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Received for review September 11, 1953. Accepted January 28, 1954. Presented before the Division of Agricultural and Food Chemistry, Fermentation Subdivision, Symposium on Non-therapeutic Uses for Antibiotics, at the 124th Meeting of the AMERICAN CHEMICAL SOCIETY, Chicago, Ill.

SOIL CONDITIONERS

Laboratory Evaluation of Polyelectrolytes As Soil Conditioners

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In the study of soil structure and its improvement with water-soluble polymers it was necessary to develop a method for comparing the soil-conditioning properties of many polymer samples in order to determine the effect of chemical composition, molecular weight, and molecular configuration. The method developed is a modification of a wet-sieve test for measuring aggregate stability. When used under closely controlled conditions the method is reproducible, is applicable to a variety of water-soluble polymers, and provides an index of the relative soil-conditioning activity of the polymer in use. The importance of a number of variables and their relationship to the test are discussed. The method is suitable for comparing different products as well as different production batches of a given product.

SYNTHETIC POLYELECTROLYTES are now an article of commerce as soil conditioners. In the manufacture of these materials it is necessary to be able to determine the relative soil-conditioning effectiveness of different chemicals and of different production batches of a given product. From the consumers' point of view, a method by which independent groups can compare the effec-

tiveness of various commercial products is also desirable.

To answer the needs of the manufacturer and the consumer, a method for evaluating polyelectrolytes as soil conditioners should give reproducible results, should be applicable to a variety of polyelectrolytes, and should provide information on the activity to be expected when the products are used as soil-conditioning

agents. Because polyelectrolytes function as soil conditioners by stabilizing soil aggregates, techniques that provide information on aggregate stability are the basis of many methods of evaluating polyelectrolytes.

In the past, several methods have been used to evaluate the effect of numerous additives upon soil structure. McCalla (1) used a pipet method to investigate

the effect of various substances upon the aggregation of the silt and clay particles of soil. Geoghegan and Brian (2) added solutions of various materials to a pulverized soil (52-mesh) under standard conditions and formed crumbs by pressing the moist soil through a sieve with 3-mm. openings. After drying, the crumbs were agitated in water and then wet-sieved. Aggregate stability was expressed by the percentage of unslaked aggregates.

Quastel and Webley (7) added a number of materials to soil with sufficient water to form a thick mud. After drying, the mass was broken into 2 to 4-mm. crumbs which were evaluated in a Warburg apparatus. Aeration in the soil at various moisture contents was determined by measuring under standard conditions the amount of oxygen used by microorganisms suspended in the water. The stability of the crumbs to water largely determined the aeration behavior observed.

Michaels and Lambe (5) have proposed a series of tests for comparing polyelectrolytes, based on the behavior and properties of a soil suspension upon treatment with the polymers.

At the Central Research Department, Monsanto Chemical Co., the development of an evaluation method was a necessary corollary to the development of polyelectrolytes as soil conditioners. A method similar to that of Geoghegan and Brian has been evolved which has proved applicable to a variety of polymers. This method was outlined by Hedrick and Mowry (3, 6). Since first described, the method has been further standardized.

Evaluation Method

Preparation of Test Soil

A standard soil is prepared from Miami silt loam dried to about 3% moisture, ground in a hammer mill through a 1/8-inch screen, and sieved to separate the fraction which will pass a 60-mesh sieve. This procedure is repeated until approximately 75% of the soil has been reduced to 60-mesh.

Soil Treatment

A 100-gram portion of pulverized Miami silt loam is placed in a 4-inch, flat-bottomed preparation dish, which is tapped on the table top to pack and level the soil. To the soil is added in one portion 30 ml. of distilled water containing the appropriate amount of the polyelectrolyte to be tested and the dish is tilted gently back and forth until all of the soil surface has been wetted and all the large bubbles covering unwetted soil have been removed.

For a 0.01% treatment, 0.01 gram of polymer would be contained in the 30 ml. of water added to 100 grams of soil. If the application of a solid polymer is being tested, the powdered sample is first

shaken with the soil in a pint jar to mix the two thoroughly; the mixture is then transferred to a preparation dish and 30 ml. of water is added. The soil surface is wetted as in the solution treatment.

