ADDITION OF POLYMERS AND LIME FOR PHOSPHORUS REMOVAL IN RAW DOMESTIC WASTEWATER

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Report to the Division of Water Pollution Control
Massachusetts Water Resources Commission
Contract Number 15-51450
ADDITION OF POLYMERS AND LIME FOR PHOSPHOROUS REMOVAL IN RAW DOMESTIC WASTEWATER

by

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ABSTRACT

In order to enable lime treatment of low alkalinity Amherst raw wastewater without requiring subsequent pH adjustments, polymers were used with lime in jar testing at a pH of 10.4 to 10.5. Results showed that several polymers, when used with lime, gave additional phosphorous and turbidity removals to that achieved by only lime. However, only Purifloc A-23, an anionic Dow Chemical Company product, gave this added removal at doses of 1.0 mg/l or less. In addition, anionic polymers produced a dense mass of solids during flocculation, with the solids settling very rapidly after flocculation.

More detailed study of Purifloc A-23 revealed that the optimum dose range was very large from 0.75 to 10.0 mg/l. A rapid mix period of 10 minutes between lime and polymer addition (lime first) was necessary for best results, while adding the two chemicals simultaneously gave poorer results than lime alone.

Although performance of the lime-polymer coagulation process varied with sewage characteristics, a pilot-scale operation of this system would better show its applicability for sewage such as that of Amherst which has low alkalinity. Lime would be added to a rapid mix basin, with Purifloc A-23 added to the flocculator or the line leading to the flocculator. The pH would be held constant at a value of 10.3 to 10.5.
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INTRODUCTION

Removal of phosphorous from domestic wastewaters has been a major concern of water pollution control authorities due to the importance of phosphorous as an algal nutrient. Since metallic phosphates are insoluble in water, chemical systems of phosphoateremoval from sewage using iron, aluminum, or calcium ion addition have been developed. Calcium addition, in the form of quicklime (CaO) or hydrated lime (Ca(OH)$_2$), has the advantages of lower chemical cost, possibility of regeneration, and addition of an anion (hydroxide) which can be removed by neutralization.

Lime is usually applied directly to raw wastewater or to secondary effluent. Two treatment options are available, single stage and two-stage. The choice of system depends primarily on the alkalinity of the wastewater. In single-stage treatment, lime is mixed with wastewater to raise pH in the range of 9.5 to 11.0. This process is well-suited to hard waters with alkalinitities above 250 mg/l as CaCO$_3$ (7); in such waters, floc particles of good settleability are more easily formed at lower pH. Two-stage lime treatment includes a primary stage with high pH, usually above 11.5, and subsequent recarbonation to remove excess calcium ions in the second stage. The high pH lime process has been found necessary with waters of low alkalinity (200 mg/l as CaCO$_3$ or less) or the low fraction of CaCO$_3$ formed will result in a poorly settleable floc.

The low alkalinity of Amherst wastewater and other New England wastewaters would generally dictate that a high pH lime process be used for phosphorous removal. This investigation was conducted to determine the
feasibility of using a low pH (single stage) lime process in conjunction with polymer addition to promote the necessary floc settleability. Such a system would be more economical and easily adapted to existing primary treatment plants.

The study used jar testing to evaluate the addition of polymers to lime-treated raw sewage at a pH in the area of 10.5. The main objectives of the testing were to:

1. Evaluate several polymers for removal of phosphorous and turbidity when used in combination with lime.
2. Study the effect of various dosages and mixing conditions on removal efficiency using the most effective polymer.

