SOIL FLOCCULANTS AND STABILIZERS

Laboratory Evaluation of Polyelectrolytes as Soil Flocculants and Aggregate Stabilizers

ALAN S. MICHAELS and T. WILLIAM LAMBE Massachusetts Institute of Technology, Cambridge 39, Mass.

The object of this work was to develop laboratory procedures whereby the efficacy of polyelectrolytes as soil flocculants and aggregate stabilizers might be simply and reproducibly compared and contrasted. Studies were conducted on three widely differing soils and three chemically different polymers. Flocculation and sedimentation tests, aggregate-stability tests and permeability and water-retention measurements were developed, which proved to be simple and reproducible. Results indicate marked differences in activity of different polyelectrolytes in different soils, and show a great dependence of durability of conditioning action on the physical conditions to which a soil is subjected. Tests of permeability and aggregate stability do not appear to correlate readily with more rapidly performed sedimentation tests. The possibility of developing a single, simple laboratory screening test for soil conditioner evaluation seems at present remote, although a series of tests of the type described may prove useful for this purpose. Extensive field testing will undoubtedly be necessary for final evaluation of the most suitable conditioner for a particular application.

 ${\rm S}^{
m ynthetic}$ polyelectrolytes as "soil conditioners" have received widespread attention and publicity in recent months, and these compounds may prove to be an important aid to agriculture and soil engineering. Although the scientific literature has attempted to explain the mechanism of polyelectrolyte action in soils (5, 6, 8, 9), few laboratory methods for either qualitative or quantitative evaluation of polyelectrolyte performance have been suggested. Field test data (1, 2, 4, 10), however, indicate that these compounds exert a pronounced beneficial influence on soil structure, and that the effects produced persist for relatively long periods of time.

If soils of poor structure—i.e., those which have a high bulk density, low permeability, and a tendency to cake and crack on drying—are adequately loosened and treated (in the presence of water) with very low concentrations of polyelec-

trolytes, certain important changes in physical properties take place: reduction in bulk density, increase in water-retention capacity, increase in permeability to air and water, reduction in tendency to "slake" or "puddle" in the presence of water, and improved resistance to erosion. In the authors' opinion (based on fundamental research now in progress) it appears likely that polyelectrolytes effect these changes both by flocculating the fine soil particles into stable, waterresistant aggregates, and by stabilizing to water such aggregates as may exist prior to addition of polyelectrolyte. It therefore appears that the ability of a polyelectrolyte to condition a particular soil will be determined by the degree to which it can cause aggregation of fine particles, and by the stability of the aggregates produced.

In the last analysis, the most reliable fashion in which soil conditioners can be evaluated is by detailed performance studies under field conditions. However, to test every potentially interesting polyelectrolyte by such methods would be an extremely time-consuming and expensive process. A need thus exists for some relatively simple, easily reproduced laboratory tests by which performance of soil conditioners in soils can be rapidly compared and contrasted. These tests must, of course, be selected with an eye toward field requirements, and must in the long run be capable of correlation with results of field tests.

The object of this investigation has been to develop test procedures which meet the requirements of simplicity and reproducibility, and which point out clearly differences in the action of certain polyelectrolytes on certain soil types. Inasmuch as the results of these tests have not yet been correlated with field behavior, it would be unwise to attempt to draw more than very rough qualitative conclusions from the experimental

	Tal	ole I. Soils Studi	ied	
Characteristics		Virginia Sandy Clay (VSC)	New Hampshire Silt (NHS)	Texas Alkali Sand (TAS)
Coarser than 0.06 mm., %		40	18	30
Between 0.06 and 0.002 mm.,	%	32	75	68
Finer than 0.002 mm., %		28	7	2
Liquid limit, %		40	27	30
Plastic limit, %		22	27	25
Composition		Quartz 40%	Quartz 55%	Quartz 40%
		Kaolinite 25%	Feldspar and	Calcite 10%
		Hydrous oxides of iron and alumi- num	mica	Organic matter and sodium chloride

data reported regarding field performance of polyelectrolytes as soil conditioners. Nevertheless, the tests employed are believed to compare under essentially identical conditions the following properties of polyelectrolytes:

Ability to flocculate soils and thus reduce the fine particle fraction.

Capacity for maintaining low bulk density of soil.

Ability to produce soil aggregates resistant to breakdown by hydraulic action.

Ability to produce aggregates resistant to breakdown on freezing and thawing.

Ability to produce aggregates resistant to breakdown on drying and wetting. Ability to increase the water-holding

capacity of soils at low moisture tension. Capacity for increasing the permeability

of soils to water.

Tests of this type will, it is hoped, make it possible to eliminate rapidly from consideration compounds whose efficacy in particular soil systems is obviously low, and to select only the more promising additives for extensive field evaluation.

