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1. INTRODUCTION

The National Pretreatment Program establishes an overall strategy for controlling the introduction of nondomestic wastes to publicly owned treatment works (POTWs) in accordance with the overall objectives of the Clean Water Act. Sections 307(b) and (c) of the Act authorize the Environmental Protection Agency to develop National Pretreatment Standards for new and existing dischargers to POTWs. The Act makes these pretreatment standards enforceable against dischargers to publicly owned treatment works.

The General Pretreatment Regulations (40 CFR Part 403) establish administrative mechanisms requiring nearly 1,500 POTWs to develop local pretreatment programs to enforce the general discharge prohibitions and specific categorical pretreatment standards. These categorical pretreatment standards are designed to prevent the discharge of pollutants which pass through, interfere with, or are otherwise incompatible with the operation of the POTW. The standards are technology-based for removal of toxic pollutants and contain specific numerical limitations based on an evaluation of specific treatment technologies for the particular industrial categories. As a result of a settlement agreement, EPA was required to develop categorical pretreatment standards for 34 industrial categories with a primary emphasis on 65 classes of toxic pollutants.

This manual provides guidance to POTWs on the application and enforcement of the categorical pretreatment standards for the battery manufacturing category. This document is based primarily on two sources: Federal Register notices, which include the official announcements of the categorical pretreatment standards, and the final development document for battery manufacturing which provides a summary of the technical support for the regulations. Additional information on the regulations, the manufacturing processes, and control technologies can be found in these sources. A listing of all references used in the development of this manual is provided at the end of this document. A Glossary of Terms is provided in Appendix A of this document to assist the reader in becoming familiar with the technical terms used in this document.

1.1 HISTORY OF THE BATTERY MANUFACTURING CATEGORY

Battery manufacturing originated in 1786 with the invention of the galvanic cell by Galvani. Electrochemical batteries and cells using silver and zinc electrodes in salt water were assembled as early as 1798 by Alessandro Volta as a result of Galvani's work. In 1868, Leclanche developed the forerunner of the modern dry cell in which he used an amalgamated zinc anode and a carbon cathode surrounded by manganese dioxide immersed in an ammonium chloride solution. Varying types of battery systems have been introduced, many of which have been displaced by newer and more advanced systems. In the last ten years lithium batteries have been developed for many applications, including heart pacemakers, and large programs have been funded for the development of electric powered automobiles and stand-by power sources for utilities. Advancing technology of materials along with new applications requirements will result in development of newer systems and the redevelopment of some older systems.

It is estimated that there are 255 battery manufacturing plants in the United States. A substantial majority of these are located in California, Pennsylvania, North Carolina, and Texas. Of the 255 identified battery manufacturing plants, 22 are direct dischargers, 150 are indirect dischargers and 83 plants do not discharge wastewater.

Categorical pretreatment standards for the battery manufacturing category were promulgated on March 9, 1984 and became effective on April 23, 1984. EPA had not previously promulgated any pretreatment regulations for the battery manufacturing category. In response to a settlement agreement, (Battery Council International v. EPA, 4th Cir. No. 84-1507) an amendment to the regulations was proposed on January 28, 1986 and promulgated on August 28, 1986. The final compliance date for the battery manufacturing categorical pretreatment standards was March 9, 1987 for existing sources and upon commencement of discharge for new sources.

be used to make categorization determinations because the codes are based on end use of the product and not the manufacturing processes.

2.2 PROCESS OPERATIONS

Manufacturing operations vary widely, depending on the particular battery application and the type of battery produced. Battery manufacturing is typically comprised of production of anodes, production of cathodes, and associated ancillary operations necessary to produce a battery such as battery assembly. These process operations are briefly discussed below:

> Anodes - Anodes, in their final or fully charged form in a battery are usually zerovalent metals. The active mass for anodes is prepared by directly cutting and drawing or stamping the pure metal or alloyed metal sheet, by mixing metal powders with or without electrolyte, by physically applying pastes of a compound of the anode metal to the support structure, or by precipitating a soluble salt of the metal onto a carrier or support structure. The final step in anode preparation for many types of batteries, especially rechargeable ones, is formation or charging of the active mass. Formation may be carried out on individual electrodes or on pairs of electrodes (anode and cathode) in a tank of suitable electrolyte. Most often the electrodes for a battery are formed in pairs and current is passed through the electrodes to charge them. For some battery types, charge-discharge cycling up to seven times is used for formation.

> Cathode Manufacturing - Although usually designated by metal type cathode active materials often consist of oxidized metals, such as lead peroxide or nickel hydroxide. Non-metals such as iodine (used in lithium-iodine batteries) and meta-dinitrobenzene (used in magnesium-ammonia reserve batteries) are other kinds of cathode active materials. Cathode active materials are weak electrical conductors and usually possess little mechanical strength. Therefore, most cathodes have a metallic current conduction support structure and conducting material, often carbon or nickel, incorporated into the active mass. The active material may be applied to the support as a paste, deposited in a porous structure by precipitation from a solution,

> fixed to the support as a compacted pellet, or may be dissolved in an electrolyte which has been immobilized in a porous inert structure. Formation processes for cathodes are similar to those used for anodes.