PRECIPITATION OF PHOSPHOROUS WITH LIME

The reactions which occur when lime is added to sewage are complex. They vary with pH, wastewater characteristics, and the dosage of lime employed. Lime reacts rapidly with bicarbonate ions to form calcium carbonate, which is virtually insoluble at high pH values. The addition of hydroxide ions raises the pH and shifts the bicarbonate-carbonate equilibrium towards carbonate formation. Orthophosphate also reacts with lime, forming hydroxyapatite:

$$5Ca^{2+} + 4OH^- + 3HPO_4^{2-} + Ca_5(OH)(PO_4)_{3+} + 3H_2O$$

The solubility of hydroxyapatite decreases rapidly with increasing pH. Precipitation occurs in two steps, first the formation of nuclei on material present in the water, then crystal growth on these nuclei (5). Both calcium carbonate and hydroxyapatite can serve as nuclei on which the
insoluble phosphorous compound can crystallize. Recirculation of solids produced by lime precipitation has therefore been found to produce marked improvement in phosphorous removal efficiency (1). Removal of phosphorous is dependent more on the alkalinity of the water than on the phosphorous content of the water, for a given lime dose, especially with phosphorous concentrations of over 10 mg/l (1,8).

COAGULATION PROCESSES

Coagulation is a physicochemical process employed to effect the destabilization and aggregation of colloidal and suspended particles in water. The aggregated material can then be removed from the suspending liquid by sedimentation and/or filtration. Normally, chemical addition and liquid agitation are necessary to accelerate the rate of this process. The addition of lime to sewage produces insoluble phosphorous-containing compounds and calcium carbonate, but these products may remain suspended as finely divided solids unless sufficient mixing occurs. Hence, coagulation involves two stages: the rapid mix, during which the chemical coagulant becomes dispersed through the system, and the flocculation period, which allows the particles to agglomerate.

The paddle rotational speed during flocculation must fall within an optimum range in order to permit good coagulation. Rotational speed determines the velocity gradient, which is a measure of the distribution of velocities within the flocculation unit. This gradient is also dependent of the viscosity of the fluid, the paddle area, the volume of the fluid, and the drag coefficient of the paddle. It is essentially a
measure of the power input to the system (10). If the velocity gradient is too low, insufficient collisions between particles will prevent efficient coagulation. If it is too high, the floc particles that form will be sheared.

Several mechanisms of colloid destabilization can occur; these vary with the nature of the impurities in water and the coagulant used. The mechanisms all involve counteracting the "stability" of the suspended and colloidal particles, i.e., their tendency to remain dispersed. Stability is largely due to repulsive forces caused by like charges on the particles, usually negative (10). In coagulation processes involving lime and polymers the principal mechanisms of particle aggregation involve adsorption and bridging phenomena.

Adsorption is the process by which charged surface-active agents such as polyelectrolytes attach to colloidal particles, reducing the net charge on them. In this case, restabilization can occur due to attachment of excess coagulant to the colloid, resulting in charge reversal. When this happens, the colloids have a net positive charge and tend to remain stable through electrostatic repulsion. In the case of phosphorous precipitation, polyphosphates tend to adsorb to precipitated orthophosphate.

The addition of polymers can result in interparticle bridging, which leads to settling of colloidal matter. The charges on the polymer molecules and their long hydrocarbon chains provide points of attachment and the opportunity to form a link between two or more colloidal particles. Although cationic polymers would be the apparent choice for destabilizing
negatively charged colloids, effective solids removal has resulted from use of anionic polymers (10,2). When divalent calcium or magnesium ions are used along with the anionic polymer, performance has been found to increase (2). Some restabilization can occur with an excess of polymer, as sites on suspended particles become used up and bridging cannot occur.
EXPERIMENTAL PROGRAM

Alkalinity Supplementation

As noted previously, the low alkalinity of Amherst sewage (about 100 mg/l on the average) would normally require that pH greater than 11 be attained in order to yield high removal of phosphorous. In practice this would be achieved using a two-stage system: lime treatment at a high pH followed by recarbonation to bring the pH down.

Initially an attempt was made to supplement the alkalinity of Amherst sewage by adding soda ash (sodium carbonate) and thereby obviate the need for two-stage treatment. It was reasoned that the artificially induced high alkalinity would allow single stage treatment to be used. This did not meet with success in jar tests run with lime because soda ash, a base, raised the pH of the water permitting only a small amount of lime to be added before the pH increased above 10.5. This effect severely limited phosphorous removals. Addition of sodium bicarbonate, a mid-range pH buffer, could prove more successful, because pH would not increase; however, its cost is much higher than that of soda ash.

