

# **CORROSIVE-CONTAINING WASTES**

**Treatment Technologies**

**by**

**L. Wilk, S. Palmer, M. Breton**



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## Foreword

Treatment technologies for corrosive-containing wastes are described in this book, which will be a comprehensive source of information for those involved in the evaluation of available waste management options.

Corrosive acids and alkalis are widely used by all segments of American industry and result in the generation of approximately 40% of all Resource Conservation and Recovery Act (RCRA)-regulated hazardous wastes. Improper management of these wastes can result in altered pH of surface waters to the detriment of aquatic organisms. Land disposal of these wastes can also lead to the solubilization of toxic (e.g., heavy metal) constituents of codisposed wastes, thereby enhancing the potential for their transport into the environment. To combat the potential negative effects associated with current disposal practices, the 1984 RCRA Amendments directed EPA to ban corrosive wastes from land disposal to the extent required to protect human health and the environment.

The land disposal ban excludes acidic corrosive wastes (pH less than or equal to 2.0) from land disposal units (excluding underground injection), effective July 8, 1987. Treatment standards for corrosives which are currently managed through underground injection were to be promulgated on August 8, 1988. Finally, alkaline corrosive wastes (pH greater than 12.5) will be banned from disposal effective May 8, 1990. In addition, standards for hazardous constituents which are commonly present in corrosive wastes, such as heavy metals and toxic organics, are also being promulgated under the 1984 RCRA Amendments. Thus, prior to land disposal, corrosive wastes will also have to meet these standards as they are promulgated.

All potentially viable technologies for treating corrosive-containing wastes are identified and discussed in the book; however, emphasis is placed on proven technologies. Each of the technologies is described in terms of actual performance in removing constituents of concern, associated process residuals and emissions, and those restrictive waste characteristics impacting the ability of a particular technology to effectively treat the wastes under consideration. Cost and capacity data are also provided to help assess the applicability of the technologies to specific waste streams.

The information in the book is from *Technical Resource Document: Treatment Technologies for Corrosive-Containing Wastes*, prepared by L. Wilk, S. Palmer, and M. Breton of Alliance Technologies Corporation for the U.S. Environmental Protection Agency, December 1987.

The table of contents is organized in such a way as to serve as a subject index and provides easy access to the information contained in the book.

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## **1. Introduction**

Section 3004 of the Resource Conservation and Recovery Act (RCRA), as amended by the Hazardous and Solid Waste Amendments of 1984 (HSWA), prohibits the continued placement of RCRA-regulated hazardous wastes in or on the land, including placement in landfills, land treatment areas, waste piles, and surface impoundments (with certain exceptions for surface impoundments used for the treatment of hazardous wastes). The amendments specify dates by which these prohibitions are to take effect for specific hazardous wastes as shown in Table 1.1. After the effective date of a prohibition, wastes may only be land disposed if: (1) they comply with treatment standards promulgated by the Agency that minimize short-term and long-term threats arising from land disposal; or (2) the Agency has approved a site-specific petition demonstrating, to a reasonable degree of certainty, that there will be no migration from the disposal unit for as long as the waste remains hazardous.

Liquid acidic wastes (i.e., pH less than or equal to 2.0) will be banned from land disposal effective July 8, 1987 with an exception granted for wastes which are disposed via underground injection. Restrictions for these wastes will be enacted by August 8, 1988. Alkaline waste (i.e., pH greater than or equal to 12.5 or wastes which are strongly corrosive to steel) and non-liquid waste disposal restrictions will be promulgated by May 8, 1990. However, the 1984 RCRA Amendments authorize the Agency to extend the effective dates of prohibitions for up to 2 years nationwide if it is determined that there is insufficient alternative treatment, recovery or disposal capacity.

