A STUDY OF THE EFFECT OF DETERGENTS ON SEEPAGE RATES

by

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CHAPTER I

INTRODUCTION

Synthetic detergents were first introduced to the public in 1932. Since that time the sale of detergents has grown to a point where they represent approximately 80 per cent of the total sales of cleansing compounds sold today. (1) This amounts to more than 4 billion pounds of production annually. If this amount were to be equally distributed in the 1150 billion gallons per day of runoff in all the streams in the United States there would be a concentration of approximately 0.8 parts per million (ppm). An equal distribution of detergent concentration in the streams is not, however, possible. The population distribution, and therefore that of the use of detergents, is not the same as the water distribution. The variation of precipitation and runoff with time further amplifies the unequal concentration of detergents in surface runoff.

During a severe drought (1952-1957), the normal surface water supply at Chanute, Kansas, was totally depleted. In 1956 the impounded sewage treatment plant effluent became the sole water supply. The detergent concentration built up over a period of six months to a level of 5 ppm. No ill effects were observed by local, state, and federal public health departments. (2)

TABLE 1

DETERGENT SALES*

Year	Soap	Syndets	Total
1948	2,491.4	401.7	2,893.1
1952	1,824.2	1,530.1	3,354.3
1956	1,525.1	2,690.3	4,015.4
1960	1,056.9	3,310.6	4,367.5
1962	1,040.0	3,750.0	4,790.0

*Millions of pounds. (3,4)

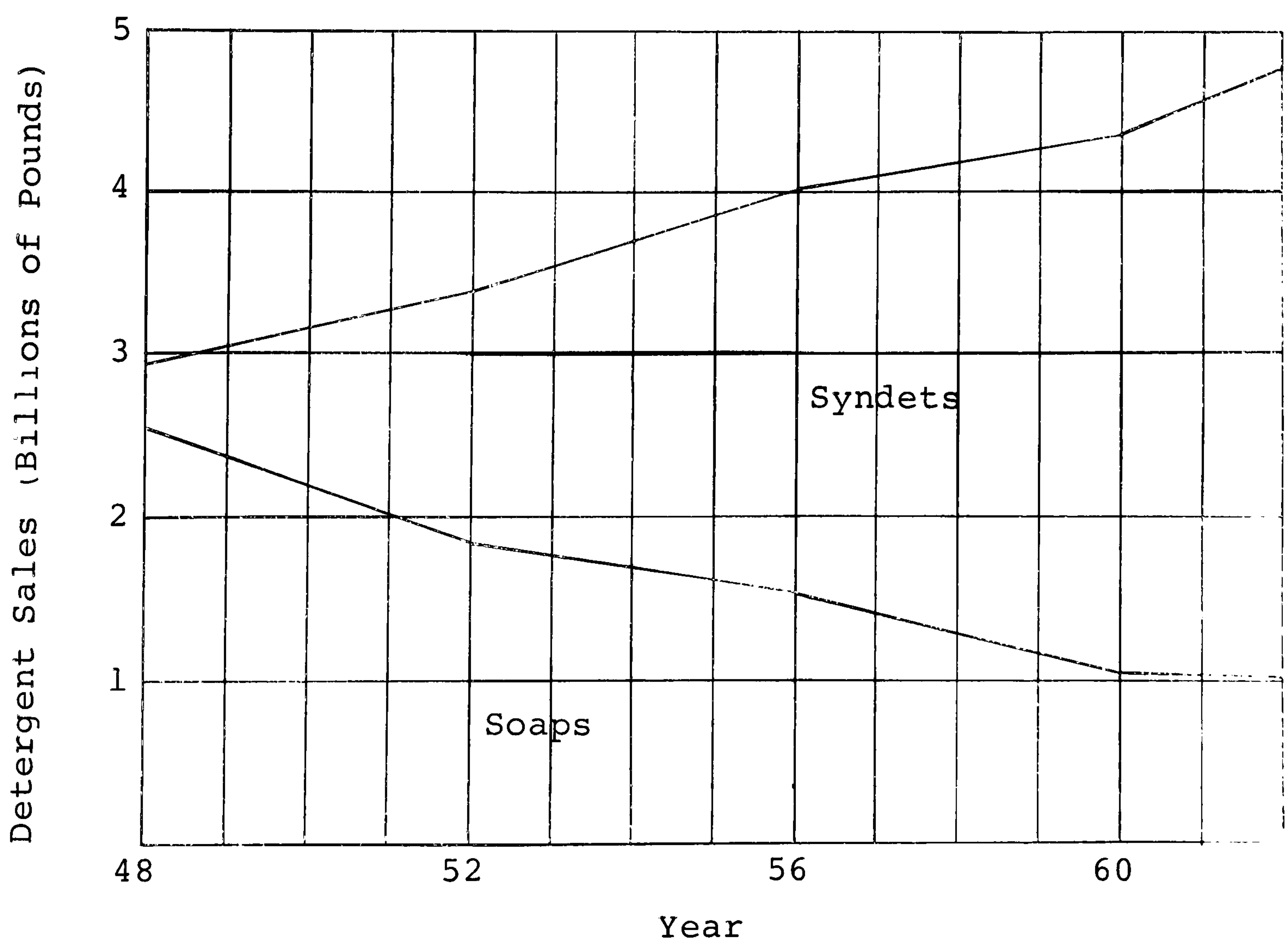


Figure 1. Detergent sales in recent years.