Polymer Screening and Jar Test Procedure

In the next phase of experimentation, a series of polymers were added to a lime coagulation system to determine which improved clarification and phosphorous removal significantly over lime used alone at pH 10.5. Dosages in the range of 0.01 to 10.0 mg/l were tried, along with a control sample in which only lime was added in the same amount as was added to the samples treated with polymer. An additional sample was treated with lime to
achieve a pH of around 11.0, as opposed to 10.5 for other samples. The purpose of this sample was to determine if any "low" pH polymer samples gave removals approaching the high pH treatment. The jar tests were conducted as follows:

1. Lime addition
2. Three minutes of rapid mix at 100 rpm
3. Polymer addition
4. Three minutes of additional rapid mix
5. Flocculation for 20 minutes
6. Settling for 15 minutes

Initially, 35-40 rpm was used for the slow-mix paddle speed. However, it was soon found that about 15 rpm produced a better floc, the higher speed tending to tear apart floc particles. Analyses were performed after the settling period on samples extracted from the supernatant.

It may be mentioned that jar test procedures given in the literature have not been standardized, due to varying conditions which dictate different mixing conditions. For example, some reported jar tests employ 2 liter samples, higher flocculation speeds, and rapid mix periods varying from 30 seconds to 10 or more minutes. Similarly, for one liter samples, paddle speed during flocculation has been cited as 25-40 rpm and 20 rpm (3), and 15 rpm (2).

When more detailed evaluation of one polymer was made, the length of rapid mix and sequence of adding the polymer was varied. The rapid mix and flocculation speed, however, were kept at 100 and 15 rpm respectively. The sample size used was one liter for all tests.
Preparation and Addition of Lime and Polymers

Lime was added as a weak slurry of 4000 mg/l or 5000 mg/l, so that 1 ml contained 4 or 5 mg of lime as CaO. This dilute concentration was made in order to facilitate dosing to attain a specific pH. The amount of lime slurry to be added was predetermined using part of the grab sample of raw sewage to be used for the following jar test. An Orion Ionanalyzer Specific Ion Meter Model 407 was used for the pH determination. The pH used in the jar tests was maintained at pH 10.4 ± 0.1.

Polymer solutions were prepared such that 1 ml contained 1 mg of polymer except for Calgon's WT-3000, WT-2700, and WT-2900, whose recommended strengths were 0.2 mg in 1 ml. Powdered polymers required about 30 minutes of vigorous stirring before completely dissolving, and these solutions tended to be quite viscous.

Analytical Procedures

Initially, residual phosphorous was used to determine the effectiveness of each polymer, but since turbidity and phosphorous concentrations showed a positive correlation (Figure 1) and turbidity is a more rapid test, this was used after a few polymers had been used. The use of turbidity permitted a more rapid screening procedure.

Turbidity: Turbidity was measured in Jackson Turbidity Units by a Hach Model 2100A turbidimeter. It should be noted that measurements of the raw sewage turbidities were imprecise, due to the large, settleable matter present which produced fluctuations in the readings.
Figure 1. Total Residual Phosphorus versus Residual Turbidity in Samples Treated with Lime and Polymer.
Phosphorous: In the detailed investigation of the most effective polymer, phosphorous determinations were made. Total phosphorous was determined by the ascorbic acid method as outlined by Jankovich, Mitchell, and Buzzell (6). Although no neutralization step is listed in this procedure, it was found that the acidified combined reagent lowered the pH of the samples beyond the range in which color development occurs in samples which required less dilution due to lower phosphorous content. Following this discovery which first occurred after the preliminary screening, all samples were neutralized to the phenolphthalein end point after digestion. Dilutions for treated samples were 10:1 and 5:1, depending on the turbidity, which gave an indication of phosphorous content. Raw sewage samples were diluted by a factor of 10 or 20, depending on their strength. A Bausch and Lomb Spectronic 20 spectrophotometer was used for absorbance readings, performed at 882 m\(\mu\).

