The Removal of ABS by a Column of Sand Coated with Iron Oxide

Wash water leaving the column was collected until ABS was no longer being removed from the column. Samples of the wash water (20 ml) were analysed by the methylene blue method at various volumetric intervals to determine the concentration of ABS in the wash water.

Data and Results for the Desorption Studies. The results of this work are found in Table IV and Figure 7. They show that ABS adsorbed by the treated sand may be removed by washing with distilled water. The results found in Figure 7 are consistent with those given in Figure 6 - the larger quantities of ABS are washed from the sand beds which contained larger quantities of iron and which had removed larger quantities of ABS in the water treatment. This is treated in detail in the Discussion section.

Permeability Determinations. Permeabilities were determined for the untreated sand, the treated sand and the treated sand saturated with ABS.

The equipment was assembled initially as it was used for the ABS removal studies (see Figure 3 and page 16). The method of storage (To avoid drying of the sand surface) was also the same as that for the ABS removal studies.

A run was made with the stopper-glass tube-stopcock assembly, removed from the discharge end of the column. Liquid flow into the column was adjusted by a pinch clamp to maintain a constant head and to provide for the unrestricted flow from the bottom of the column. Permeabilities of the untreated and treated sand columns were obtained using distilled water. The permeabilities of treated sand saturated with ABS were obtained with water containing 5 mg/l ABS. In each run the flow rate through a given bed depth was adjusted until a constant

TABLE IV

The Removal of ABS from a 12 Inch Treated Sand Column*

Total Volume of Elutrant ml	Volume Analyzed ml	Mean Absorbance at 652 mμ	ABS in Elutrant** mg/l
7.7×10^{-6} gm Fe/gm sand			
100	20	--	--
125	20	0.220	5.00
150	20	0.148	3.50
200	20	0.096	2.30
300	20	0.018	0.45
350	20	0.000	0.00
15.4×10^{-6} gm Fe/gm sand			
100	20	--	--
125	20	0.220	5.00
150	20	0.178	4.25
200	20	0.140	3.35
300	20	0.093	2.25
400	20	0.038	0.95
450	20	0.000	0.00
30.8×10^{-6} gm Fe/gm sand			
100	20	--	--
125	20	0.220	5.00
150	20	0.200	4.75
200	20	0.167	4.00
300	20	0.120	2.85
400	20	0.083	2.00
500	20	0.062	1.50
600	20	0.030	0.75
700	20	0.012	0.30
800	20	0.000	0.00

* Treated sand column saturated with ABS

** Distilled water used as feed to column
Average flow rate: 100 ml/hr
Total head: 42 inches water

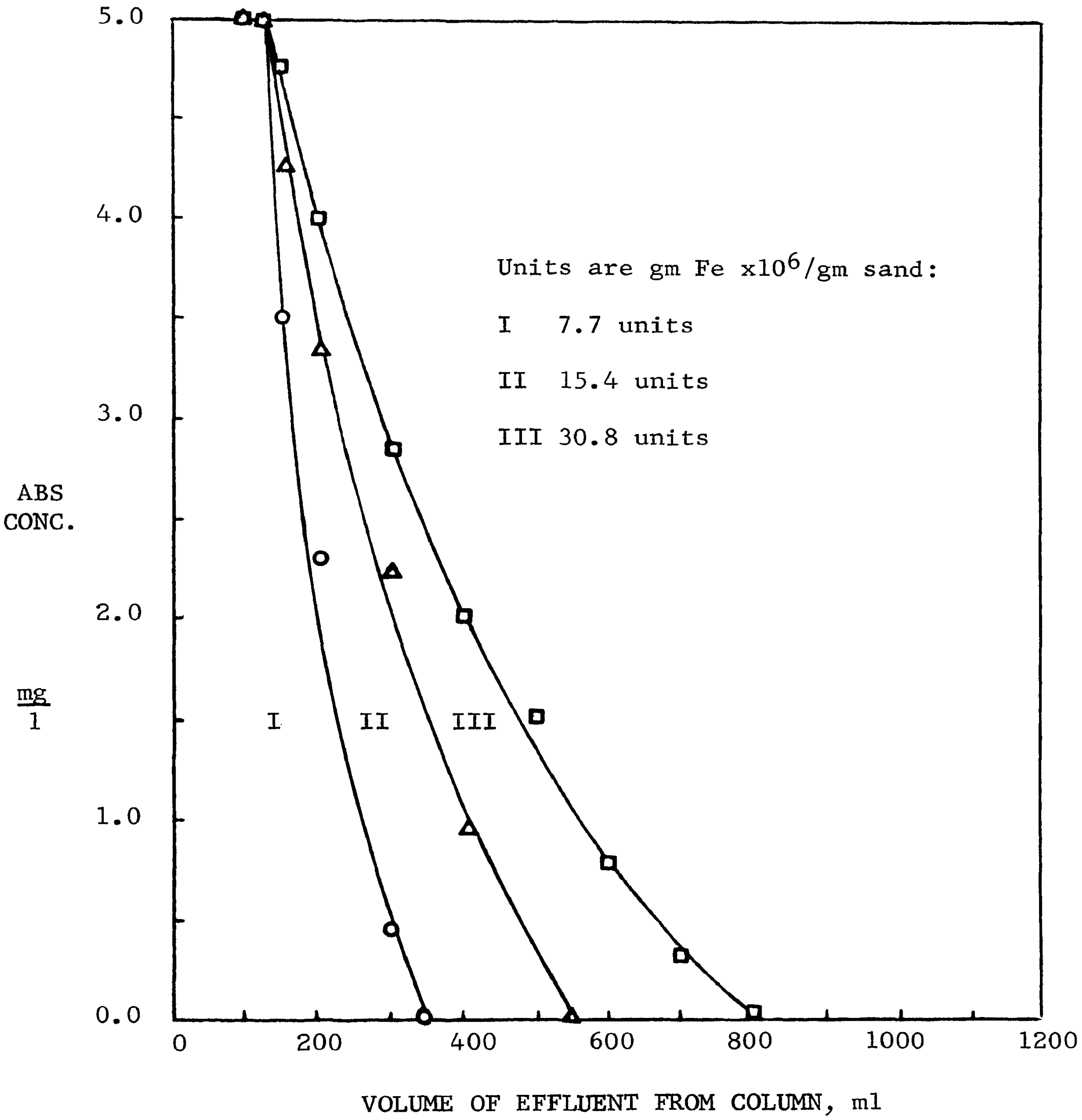


FIGURE 7. The Removal of ABS from a 12 Inch Treated Sand Column

head was maintained.

Data and Results from Permeability Studies. The method used to determine permeabilities of sands is discussed in the Literature Review section (equations 4, 5, and 6 on page 10). Appendix D shows a detailed sample calculation to illustrate the applications of the theory.

