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CHAPTER 5
CYANIDE WASTES

A. INTRODUCTION

Cyanide waste streams are produced by several industries in California, including ore extraction, photographic processing, synthetics manufacturing, and metal finishing.

Cyanide-containing wastes include metal finishing contaminated rinse water, spent process solutions, and accidental spills. Metal finishers use cyanide baths to hold metal ions such as zinc and cadmium in solution during the electroplating operation. Metal platers may also use cyanide in their stripping solutions.

Contaminated rinse waters generally have cyanide concentrations under 100 milligrams per litre (mg/l), and typically at about 10 mg/l to 20 mg/l. These dilute wastes are usually treated to meet municipal pretreatment requirements and are then discharged to sewers.

Spent cyanide process solutions typically have concentrations above 1,000 mg/l. Batch discharges of these spent solutions occur periodically when the quality of the solution is no longer suitable for the plating operation. The relative volumes of spent process solution wastes are not large, but the cyanide concentrations are high.

As of June 1, 1983, liquid hazardous wastes containing free cyanides at concentrations greater than or equal to 1,000 mg/l were prohibited from land disposal in California. These wastes are now being treated on site, or at one of four off-site facilities in California. Methods used by the off-site facilities are described in this chapter.

B. TREATMENT PROCESSES FOR CYANIDE WASTES

Several processes can be used to treat aqueous cyanide wastes. Treatment of aqueous cyanide typically requires chemical oxidation, or conversion to thiocyanate. Cyanide treatment processes are described below, with examples of available off-site facilities included for each process where applicable.

Oxidation With Chlorine and Hypochlorites (Figure 5-1) -- This has been the most widely accepted method of cyanide treatment during the past 30 years, and is still the most common method. Cyanide is first oxidized to cyanate at pH 9 to 11. Cyanate is then converted to bicarbonate and nitrogen gas at pH seven to nine. The theoretical chlorine requirement is 6.8 pounds of chlorine per pound of cyanide. The actual chlorine requirement for a given waste is always greater due to the presence of other oxidizable constituents. Additional chlorine helps to speed up the reaction.

Chlorine or hypochlorite oxidation is convenient because it can be carried out at ambient temperature and it is suitable for automatic control.

Most chlorine and hypochlorite treatment units for on-site use are designed to treat only dilute cyanide solutions and rinse waters. These batch-type units may be modified so that plating baths with cyanide concentrations up to 5,000 mg/l can be treated. Solutions with cyanide concentrations above 5,000 mg/l or solutions that are heavily complexed with iron or nickel generally require greater expertise in treatment control than the average plating shop can provide. Treatment of concentrated cyanide solutions produces a great deal of heat and undesirable side reactions can take place unless the operation is well controlled. Currently, equipment is not generally available for on-site treatment of high concentration or heavily complexed cyanide waste. High concentration cyanide wastes should be treated at a centralized facility.

Some disadvantages of cyanide oxidation with chlorine or hypochlorite include: the possible emission of volatile intermediate reaction products, and chemical interference in the treatment of mixed waste.

Improper chlorination of cyanide ion, hydrogen cyanide, or thiocyanate ion, particularly under conditions below pH ten, will result in increased evolution of cyanogen chloride, which is as hazardous as hydrogen cyanide.

The presence of nickel, cobalt, iron, silver, and gold slow the oxidation of cyanide. The reaction will take place if sufficient time is provided.

Many companies, including several listed in California, offer prepackaged and custom designed chlorine and hypochlorite oxidation units for wastewater treatment for metal finishers. Most of these are designed to both treat the cyanide wastes and to remove heavy metals from the rinse waters before discharge to municipal sewers. The sizes of these treatment units range from batch units with capacities of 100 gallons per day to continuous units which can handle hundreds of thousands of gallons per day. These units vary in complexity depending on the metal finishing process employed, the requirements of the local sewage treatment plant, and the space available for the treatment facilities.