Alkalinity: Alkalinity measurements were taken on the raw sewage samples to determine whether the alkalinity variations produced changes in the requisite lime dosage and also whether they influenced removal efficiencies. The measurement was made with standardized .02N \(\text{H}_2\text{SO}_4\) and methyl orange indicator according to the procedures used in Standard Methods (11).

Total Organic Carbon: TOC was measured on two samples to evaluate the degree of change in organics removal produced by the polymer which gave greatest improvement in turbidity and phosphorous removals. A Beckman Model 915 A organic carbon analyzer was used to measure TOC, using 20 \(\mu\)l aliquots.
EXPERIMENTAL RESULTS

Polymer Screening

Sixteen different polymers of various types were tested to determine their effectiveness as a coagulant aid in lime treatment of wastewater at pH 10.5. The polymers used are listed in Table 1. Results obtained in jar tests for each individual polymer are discussed in the following paragraphs. First it is important to point out that results for a given polymer could not be reliably duplicated using raw wastewater samples. Hence, meaningful comparisons can only be made within a given test and not between tests. It follows that comparing absolute values of the measured parameters does not give a true indication of the advantages of one polymer over another, since the wastewater variation in each grab sample can produce large changes in coagulation effectiveness.

Cat Floe B had no positive effect on phosphorous removal. The settling characteristics after flocculation showed little variation from adding lime only. In addition to the test plotted in Figure 2, a second run, not shown, produced high turbidity in all samples.

Purifloc M-11, cited as an effective coagulant aid in lime treatment at Lake Tahoe (4) also gave no important change in water quality after flocculation as shown in three tests plotted in Figure 3. The differences in results of the three tests may be attributed to varied wastewater characteristics and to the fact that one test was conducted at pH 10.0 rather than 10.5. As would be expected, results were much poorer at the lower pH.
Table I. List of Polymers Used

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Company</th>
<th>Ionic Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAT FLOC B</td>
<td>Calgon</td>
<td>Cationic</td>
</tr>
<tr>
<td>PURIFLOC N-11</td>
<td>Dow</td>
<td>Nonionic</td>
</tr>
<tr>
<td>NALColyte 605</td>
<td>Nalco</td>
<td>Cationic</td>
</tr>
<tr>
<td>PURIFLOC A-23</td>
<td>Dow</td>
<td>Anionic</td>
</tr>
<tr>
<td>CALGON S.T.-270</td>
<td>Calgon</td>
<td>Nonionic</td>
</tr>
<tr>
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</tr>
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</tr>
<tr>
<td>CALGON WT-2700</td>
<td>Calgon</td>
<td>Weakly Anionic</td>
</tr>
<tr>
<td>CALGON WT-2900</td>
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<td>Strongly Anionic</td>
</tr>
<tr>
<td>CALGON COAGULENT AID 227</td>
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<td></td>
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<tr>
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<td>Calgon</td>
<td></td>
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<td>CALGON COAGULENT AID 50</td>
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<td>CALGON COAGULENT AID 252</td>
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<tr>
<td>CALGON ST-269</td>
<td>Calgon</td>
<td>Nonionic</td>
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<td>CALGON COAGULENT AID 223</td>
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<tr>
<td>HERCULES RETEN A-5</td>
<td>Hercules</td>
<td>Anionic</td>
</tr>
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Figure 2. Total Residual Phosphorus versus Dosage of CAT FLOC B at pH 10.5.
Figure 3. Total Residual Phosphorus versus Dosage of PURIFLOC N-11 at pH 10.0 and 10.4.
Figure 4 shows the results of addition of Nalcoyte 605. Some improvement in phosphorous removal can be noted with doses of 1.0 mg/l and greater. On the other hand, this improvement was neither large nor consistent. Additionally, little improvement in settleability was noted.