The Surgeon General, with the help of extensive committee studies, has established a limit of 0.5 ppm of alkyl benzene sulfonate (ABS) in municipal water supplies. (5) This limit was set for esthetic reasons in that 0.5 ppm does not foam. The principal reason for this criterion is that the permitting of a higher concentration might lead to use of other supplies of water which do not foam but may not be properly protected otherwise.

Toxicity tests indicate that ABS has no ill effects on the health of animals by ingestion with food or water. (6) Tests have been conducted on men at the level of 100 milligrams per day for 4 months, on dogs at a level of 1 gram per day for 6 months, and on white rats at a level of 1 per cent in the diet for 2 years.

Work done by S. A. Klein, D. Jenkins, and P. H. McGauhey showed no ill effect on plants grown in soil but adverse effects on those grown in water cultures. (7) Plants grown in water cultures of 10 mg/l ABS had growth retarded to about 70 per cent of normal. Plants grown in soil irrigated with sewage effluent containing up to 15 mg/l ABS far surpassed those irrigated with water and ABS, regardless of soil fertility.

As an expanding population puts ever-increasing demands on the relatively fixed water resource, inevitably, a greater portion of the supply will come from re-use of waste water. At the present time, 40 per cent of the population is using water that has been used at least once for domestic or industrial use. (5)

Irrigational use of water is generally low on the list of preferential use set up by most states. Domestic, municipal, and industrial uses of water are responsible for the bulk of detergents in waste water. After re-use by these same users, the concentration of detergents will increase as seen by the instance at Chanute, Kansas. This water may well be used for irrigational purposes with detergent concentrations well above the 5-10 ppm now in sewage effluent (see Table 2).

In irrigated areas water is usually the limiting factor in the number of acres irrigated. It is only natural to seek the use of sewage effluent. Any progressive farmer will recognize that the fertilizer contained therein will be of considerable benefit. There may be other benefits not normally thought of. The wetting action of detergents may or may not alter the seepage rates of soils. Any benefit derived from detergents in an irrigation supply may depend upon the characteristics of the soil and physical character of the irrigation system.

The purpose of this work is to attempt to determine if there is any immediate effect on seepage rates of a typical soil of the Lubbock, Texas region.

TABLE 2

MBAS* LEVELS IN WATERS AND WASTE

	ppm MBAS
Wash Water	
From Household Use of Syndets (8)	1000 to 5000
Raw Municipal Sewage (1)	2 to 15
Effluent from Activated Sludge	
Sewage Treatment Plant (1)	1 to 10
River Water	
Important U. S. Streams (1,9)	0.5 to 1
Ground Water	
Municipal Deep Wells	Rarely Above 0.1
Individual Wells in Unsewered Areas (1)	0 to 5
Drinking Water from	
Municipal Water Treament Plants (1)	0 to 0.5
A Single Isolated Case (2)	5.0

*Methylene Blue Apparent ABS--method of determining ABS content.

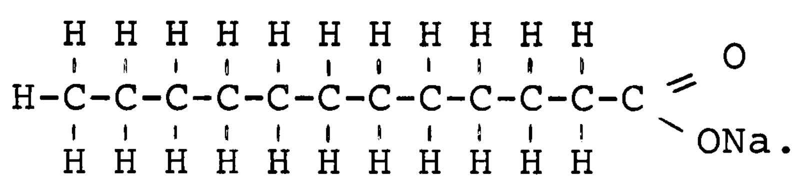
CHAPTER II

DETERGENTS

Soap is a detergent, but acids and constituents of hard water destroy its detergent potential. Soap, made by the alkali saponification of animal or vegetable fats, is a long-chain organic fatty acid of sodium or potassium salts. The chemical formula (10) for a soap of sodium salt is

$$C_{11}H_{23} - CO_2Na$$

or:



Manufacturers, seeking to produce a reliable detergent, look for the following characteristics in the product.

1. It is readily soluble in water.
2. The water-detergent solution will penetrate capillaries by lowering the interfacial tension (wetting action).
3. It breaks up or separates particles (dispersing action) that have agglomerated (gathered together).
4. It links the dirt and/or oil particles with the water (emulsifying action) rather than with each

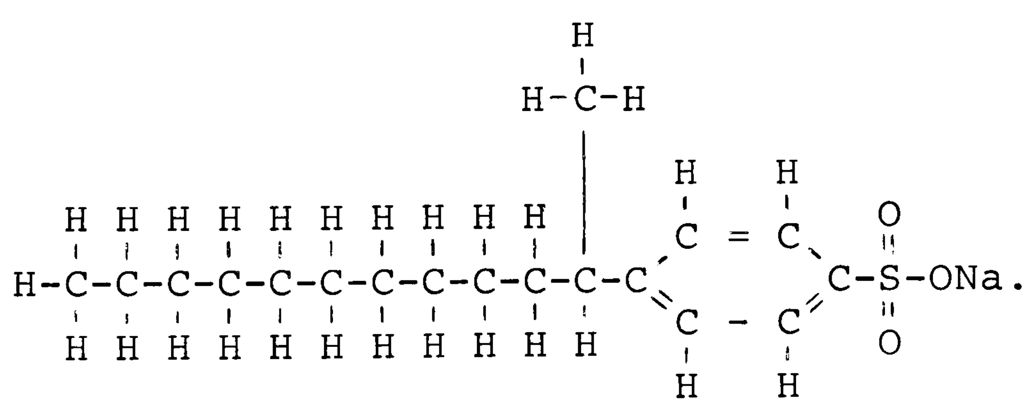
other or with the substance being cleaned.

