Recovery and Reuse of Coagulants from Treatment of Water and Wastewater

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PREFACE

The focus of water quality research in the decade ahead will emphasize the development of processes which will enable reclamation and reuse as opposed to wastewater treatment and disposal to a nearby water course. In this regard the importance of chemical treatment processes similar to those utilized by the water utility industry for many years is now well established. Two problems in this type of system are the increasing expense and scarcity of appropriate chemicals and the resulting large volumes of sludge. The use of coagulant recovery techniques promises to alleviate both problems. Until economical coagulant recovery schemes have been developed, the potential benefits associated with water reuse cannot be fully realized.

The primary objectives of this research were to evaluate the possibilities and procedures for coagulant recovery in chemical treatment processes employed in water and wastewater treatment systems. Attention was focused on the extent of coagulant recovery achievable; the separation, dewatering, and ultimate disposal of the remaining solids after recovery; the effectiveness of the recovered coagulant during reuse; and the economic considerations which determine the feasibility of utilizing the proposed processes.

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Coagulants used in many water treatment processes are increasing in cost and supply problems. For this reason, finding more efficient means for reclaiming and reusing these chemicals would offer substantial economic benefits in the operation of water and wastewater treatment systems. This was the objective of the research project reported herein. In laboratory experiments, it tested procedures for economical recovery of hydrolyzed metallic coagulants used in treatment of polluted surface waters and selected wastewater discharges. Investigations focused on treatment systems using aluminum and iron salts as coagulants and precipitants.

The experiments sought answers to three principal questions: (1) How much coagulant can be recovered? (2) What is the best means of separating and dewatering the remaining solids? (3) How effective is the recovered coagulant during reuse?

The investigation included an economic analysis to estimate the capital cost of implementing the process, and to determine what savings may be expected in chemical costs. In addition, a computer model was developed for determining, under selected conditions, the economic break-even point with reference to treatment plant capacity.

Research findings indicate that recovery of both aluminum and iron salts is technically feasible, though the potential for aluminum recovery appears greater. Among additional benefits from the process described are large reductions in sludge volume and improved settleability and filterability of the remaining sludge. Laboratory tests also indicate that the efficiency of recovered metal in coagulating suspended solids is not materially reduced from that of fresh coagulant.
INTRODUCTION

Aluminum and iron salts have been used as coagulants in water and wastewater treatment for many years. In the early days of recorded history, alum was used for water clarification and paper manufacturing in China. The initial use of iron salts dates back to the late nineteenth century. It was not until this time that alum was also used in municipal water treatment prior to rapid sand filtration. Today, except in the case of water softening, alum and iron salts are used almost exclusively as coagulants in the water utility industry. Installations using alum far outnumber those which employ iron salts.

Alum and iron salts are also used as polishing agents in tertiary wastewater treatment. Although the concept of using coagulants to treat raw sewage was suggested more than 60 years ago, the practice was not widely adopted, mainly because of the engineering difficulties involved and the volume of sludge which the process produced. Another important reason for the failure of coagulation of sewage to achieve recognition until recently is the lack of public pressure to produce better effluents from wastewater treatment plants.

In recent years the attention of the water utility industry has been increasingly focused on the economic disposal of the sludges produced by water treatment plants. Prior to this time the normal practice was to discharge these materials directly to the nearest watercourse. Many investigators have sought to find a way to solve the sludge disposal problem resulting from coagulation with aluminum or iron salts and a number of conditioning and disposal methods have been suggested. In a report by the American Water Works Association Research Foundation (Ref. 1), the following methods are described and discussed: direct discharge to water bodies, discharge to sanitary sewer, lagooning, sand bed drying, vacuum filtration, filter pressing, centrifugation, freezing, heating and pressuring, polyelectrolyte-aided thickening, land disposal, and coagulant recovery. Of all the methods mentioned, only coagulant recovery has the potential of profit, or, at least, cost saving resulting from reusing the reclaimed chemical.

The concept of using a recovery system for coagulant reuse is by no means new. Although a considerable number of studies have been directed toward reutilization of various coagulants, particularly alum, most of these have been concerned with the solution of a local problem. Many investigators have noted difficulties in achieving satisfactory process control. Very few studies have demonstrated the differences that may be experienced with sludges obtained from a variety of sources. In addition, there has been little attempted in terms of developing a method to analyze laboratory data and
translate it into economic terms that will enable the decision makers to come to a logical conclusion regarding the suitability of utilizing a coagulant recovery process at a particular location.

The purposes of this investigation were to define the extent of alum and iron salts recovery achievable using selected water and wastewater treatment plant sludges, to demonstrate the effectiveness of recovered coagulant as compared to fresh chemical in coagulation, to characterize and define the properties of the remaining sludge after chemical addition and separation of the recovered metal, to estimate the capital cost of the process as well as the savings in chemical cost, and finally to develop a method for determining the economic characteristics for employing coagulant recovery in terms of treatment plant size.
REVIEW OF LITERATURE

Alum in Aqueous Solutions

The use of alum has been an integral part of the purification of water for many years. The hydrolysis of the trivalent aluminum ion in aqueous solutions has been studied in detail by numerous investigators. Different chemical formulas of the hydrolysis of aluminum ions to yield various polynuclear species have been postulated. Controversies have been raised and no definite conclusion has ever been achieved.

Sullivan and Singley (Ref. 2) showed that under equilibrium conditions, aluminum existed primarily as the insoluble Al(OH)₃. But under nonequilibrium conditions existing in water treatment plant coagulation, they showed that the predominant form might not be Al(OH)₃, but a positively charged species. As shown in Figure 1, the species formed in the aqueous solution depends heavily on the concentration of aluminum in solution and the system pH. The figure also shows that the aluminum will leach out in the form of Al³⁺ at an aluminum concentration of 0.1 moles per liter when the pH of the system drops to about 3.5. On the other hand, the system pH must be raised to about 12.0 before the aluminum, in the form of Al(OH)₄⁻, reaches the same concentration in the solution. This phenomenon seems to make the acid method of recovery of alum relatively more attractive than the alkaline scheme.

Matijevic et al. (Ref. 3, 4) reported systematic investigations on coagulation and reversal of charge of silver iodide and silver bromide sols by aluminum nitrate and aluminum sulfate as a function of pH and the age of aqueous solutions. The entire domain of stability in the plot of the log of aluminum salt concentration versus pH for silver halide sols was established. The investigation of the reaction of aluminum nitrate with silver halide sols led to the formulation of hydrolyzed aluminum ions, which is consistent with the species Al₈(OH)₂⁰⁺⁴. In the case of aluminum sulfate, the formulate Al₈(OH)₁₀(SO₄)₄²⁻ was suggested. The results of this study generally agreed with the work of Brosset (Ref. 5, 6), who postulated an aluminum-to-hydroxide ratio of 1.0:2.5.

