



Wastewater Technology Fact Sheet Chemical Precipitation

DESCRIPTION

Chemical precipitation is a widely used, proven technology for the removal of metals and other inorganics, suspended solids, fats, oils, greases, and some other organic substances (including organophosphates) from wastewater. Generally speaking, precipitation is a method of causing contaminants that are either dissolved or suspended in solution to settle out of solution as a solid *precipitate*, which can then be filtered, centrifuged, or otherwise separated from the liquid portion. A voluminous precipitate can capture ions and particles during formation and settling, in effect “sweeping” ions and particles from the wastewater. (Tchobanoglous and Burton, 1991). Precipitation is assisted through the use of a coagulant, an agent which causes smaller particles suspended in solution to gather into larger aggregates. Frequently, polymers are used as coagulants. The long-chain polymer molecules can be either positively or negatively charged (cationic or anionic) or neutral (nonionic). Since wastewater chemistry typically involves the interaction of ions and other charged particles in solution, these electrical qualities allow the polymers to act as bridges between particles suspended in solution, or to neutralize particles in solution (Amirtharajah and O’Mella, 1990; Jacangelo, 1987). The specific approach used for precipitation will depend on the contaminants to be removed, as described below.

Metals Removal

Water hardness is caused primarily by the dissolution of calcium and magnesium carbonate and bicarbonate compounds in water, and to a lesser extent, by the sulfates, chlorides, and silicates of

these metals. The removal of these dissolved compounds, called water softening, often proceeds by chemical precipitation. Lime (calcium oxide), when added to hard water, reacts to form calcium carbonate, which itself can act as a coagulant, sweeping ions out of solution in formation and settling. To do this with lime alone, a great deal of lime is typically needed to work effectively; for this reason, the lime is often added in conjunction with ferrous sulfate, producing insoluble ferric hydroxide. The combination of lime and ferrous sulfate is only effective in the presence of dissolved oxygen, however. Alum, when added to water containing calcium and magnesium bicarbonate alkalinity, reacts with the alkalinity to form an insoluble aluminum hydroxide precipitate.

Soluble heavy metal ions can be converted into insoluble metal hydroxides or carbonates through the addition of hydroxide compounds. Additionally, insoluble metal sulfides can be formed with the addition of ferrous sulfate and lime. Once rendered insoluble, these compounds will tend to precipitate and settle. The solubility of the metal compounds thus formed is pH dependent; most tend to be least soluble in alkaline solutions. Since the optimal pH for precipitation depends both on the metal to be removed and on the counter ion used (hydroxide, carbonate, or sulfide), the best treatment procedure must be determined on a case-by-case basis. Metal solubility data are available in Benefield and Morgan, 1990, as well as in many other sources.

Once the optimal pH for precipitation is established, the settling process is often accelerated by addition of a polymer coagulant, which gathers the insoluble metal compound particles into a

coarse floc that can settle rapidly by gravity.

Removal of Fats, Oils and Greases

Fats, oils, and greases are typically organic substances which tend to bead together or form “slicks” on the surface of aqueous solutions. They behave in this way because these organic, non-polar substances are typically insoluble in water, which is inorganic and polar. Because they tend to be less dense than water, they float to the surface rather than settling to the bottom. In situations where the oily substance is free floating in slicks, skimming the surface of the solution is often the best way to remove most of the material. However, oils, fats, and greases can become *emulsified* in aqueous solution, meaning that small globules of the oily product can become suspended throughout the water. These globules are localized, particle-like aggregations of compatibly charged molecules existing in an incompatible aqueous medium—which is to say that these molecules are *hydrophobic* (“water-fearing”). Often times, other substances (especially products like soaps and detergents) in solution can act as aids to making hydrophobic substances soluble in water.

To remove emulsified oils and greases, the emulsion must be broken up by destabilizing the electrical charge attractions that keep the localized clusters of oily molecules stable in solution. This can be done with the addition of a polymer designed for charge neutralization. In this way, the charge attraction of the oily particles is disrupted, allowing them to separate from the aqueous solution.

Phosphorus Removal

Metal salts (most commonly ferric chloride or aluminum sulfate, also called alum) or lime have been used for the removal of phosphate compounds from water. When lime is used, a sufficient amount of lime must be added to increase the pH of the solution to at least 10, creating an environment in which excess calcium ions can react with the phosphate to produce an insoluble precipitate (hydroxylapatite). Lime is an effective phosphate removal agent, but results in a large sludge volume. When ferric chloride or alum is used, the iron or

aluminum ions in solution will react with phosphate to produce insoluble metal phosphates. The degree of insolubility for these compounds is pH-dependent. Moreover, many competing chemical reactions can take place alongside these, meaning that the amount of metal salt to add to the solution cannot simply be calculated on the basis of the phosphate concentration, but must be determined in the laboratory for each case (Tchobanoglous and Burton, 1991).