Detergent, household syndet, syndet, surfactants, or ABS are synonyms for the synthetic detergents presently being manufactured. Detergents are also termed "hard" or "soft" detergents, according as they are extremely hard to degrade (destroy) or are more easily degraded. The extent of degradation depends on (a) the presence of microbes and (b) suitable conditions for the microbes to thrive. For instance, completely bio-degradable materials will not degrade in sterile water. In activated sludge treatment plants about 50 per cent of the detergents are broken down.

Hard detergents are a branched-chain hydrocarbon of the alkyl benzene sulfonate group. (10) For example:

$$C_{12}H_{25} - C_6H_4 - SO_3Na$$

or:

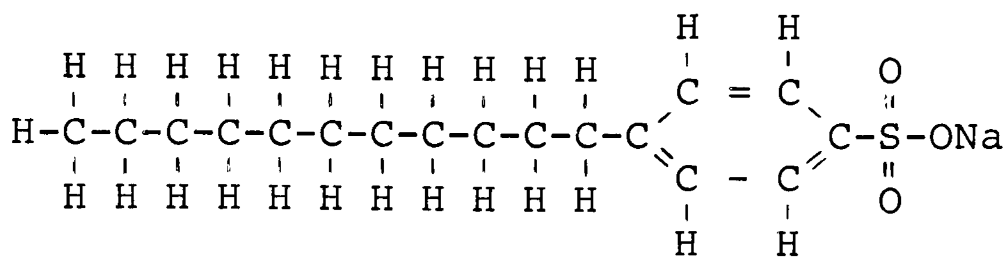


Soft detergents are of the straight-chained group. The straight-chain is broken or destroyed more readily than the branched-chain.

An example of the straight-chain detergent is (10):

$$C_{12}H_{25} - C_6H_4 - SO_3Na$$

or:



From these examples it may be seen that there can be some 3000 isomers for the $C_{12}H_{25}$ hydrocarbon group. Detergents include the C_{10} to C_{15} group and from this group upward of 80,000 structures are possible. (10) A brand-name detergent may be made up of several of these various chain length groups with variations within the same group. Synthetic detergents contain a detergent such as alkyl benzene sulfonate and builders. Builders are additives which improve the detergent action. Those generally included are the polyphosphates, sodium silicates, and sodium carboxymethyl cellulose (a dirt-suspending agent).

The major portion of a synthetic detergent is made of builders. The builders aid the detergent and may have as great an influence on the surface tension as the surface-active agents themselves. Table 3 shows the typical formulation of synthetic detergents.

The ability to reduce surface tension is the most important property of a detergent. As little as 10 ppm will reduce the surface tension by about 20 per cent (Figure 2). The range of reduction in surface tension for the majority of surfactants remains about the same after reaching a concentration of 0.2 per cent or 2000 ppm (Figure 3).

TABLE 3

EXAMPLES OF DETERGENT FORMULATIONS

Component	Quantity in % (Approximate)
Heavy Duty Detergent	
Surfactant	
Alkyl Aryl* Sulfonate	20
Builders	
Sodium Tripolyphosphate	40
Sodium Metasilicate	10
Sodium Sulfate	28
Carboxymethyl Cellulose	2
Packaged Household Detergent	
Surfactant	
Alkyl Aryl Sulfonate	30
Builders	
Tripolyphosphate	28
Sodium Silicate	6
Sodium Carboxymethyl Cellulose	1
Sodium Sulfate Sodium Chloride Moisture	35

*Aryl--a univalent aromatic radical characterized by the benzene ring.

Detergents are classified on the basis of their ionization in water as anionic (negative), cationic (positive), or nonionic (neutral). Alkyl benzene sulfonate, which is