Inverse flow rates are plotted as a function of untreated sand depth in Figure 8. The method of least squares (Appendix C) was used to evaluate the slope and intercept of the straight line relationship which fit the data. The relationship of the data to the curves in Figure 8 indicated that the overall reproducibility of the data was consistent with results common in this type of work. The magnitude of the intercept also verified the reproducibility of the data and in addition, indicated that construction of the column was such that resistances (such as that of the retainer assembly) other than the sand bed were insignificant. Small auxiliary resistance is consistent with desirable filter operations discussed by Foust and others(8). The linear relationship also indicated that the experimental procedure derived from the Carman-Kozeny relationship (see Literature Review, pages 8 to 10) served as a valid basis for the evaluation of permeabilities. It further confirms that the total head was the correct value for an evaluation which involves free flow through a sand packed column.

The permeability (ft^2) of the untreated sand was calculated from the slope of the curves in Figure 8. These results were tabulated with the original data in Table V. The permeabilities (3.645 and 3.75×10^{-10} ft^2) calculated for two different heads (36 and 42 inches of water respectively) check within three per cent. This reproducibility is

TABLE V

The Determination of the Permeabilities of an Untreated Sand Column

Run No.	Height of Sand in	Height of Water in	Time sec	Volume of Sample ml	$\Delta t/\Delta V$ sec/ml	Mean $\Delta t/\Delta V$ sec/ml
Total Head:	36 inches					
1	12	24	300	350	0.85	
	12	24	300	348	0.86	
	12	24	300	348	0.86	0.86
2	18	18	300	233	1.28	
	18	18	300	236	1.27	
	18	18	300	238	1.26	1.27
3	24	12	400	226	1.77	
	24	12	400	227	1.76	
	24	12	400	226	1.77	1.76
Total Head:	42 inches					
4	6	36	300	1083	0.27	
	6	36	300	1083	0.27	
	6	36	300	1085	0.27	0.27
5	12	30	300	422	0.71	
	12	30	300	422	0.71	
	12	30	300	422	0.71	0.71
6	18	24	300	278	1.07	
	18	24	300	272	1.10	
	18	24	300	270	1.11	1.09
7	24	18	400	280	1.42	
	24	18	400	282	1.42	
	24	18	400	278	1.43	1.42
8	30	12	400	212	1.87	
	30	12	400	213	1.87	
	30	12	400	214	1.87	1.87
9	36	6	400	190	2.11	
	36	6	400	190	2.11	
	36	6	400	190	2.11	2.11

From Figure 8:
For 36 inches head: Slope = 0.07300; Permeability = 3.665×10^{-10} ft^2
For 42 inches head: Slope = 0.06097; Permeability = 3.75×10^{-10} ft^2

Permeability, as ft^2, may be converted into darcies (cm^2), by multiplying by the factor $(\text{cm/ft})^2 = (30.48)^2 = 929.03$

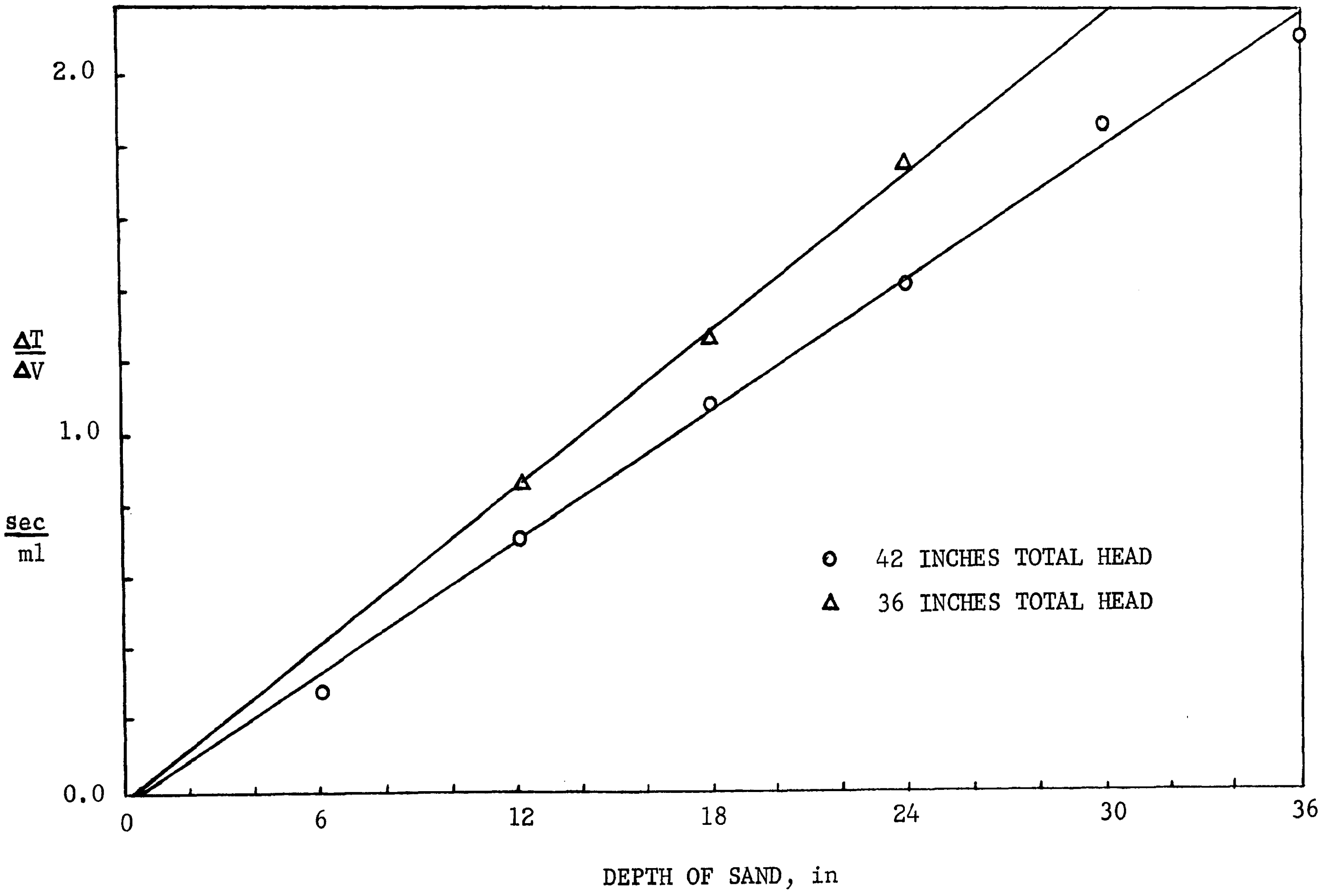


FIGURE 8. The Determination of the Permeability of an Untreated Sand Column

consistent with data of this type. Further, the sand may be considered to be incompressible, within the reproducibility limitations, a condition to be expected at the low pressure differentials utilized in this analysis.