The tests described are merely representative of general laboratory procedures which, in the opinion of the writers, point out differences in performance of soil conditioners. Specific test conditions such as operating temperatures, dimensions of equipment, flow rates, and pressures were selected purely on a basis of convenience, except where otherwise noted. Much more rigid specifications of operating conditions will have to be formulated, however, if tests of this nature are to be standardized for general use.

Polyelectrolytes and Soils Studied

In order to obtain a fairly broad picture of polyelectrolyte behavior in soils, three polymers of markedly different chemical structure and three "problem" soils of widely different composition were selected for study.

Polyelectrolytes. A 15% aqueous solution of sodium polyacrylate prepared by the incomplete caustic hydrolysis of polyacrylonitrile (designated as A in tables and graphs).

The calcium salt of a copolymer of maleic acid and polyvinyl acetate (designated as M in tables and graphs).

A copolymer of styrene and N-methyl-2-

vinyl pyridine methosulfate, molecular weight approximately 200,000 (designated as P in tables and graphs).

Soils. The textural, plastic, and compositional characteristics of the three soils are summarized in Table I.

The Virginia clay is a red, residual, wellgraded soil typical of the region. It becomes muddy when wet and cakes when dried and, therefore, presents many engineering and agricultural problems. The silt from Manchester, N. H., is a uniform, glacial deposit and is representative of New England silts. The silty sand from Texas is a black, alkali soil of considerable agricultural importance.

Flocculation Efficiency and Sediment Density Tests

One important action of polyelectrolytes in soils appears to be flocculation of fine particles. Relatively simple laboratory tests are available for determining the size of particles present in soils, one of which has been adapted for use in this study as a means of determining changes in apparent particle size which result from polyelectrolyte addition. This test. which involves sedimentation of soils suspended in water, also permits measurement of corresponding changes in bulk density of the sedimented soil.

Fifty grams of dry, untreated Procedure soil were introduced into a 1liter graduate containing somewhat less than 1 liter of water, and suspended in the water by shaking. A measured amount of polyelectrolyte in aqueous solution was added to the suspension, the volume brought to exactly 1 liter with additional water, the mixture reagitated, and the solid then allowed to settle for 2 hours. The particle size distribution of the sediment was measured by the hydrometer procedure (3), and the volume occupied by the sediment was determined.

Soil	Additive	Additive Concn., G./100 G. Dry Soil	% of Soil Weight Finer than 0.06 Mm.	Sediment Density, G. Dry Soil/Cc.	Flocculation Index, %	Sediment Densit Index, %
VSC			15.5	0.833		
	A	0.05	0.0	0,575	100	31
	А	0.10	0.0	0.445	100	47
	M	0.05	5.0	0.695	68	17
	M	0.10	3.8	0.658	75	21
	P	0.05	1.0	0,746	94	10
	P	0.10	1.0	0.715	94	14
NHS			65.0	0.910		
	А	0.05	0.0	0.463	100	49
	А	0.10	0.0	0.495	100	46
	М	0.05	8.0	0.641	88	30
	М	0.10	7.2	0.770	89	15
	Р	0.05	3.1	0.770	95	15
	Р	0.10	4.7	0.794	93	13
TAS			37.4	1.000		
	А	0.05	6.1	0.715	84	29
	Α	0.10	9.4	0.746	75	25
	М	0.05	20.9	0.725	44	28
	М	0.10	23.4	0.715	37	29
	Р	0.05	25.0	0.735	33	27
	Р	0.10	12.5	0.650	67	35

- - -

The results of these tests are Results summarized in Table II. Of Tests The effect of polyelectrolytes on particle size is expressed in terms of the fraction of the soil weight remaining as particles smaller than 0.06 mm. (Particles smaller than 0.06 mm. are commonly classified as "silt," while particles larger than this are considered "sand.") To facilitate comparison of the effects of polyelectrolytes upon both particle size and density of the soils, the changes in these properties have been expressed as percentages of the values for the untreated soils. These are referred to as indexes in the subsequent discussion.

The acrylate polymer has the most beneficial effect on the particle size of the three soils. It is also most effective in reducing the density of the Virginia clav and the New Hampshire silt, but is inferior to the pyridine polymer in this respect with the Texas sand. While there appears to be no significant correlation between flocculation index and sediment-density index, there is no case where marked reduction in density is accomplished without a significant increase in particle size. These observations lend credence to the hypothesis that an increase in soil porosity by polyelectrolyte treatment is caused by flocculation, but that flocculation alone need not necessarily bring about an increase in porosity. Consequently, it may be concluded that reduction in sediment density (or increase in density index) is a better measure of polyelectrolyte efficacy in improving soil structure than is the flocculation index.

The effect of polyelectrolyte concentration upon the above properties of the soils studied is erratic. With the clayey soil, the higher concentrations of the three polymers are more effective than the lower concentrations. With the New Hampshire silt, the converse is true. With the Texas soil, the effect of increasing concentration varies among polymers. Undoubtedly, the concentration of polyelectrolyte required to cause maximum improvement in soil structure depends to a large extent upon the adsorptive selectivity of the soil for the polymer added, and the specific surface area of the Simple sedimentation tests of the soil. type described above may prove to be a rapid means of determining the range of concentration in which a polyelectrolyte will cause a substantial improvement in the physical properties of a given soil.