Iron in Aqueous Solutions

The hydrolysis of trivalent iron ion in aqueous solutions has been studied in detail. Most investigators agree that the effects of iron salts on coagulation are brought about by the hydrolysis products of the salts and not by the simple
aquo-metal ions (Ref. 7). The hydrolytic reactions which occur take the form:

\[
[\text{Fe(H}_2\text{O)}_6]^{3+} + \text{H}_2\text{O} = [\text{Fe(H}_2\text{O)}_5(\text{OH})]^{2+} + \text{H}_3\text{O}^+
\]

Additional ferric hydroxo complexes may be produced by similar reactions. These complexes have a pronounced tendency to polymerize, and the simplest reaction leading to a dimeric species is:

\[
2[\text{Fe(H}_2\text{O)}_5(\text{OH})]^{2+} = [\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2]^{4+} + 2\text{H}_2\text{O}
\]

This dimer, which contains hydroxo bridges between the metal ions, may undergo further hydrolytic reactions and form higher hydroxide complexes. As the ferric iron is progressively coordinated with hydroxo groups, the repulsion between ions decreases and the tendency toward polymerization increases. Eventually, colloidal hydroxo polymers and, ultimately, insoluble hydrous ferric oxide precipitates are formed (Ref. 8).

Black and Singley (Ref. 9) studied the distribution of the hydrolyzed species of iron (III) in dilute solutions. They showed that the equilibrium system is dominated by the insoluble neutral form Fe(OH)$_3$. But under nonequilibrium conditions existing in water treatment, they demonstrated that several positively charged species could exist. The number of hydroxides bound to each ferric ion varied with the concentration of iron and the system pH. Figure 2 illustrates this phenomenon. The figure indicates that the iron will leach out in the form of Fe$^{3+}$ at an iron concentration of 0.01 moles per liter when the pH of the system drops to about 2.0. When the system pH is raised to about 12.0, the soluble iron, in the form of Fe(OH)$_4^{-}$, is present at a concentration of only $10^{-7}$ moles per liter. This effect seems again to favor an acid method of recovery.

**Characteristics of Alum Sludge**

Although all chemical coagulation sludges vary significantly from plant to plant and even in a single plant due to seasonal changes, the basic characteristics are quite similar. Alum sludge is a bulky, gelatinous substance composed of aluminum oxides and hydroxides, inorganic particles such as clay or sand, color colloids, microorganisms, including plankton, and other organic and inorganic matter removed from the water or wastewater being treated.
Solids. Solids content varies widely, and no set pattern exists to predict its value. Generally speaking, solids level is influenced by the turbidity and impurities in the raw water, the amount of alum added as coagulant, the means of and intervals between withdrawing of sludge, and the depth of sludge in the sedimentation basins. From various sources, total solids values from 0.1% to 4% have been reported (Ref. 1). Despite this wide range of values of total solids, suspended solids usually account for 75 to 90% of the total. The volatile content ranges from 20 to 35% of total solids.

pH. Because of the amphoteric nature of aluminum, the pH of alum sludge is normally in the range between 6.0 and 7.0.

Settleability. Although there is not sufficient data to characterize the settleability of alum sludge, Gates and McDermott (Ref. 10) reported an inverse linear relationship between the log of the total solids of the sludge and the log of the initial settling rate of the sludge-liquid interface. The higher the solid content observed, the lower was the initial settling rate. During their settling tests of raw alum sludge, Roberts and Roddy (Ref. 11) experienced some extreme results. The liquid-solids interface position of the alum sludges in 1000-ml graduated cylinders after one hour of gravitational settling varied from the 950-ml to the 100-ml mark. They concluded that these differences were the result of the type of floc formed during the coagulation of the highly variable surface supply at Tampa, Florida.

Filterability. Filterability of alum sludge is usually evaluated using both the gravity drainage technique and the vacuum filter technique. For the gravity system a sand bed drainage test is normally performed, and data obtained are used to design gravity drying beds. Various tests under pressure are used to design vacuum filter and filter press systems, but among those the specific resistance test is the most widely adopted. This analytical method was developed by Carman (Ref. 12) as early as 1933 and was later modified by Coackley and Jones (Ref. 13) for application of Carman’s theory to vacuum sludge filtration. Specific resistance can be described quantitatively as:

\[ r = \frac{2PA^2b}{\mu C} \]

where \( r \) = specific resistance, cm/gm
\( P \) = pressure of vacuum applied to filtration, gm/cm\(^2\)
\( A \) = filter area, cm\(^2\)
\( b \) = slope of \( T/V \) versus \( V \) curve sec/cm\(^6\)
Although numerous investigators have attempted to define the filterability of alum sludge in terms of specific resistance, little appreciable progress has been accomplished. The major reasons for this failure are the dependence of specific resistance on pressure of filtration, volume of sludge applied, and solids concentration. Even if all the experimental conditions are the same, it has been found to be difficult to compare values of specific resistance because of the different sludge characteristics at various locations. Thus it can be concluded that specific resistance is a qualitative but not a quantitative test of sludge filterability.

**Characteristics of Iron Sludge**

Ferric salt sludge is a bulky substance, reddish-brown in color, similar in many respects to alum sludges.

**Solids.** Ferric sludge solids content varies widely and is difficult to predict. The total solids content of sedimentation basin iron sludge is usually higher than that of alum systems. From various sources, total solids values from 0.26% to 3.5% have been reported (Ref. 14, 15). Suspended solids typically account for about 80% of total solids.

**pH.** The pH of iron sludge produced in water treatment is normally in the neutral range and approximately that of the treated water.

**Settleability.** There is not sufficient data to characterize the settleability of iron sludge. Generally, an inverse relationship exists between the solids content and the initial settling rate.

**Filterability.** The specific resistance of iron sludges varies depending on the sludge characteristics and experimental conditions, particularly solids concentration and volume of the sludge sample used. The dewatering characteristics of ferric sludges are normally superior to those of alum sludges (Ref. 15).

**Coagulant Recovery**

Most of the interest in coagulant recovery has centered on the reuse of alum.
Little attention has been given to iron sludges. In 1954 Palin (Ref. 16) reported little success in acidification of wet alum sludge. He stated that the aged alum precipitates did not readily dissolve in acid and that the sludge volume was not appreciably diminished. He found, however, that almost full alum recovery could be accomplished by adding sulfuric acid to a dried sludge containing Al₂O₃.