## 2 Corrosive-Containing Wastes

TABLE 1.1. SCHEDULING FOR PROMULGATION OF REGULATIONS BANNING  
LAND DISPOSAL OF SPECIFIED HAZARDOUS WASTES

| Waste category  | Effective date <sup>a</sup> |
|---|-----------------------------|
| Dioxin containing waste   | 11/8/86                     |
| Solvent containing hazardous wastes<br>numbered F001, F002, F003, F004, F005  | 11/8/86                     |
| California list:  |                             |
| - Liquid hazardous wastes, including free liquids<br>associated with any solid or sludge containing:                        |                             |
| - Free or complex cyanides at $\geq 1,000$ mg/L   |                             |
| - As $\geq 500$ mg/L  |                             |
| - Cd $\geq 100$ mg/L  |                             |
| - Cr <sup>+6</sup> $\geq 500$ mg/L  |                             |
| - Pb $\geq 500$ mg/L  | 7/8/87                      |
| - Hg $\geq 20$ mg/L   |                             |
| - Ni $\geq 134$ mg/L  |                             |
| - Se $\geq 100$ mg/L  |                             |
| - Ti $\geq 130$ mg/L  |                             |
| - Liquid hazardous wastes with:   |                             |
| - pH $\leq 2.0$   | 7/8/87                      |
| - PCBs $\geq 50$ ppm  |                             |
| - Hazardous wastes containing halogenated organic<br>compounds in total concentration $\geq 1,000$ mg/kg                    | 7/8/87                      |
| Other listed hazardous wastes (§§261.31 and 32), for<br>which a determination of land disposal prohibition<br>must be made: |                             |
| - One-third of wastes   | 8/8/88                      |
| - Two-thirds of wastes  | 6/8/89                      |
| - All wastes  | 5/8/90                      |
| Hazardous wastes identified on the basis of<br>characteristics under Section 3001   | 5/8/90                      |
| Hazardous wastes identified or listed after enactment   | Within 6 months             |

<sup>a</sup>Not including underground injection for which land disposal restrictions  
will be promulgated by 8/8/88.

## PURPOSE AND SCOPE

This Technical Resource Document (TRD) for corrosive RCRA wastes identifies recovery and treatment alternatives to land disposal for these wastes and provides performance data and other technical information needed to assess potentially applicable alternatives. This document is one of a series of documents designed to assist regulatory agency and industrial personnel in meeting the land disposal restrictions promulgated by the 1984 RCRA Amendments. To minimize redundancy, emphasis has been placed on treatment technologies (i.e., neutralization) which specifically address the corrosive nature of RCRA wastes. Similarly, discussion of recovery practices has been restricted to methods which are capable of achieving adequate performance at extreme conditions of pH. Although emphasis is placed on performance data for these processes, cost data and technical factors affecting performance (e.g., restrictive waste characteristics) are discussed to assist in the evaluation of alternative approaches to land disposal.

## DOCUMENT ORGANIZATION AND CONTENT

The following section (Section 2) will identify the hazardous wastes of concern which meet the RCRA definitions of corrosive wastes. Available information concerning waste stream characteristics, generation, and management practices will be provided in Section 3. Following sections (Sections 4 and 5) will discuss neutralization and recovery practices, which are available as alternatives to land disposal. Each process will be reviewed with regard to the following four factors:

1. Process description, including design and operating parameters, applicable waste types, pretreatment requirements, and post-treatment and disposal of residuals;
2. Case study and performance data which identifies the range in potential applications, processing equipment, and system configurations;
3. Cost of treatment; and
4. Present status of the process.

#### 4 Corrosive-Containing Wastes

Virtually all corrosive wastes will have to undergo some form of neutralization as part of the treatment/disposal process. Thus, handling of non-corrosive waste constituents will be discussed as pre- or post-treatment (neutralization), as appropriate. Treatment and disposal alternatives for these non-corrosive constituents and treatment residuals will be identified. However, the reader is referred to related Technical Resource Departments for detailed performance data since this was beyond the scope of this document.

A final section (Section 6) provides approaches to identifying and selecting appropriate technologies for corrosive waste streams. Although emphasis is placed on technical approaches, economic and institutional concerns are also discussed to assist in process selection.

## 2. Identification of RCRA Corrosive Wastes

As specified in the EPA regulations for identifying hazardous waste, a waste is defined as a RCRA corrosive waste if it meets either of the following criteria:<sup>1</sup>

- It is aqueous and has a pH less than or equal to 2.0 or greater than or equal to 12.5; or
- It is a liquid and corrodes steel (SAE 1020) at a rate greater than 0.25 in./yr at a test temperature of 130°F.