Hydraulic Stability Tests

The object of the tests described below was to determine the fraction of the weight of a polyelectrolyte-treated soil which remains as aggregates larger than approximately 0.07 mm. (200 mesh) after exposure to flowing water for an extended period. Since soils composed of particles (or aggregates) larger than 0.07 mm. generally exhibit the relatively high permeability and other desirable structural properties characteristic of sands, it is believed that this size range is the most convenient and equitable point to draw the line of demarcation between aggregates which are "too small" or "just large enough" to give desirable structural properties to a soil.

Procedure Twenty-five grams of dry soil were added to 50 ml. of water containing a known quantity of dissolved polyelectrolyte. The mixture was

gently stirred to assure uniform contact between soil and solution, and then transferred to a standard 200-mesh sieve 8 inches in diameter.

The sieve was then placed in a waterfilled vessel, in which the water level was adjusted to reach about 1/4 inch above the wire screen. Water (at 10° to 12° C.) was then allowed to flow downward through the sieve at a rate of about 2 liters per minute for 15 minutes. The water was introduced into the sieve via a horizontal tee-connection in order to prevent direct impingement of the stream upon the soil sample. The sieve was shaken gently every few minutes during the washing process to redistribute the soil over the screen and permit escape of fine particles.

At the end of the washing period, the residue on the sieve was flushed into a Büchner funnel, allowed to drain free of water, dried at room temperature, and weighed.

Preliminary experimentation with this procedure showed clearly that the rate of loss of soil after 15 minutes' washing was very low, and that the frequency of shaking of the sieve of variation in the water flow rate over a wide range (1 to 3 liters per minute) had little effect on the fraction of the soil sample retained. Results were found to be reproducible within ± 0.5 gram ($\pm 2\%$ of the sample weight.)

Results Of Tests The results of these tests are summarized in Table III. A "hydraulic stability index," defined as the percentage decrease in weight loss on washing due to polyelectrolyte action, has been calculated for each run.

The data indicate that the three polyelectrolytes examined have a significant beneficial effect upon the resistance of soil to hydraulic breakdown. The acry-

Table III. Hydraulic Stability Characteristics of Polyelectrolyte-Treated Soils

Soil	Additive	Concn., G./100 G. Dry Soil	Weight Lost from 25 G. Sample, G. (±0.5)	Weight Loss on Washing, % (±2)	Hydraulic Stability Index, %
VSC			5.4	22	
	А	0.05	2.2	9	$59(\pm 10)$
	А	0.10	1.6	6	$70(\pm 10)$
	М	0.05	2.2	9	$59(\pm 10)$
	М	0.10	2.2	9	$59(\pm 10)$
	Р	0.05	4.0	16	$26(\pm 10)$
	Р	0.10	3.0	12	$44(\pm 10)$
NHS			17.7	71	
	А	0.05	0.9	4	95 (±3)
	А	0.10	1.0	4	94 (±3)
	М	0.05	11.4	46	$36(\pm 3)$
	Μ	0.10	15.1	60	$15(\pm 3)$
	Р	0.05	12.6	50	29 (±3)
	Р	0.10	17.2	69	3 (±3)
TAS			15.5	62	
	А	0.05	9.4	38	$39(\pm 3)$
	А	0.10 /	10.0	40	$36(\pm 3)$
	М	0.05	12.5	50	$19(\pm 3)$
	М	0.10	12.1	48	$22(\pm 3)$
	Р	0.05	12.6	50	$19(\pm 3)$
	· P	0.10	6.3	25	$59(\pm 3)$

late polymer appears superior to the other two compounds in the Virginia sandy clay and in the New Hampshire silt. While the cationic pyridine polymer is of inferior effectiveness in these two soils, it is superior to the anionic polymers (at 0.1% concentration) in the Texas alkali soil. The effects of polymer concentration on hydraulic stability (as on sediment density) are erratic, and emphasize the importance of controlling conditioner concentrations in the field.

It is interesting to compare the percentage loss in soil weight during the washing process with the percentage of particles finer than 0.06 mm. determined in the corresponding flocculation tests. In all cases, the loss on washing on the 200-mesh sieve (screen opening 0.07 mm.) exceeds the latter figure by an appreciable margin. (It has generally been observed that the weight fraction of particles smaller than 0.06 to 0.07 mm. present in a soil, as determined by sedimentation methods, is usually less than that obtained by direct sieving. The differences are normally only of the order of a few per cent, and are thus small compared with the differences noted here.) The difference between these two figures must equal very nearly the fraction of the soil weight consisting of aggregates larger than 0.06 to 0.07 mm. which break down during washing. Employing this difference as a more precise measure of aggregate stability to hydraulic action, it is noted that the maleate polymer is most effective in the Virginia sandy clay, the acrylate polymer in the New Hampshire silt, and the pyridine polymer in the Texas alkali soil. These observations serve to empha-

size that the ability of a polyelectrolyte to flocculate a large fraction of a soil mass is not necessarily a criterion of aggregate stability.