Vahidia and Issac (Ref. 17) found that the amount of aluminum hydroxide dissolved by sulfuric acid was a function of the quantity of acid added to the sludge. They further reported that the remaining sludge dewatered more rapidly than untreated sludge. Results of centrifugation of acid-treated sludge showed that the volume of remaining sludge decreased with increasing percentage of alum recovered. The investigators concluded that the coagulation efficiency of the treated supernatant was lower than that of fresh alum due to the organic color recovered.

Several alum recovery investigations have been conducted on a pilot plant scale and, in a few cases, extended to full-scale plant operations. During the 1960's Roberts and Roddy (Ref. 11) worked on a sludge acidification process in Tampa, Florida. From batch studies, they determined that the optimum pH range for recovery of alum was between 1.5 and 2.5. The reclaimed alum was nearly as efficient a coagulant as fresh alum. In actual plant operations, there was no noticeable interference from any acid-insoluble material or any change whatsoever in the treated water quality. The operational scheme utilized is shown in Figure 3.

Other large-scale recovery systems include the facilities at Daer, Scotland, and Tokyo, Japan. At Daer Water Treatment Works, Webster (Ref. 18) operated a pilot plant on a batch basis, where the sludge and supernatant were pumped from their units every twenty-four hours. After acid treatment, only about 5.6% of the sludge was unreclaimed Al₂O₃, and sludge solids were increased to 10% (Ref. 14). The Asaka Purification Plant near Tokyo has been recovering alum on a continuous flow basis for some time (Ref. 19).

Alum sludge from wastewater treatment plants was almost nonexistent a decade ago, but since then public pressure for better quality effluents has resulted in a gradual increase in alum usage in wastewater treatment. Because aluminum sulfate can serve both as a coagulant to remove suspended solids and as an agent to remove phosphate, more and more wastewater treatment plants are considering using it in tertiary treatment. Very few investigators have reported work on the recovery of alum from wastewater treatment plant sludges.
The first attempt to recover aluminum from tertiary alum sludge was made by Lea et al. (Ref. 20) at Madison, Wisconsin. The chemical reactions involved were shown by the following equations:

\[ \text{Al(OH)}_3 \cdot \text{PO}_4^- + 4\text{NaOH} \rightarrow \text{NaAlO}_2 + \text{Na}_3\text{PO}_4 + 2\text{H}_2\text{O} + 3\text{OH}^- \]

\[ 2\text{Na}_3\text{PO}_4 + 3\text{CaCl}_2 \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 6\text{NaCl} \]

The aluminum hydroxide phosphate floc mixture was first reacted with sodium hydroxide to produce sodium aluminate and sodium phosphate. Then calcium chloride was added to precipitate phosphate in the form of calcium phosphate. At a pH of 11.9, approximately 93% of the aluminum was recovered, and after addition of the calculated amount of calcium chloride, only 12% of the phosphate remained in solution. This small amount of phosphate in solution did not affect the efficiency of the sodium aluminate when it was reused for phosphate removal.

From the results of pilot plant experiments, the investigators showed no appreciable difference in phosphate removal efficiency when using recovered aluminate and fresh alum; but after careful evaluation of their data, the author found that the aluminum-to-phosphorus molar ratio used in their studies was as high as 4.2, which is double the Al:P molar ratio most investigators found to be required for optimum phosphate removal.

Slechta and Culp (Ref. 21) attempted three processes of recovering aluminum from tertiary alum sludge at Lake Tahoe, California. First, they tried virtually the same process Lea et al. (Ref. 20) developed, except that the aluminum-to-phosphorus molar ratio was reduced to about 2.0. They found that at this ratio the reclaimed aluminum, in the form of sodium aluminate, was not an effective coagulant. Fifty percent fresh alum was required at a total alum dose of 400 milligrams per liter to achieve the same turbidity and phosphate removals as those achieved by 200 mg per liter of fresh alum alone. The requirement of large quantities of make-up alum for effective coagulation and phosphate removal made this method of alum recovery uneconomical.

Another alkaline scheme of alum recovery from wastewater sludge using lime was also studied by Slechta and Culp (Ref. 21). Although the cost of lime is lower than that of sodium hydroxide, and calcium chloride and lime are much easier to handle, alum was poorly recovered. At pH 10.2 using
separation by sedimentation, only 20% of the aluminum was recovered. This poor recovery was probably due to the calcium ion reacting to form insoluble calcium phosphate. This method was also concluded to be impractical.

Sulfuric acid was then used by Slechta and Culp (Ref. 21) to recover aluminum at low pH. Excellent recovery of alum was obtained when the pH of the alum sludge was lowered to 2.5, but phosphate was also recovered at this pH. The recovered alum was found to be as effective as fresh alum after 10 cycles of reuse. The only problem involved in this method is the continual, concurrent recovery of phosphate. Ion exchange and phosphate adsorption on activated alumina were studied for separation of phosphate from the recovered alum, but the cost of these methods was prohibitively high. Thus, Slechta and Culp concluded that alum recovery was only attractive when phosphate removal is not required.

As previously mentioned, little work has been done on iron recovery from sludges. Cities Service Company, Atlanta, Georgia, claims to have attempted recovery of iron at low pH from water treatment plant sludge, but no experimental data is available. So far as can be discovered, no studies on iron recovery from water treatment plant sludge have been published. One would predict, however, that iron coagulants could be reclaimed in somewhat the same manner as alum. As previously noted, the hydrolyzed species of aluminum and iron are not dissimilar, and the solubilities as a function of pH follow the same general trend.
EXPERIMENTAL METHODS

Sources of Sludge

All samples of water treatment plant alum sludges were collected from the sedimentation basins of four typical, conventional water treatment plants in Virginia: the City of Radford; Food Processors Water Cooperative, Incorporated, of Timberville; the City of Harrisonburg; and Blacksburg-Christiansburg-V.P.I. Water Authority. Alum is employed at all four plants as the primary coagulant. Lime or soda ash is used for pH adjustment, and chlorine is used for final disinfection. All four plants are equipped with flash-and slow-mixing basins, sedimentation basins, and rapid sand filters. Activated carbon is occasionally used at the Radford plant when organic color in the raw water is extensive.