Purifloc A-23 produced results superior to any of the other polymers tested. Addition of 0.5 mg/l or more gave a very large floc, even during the rapid mix period, which formed one mass of solids after only a few minutes of flocculation. This mass of solids required virtually no settling period; as soon as the paddles stopped, most of the solid matter settled rapidly. In addition, reductions in phosphorous were obtained in all tests when 1.0 or 10.0 mg/l were added as shown in Figure 5. The effect of consolidation of the solids in the system comes about most likely from the bridging effect. Further tests were conducted with this polymer which are discussed later in this report.

Figure 6 shows the results of jar tests using three different Calgon polymers: ST-2640, ST-270, and WT-2900. Calgon ST-270 produced the same kind of consolidation effect with 1.0 and 10.0 mg/l as occurred with Purifloc A-23, but little improvement in turbidity removal was noted in the jar tests over the control sample containing no polymer. Addition of Calgon WT-2640 resulted in some additional turbidity removal with a 10.0 mg/l dose along with more rapid settling than treatment with only lime. The improvement in turbidity, however, as seen by the graph, was only slight. Calgon WT-2900, a strongly anionic polymer, gave a consolidated floc which settled very rapidly with doses of 1.0 and 10.0 mg/l. All tests showed that greater than 1.0 mg/l was necessary to produce the largest increment in turbidity removal.
Figure 4. Total Residual Phosphorus versus Dosage of NACOYLTE 605.
Figure 5. Total Residual Phosphorus versus Dosage of PURIFLOC A-23.
Figure 6. Residual Turbidity versus Dosage of CALGON WT-2900, ST-270 and WT-2640.
In Figure 7, results of jar testing with two more Calgon polymers are shown; two duplicate tests were run for each polymer on different wastewater samples. Calgon WT-3000, which is strongly anionic, produced significantly improved turbidity removals with the larger doses. The settling improved with a 10.0 mg/l dose. The plots reveal that, for each polymer, one test gave much more improvement than the other, so further study is necessary to reveal the effectiveness and consistency of this polymer when used with lime. Calgon WT-2700, described as weakly anionic, improved settleability of the floc, but only a small change in residual turbidity was noted as compared to using lime alone. These results indicate that a strongly anionic polymer has more effect on turbidity removal than weakly anionic polymers.

Calgon Coagulant Aid 227 gave vast improvement in turbidity removal when dosages greater than 1.0 mg/l were used (Figure 8). However, the large dose required for the bulk of this improvement would likely result in too great a cost on a large-scale system. From the plots it is evident that most of the reduction in residual turbidity over using lime only occurs between 1.0 and 10.0 mg/l. Figure 8 also shows the results of Calgon Coagulant Aid 50. This polymer produced no significant differences from the control samples, either with turbidity or settleability.

Figure 9 shows the results of jar tests of five additional polymers, none of which gave any increase in turbidity removal over just lime addition. Four of these polymers (Calgon ST-269, Calgon Coagulant Aid 240, Hercules Reten A-5, Calgon Coagulant Aid 252) gave poorer turbidity removals than did the addition of lime only to the same sewage sample.
Figure 7. Residual Turbidity versus Dosage of CALGON WT 2700 and WT 3000.
Figure 8. Residual Turbidity versus Dosage of CALGON AIDS 50 and 227.
Figure 9. Residual Turbidity versus Dosage of CALGON AIDS 223, 240, and 242, HERCULES RETEN A-5 and CALGON ST-269.
All except Calgon Coagulant Aid 223 produced more rapid settling with 10.0 mg/l, with Hercules Reten A-5 producing a mass which required virtually no settling period. Polymers such as these would be beneficial in an hydraulically overloaded basin but would not be useful for improving effluent clarity.

Choice of Most Effective Polymer

Of the sixteen polymers tried, the testing indicated that Purifloc A-23 is the most effective in providing additional removal of turbidity as well as phosphorous. While other polymers in conjunction with lime, notably Calgon WT-3000, Calgon WT-2900, and Calgon Coagulant Aid 227, produced reduced residual turbidities after jar testing compared to lime alone, only Purifloc A-23 gave the bulk of this reduction with a dose as low as 1.0 mg/l. Therefore, Purifloc A-23 was chosen for further study.