Freeze-Thaw Stability Tests

The stresses which are set up in a wet soil aggregate when subjected to freezing are probably large, and may cause disintegration of the aggregate on subsequent thawing. The object of this test was to determine the extent of aggregate deterioration (into particles less than 200-mesh) when treated soils are subjected to repetitive freezing and thawing.

Twenty-five-gram polyelec-Procedure trolyte-treated soil samples, prepared as described above, were transferred to filter paper and drained of excess water in a Büchner funnel. The samples were placed in a deep-freeze unit at -23° C. until frozen solid, allowed to thaw completely at room temperature without evaporation of water, and refrozen. Samples of each soil polyelectrolyte combination were subjected to two freeze-thaw cycles; duplicate samples were subjected to four cycles. After the final thawing, each sample was flushed with water into a porcelain dish, agitated gently to break up large clumps, transferred to a 200-mesh sieve, and subjected to the washing test.

The results of these tests are Results shown in Table IV and **Of Tests** Figure 1. Comparison of polyelectrolyte performance in terms of a "freeze-thaw index" (defined as percentage reduction in loss of treated soil after four freeze-thaw cycles relative to that of untreated soil under similar conditions) shows:

With the three soils employed the three polyelectrolytes examined cause



Figure 1. Freeze-thaw stability of polyelectrolyte-treated soils

significant increase in stability of aggregates to freezing and thawing.

With the Virginia sandy clay, the maleate polymer appears superior to the acrylate polymer in this respect, in spite of the fact that the latter has a greater beneficial effect on hydraulic stability. The stabilizing effect of pyridine polymer is somewhat more rapidly lost by freezing and thawing than that of the other two polyelectrolytes.

Soil	Additive	Additive Concn., G./100 G. Dry Soil	Wt. of 25 G. Sample Lost on Wash after Two Freeze-Thow Cycles, G. (±0.5)	Loss after Two Cycles, %	Wt. Loss after Four Cycles, G.	Loss after Four Cycles, % (+2)	Freeze-Thaw Index, の人
VSC		, ,	6.1	24	6.2	25	/0
100	Δ.	0.05	4.0	16	0.2	25	0 (1 10)
	а А	0.03	4.0	10	4.7	23	$0(\pm 10)$
	A A A A A A A A A A A A A A A A A A A	0.10	7.5	10	4.7	19	$24(\pm 10)$
	M	0.00	J.I 2 1	12	J.0 2.0	14	$42(\pm 10)$
	p	0.10	2.1	20	5.0	12	$52(\pm 10)$
	P	0.10	3.3	13	5.4	22	$13(\pm 10)$ $10(\pm 10)$
NHS			24.0	96	24.1	96.5	
	А	0.05	10.9	44	20.2	81	$16(\pm 2)$
	А	0.10	4.9	20	13.6	54	$44(\pm 2)$
	М	0.05	14.4	58	21.6	86	$10(\pm 2)$
	Μ	0.10	16.1	64	17.6	70	$27(\pm 2)$
	Р	0.05	14.1	56	23.2	93	4(+2)
	Р	0.10	17.7	71	22.9	92	$5(\pm 2)$
TAS			17.9	72	18.4	74	
	А	0.05	12.4	50	14.3	57	$22(\pm 3)$
	А	0.10	8.4	34	10.5	42	$43(\pm 3)$
	М	0.05	14.2	57	16.2	65	$12(\pm 3)$
	М	0.10	13.7	55	15.2	61	$17(\pm 3)$
	Р	0.05	15.5	62	16.7	67	$9(\pm 3)$
	Р	0.10	8.0	32	10.7	43	$42(\pm 3)$

.



Figure 2. Wet-dry stability of polyelectrolyte-treated soils

With New Hampshire silt, the relatively greater stabilizing influence of the acrylate polymer exhibited in the washing test persists through the freezing and thawing process. While the maleate polymer improved the hydraulic stability of this soil to only a moderate extent, its effect upon freeze-thaw stability is relatively more satisfactory. The pyridine polymer appears to be inferior in freeze-thaw stability to the other compounds with this soil, as with the sandy clay.

With the Texas alkali sand, although the pyridine polymer effects greatest stabilization to hydraulic breakdown, the acrylate polymer proves most durable in the freeze-thaw tests.

