Chapter 15
Precipitation

15-1. General

The process of precipitation, its applications, and resulting waste streams are described in the first section of the chapter. The chapter's second portion is a hazard analysis with controls and control points listed.

15-2. Technology Description

a. Process.

Precipitation is a treatment process in which soluble metals and inorganics are precipitated into relatively insoluble metals and inorganic salts by the addition of a precipitating agent (see Figure 15-1). Precipitates, which are small or colloidal, are then settled or filtered out of solution, leaving a lower concentration of metals and inorganics in the effluent. Precipitating agents include soluble hydroxide, sulfide, carbonate, and xanthate compounds. If the precipitate does not settle rapidly, a polymer may be added as a coagulant to increase agglomeration and settling. Inorganic iron and aluminum derivatives, such as ferric chloride and aluminum, may also be used to enhance coagulation. The solids are settled in a clarifier, and the supernatant liquid is discharged or sent to primary treatment. The thickened solids are then disposed of.

b. Applications.

Precipitation is a primary method of treating metal-contaminated aqueous waste streams. Most metals will precipitate from solution at some concentration of their hydroxide, sulfide, or carbonate salts. Additions of more soluble salts of these compounds to an aqueous stream may precipitate metals whose salts have a lower solubility than the additive ions.

Precipitation is a candidate technology for the remediation of groundwater contaminated with heavy metals (including radionuclides) and is an effective pretreatment method for other remediation technologies (such as chemical oxidation or air stripping) where the presence of metals may interfere with the treatment process.

c. Resulting Waste Streams.

Precipitation reactors will produce two streams that may require additional handling:

- The treated effluent wastewater stream.
- Sludges (such as metal hydroxide sludges) that must pass TCLP tests for land disposal.

Adequate solids separation techniques (such as clarification, coagulation, flocculation, or filtration) are required for efficient treatment. Treated effluent may be adversely affected by the rate of addition of reagents or by pH adjustment, which must be controlled to prevent unacceptable concentrations of total dissolved solids in the treatment effluent.

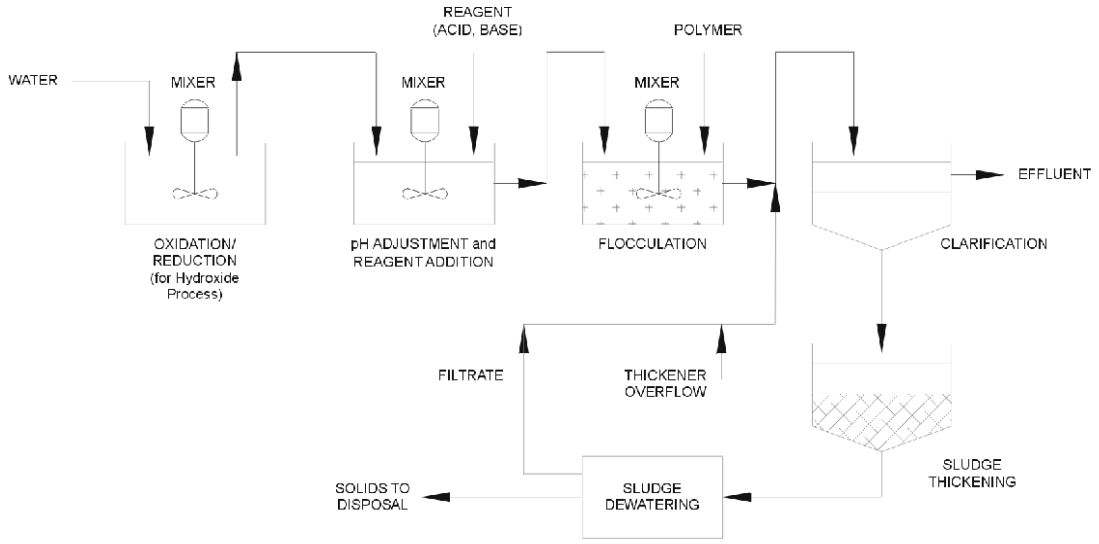

FIGURE 15-1. TYPICAL PROCESS FLOW FOR PRECIPITATION

For additional information on similar processes, see Chapter 16 and 18.