Dishes containing the moist, treated soil are stacked together to prevent evaporation and allowed to stand 2 hours. If any of the soil has not been wetted at the end of this period, the soil is sliced gently with a spatula to distribute the dry soil and allow it to become wetted. The soil should not be mixed unnecessarily, as some polymer treatments are sensitive to the amount of mixing given the moist soil. All of the soil is transferred by means of a stainless steel spatula, 1.25 inches in width, to an 8-inch sieve with 4-mm. openings and pressed with the spatula through a small area of the sieve to form crumbs. It is important that each sample be pushed through approximately the same sized area, as this controls the compaction of the crumbs. The crumbs are placed in a 6-inch Petri dish and dried for 2 days at 25°C. and at a relative humidity of 40 to 50%.

Wet-Sieving A 40-gram sample of dried crumbs is wet-sieved by a modification of the Yoder (8) method. The apparatus is a device for raising and lowering any number of sets of sieves in water, and a variety of designs have been used. The apparatus used in the present study is shown in Figure 1.

Three sieves are used, with openings of 0.84, 0.42, and 0.25 mm., stacked in order of decreasing size from the top. The weighed soil crumbs are placed on the top sieve and the water level is allowed to rise in the tank until the soil begins to wet from below. The water level is then held constant until the crumbs are completely wetted by capillarity. The final water level is such that the top screen is at the surface of the water when the sieves are at the top of the cycle. The sieves are set in motion and are raised and lowered through a distance of 1.5 inches at a rate of 30 cycles per minute for 30 minutes. The sieves are allowed to drain and are dried in a circulating air oven at 110°C. The dry aggregates are removed from each sieve and weighed. The results are usually expressed as the aggregation value, which is the percentage of the soil retained as aggregates larger than 0.25 mm.

$$\text{Aggregation value} = \frac{\text{total weight (grams) recovered}}{40} \times 100$$

Application to Quality Control

For quality control of production of a single polymer the method has sometimes been modified by oven-drying treated soil crumbs or by wet-sieving undried crumbs. This elimi-

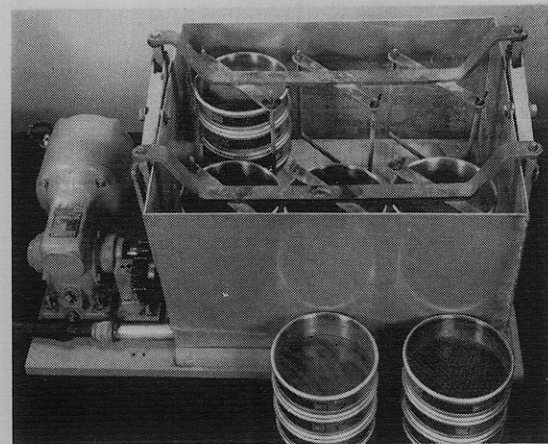


Figure 1. Wet-sieve apparatus

nates the 2-day air-drying period and allows the comparison of polymer samples in a few hours. Results obtained with samples of a given polymer by means of procedures so modified can be compared with each other, but are not necessarily regarded as indicative of the true aggregate-stabilizing properties of the product.

Although modifying the conditions of the test may change the magnitude of the aggregation values, the relative rating of polymer samples is usually not changed. Whenever a modification is made, however, it must be followed rigorously in order to obtain comparative data.

Interpretation of Evaluation

The reproducibility of the method is shown by the data in Table I. In this experiment each replicate was run on a different day and was independent of the others, even to the weighing of the polymer samples and the preparation of the standard solutions.

To obtain a true picture of the aggregate-stabilizing properties of a given polyelectrolyte, the polyelectrolyte should be evaluated at several rates of application and the results of solution and solid applications should be compared. The range of rates will depend upon the effectiveness of the materials being tested; 0.005 to 0.1% is a useful range for most of the polyelectrolytes that show promise as soil conditioners. Comparison of polymer samples can best be made when aggregation values are in the range of 20 to 70. The aggregation value is defined on the more or less arbitrary basis of aggregates larger than 0.25 mm. This value was selected because noncapillary porosity of soil is determined almost entirely by aggregates larger than 0.25 mm. (7).