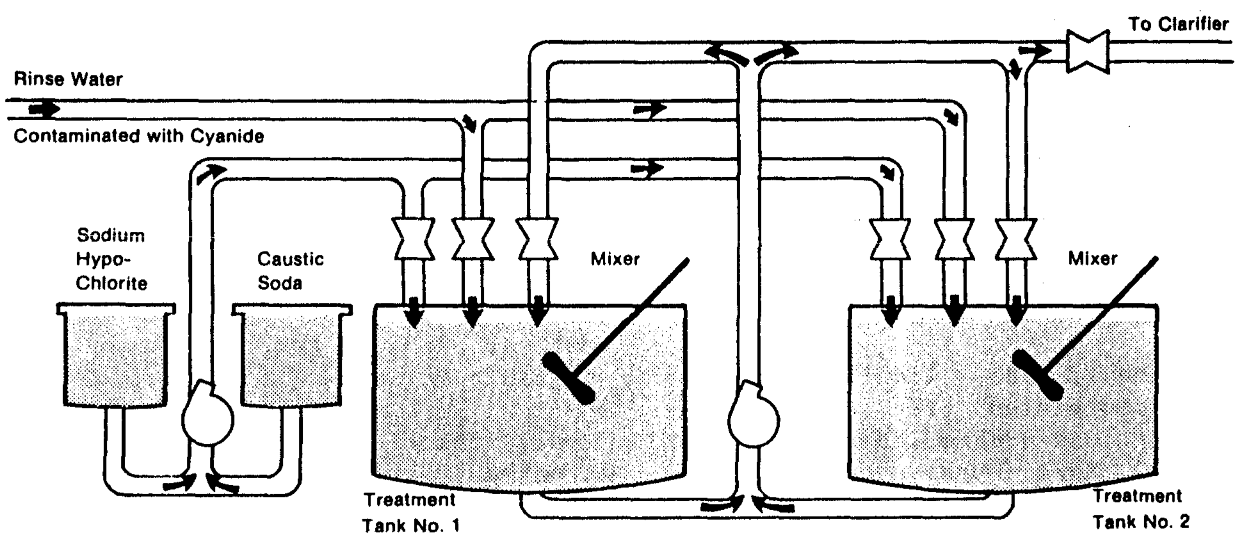

Figure 5-1 Batch Treatment of Cyanide with Sodium Hypochlorite.

Capital costs for chlorine hypochlorite treatment systems vary considerably. The minimum equipment costs for a small batch system (about 200 gallons per day) is around $10,000. Continuous flow systems which treat cyanide and remove dissolved metals range in cost from $50,000 for moderate units (around 20 gallons per minute) to hundreds of thousands of dollars for high flow custom systems. The cost to install the treatment unit can be comparable to the purchase price. Operating cost using chlorine or hypochlorite to treat cyanide ranges from $2.50 to $7 per pound of cyanide for on-site treatment. Examples of commercial chlorination units are presented in Table 5-1.

Industrial waste treatment services which exist in the eastern United States charge $3 to $4.50 (1982 dollars) per pound of cyanide for treatment. Such facilities have a much longer operating experience than similar facilities in California and may be indicative of stable costs for treatment of cyanide. The costs vary depending on the initial concentration of cyanide, interference from heavily complexed metals such as iron and nickel, and the stringency of local discharge requirements when the effluent is discharged to sewers.

TABLE 5-1

EXAMPLES OF COMMERCIALLY AVAILABLE CHLORINATION UNITS

Manufacturer	Capacity of Units	Units in Service	Cost Examples
Advanced Metal Finishing, Inc.	1,000 gallons per day to 350 gallons per minute	More than 300	20 gpm...$50,000 120 gpm..$125,000
Advanced Chemical Systems, Inc.	5 gallons per hour to 1,000 gallons per minute	50	50 gpm..$100,000

Oxidation by Hydrogen Peroxide -- A hydrogen peroxide solution with formaldehyde may be used to oxidize sodium cyanide, potassium cyanide, and cadmium cyanide. This process is usually operated at a temperature of 50°F to 60°F and at a pH between 10 and 11.5. The effluent from this process has a high biochemical oxygen demand and requires biological treatment before discharge to sewers. Effective oxidation by hydrogen peroxide may require a catalyst. This process is not usually suitable for treatment of copper plating wastes.