15-3. Hazard Analysis

Principal unique hazards associated with precipitation, methods for control, and control points are described below

a. Physical Hazards.

(1) *Incompatible Treatment Materials and Reagents*.
Description. Chemical reagents (e.g., soluble hydroxide, sulfide, carbonate, and xanthate compounds, polymers added as a coagulant to increase agglomeration and settling), inorganic iron and aluminum derivatives, such as ferric chloride and aluminum, may be used. The system design and materials of construction must be compatible with the reagents. Incompatible reagents and materials may cause corrosion, leaks, joint failures, flow obstructions, and over pressurization of lines.

Control. Controls for incompatible treatment materials and reagents include:
- Train operators in the system chemistry involved in the plant operation.
- Perform a Process Hazard Analysis (PHA) prior to startup and correct all deficiencies found.
- Use liquid transfer equipment (pumps, piping, pipe fittings, valves, and instruments) fabricated from materials that are chemically inert to the liquid streams. Use EM 1110-1-4008, “Liquid Process Piping,” for materials selection.

- Place automatic alarms (e.g., pH, temperature, pressure, reactant off-gas concentration detectors) with sensors at critical points throughout the system to monitor all reactions.
- Utilize appropriate chemical storage and handling procedures to prevent contact or mixture of incompatible reagents and materials.
- The design engineer's authorization is required for any equipment and material substitutions made during construction.
- Train operators in emergency procedures in case of a treatment system failure, in life saving first aid procedures including halting chemical reactions, extracting, decontaminating and stabilizing victims, and in emergency system isolation and shutdown procedures.

(2) *Plugged or Overpressured Waste Lines*.
Description. Precipitate may plug waste lines if the formation rate exceeds the rate of removal. Plugged lines may cause tanks to overflow; broken lines and pumps can cause slippery conditions, worker exposure, and environmental damage. Also, because of the wet environment and the use of electrical equipment, workers may be exposed to electrocution.

Control. Controls for plugged or overpressured lines include:
- Use auger-equipped waste lines to prevent plugged lines.
- Use flow controls to prevent plugged lines and overflowing tanks.
- Install alarms to alert operators of system over-pressurization.
- Allow adequate space for maintenance between equipment.
- Install slip resistant walking and working surfaces.
- Verify that drawings designate the hazardous area classifications as defined in NFPA 70, Chapter, 5 500.1 through 500.10.
- Use controls, wiring, and equipment, both temporary and permanent, that conforms to EM 385-1-1, Section 11, and NFPA 70 for each of the identified hazard areas.
- Use grounded equipment or equipment provided with ground fault circuit interrupter (GFCI) protection if required by EM 385-1-1, Section 11, or NFPA 70.
- Permit only trained and experienced workers in the areas.

CONTROL POINT: Design, Operations, Maintenance

(3) *Tank Mixing/Sludge Handling Equipment*.
Description. Tank mixing equipment may splash chemical reagents (e.g., acids or hydroxides) or may entangle workers who come in contact with propellers or shafts. Sludge press areas are notoriously wet and congested work areas with slips, trips, and falls present as ongoing hazards.

Control. Controls for mixing equipment include:
- Train the operators in the operating characteristics of the tank mixing equipment, in all potential pinch points and rotating part or splash exposures from

the equipment, in the chemistry involved, in the heat of reaction of the chemical reactions, and in handling and transferring the chemicals.

- Use tanks designed to protect people from harmful splashing of rotating mixers or entanglement with shafts or motors.
- Install deadman switches on the equipment and implement lock-out/tag-out procedures when performing maintenance on the mixers.
- Treat floor surfaces around mixing and precipitation equipment, such as sludge handling equipment, with no-skid floor coverings.
- Train workers in potential chemical contact hazards and control measures (see 29 CFR 1910.1200). Train the operators in emergency procedures in the event of a chemical splash exposure or physical entanglement, in life saving first aid procedures including emergency de-energizing equipment, halting and neutralizing chemical reactions, extracting, decontaminating, and stabilizing victims, and in emergency sludge system isolation and shutdown procedures.
- Install, and maintain emergency eyewash/showers at critical points with easy access to the mixing tank equipment. (See American National Standards Institute ANSI Z 358.1 – 1998.)