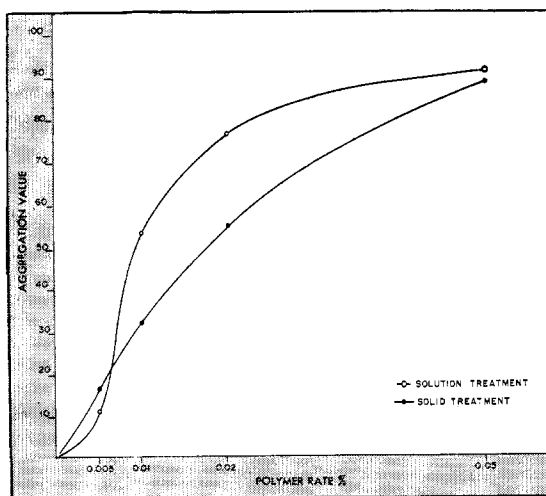
Application of a polyelectrolyte to the soil in aqueous solution normally gives higher aggregation values in the laboratory than application of the same amount of the polymer as a solid. A comparison of solution and solid applications of a

typical polyelectrolyte is given in Figure 2. The reason for the greater effectiveness of the solution treatment lies in fact that solution application assures uniform distribution of the polymer and maximum opportunity for adsorption on the soil. In a solid treatment uniform distribution is difficult to attain. Moreover, the aggregation value obtained from application of a solid product depends upon particle size, ease of solubility, and the viscosity of the resulting aqueous solution of the polyelectrolyte in the soil, as well as upon the inherent activity of the polymer being tested. Formulation with inert diluents may result in better distribution of the polyelectrolyte in the soil in practical applications; formulation rarely raises the aggregation value in a laboratory evaluation by the method described. The effect of particle size upon the aggregation values obtained by solid incorporation of one polyelectrolyte is shown in Table II. These data show that the aggregation value increases as the polymer is pulverized, because of better distribution and solubility of the polymer.

A method used to compare the aggregate-stabilizing properties of polyelectrolytes must take into account the different sensitivities of various polyelectrolytes. For example, some products are much more sensitive than others to the amount of mixing which can be given the moist, treated soil in the formation of crumbs without causing a decline in the aggregation value. In the procedure described above the treated soil is not mixed at all prior to the formation of crumbs. Some polymers are more sensitive than others to the temperature or humidity during the drying of the crumbs. For this reason both the temperature and humidity should be controlled.

This method has been used to evaluate several thousand polymer samples at the Central Research Department.

Figure 2. Comparison of solution and solid applications of polyelectrolyte



Effect of Variables

Composition Of Test Soil

The composition of the test soil is an important factor in the evaluation of polyelectrolytes as soil conditioners. Soils high in sand have low dry strength and crumbs made from such soils crumble on handling. Soils high in clay are gummy, and crumbs made with clayey soil and water alone do not slake rapidly on wet-sieving. Thus, while a clayey soil responds well to treatment of polyelectrolytes (as evidenced by improved workability and reduced stickiness), the improved structure is not always best measured by aggregate stability, as determined by wet-sieving. Miami silt loam which has been used is of more nearly average composition, containing 22% clay, 47% silt, and 31% sand. It forms crumbs which can be handled easily when dry, but have little stability to wet-sieving when no aggregate-stabilizing material has been added. Its original structure is more or less unimportant, since the soil is mechanically pulverized to destroy structure.

Because all of the variables are not known which determine the response of a given soil to polyelectrolyte soil conditioners, the aggregation value obtained with a polymer in Miami silt loam may not be a measure of its effectiveness as a soil conditioner in any other soil. However, the comparison on Miami silt loam has proved reliable on many other soils. The test might be expected to determine the response of polyelectrolytes in other soil types by substitution of that soil in the test, providing attention is given to determining optimum moisture content during treatment, the proper length time of sieving, etc.

Preparation Of Test Soil

In order to destroy natural aggregates larger than 0.25 mm., the test soil is pulverized, and then sieved to remove rocks and debris. The conditions under which the test soil is pulverized and the extent of pulverization affect the behavior of the soil during the test. For example, Miami silt loam containing 1.8% moisture when pulverized in a hammer mill gave lower aggregation values with a standard polyelectrolyte treatment than did Miami silt loam pulverized while containing 3% moisture. Grinding the soil at the lower moisture content appeared to shatter the natural soil aggregates into smaller fragments, which require more polymer for stabilization.