Purifloc A-23 has been used in practice as a coagulant aid in conjunction with iron salts and lime (7). Doses used have ranged from 0.3 to 0.7 mg/l. Two points of addition have been noted in the EPA design manual on phosphorous removal (7). One plant in Michigan added it just ahead of a rapid mix basin, but after an aeration chamber to which ferrous chloride and lime were added. A system in New York added it to the line leading to the flocculator.

Effect of Dose on Purifloc A-23 Performance

Figures 10 and 11 show the results of several jar tests using varying dosages of Purifloc A-23. The plots show that the major reduction in turbidity and total phosphorous occurs with polymer doses between 0.1 and 1.0 mg/l. An increase in residual turbidity can be noted when the doses exceed 10 mg/l. This increase was accompanied by some dispersion
Figure 10. Total Residual Phosphorus versus Dosage of PURIFLOC A-23.
Figure 11. Residual Turbidity versus Dosage of PURIFLOC A-23.
of the floc as opposed to the tightly bound mass of solids which characterized the 0.75 and 1.0 mg/l doses. Settling of these dispersed particles was relatively slow; the particles were fairly large, but appeared to consist of a dispersed gelatinous matter. The dispersion and the higher turbidities observed with larger doses indicates that restabilization occurs with an overdose of Purifloc A-23. This overdose could vary with the strength of the sewage (solids content, phosphorous concentration). The bridging form of particle destabilization appears to be the predominant mechanism by which this polyelectrolyte removes solids and precipitates phosphorous.

Effect of Mixing Time and Sequence of Purifloc A-23 Addition

The effect of length of rapid mixing was evaluated by adding the polymer at different lengths of time following the initial addition of lime. It was found that as the length of rapid mix before addition of Purifloc A-23 increased, performance of the polymer also increased (Figure 12). Increasing the rapid mix time for samples to which only lime was added also increased removal efficiencies.

Addition of Purifloc A-23 to the samples at the beginning of the flocculation period produced enlargement of the floc and very rapid settling after flocculation. It appears that, as reported by Culp and Culp (4), these polymers can be added to the flocculation tanks in a full-scale system.

When the lime and Purifloc A-23 were added at the same time, the polymer actually inhibited turbidity and phosphorous removal. The floc did not consolidate into one mass during flocculation, and residual turbidity was high in all samples treated in this fashion. In order to
1.0 mg/l PURIFLOC A-23
3 MIN. RAPID MIX AFTER POLYMER ADDITION
20 MIN. FLOCCULATION PERIOD

Figure 12. Effect of Time Elapsed Between Lime and Polymer Addition for Two Runs.
maximize phosphorous and turbidity removals, the phosphorous must be rendered insoluble first, followed by the adsorption and bridging effect of the polymer. Possibly, the anionic polymer reacts with some of the calcium ions from the lime before they have a chance to react with the phosphate and bicarbonate/carbonate ions. A thorough knowledge of the equilibria involved in the reaction, if any, between this polymer and calcium ions would be needed in order to predict how much, if any, Ca^{++} is tied up by reaction with the polymer.

**Effect of Purifloc A-23 on TOC Removal**

Removals of total organic carbon are shown in Table 2 along with corresponding phosphorous removals. The results of these limited tests indicate that Purifloc A-23 has little or no effect on TOC removal as compared with lime alone. Evidently, the added turbidity removal comes from added precipitation of suspended insoluble inorganics - probably consisting largely of calcium carbonate and hydroxyapatite.