The data is treated further to give specific cake resistances (α'), the viscous resistance coefficient (α), and permeabilities ($1/\alpha$). These results are found in Table VIII, where a comparison is made between the untreated sand, treated sand, and treated sand saturated with ABS. Details relevant to the calculation of the various terms in Table VIII are given in Appendix D.

The data for sand which had been treated with various quantities of $FeCl_2$ are given in Table VI and Figure 9 as well as Table VIII. Calculations, based upon a total head of 42 inches of water, are identical to those for the untreated sand. The experimental procedures can be justified as in the case of the untreated sand. Reproducibilities are also similar. One notes that the permeabilities increased from a small value of 2.87×10^{-10} ft^2 for the sand containing the largest amount of iron to 2.97 and 3.21×10^{-10} ft^2 for the lower concentrations. This is consistent with the results for the untreated sand (3.75×10^{-10} ft^2).

Table VII and Figure 10, present the data for treated sand saturated with ABS. In this case the water used in the determination of flow rates through the sand bed contained 5 mg/l ABS. A comparison between the data for treated sand saturated with ABS and the ABS free treated sand given in Table VIII showed that complexed ABS caused no significant decrease in the permeability of the treated sand.

TABLE VI

The Determination of the Permeabilities of a $FeCl_2$ Treated Sand Column

Run No.	Height of Sand in	Height of Water in	Time sec	Volume of Sample ml	$\Delta t/\Delta V$ sec/ml	Mean $\Delta t/\Delta V$ sec/ml
7.7×10^{-6} gm Fe/gm sand						
1	12	30	300	349	0.86	
	12	30	400	355	0.84	
	12	30	300	355	0.84	0.85
2	18	24	300	231	1.29	
	18	24	300	230	1.30	
	18	24	300	230	1.30	1.28
3	24	18	300	182	1.65	
	24	18	300	176	1.70	
	24	18	300	171	1.75	1.70
15.4×10^{-6} gm Fe/gm sand						
4	12	30	300	333	0.90	
	12	30	300	326	0.92	
	12	30	300	329	0.91	0.91
5	18	24	300	222	1.35	
	18	24	300	216	1.39	
	18	24	300	224	1.40	1.38
6	24	18	300	166	1.81	
	24	18	300	162	1.85	
	24	18	300	164	1.83	1.83
30.8×10^{-6} gm Fe/gm sand						
7	12	30	300	309	0.97	
	12	30	300	310	0.96	
	12	30	300	308	0.97	0.97
8	18	24	300	210	1.43	
	18	24	300	208	1.44	
	18	24	300	214	1.40	1.42
9	24	18	300	156	1.92	
	24	18	300	157	1.91	
	24	18	300	157	1.91	1.91

From Figure 9; where units indicated are gm Fe x 10^{-6}/gm sand:
7.7 units treated sand: Slope = 0.07237; Permeability = 3.15×10^{-10} ft^2

15.4 units treated sand: Slope = 0.07837; Permeability = 2.92×10^{-10} ft^2

30.8 units treated sand: Slope = 0.08240; Permeability = 2.77×10^{-10} ft^2

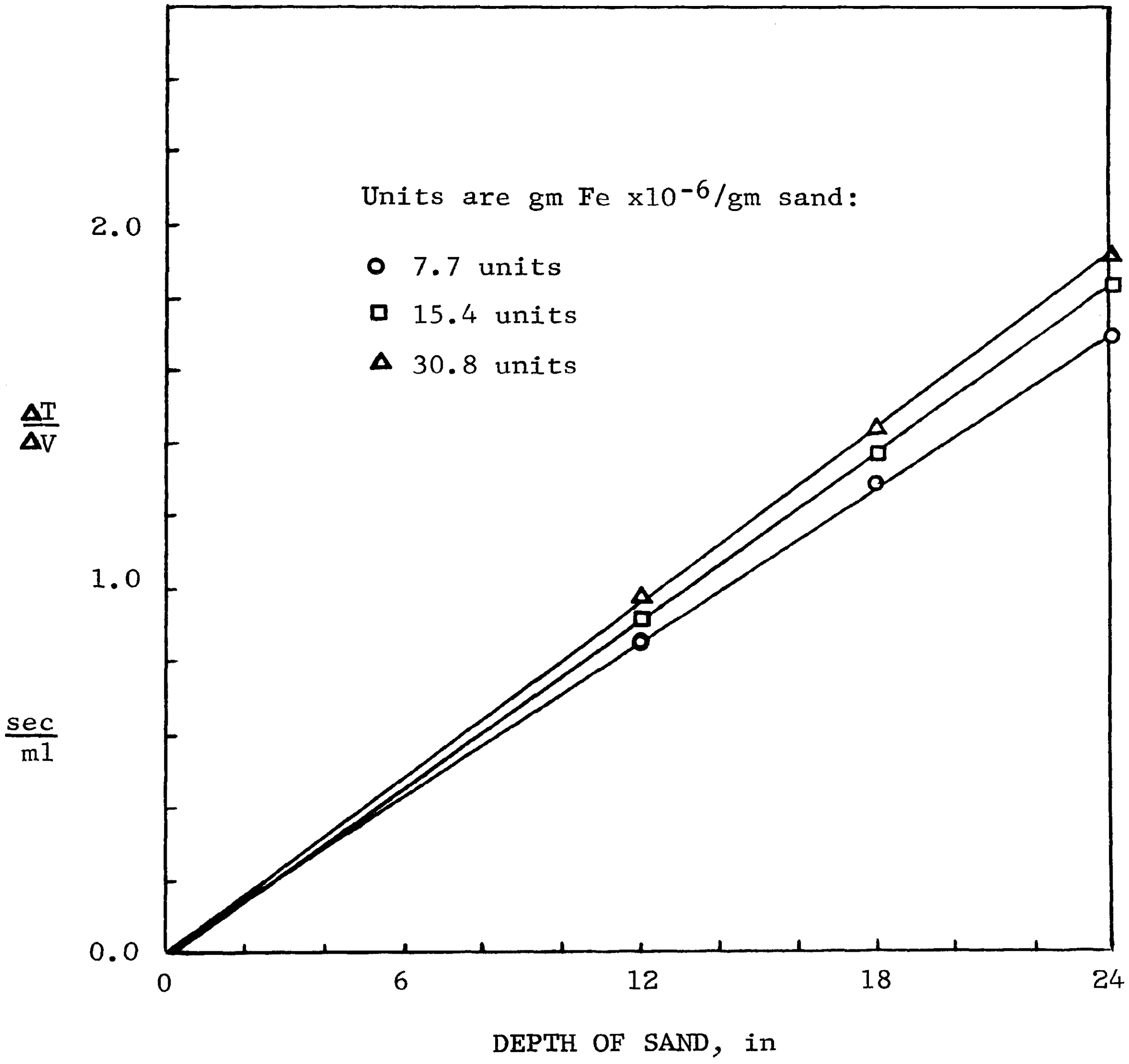


FIGURE 9. The Determination of the Permeability of a $FeCl_2$ Treated Sand Column

