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**Bulletin 52
TREATMENT OF WASTE SLUDGES
FROM WATER PURIFICATION PLANTS**

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The work upon which this publication is based was supported in part by funds provided by the United States Department of the Interior, Office of Water Resources Research, as authorized under the Water Resources Act of 1964.

OWRR Project A-030-VA

Water Resources Research Center
Virginia Polytechnic Institute
and State University
Blacksburg, Virginia
September 1972

VPI-WRRC-BULL 52

PREFACE

Accelerated interest in water pollution control has led to increased concern about a wide variety of polluting substances. One of these is the waste sludge from water treatment plants. A frequent practice is to discharge these wastes, without treatment, into the nearest available watercourse. There are two major reasons for this expediency. First, state anti-pollution agencies have, until recently, expressed little concern about these discharges, and second, little work has been done to demonstrate the available methods for treatment, dewatering, and ultimate disposal of these sludges.

The primary objective of this research was to study in detail possible methods for concentration, dewatering, and ultimate disposal of various types of water treatment plant sludges resulting from conventional processes. The use of newly-developed synthetic organic polyelectrolytic coagulant aids was investigated as a pretreatment method in combination with both open sand bed drying and vacuum filtration. The suitability of the dried product for ultimate disposal as landfill was evaluated.

The authors would like to acknowledge the contributions to this work of William B. Kirchman, Ernest W. Spradlin, C. D. Getgood, Dr. Clifford W. Randall, Walter S. Medding, Dr. Jerry A. Caskey, Russell MacNair, and E. G. Willard.

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INTRODUCTION

Recent years have seen efforts toward enhancement of water quality greatly intensified and broadened. Among the beneficiaries of such efforts are the many owners of municipal and industrial water treatment plants. Improved conditions in surface streams result in decreased variation in raw water quality and in reduced water treatment costs. On the other hand, the comprehensiveness of this water pollution program has focused attention on waste discharges which have previously been considered unimportant or insignificant. A good example of such wastes are those from water treatment plants. Historically, water treatment plants have disposed of waste resulting from coagulation, softening, and backwashing of filters by direct discharge to the nearest available watercourse. The Environmental Protection Agency has required that specific provisions for the control of water treatment plant wastes be included in all stream standards. Hence, it has become apparent that economic means of disposing of these wastes without contributing to the pollution load on surface waters must be developed.

Wastes from water treatment plants are generated in the separation of solids from the product water accomplished in the softening, chemical coagulation, settling, and filtering processes. There is a wide variation in the nature of the waste due to differences in raw water quality, plant operation, amount and type of chemicals added, seasonal influences, and the efficiency of the process. Total solids concentrations for sedimentation basin sludges generally range from 0.15 to 3.5%. Although this sludge does settle rapidly, its gelatinous nature renders it difficult to dewater without conditioning.

The pollution potential of water plant wastes has been questioned by many who reason that the waste is primarily the solids that were originally present in the stream. The fact that the solids in the waste flow have been concentrated many times is not considered. These wastes are definitely pollutants since they may inhibit biological activity in a lake or stream due to both the smothering action of the settled material as well as the toxic metals present in the chemically coagulated solids. Since the solids produced are light, flocculent, and easily stirred by current action, they may produce esthetically objectionable conditions. These wastes are also capable of causing serious oxygen depletion in the receiving streams.

The data collected from these studies were analyzed in such a manner as to enable choice of a suitable alternative for sludge conditioning prior to disposal. Recently much federal, state, and local concern has been given to water treatment plant wastes. However, very little qualitative or quantitative research has been conducted in this area. It is anticipated that the results obtained from this investigation will contribute significantly to the development of satisfactory sludge disposal methods for water treatment plant wastes.

Gates and McDermott¹⁷ investigated the effects of four polyelectrolytic conditioners on alum sludge with specific resistance determinations. They observed specific resistance values for untreated alum sludge ranging from 0.1×10^{10} to 0.44×10^{10} sec²/gm. These values were comparable to those reported by Eckenfelder and O'Connor¹⁴ for primary sedimentation basin sewage sludge. Minimum specific resistance values reported for polyelectrolyte conditioned alum sludges of 4.05% solids were as follows: cationic, 0.41×10^{-8} ; nonionic, 1.08×10^{-8} ; and anionic, 2.25×10^{-8} . The results indicated that the specific resistance relationship was a valid measure of the effect of polyelectrolyte dosages on the dewaterability of the alum sludges tested.