CONTROL POINT: Design, Operations, and Maintenance

(4) *Electrical Shock.*
Description. Electrical systems in wet or damp areas can cause electrical shock to operating personnel.

Control. Controls for electrical shock include:

- Train operators in the electrical systems used and in the potential electrocution hazards.
- Use ground-fault protected electrical systems in areas that could become wet or damp. Electrical system design must follow "National Electrical Code" NFPA 70 and UFGS 16415A, "Electrical Work, Interior."
- Perform all electrical work according to code and under the supervision of a state licensed master electrician.
- Use grounded or GFCI-protected equipment if required by EM 385-1-1, Section 11, or NFPA 70.
- Never allow the use of ungrounded temporary wiring or electrical cords during minor maintenance work on the units, or grounded temporary wiring in contact with water, or wet or damp surfaces that is not approved for these applications.

CONTROL POINT: Design, Construction, Operations, Maintenance

(5) *Emergency Wash Equipment.*
Description. Emergency shower/eyewash equipment required per 29 CFR 1910.151 is not always provided with adequate floor drains, thereby creating potential electrical hazards or walking surface hazards during required testing and use.

Control. A control for emergency wash equipment includes:

- See American National Standards Institute ANSI Z 358.1 – 1998: "Emergency Eyewash and Shower Equipment" for design requirements.
- Equip showers/eyewash equipment with accompanying functional drains to isolate and collect the shower/eyewash water from unprotected electrical equipment and walking surfaces that, when wet, create slipping hazards.

CONTROL POINT: Design

(6) *Confined Spaces.*

Description. Process tanks are considered to be permit-required confined spaces. Entering process tanks and vessels for inspection and maintenance requires that adequate precautions be taken. Hazards associated with entry into confined space include asphyxiation from the lack of oxygen, exposure to toxic chemical vapors and gases, or poisonous gases from the reagents such as soluble hydroxides, sulfides, hydrogen sulfide, or acids and bases or treatment contaminants or slurries and sludge.

Control. Controls for confined-space entry include:

- Thoroughly train operators and workers in confined space hazards and on safety procedures to be employed in confined space entry.
- Design the mixing tanks and vessels to maximize easy operation, physical cleaning, and maintenance to include accessible, adequately sized access doors or entry ports; and to minimize the frequency, duration, and extent of cleaning and maintenance required.
- Utilize pre-entry confined space permits as detailed in a confined-space entry program that includes a hazard assessment (see 29 CFR 1910.146) including interior atmosphere testing prior to and throughout the work planned.
- Ventilate tank and vessel interiors prior to and during the confined space entry to eliminate the oxygen-deficient or toxic and poisonous atmosphere (hydrogen sulfide or acid gas).
- Complete the mixing tank/vessel manufacturer's shutdown procedures and lock-out/tag-out of associated mixing, pumping or electrically energized systems prior to entry. Eliminate possible buildup of static electricity.
- Use air-supplied respirators to control inhalation exposures to toxic chemicals and poisonous gases to prevent any potential for asphyxiation in situations where only constant mechanical ventilation prevents the buildup of a toxic or inert gas environment.

CONTROL POINT: Design, Operations, and Maintenance

(7) *Design Field Activities.*

Description. Design field activities associated with subsequent construction may include surveying, biological surveys, soil gas surveys, geophysical sur-

veys, trenching, drilling, stockpiling, contaminated groundwater sampling, and other activities. Each of these field activities may expose the survey personnel to physical, chemical, radiological, and biological hazards.

Control. Controls for hazards resulting from predesign field activities include

- Prepare an activity hazard analysis for predesign field survey activities. EM 385-1-1, Section 1, provides guidance on developing an activity hazard analysis.
- Train workers in hazard identification processes and control practices.

CONTROL POINT: Design

b. Chemical Hazards.