TABLE VII

The Determination of the Permeabilities of a $FeCl_2$ Treated Sand Column after Saturation with ABS

Run No.	Height of Sand in	Height of Water in	Time sec	Volume of Sample ml	$\Delta t/\Delta V$ sec/ml	Mean $\Delta t/\Delta V$ sec/ml
7.7×10^{-6} gm Fe/gm sand						
1	12	30	300	352	0.85	
	12	30	300	349	0.86	
	12	30	300	344	0.87	0.86
2	18	24	300	230	1.30	
	18	24	300	233	1.29	
	18	24	300	229	1.31	1.30
3	24	18	300	173	1.73	
	24	18	300	174	1.72	
	24	18	300	171	1.75	1.73
15.4×10^{-6} gm Fe/gm sand						
4	12	30	300	317	0.94	
	12	30	300	319	0.94	
	12	30	300	321	0.93	0.94
5	18	24	300	211	1.42	
	18	24	300	212	1.41	
	18	24	300	214	1.40	1.41
6	24	18	300	161	1.87	
	24	18	300	158	1.90	
	24	18	300	161	1.87	1.88
30.8×10^{-6} gm Fe/gm sand						
7	12	30	300	306	0.98	
	12	30	300	305	0.97	
	12	30	300	303	0.99	0.98
8	18	24	300	201	1.49	
	18	24	300	200	1.50	
	18	24	300	207	1.45	1.48
9	24	18	300	150	2.00	
	24	18	300	151	1.98	
	24	18	300	154	1.94	1.97

From Figure 10; where units indicated are gm Fe x 10^{-6}/gm sand:

7.7 units treated sand: Slope = 0.07237; Permeability = 3.15×10^{-10} ft^2

15.4 units treated sand: Slope = 0.07837; Permeability = 2.92×10^{-10} ft^2

30.8 units treated sand: Slope = 0.08240; Permeability = 2.77×10^{-10} ft^2

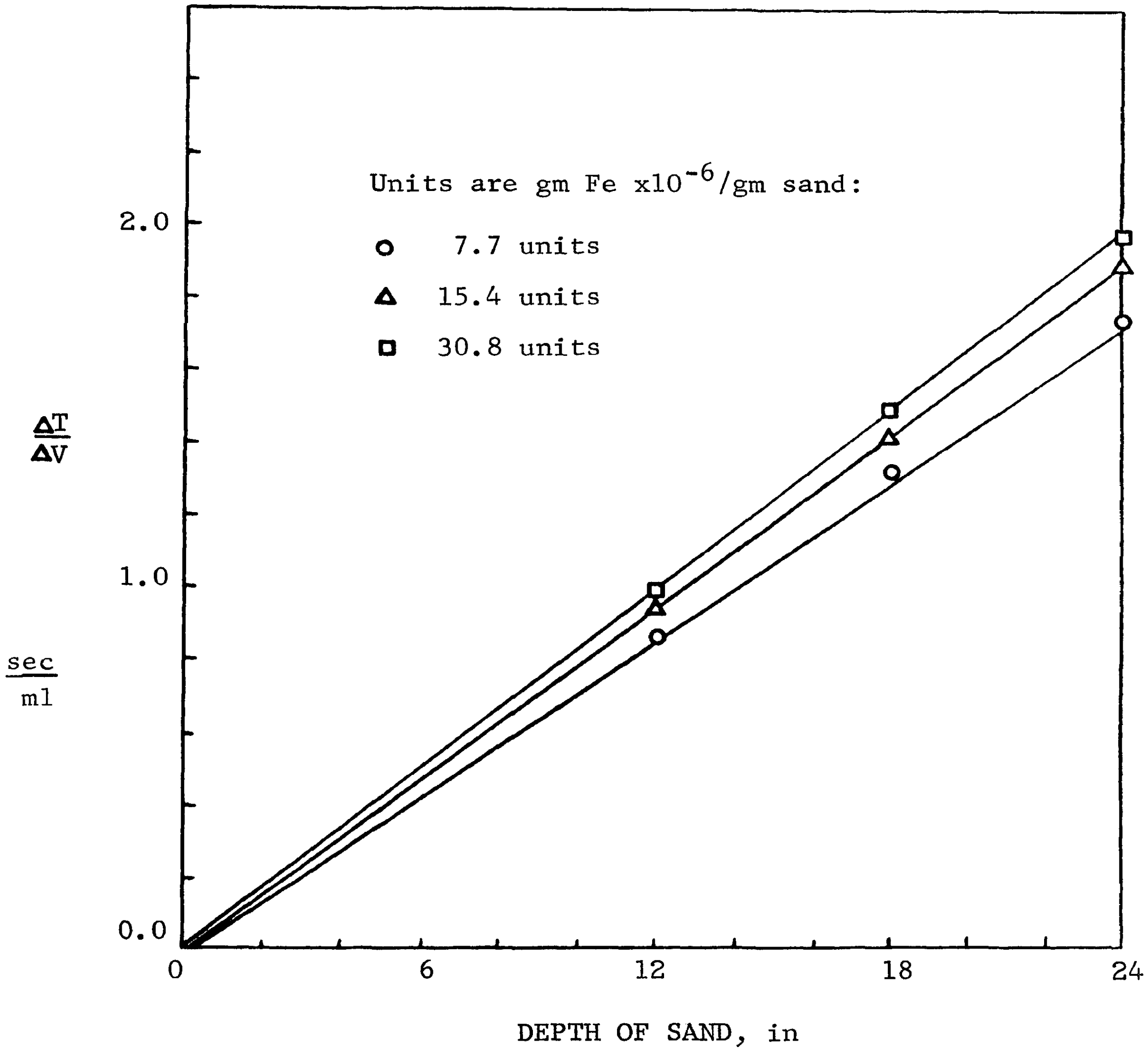


FIGURE 10. The Determination of the Permeability of a $FeCl_2$ Treated Sand Column after Saturation with ABS