Summary

The great concern relevant to disposal of water treatment plant wastes in recent years has promoted investigation of many methods of treatment and disposal. Unfortunately, most of these methods either are unsatisfactory or have not been thoroughly researched. The development of new synthetic polyelectrolytes has led to successful uses in other areas of waste treatment, especially in sewage sludge conditioning. Polymer use in water plant sludge conditioning has been classified by some as unsatisfactory and has been completely overlooked by others. In addition, the mechanisms involved in sludge conditioning with polyelectrolytes have not been clearly understood by practitioners in the field of sanitary engineering. The conventional theories of colloid destabilization often do not apply to polymer conditioning. This brief review of some pertinent literature illustrates the need for a study of the factors which affect polymer conditioning of water plant sludges. In addition, the mechanism responsible for bringing about the conditioning process needs clarification. The purpose of this research was to conduct experiments with the intent of developing information to fill these gaps in current knowledge.

REVIEW OF SOME PERTINENT LITERATURE

The present interest in the disposal of wastes from water treatment plants began in 1946 with the appointment of an American Water Works Association Committee whose objective was to report on the disposal of wastes from water purification and softening plants.¹ This early interest in water treatment plant waste disposal was primarily focused on the wastes from water softening plants. In 1953 Dean² surveyed the waste load from water filtration plants over the United States. A total of 1,925 plants were covered by this survey. Of the plants investigated with coagulation and settling basins, 96% discharged sludge which eventually reached streams and lakes without treatment. In a more recent survey conducted by the Washington Aqueduct Division of the U.S. Army Corps of Engineers,³ 21% of the plants surveyed stored wash water in lagoons and about 18% returned reclaimed wash water to the influent stream of the plant. Only 11% of the surveyed plants lagooned sedimentation basin sludge. Clearly, this problem must be attacked with increasing vigor over the course of the next few years.

Coagulation and Flocculation Theory

Solution of the water treatment plant sludge disposal problem depends on an understanding of coagulation theory. In the coagulation of colloidal particles there are two basic steps involved: (1) transport of the particle which in turn results in contact with other particles and (2) particle destabilization which enhances attachment when contact occurs. Transport of the particle is a physical phenomenon that is caused by fluid movement or Brownian movement. Particle destabilization, on the other hand, is a colloid-chemical reaction that can be affected by physical and chemical properties of the liquid, colloid, or coagulant.⁶ Although there is agreement on the processes involved in the transportation of the particle, there are differences of opinion on the mechanism involved in particle destabilization. La Mer breaks particle destabilization down into two categories: (1) reactions that cause a reduction in the potential energy of interaction between the electrical double layers of the two particles and (2) reactions that cause the formation of chemical bridges that result in a three dimensional floc network of particles. The first category is exemplified by the charge neutralization caused by the addition of an electrolyte of opposite charge and is usually termed coagulation. The term applied to the second category is flocculation and is demonstrated by the destabilization of a negatively charged colloidal dispersion by an anionic polyelectrolyte.⁷ A knowledge of the colloidal particles present in a dispersion is necessary in order to understand the mechanisms of destabilization that occur.

In the coagulation basins of a water treatment plant two basic types of colloidal particles exist: (1) those which were formed by the addition of the

coagulant aids and (2) those present in the raw water initially. These particles vary both chemically and physically, and the charge possessed by each particle is dependent upon several factors.⁸ It may be the result of an ionization of one of the functional groups on the surface of the particle, for example, a carboxylic or hydroxyl radical may be formed. Adsorption of ions from solution as well as isomorphic substitution can also help determine the charge existing on the particle. As stated before, in destabilization chemical reactions occur between the reactive groups resulting in the formation of complexes with the coagulant aids, as well as counter-ion adsorption by the colloidal particles.

Stumm and Morgan have emphasized that the effects of ferric and aluminum salts upon coagulation are brought about by the hydrolysis products of the salts and not by the simple aquo-metal ions themselves.⁸ This hydrolysis is accomplished by a stepwise consecutive replacement of water molecules in the hydration shell by hydroxide ions. The products of this hydrolysis are termed multinuclear hydroxo-metal complexes and are usually highly charged. The complexes can be nonionic, cationic, or anionic, depending upon the species existing. Some of the species formed in the hydrolysis steps tend to polymerize. Stumm and O'Melia have concluded that after the hydrolysis has been completed the following steps will then occur in the time dependent coagulation mechanism: (1) adsorption of the hydrolysis species into the colloidal particles followed by destabilization; (2) the destabilized colloidal particles then aggregate and interparticle bridging occurs; (3) aging of the flocs that were formed leads to a chemical change in the multinuclear hydrolysis products and the sorbability of the floc; and (4) precipitation of the metal hydroxide is completed.⁸

Polyelectrolytes utilized as flocculation aids are high molecular weight (15,000 to several million), long chain organic molecules containing several ionizable sites along the chain. They are classified as either natural organic or synthetic organic compounds. The properties of polyelectrolytes depend on the net charge, molecular weight, and the type of reactive sites. The three basic types of polyelectrolytes are anionic, cationic, and nonionic, which are determined by whether the net charge on the molecule is negative, positive, or neutral.