In general, the higher concentration (0.1%) of each polyelectrolyte lends greater freeze-thaw stability to each soil examined than the lower concentration. These results could not have been predicted from hydraulic stability data alone, in which frequently the lower concentrations of polyelectrolyte (particularly with the New Hampshire silt) appear to give more satisfactory results. These observations suggest that the freezing and thawing process not only ruptures aggregates but also permits adsorbed polymer to be extracted by water, with the result that the active polyelectrolvte content of the soil is gradually reduced. On the whole, the deterioration of conditioner-stabilized aggregates resulting from repetitive freezing and thawing is considerably greater than that caused by hydraulic action alone; this suggests that the field durability of soil conditioners in areas subject to frequent freezing and thawing may be poorer than in other areas.

Wet-Dry Stability Tests

The capillary forces produced by removal or addition of water to soil aggregates are responsible to a great extent for aggregate breakdown, and hence for gradual loss of desirable structural characteristics of soils. These tests were intended to ascertain the resistance to breakdown on cyclic wetting and drying of polyelectrolyte-stabilized aggregates.

Twenty-five-gram samples of Procedure polyelectrolyte-treated soils were allowed to dry completely in an oven at 60 ° C. The samples were removed from the oven, allowed to cool to room temperature, rewet with 25 ml. of water, agitated briefly to ensure thorough contact of soil and water, and allowed to stand for 15 minutes. They were then replaced in the oven to dry again. One set of samples was subjected to two such drving and rewetting cycles, and another to four cycles. After the final rewetting, the samples were transferred to a 200-mesh sieve, and subjected to the wash test described above.

Results Of Tests The results of these tests are summarized in Table V and Figure 2.

The three polyelectrolytes studied exert a marked stabilizing effect upon aggregates of the soils examined when subjected to repetitive drying and wetting.

With Virginia sandy clay, the maleate polymer (at 0.1% concentration) is most satisfactory. The trends observed with this soil parallel rather closely those observed in the corresponding freeze-thaw tests.

With New Hampshire silt, consistent with the hydraulic stability and freezethaw tests, the acrylate polymer performs most satisfactorily during cyclic drying and wetting. Relative differences between the acrylate and maleate compounds in terms of wet-dry resistance are somewhat more marked than those observed in the previously described tests involving this soil.

Table V. Wet-Dry Stability of Polyelectrolyte-Treated Soils

Soil	Additive	Additive Concn., G./100 G. Dry Soil	Wt. of 25 G. Sample Lost on Wash after Two Wet-Dry Cycles, G. (±0.5)	Loss after Two Cycles, % (±2)	Wt. Loss after Four Cycles, G. (土0.5)	Loss after Four Cycles, % (±2)	Wet-Dry Index, %
VSC			7.3	29	9.7	39	
	А	0.05	5.4	22	8.9	36	$8(\pm 10)$
	Α	0.10	4.9	20	7.5	30	$23(\pm 10)$
	М	0.05	5.1	20	7.6	30	$22(\pm 10)$
	М	0.10	3.9	16	5.1	20	$47 (\pm 10)$
	Р	0.05	7.6	30	8.6	34	$11(\pm 10)$
	Р	0.10	6.6	26	7.4	30	$27(\pm 10)$
NHS			24.0	96	24.1	96.5	
	Α	0,05	15.2	61	16.8	67	$30(\pm 2)$
	А	0,10	10.3	41	10.7	43	56 (±2)
	М	0.05	16.2	65	20.5	82	$15(\pm 2)$
	М	0.10	16.2	65	17.5	70	$27 (\pm 2)$
	Р	0.05	23.0	92	23.8	95	$1(\pm 2)$
	Р	0.10	21.8	87	21.4	86	$11(\pm 2)$
TAS		· · · ·	16.5	66	16.4	66	
	А	0.05	10.1	40	10.8	43	$34(\pm 3)$
	А	0.10	9.5	38	9.7	39	41 (± 3)
	М	0.05	13.0	52	13.4	54	$18 (\pm 3)$
	М	0.10	12.2	49	12.5	50	24 (±3)
	Р	0.05	13.3	53	14.2	57	$13(\pm 3)$
	Р	0.10	16.9	68	17.3	69	0 (±3)



Figure 3. Water retention capacity of polyelectrolyte-treated soils as a function of bulk density after drainage

With the Texas sand, the acrylate polymer was found to yield aggregates most stable to wetting and drying. This soil (without treatment) underwent less breakdown on cyclic drying and wetting than on freezing and thawing; the same observations apply to this soil when treated with the acrylate and maleate polymers. Why the rate of deterioration of this soil is so rapid when treated with 0.1% of the pyridine polymer and subjected to drying and wetting is not clear.

The higher concentrations of polyelectrolytes generally lend greater resistance to breakdown of the soil studied during drying and wetting than do the lower concentrations. Aggregate breakdown on drying and wetting is more rapid (irrespective of the polyelectrolyte added) than freeze-thaw breakdown for the Virginia sandy clay, but the opposite is true for the other two soils. Observations of this nature, combined with climatological information about the area of origin of a soil, may permit reasonably sound qualitative predictions of the probable efficacy of a given polyelectrolyte under field conditions.