Suspended Solids

Finely divided particles suspended in solution can elude filtration and other similar removal processes. Their small size allows them to remain suspended over extended periods of time. More often than not, the particles populating wastewater are negatively charged. For this reason, cationic polymers are commonly added to the solution, both to reduce the surface charge of the particles, and also to form bridges between the particles, thus causing particle coagulation and settling (Tchobanoglous and Burton, 1991).

Alternatively, lime can be used as a clarifying agent for removal of particulate matter. The calcium hydroxide reacts in the wastewater solution to form calcium carbonate, which itself acts as a coagulant, sweeping particles out of solution.

Additional Considerations

The chemical agents most frequently used for chemical precipitation are shown in Table 1. The amount of chemicals required for treatment depends on the pH and alkalinity of the wastewater, the phosphate level, and the point of injection and mixing modes, among other factors. Competing reactions often make it difficult to calculate the quantities of additives necessary for chemical precipitation. Accurate doses should be determined by jar tests and confirmed by field evaluations. Chemicals are usually added via a chemical feed system that can be completely enclosed and may also include storage space for unused chemicals. Choosing the most effective coagulant depends on jar test results, ease of storage, ease of transportation, and consideration of the operation and maintenance costs for associated equipment.

TABLE 1 CHEMICALS USED IN WASTEWATER TREATMENT

Lime – Calcium Oxide, CaO
Produces calcium carbonate in wastewater which acts as a coagulant for hardness and particulate matter. Often used in conjunction with other coagulants, since: (1) by itself, large quantities of lime are required for effectiveness, and (2) lime typically generates more sludge than other coagulants.
Ferrous Sulfate – Fe(SO₄)₃
Typically used with lime to soften water. The chemical combination forms calcium sulfate and ferric hydroxide. Wastewater must contain dissolved oxygen for reaction to proceed successfully.
Alum or Filter Alum – Al₂(SO₄)₃·14H₂O
Used for water softening and phosphate removal. Reacts with available alkalinity (carbonate, bicarbonate and hydroxide) or phosphate to form insoluble aluminum salts.
Ferric Chloride – FeCl₃
Reacts with alkalinity or phosphates to form insoluble iron salts.
Polymer
High molecular weight compounds (usually synthetic) which can be anionic, cationic, or nonionic. When added to wastewater, can be used for charge neutralization for emulsion-breaking, or as bridge-making coagulants, or both. Can also be used as filter aids and sludge conditioners.

Source: U.S. EPA, 1980.

Although chemical precipitation is a well established treatment method, research continues to enhance its effectiveness. Much recent research concentrates on combining chemical precipitation with other treatment methods such as photochemical oxidation, reverse osmosis, and biological methods to optimize performance.

APPLICABILITY

Chemical precipitation can be used to remove contaminants from both municipal and industrial wastewaters. It can be used for water softening, heavy metal removal from metal plating wastes, oil and grease removal from emulsified solutions, and phosphate removal from wash-waters and other wastewater. It is an effective tool for wastewater polishing and removal of particulate matter.

ADVANTAGES AND DISADVANTAGES

Before deciding whether chemical precipitation meets the needs of a municipality, it is important to understand the advantages and disadvantages of this methodology.

Advantages

- C Chemical precipitation is a well-established technology with ready availability of equipment and many chemicals.
- C Some treatment chemicals, especially lime, are very inexpensive.
- C Completely enclosed systems are often conveniently self-operating and low maintenance, requiring only replenishment of the chemicals used. Often times, a sophisticated operator is not needed.

Disadvantages

- C Competing reactions, varying levels of alkalinity and other factors typically make calculation of proper chemical dosages impossible. Therefore, frequent jar tests are necessary for confirmation of optimal treatment conditions. Overdosing can diminish the effectiveness of the treatment.
- C Chemical precipitation may require working with corrosive chemicals, increasing operator safety concerns.
- C The addition of treatment chemicals, especially lime, may increase the volume of waste sludge up to 50 percent.
- C Large amounts of chemicals may need to be transported to the treatment location.
- C Polymers can be expensive.

Table 2 provides a summary of properties and considerations appropriate to chemicals commonly used for precipitation.