Stumm and O'Melia have stated that destabilization of colloidal dispersions by polyelectrolytes cannot always be explained through the double layer model, but instead a chemical bridging or flocculation theory must be used.⁸ La Mer and his co-workers were the first to propose a mathematical model of the chemical bridging theory to explain the action of polyelectrolytes in destabilization of colloidal dispersions.⁷ Earlier work on the chemical

bridging theory was done by Ward and Ruehrwein. Through their tests dealing with the adsorption of polymethacrylate on kaolinite clay dispersions they helped establish and confirm the chemical bridging theory.¹⁰ Since this early work, much more data has been obtained to support this hypothesis.

The chemical bridging theory states that polyelectrolyte molecules may attach themselves to colloidal particles at one or more adsorption sites. The remainder of the molecule that is not attached extends out into the solution containing the colloidal particles. If this extended segment makes contact with a colloidal particle, the particle becomes attached to the segment. As this process continues for the many extended segments of one polyelectrolyte molecule, bridges are formed between colloidal particles. If adsorption is effective for all the polyelectrolyte molecules present, the net result is that the colloidal particles are aggregated into small packages that continue to grow in size. Factors limiting this growth are the amount of polyelectrolyte initially adsorbed on the surface and the shear gradient imposed by the amount of agitation necessary in promoting particle-polyelectrolyte contacts.

Black, Birkner, and Morgan¹¹ have found that the kinetics of polyelectrolyte adsorption are very rapid, with 85% of the equilibrium value being adsorbed in only 30 seconds. They have broken the kinetics down into two steps: (1) the rate at which the polymer is adsorbed from solution and (2) the rate at which the initial particles agglomerate to form secondary, tertiary, and n-unit particle aggregates. Anionic polyelectrolytes have been found to be readily adsorbed on negatively charged clay particles. Tests with a polyacrylamide by Kane, La Mer, and Linford¹³ indicated that with increased hydrolysis and negative charge, the polyelectrolyte did a progressively better job of destabilizing negatively charged silica particles. Thus, anionic polyelectrolyte destabilization is strictly by a flocculation mechanism. The proposed mechanism for destabilization by cationic polyelectrolytes, on the other hand, is a combination of flocculation-coagulation process. The cationic polyelectrolyte serves first as a coagulant by reducing the repulsive charges between particles, and then chemical bridging takes place as the rate controlling reaction.¹¹ Nonionic polyelectrolytes exhibit both forms of destabilization shown by the cationic and anionic polyelectrolytes but to a smaller degree.

Zeta potential is a measure of the electrokinetic charge that surrounds a colloidal particle.¹⁸ It is the potential that exists at the plane of shear between the particle and the bulk of the solution. Particle zeta potential thus describes the forces of repulsion in a colloidal system. As a result of these repulsive forces, the particle is kept in solution. The more negative or positive

the zeta potential, the more stable the colloidal solution. Most systems of interest in water treatment are negatively charged.

Since zeta potential is proportional to the rate of movement of the colloidal particle in an electric field, it can be calculated by the following formula.¹⁸

$$ZP = \frac{4\pi UV_t}{D_t}$$

where:

- U = electrophoretic velocity of the colloidal particle
- V_t = viscosity
- D_t = dielectric constant of the suspending liquid.

Many recent theories regarding coagulation are the result of increased knowledge about the zeta potential of colloids. However, in some situations zeta potential is not an appropriate process control parameter, particularly when chemical bridging is important. In these situations particle agglomeration may be accomplished at zeta potential levels substantially greater or less than zero, and measurement of the zeta potential serves only to confirm that the mechanism responsible for coagulation is not particle charge neutralization.

Sludge Drainability and Dewatering Processes

Sludge produced in the coagulation-sedimentation-filtration processes at water plants, as well as the sludges produced in primary and secondary sewage treatment, usually require dewatering by filtration before final disposal. The most common method of dewatering sludge has been by sand beds. Two mechanisms are involved in such dewatering processes, filtration action by the sand resulting in gravity drainage of water, and evaporation of water from the sludge surface. For sewage sludge, filtration is usually complete in one to two days and solids concentrations may be increased to 13 to 22% depending on the nature of the sludge. The filtration rate can generally be increased by the addition of a coagulant. When the sludge is exposed to air, it will further dry to an equilibrium moisture content which depends upon the temperature and relative humidity of the air in contact with the sludge.¹⁴

Sand beds usually consist of 4 to 6 inches of sand covering an underdrain system composed of 8 to 10 inches of graded gravel and 6- or 8-inch drain tiles. Such beds may be both technically and economically feasible for water plant sludge dewatering if facilities for proper sludge conditioning are provided. Neubauer's¹⁵ studies with bench scale drying beds, each having an area of 0.5 sq ft and an underdrain of gravel and coarse sand, indicated that water plant sludge could be concentrated to 20% total solids in 70 to 100 hours.

