

Chemical Precipitation
Methods
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III. CHEMICAL PRECIPITANTS AND APPLICATION TECHNIQUES AND STRATEGIES

Phosphorus Inactivation-
Chemical Precipitants and Strategies

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Introduction:

Chemical coagulation and clarification are important means of nutrient inactivation and management in surface waters. The precipitation and removal of the phosphorus from the water column and subsequent deposition and sealing in sediments has a good history of lake restoration when used in conjunction with sound watershed management practices. The impetus of providing high quality recreational waters is underscored by the agenda for improving surface water qualities used as potable water sources. Microbial proliferation will manifest as the NOM (natural organic matter) -the disinfection by product precursors that can "ignore" activated carbon and must be chemically coagulated out of the water supply; and color and taste and odor causing compounds (themselves potential DBP's) that often don't respond to adsorbents and oxidants. So coagulants are one of the most important chemicals fed to purify drinking water supplies and manage the quality of the source waters. What follows is an overview of the major types of coagulants and precipitant and the variable properties that are important in making certain that the money spent is buying the best product for the job rather than the cheapest.

Chemicals Used in Phosphorus Inactivation

Aluminum sulfate

The most widely used coagulant, aluminum sulfate has been treating water for centuries. Aluminum sulfate is also used for papermaking; hide preservation and tanning; food processing; as a dye mordant; producing aluminum chemicals, and in pharmaceuticals applications. The passing of wastewater discharge limits for suspended solids, BOD and phosphorus caused the largest growth for aluminum sulfate in the wastewater treatment industry. Its success in precipitating phosphorus from wastewater was mirrored by successful lake restoration applications in the early 1970's

Alum is produced by dissolving or digesting an aluminum source in sulfuric acid and water. The aluminum sources commonly used are chemical grade bauxite (lower iron and heavy metals than metallurgical grades), bauxitic or high aluminum clays, and aluminum trihydrate. Bauxite and

Liquid alum is approximately a 47-49 % solution of dry alum. Some manufacturers may produce and sell standard (unmodified) liquid alum at significantly lower strengths, but only a few regional suppliers fall far away from the AWWA Standard. This dry alum equivalence shifts as the assay of liquid alum is higher or lower than the 4.2% Al.

Accounting for usage of dry alum is easy - count the bags used or the number of pounds fed through a gravimetric feeder.

Liquid can be accounted for either as its dry equivalent or on a straight liquid basis. Most utilities and paper mills use dry basis since that has been the historical method and the way the majority of suppliers bill. Lake treatment technologists will use either method, however the use of a liquid on an as is basis, (4.2% Al) is becoming more common since it allows for quick stoichiometric conversions for Phosphorus removal calculations. The typical conversion factor is 5.4 pounds of dry alum per gallon (US). This is a close approximation of the actual usage and it assumes the liquid alum weighs 11.1 lb. per gallon and is a 48.5 % solution of dry alum. Treatment chemical assays for strength are not static numbers but vary batch to batch. Variations may be minimized by choosing a supplier that uses SQC or is ISO certified. Specific gravity determinations on the chemical as received can be used to determine (in lieu of actual chemical analysis) the strength of the product. The manufacturer or supplier can provide a specific gravity versus strength chart for their liquid products. This number should be used to better calculate the actual density and dry weight equivalence.

A common misconception is that iron concentration leads to deposit and crystallization problems in the storage and feed systems. This is somewhat true if the iron content of the alum is greater than 2% (20,000 PPM). Most standard grade alums are less than 0.3% as Fe (3000 PPM) and iron does not produce a precipitation or deposit problem. The familiar deposit from standard grade alums is mostly due to strength - the 4.3 % Al is a saturated solution of aluminum sulfate. As such any evaporation will cause crystallization. The iron in standard grade (bauxite based) actually is a benefit to surface water treatment since it provides additional precipitant and allows for stronger alum to be shipped without the threat of crystallization.