In order to be able to compare evaluation data, it is important that a large batch of test soil be prepared for use over a long period of time.

pH of Soil The pH of the soil may be a factor in the response of certain polyelectrolytes. It is desirable, therefore, to compare polyelectrolytes in a test soil having a pH

Table I. Replicated Evaluation of a Polymer Sample at Two Rates of Application

Replicate	Aggregation Value	
	0.005% Application	0.01% Application
1	13.8	57.8
2	15.8	58.5
3	17.8	60.0
4	11.8	55.5
5	12.0	58.0
6	16.8	60.3
Mean	14.7	58.4
Standard deviation	2.30	1.58
Range	6.0	4.8
95% confidence limits	±2.65	±1.82

Table II. Effect of Particle Size upon Aggregation Values Obtained by Treatment with Solid Polyelectrolyte

Particle Size of Polyelectrolyte, Mesh	Aggregation Value
10-20	12.4
20-40	13.2
40-60	22.8
60-140	25.5
140-200	29.8
<200	36.3

in the same range as the soil in which the conditioner is to be used. Miami silt loam has a pH of 6.5.

Moisture Content Of Soil During Treatment

The moisture content of the soil during treatment is one of the most critical of the factors that affect the aggregation value. Figure 3 shows the effect upon the aggregation value of adding the polymer in different amounts of water. The treatments made at higher than 30% moisture were allowed to dry to that moisture content before being pressed through a 4-mm. sieve to form crumbs. The crumbs formed were, therefore, fairly consistent in size and degree of compaction. Maximum aggregation was obtained at the 30 to 35% moisture range, while at moisture contents above 50% the aggregation value dropped off rapidly. Because polymer adsorption is relatively slow, some of the response of a normal 30% moisture treatment was undoubtedly obtained when soil at higher moisture content was dried to 30% moisture.

These results show that the soil particles are not bound together as effectively when they are widely separated by water. It, therefore, appears that when the polymer is adsorbed at high soil-moisture content less polymer bridging between particles occurs and polyelectrolytes are less efficient as aggregating-cementing materials.

Figure 4 shows the effect of moisture content during treatment upon the aggregation values obtained when the treated soil slurry was wet-sieved without being dried and without the formation of crumbs by pressing through a sieve.

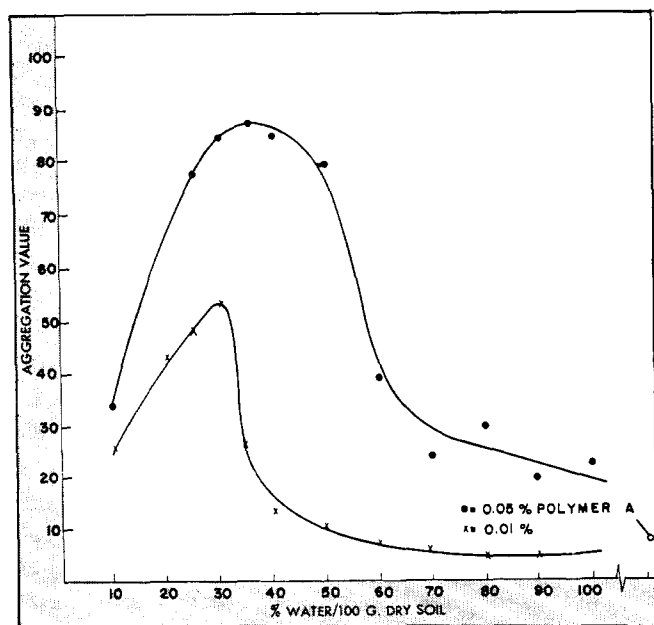


Figure 3. Effect of soil moisture content during treatment with polyelectrolyte

All samples with more than 30% water were dried to that moisture content before forming crumbs