Theoretical work done by Hatschek in 1908 and Ruth and Carman in 1933 led to the introduction of the concept of "average specific resistance." Average specific resistance is determined in a relatively simple laboratory test and is defined as the resistance of a unit weight of filter cake per unit area at a given pressure and is commonly expressed in terms of sec^2/gm .¹⁶

The relationship describing specific resistance is:¹⁶

$$r = \frac{2PA^2b}{\mu c}$$

where

- r = specific filtration resistance, sec^2/gm
- P = pressure of filtration, $\text{gm}/\text{sq cm}$
- A = filter area, sq cm
- b = slope of T/V versus V curve, sec/cm^6
where T = time, sec
and V = volume of filtrate, ml, in time T
- μ = filtrate viscosity, poise
- c = ratio of grams of dry cake solids per gram of liquid before filtration, gm/cm^3 .

Laboratory experiments, conducted to determine the accuracy of specific resistance in describing the results of filtration tests, confirmed the applicability of Carman's work. Experiments with thickened, digested sludge diluted to various concentrations with tap water revealed that specific resistance remained practically constant over a solids content range from 1.5 to 8.5%. Large decreases in feed solids concentration have been shown by Eckenfelder and O'Connor¹⁴ to decrease specific resistance slightly.

EXPERIMENTAL METHODS AND MATERIALS

The experimental work described herein was aimed at developing appropriate methods for concentrating and dewatering water plant sludges. The purpose of this chapter is to describe the apparatus used, the experimental procedures employed, and the analytical techniques utilized.

Sources of Sludge

All sludge samples used in this research were obtained from conventional treatment plants. Samples of alum sludge were pumped periodically from the bottom of the sedimentation basins at the Blacksburg-Christiansburg-V.P.I. Water Authority Plant near Blacksburg, Virginia.

Samples of ferric sludge were collected from the holding pond at the Carvin's Cove Water Plant near Hollins, Virginia. This plant is very similar in operation to the Blacksburg-Christiansburg-V.P.I. Plant.

Samples of lime sludge were pumped from the bottom of the sedimentation basin of the United Piece Dye Works Plant in Bluefield, Virginia. This sludge is a result of an excess lime treatment process used to remove color from a textile dyeing and finishing waste. A second lime sludge was obtained following lime treatment of the secondary effluent of the Strouble's Creek trickling filter sewage treatment plant located near Blacksburg, Virginia.

Preparation of Polymer Solutions

For each polymer used, Table I shows the nature of the charge and the molecular weight, or viscosity data where molecular weight was not available. High molecular weight polyelectrolytes are often difficult to dissolve. The dissolving rate increases with temperature. Therefore, the polymer solutions were prepared on a magnetic heat-stirrer apparatus which heated the polymer solution to a range of 120° to 150°C. Temperatures over 150°C may cause degradation of polyelectrolyte solutions.

Sludge Filterability Test

The initial studies were primarily concerned with developing a test procedure for determining sludge drainability. The specific resistance test as described by Coakley and Jones¹⁶ was adopted as the primary tool.

TABLE I
POLYELECTROLYTE DATA

<u>Polymer</u>	<u>Charge</u>	<u>Molecular Weight or Viscosity</u>
Nalco 605 ⁽¹⁾	Cationic	400 cps @ 75°F
Nalco 610	Cationic	1,000,000 +
Nalco 632	Cationic	320 cps @ 77°F
Nalco 670	Nonionic	1,000,000 +
Nalco 671	Nonionic	1,000,000 +
Nalco 672	Anionic	1,000,000 +
Nalco 673	Anionic	1,000,000 +
Nalco 675	Anionic	1,000,000 +
Dow-N-17 ⁽²⁾	Nonionic	1,000,000 +
Dow-A-23	Anionic	1,000,000 +
Dow-C-31	Cationic	225 cps @ 25°C
Calgon 23-N ⁽³⁾	Nonionic	--
Calgon 243-A	Anionic	--
Magnifloc 835-A ⁽⁴⁾	Anionic	15,000,000
Magnifloc 905-N	Nonionic	15,000,000

- (1) A trade name of Nalco Chemical Company.
 (2) A trade name of Dow Chemical Company.
 (3) A trade name of Calgon Corporation.
 (4) A trade name of American Cyanamid.

The specific resistance apparatus is shown in Figure 1. Some of the polyelectrolytes used to condition the sludge agglomerated the solids to such an extent that the sludge became very lumpy. For this reason no single constant volume of sludge was used. The sludge sample was mixed well and quickly poured into the Buchner funnel in an attempt to maintain homogeneity in the sample. A constant pressure differential of 12 inches of mercury was maintained by a mercury manometer and a bleedoff regulated by a screw clamp. After the pressure differential was adjusted and 10 to 15 seconds allowed for cake formation by sedimentation, another screw clamp located between the Buchner funnel and the 250 ml cylinder was quickly released. For slow filtering samples the amount of filtrate collected in the graduated cylinder was read every 15 seconds for the first 4 minutes, every 30 seconds for the next 3 minutes, and every minute until the cake cracked, the pressure dropped, or the filtrate volume became constant. Readings were taken every five seconds in the case of rapidly filtering samples.