Iron free and low iron alums at the same concentration as standard grade (4.2-4.3% Al) will crystallize more quickly than the standard grade. Often these products are marketed to have fewer deposits due to the iron content. This problem is circumvented in reality by supplying a weaker low iron alum product at 4.0 - 4.15% Al (7.6 - 7.8 % as Al_2O_3). Whereas this reduces the likelihood of a deposit it means more alum must be used to do the same job. A price quoted on this weaker

material may appear to be a better deal, but until the price is equalized against the actual Al concentration, total costs cannot be established.

Other causes of crystallization or deposit problems are calcium, potassium and ammonium ion. These substances are not harmful but can cause deposits and can be found in any type of alum - standard, low iron or iron free. These elements are usually introduced into the alum through transport contamination or off spec raw materials. Periodic confirmation of strength and purity is advised on all alum shipments and grades.

The purity of alum will vary with aluminum and acid sources. The majority of these contaminants are heavy metals that do not impact on the quality of the water being treated because they are mostly insoluble and are at low concentrations. However they can contribute to the metals burden of the precipitant residue. Since the whole idea of nutrient inactivation is as a *restoration* technique, it seems somehow silly to use low quality chemicals that could introduce heavy metals to the lake sediment. Manufacturers can supply typical heavy metal analyses. Generally the difference in cost for a cleaner product is minimal (until one approaches food grade quality).

Polyaluminum Hydroxychlorides

This group of coagulants has been expanding as it finds varied success in replacement of more traditional iron and alum applications. These materials are more specialty in nature and performance and chemical characteristics vary with the manufacturing technique used. Several permutations exist, but fundamentally aluminum, in the form of aluminum metal or aluminum hydroxide is dissolved in hydrochloric acid. Heat, time of reaction, raw materials, pressure and mixing intensity are all variables in producing a family of products to meet specific end uses. Some processes are only capable of producing one specific product, others can produce a wide array of product chemistry. Some of the more familiar synonyms are below. The accepted acronym is PACl (often PAC is used, but PAC is actually short for Powdered Activated Carbon).

- Polyaluminum chloride
- Polyaluminum chlorosulfate
- Aluminum chlorohydrate - the highest aluminum concentration product type
- Basic aluminum chloride
- Polyhydroxyaluminum chloride
- Neutralized aluminum chloride

PACIs vary in many physical and chemical characteristics that can be grouped into three major categories:

- Aluminum concentration - typically from 3% to 13% Al by weight "as is" or liquid
- Basicity - the amount of hydroxide (OH) in the product. This is proportional to the amount of aluminum and chloride in the product as well. It is expressed in the formula :

- $\text{Basicity \%} = \frac{[\text{OH}]}{3[\text{Al}]} * 100$

Higher basicity products tend to have higher cationic (positive) charges and thus are more efficient in coagulating the negatively charged contaminants in the water. Basicity is also a measure of the "prehydrolysis" of the material. Thus PACI with a higher basicity will have more (OH) and exhibit a far lower pH depression and alkalinity impact on the water. Basicity will be expressed as a percent greater than zero and less than one hundred. The most commonly found products are in the ranges :

- <30%, Low Basicity
 - 45-50%, Moderate Basicity and most common in Drinking Water Treatment
 - 75 - 83%, High Basicity including Aluminum Chlorohydrate (ACH)
- Additives and artifacts - this could be sulfate or calcium from the raw materials; added phosphorus or polyelectrolytes; or anything else the manufacturer feels adds performance. Typical concentrations will be less than 5% for calcium or sulfate and up to 50% for polymers and polyelectrolytes.

The wide variability in PACI products makes it more difficult to find equivalent products for bidding. The performance of these products is often well worth the extra testing and evaluating. The formulas given for PACI are only used to approximate the actual make up. In order to find the best product at the best overall cost, it is critical to evaluate the individual product and not "commoditize" them by gross characteristics that do not describe the function of the chemical.

PACI is most often sold on a neat, liquid, 100% or "as is" basis. Early on, the PACI was dosed on a dry basis. Although a vestige of the introductory days, it still persists and the purchaser should clarify the basis for the price.