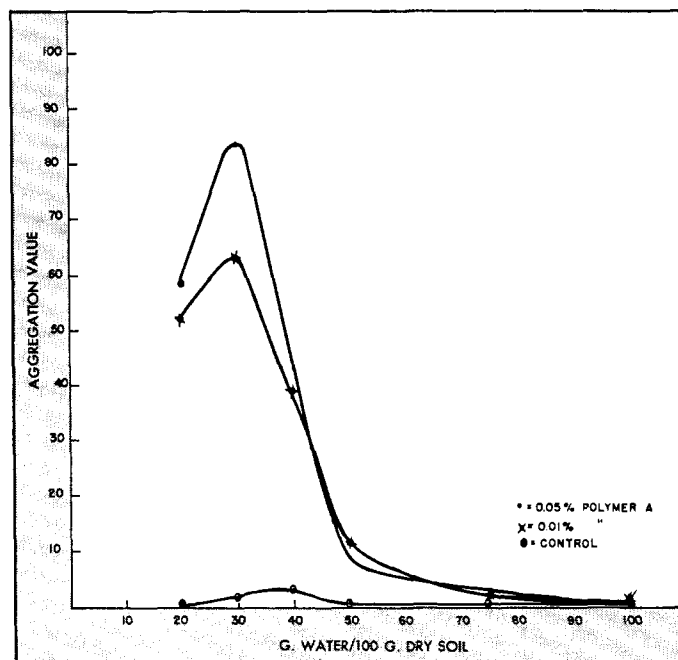


Figure 4. Effect of soil moisture content during treatment with polyelectrolyte

Soil slurries not dried before wet-sieving

Maximum aggregation was found when treatment was made at 30% moisture, whereas almost no aggregation was found when treatment was made above 75% moisture. When this method was used, the size of the soil crumbs formed was not uniform, but decreased with increasing moisture content. The aggregation value obtained at high moisture content was low because of this effect as well as because of reduced bridging of soil particles by polymer chains.

In the test developed at Dayton, the level of 30% moisture is specified because a 100-gram sample of test soil is completely wetted by 30 ml. of water, Miami silt loam treated at this moisture level has good structure and good workability, and, finally, the polyelectrolytes are used more efficiently in binding together particles of Miami silt loam containing this percentage of water.

The specified treatment at 30% moisture content differs from the treatments at 200% moisture used by Michaels and Lambe for their hydraulic stability and permeability tests on soils treated with polyelectrolytes. The very small aggregates prepared under the conditions of high moisture content may improve aggregation and porosity somewhat, but to a much smaller degree than aggregates as large as 0.5 to 1.0 mm. (7). In the author's experience the results obtained by treatment at 30% moisture have agreed well with the relative behavior of various polyelectrolyte samples used for field applications and provide good indication of the activity of the polymer to be expected in use. Moreover, the test has been useful in elucidating the effect of chemical composition,

molecular weight, and molecular configuration on the aggregate-stabilizing property of polyelectrolytes.

Mechanics of Wet-Sieving

Conditions for wet-sieving for the determination of aggregate stability in determination of natural soil structure vary somewhat as carried out by different soil scientists. The sizes and number of sieves used, the rate and distance of movement of the sieves in water, and the time of sieving have not yet been standardized. Most of the variations of wet-sieving in use will probably give the same relative rating to various polymer samples. Time of wet-sieving may be an exception with some soils. With Miami silt loam it has been the author's experience that when dry soil crumbs are subjected to wet-sieving any slaking action by water is very rapid; untreated soil crumbs completely disintegrate in water in a few minutes. The 30-minute wet-sieve period is adequate to measure aggregate-stability, since aggregate breakdown occurring during a longer wet-sieving period is largely mechanical.

Summary

The method for laboratory evaluation of polyelectrolytes as soil conditioners described has been used for the comparison of thousands of polymer samples. It is applicable to solution and solid treatments, is reproducible when rigorously followed, and allows comparison of different polymers as well as various batches of the same polymer. By proper modification it can be satisfactorily used as a control procedure.

The moisture content at the time of treatment is a most critical factor. Treatment at 30% moisture has been found most satisfactory for Miami silt loam and is believed to give results that correlate well with practical application of soil conditioners in greenhouse and field use. Other variables are the composition, preparation, and pH of test soil and mechanics of wet-sieving.

Acknowledgment

The author is indebted to D. T. Mowry for his advice and counsel and to W. P. Phillips and J. G. Villars for aid in the development of the techniques described.

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Received for review September 17, 1953. Accepted January 28, 1954. Presented before the Division of Fertilizer and Soil Chemistry, Symposium on Soil Chemistry, at the 124th Meeting of the AMERICAN CHEMICAL SOCIETY, Chicago, Ill.