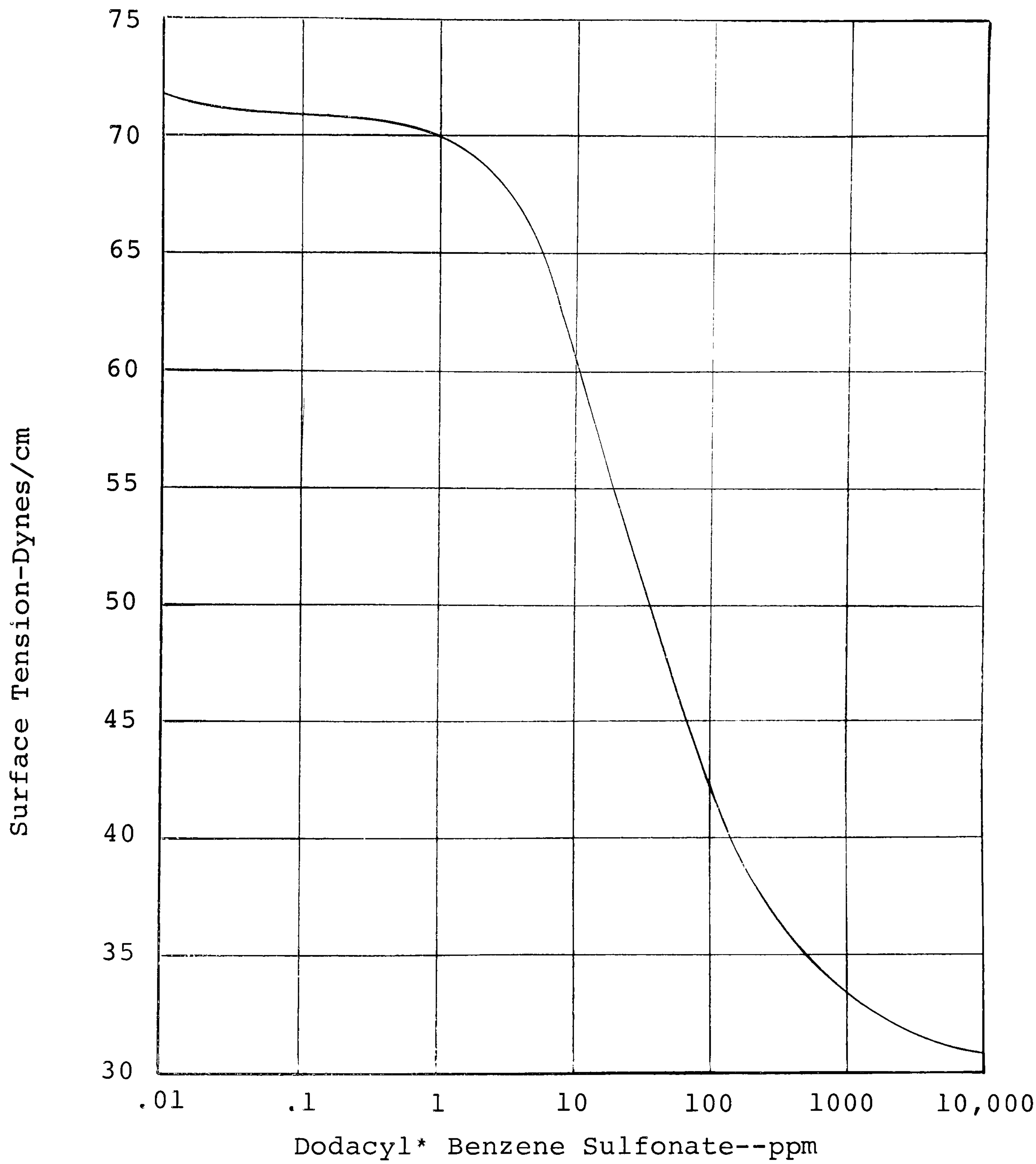


Figure 2. Effect of anionic surfactant on surface tension. (10)

*Dodacyl is a mixture of branch-chain alkyl radicals averaging $C_{12}H_{25}$ in length.