TABLE VIII

Results from Permeability Studies

Condition	Slope n $\frac{\text{sec}}{\text{cm}^3\ \text{in}}$	Viscous Resistance Coefficient α $\text{ft}^{-2}\text{x}10^{-9}$	Permeability $1/\alpha$ $\text{ft}^{-2}\text{x}10^{10}$	Specific Resistance α' $(\text{ft/lb})\text{x}10^{-7}$
Untreated sand	0.06097	2.670	3.75	2.87
7.7 units* treated sand	0.07091	3.118	3.21	3.35
15.4 units treated sand	0.07638	3.370	2.97	3.62
30.8 units treated sand	0.07950	3.490	2.87	3.75
Plus ABS**				
7.7 units treated sand	0.07237	3.176	3.15	3.41
15.8 units treated sand	0.07837	3.430	9.92	3.69
30.4 units treated sand	0.08240	3.620	2.77	3.89

* Units indicated are gm Fe x 10^{-6}/gm sand

** Treated sand saturated with ABS

IV. DISCUSSION

The Results. The exploratory work (page 18 through 23) indicated that soluble ferrous forms, produced by the hydrolysis and neutralization of $FeCl_2$ at pH values lower than 9, were not capable of removing significant amounts of ABS from solution. On the other hand, iron concentrations of 8 mg/l (2 ml 0.0071 N $FeCl_2$ mixed with 100 ml ABS solution) reduced concentrations of 5 and 10 mg/l ABS by a factor of one-half where the pH of the final solution was 12 or above and the iron was in the higher oxidation state. These results approximate those obtained at the South District Filtration Plant, Chicago, Illinois, in studies made with ferrous sulfate(22).

Relatively small amounts of iron may be used to treat river sand and produce a surface active material. A simple mixing procedure followed by drying and heating at a relatively low temperature produced a uniformly treated sand product in which the adhering properties of the deposited iron were stable. Since the higher oxidation state of iron is the normal state under atmospheric conditions and since ferric iron was also required for the removal of ABS from water, the treated sand product may also be considered chemically stable. These results are consistent with the factors discussed by Sanford and Gates(14), and Stern(24) and referred to in the Literature Review (pages 6 and 7).

The sand packed column was used successfully to study the removal of ABS with $FeCl_2$ treated sand. The results from the studies made with solutions of ABS and $FeCl_2$, and with ferric iron (page 24), indicated that if similar iron products could be deposited upon the sand, equilibrium would be such that ABS would be removed in the treated column until the sand became saturated with ABS. This fact was verified with flow rates through the treated sand column reduced to provide ample time to achieve equilibrium. The quantity of ABS required to saturate the treated sand column was found to increase with the amount of iron deposited upon the sand (page 28). Integration of the graphical relationship between the concentration of ABS and the total volume of the effluent from the treated column (Appendix E) showed that within experimental limitations the total amount of ABS adsorbed by the sand was proportional to the amount of iron deposited per unit weight of sand. Representative ratios (for sand with the higher iron content) consistent with this fact were: 3.9×10^{-6} gm ABS/gm sand, 30.8×10^{-6} gm iron/gm sand. These ratios combined are equivalent to 0.12 gm ABS/gm iron.

The ABS was quantitatively removed from sand which contained less than 15.4×10^{-6} gm iron/gm sand (20 ml 0.0071 N $FeCl_2$ for 516.9 gm sand) by washing the ABS saturated column with distilled water. Similar treatment of the column containing 30.8×10^{-6} gm iron/gm sand resulted in recovery of only about 62 per cent of the ABS (Appendix E and F). This data corresponded to a ratio of 0.049 gm ABS/gm iron easily retained by the treated sand (not removed by washing with distilled water).

A possible explanation of these results is that the surface activity of sand increases as the surface concentration of iron is increased. Forces of attraction between negative or similar polar ABS molecules and the positive iron treated surface increased to the point at which the retention of the ABS on the sand (38 per cent) was significant and could not be disregarded because of experimental limitations. Such an explanation is consistent with the general theories proposed by Langmuir and others(25).

The simple procedure employed in the permeability studies with the sand packed column (pages 32 through 40) gave meaningful results. The order of magnitude (10^7 ft/lb) of the specific resistances evaluated with the sand column compares favorably with values given in the literature by Foust and others(8).

The specific resistance of the sand was increased consistently by the addition of incremental quantities of precipitated iron to the sand surfaces. Although similar, incremental increases for the ABS saturated treated column were relatively small, the consistency of the increases gave credence to the results. The increase in the specific resistances of the treated sand (compared to untreated sand) varied from 17 to 31% while that for the ABS saturated treated sand ranged from 19 59 36% (Table VIII).

The effect of the adsorbed ABS upon the specific resistances in the sand filter was much less than would be expected. Large reductions of water treatment flow rates found in the literature and attributed solely to ABS(13) might have been caused by foaming and related surface tension effects rather than the effects studied in this investigation.

<u>Recommendations</u>. The study of a method of removal of ABS from water may seem to be redundant because of recent developments with biodegradable type surfactants. Studies of this type, however, permit comparisons to be made with other methods previously studied. Since ABS is present in polar form in aqueous solution, any study involving ABS may prove valuable as a guide to the treatment of similar materials,

some of which may be toxic, present as waste in sewage or other water. The recommendations which are made with respect to ABS therefore apply equally well to other similar waste materials.

A study of the effect of the size and shape of the sand particles used in the water treatment as well as the effect of the amount of iron deposited on the sand and the depth of the sand bed would give more quantitative results to aid in the operation and construction of treated sand columns and filters. Hopefully, fundamental information relative to the coverage of the sand particles and the nature of the deposited iron would also be obtained in such studies.

The iron-sand system is significant because of the wide use of sand filters and the low cost of the two materials. The potential for studies involving other precipitants and other solids in various combinations, as well as the techniques necessary for the preparation of effective materials, is unlimited.

Studies should be made to obtain information on rates of adsorption, information fundamental to this type of surface reaction. The selection of an optimum bed depth which would comprise the equilibrium capacity of the treated bed would be facilitated by a study of this type.

The effects of sewage products upon the performance of the treated filter should be investigated. The work described herein may repeated with sewage substituted for the distilled water.

Limitations. The obvious limitation to a study of this type is implied in the last recommendation. The capacity of the treated sand described in this investigation has not been checked using either sewage or raw water.

The sand used in this investigation was carefully screened, washed and blended to give a uniform product. Undoubtedly systematic effects, which might be difficult to evaluate, would result if this were not possible.