Similar to chlorination, oxidation with hydrogen peroxide is a simple process easily automated and which takes place at ambient conditions. Limitations of this process include: possible chemical interference, the limited shelf life of hydrogen peroxide, and incomplete oxidation of cyanide beyond the cyanate level.

Manufacturers and suppliers of hydrogen peroxide generally provide all equipment for storing and handling the hydrogen peroxide solutions. However, the generator must usually retain a specialist to design and install the treatment equipment, tanks, and control systems.

Capital and operating costs for cyanide treatment with hydrogen peroxide are comparable to those for chlorine treatment.

Ozonation -- Ozone, a molecular form of oxygen, effectively oxidizes cyanide. Commercial units are available which include on-site ozone generation. Ozonation shares many of the advantages and disadvantages with other chemical oxidation processes for cyanide. The reaction takes place at ambient temperature and is well suited to automatic control. Oxidation beyond the cyanate level is slow. Chemical interference may be a problem when mixed wastes are treated. Oxidation of strong cyanide complexes, especially iron complexes, is slow. In general, ozone oxidation of cyanides is enhanced by copper ions, high pH, and intimate contact of the cyanide with the ozone.

A small number of vendors, including west coast suppliers, offer ozone oxidation units for treating cyanide wastes on site. Ozone oxidation is probably not economical for small generators. A 50-gallon per minute unit for dilute wastes costs approximately $300,000. Operating costs are approximately half that of chlorine oxidation units.

Electrochemical Oxidation -- Electrochemical oxidation is used to treat free cyanide and cyanate at high concentrations. A direct electrical current oxidizes the cyanide to nitrogen, carbon dioxide, and ammonia. Operating temperatures are around 200°F. Effluent from electrolytic oxidation containing less than 100 mg/l of cyanide can be further treated by chlorination. Wastes containing several thousand milligrams per liter of cyanide have been treated, but the time required to destroy such high concentrations is on the order of several days.

Electrolytic treatment systems are presently available as off-the-shelf units. These systems are modular, expandable, and allow flexibility to treat high concentration cyanide wastes.

Costs for electrolytic oxidation equipment run from $15,000 for a system to treat one pound of cyanide per hour to $30,000 for a system to treat four pounds of cyanide per hour. The major cost of operation is for electricity. An estimated average operating cost is $4 per pound of cyanide removed.

Treatment With Sulfur -- Metallic cyanides react with elemental sulfur to form inorganic thiocyanates. In some cases, polysulfide compounds, calcium polysulfide, or sodium polysulfide can be substituted for elemental sulfur. The reaction is carried out in a reactor at a pH of ten. The reaction is slow, with residence times of two to six days. Thiocyanates are relatively chemically stable, are soluble in water, and are considerably less hazardous than their cyanide precursors.

There is no off-the-shelf equipment available. All equipment is custom designed and built.

Costs for this process are dependent on the availability of an inexpensive source of sulfur.

Only one off-site facility in California offers the sulfur treatment process, Chemical Waste Management, in Kettleman Hills (Table 5-2).

Hydrolysis -- The hydrolysis process provides the plating industry with a simple, effective, and economical alternative for on-site disposal of cyanide wastes. Cyanide is converted to ammonia and formate (formic acid) without expensive chemicals. In hydrolysis, the cyanide waste is placed under a pressure of 250 to 600 pounds per square inch (psi) at a temperature of 475°F to 525°F. In bench-scale tests, cyanides at concentrations of 50,000 mg/l of total cyanide have been reduced to less than 30 mg/l within 60 minutes.

The American Electroplating Society completed tests on a full-scale commercial prototype hydrolysis reactor. The size of the reactor was 150 gallons. The unit was also designed to hold a 55-gallon drum of cyanide sludge for treatment. Operation of the commercial size unit confirmed the same high efficiencies (99.99 percent) obtained in an earlier laboratory program. Although drummed inorganic cyanide sludge was successfully treated, wastes containing organic material did not readily solubilize. The hydrolysis treatment is followed by either oxidation with potassium permanganate to destroy chelating agents and allow precipitation of metal hydroxides, or by sodium sulfide addition to precipitate dissolved metals in order to produce effluent suitable for discharge to sewers.