The manufacturing of PACI in North America is done with very pure raw materials. Heavy metal impurities are generally less than even the cleanest standard alum. Purchasers should ask for typical analyses as part of their chemical audits, however routine load analyses should require product strength and basicity and additives as specified.

For restoration and nutrient inactivation the most important features of a PACl type product would be the aluminum content and the basicity. The aluminum content should be high to provide the most Al for P inactivation. The high basicity will provide good clarification at a minimum pH depression. Also free aluminum (analogous to aluminum residual in drinking water) is minimal with the high basicity materials. The high basicity products also are the highest strength aluminum, therefore a PACl with 23% Al_2O_3 and >73% basicity would be a good choice for lake treatment.

Ferric Sulfate

Enjoying a renaissance in surface water treatment as more reliable, high quality producers of this coagulant enter the marketplace, ferric sulfate has been around in the water treatment industry since the late 1800's. Ferric sulfate can either be manufactured or reprocessed. The reprocessed material, or co-product, was formerly disposed of as a waste from various iron mills, foundries and pickling operations. Cleaning up this material by oxidizing and filtering out much of the gross heavy metal contamination makes a chemical suitable for water treatment. Various iron ores or scrap iron sources are digested with sulfuric acid to manufacture "from scratch". Depending upon the purity of the iron source or raw materials the product can be quite clean.

Dry ferric sulfate is available from a few sources, both domestic and imported. This product is either an industrial co-product from oxidized pigment waste liquors or digested copper mine tailings. The dry material made from pigment manufacturing has the lower metals and insoluble material. The copper mine source has trace metals (obviously copper) that would *not* make it a good choice for lake treatment. As dry materials they are >25% iron as Fe and are used where freight from the nearest liquid producing location would be prohibitive, or very small applications. Since they dissolve slowly the dry ferric sulfate needs to be dissolved prior to use, generally on shore. The high water insoluble content of the solution may plug applicator spray bars.

Ferric sulfate liquid will vary in strength from <10% iron to >12% iron. Generally the manufactured materials (versus the reprocessed) have better control over the sources and are able to make stronger products and provide superior quality control. Specific gravity and iron content should be routine procedures for assaying the chemical. Dosage fluctuations and treatment excursions can occur through strength variations. As in the case with alum it may be that a weaker material is quoted at a seemingly lower price, but when adjusted for the iron content the "cheaper" product is not less costly.

Impurities can also have an impact on the cost of ferric sulfate. The costs of cleaning the chemical and ability to use poorer quality raw materials can allow lower quality materials to be priced lower. The impurities and excess acid also lend weight to the liquid material. Excess acid will have a

higher pH depression in lake and surface water treatment. Therefore merely running a specific gravity may show a false high level of iron when the measurement is assessing the dirt too. It is suggested to require typical analyses on ferric sulfate.

Ferric Chloride

Ferric chloride is the most widely used iron salt. Second only to alum in the amount of water it treats in North America, it is feeling some pressure from ferric sulfate and PACl as replacement chemicals. Produced in analogous ways to ferric sulfate it, too can vary widely in quality from batch to batch or vendor to vendor. Ferric chloride made from reprocessed titanium dioxide waste liquors can have elevated amounts of ferrous iron and manganese that can pass through unprecipitated. Potentially phytotoxic heavy metals are also potential contaminants. As in any treatment chemical that is used in treating surface or drinking waters, it is critical to demand quality and quality control from the supplier.

Ferric chloride is available in 30 to 40% ferric chloride solutions containing 10 to > 13% iron as Fe. Excess acid not reacted with iron, impurities, and heavy metals can increase the specific gravity, alkalinity consumption, and corrosivity of the material. In evaluating bulk deliveries it is worthwhile to perform (or have performed) chemical analyses of the strength of the coagulant to ensure the using location is receiving what is paid for. Dry ferric chloride is available but it is rare and expensive. Solution and application problems preclude using the dry ferric chloride.