Percentage errors in the analysis of water samples for either ABS or iron concentration are inherently greater when measured quantities (or percentages) are small. The effect of limitations in the measurements of ABS concentrations, for the sand (516.9 gm) prepared with 10 ml of 0.0071 N $FeCl_2$, upon the evaluation of the amount of ABS adsorbed by the sand can be shown by comparing the results found in Appendix E with those in Appendix G. The values of ABS concentrations in Appendix G have been obtained by adjusting the compositions in Appendix E by an amount equal to the expected limitation measurements. The quantity of ABS adsorbed as calculated from the adjusted values compares more favorably with the quantity of ABS removed and shown in Appendix F. These comparisons illustrate the limitations in the results obtained with relatively low iron to sand ratios and with a column of sand containing a relatively small quantity of iron. Although the use of a greater sand depth would require a correspondingly greater head of water (and taller equipment) to provide for suitable flow rates in permeability determinations, these effects would be offset by more accurate results which are necessary if a study of the transfer mechanism is to be made.

V. CONCLUSIONS

In consideration of the facts brought out by this study, one may conclude that a sand column, treated with iron in the higher oxidation state, can be utilized to remove ABS at low concentrations from distilled water.

VI. APPENDICES

APPENDIX A

METHYLENE BLUE METHOD

Experimental Procedures. The method which was used to analyze for ABS content was taken from "Determination of Synthetic Detergent Content of Raw-Water Supplies"(20). The procedure used in this investigation is as follows:

(1) Dissolve 0.1 g of methylene blue in 100 ml of distilled water. Transfer 30 ml of this solution to a 1-liter volumetric flask. Add 500 ml distilled water, 6.8 ml concentrated H_2SO_4 and 50 gm of the monosodium phosphate. Shake until the solution is complete. Dilute to 1-liter mark.

(2) Add 6.8 ml of concentrated H_2SO_4 to 500 ml distilled water in a 1-liter flask. Introduce 50 gm of monosodium dihydrogen phosphate monohydrate, and shake until the solution is complete. Dilute to the 1-liter mark as wash solution.

(3) Prepare a standard solution by weighing out 1.825 gm ABS. Dissolve in distilled water and dilute to 2 liters. Pipet 50 ml of the solution into a 250 ml volumetric flask and dilute to volume with distilled water. Transfer 0, 1, 3, etc., ml of dilute ABS solution into a series of 100 ml volumetric flask and add sufficient distilled water to make the total volumes 100 ml respectively.

(4) 20 ml of each solution are used as the test sample. Pipet each sample into a separatory funnel.

(5) Make the solution alkaline by adding 20% NaOH (phenolphthalein indicator). Then acidify with 4N H_2SO_4.

(6) Add 10 ml of chloroform and 25 ml of methylene blue. Shake

vigorously for 30 sec and allow phase separation.

(7) Draw off the chloroform layer into a second separatory funnel. Rinse the delivery tube of the first separatory funnel with a small amount of chloroform. Repeat the extraction three times, using 10 ml of chloroform each time if the blue color in the water phase becomes faint and disappears add 25 ml more dilute methylene blue.

(8) Combine all extracts in the second separatory funnel. Add 50 ml of wash solution and shake vigorously for 60 sec. Allow contents to settle and draw off the chloroform layer through the glass wool into the volumetric flask. Repeat the washing twice more with 10 ml of chloroform each time. Rinse the glass wool and the funnel with chloroform. Collect the washing in the volumetric flask, dilute to the mark and mix well.

(9) Determine the absorbance of the solution at 652 mμ, using a 1 cm width rectangular cell against a blank of chloroform, on a Beckman model B. spectrophotometer. The absorbance reading is repeated three times on each sample. Three samples of each solution are tested.

(10) The ABS content for each sample is obtained from a calibration curve developed by the above method and shown in Figure 4.

Construction of the ABS Calibration Curve. The calculations for the calibration curve referred to above were obtained from the observations shown in Table I and plotted in Figure 4.

A linear relationship was assumed between the concentration and the absorbance of a solution. This relationship was :

$$y = a + b\,x \qquad \text{(A-1)}$$

where,

y = concentration, mg ABS/100 ml $CHCl_3$

a = the intercept on the ordinate axis, units consistent with y

b = slope of the linear relationship

x = absorbance of the chloroform extract of the ABS-methylene blue complex

The method of least squares was used to evaluate the slope and intercept of the above relationship from the residual equations obtained from the data in the manner outlined in Appendix C. The results of this work is :

$$y = 0.001095 + 0.471\ x \tag{A-2}$$

This equation was used to plot the curve in Figure 4. The small value of <u>a</u> and the relative position of data points with respect to the straight line relationship verify the fact that the correlation is valid within experimental limitations.

Values of percentage deviation are obtained from the difference between the observed data and values calculated using the above correlation. These are shown in Table I.

The absorbancies listed in Table I are for solutions of ABS in chloroform. 100 ml chloroform was used to extract 20 ml of water sample. For the case where the concentration of the water sample is known:

$$\frac{\text{mg ABS in } CHCl_3}{100 \text{ ml } CHCl_3} = (\text{mg ABS/1 } H_2O) \quad \frac{\text{mg ABS in } H_2O/\text{gm } H_2O}{\text{mg ABS/1 } H_2O}$$

$$\frac{\text{mg ABS in } CHCl_3}{\text{mg ABS in } H_2O} \quad \frac{\text{gm } H_2O}{\text{ml } H_2O} \quad \frac{\text{ml } H_2O}{100 \text{ ml } CHCl_3}$$

For 5 mg ABS/l H_2O:

$$(5)\ \left(\frac{0.001}{1}\right)\ (1)\ (1)\ \left(\frac{20}{1}\right) = (100)\ (0.001) = 0.1\ \frac{\text{mg ABS in CHCl}_3}{\text{100 ml CHCl}_3}$$

Other concentrations of ABS in water are used to evaluate concentrations in the chloroform in a similar manner.

If the volume of water, necessary for the extraction with 100 ml of $CHCl_3$, differs from the 20 ml used in this procedure, the concentration of an unknown aqueous solution may be determined from the calibration curve by

$$\text{mg ABS/l H}_2\text{O} = \frac{\text{mg ABS in CHCl}_3}{\text{100 ml CHCl}_3} \quad \frac{1000}{\text{ml H}_2\text{O sample}}$$

APPENDIX B

PROCEDURE FOR THE DETERMINATION OF IRON BY THE PATASSIUM DICHROMATE METHOD

The determination of iron concentration in solution(2) used in this investigation is described as follows:

(1) Weigh out 4.903 gm of the pure potassium dichromate salt, dissolve it in water and dilute to 1000 ml as a 0.1 N solution. Pipet 10 ml into a 100 ml volumetric flask and dilute with distilled water to 100 ml mark to form a 0.01 N solution.

(2) Dissolve 30 gm $SnCl_2$ $2H_2O$ in 100 ml conc. HCl. Add water to make a total volume of 200 ml. This solution should be either fresh or when stored should contain a tin bead.

(3) Dissolve 5 gm $HgCl_2$ in 95 ml distilled water.