Determination of Optimum Conditions
for Sludge Drainability

The total volume of the sludge samples used in each experiment throughout the investigation, after pH adjustment and addition of polymer solutions, was approximately 1 liter. A conventional multiple jar stirring device was employed to mix the samples in 1-liter beakers. The desired pH of the samples was achieved with concentrated sulfuric acid and a 50% solution of sodium hydroxide. Polyelectrolyte dosages ranging from 0 to 100 ppm were applied to the sludge samples and rapidly mixed (at stirrer speeds of 100 rpm or greater) on the multiple jar stirring device for 1 to 2 minutes depending on the appearance of the sludge. A rapid mix was necessary to prevent the heavy polymer solutions and the solids which had adsorbed large doses of polymer from settling and to obtain a homogeneous sample in which all solids present could adsorb polymer molecules equally. An increased time of agitation was observed to destroy the floc.

After mixing, the samples were allowed to settle for 15 minutes, the supernatant was decanted, and the specific resistance of the remaining sludge was determined. Specific resistance tests were used to determine the optimum pH, polymer dosage, and time of agitation. The same basic procedure was employed to determine the effects of temperature and solids concentration on the optimum dosage of polyelectrolyte.

Freeze and Thaw Tests

For these tests the sludge was frozen for 24 hours, completely thawed, and the supernatant decanted. Drainability tests involved filtering 100-ml portions of the sludge samples in 9-cm Buchner funnels, using in each a layer of sand 10 mm thick. The sand used was characteristically retained on a No. 30 soil sieve and passed a No. 12 sieve. Each funnel was attached to a 250-ml graduated cylinder to enable filtrate volume determinations. Sludge samples of 100 ml were placed in the funnels and allowed to drain for 7 days.

Zeta Potential Test

A Standard Zeta Meter was used to determine zeta potential in supernatant from conditioned and unconditioned samples. Most conditioned sludge samples yielded a rather clear supernatant that could be used as a test sample. On the other hand, unconditioned and conditioned sludge samples that did not settle well had to be centrifuged and reconstituted to obtain a relatively clear sample. The laboratory centrifuge was found to be capable of clarifying the samples in approximately 5 minutes. The reconstituted sample after centrifuging was then used in zeta potential determinations. Relatively little solids in the supernatant is a prerequisite to valid zeta potential readings.

Bench Scale Sand Bed Studies

Sand bed studies were conducted using plexiglass beds 1 square foot in cross-sectional area. The beds were constructed with 3/8-inch plexiglass sides and a funnel shaped plexiglass device to collect filtrate that had drained from the sludge sample. The filtrate was then conveyed from the funnel device by a rubber hose to a 2 liter graduated cylinder where it was measured. The filter medium consisted of a 1-inch layer of coarse sand, which was retained on a No. 10 soil sieve, covered by a 3-inch layer of lightweight Weblite aggregate sand with a uniformity coefficient of 2.89 and an effective size of 0.40 mm. The medium was supported on the bed by fine wire mesh screens. The distance from the top of the Weblite sand to the top of the plexiglass side was approximately 9 inches.

Samples of 14 liter size at 3.6% solids were used in the studies and were poured into a 30-liter, wide-mouth Pyrex jar after which the proper polyelectrolyte dosage was added. A short "flash" mix at 100 rpm was applied, then the sample was quickly applied to the bed. Filtrate volume

measurements were taken at various times during the filtration action. Moisture content of the sludge during the air drying phase was determined gravimetrically.

EXPERIMENTAL RESULTS

Initial studies were aimed at determining optimum experimental conditions for a variety of polyelectrolytes. The effect of mixing time after polymer addition on the specific resistance of conditioned alum sludge was determined for a number of polyelectrolytes. A typical result is given in Figure 2. As noted, an increase in mixing time in general led to a deterioration in the specific resistance of the resulting sludge cake. The increased energy fed into the system caused the agglomerated floc to break up. On the basis of these data, a mixing time of 1 to 2 minutes was employed for the remainder of the experimental work.

The effect of system pH on specific resistance of alum sludge for a variety of polymer conditioning agents is noted in Figure 3. The considerable improvement related to the use of polyelectrolytes as chemical conditioners is illustrated by these data. In most cases the polymers are effective over a reasonably wide pH range, except for the cationic polymers which are effective only at relatively low pH values. The anionic and nonionic polymers are useful in the pH range of 6.0 to 10.0, and lower system pH levels result in sharply increasing values of specific resistance. On the basis of these data, further work was done at the unadjusted pH of the alum sludge, 6.5 to 6.7.