TABLE 2 COMMERCIAL FORMS OF CHEMICAL PRECIPITATION CHEMICALS

Chemical	Commercial Characteristic
Alum	Alum is an off-white crystal which, when dissolved in water, produces acidic conditions. As a solid, alum may be supplied in lumps, but is available in ground, rice, or powdered form. Shipments range from small 100 lb bags, to bulk quantities of 4000 lbs. In liquid form, alum is commonly supplied as a 50% solution delivered in minimum loads of 4000 gal. The choice between liquid and dry alum depends on the availability of storage space, the method of feeding, and economics.
FeCl ₃	Ferric chloride, or FeCl ₃ , is available in either dry (hydrate or anhydrous) or liquid form. The liquid form is usually 35-45% FeCl ₃ . Because higher concentrations of FeCl ₃ have higher freezing points, lower concentrations are supplied during the winter. It is highly corrosive.
Lime	Lime can be purchased in many forms, with quicklime (CaO) and hydrated lime (Ca(OH) ₂) being the most prevalent forms. In either case, lime is usually purchased in the dry state, in bags, or in bulk.
Polymer	Polymers may be supplied as a prepared stock solution ready for addition to the treatment process or as a dry powder. Many competing polymer formulations with differing characteristics are available, requiring somewhat differing handling procedures. Manufacturers should be consulted for recommended practices and use.

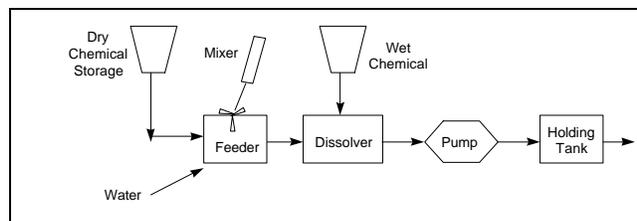
Source: U.S. EPA, 1980.

DESIGN CRITERIA

Chemical precipitation is normally carried out through a chemical feed system, most often a totally automated system providing for automatic chemical feeding, monitoring, and control. Full automation reduces manpower requirements, allows for less sophisticated operator oversight, and increases efficiency through continuous operation.

An automatic feed system may consist of storage tanks, feed tanks, metering pumps (although pumpless systems do exist), overflow containment basins, mixers, aging tanks, injection quills, shot feeders, fittings, and valves.

Chemical feed system storage tanks should have sufficient capacity to run for some time without running out and causing downtime. At least a one month supply of chemical storage capacity is recommended, though lesser quantities may be justified when a reliable supplier is located nearby, thus alleviating the need for maintaining substantial storage space. Additive chemicals come in liquid and dry form (see Table 2). Figure 1 shows a simplified flow chart of a chemical feed system.



Source: Adapted from U.S. EPA, 1980.

FIGURE 1 FLOW DIAGRAM OF A CHEMICAL FEED SYSTEM

When working with dry chemicals, a volumetric feeder or a gravity feeder can be used to measure the amount of chemical to be dissolved in water. Gravimetric feeders measure the chemical as a weight per unit time; volumetric feeders, by contrast, measure the chemical volume per unit time. While gravimetric feeders are more expensive than volumetric ones, they are also more accurate. Even so, volumetric feeding systems are more commonly used. In either case, the type of feeding mechanism required depends on the feed rate anticipated. Table 3 summarizes the types of feeding mechanisms available with associated feed rates.

In choosing a feed system, one must be certain that the materials used to build the system are chemically compatible with the chemicals to be used. Equipment manufacturers' chemical resistance charts should be used in selecting appropriate construction materials.

TABLE 3 TYPES OF FEED MECHANISMS WITHIN VOLUMETRIC AND GRAVIMETRIC FEEDERS

Dry Feed Mechanism	Feed Rate (lbs/hr)
Rotating disk	10
Oscillating	10 - 100
Rotary gate	200 - 500
Belt	500 - 20,000
Screw*	10 - 24,000

* Typically for volumetric feeders

Source: Benefield *et al.*, 1990.

PERFORMANCE

Jar Testing

For any given wastewater, the optimal treatment strategy should be determined by jar testing. Commercial chemical vendors provide testing guidelines to determine the most appropriate chemical(s) and the most effective dosage. Laboratory bench-scale jar testing apparatuses (available through scientific product supply companies) typically allow for six samples, each one liter in size, to be tested simultaneously. One central control operates the mixing of all jars, hence one variable (for example, polymer dosage) can be manipulated in a test group while all other factors, including mixing rates and times, can be kept constant. Inconclusive and incorrect interpretation of the results may be the result of using too small a sample for stock solution (1-2 ml of stock solution equals a 1-20 percent error in final concentration), adding chemicals inconsistently, erroneous data recording, using old chemicals, choosing improper flocculation and settling conditions (time, duration), using different people to perform tests, and choosing too narrow a dosage range. (Molina, *et al.*, 1998).

DoD Facility Reduces Plating Waste and Reduces Costs Using Chemical Precipitation.