(4) Heat the 25 sample solution nearly to boiling and add $SnCl_2$ dropwise until the yellow color of the solution just disappears. Add no more than 1-2 drops in excess. Dilute to 150 ml and add rapidly 15 ml of 5% $HgCl_2$ while swirling the flask contents. Cover the flask with a watch glass, and allow it to stand 5 minutes.

(5) Add sufficient water to 20 ml conc. H_2SO_4 and 15 ml conc. H_3PO_4 to give a total volume of approximately 250 ml. Cool to room temperature under water tap. Add 8 drops of diphenylamine as indicator. Titrate with $K_2Cr_2O_7$, swirling constantly.

APPENDIX C

THE METHOD OF LEAST SQUARES

The method of least squares was used to evaluate the relationship between the spectrophotometric reading (absorbance) and the concentration in the chloroform extract obtained in the methylene blue method. The method was also used to evaluate the slope of the linear relationships between dt/dv and the height of sand (as an example those listed in Table V where the total head is 42 inches) required to evaluate permeabilities and related terms. The determination of permeability is used to illustrate the method in detail in the following example.

A linear relationship is assumed as:

$$y = a + b\,x \tag{C-1}$$

Where,

y = value of dt/dV, sec/cm^3

a = the intercept on the ordinate, same as y

b = slope of the line, sec/cm^3 in

x = L, the depth of sand, in

For a total head 42 inches of untreated sand, the residual equations obtained from data in Table V are:

$\epsilon_1 = a + 0.0\,b - 0.0000$

$\epsilon_2 = a + 6.0\,b - 0.2773$

$\epsilon_3 = a + 12.0\,b - 0.7110$

$\epsilon_4 = a + 18.0\,b - 1.0990$

$\epsilon_5 = a + 24.0\,b - 1.4286$

$\epsilon_6 = a + 30.0\,b - 1.8752$

$$\epsilon_7 = a + 36.0\ b - 2.1100$$

Two simultaneous equations are obtained from the residual equations,

$$7a + 126\ b - 7.4009 = 0 \qquad \text{(C-2)}$$

$$126a + 3276\ b - 196.4742 = 0 \qquad \text{(C-3)}$$

a and b were found by the simulataneous solution of equations D-2 and D-3 to be -0.0259 and 0.06097 respectively.

Then,

$$y = -0.0259 + 0.06097\ x \qquad \text{(C-4)}$$

The intercept and slope of this equation were used to plot the curve in Figure 8.

The slope 0.06097 was used to calculate the permeability of sand by the method indicated in Appendix D.

APPENDIX D

THE CALCULATION OF PERMEABILITY AND RELATED TERMS

The calculations necessary to evaluate the results given in Table V, VI, VII and VIII are based upon equations 1, 2, 3 and 4. The definitions of terms listed for equations 1, 2 and 3 are the same as those used in this discussion.

From equations 1, 2 and 3, for the case where the resistances other than the sand are insignificant ($L_e = 0$):

$$\frac{dt/dV}{L} = n = \alpha \frac{\mu}{g_c\ (-\Delta p)\ A} = \alpha'(1-\epsilon)\rho_s \frac{\mu}{g_c\ (-\Delta p)\ A} \qquad \text{(D-1)}$$

where,

n = slope from the plot of dt/dV vs L, $\frac{sec}{cm^3\ in}$

$$\alpha = n\,\frac{g_c\ (-\Delta p)\ A}{\mu} = \frac{n\ g_c\ (-\Delta p)(\pi D^2)}{4\ \mu} \qquad \text{(D-2)}$$

$$\frac{1}{ft^2} = \left(\frac{sec}{cm^3\ in}\right)\left(\frac{ft\ lb}{sec^2\ lb_f}\right)(in\ H_2O)(in^2)\left(\frac{ft\ sec}{lb}\right)\left(\frac{cm^3}{ft^3}\right)\left(\frac{in}{ft}\right)\left(\frac{lb_f}{in\ H_2O\ in^2}\right)$$

For the case of untreated sand, where the total head is 42 inches of H_2O, the slope ($n = 0.06097\ \frac{sec}{cm^3\ in}$) is obtained (Figure 8). The viscosity of the water (and 5 mg/l solutions) is considered constant within error limitations, $\mu = 1\ cp = 0.000672\ \frac{lb}{ft\ sec}$. The cross-sectional area of the filter (1.5 inch inside diameter) is also constant. $A = 1.766\ in^2$.

Substituting into equation E-2:

$$\alpha = n\left(\frac{32.17 \times 42 \times 1.766}{0.000672}\right)(2.54^3 \times 12^4)\left(\frac{14.7}{406}\right)$$

$$= n(42)(1.043 \times 10^9) = (0.06097)(4.38 \times 10^{10})$$

$$= 2.67 \times 10^{9} \text{ ft}^{-2}$$

$$1/\alpha = 3.75 \times 10^{-10} \text{ ft}^{2}$$

Furthermore for the specific bed resistance:

$$\alpha' = \frac{\alpha}{(1-\epsilon)\rho_s} \qquad \text{(D-3)}$$

note that

$$\rho_s = \frac{W_s}{V_t\ (1-\epsilon)} \qquad \text{(D-4)}$$

where,

W_s = mass sand in a total volume including voids, lb

V_t = total volume, ft^3

$1-\epsilon$ = fraction of total volume occupied by sand, $\frac{\text{ft}^3}{\text{ft}^3}$

The units of equation D-4 are defined as:

$$\left(\frac{\text{lb sand}}{\text{ft}^3 \text{ sand}}\right) = \left(\frac{\text{lb sand}}{\text{ft}^3 \text{ sand} + \text{ft}^3 \text{ voids}}\right)\left(\frac{\text{ft}^3 \text{ sand} + \text{ft}^3 \text{ voids}}{\text{ft}^3 \text{ sand}}\right)$$

Then,

$$\alpha' = \frac{\alpha}{(1-\epsilon)} \ \frac{V_t\ (1-\epsilon)}{W_s} = \frac{\alpha}{\rho_s'} \qquad \text{(D-5)}$$

Where,

$$\rho_s' = \text{bulk density, } \frac{\text{lb sand}}{\text{ft}^3 \text{ total volume}}$$

For the 12 inches column:

$$\rho_s' = \left(\frac{\text{gm}}{\text{in}^3}\right)\left(\frac{\text{in}^3}{\text{ft}^3}\right)\left(\frac{\text{lb}}{\text{gm}}\right) = \frac{\text{lb}}{\text{ft}^3}$$

$$= \left(\frac{516.9}{1.766 \times 12}\right)\left(\frac{12^3}{453.6}\right) = 93$$

$$\alpha' = \frac{2.67 \times 10^{9}}{93} = (1.075 \times 10^{-2})(2.67 \times 10^{9})$$

$$= 2.87 \times 10^7 \text{ ft/lb}$$

The bulk density of the sand is assumed constant (93 lb/ft^3) within experimental limitations for all of the operations encountered in this investigation.