Water-Retention Tests

From the agricultural standpoint, another important soil property is undoubtedly the capacity to hold water. There are, however, two mechanisms by which a soil may pick up and retain water under field conditions: The soil may imbibe subsurface water by capillarity, and it may absorb rain or other surface water to a certain extent before runoff or puddling occurs. Fine-textured soils generally have a greater capacity to retain water under high capillary tensions than do coarser grained soils; consequently, addition of polyelectrolytes to fine-grained soils, by increasing the mean pore size, might be expected to decrease the ability of such a soil to imbibe water at high tensions. Recent data (7) seem to substantiate this prediction. On the other hand, polyelectrolyte treatment of soil, by increasing soil porosity, would be expected to increase the capacity of a soil to hold surface water without runoff or puddling. As it is unlikely that more than the top 6 to 12 inches of the soil would ever be treated with polyelectrolyte in an agricultural application, it would appear that surface water retention capacity would be the more important property to consider in evaluating relative performance of polyelectrolytes. For this reason, water retention under low (8 to 13 cm.) tension was determined.

To 300 ml. of water contain-Procedure ing the desired amount of dissolved polyelectrolyte were added 200 grams of air-dry soil, and the mixture was gently agitated. The suspension was transferred to a Lucite tube (inside diameter 5 cm.), the bottom of which was fitted with a 200-mesh supporting screen. The tube was connected to a constant-head reservoir which maintained the water level precisely at the bottom of the soil column. The soil sample was allowed to drain by gravity for 3 days; measurement of the initial and final height of the soil column, and the final weight of soil and water retained, permitted calculation of the initial and final bulk density, and final water content. From these data was calculated the final "degree of saturation," defined as the percentage of void space in the soil which is filled with water.

Results Of Tests The results of these tests are summarized in Table VI.

The acrylate polymer appears to effect the greatest increase in waterretention capacity for the Virginia sandy clay and the New Hampshire silt, while the pyridine polymer has the greatest effect in the Texas alkali sand. The maleate polymer at 0.1% concentration appears to exert a significant lowering of the degree of saturation of the Virginia sandy clay. The reason for this phenomenon is obscure, but it may possibly be explained by a reduction in water-soil contact angle or "wettability" caused by the nature of the orientation of this polymer on the particle surfaces.

The increase in water retention capacity brought about by polyelectrolyte addition is, as might be expected, greatest for the New Hampshire silt, which exhibits the greatest reduction in bulk density on polyelectrolyte treatment. There is, moreover, a correlation between









bulk density after drainage of water from a treated soil and water retention by the soil, as shown in Figure 3. This plot suggests that the water-retention capacity of a treated soil can in most cases be predicted from a knowledge of its bulk density, irrespective of the nature of the soil or of the polyelectrolyte used.

An attempt has been made to correlate graphically the bulk density of a conditioner-treated soil as determined by a simple sedimentation test with bulk density after drainage (Figure 4) and with water-retention capacity (Figure 5). Figure 4 indicates that the sediment density of a treated soil is considerably lower than the bulk density after drainage, and that the difference between these two densities is greater for more porous soils. These observations reflect the frequently noted fact that low-density flocculated soils are usually more compressible than more compact, higher density soils. Figure 5 indicates a general trend toward higher water-retention capacity with soils of low sediment density.

Although the scatter of the experimental data about the best lines drawn in Figures 4 and 5 is appreciable, over 80%of the points lie within $\pm 6\%$ of the mean final water content, and within ± 0.04 gram per cc. of the mean final bulk density. Inasmuch as these data represent the behavior of three different polyelectrolytes and three soil types, the correlation may be of practical utility. If continued experimental measurements substantiate the observed trends, it may prove possible to employ an easily determined sediment density measurement as a means of predicting the porosity and water-retention characteristics of polyelectrolyte-treated soils, irrespective of soil type or conditioner composition.

Permeability Tests

One of the most important properties of soil in both agricultural and engineering applications is its permeability to fluids. The object of the test described below was to determine the effect of polyelectrolytes upon the permeability of soils to water, to measure changes in permeability of treated soils resulting from prolonged water flow, and to determine the causes of such changes in permeability.

Apparatus Permeability measurements were made using a specially designed Lucite permeameter shown in Figure 6. The permeameter was fitted with two piezometer outlets 10 cm. apart to permit determinations of permeability at intermediate points in the soil sample. All measurements were made at an applied hydrostatic head of 244 cm. of water.

Procedure To 500 grams of dry soil were added 400 ml. of water containing the required amount of chemical in solution. After being mixed 15 seconds with a power stirrer, the slurry was introduced into the permeameter, using a small dump bucket to minimize particle segregation. Water was allowed to flow through the sample for about 35 hours. Volumetric flow rate, piezometer pressure, temperature, and bed height were measured periodically throughout the test.