A recent study of a Department of Defense (DoD) facility demonstrated the ability to use chemical precipitation to reduce plating waste and costs

(Hewing, *et al.*, 1995). The decision to treat concentrated plating waste as well as to dilute wastes already being treated at the facility was cost driven. Chemical precipitation was selected over reverse osmosis, demineralization, electro dialysis reversal, evaporation, and electrolytic precipitation, primarily because of space limitations. The decision also reflected sludge disposal costs, equipment requirements and cost, and safety considerations.

The facility compared the performance of ferrous sulfate, dithiocarbamate, borohydride, and aluminum as precipitating additives. Treatment was needed for waste streams containing high concentrations of potassium persulfate, copper sulfate, ammonium chloride/hydroxide, and pyrophosphate, with copper concentrations ranging from 20,000 to 150,000 ppm. Persulfates accounted for more than half of the generated waste and presented numerous safety challenges since they are strong oxidizers.

Table 4 shows the final treatment costs for the four chemicals studied. Overall treatment costs included initial chemical costs, stoichiometric volumes, and dry sludge weight.

TABLE 4 COMPARATIVE TREATMENT COSTS

Chemical	Chemical Cost/lb	Treatment Cost/gal
Ferrous sulfate	\$0.17	\$1.03
Dithiocarbamate	\$0.95	\$0.82
Borohydride	\$2.86	\$0.76
Aluminum	\$0.50	\$0.04

Source: Hewing, *et al.*, 1995

Ferrous sulfate generated large sludge volumes, making it too expensive for consideration. Dithiocarbamate produced less sludge but presented an occupational health hazard due to generation of noxious carbon disulfide. Sodium borohydride

produced less sludge but presented a safety problem due to its chemical properties.

Aluminum presented no occupational health problems, generated the least amount of sludge, and resulted in a final wastewater concentration of 5-10 ppm copper. The overall cost was \$0.04 per gallon.

Further testing helped identify optimum conditions for the use of chemical precipitation by the facility using aluminum.

OPERATION AND MAINTENANCE

A routine O&M schedule should be developed and implemented for any type of bulk chemical feed/handling system. Many systems are now completely enclosed, factory mounted/piped/wired systems. All manufacturer O&M recommendations should be followed, including testing and calibration. Regular O&M includes the following:

- C Occasional flushing of the system, if this is not provided automatically.
- C Inspecting and replacing pump seals, bags, dust filters, pH and ion specific electrodes, and other components..
- C Periodically lubricating bearings, motor, and other moving parts.
- C Developing an emergency response plan for onsite storage of chemicals.

When using chemical precipitation to treat wastewater, it is important to properly and safely store all chemicals. For further details on the safe use and storage of chemicals, refer to Material Safety Data Sheets (MSDSs) provided by the chemical manufacturers.

COSTS

The overall cost of chemical precipitation depends on many variables, including the characteristics of the wastewater, the chemicals and dosages to be used, the volume of water to be treated, and the level of water purity desired. Moreover, chemical costs can vary widely depending on the form and

quantity of material to be procured. Material prices fluctuate according to the region of the country. Chemicals provided in bags or measured batches are more expensive than when purchased in bulk quantities.

Table 5 summarizes some chemical prices as of January, 2000, as reported by the *Chemical Market Reporter* (ChemExpo, 2000).

TABLE 5 COSTS OF SELECTED CHEMICALS

Product Description	Cost (per Ton)
Aluminum sulfate, liquid, in tanks, iron-free	269
Aluminum sulfate, liquid, in tanks, NOT iron-free	152
Aluminum sulfate, dry, 100 lb bags, iron-free	250
Aluminum sulfate, dry, 100 lb bags, NOT iron-free	245 - 280
Ferric chloride, technical grade, in tanks	255 - 300
Ferrous sulfate, monohydrate, granulated, bulk	222.50 - 240
Lime, chemical, hydrated, bulk	70

Source: ChemExpo, 2000.

It should be noted, however, that estimation of treatment cost cannot be determined solely on the price of the chemicals. For example, one study found that while it was less expensive to purchase alum than ferric sulfate, overall treatment costs were less using ferric sulfate (Hook *et al*, 1992).

Generally speaking, lime is readily available and the least expensive of common treatment options. A completely enclosed lime chemical handling system costs between \$110,000 and \$130,000, with the lower prices reflecting gravity versus pump systems. The more expensive lime systems include a slaker to convert calcium oxide to calcium hydroxide. These systems can consume up to 2,000 lbs of lime per hour and include storage for up to 60,000 lbs of lime. The trade-off in using lime, however, is in the large sludge volumes that result from its use. For this reason, lime is often used in tandem with more expensive additives. These

trade-offs must be kept in mind when performing jar tests and developing the optimal treatment strategy for each situation.

REFERENCES

Other Related Fact Sheets

Other EPA Fact Sheets can be found at the following web address:

<http://www.epa.gov/owmitnet/mtbfact.htm>

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