Alum sludge resulting from tertiary wastewater treatment was generated in the laboratory. Secondary effluent from the final clarifier at the Stroubles Creek Wastewater Treatment Plant near Blacksburg, Virginia, was collected in five-gallon, polyethylene carboys. The carboys were carried back to the laboratory and emptied into a 50-liter glass tub. The dissolved orthophosphate concentration in the samples was measured before an alum dose, which produced an aluminum-phosphorus molar ratio of 2.5, was added. Flash-mixing each sample for one minute was followed by 30 minutes of slow mixing. One hour of sedimentation was allowed before the supernatant was pumped out and discarded. The remaining sludge was preserved and was concentrated to about 1% solids before any further experiments were performed. Because of the high organic content, the sludge was stored in a refrigerator, but freezing of the sludge was carefully avoided.

The ferric sludge samples were collected from the sedimentation basins of the 11 MGD water treatment plant serving the city of Kingsport, Tennessee. The Kingsport plant is a typical water filtration facility. A ferric sulfate coagulant, "Ferri-floc" (Cities Service Company, Atlanta, Georgia), is employed for treatment of a surface water supply. Lime is used for pH adjustment, and activated carbon is added in small amounts for the removal of organic color. The plant is equipped with flash-mixing and baffled slow-mixing basins, sedimentation basins, and both conventional and high-rate rapid sand filters. Chlorine is added in the flash mix unit for disinfection and odor- and algae-control.
Settleability Test and Recovery Procedure

Sludge samples were allowed to settle for an indefinite period until no further appreciable settling was observed. The supernatant liquid was then carefully decanted. The remaining sludge was diluted to various solids concentrations with the decanted liquid. These sludge samples with different solids concentrations were poured into graduated cylinders. The position of the solid-liquid interface was recorded at various time intervals. Usually the test lasted for one hour.

Various amounts of acid or alkali were added to the sludge containing a selected solids concentration. Although the reaction is exothermic, the mixture was stirred at 30 rpm for 30 minutes. The remaining sludge was settled by gravity for an hour. The position of the liquid-remaining solids interface was recorded at various time intervals. The supernatant was then decanted for pH and metal ion coagulant content measurements. In the case of recovered alum from wastewater treatment sludge, dissolved orthophosphate was also measured. The remaining settled sludge, after one hour of gravitational settling, was used for the filterability determination accomplished by using the Buchner funnel, specific resistance test. The decanted supernatant was preserved for coagulation testing.

Aluminum Determination

The experimental procedure used in this study to determine aluminum concentration was developed by Rich and Singh (Ref. 22). The elements of the procedure are described as follows:

1. After the alum sludge was chemically treated, a suitable proportion of the supernatant, usually containing about five milligrams of aluminum, was measured into an Erlenmeyer flask. If the supernatant was high in color, it was run through an activated carbon column before proceeding to the next step.

2. Twenty-five milliliters of buffer solution (144 grams of ammonium acetate and 100 ml of glacial acetic acid were dissolved in distilled water, made up to one liter with distilled water, and pH-adjusted to 4.8 by adding ammonium hydroxide or acetic acid) and 25 ml of distilled water were added to the sample.

3. pH of the mixture was adjusted to 4.8 by adding ammonium hydroxide or acetic acid.
4. Five to ten milliliters of 0.05 M disodium ethylene-diaminetetra-acetate dihydrate (sodium salt of E.D.T.A.) was added to the sample. Exact amount added was recorded.

5. The mixture was brought to a boil and cooled to room temperature.

6. One milliliter of sulphosalicylic acid indicator (10 gm of sulphosalicylic acid dissolved in 50 ml distilled water and pH of the solution adjusted to 4.8 by adding 2 N sodium hydroxide) was added.

7. The resulting solution was titrated with 0.025 M ferric chloride solution (6.8 gm of FeCl$_3$·6H$_2$O dissolved in distilled water and 25 ml of concentrated hydrochloric acid added to the solution and diluted to one liter with distilled water). The color changed from a light yellow to light brown at the end point.

The end point is very sharp, usually taking only a fraction of a drop of ferric chloride solution to effect, but the color change is not very dramatic. Although it takes some practice to master the determination of the end point of the titration, the method is extremely accurate. An error of less than 1% is possible.

**Iron Determination**

After the iron sludge was chemically treated, portions of the decanted supernatant were digested in preparation for measurement of iron content. Iron concentration was determined using the phenanthroline method as outlined in *Standard Methods* (Ref. 23) and verified by atomic absorption spectrophotometry.

**Solids Determinations**

Total and volatile solids and total and volatile suspended solids concentrations were determined prior to chemically treating the sludge samples. After acidification and settling, the decanted supernatant was analyzed for dissolved and volatile dissolved contents. The remaining sludge was tested for total and volatile solids concentrations. All tests were performed using the procedures outlined in *Standard Methods* (Ref. 23).
Filterability Test

Filterability of the chemically-treated sludges was determined using the Buchner funnel specific resistance test. Testing procedures were as follows:

1. One piece of Whatman Number 4 filter paper was placed on the bottom of the Buchner funnel. A proportion of distilled water was poured into the funnel, and vacuum was applied to drain off the liquid to properly seat the filter paper.

2. The vacuum was relieved and the Mohr burette was emptied.

3. A 50-ml sample was poured into the funnel. The vacuum was applied, and the stopwatch was started as the filtrate reached the 100-ml mark. Time readings were taken at various volumes for about two minutes. The applied pressure was recorded from the manometer.

The values of specific resistance to dewatering were then calculated according to the equation noted in the previous chapter.

Evaluation of the Coagulation Efficiency of Recovered Metal Ion

The supernatant above the acidified sludge was preserved for coagulation tests. Prior to testing, samples were again carefully decanted to insure the removal of all settleable solids. Two raw waters were used in coagulation testing, one natural and the other artificial. The natural water was taken from the New River, a source which normally maintains sufficient alkalinity for alum or iron coagulation. The artificial water samples were made from distilled water to which various amounts of finely ground kaolin were added. The alkalinity was adjusted to 100 mg per liter by adding sodium bicarbonate.

Both the recovered coagulant solution and a comparable fresh reagent solution were used as coagulants. Different amounts of either coagulant were added to 1000-ml raw water samples in 1500-ml beakers, which were placed on a six-phase stirring apparatus. One minute of rapid-mixing was followed by 30 minutes of flocculation at 20 to 30 rpm. The stirring paddles were then removed, and the flocculated solution was allowed to settle quiescently for another 30 minutes before the supernatant was withdrawn. Residual turbidity of the supernatant was measured using a Hach Model 2100A turbidimeter.