**Importance of Wastewater Characteristics**

From inspection of the graphs of each polymer, as well as from observations, lower residual phosphorous after treatment in these jar tests occurred when the raw sewage phosphorous was lower. Figure 13 shows the range of raw sewage phosphorous concentrations measured. Note that only one sample had a phosphorous concentration of over 10 mg/l. Although at higher phosphorous concentrations, the removal efficiency is essentially independent of initial concentration, the dependency on phosphorous concentration takes effect at concentrations under 10 mg/l (8). Figure 14 shows the relationship between residual phosphorous in samples treated
Table 2. Residual TOC and Phosphorus for Two Jar Tests

<table>
<thead>
<tr>
<th>Sample</th>
<th>Residual Phosphorous mg/l</th>
<th>Residual TOC mg/l</th>
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<td>Lime pH 10.5</td>
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<tr>
<td>Lime pH 11.0</td>
<td>0.7</td>
<td>31</td>
</tr>
<tr>
<td>Lime and 1 mg/l Purifloc A-23 pH 10.5</td>
<td>1.0</td>
<td>31</td>
</tr>
<tr>
<td>Test No. 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lime pH 10.1</td>
<td>3.05</td>
<td>27</td>
</tr>
<tr>
<td>Lime pH 11.0</td>
<td>0.75</td>
<td>25</td>
</tr>
<tr>
<td>Lime and 1 mg/l Purifloc A-23 pH 10.5</td>
<td>1.27</td>
<td>29</td>
</tr>
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</table>
Figure 13. Distribution of All Raw Sewage Phosphorus Concentrations in Samples Used for Jar Testing.
Figure 14. Residual Total Phosphorus versus Raw Sewage Total Phosphorus Lime Addition Only.
with lime (no polymer added) at a pH of 10.5 and initial phosphorous concentration. Only a general trend toward increased residual phosphorous with higher raw sewage phosphorous can be seen, but some dependence is evident.

The scattered nature of these points indicates, however, that the large variation in effectiveness of jar testing depended on much more than phosphorous content of the sewage. As a rule, the residual turbidity and phosphorous were low when a sample had relatively low turbidity to start with. "Weak" samples, such as ones collected early in the morning or after rainfall, gave good solids removal and low residual phosphorous. Samples which had an excessive amount of solids and turbidity yielded higher values of turbidity and phosphorous after jar tests using lime, a polymer, and pH of 10.5. Generally, samples collected in the morning gave better results than those collected in the afternoon, which can be attributed to the increased strength of the sewage as the day goes on.

Alkalinity measurements gave little correlation with removal efficiencies. In some cases, the efficiency increased with increasing alkalinity; in others, the reverse was true. Low alkalinity samples which were associated with rain-diluted or early morning sewage, however, gave better results than those with average or high (for Amherst wastewater) alkalinitities.

Lime dosage for attaining a pH of 10.5 also did not appear to affect the final results. If there was any trend in a relationship between
residual phosphorous and lime dose, removals went inverse to the lime added to reach a constant pH. For example, addition of only 64 mg/l of lime as CaO and 1.0 mg/l of Purifloc A-23 in one sample (Figure 5) yielded only 0.22 mg/l of total residual phosphorous. Other samples to which over 110 mg/l of CaO could be added before the pH reached 10.5 gave much higher values of phosphorous after coagulation. These samples as a rule had more turbidity and higher phosphorous concentrations. Some of the phosphorous which has been rendered insoluble likely remains in suspension in these cases.

**Lime Dose and Alkalinity**

The dose of lime required to reach a pH in the range of 10.5 to 11.0 should be dependent on the alkalinity of the water. The results of the lime dosing in the jar tests show some correlation between lime dose and alkalinity (Figure 15). However, it is difficult to arrive at a definite relationship because factors other than alkalinity may be involved.

**Effect of pH**

While most jar tests were run with a pH in the area of 10.5 after lime addition, some samples were treated with lime and polymer at a pH of 10.0. These yielded phosphorous concentrations on the order of two to three times greater than samples to which lime was added to reach a pH of 10.5. Removal efficiencies for these samples averaged about 50%. This indicates that a pH of 10.0 is insufficient for good phosphorous removal with lime and Purifloc A-23.
Figure 15. Lime Dosage to Reach pH 10.5 versus Alkalinity.
Other samples were treated with lime at a pH of about 11.0 in order to compare with the use of a slightly lower pH and polymer addition. These samples, run in parallel with ones with Purifloc A-23 added, gave better phosphorous removals (Figure 16). This would lead to the conclusion that low pH (single stage) lime treatment, even with polymer addition, is not as effective as high pH (two-stage) lime treatment. However, if settling efficiency plays an important role, the use of Purifloc A-23 would still merit consideration.