Thus, wastes which are all solids are not subject to restrictions applicable to RCRA corrosive wastes. However, wastes which contain both liquids and solids may be classified as RCRA corrosive wastes depending upon the characteristics of the liquid fraction. EPA has established a test protocol called the paint filter test<sup>2</sup> which is designed to separate free liquids by gravity from the waste matrix. If the recovered liquid meets the above criteria for corrosive waste, the entire waste is considered to be corrosive. The term "solids" is used throughout this document. It is assumed that corrosives which were characterized as "solids" in the literature, actually contain residual quantities of liquid which meet the definition of corrosive waste.

Corrosiveness was determined to be a hazardous characteristic because<sup>3</sup> improperly managed highly acidic or alkaline wastes can present a danger to human health and the environment through the following mechanisms:

- Harm to transporters and other persons coming into contact with the waste;
- Solubilization of toxic constituents of solid wastes thereby enhancing their transport into ground and surface water;

## 6 Corrosive-Containing Wastes

- Chemical reactions with co-disposed wastes which can result in generation of heat or toxic fumes; and
- Altered pH of surface waters to the detriment of aquatic organisms.

Although these effects occur below pH of 3 and above pH of 12, EPA ultimately promulgated less restrictive standards (i.e., pH less than or equal to 2.0 or greater than or equal to 12.5) in order to exclude certain materials from regulation. Specifically, these include otherwise non-hazardous wastes such as lime stabilized sludges (pH 12.0 to 12.5), which can be put to agricultural or other beneficial uses, and substances such as cola drinks and many industrial wastewaters (pH 2.0 to 3.0).<sup>3</sup> EPA felt that these less restrictive limits would still encompass those wastes which are most likely to involve damage to the skin, solubilization of toxic substances or harmful chemical reactions.

In addition to pH, EPA has elected to express corrosiveness in terms of the metal corrosion rate since many RCRA wastes are stored, transported and land disposed in steel containers. Therefore, the metal corrosion rate is indicative of a compound's ability to escape from its container or corrode other containers thereby increasing the potential for adverse chemical reactions or hazardous substance release. The EPA standard for metal corrosion rate was adopted from the Department of Transportation classification for compounds which exhibit severe rates of corrosion at temperatures which may be encountered during handling of hazardous materials.

EPA has listed two wastes from specific sources (K062, K111) and five discarded commercial chemical products and associated off-specification materials, containers, and spills (U006, U020, U023, U123, U134) as materials which meet the criteria for corrosive hazardous wastes.<sup>1</sup> As shown in Table 2.1, certain other listed hazardous wastes have also been reported which were characterized by the generators as corrosive. Finally, the waste code D002 has been assigned to wastes which also meet the definition of corrosive wastes but are not identified as hazardous in Part 261, Subpart D. These non-toxic corrosive compounds and other compounds which can react with water to form corrosive wastes are also listed in Table 2.1.<sup>4</sup>



TABLE 2.1. CORROSIVE AND POTENTIALLY CORROSIVE WASTE MATERIALS

A. RCRA Wastes Listed Due to Corrosivity

- D002 - Any waste not listed in Subpart D which has either: 1)  $12.5 \leq \text{pH} \leq 2$ , or 2) corrodes SAE1020 steel at a rate greater than 0.25 inch per year at 130°F
- K062 - Spent pickle liquor generated by steel finishing operations of plants that produce iron or steel
- K111 - Product washwaters from the production of dinitrotoluene via nitration of toluene
- U006 - Acetyl chloride
- U020 - Benzenesulfonyl chloride
- U023 - Benzotrichloride
- U123 - Formic acid
- U134 - Hydrogen fluoride; hydrofluoric acid

B. Potentially Corrosive RCRA Listed WastesACIDS -

- K039 - Filter cake from the filtration of diethylphosphorodithioic acid in the production of phorate
- K050 - Heat exchanger bundle cleaning sludge from the petroleum refining industry
- K100 - Waste leaching solution from acid leaching of emission control dust/sludge from secondary lead smelting
- |                               |  |
|-------------------------------|--|
| U008 - Acrylic acid           | U114 - Ethylenebis (dithiocarbamic acid)                 |
| P010 - Arsenic acid           | P058 - Fluoroacetic acid, sodium salt                    |
| U136 - Cacodylic acid         | P063 - Hydrocyanic acid, hydrogen cyanide                |
| U052 - Cresylic acid          | U147 - Maleic anhydride                                  |
| U088 - Diethyl phthalate      | U156 - Methyl chlorocarbonate                            |
| U102 - Dimethyl phthalate     | U162 - Methyl methacrylate                               |
| U103 - Dimethyl sulphate      | P043 - Phosphorofluoric acid, bis (1-methyl-ethyl ester) |
| U113 - Ethyl acrylate         | U204 - Selenium dioxide                                  |
| U119 - Ethyl methanesulfonate |  |