The design is simple and no exotic equipment is needed. Complete details are available from the American Electroplaters Society, Research Project 53A, 1201 Louisiana Avenue, Winter Park, FL 32789. Their prototype hydrolysis reactor was constructed of stainless steel. However, reactors can be built locally.

The capital and installation costs for a unit to treat 300 gallons per day of wastes containing 50,000 mg/l cyanide are estimated to be as low as $20,000 to $50,000 for a unit designed to treat both liquids and sludges. Estimated overall cost of treatment of liquid cyanide waste, including posttreatment, maintenance, labor, energy, and capital cost, are from $.62 to $1.88 per pound of cyanide. For treatable sludges, the costs range from $1.07 to $1.78 per pound of cyanide.

<u>Other Technologies for Cyanide Wastes</u> -- Cyanide wastes can be treated by many of the techniques used to treat organic waste streams. Both waste types are generally decomposed by oxidation. Biological oxidation is routinely used to decompose dilute cyanide wastes. In the petrochemical industry, cyanide wastes up to 100 ppm are treated with activated sludge and trickling filter processes. A rotating biological contactor has been used to treat gold mine wastewaters with cyanide levels of approximately 30 ppm.

Biological oxidation of cyanides requires caution. A sudden increase in the concentration of cyanide (shock load) can kill the biomass with consequent accumulation of untreated wastes and risk of environmental contamination. Decomposing organisms often require acclimation before decomposing cyanide.

Wet air oxidation (WAO), another technique applied to organic wastes (Chapter 6), also decomposes cyanide wastes. In WAO, materials are oxidized by oxygen at elevated temperatures (350°F to 650°F). High pressures are required to prevent volatization and to increase the dissolved oxygen content in the water. The oxygen is usually supplied in the form of air.

A WAO developed by Zimpro Corporation was placed into operation at Casmalia Resources in Santa Barbara County (Table 5-2) for off-site treatment in 1983. This unit has the capability of treating cyanides and several categories of organic wastes. This unit can achieve destruction efficiencies of better than 99.5 percent; in one case, a cyanide concentration was reduced from 25,000 mg/l to 82 mg/l.

Capital costs for WAO units are from $1 to $2 million for a 10-gallon per minute unit and from $3.5 to $5 million for an 80-gallon per minute unit. The operating costs depend strongly on the waste composition.

Cyanide sludges can be treated by hydrolysis and wet-air oxidation. However, incineration is still the best available technology for the treatment of cyanide sludge, especially for sludge with a high concentration of organics. A complete description of available incineration technology may be found in Chapter 9.

TABLE 5-2

OFF-SITE TREATMENT OF CYANIDE WASTES

Operator and Location	Treatment	Storage Capacity	Treatment Capacity or Batch Size	Cost 1/
IT-Martinez	gaseous chlorine	7,500 gal	5,000 gal tank or 1,600 gal per day	specific quote only
BKK-Chula Vista	sodium hypoclorite	18,000 gal and 13 55-gal drums	up to 10,000 gal per day	$.65 to 4.00 per gallon
Casmalia Resources-Casmalia	wet air oxidation	70,000 gal	15,000 tons per year 2/	$.05 to 1.00 per gallon
Chem Waste Mgmt., Kettleman Hills	calcium polysulfide		4,600 tons year 2/	$.05 to 1.00 per gallon

Supercritical water technology, a noncombustion thermal process, can destroy cyanide wastes. Water heated above 705°F and above 3,200 psi becomes supercritical; at this point, many normally insoluble compounds become highly soluble. Under these conditions, complex molecules are decomposed to low molecular weight compounds. Oxygen, usually added as air, rapidly oxidizes the carbon and hydrogen of the newly-formed low molecular weight compounds.

Under process conditions, the inorganic salts formed are almost completely insoluble; they precipitate out, and can be removed by filtration. The remaining stream of supercritical water at high temperature and pressure can be used for process heat or fed to a turbine for generating power.

The supercritical water process has generally been applied to organic wastes. A complete description of the supercritical water process is therefore presented in Chapter 9.

1/ Costs depend largely on concentration.

2/ Assumes equipment is not used for any other waste streams.

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