The supernatant above the acidified wastewater alum sludge was also preserved for coagulation tests. The wastewater sample used for coagulation
tests also was taken from the secondary effluent of the final clarifier of the Stroubles Creek Wastewater Treatment Plant. Different amounts of either fresh or recovered alum solution were added to the wastewater samples. One minute of flash-mixing was followed by 30 minutes of flocculation at 30 rpm in a jar test apparatus. The flocculated solution was allowed to settle for another 30 minutes before the supernatant was decanted. Dissolved orthophosphate, pH, suspended solids, and chemical oxygen demand of the supernatant were measured. Dissolved orthophosphate was measured by the stannous chloride method. pH was measured with a glass electrode pH meter. Experimental procedures for all of these methods were as outlined in Standard Methods (Ref. 23).
EXPERIMENTAL RESULTS

Sludge Characteristics

The sludge characteristics of the four selected water treatment plants in Virginia utilizing alum, the one wastewater treatment alum sludge generated in the laboratory, and the ferric sulfate sludge from Kingsport, Tennessee, are listed in Table I. Total and volatile solids, aluminum contents, pH, specific resistance, and initial settling velocity were measured in each case.

It may be noted that the total solids contents of the Timberville sludge and the wastewater treatment alum sludge are comparatively low. The dilute nature of the wastewater sludge could be due to lack of compression. At Timberville the sedimentation basins were cleaned a few days before the sample was collected. Independent of the solids contents of the sludge samples, the volatile fraction of the solids is consistently between 20 and 30% of the total solids. This same result was also noted by other investigators (Ref. 10, 24, 25). This result does not necessarily imply that all the measureable volatile solids are organic matter. Much of the measured volatile solids is possibly due to previously bound water of hydration not released at 103°C.

Recovery of Alum from Sludge Samples

A preliminary study of alum recovery using various chemicals was performed on alum sludge samples obtained from Blacksburg-Christiansburg-V.P.I. Water Authority Plant. Four different chemicals were used for this purpose: sulfuric acid, hydrochloric acid, sodium hydroxide, and calcium hydroxide. The following chemical reactions are anticipated in each case:

\[
2\text{Al}_x(\text{OH})_{3y} \rightarrow 3\text{H}_2\text{SO}_4 + x\text{Al}_2(\text{SO}_4)_3 + 2y\text{H}_2\text{O} + (6x-2y)\text{H}^+ 
\]

\[
\text{Al}_x(\text{OH})_{3y} + 3\text{HCl} \rightarrow x\text{AlCl}_3 + y\text{H}_2\text{O} + (3x-y)\text{H}^+ 
\]

\[
\text{Al}_x(\text{OH})_{3y} + x\text{NaOH} \rightarrow x\text{NaAlO}_2 + (y-x)\text{H}_2\text{O} + (3x-y)\text{H}^+ 
\]

\[
2\text{Al}_x(\text{OH})_{3y} + x\text{Ca(OH)}_2 \rightarrow x\text{Ca(AlO}_2)_2 + 2(y-x)\text{H}_2\text{O} + (6x-2y)\text{H}^+ 
\]
<table>
<thead>
<tr>
<th></th>
<th>Radford</th>
<th>Timberville</th>
<th>Harrisonburg</th>
<th>Blacksburg</th>
<th>Wastewater Alum Sludge</th>
<th>Kingsport Ferric Sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total Solids (mg/l)</strong></td>
<td>29,800</td>
<td>13,500</td>
<td>21,000</td>
<td>30,800</td>
<td>7,500</td>
<td>40,800</td>
</tr>
<tr>
<td><strong>Volatile Solids (mg/l)</strong></td>
<td>9,450</td>
<td>2,980</td>
<td>5,500</td>
<td>9,250</td>
<td>2,680</td>
<td>6,895</td>
</tr>
<tr>
<td><strong>Aluminum or Iron (mg/l as metal)</strong></td>
<td>3,480</td>
<td>1,175</td>
<td>1,620</td>
<td>1,383</td>
<td>873</td>
<td>2,350</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>6.70</td>
<td>7.10</td>
<td>7.20</td>
<td>6.85</td>
<td>6.25</td>
<td>7.60</td>
</tr>
<tr>
<td><strong>Specific Resistance</strong></td>
<td>$16.5 \times 10^{10}$</td>
<td>$54.0 \times 10^{10}$</td>
<td>$36.0 \times 10^{10}$</td>
<td>$41.0 \times 10^{10}$</td>
<td>$209.0 \times 10^{10}$</td>
<td>$195.0 \times 10^{10}$</td>
</tr>
<tr>
<td><strong>Initial Settling Velocity (cm/sec)</strong></td>
<td>0.060</td>
<td>0.074</td>
<td>0.095</td>
<td>0.150</td>
<td>0.035</td>
<td>0.007</td>
</tr>
</tbody>
</table>
Chemicals were added to the alum sludge samples at various concentrations. Aluminum contents of the supernatant were then determined. The results are shown in Figure 4. The dotted line is the predicted relationship if the stoichiometry of the reactions in the above equations is followed. It was found that both the sulfuric acid and the hydrochloric acid followed stoichiometry while both sodium and calcium hydroxide did not. The poor recovery of aluminum by calcium hydroxide could be due to the concentration of aluminum by calcium ions in the form of calcium aluminate. Sodium hydroxide and calcium hydroxide were then eliminated from further aluminum recovery studies. Dean (Ref. 1) stated: “According to the literature, if alum is not exhausted as a precipitant, it should be possible to recover soluble aluminum chloride with only one mole of hydrochloric acid. Three moles of sulfuric acid would probably be needed.” However, from the previously cited formula and the experimental results shown in Figure 4, one and a half moles of sulfuric acid and three moles of hydrochloric acid would be needed to recover one mole of aluminum. Since there was no apparent advantage chemically in using hydrochloric acid, and since its cost was prohibitively higher than that of sulfuric acid, it was also eliminated from further studies.

As noted previously, it may be anticipated that the amount of aluminum recovered is stoichiometrically related to the quantity of sulfuric acid added in the recovery process. Different amounts of sulfuric acid were added to the alum sludge samples, and the aluminum concentration in the resulting supernatant was then determined. The data collected during this study, as shown in Figure 5, strongly indicate the stoichiometric relationship. With the exception of the Radford sludge, which appears to have an immediate acid demand unrelated to the aluminum recovery process, all samples showed a remarkable alignment with the relationship predicted by the stoichiometry. The several data points of Harrisonburg sludge and the wastewater treatment sludge which are above the line determined by stoichiometry may or may not be due to experimental errors. The authors suspect that when a sufficient amount of sulfuric acid was added to the alum sludge, large aluminum hydroxide floc particles were broken up and minute floc was suspended in the supernatant. Since the supernatant was not passed through a fine filter paper before the supernatant aluminum concentration was measured, the aluminum in the suspended floc was also measured, resulting in a higher aluminum ion concentration in the supernatant.