APPENDIX E

Sample Calculation of ABS Removed by Treated Sand Column*

Run No.	Volume of Sample ml	Concentration of Sample mg/l	Graphical Intergration of $\int C_{ave} dV$		
			Average Concentration mg/l	ΔV ml	$C_{ave}\Delta V$ gm(10^6)
	a	b	c	d	e=cd
	125 ($125-E_V$)**	0.00	--	-	--
	150	1.50	0.750	25 ($25+E_V$)	18.75 ($18.75+0.75E_V$)
	200	4.10	2.800	50	140.00
I	300	4.65	4.375	100	437.50
	400	4.80	4.725	100	472.50
	500	4.98	4.860	100	486.00
				TOTAL	1554.75
			Unadsorbed ABS in solution		1550 ($1554.75+0.75E_V$)
	375	5.00	ABS in feed solution		1875 ($1875.00+5.00E_V$)
			ABS adsorbed		325 ($320.25+4.25\ E_V$)

* Values from Table III and Figure 6.

** Values in parenthesis indicate effects of a systematic error in volume measurements, E_V,; these calculations are shown on page 60.

APPENDIX E (Continued)

Run No.	Volume of Sample ml	Concentration of Sample mg/l	Graphical Intergration of $\int C_{ave} dV$		
			Average Concentration mg/l	ΔV ml	$C_{ave} \Delta V$ gm(10^6)
	a	b	c	d	e=cd
II	125(125-E_V)	0.00	--	-	--
	150	0.10	0.050	25(25+E_V)	1.25(1.25+0.05E_V)
	200	0.75	0.425	50	21.25
	300	2.50	1.625	100	162.50
	400	4.15	3.325	100	332.50
	500	4.40	4.275	100	427.50
	700	5.01	4.705	200	941.00
				TOTAL	1885.90
			Unadsorbed ABS in solution		1890 (1885.90+0,05E_V)
	575	5.00	ABS in feed solution		2875 (2875.00+5.00E_V)
			ABS adsorbed		985 (989.10+4.95 E_V)

APPENDIX E (Continued)

Run No.	Volume of Sample ml	Concentration of Sample mg/l	Graphical Intergration of $\int C_{ave} dV$		
			Average Concentration mg/l	ΔV ml	$C_{ave}\Delta V$ gm(10^6)
	a	b	c	d	e=cd
	125(125-E_V)	0.00	--	-	--
	200	0.15	0.075	75(75+E_V)	5.63(5.63+0.075E_V)
	300	0.16	0.155	100	15.50
	400	0.80	0.480	100	48.00
III	500	2.00	1.400	100	140.00
	600	3.75	2.875	100	287.50
	800	4.70	4.225	200	845.00
	1000	5.00	4.850	200	970.00
				TOTAL	2311.63
			Unadsorbed ABS in solution		2310 (2311.63+0.075E_V)
	875	5.00	ABS in feed solution		4375 (4375.00+5.00 E_V)
			ABS adsorbed		2065 (2063.37+4.925E_V)#

E_V is an error term used to explain back mixing and dilution effects indicated on page
The calculation of E_V using values from Runs II and III are as follows:

$$\frac{2063.37 + 4.925E_V}{989.10 + 4.950E_V} = \frac{2}{1} \; ; \; E_V = 17.3$$

The error attributed to dilution and back mixing are small when one considers the concentration as (17.3)(0.15) = 2.6. Then (100)(2.6)/2311.63 = 0.11%

APPENDIX F

Sample Calculation of ABS Eluted from Treated Sand Column with Distilled Water*

Run No.	Volume of Sample	Concentration of Sample	Graphical Intergration of $\int C_{ave}dV$		
			Average Concentration	ΔV	$C_{ave}\Delta V$
	ml	mg/l	mg/l	ml	gm(10^6)
	a	b	c	d	e=cd
I	125	5.00	--	-	--
	150	3.50	4.250	25	106.250
	200	2.30	2.875	50	143.750
	300	0.45	1.375	100	137.500
	350	0.00	0.250	50	12.500
					400.000
				ABS in solution leaving:	400
II	125	5.00	--	-	--
	150	4.25	4.625	25	115.625
	200	3.35	3.800	50	190.000
	300	2.25	2.750	100	275.000
	400	0.95	1.600	100	160.000
	550	0.00	0.475	150	71.250
					811.875
				ABS in solution leaving:	810
III	125	5.00	--	-	--
	150	4.75	4.875	25	121.870
	200	4.00	4.375	50	218.750
	300	2.85	3.425	100	342.500
	400	2.00	2.425	100	242.500
	500	1.50	1.750	100	175.000
	600	0.75	1.125	100	112.500
	700	0.30	0.525	100	52.500
	800	0.00	0.150	100	15.000
					1280.620
				ABS in solution leaving:	1280

* Values from Table IV and Figure 7

APPENDIX G

Sample Calculation of ABS Removed by Treated Sand Column
Effect of Limitations in Analysis*

Run No.	Volume of Sample ml	Concentration of Sample mg/l	Graphical Intergration of $\int C_{ave} dV$		
			Average Concentration mg/l	ΔV ml	$C_{ave}\Delta V$ gm(10^6)
	a	b	c	d	e=cd
	125	0.000	--	-	--
	150	1.425	0.7125	25	17.81
	200	3.895	2.6600	50	133.00
	300	4.435	4.1650	100	416.50
I	400	4.560	4.4975	100	449.75
	500	4.731	4.6455	100	464.55
	600	4.850	4.7905	100	479.05
	700**	5.000	4.9250	100	492.50
				TOTAL	2453.16
			Unadsorbed ABS in solution		2450
	575	5.000	ABS in feed solution		2875
			ABS adsorbed		425

---

* Concentrations shown in Appendix E for the Run No. I have been decreased by 5% - an error assumed to illustrate the effects of errors of this type.

** Volume extrapolated to give a continuous relationship as in Figure 6.

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IX. VITA

The author was born on June 5, 1941, in Hofei, Anwei, China. After World War II, he came to Taiwan, China from Naking, the capital of the Republic of China. He attended primary and high schools at Taipei, Taiwan. Upon graduation from high school in June, 1959, the author attended Chung-Yuan College of Science and Engineering, Chung-Li, Taiwan, China, where he obtained a Bachelor of Science degree in Chemical Engineering in June, 1963.

After graduation, the author served one year with the Chinese Army as a Second Lieutenant.

In September, 1964, the author came to the United States and enrolled at the University of Missouri at Rolla, for his graduate studies in Chemical Engineering. He is a member of American Institute of Chemical Engineers.