The effect of polymer dosage on specific resistance for several of the polymers tested is shown in Figure 4. The solids content for each alum sludge used in this experiment was approximately 2%, and the system pH was 6.6. In terms of the nature of the polyelectrolyte, the performance of the anionic polymers was somewhat superior to the nonionic polyelectrolyte and substantially more effective than the cationic polymer. The specific resistance continued to decrease with increasing polymer dosage and there was no tendency toward reversibility of this effect within the range of polyelectrolyte dosages tested at this particular solids concentration.

The variability of specific resistance with solids concentration noted in these experiments is illustrated in Figure 5. These data were obtained for anionic polymer-conditioned alum sludge with a system pH of 6.5 and a polyelectrolyte dosage of 90 ppm. The deterioration in specific resistance noted at a very low solids concentration strongly suggests that it is possible to overdose a system of this type with an anionic polymer. This effect was not noted in Figure 4 because of the solids concentration utilized and the limited range of polymer dosage applied.

Zeta potential data were also collected as an aid in postulating the mechanism involved in the conditioning process. Results of this work are typified by data shown in Figure 6. The variation of zeta potential with pH for unconditioned and for anionic polyelectrolyte conditioned alum sludge at a dose of 100 ppm and a solids concentration of 3.2% is shown. The influence of anionic polymer dosage on zeta potential at a constant pH of 8.0 is also indicated. This system pH was selected because it has previously been shown to be the optimum for treatment with this particular polyelectrolyte. The data indicate that for both conditioned and unconditioned sludge the zeta potential reaches zero at a system pH of 4.0. Higher pH levels are associated with increasingly negative values of zeta potential. The presence of the anionic polymer results in large increases in measured zeta potential. As would be expected, zeta potential increased rapidly with increasing concentration of applied anionic polymer. It is particularly significant to note that zeta potential reaches its peak value, in excess of -20 millivolts, at the point of lowest specific resistance for alum sludge conditioned with 100 mg/l of polymer at a system pH of 8.0.

In an effort to define the effect of the conditioning process on a system for dewatering the drying alum sludge, bench scale sand bed studies were conducted. Results of this work are shown in Figure 7. The solids content of both sludges at the time of application to the beds was 4.2%, and the conditioned sludge was treated with 100 mg/l of anionic polyelectrolyte. The large increase in water released by gravity drainage associated with the conditioning process is clearly indicated. A volume reduction of 46% of the conditioned sludge was achieved in 1 hour as opposed to only a 5% decrease for the unconditioned sludge. Gravity drainage of the conditioned sludge was completed in about 1 day but continued for about 5 days with the untreated material. The air drying rates of the two sludges, as shown in Figure 7, appeared to be similar.

Alum sludge samples were tested with and without polyelectrolyte addition before freezing and thawing. Samples treated with polyelectrolytes originally contained 2.95% total solids and were treated with 100 ppm Nalco 675. Results involving freezing and thawing of alum sludge are shown in Tables II and III. The only advantage of polyelectrolyte use in freezing and thawing appears to be in concentrating the solids before freezing. The solids dewatered rapidly and dried to a loose state like that of dry sand. The solids no longer exhibited the gelatinous nature typical of unfrozen samples. The laboratory results suggest that alum sludge will, upon freezing, thawing, and allowing to drain, dry to a consistency which can be handled easily.

TABLE II
SLUDGE VOLUME REDUCTIONS BY FREEZING

Polymer Dosage mg/l	Total Solids Before Freezing, %	Sludge Volume Reduction After Thawing, %	Total Solids in Supernatant After Thawing, mg/l	Total Solids of Sludge After Thawing, %
0	2.96	86.2	396	18.2
100	5.93	64.2	795	17.2

TABLE III
DRAINABILITY TESTS RESULTS

Sample*	Feed Solids, %	Filtrate Volume After 15 min., ml	Moisture Content After 7 days, %
F-T-no P	18.2	30	10.3
F-T-P	17.2	34	11.2
F-T-P	17.2	34	11.1
P	7.58	31	53.9
no P	2.95	73**	

*F = freeze, T = thaw, and P = polymer.

**Solids escaped through sand.

A second series of experiments was conducted using ferric sulfate sludge collected from the Carvin's Cove Water Treatment Plant at Roanoke, Virginia. A typical solids content for sludge pumped from the sedimentation basins was 3.5%. A volatile fraction of about 20% of the total solids was observed. COD values on the order of 5,500 mg/l were measured indicating a possible deleterious effect if this sludge were to be discharged directly into a receiving watercourse.

The effect of polymer type and dosage on the specific resistance of the ferric sulfate sludge for selected sludge solids concentrations is given in Figures 8 through 10. In each case the pH of the system was held constant at 7.5. The improvement in filterability resulting from the polymer conditioning step is clearly evident from these data. In terms of the nature of the polyelectrolyte, there appeared to be little difference between the anionic and cationic materials, both being clearly superior to the nonionic polymer tested. The major influence of solids concentration was in the polymer dosage required for maximum improvement in specific resistance. This result was especially evident with the cationic polymer (C-31).