(1) *Chemical Reagents.*

Description. Precipitation treatment may expose workers to corrosive chemical reagents, e.g., HCL, lime, sodium hydroxide, carbonate salts, sulfide salts, etc. The reagents can be powder or liquid and may pose an exposure hazard through either inhalation, dermal, or ingestion routes. They may corrode piping system components. Some chemicals used in the precipitation process are hygroscopic and may develop unwanted reactions in the presence of moisture.

Control. Controls for chemical reagents include:

- Label all tanks and piping systems.
- Store all chemicals and reagents in accordance with NFPA, manufacturer, and Material Safety Data Sheet (MSDS) requirements. Do not store a greater chemical inventory than can be used within the acceptable storage period.
- Use temperature and moisture control in storage areas if advised by the manufacturer.
- Segregate acids, bases, and other reactive chemicals with dikes in storage areas.
- Determine reagent compatibility prior to placement in storage following their introduction into the system.
- Use a closed system for the delivery of chemical reagents (e.g., lime, sodium hydroxide solutions, etc.).
- Use the Buddy System and mix all chemical reagents in the mixing tanks in accordance with NFPA and manufacturers requirements, employing all prescribed protective equipment (PPE) including respirators, face shields, and chemical splash resistant suits.
- Install and maintain emergency eyewash/showers at critical points with easy access to the mixing tank equipment and the chemical storage areas. (See ANSI Z 358.1 – 1998.)
- Use PPE such as an air-purifying respirator using cartridges appropriate to the reagents.

- Consult MSDS prior to handling reagents to determine the specific chemical hazards and face shields, gloves, and aprons required.
- Train operators in the characteristics of the tank mixing equipment, splash exposures from mixing reagents, in the chemistry involved, in the heat of reaction and toxicity of the chemical reactions in handling and transferring the chemicals.
- Train operators in the emergency procedures in case of a chemical splash or toxic vapor exposure, in life saving first-aid procedures including emergency de-energizing equipment, halting and neutralizing chemical reactions, extracting, decontaminating, and stabilizing victims and in emergency reaction tank system isolation and shutdown procedures.
- Use appropriate materials in the design of piping and system components.

CONTROL POINT: Design, Operations, Maintenance

(2) *Uncontrolled Reactions.*
Description. If adding reagents in the oxidation/reduction reactions is not properly controlled, the reactions can cause heat and pressure buildup, producing a system release. The release may expose workers to chemical reagents or waste material. Exposure may cause irritation or chemical burns to eyes, skin, and respiratory tracts.

Control. Controls for reactions include:
- Use flow controls to help prevent addition of excessive amounts of chemical reagents (e.g., hydrochloric acid, sodium hydroxide, lime, etc).
- Store the oxidation/reduction reagents in separate areas under cool, dry conditions.
- Include pressure-relief systems and over-pressurization alarms as mandatory components in process design.
- Install an automatic shutoff to prevent the overflowing of storage tanks.
- Locate chemical piping low to the ground, if possible, in case of rupture.
- Provide insulation on pipes to prevent slipping hazards if pipes have moisture buildup.

CONTROL POINT: Design

(3) *High pH Sludge.*
Description. Sludge from the treatment process may have a high pH, which may cause skin burns for workers handling the material.

Control. Controls for high pH include:
- Train operators in the chemical safety and health hazards associated with sludge handling operations.
- Neutralize sludge prior to handling.
- Use PPE such as rain gear, rubber gloves (e.g., butyl rubber for hydrochloric acid or sodium hydroxide), and splash shields.

CONTROL POINT: Design, Operations, Maintenance

(4) H*ydrogen Sulfide Exposure*.
Description. The process may form metal sulfides, which may generate toxic gases, such as hydrogen sulfide (H_2S) or the sulfide sludge may spontaneously combust. If sulfide salts are used as a precipitating agent, H_2S will be generated if the solution is acidic.