From the data of Slechta and Culp (Ref. 21), Webster (Ref. 18), Bugg (Ref. 26), and the authors, it may be noted that system pH is generally an unsatisfactory control parameter for acidified aluminum recovery systems.
Although maximum recovery may consistently be obtained at a given pH at any one particular plant, it is not possible to translate this pH to another location. The relationship between pH and extent of aluminum recovered from the sludge samples utilized in this study and the data collected by other investigators (Ref. 26, 21, 25), as depicted in Figure 6, lend substantial support to this statement. As noted in these data, the pH level at which maximum aluminum recovery was achieved varied from 3.0 to as low as 1.0. It can be said that system pH is not a good control parameter alone, and the stoichiometric amount of sulfuric acid, according to the previously described equations, should be taken into consideration. By knowing the amount of sulfuric acid added, the amount of aluminum recovered can be calculated. By measuring the system pH, the possibility of a large overdose of sulfuric acid in an operating system can generally be eliminated. As indicated in Figure 6, except for one instance, pH value of 2.5 can account for about 90% aluminum recovery for each of the sludges studied.

When aluminum was recovered from the wastewater treatment sludge, phosphate was recovered at the same time. This phenomena was also observed by other investigators (Ref. 27, 20, 21). Lea et al. (Ref. 20) tried to use calcium chloride to precipitate the phosphate ions, and, later, Farrel et al. (Ref. 27) used calcium hydroxide to achieve the same purpose. But these two investigations involved the alkaline scheme of alum recovery which Slechta and Culp (Ref. 21) concluded to be uneconomical. When the acidic method was used to recover alum, Slechta and Culp stated that this process had to be limited to instances where clarification only and not phosphate removal was desired. In this study attempts were made to evaluate the degree of phosphate recovery when alum was partially recovered. The aluminum and phosphate contents of the supernatant above the partially acidified alum sludge samples were determined. The results are shown in Figure 7. If the stoichiometry is followed, the percentage of phosphate recovered should be the same as that of the aluminum. The data presented in this study shows a commensurately higher recovery of aluminum than of phosphate. The authors believe that only a portion of the alum added reacts with the dissolved orthophosphate while the other portion forms aluminum hydroxide floc, which is responsible for the coagulation of the suspended matter in the wastewater. During the addition of sulfuric acid, the portion of alum floc responsible for the coagulation of the suspended matter in the wastewater reacts first with the acid and then the alum-phosphate precipitate begins to redissolve.
Settleability of the Acidified Sludges

In any practical coagulant recovery process, separation of remaining solids from supernatant following acidification must be accomplished expeditiously. The initial settling velocity, defined as the steepest slope of the height of the liquid-solids interface versus time curve, was used in this study to evaluate the settleability of the acidified sludge samples. The relationship noted between the initial settling velocity and the percent recovery of the total aluminum in the alum sludge systems is given in Figure 9. As noted therein, the observed initial settling velocity consistently increased with increasing extent of aluminum recovery. Initial settling velocity increased substantially when the portion of aluminum recovered was more than 40%. Particularly favorable settling velocity was achieved when aluminum recovery exceeded the 60 to 80% level, although the value of the observed settling velocity varied substantially with the source of the sludge.

Corresponding settling velocity measurements for the iron system were also conducted. Data for this work is summarized in Figure 10, which gives the initial settling velocity as a function of pH. As noted therein, the observed settling velocity consistently increased with decreasing pH.

Filterability of the Acidified Sludges

A practical process for coagulant recovery must result in remaining sludge that can be readily dewatered. Figure 11 indicates the specific resistance of the remaining sludge in each of the alum experiments as a function of the extent of aluminum recovered. Acid addition sharply improved the filterability of the system sludge, and specific resistance reached a minimum when aluminum recovery was in the range of 60 to 80% of the total aluminum contained in the original sludge. Further improvement in filterability may well be achieved by judicious use of a properly chosen polyelectrolyte (Ref. 26). Similar results were obtained for the ferric sulfate sludge, as seen in Figure 12. Acid addition sharply improved the filterability of this sludge, although deterioration was noted when the system pH was decreased below 2.0.

Effectiveness of the Recovered Coagulants

The results obtained during the testing of the effectiveness of the recovered alum from the acidified water treatment plant alum sludge in a typical
coagulation process are indicated in Figure 13. Raw water turbidity is plotted against the critical coagulation concentration of aluminum. The critical coagulation concentration (c.c.c.) was obtained by extrapolation to zero turbidity of the steepest portion of the curve of residual turbidity versus alum dosage. From the data presented it may be noted that for low turbidity raw water, the recovered alum was marginally superior to fresh alum. At higher turbidity levels, fresh alum was somewhat more efficient. A possible explanation for this result is that the impurities and foreign particulates in the recovered aluminum solution provided some nucleation to aid in the coagulation of the low turbidity waters.

The effectiveness of the recovered alum from the acidified wastewater treatment alum sludge was also tested. The results are indicated in Figures 14 and 15, where the efficiency of phosphate removal and chemical oxygen demand removal are shown, respectively. It may be noted from these two figures that the recovered alum is at least as effective as fresh alum in removing phosphate and chemical oxygen demand. It should be noted that the phosphate recovered in the alum solution was already included in the aluminum to phosphorus molar ratio shown on the abscissas. This result indicates that full alum recovery does not represent an optimum operating system for the type of wastewater treatment contemplated in this portion of the study.

Coagulation tests were also performed using reagent grade ferric sulfate and recovered iron as coagulants. Although the pH value and volume of coagulant added varied, the raw water pH level never decreased by more than one-half of a pH unit. The data given in Figure 16 are representative of the results obtained. As noted therein, the raw water used in this series was a kaolinite suspension having moderate turbidity and alkalinity. From the data presented, it may be noted that, while fresh iron coagulant resulted in a slightly lower residual turbidity, the critical coagulation concentration was less when recovered iron was used.