The considerable effect of system pH on the results of the polymer conditioning process is indicated in Figure 11. pH levels of 4.0, 6.0, 7.5, and 10.0 were utilized. In addition the cationic polymer was tested at pH 2.0. In general the polymers were effective over a reasonably wide pH range with the cationic polymer being especially well adapted to mildly acidic conditions. The performance of all systems tended to deteriorate as pH deviated from neutrality, especially when this deviation was toward the basic side.

Zeta potential data were collected as an aid in postulating the mechanism involved in the conditioning process. A typical result of this work is summarized in Figure 12. These data are for a system of constant pH and variable polymer dosages for a sludge solids concentration of 3.6%. The cationic polyelectrolyte, as expected, brought about a decrease in zeta potential while the use of the anionic polymer resulted in marginally increased zeta potential. In correlating these data with Figures 8 through 10, it may be seen that improved filterability was largely unrelated to changes in zeta potential. Figure 13 shows the effect of system pH on the zeta potential of polymer conditioned systems with an initial sludge solids concentration of 3.6%. Peak zeta potential occurred for the anionic and nonionic systems at pH 7.5, while little change was noted in the cationic system over the range of pH values studied. Again, there was no positive correlation between reduced zeta potential and improved sludge filterability.

Sand bed studies were conducted to determine the effect of the conditioning process on gravity dewatering and air drying of ferric sulfate sludge. Results are shown in Figures 14 and 15. The initial solids content of the sludge was 3.6% and the system pH was 7.5. Polymer dosages were those determined to result in maximum decrease in specific resistance. As noted in Figure 14, the polymer conditioning step resulted in much more rapid gravity drainage than was apparent in the unconditioned system. However, the unconditioned sludge also drained relatively rapidly and released substantially all of its drainage water in about 30 hours as opposed to approximately 25 hours for

the polymer conditioned systems. The results of air drying of the drained sludge showed that after 20 days the polymer conditioned systems typically had marginally higher rates of drying. For example, at the end of the drying period the A-23 system had a cake moisture content of 70% as opposed to 75% in the unconditioned system.

A final series of experiments was concerned with the effect of polymer dosage on specific resistance of a representative lime clarification sludge. Typical results of this work are given in Figure 16. The initial solids content for each sludge was 4.3% and the system pH was 11.8. Only the anionic polymer, Nalco 673, was effective in conditioning this sludge. Specific resistance decreased with increasing dosage of this polymer until about 75 ppm was reached at which time there was a leveling off of the measured value.

Figure 17 shows the effect of solids content on specific resistance and optimum dosage of polyelectrolyte required for conditioning the lime clarification sludge with Nalco 673. Sludge solids contents utilized were 1.3, 2.2, and 3.9%. These results indicated that solids concentration does affect the specific resistance of Nalco 673 conditioned sludge. The optimum polyelectrolyte dosage was also affected by the initial solids content of the sludge.

Sand bed studies were made using sludge which had an initial solids content of 2.3% and a pH of 10.9. Sludges conditioned with dosages of 25 ppm, 50 ppm, and 75 ppm of Nalco 673 were applied to three of the beds, while the remaining bed was covered with an unconditioned sample. The results of gravity drainage are shown in Figure 18. Gravity drainage for the unconditioned sample lasted for 32 hours, producing a cake moisture of 96%. Gravity drainage for the sample conditioned with 25 ppm of Nalco 673-A also lasted for 32 hours. A resultant cake moisture of 95.4% was obtained. Gravity drainage for the sludge conditioned with 50 ppm Nalco 673-A was much faster and lasted about 12 hours. In only four hours, the volume of sludge had been reduced by one-half. The final cake moisture obtained by gravity drainage was 92.2%. The fastest gravity drainage rate was observed for the sample conditioned with 75 ppm Nalco 673-A. In only 1 hour gravity drainage resulted in a volume reduction of one-half. Gravity drainage ended in approximately 10 hours resulting in a cake moisture of 92.3%. The air drying rates of the various sludges, as indicated by Figure 19, appeared to be similar.

DISCUSSION OF RESULTS

All the polyelectrolytes investigated in this study improved the dewatering characteristics of alum sludge. Under the experimental conditions employed, anionic polymers were somewhat superior to nonionic agents and were significantly better than cationic chemicals. In considering the mechanism by which this improvement is achieved, the data suggest that the molecular bridging theory previously described offers a satisfactory explanation of the conditioning process. Zeta potential data strongly indicate that electrostatic forces are apparently overwhelmed by the stronger, short-range chemical forces. This effect explains the fact that anionic polymers are effective in conditioning the negatively charged alum sludge. It also leads to the definite conclusion that zeta potential is not an important control parameter in selection of an appropriate polyelectrolyte and in the determination of a proper polymer dosage.