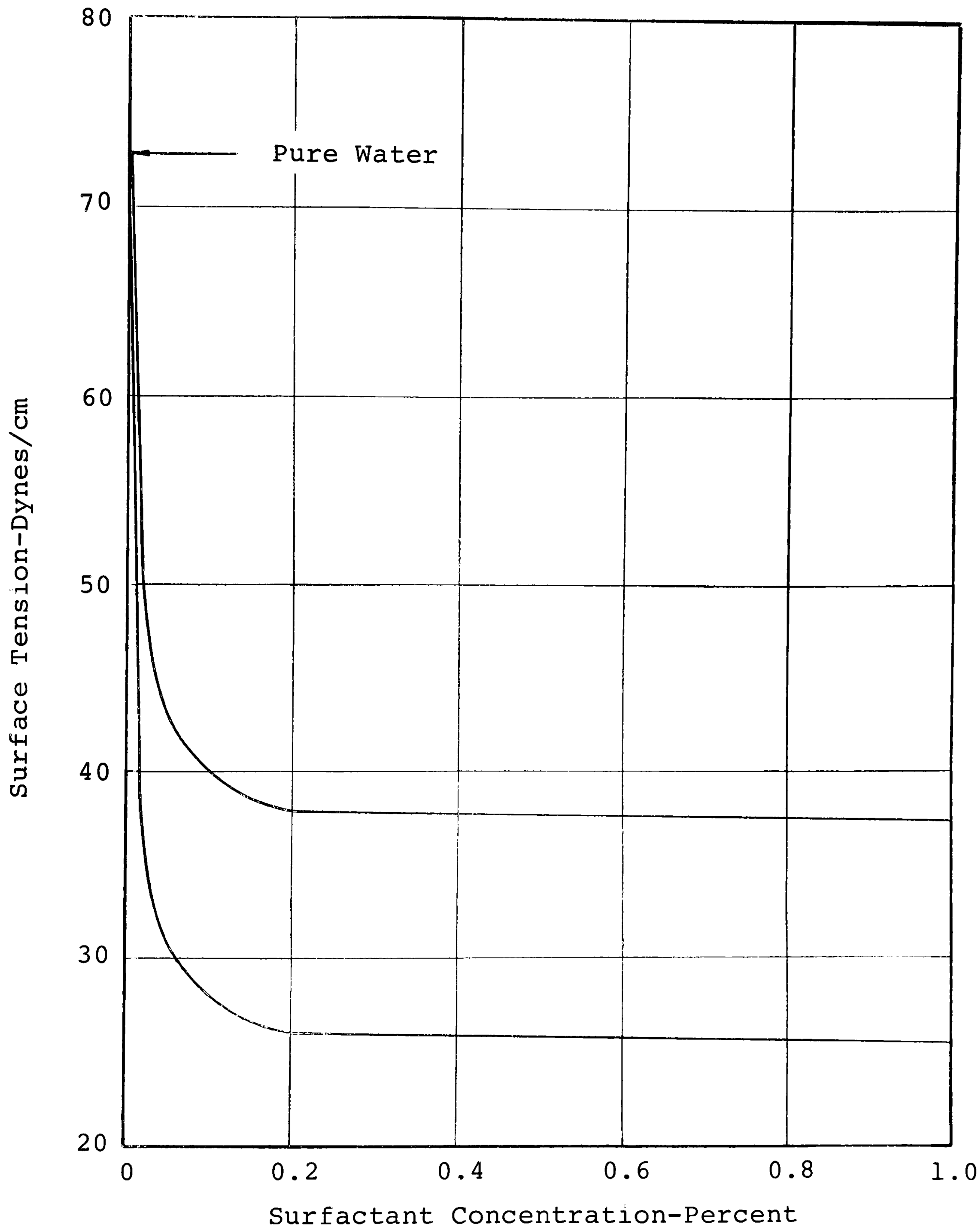


Figure 3. Reduction of surface tension. Values in the shaded area apply to the majority of surfactants. (10)

anionic, is by far the most widely used detergent. In solution the anionic detergents will react with any cationic detergent, rendering the combination nonionic. This leaves the nonionic and the excess anionic detergents to be reckoned with in sewage effluent.

Physical adsorption is a reversible process which is developed in layers on the surface of a solid. Theoretically the adsorbed film is considered to be monomolecular (one layer at a time); it will continue to develop until a state of equilibrium is reached. Soil particles will adsorb alkyl benzene sulfonate and desorb it to an extent of approximately 80 percent of the original adsorption. The amount of adsorption follows the "plate" theory. The greatest adsorption will take place in the first inch of soil. After this, the concentration of adsorbed ions decreases as the concentration of the solute decreases. (10) A soil will adsorb approximately 50 per cent of the theoretical monolayer adsorption values (Figure 4). The soil-solute combinations will reach equilibrium after about forty hours of saturation. (11) An example of ion surface area coverage calculation follows:

Given:

Alkyl benzene sulfonate = 350 grams per mole = 6.02×10^{23} ions per mole

Solution contains 10 mg/l ABS.

Cross-sectional area of ABS molecule is 20 A^2.

(A^2 is 1 angstrom squared or 10^{-16} cm^2.)

The number of ions per liter will be

$$\frac{(1 \times 10^{-2}) \text{ gms} \quad (6.02 \times 10^{23}) \text{ ions per mole}}{350 \text{ gms per mole}} =$$