(continued)

TABLE 2.1 (Continued)

BASES -

K060 - Ammonia still lime sludge from coking operations

U012 - Aniline

U133 - Hydrazine

U092 - Dimethylamine

U167 - 1-Naphthylamine

U098 - 1,1-dimethylhydrazine

U174 - N-Nitrosodiethylamine

P046 - Ethanamine, 1,1-dimethyl-  
2-phenyl-

U194 - n-Propylamine

P053 - Ethylene diamine

U196 - Pyridine

U221 - Toluenediamine

C. Potentially Corrosive Non-Listed WastesACIDS -

Acetic acid

Hydrogen chloride

Acetimidic acid

Hydrogen peroxide

Adipic acid

Isocyanic acid

Butanoic acid

Methanesulfonic acid

Carbamic acid

Nitric acid

Chlorosulfonic acid

Oxalic acid

Chromic acid

Phosphoric acid

Citric acid

Phosphorofluoric acid

Dithiocarbamic acid

Propionic acid

Fulminic acid

Sulfuric acid

Hydrochloric acid

Vanadic acid

BASES -

Aminoethanolamine

Morphaline

Ammonium hydroxide

Potassium hydroxide

Caustic potash Solution

Sodium carbonate

Caustic soda Solution

Sodium hydrosulfide

Cyclohexylamine

Sodium hydrosulfite

Diethanolamine

Sodium Hydroxide

Diethylenetriamine

Triethanolamine

Diisopropanolamine

Triethylamine

Dimethylformamide

Triethylenetetramine

Hexamethylenediamine

Trimethylamine

Hexamethylenetetramine

Urea

Methylethylpyridine

Monoethanolamine

Monoisopropanolamine

(continued)

F 9/02 X5

B1

TABLE 2.1 (Continued)

D. Chemicals that React in Water to Give Acids

| <u>Compound</u>         | <u>Resulting Acid</u>                      |
|-------------------------|--|
| Acetic anhydride        | Acetic acid                                |
| Aluminum chloride       | Hydrogen chloride + aluminum hydroxide     |
| Benzoyl chloride        | Hydrogen chloride + benzoic acid           |
| Bromine                 | Hypobromous acid                           |
| Chlorosulfonic acid     | Hydrogen chloride + sulfuric acid          |
| Maleic anhydride        | Maleic acid                                |
| Nitrogen tetroxide      | Nitric acid + nitric oxide                 |
| Nitrosyl chloride       | Hydrogen chloride + nitrous acid           |
| Oleum                   | Sulfuric acid + sulfur trioxide            |
| Phosphorus oxychloride  | Hydrogen chloride + phosphoric acid        |
| Phosphorus pentasulfide | Hydrogen sulfide + phosphoric acid         |
| Phosphorus trichloride  | Hydrogen chloride + phosphoric acid        |
| Polyphosphoric acid     | phosphoric acid                            |
| Sulfur monochloride     | Hydrogen chloride + sulfuric acid + others |
| Sulfuryl chloride       | Hydrogen chloride + sulfuric acid          |
| Titanium tetrachloride  | Hydrogen chloride + tri-hydroxyhalides     |

E. Chemicals that React with Water to Give Bases

| <u>Compound</u>          | <u>Resulting Base</u>                             |
|--------------------------|---|
| Anhydrous ammonia        | Ammonium hydroxide                                |
| Ethylene imine           | Monoethanolamine                                  |
| Lithium aluminum hydride | Lithium hydroxide + hydrogen + aluminum hydroxide |
| Sodium                   | Sodium hydroxide + hydrogen                       |
| Sodium amide             | Ammonia + sodium hydroxide                        |
| Sodium hydride           | Sodium hydroxide + hydrogen                       |

Sources: References 1, 4, 5 and 6.