Evaluation of Lime-Polymer System

Figure 17 shows the distribution of results of jar testing using set dosages of Purifloc A-23 and lime at a pH of 10.5. These graphs show that little change in overall phosphorous reduction occurs with 0.1 and 0.5 mg/l of polymer. Doses of 1.0 and 10.0 mg/l show a noticeable, but not great, reduction in phosphorous. This improvement does not appear to have great promise by itself in a treatment system, the increment probably being offset by the chemical cost.

On the other hand, addition of Purifloc A-23 produced very rapid settling, as already stated. Although the ease of handling the solids produced is not certain, Purifloc A-23 has been used as a dewatering agent (7). The rapid settling of the large mass produced would enable a much smaller settling basin to be used. Greater flowrates through an existing system could also be handled. Figure 18 shows a typical run using lime with and without Purifloc A-23. Note that turbidity during flocculation almost approached the lowest level attained during settling when 1.0 mg/l
Figure 16. Distribution of Total Residual Phosphorus With and Without Addition of 1 mg/l PURIFLOC A-23.
Figure 17. Distribution of Total Residual Phosphorus at Varying Dosages of PURIFLOC A-23.
Figure 18. Residual Turbidity versus Time in Jar Tests With and Without Addition of PURIFLOC A-23.
of the polymer was used. Pilot-scale testing of this system would give better evidence as to the possibility of using lime and a polymer in a primary step of sewage treatment with low alkalinity wastewater. The jar testing system is prone to greater changes in strength and other characteristics of sewage than a continuous system. Around-the-clock testing of the effluent and evaluation of the settleability of solids produced would be needed to determine the feasibility of such a chemical addition process. In order to maintain the pH level, a feed forward or feedback control would have to be used.

Many other polymers remain to be studied. Products of several other chemical companies were available and some Calgon, Nalco, Hercules, and Dow products remained untested. On the basis of the polymers studied, however, it appears that anionic polyelectrolytes give the most significant improvement in coagulation of raw wastewater. Most of the anionic polymers, although not necessarily removing turbidity or phosphorous better than lime alone, still produced a large mass of solids which settled out rapidly.
CONCLUSIONS

On the basis of jar testing of polymers and lime to produce a final pH of 10.5, several conclusions can be made with regard to this system:

1. Lime treatment of Amherst wastewater gives insufficient phosphorous and turbidity removals when the pH obtained is 10.0 or less.

2. Of 16 polymers tested, only Purifloc A-23 makes a significant improvement in phosphorous and turbidity removals in conjunction with lime at a pH of 10.5 at a dose of 1.0 mg/l or less over the use of lime alone. Optimum range is 0.75 to 10 mg/l with the lower range desired due to chemical costs.

3. The increase in removal efficiency by Purifloc A-23 does not mark a large improvement over the use of lime only at the same pH. Using a lime dosage for a pH of 11.0 to 11.2 gives slightly higher removal efficiency than the lime-polymer system at pH 10.5.

4. Purifloc A-23 and most of the anionic polymers tested produce a large mass of solids which settle even during flocculation. Under quiescent conditions these solids settle almost immediately and therefore polymers could prove valuable in a hydraulically overloaded plant.

5. Purifloc A-23 should be added after at least 3 minutes of rapid mix following lime addition. Addition of lime and polymer simultaneously gives poor results; poorer removals than using only lime. The polymer can be added to the flocculation unit or the line to the flocculator to provide mixing, but an extended rapid mix for this polymer appears unnecessary.
6. Removal of TOC shows little effect with addition of Purifloc A-23 in comparison with lime alone.

7. Pilot scale tests using the lime-polymer treatment should be made in order to determine more fully the practicality of this coagulation method. Special notice should be made of the settleability of the solids. Handling of the sludge produced should also be studied, for ease of dewatering and possibility of lime recovery. Recirculation of some of the solids should be considered on a continuous system.
REFERENCES