Results Of Tests Figure 7 summarizes all permeability tests performed on Virginia sandy clay treated with the three polyelectrolytes described above. In all cases, the permeability decreases markedly with the quantity of water passed through the soil, approaching a nearly constant value after pro-



Figure 6. Permeability measuring apparatus

longed flow. Differences in behavior of the polyelectrolytes are illustrated more clearly in Table VII, which shows the permeability of the treated soil both early in the permeation test (after 1 ml. of water per cc. of sample volume has passed through the bed) and toward the end of the test (after 33 ml. of water per cc. of sample volume have passed through

Table VI. Water-Retention Characteristics of Polyelectrolyte-Treated Soils

of on Increase	Degree of Saturation after Drainage, %	Water Content, G. H ₂ O/100 G. Dry Soil	Density, Cc. (±0.04)	Bulk E G. Dry Soil/	Additive Concn., G./100 G. dditive Dry Soil		Soil
e, in Water Retention, %		after Drainage (±3)	After drainage	Before drainage		Additive	
	98	60	1.02	1.01			VSC
4	89	62	0.94	0.93	0.05	А	
19	93	71	0.88	0.83	0.10	А	
3	88	61	0.94	0.93	0.05	М	
-10	78	54	0.95	0.94	0.10	М	
4'	89	62	0.94	0.91	0.05	Р	
6	86	63	0.90	0.89	0.10	Р	
	95	42	1.23	1.21			NHS
63	97	69	0.94	0.86	0.05	Α	
65	97	70	0.93	0.83	0.10	Α	
25	93	53	1.07	0.97	0.05	М	
31	94	55	1.05	0.98	0.10	М	
18	94	50	1.11	1.02	0.05	Р	
33	93	56	1.03	0.97	0.10	Р	
· · · ·	96	54	1.06	1.01			TAS
6	96	57	1.03	0.98	0.05	А	
1	92	54	1.04	1.00	0.10	Α	
2	94	54	1.04	1.01	0.05	М	
-2	93	53	1.05	1.04	0.10	М	
18	95	63	0.94	0.89	0.05	Р	
18	93	63	0.94	0.86	0.10	Р	
	96 96 92 94 93 95 93	54 57 54 53 63 63	1.06 1.03 1.04 1.04 1.05 0.94 0.94	0.98 1.00 1.01 1.04 0.89 0.86	0.05 0.10 0.05 0.10 0.05 0.10	A A M M P P	145



Figure 7. Permeability of polyelectrolyte-treated Virginia sandy clay as a function of volume of water through sample

the bed). The greatest initial improvement in permeability was produced by the pyridine polymer, but soil treated with this compound suffered the greatest reduction in permeability with water flow. Although the acrylate polymer caused a much smaller initial permeability improvement, its effect proved to be most durable, yielding the most permeable soil after prolonged water flow.

These data thus show clearly that the initial increase in soil permeability effected by polyelectrolyte addition does not necessarily signify permanence of structural improvement. The nature of the reduction in permeability with water flow is elucidated by measuring the variation of permeability of various segments of the soil column during flow.

Figure 8 presents these measurements for polyacrylate-treated soil, and indicates a greater reduction in permeability with time in the lower sections of the bed than in the upper sections. These changes become more apparent when the permeability of each segment of the soil column at any instant is divided by the average column permeability at the same instant, as shown in Figure 9. The variations observed can most readily be explained in terms of gradual transport of fines from the top toward the bottom of the column. Such transport will tend to free the voids in the upper segment of the bed from obstructions and thereby increase permeability, while accumulation of fine particles in the lower regions will plug the voids and thereby decrease permeability. Since, however, the permeability of all sections of the bed decreases with time, it appears that hydraulic disintegration of aggregates generates fine particles at a rate greater than that at which the fines are transported downward through the soil mass.

Figure 10 shows similar data for pyridine polymer-treated soil. In this case, it appears that the initial rate of aggregate breakdown greatly exceeds the rate of transport of fines, as evidenced by the relative reduction in permeability of the upper segments of the soil column. The relative increase of permeability of the lowest segment of the column is undoubtedly due to the leaching of fines out of the bed through the 200-mesh retaining screen at the bottom of the permeameter.

That plugging of the soil voids with fine particles is the explanation for the observed reductions in permeability is further substantiated by the observation

that the average bulk density of the soil column increases very little during flow.

Figure 8. Permeability of polyacrylate-treated Virginia sandy clay, showing variations in permeability in isolated segments of the soil column



Attempts to correlate quantitatively the effects of polyelectrolytes upon soil permeability, or upon changes in permeability with water flow, with previously discussed criteria of polyelectrolyte action have met with failure. Evidently a combination of factors, including the size and size distribution of the aggregates formed, the density or porosity of the treated soil, and the hydraulic stability of the aggregates, determines the water permeability and permeability decrease during flow for a given soil mass. Qualitatively, it may be assumed that a polyelectrolyte which, when added to a particular soil, (1) reduces the fraction of fine particles to a very low value, (2) causes marked reduction in sediment density, and (3) yields aggregates which are stable to hydraulic action, may be expected to improve appreciably the soil permeability. If, however, the additive fails to meet any one of these three requirements, little or no improvement in permeability may be realized.