The data illustrating the effect of system pH on chemical conditioning indicate that selection of an anionic polyelectrolyte will eliminate the need for pH adjustment as a part of the treatment process. The data on solids concentration underscore the possibility of deleterious effects associated with an overdose of polymer. It would appear that polyelectrolyte dosage should be based on a weight per unit weight of solids contained in the system rather than a weight per unit volume of sludge basis. The reversibility effect is explained in terms of the bridging model by noting that optimum treatment is obtained under a condition of optimum floc surface coverage by the adsorbed polymer. Greater surface coverage reduces the opportunities for effective molecular bridging and thus increases the tendency toward restabilization.

The results of the ferric sulfate studies indicate the ability of synthetic organic polyelectrolytes to improve dewaterability of ferric sludges. All of the polymers investigated improved drainage rates, although improvement is not as dramatic as was observed for alum sludge. The cationic and anionic species tested were superior to the nonionic material utilized. The lack of correlation between zeta potential data and improved specific resistance and the similar ability of anionic and cationic polymers again strongly implies that the mechanism by which this improvement is achieved is chemical bridging rather than reduction of electrostatic forces of repulsion.

Sludge solids content is again shown to play an important role in the polymer conditioning process. The data collected strongly indicate that optimum performance is achieved in a given system at a given polymer dosage per unit

of solids to be treated. The relationship of this ratio to specific resistance for each of the anionic and cationic polyelectrolytes tested is shown in Figures 20 through 22. As noted in these figures, the ratio of polymer dosage to solids in the sludge at which optimum performance was noted remained substantially constant over the range of solids concentration tested.

The pH of the system has a definite effect on the performance of the polymer conditioning process. The pH not only influences the surface properties of the sludge particles, but also affects the extent of the hydrolysis of the polyelectrolyte. The data indicate that optimum performance occurred in a pH range near neutrality. Thus, in most chemical treatment systems using ferric chloride a pH adjustment of the sludge prior to the conditioning would not be required.

The sand bed studies on ferric sulfate sludge illustrate a practical means for sludge treatment in situations where sufficient land is available to construct adequate sludge drying beds. Polymer conditioning improved the rate of gravity drainage. However, the unconditioned ferric sludge also drained rapidly, indicating that the use of polymer in this situation might not be warranted. Air drying rates and final moisture content were somewhat improved by the polyelectrolyte conditioning step, perhaps because of the tendency of the polymer to produce an open, porous floc structure. This latter feature was especially true of the anionic polymer conditioned systems which performed best during the air drying phase of the study.

Studies utilizing lime clarification sludges showed that anionic polymers were most effective in bringing about improved dewaterability. The failure of nonionic and cationic polymers to function effectively may be explained by the high pH of the system. The excess hydroxide ions in solution may be adsorbed onto the charged sites of a cationic and nonionic polymer. The result would be a deactivation of these adsorptive sites with hydroxide ions, and the chemical bridging effect would be impaired. This effect could not occur in anionic conditioning. The negative hydroxide ions would be repelled by the negatively charged polymer. Thus, the adsorptive sites would remain available for solids adsorption and subsequent chemical bridging.

Bench scale sand bed studies again revealed that polyelectrolytes did improve sludge dewaterability. Sludge conditioned with 50 ppm Nalco 673 produced the lowest cake moisture after 15 days. Samples conditioned with 50 ppm and 75 ppm Nalco 673 produced a porous open floc which dewatered readily. The unconditioned sample as well as the sample conditioned with 25 ppm Nalco 673 produced a more compact floc which failed to dewater as readily.

The need for development of economic treatment and disposal methods for chemical sludges is clearly evident both in the water utility industry and in wastewater treatment systems using coagulation processes. The use of synthetic organic polyelectrolytes as sludge conditioning agents prior to vacuum filtration or gravity drainage and drying on open beds appears to offer considerable promise. The data presented in this paper suggest that polymer conditioning of chemical sludges may lead to substantial improvement in filterability as indicated by the specific resistance data and accelerates to a significant degree the rate of gravity drainage and air drying.

CONCLUSIONS

1. Both polymers and freezing and thawing are effective conditioning agents leading to rapid dewatering of typical water treatment plant sludges.
2. Selection of an appropriate polymer is related to a number of factors, including primary coagulant and system pH.
3. Optimum polymer dosage is directly related to sludge solids concentration.
4. Dewatering of polymer conditioned sludges may be accomplished by either gravity drainage or vacuum filtration.
5. Alum sludge is relatively more difficult to dewater than sludge resulting from the use of iron salts. However, polymer conditioning of alum sludge brings about dramatic improvement and tends to greatly diminish this difference.
6. Anionic polymers are particularly effective conditioning agents for lime clarification sludges. Anionic polyelectrolytes are also normally superior for alum and ferric salt sludges.

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FIGURES