As previously described, a natural raw water sample was also used in coagulation tests. The data given in Figure 17 are typical of those collected. The characteristics of the New River water are somewhat different from those of the artificial samples. Even so, the results are quite similar to those previously shown, except the residual turbidity levels are higher. Again, the use of recovered iron resulted in the lower critical coagulation concentration and a higher residual turbidity.
Additional Experimental Work

Extensive data was collected in the wastewater alum sludge system in an effort to define the predominant aluminum phosphate species on the basis of mass balance considerations. In addition, a proposed molecular structure for the postulated species was developed. At pH 5.0 the proposed formula of the complex is:

\[ \text{Al}_{13} \text{(OH)}_{30} \cdot 18\text{H}_2\text{O} \cdot (\text{H}_2\text{PO}_4)_9 \]

This material has an aluminum-to-phosphorus molar ratio of 1.44. A full discussion of this phase of the study has been previously published (Ref. 28).
ECONOMIC ANALYSIS OF ALUM RECOVERY

From the experimental results previously presented, it may be concluded that the acidic method of both alum and iron salt recovery is technically feasible. The remaining problem stems from the economic aspects of this process. In the literature reviewed, only a few investigations touched on this problem, and those investigations were limited to simple chemical cost analyses. In this chapter the experimental results were utilized to design an operable process and to analyze the capital costs as well as the operation and maintenance costs involved in alum recovery.

Costs Analysis of Alum Recovery from Water Treatment Sludge

The cost analysis in this study is based on a treatment scheme illustrated by the flow diagram shown in Figure 18. Sludge from the sedimentation basins and backwash wastewater are equalized first in an equalization tank or lagoon, and then a thickener is used to concentrate the sludge. The supernatant of the thickener is introduced back to the water intake, while the underflow is led to the reactor for mixing with sulfuric acid. The acidified mixture is next separated, with its supernatant going directly back to the flash mix unit. Lime is added to neutralize the remaining sludge to a suitable pH range for ultimate sludge disposal.

Detailed design of this proposed scheme of alum recovery was conducted using the following assumptions:

1. All alum floc is either intercepted by the sedimentation basins or the rapid sand filters.

2. All backwash wastewater is recycled.

3. Solids content of sludge from sedimentation basins is 10,000 mg per liter, or 1%. Sludge is continuously removed and sludge flow is 0.5% of the total plant production.

4. Backwash wastewater has a solids content of 400 mg per liter, or 0.04%. It also has the same characteristics and constituents as the sludge from the sedimentation basins.

5. Number of filters follows Morrill's formula:

\[ N = 2.7(Q)^{0.5} \]
where \( Q \) = plant capacity in million gallons per day; and \( N \) = number of filters, which is rounded off to the next highest even number.

6. Filtration is considered to be accomplished at a 4 gal./minute/sq. ft. rate, filter runs are uniformly set at 24 hours, and a backwash rate of 15 gal./minute/sq. ft. for ten minutes is assumed.

7. Aluminum content of the sludge is considered to be 10% of the dry weight and is assumed to be 95% recoverable according to stoichiometry and 90% as effective as fresh alum.

A computer program which indicated an optimum design for the proposed alum recovery system was developed. Thickener design was based on observed settling rates and utilized the theory of Kynch (Ref. 29). Reactor volume was based on a required retention time of five minutes. Design of the separation unit following acidification was accomplished in a manner similar to that used for the initial thickener.

Cost of the alum recovery process was analyzed in accordance with the following assumptions:

1. An interest rate of 6% compounded annually and a useful life for the equipment of 25 years are selected.

2. Maintenance cost is taken to be 5% of capital cost, and two extra operators at an annual cost of $10,000 per man are assumed to be required.

3. Insurance is taken to be 2% of capital cost.

4. Land is assumed to be available at a cost of $20,000.

5. Cost of cast-concrete structures is based on an Engineering News Record Index of 1,750 where erection and construction are included in the cost.

6. Cost of other equipment is based on a Marshall and Stephens Equipment Cost Index of 340 where erection and construction are not included. The total in-place cost is obtained by multiplying by a factor of 4.0.

7. Chemicals costs were: fresh alum at $62.80 per ton; commercial lime at $20.00 per ton; and sulfuric acid at $33.75 per ton.
The computer program was designed for optimizing the annual saving or minimizing the annual cost. Two variables were fixed at any one time of calculation. The plant capacity used in the calculation varied from 10 million gallons per day to 100 million gallons per day, with an increment of 10 million gallons per day. The underflow solids concentration of the thickener varied from 1.0% to 5.0%, with an increment of 0.1%. The underflow solids concentration of the separator varied from 7.0% to 15.0%, with an increment of 1.0%. The annual saving (or annual cost), capital cost of this process, and the optimum solids concentration from the thickener and the separator were determined. The annual saving (or annual cost) and the capital cost of the process are plotted against the plant capacity in Figure 19.

Cost Analysis of Alum Recovery from Wastewater Treatment Sludge

The recovery scheme of alum from a tertiary wastewater treatment sludge is virtually the same as shown in Figure 18. Additional assumptions used in designing the process are listed as follows:

1. Phosphate content in the secondary effluent from the wastewater treatment plant is assumed to be 10 mg/liter as phosphorus.

2. Aluminum is 10% by weight of total solids from the sedimentation basins and backwash wastewater.

3. Sludge from sedimentation basins has a solids content of 5,000 mg/liter or 0.5%. Solids content of backwash wastewater is 500 mg/liter or 0.05%.

4. Filtration of chemically-treated effluent is considered to be accomplished at a 4 gal./minute/sq. ft. rate, filter runs are uniformly set at 8 hours, and a backwash rate of 15 gal./minute/sq. ft. for ten minutes is assumed.

5. An aluminum-to-phosphorus molar ratio of 2.5 is required for effective plant operation using either fresh or recovered alum.

Four variables are involved in this recovery process—the plant capacity, the underflow solids concentrations of the thickener and the separator, and the fraction of alum recovered \( F_A \). The plant capacity is a fixed variable, and the other three are operational variables.
The same computer program designed for the optimization of annual saving of the water treatment alum sludge recovery process was also used for this purpose, except another variable ($F_A$) was added. The plant capacity used in the calculation varied from 10 million gallons per day to 100 million gallons per day, with an increment of 10 million gallons per day. The underflow solids concentration of the thickener varied from 0.3% to 1.5%, with an increment of 0.1%. The underflow solids concentration of the separator varied from 1.2% to 2.0%, with an increment of 0.1%. The fraction of alum recovered varied from 0.30 to 0.70, with an increment of 0.05. The annual cost of this process, cost per thousand gallons wastewater treated, and the optimum values of the three operation variables at different plant sizes were determined. The annual cost and the cost per thousand gallons of wastewater treated are plotted against plant capacity in Figure 20.
CONCLUSIONS

From the study of coagulant recovery from both water and wastewater alum and iron sludges, the following conclusions have been drawn:

1. The acidic method of alum recovery from water and wastewater alum sludge is technically feasible. The amount of alum recovered follows a stoichiometric relationship. Both sulfuric acid and hydrochloric acid can be used for this process, but for economic reasons sulfuric acid is superior.