Sodium Aluminate

Sodium aluminate is on the opposite end of the pH scale from alum, PACl and iron salts. All these materials are metal reacted with an acid to make a coagulant. Sodium aluminate is aluminum dissolved in sodium hydroxide (caustic soda). The same aluminum raw materials used in making alum can be used to make sodium aluminate. Major producers of sodium aluminate include aluminum companies. The costs of sodium aluminate relegate it to use in small doses in softening; waters where the sulfate or chloride from another coagulant would be undesirable; in very soft or low pH water, or as a supplement to an alum program. Sodium aluminate will supply alkalinity to a restoration and nutrient inactivation program. It functions like alum; that is the same pH solubility curves and precipitation stoichiometry. Since the aluminum demand is often independent of the alkalinity requirement it could be possible to overdose the caustic portion and raise the pH past where it forms an insoluble precipitate (pH 8.5±). The high free aluminum will be as a soluble aluminate and may cause problems. Therefore, except in very acidic lakes, sodium aluminate is used in conjunction with alum for treatment of low alkalinity systems.

Most sodium aluminates are as free from impurities as alum or low iron alums. The high pH at which sodium aluminate is made minimizes the amount of heavy metals that can be dissolved into the chemical. Waste caustic streams are utilized by some processors and contain rather large quantities of undesirable organics and heavy metals.

Sodium aluminate is available in several grades and strengths, most common are 32 to 45% solutions (9 - 12 % as Al) and dry crystal with 30 - 34 % aluminum as Al.

Polymers and Polyelectrolytes

Synthetic organic polymers have enjoyed wide acceptance as partial replacements for aluminum and iron based coagulants in drinking water treatment. There is little application in lake treatment except in specific instances where high suspended solids are involved. Lagoon and pit treatments are the most common "cousin" to lake treatment where polymers are most accepted. Often alum, iron or PACl blended with a little (5-10% polymer by weight) is sufficient to remove suspended solids and reduce P. Polymers do not precipitate soluble phosphorus, they can only flocculate out particulate P. They also do not "seal" the P into an insoluble complex, thus P is released upon biological decomposition of the floc. Purchasing a flocculant when a coagulant is needed will not produce the highest degree of efficiency.

For information purposes it is useful to review the predominant chemistries for coagulant applications - poly DADMAC and EPI/DMA. These acronyms are for dimethyl diallyl diammonium chloride and epichlorohydrin dimethylamine. The manufacturing of both of these are specific to the individual companies that make them and finished polymers will vary by concentration (percent active solids), molecular weight, charge density and impurities. Various organic contaminants and unreacted raw materials can be left in the products. These can have serious implications on water quality. The products with the lowest monomer and organic contamination are often favored for potable water and would make sense for restoration applications as well.

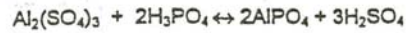
Phosphorus Removal

The inactivation of phosphorus by metal salts involves a "simple" precipitation of the phosphorus as a metal phosphate. The above hydrolyzing metals have been used extensively for P removal. Lime (CaO and $\text{Ca}(\text{OH})_2$) has also been used in wastewater treatment, but raise the pH to >10 for optimal effect - not the pH most lakes would like to be. The reactions proceed at normal pH values found in surface waters and are dependent on concentration, temperature and alkalinity. Alum, ferric sulfate, ferric chloride and PACl are powerful sources of cationic charge and will have strong tendencies to coagulate the colloidal and particulate matter and NOM (water color). Additionally

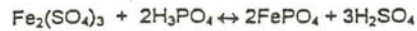
the metal will hydrolyze to form aluminum or iron hydroxide precipitates (floc) that increase the amount of metal required for P precipitation.

The following typical reactions and metal requirements are theoretical only and will be altered as the water quality puts more or less perturbation on the P removal chemistry.

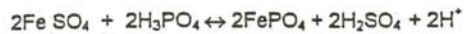
- Aluminum Sulfate



- Ferric Sulfate



- Ferrous Sulfate



The reactions are essentially the same for the chloride salts of aluminum, iron (II) and iron (III). The major difference in using a sulfate versus a chloride is in turbidity removal wherein the sulfate tends to catalyze and broaden the effective dose/pH range.