Control. Controls for hydrogen sulfide exposure include:
- Ventilate to remove gas from the work area, process tanks, and vessels.
- Use pH control to keep the sulfides alkaline.
- Use water control systems to keep sulfide filter cakes moist.
- Install a H_2S monitor to avoid fatal overexposure where the generation of H_2S is most probable. Set monitors to alarm at 10 ppm.
- Make emergency escape respirators available for all operators in the event of a catastrophic system rupture or uncontrolled reaction.
- Train workers in hazard identification and control and in the chemistry and toxic reactions and effects of hydrogen sulfide.

CONTROL POINT: Design, Operations, Maintenance

(5) *Acids and Bases*.
Description. Workers may be exposed to acids or bases used for pH adjustment.

Control. Controls for acids and bases include:
- Construct secondary containment storage areas for acids and bases of compatible materials.
- Mark storage containers clearly.
- Store acids and bases in separate areas.
- Locate emergency showers and eye wash stations that comply with 29 CFR 1910.151(c) and the design requirements specified in ANSI Z358.1 - 1998 near the reagent storage areas.
- Automate handling of pH agents to the extent practical.
- Prepare an emergency plan and train workers in safe acid/base handling techniques.
- Restrict manual handling of acids and bases to trained and authorized personnel.
- Use PPE such as leather or rubber acid-resistant boots, chemical-resistant coveralls, goggles and face shields, air-purifying respirators (as indicated by the reagent), and rubber or other acid and base resistant gloves (e.g., nitrile) or gauntlets.

CONTROL POINT: Design, Operations, Maintenance

(6) *Treatment Buildings*.
Description. Permanent or semi-permanent treatment buildings may present life safety hazards such as inadequate egress, fire suppression systems, or emergency lighting systems.

Control. Controls for treatment buildings include:

- Meet the following construction requirements for permanent and semi-permanent treatment system buildings: ANSI 58.1, "Minimum Design Loads for Buildings and Other Structures," the "National Fire Code," the "National Standard Plumbing Code," "Life Safety Code," and the "Uniform Building Code."
- Make sure structures comply with either the Air Force Manuals on Air Force bases, the USACE Technical Manuals on Army installations, or local building codes on Superfund, Base Realignment and Closure (BRAC) or Formerly Used Defense Sites (FUDS) sites.

CONTROL POINT: Design, Operations

c. Radiological Hazards.

(1) *Radioactive Materials*.
Description. Many radioactive materials and naturally occurring radioactive materials (NORM) are metals that, if present in the water, can precipitate and be concentrated. This hazard may be considered out of the ordinary for this technology. Some radioactive materials may present an external exposure hazard. All radioactive materials may present an internal exposure hazard through inhalation or ingestion.

Control. Controls for radioactive materials include:

- Consult a qualified health physicist to determine the exposure potential, any necessary engineered controls, or required PPE.

CONTROL POINT: Maintenance

(2) *Radioactive Devices*.
Description. Fire and smoke detection devices, fluid level devices, and other process monitors and switches may contain radioactive devices potentially exposing workers through lack of identification or mishandling.

Control. Controls for inadvertent handling or exposure to radioactive devices include:

- Workers should be prevented from and warned against tampering with the devices.
- The location of the devices should be recorded so as to safely retrieve and dispose devices in case of a system failure and equipment replacement.

CONTROL POINT: Design, Operations and Maintenance

d. Biological Hazards.

Opportunistic Insects and Animals.
Description. For all sites but especially in cooler climates, opportunistic insects or animals can nest in and around warm process equipment. Vermin, insect and arthropod control measures should be considered in any design.

Control. Control of opportunistic insect and animals include:

- Electrical cabinets and other infrequently opened enclosures should be opened carefully and checked for black widow and brown recluse spiders, and evidence of rodents. As rodents can cause damage to electrical cables, all wiring should be inspected regularly.
- Ensure all storage is off the ground, palleted, and kept dry. Damp areas attract scorpions, rodents, and the snakes that eat them.
- Design ceiling corners and other high areas to discourage nesting by swallows, pigeons, and other birds. Birds are carriers of diseases, especially in their droppings, which can foul cranes and process equipment.

CONTROL POINT: Design, Operations and Maintenance