Conclusions

A series of laboratory tests, aimed at measuring the ability of polyelectrolytes to improve soil structure and to maintain such improved structure under adverse





Figure 9. Variations in relative permeability with water flow for isolated segments of soil column; polyacrylate-treated Virginia sandy clay

conditions, yields reproducible results, and shows significant differences in polyelectrolyte activity in soils.

Both cationic and anionic polyelectrolytes appear to exert a significant and durable flocculation and aggregatestabilizing action on three widely different soil types.

Acrylate and maleate polymers exert a somewhat more durable aggregate-stabilizing action on the soils examined than a cationic pyridine polymer.

There appears to be a correlation between the water-retention capacity of a polyelectrolyte-treated soil and the sediment density of the soil as measured in a simple sedimentation test. Other important characteristics of polyelectrolytetreated soils. such as hydraulic stability, freeze-thaw and wet-dry resistance, and water permeability, do not appear to correlate satisfactorily with such easily measured soil properties.

The ability of polyelectrolytes to increase water permeability of soils is very marked. There is, however, a significant loss in permeability with water flow

for treated soils, which appears to be caused by the plugging of voids by fine soil particles. Pore size, the quantity of unflocculated soil particles initially present, and the rate of aggregate breakdown by hydraulic action are all believed to influence the magnitude of reduction in permeability caused by water flow.

The ability of a polyelectrolyte to produce and maintain significant improvement in soil structure is profoundly influenced by soil type and the physical conditions to which the soil is to be subjected. For these reasons it seems unlikely that a single, simple laboratory screening test will be developed by which polyelectrolyte efficacy in soils can be accurately determined.

Acknowledgment

The authors wish to acknowledge the assistance of the American Polymer Corp., which sponsored this research. Thanks are also due to C. N. Baker and J. K. Mitchell for help in the experimental work.



Figure 10. Variations in relative permeability with water flow for isolated segments of soil column; polyvinyl pyridinetreated Virginia sandy clay

Literature Cited

- (1) Allison, L. E., Soil Sci., 73, 443 (1952).
- (1952).
 (2) Hedrick, R. M., and Mowry, D. T., *Ibid.*, **73**, 427 (1952).
 (3) Lambe, T. W., "Soil Testing for Engineers." New York, John
- Wiley & Sons, 1951.
 (4) Martin, W. P., *et al.*, Soil Sci., 73, 455 (1952).
- (5) Michaels, A. S., "Altering Soil-Water Relationships by Chemical Means," p. 59, Proceedings of Conference on Soil Stabilization, Mass. Institute of Technology, June 18-20, 1952. (6) Michaels, A. S., "Some Colloidal
- and Physico-Chemical Aspects of Soil-Chemical Interactions," address before Northeastern Section, AM. CHEM. Soc., Cam-
- (7) Peters, D. B., Hagan, R. M., and Bodman, O. S., *Soil Sci.*, **75**, 476 (1953)
- Quastel, J. H., Ibid., 73, 419 (1952).
- (9) Ruehrwein, R. A., and Ward, D. W., *Ibid.*, 73, 485 (1952).
- Weeks, L. E., and Colter, W. G., *Ibid.*, **73**, 473 (1952). (10)

Received for review March 12, 1953. cepted September 2, 1953. Ac-

Table VII. Permeability Coefficients

(virginia sanay ciay)								
Additive	Additive Concn., G./100 G. Dry Soil	Initial Bulk Density, G. Dry Soil/Cc.	Initial Permeability Coefficient, Cm./Sec. 🗙 104	Final Bulk Density, G. Dry Soil/Cc.	Final Permeability Coefficient, Cm./Sec. 🗙 104	Final Permeability, % of Initial		
None A A M	0.05 0.10 0.05	1.22 1.14 1.15 1.16	$\begin{array}{c} 4.4 \pm 0.4 \\ 9.9 \pm 1.0 \\ 10.8 \pm 1.1 \\ 10.3 \pm 1.0 \end{array}$	1.23 1.14 1.15 1.18	$ \begin{array}{r} 1.4 \pm 0.1 \\ 4.0 \pm 0.4 \\ 3.5 \pm 0.4 \\ 2.2 \pm 0.2 \end{array} $	31 ± 8 40 ± 10 32 ± 10 21 ± 5		
M P P	0.10 0.05 0.10	1.17 1.13 1.10	$12.7 \pm 1.3 \\ 18.6 \pm 1.9 \\ 32.5 \pm 3.3$	1.18 1.15 1.13	$ \begin{array}{r} 2.1 \pm 0.3 \\ 2.7 \pm 0.3 \\ 1.9 \pm 0.2 \end{array} $	$ \begin{array}{r} 21 \pm 0 \\ 24 \pm 6 \\ 15 \pm 4 \\ 6 \pm 1 \end{array} $		