The stoichiometric amounts of metal per part of elemental P can be used to estimate precipitant dosage requirements as shown in Table 2.

Table 2
Theoretical Metal : Phosphorus Requirements

Metal	Metal : P Requirement	Chemical Name
Aluminum	0.87:1	Alum, Aluminum Chloride, Sodium Aluminate, PACl
Ferric Iron (Fe ³⁺)	1.8:1	Ferric Sulfate Ferric Chloride Chlorinated Copperas
Ferrous Iron (Fe ²⁺)	1.8:1 3.2:1	Ferrous Sulfate Ferrous Chloride Pickle Liquor Copperas
Calcium (Ca ²⁺)	1.93:1	Lime Quicklime Calcium Oxide Calcium Chloride

Dosage Estimation

Using these theoretical requirements a dosage can be estimated.

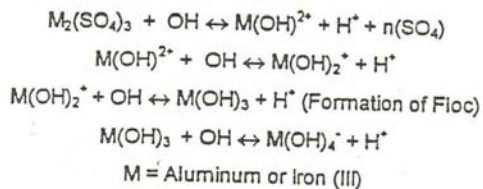
- Desired P removal = 10 PPM
- Coagulant = Alum at 4.2% Al liquid basis
- Water Volume treated 10 million gallons (approx 30 acre-feet)
 - $10 \text{ PPM P} \times 0.87 = 8.7 \text{ PPM Al Required}$
 - $8.7 \text{ PPM Al} / 4.2\% \text{ Al in Alum} = 207 \text{ PPM Alum}$
 - $207 \text{ PPM} \times 8.34 = 1728 \text{ lb. Liquid Alum/million gallons or } 17280 \text{ lb. Total}$
 - $17280 \text{ lb.} = 1556 \text{ gallons; about } 4/10 \text{ full truckload (43,000 lb. } \approx \text{ full truck)}$

These are theoretical dosages and tend to be higher than those actually experienced for water column applications. Sediment applications tend to require proportionately higher dosages, but the P loadings really are the determining factors. Other factors to keep in mind when estimating dosages are:

- Not all P is soluble and require the full stoichiometric amount
- Formation of Insoluble Hydroxides (below) as floc will remove particulate and colloidal P compounds and biomass.

Hydrolysis and Alkalinity Consumption

The phosphorus precipitant products also consume alkalinity in hydrolysis and therefore reduce the alkalinity of the water being treated.



The theoretical Alkalinity Consumption can also be calculated based on the concentration of commercially available precipitants. Table 3 lists the relative effect of various treatment chemicals on alkalinity.

Table 3
Alkalinity Supplementation or Consumption of Common
Treatment Chemicals

Chemical (basis)	Change in Alkalinity PPM as CaCO ₃ per PPM Product
Ferric Chloride/Sulfate (liquid)	-1.0
Aluminum Sulfate (dry basis)	-0.5
Aluminum Chloride (liquid)	-0.3
PACl (liquid)	-0.3—0.05 (varies w/product)
Lime (dry)	+1.45
Sodium Hydroxide (dry)	+1.26
Soda Ash (sodium carbonate) (dry)	+0.96
Sodium Bicarbonate (dry)	+0.6
Sodium Aluminate (liquid)	+0.4-0.6 (varies w/product)

Product Choice

Which precipitant to choose will depend largely on the project goals and the desired long term effects. Both iron and aluminum will effectively precipitate P. Iron phosphate precipitate will, under anoxic (negative redox) conditions in the sediments or water column, resolubilize and release the nutrient back into the water column. Iron is itself a plant nutrient and will assist in the proliferation of algae. A water utility uses iron chloride to maintain a low P level in its source water reservoirs by injecting the material into incoming watercourses and keeping an air supply (compressed microbubble system) in the deep holes to prevent resolubilization of the iron phosphate. The release of iron phosphates is a burst of fertilizer for algae and macrophytes.

Aluminum phosphate will not release the nutrient back into the water column regardless of sediment redox.