2. The control of the alum recovery process is not difficult. The amount of alum recovered can be calculated from stoichiometry. pH measurements may be used to prevent an overdose of acid.

3. Phosphate is recovered simultaneously when acid is added to recover aluminum from wastewater sludge. However, phosphate is not extensively leached until after a certain proportion of aluminum is recovered.

4. The efficiency of alum recovered from wastewater for removing turbidity, phosphate, and COD is not appreciably reduced from that of fresh alum. Since a certain amount of alum is wasted with the remaining sludge after each cycle, the effectiveness of impurities is not cumulative. The remaining sludge after acidification showed better filterability and drainability properties than the untreated alum sludge.

5. Using a number of assumptions, the break-even plant size for alum recovery from water treatment alum sludge is about 25 MGD. The unit cost for wastewater treatment alum sludge is also a function of plant size.

6. The acidic method of iron recovery is technically feasible. Both sulfuric acid and hydrochloric acid can be used for this process, but for economic reasons sulfuric acid is again superior.

7. Acid addition resulted in a dramatic reduction in sludge volume for both alum and iron systems. However, volume reduction and coagulant recovery did not occur simultaneously at a given pH.

8. Acid addition greatly improved the settleability and the filterability of the remaining sludge.

9. The efficiency of recovered metal in coagulation of suspended solids is not appreciably reduced from that of fresh coagulant.
REFERENCES


LIST OF FIGURES
Figure 1
Solubility of Aluminum Hydroxide as a Function of pH

Water Treatment Plant Operation Region

Log (Al III) Total, moles/l

$pH$

$Al(OH)_3(s)$

$Al(OH)_4^-$

$Al_2(OH)_2^{4+}$

$Al_6(OH)_{15}^{3+}$

$Al^{3+}$

$Al(OH)^{2+}$
Figure 2

Solubility of Iron Hydroxide as a Function of pH
Figure 3

Operational Scheme for Alum Recovery Process
at Tampa, Florida

Plant Influent

Slow Mixing Basins

Settling Basins

Effluent to Filters

Acid

Mixer Tank

Sludge Concentration Tank

Wet Well
Relationship Predicted by Stoichiometry
Figure 5

Percent Aluminum Recovered as a Function of Amount of Sulfuric Acid Added

- Radford
- Timberville
- Harrisonburg
- Blacksburg
- Wastewater Alum Sludge

Relationship Predicted by Stoichiometry

% Aluminum Recovered vs. % Stoichiometric Amount of Sulfuric Acid Added for Total Aluminum Recovery
Figure 6

Aluminum Recovered as a Function of System pH

- Radford
- Timberville
- Harrisonburg
- Blacksburg
- Slechta & Culp (42)
- Webster (47)
- Bugg (5)
- Wastewater Alum Sludge
Figure 7

Percent Aluminum or Phosphorus Recovered as a Function of Amount of Sulfuric Acid Added

- ○ Al
- △ P

Relationship Predicted by Stoichiometry

% Stoichiometric Amount of Acid Added for Total Aluminum Recovery
Figure 8

Iron Recovered as a Function of pH Using Two Acids

Iron Recovered $\times 10^{-3}$ (mg/l)

<table>
<thead>
<tr>
<th>pH</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>△</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- O: Sulfuric Acid Addition
- △: Hydrochloric Acid Addition
Figure 9

Initial Settling Velocity of Remaining Sludge after Acidification

- Radford
- Timberville
- Harrisonburg
- Blacksburg
- Wastewater Alum Sludge

Initial Settling Velocity (cm/sec)

% Aluminum Recovered
Figure 10

Initial Settling Velocity of Remaining Sludge after Acidification
Figure 11

Variation of Specific Resistance of Remaining Sludge as a Function of Percent Aluminum Recovered
Specific Resistance of Remaining Sludge as a Function of pH

Initial Specific Resistance = $19.5 \times 10^{12}$ m/kg
Figure 13
Critical Coagulation Concentration as a Function of Turbidity Level of Raw Water

<table>
<thead>
<tr>
<th>Raw Water Sources</th>
<th>Critical Coagulation Concentration of Al (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh Alum</td>
<td>●</td>
</tr>
<tr>
<td>Stroubles Creek Water</td>
<td>▲</td>
</tr>
<tr>
<td>Kaolin Water</td>
<td>○</td>
</tr>
</tbody>
</table>

Raw Water Turbidity (U.T.U.)

Critical Coagulation Concentration of Al (mg/l)
Figure 14

Phosphate Removal Efficiency as a Function of Total Aluminum Phosphorus Molar Ratio

- Fresh Alum
- Recovered Alum Al/P = 3.80
- Recovered Alum Al/P = 2.79

% Phosphate Removal vs. % Phosphate Removal

Al/P Molar Ratio

52
Figure 15

COD Removal Efficiency as a Function of Aluminum Phosphorus Molar Ratio

- Fresh Alum
- Recovered Alum Al/P = 3.80
- Recovered Alum Al/P = 2.79

COD % Removal vs Al/P Molar Ratio
Figure 16

Residual Turbidity as a Function of Iron Dosage

- △ Recovered Iron
- ○ Fresh Iron

Kaolinite Suspension
Raw Water Turbidity = 22 J.T.U.
Alkalinity = 100 mg/l
pH = 7.5
Residual Turbidity as a Function of Iron Dosage Using New River Raw Water Sample

- Fresh Iron
- Recovered Iron

New River Sample
- Raw Water Turbidity = 20 J.T.U.
- Alkalinity = 63 mg/l
- pH = 7.3

Iron Dosage (mg/l as Iron)

Residual Turbidity (J.T.U.)
Figure 18

Flow Diagram of Proposed Alum Recovery System

1. Equalization Tank or Lagoon
   - Backwash Waste from Filters
   - Sludge from Sedimentation Basin

2. Sludge Thickener
   - Supernatant to Water Intake
   - Supernatant to Flash Mix
   - Acid Tank

3. Reactor
   - Lime Addition

4. Separator
   - Sludge Disposal
Figure 19

Capital Cost and Annual Savings of Alum Recovery System for Various Water Treatment Plant Capacities
Figure 20

Annual Cost and Cost per 1,000 Gallons Waste Treated of Alum Recovery Process for Various Wastewater Treatment Plant Capacities