1.72×10^{19} ions per liter,

and the surface area (X) of solid that can be covered will be

$$X = (20A^2) \quad (1.72 \times 10^{19} \text{ ions})$$

$$= (20 \times 10^{-16} \text{ cm}^2) \; (1.72 \times 10^{19} \text{ ions})$$

$$= 34{,}400 \text{ cm}^2.$$

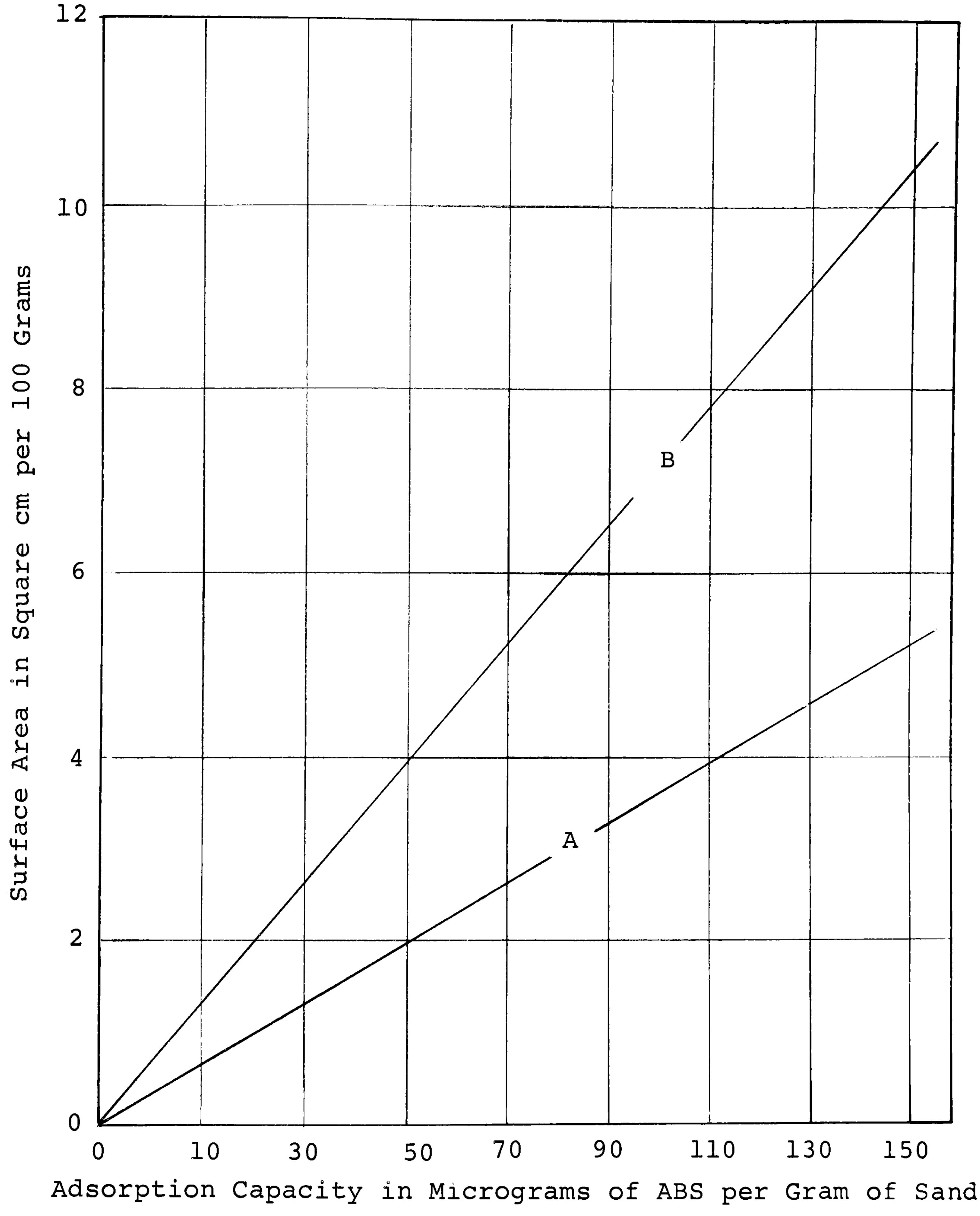


Figure 4. Adsorption of ABS on "Ottawa Sand" as a function of surface area. A represents adsorption capacity calculated for a monolayer and B represents experimental results. (11)

CHAPTER III

PERMEABILITY

Permeability is the hydraulic conductivity of a porous material. Darcy, in 1856, was the first to develop a relation for expressing permeability numerically. Darcy's law (12) may be expressed as

$$Q = KiA,$$

where Q represents the volume rate of flow, K is the permeability coefficient, i is the hydraulic gradient, and A is the cross-sectional area. Since $\frac{Q}{A}$ has the dimensions of length divided by time, it, and therefore Ki, have the characteristics of velocity. If A be taken to be the total cross-sectional area, Ki will be the velocity of flow through a tube of the same area as is occupied by the porous medium. The velocity of the fluid in the pore space is greater, its value depending upon the total pore space at any cross-sectional area in the flow-tube.

Factors Affecting Permeability of Porous Material

Compaction has a definite effect on permeability if the yield under compaction is great. Fibrous materials undergo a great reduction in permeability whereas hard unconsolidated materials such as sand require large compaction pressures to produce any significant change in permeability.

Swelling of clays can alter the permeability of a soil to a considerable degree. Montmorillonite-type clays absorb fresh water readily. The addition of sodium or potassium salts will, however, eliminate the swelling of clays in most cases.

The leaching of minerals from soils can change the pore size and thus change the permeability. This is especially true in limestone, since calcium carbonate is readily soluble in fresh water.

Mechanical alteration or rearrangement of particles due to the forces of a fluid flowing through a soil may also alter the permeability by changing the pore size.

The viscosity of the influent used will affect the permeability. A "heavy" liquid will not flow readily due to internal friction (viscosity). Viscosity is, in turn, related to temperature. For liquids, the viscosity decreases as the temperature increases. Surface tension or interfacial tension determines the size of pores which a fluid will penetrate. If more of the smaller pores are penetrated, thus increasing the effective pore space, the permeability will increase.

Barometric pressure will affect permeability to some extent. If air be entrapped in a soil sample, changing barometric pressure will change the volume of this air, thus changing the effective pore space.

The depth of sample has little effect on the permeability. Although the air permeability decreases rapidly as the depth increases, permeability to water of the total depth is controlled by the most impermeable layer.

CHAPTER IV

PROCEDURE AND RESULTS

Soil Used

The soil used for this test is an Amarillo fine sandy loam. (13) The samples were taken from the South Half (S ½) of the Southeast Quarter (SE ¼) of the 160 acre farm located in the Southwest Quarter (SW ¼) of Section Seventy-three in Block A, Lubbock County, Texas. This farm is owned by Mr. Ed Schoppa and operated by Mr. Sylvin Schoppa.

Amarillo fine sandy loam soil under cultivation has the general profile indicated below. The A horizon ranges from 7 to 14 inches thick and is a brown, fine, sandy loam. It has a weak, fine granular structure that is slightly hard and friable with few to many fine pores. The pH is 6 to 8.

The B horizon is 10 to 25 inches thick. It is a reddish brown, light, sandy clay loam with compound moderate very coarse prismatic, and weak medium subangular blocky structures. This horizon is generally very hard. It has many fine and medium pores. The pH is the same as that of the A horizon. (14)

According to Allen (15), the ion exchange capacity of a soil can be considered to be 60 per cent of the clay content of the soil. The ion exchange capacity is measured in terms of micrograms of adsorbed ions per gram of soil. The clay content for the A horizon is 48.8 per cent and that of the B horizon is 66.8 per cent. (13) The ion exchange would be 29 micrograms of ABS per gram of soil in the A horizon and 40 in the B horizon.