For low alkalinity systems a combination alum/aluminate or alum/soda ash treatment is often preferable. Partially neutralized aluminum compounds or buffered alums are available and offer some convenience to handling two chemicals. Another alternative is the use of high basicity PACl that does not consume nearly as much alkalinity as the more traditional coagulants.

Storage and Handling

The use of precipitants for nutrient inactivation requires knowledge of the product's chemistry from a handling and safety standpoint. That each of these familiar materials are used to treat drinking water nearly everywhere should not be a basis for taking these products lightly. In a treatment plant they are dosed in a more controlled environment. Any of these products released to the environment in a catastrophic or uncontrolled manner in large quantities will have serious impact.

The manufacturer should be consulted for safety, storage and handling advice prior to any chemical being ordered and used. Always read and understand the material safety data sheets for each product used.

A few points are standardized that can be summarized.

1. No copper, aluminum, iron, galvanized or other non corrosion resistant pipes, tanks, valves, fittings whatsoever. Only Corrosion resistant metals like stainless steel or Hastelloy except:
 - No Stainless Steel for Ferric/Ferrous Chloride, Aluminum Chloride and some PACI and high chloride Ferric Sulfate
2. Personal Protective gear must be worn; Goggles, gloves, boots, hard hat, long sleeve shirts, long pants, etc.
3. Polyethylene tanks can be used for some temporary storage. Use heavier wall construction than would normally be anticipated. That is alum has a specific gravity of 1.333. To err on the side of caution a plastic tank with a specific gravity rating of >1.4 would be best. Also, many of these chemicals may be shipped hot, especially if they are used in a large project and the manufacturer is pushing the production to meet the project needs. Alert the tank manufacturer that delivery temperatures might be >100°F.
4. Sodium aluminate has a freezing point of around 50°F depending on product strength. Supplemental heat may be necessary for spring and fall projects in northern climes. All other chemicals freeze well below 32°F.
5. Truck transports can be used for temporary storage and provide easy set up and knock down of the project. Keep in mind
 - Trucks and Trailers weigh 60,000 ± lb. loaded. Good, solid roads are necessary.
 - The turning radius will vary by truck, but maneuverability is important. Avoid tight and serpentine access.
 - Truck transports will either off load by pump or air compressors. Many transport companies may assume the site has an air supply. Specify if the transport needs a pump or on board compressor. A typical compressor is set for 25 psi. If the receiving tank is not vented or cannot handle 25 psi do not use air to offload, rather ask the supplier's transport company to provide a trailer with a pump.

- Most trailers will have 40-60 feet of hose. If the truck can not get this close, alert the supplier who can request more hose.
 - Provide containment for storage and transfer pumps. A quantity of neutralization chemicals (lime or soda ash) may be required by the state or local authorities in case of chemical spills.
 - Transports will have 2 or 3 inch chemical hose with quick connect adapters. Consult with the supplier so that the job site's system can have the same fittings.
6. If a combination precipitant - pH adjustment program is being used like alum/soda ash or alum/aluminate - do not mix the two chemicals. They will react with each other, perhaps violently. They should be stored and handled separately. Hoses, tanks etc. should be thoroughly flushed with water if used for more than one chemical.
 7. If using a combination iron - aluminum program do not mix the two chemicals. Although both acidic in nature they can react with each other and solidify.

If anxiety about the actual application is high, several reputable applicators can assist in the actual chemical application. They have the technology at their disposal and the experience to choose and dose effectively. Often local authorities and extension services have access to specialists skilled in the application. Chemical suppliers may work with the more reputable applicators and can be a source of contacts. Insist on references and "testimonials" - often there is only one chance to treat the problem due to funding and logistics. Bad application can be disastrous.

The use of chemicals for nutrient inactivation has a long successful history. The variety of phosphorus precipitants available, whereas at times confusing, allows for a number of opportunities to get the best, long term treatment technology. For example, the ability to use prehydrolyzed aluminum compounds like PACl brings a one product approach to some low pH water systems. Combination programs of alum and soda ash also provide nutrient inactivation and pH adjustment. The cooperation of applicators, limnologists, researchers, regulators and suppliers will provide safe and effective nutrient inactivation.