Detergent Used

A combination of equal parts of Dupan and KloroKol, to give a standard solution of 6600 ppm, was used for this experiment. Solutions of 10, 50, and 100 ppm of detergents were made by diluting the standard solution with an appropriate amount of tap water. Dupan was chosen because it is typical of the household detergents now on the market. Dupan is an anionic detergent. KloroKol is typical of the detergents used by commercial establishments and contains 1 per cent of a solution of chlorine of over 150 ppm. KloroKol is nonionic in nature. This mixture approximates what appears in sewage effluent. The pH of each product is 7. These products are manufactured and were supplied by Dubois Chemical Company, a division of W. R. Grace and Company.

Taking Soil Samples

Four-inch conduit was cut into 20 inch lengths with a beveled edge on one end (Figure 5). The cylinders were forced into the ground with a hydraulic jack to a depth of

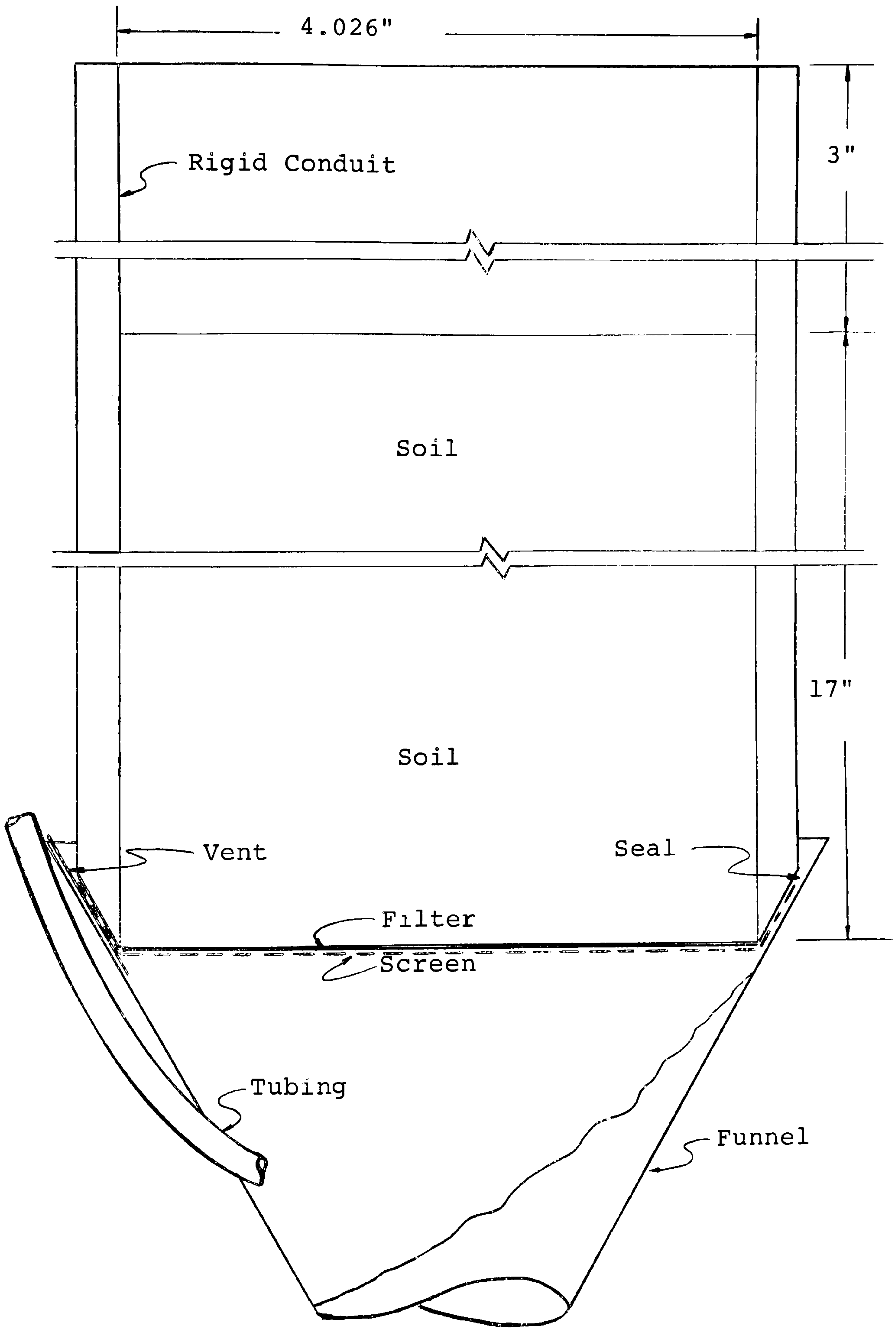


Figure 5. Cross-section of Permeameter.

18 inches. Eighteen-inch depths were chosen to include the root zone of most plants. The forcing of the cylinders into the soil results in compaction of the surrounding soil. Samples were taken 2 feet apart to minimize the effect of compaction. The cylinders were then removed from the ground by digging around and under the cylinders to avoid breaking the sample inside the cylinder. A hacksaw blade with the set removed from the teeth was used to cut the excess soil protruding from the cylinder.

Preparation of Samples

Filters were cut from a desk blotter pad and placed on the bottom of each cylinder. The filters were held in place by a wire screen which was placed across the bottom of the cylinders and attached to the beveled edge with epoxy glue. The cylinders were then placed, beveled edge down, in a funnel (Figure 5). The area between the cylinder and funnel was then sealed with fiberglass plastic. A hole was drilled through the fiberglass plastic for a vent to release air from the funnel. This was essential when charging the sample with solute. A tube was soldered into the funnel for bottom feeding during saturation periods. This was done to minimize the possibility of air entrapment and short circuiting or channeling during the tests.

Test Procedure

All samples were bottom fed for complete saturation for each test. Tap water without detergent was used first to determine the control. The control, or standard, is the basis for comparison of results of tests conducted with various levels of detergent solute after the standard was established. Tap water with 10, 50, and 100 ppm of detergent was used for various tests. Samples were saturated for 2 days when using the detergent solutions to enable the soil-solute to reach equilibrium. At this point the container was opened at the bottom and all excess allowed to drain off. The soil was kept inundated to prevent air from re-entering the soil sample from the top.

At the beginning of each test the containers were filled with solute to a depth of 2 inches. A measurement was made to the water surface and a container was placed under the funnel. The time was noted for each. Before all the solute had entered the soil, or at 12 or 24 hour periods, the depth to the water surface and the amount of water percolating through the soil samples were measured. The change in head measurements served as a check on the amount of water percolating through each sample. In the event of any large discrepancies, the test was not used. Another test was always conducted to confirm or deny the results.

Results

Seepage Tests

Five soil samples were tested.

Each test was conducted for 24 hours except where indicated.

The tests are reported in the sequence in which they were conducted.

Each test reported is an average of the results of several trials.

Sample 1 (12 hour tests)

Solute (ppm)	Seepage (ml/12 hr)
0	305
50	410
10	395
100	430
0*	420

*No saturation period between 100 and 0 ppm test.

Sample 2

Solute (ppm)	Seepage (ml/24 hr)
0	20
10	NC*
50	NC
100	NC

*No change.

Sample 3 (12 hour tests)

Solute (ppm)	Seepage (ml/12 hr)
0	182
100	330
10	241*
50	281
0	285

*The first result was rather high in comparison with the others for this series of tests at 10 ppm.

Sample 4

Solute (ppm)	Seepage (ml/24 hr)
0	50
50	NC
100	NC
10	NC

Sample 5

Solute (ppm)	Seepage (ml/24 hr)
0	165
10	165
100	208
50	190

TABLE 4

CONDENSED SUMMARY OF RESULTS

Sample	Standard	Detergent Levels		
		10 ppm	50 ppm	100 ppm
1*	305	395	410	430
3*	182	241	281	330
2	20	NC	NC	NC
4	50	NC	NC	NC
5	165	165	190	208

*Seepage rates in ml/12 hrs--others in ml/24 hrs.

Samples 2 and 4 showed no change in seepage rate for any level of detergent concentration. These samples were very impermeable as indicated by the 20 and 50 ml/day seepage rates. Changes occurred in all of the other tests conducted. A high initial change of seepage rates is indicated between the standard and solute tests for samples 1 and 3. There was no change between the standard and the 10 ppm solute test of sample 5. This would seem to be due to a continued adsorption of ABS by the soil. In this case the 10 ppm test was the first conducted after the standard was established. The saturation of the sample with 10 ppm either had not reached equilibrium because of the lower permeability, or the adsorption capacity was greater than the available ABS.

The last test conducted on sample 1 indicates a continued effect of ABS. A saturation period was not used between the last 100 ppm and the 0 ppm test. The seepage rate is less than the 100 ppm test, but greater than the 10 or 50 ppm tests. This indicates desorbtion of ABS by the water.

Sample 3 also indicates a continued effect of ABS by the first 10 ppm solute test being high. The effect of ABS is not obvious, as indicated by the last 0 ppm test. A saturation period of 0 ppm was used between the last 50 ppm test and the 0 ppm test. This sample follows the pattern set in sample 5 when the high result of the first 10 ppm test is considered. If the effect from desorbtion of ABS is taken into account this series of tests would have a much lower seepage rate.

CHAPTER V

SUMMARY AND CONCLUSIONS

Five samples of Amarillo fine sandy loam soil were used to study the effect of detergent on seepage rates. A combination of a nonionic and an anionic detergent was used to approximate the detergent that would be found in sewage effluent.

The tests revealed that detergents at any level used had no effect on seepage rates of very impermeable soils. There is a definite effect on the more permeable samples used. The range of seepage rates of the various levels of detergent concentrations is not as great as the change between the standard and solute tests for the most permeable sample. Sample 5, which is less permeable, showed less effect on seepage rates. This follows the pattern of variation from no effect on very impermeable soil to a marked effect on the more permeable samples.

Sample 3, which is in the intermediate range of permeability, tends to follow the same pattern as sample 5 when the high initial test at 10 ppm is taken into consideration.

No attempt was made to determine if the other contents of sewage effluent would alter the effects of detergents on seepage rates.

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