> Ancillary Operations - Ancillary operations are those operations unique to the battery manufacturing category that are not specifically included under anode or cathode fabrication. Ancillary operations are primarily associated with cell and battery assembly and chemical production of anode and cathode active materials. Ancillary operations also include battery washing (both intermediate and final product), and washing of equipment, floors, and operating personnel as well as some dry operations.

The reactive materials in most modern batteries include one or more of the following toxic metals: cadmium, lead, mercury, nickel, and zinc. These toxic metals are often found in wastewater discharges and solid wastes from battery plants. Water is used throughout the manufacturing process, specifically in preparation of electrolytes and electrode active masses, in deposition of active materials on electrode supporting structures, in charging electrodes and removing impurities, and in washing finished batteries, production equipment, and manufacturing areas.

2.3 SUBCATEGORIZATION

The battery manufacturing category was subcategorized based on anode material and electrolyte composition. The rationale for this subcategorization is that many battery manufacturers produce batteries with different anode-cathode pairs but with a common anode material. The seven subcategories to which this regulation applies are:

- Cadmium
- Calcium
- Lead

- Leclanche (zinc anode with an acid electrolyte)
- Lithium
- Magnesium
- Zinc (with alkaline electrolyte)

These subcategories are represented by Subparts A-G of the categorical standards.

These subcategories are further subdivided into manufacturing process elements frequently referred to as "building blocks" specific to basic manufacturing operations within the subcategory. Promulgated standards are specific to these elements. At the element level water use and pollutant characteristics can be related to a specific measure of production. This factor is referred to as a production normalizing parameter (PNP). The PNP may be different in the different subcategories or even different for each element. For example, in the case of plants subject to the lead subcategory standards, the PNP for all process elements for which discharge allowances are provided (except for the truck wash process element) is the total lead weight used (consumed) in the type of battery manufactured. The PNP for truck wash is the weight of lead in batteries (not total weight of batteries) moved in trucks. This does not apply to truck washing at plants that have battery cracking or secondary lead smelting which is covered under nonferrous metals manufacturing.

The seven subcategories, their manufacturing operations and resulting wastewater characteristics are described briefly in this section. The application of the battery manufacturing categorical standards may be difficult for those unfamiliar with the processes and terminology used. As a general guide, the Control

Authority should ask the manufacturer the questions listed in Table 2.1 to determine the applicable subcategories and standards. If further technical assistance is needed the Control Authority is encouraged to contact the EPA Industrial Technology Division project officer (Mary L. Belefski at (202) 382-7153).

2.3.1 Cadmium Subcategory

The Cadmium Subcategory encompasses the manufacture of all batteries in which cadmium is the reactive anode material. Cadmium cells currently manufactured are based on nickel-cadmium, silver-cadmium, and mercury-cadmium couples. Three general methods for producing anodes are employed:

1) The manufacture of pasted and pressed powder anodes by physical application of the solids;
2) Electrodeposited anodes produced by means of electrochemical precipitation of cadmium hydroxide from a cadmium salt solution;
3) Impregnated anodes manufactured by impregnation of cadmium solutions into porous structures and subsequent precipitation of cadmium hydroxide.

Five cathode manufacturing process elements are employed in this subcategory, three of which are specifically for production of nickel cathodes and two are for production of silver and mercury cathodes. They include:

(1) Nickel pressed powder cathodes
(2) Nickel electrodeposited cathodes
(3) Nickel impregnated cathodes
(4) Silver powder pressed cathodes
(5) Mercuric oxide powder pressed

TABLE 2.3

CALCIUM SUBCATEGORY ANALYSIS

Grouping	Element	Specific Wastewater Sources (Subelements)
Anode Manufacture	Vapor Deposited	• No Process Wastewater
	Fabricated	• No Process Wastewater
Cathode Manufacture	Calcium Chromate	• No Process Wastewater
	Tungstic Oxide	• No Process Wastewater
	Potassium Dichromate	• No Process Wastewater
Ancillary	Heating Component Production:	
	Heat Paper	• Slurry Preparation • Filtrate Discharge
	Heat Pellet	• No Process Wastewater
	Cell Testing	• Leak Testing

much as possible. The most significant pollutants found in these wastewaters are chromium (especially hexavalent chromium from barium chromate) and asbestos. Both of these pollutants are from raw materials used in the manufacture of heating components.

2.3.3 Lead Subcategory

The Lead Subcategory, which is the subcategory with the largest number of plants and volume of production, includes batteries which use lead anodes, lead peroxide cathodes, and acid electrolytes. The subcategory includes lead acid reserve cells and the more familiar lead acid storage batteries. Lead acid batteries include cells with immobilized electrolytes for use in portable devices; batteries used for automotive starting, lighting, and ignition (SLI) applications; and a variety of batteries designed for industrial applications. Lead reserve batteries are similar to dehydrated plate lead batteries and are produced from lead electroformed on steel which is immersed in an acid electrolyte when placed in use.

SLI and industrial type batteries are manufactured and shipped as "dry-charged" (shipped without acid electrolyte) and "wet-charged" (shipped with acid electrolyte) units. Batteries shipped without electrolyte include damp-charged batteries (damp batteries) and dehydrated plate batteries (dehydrated batteries). Damp batteries are usually manufactured by charging the electrodes in the battery case after assembly (closed formation), and emptying the electrolyte before final assembly and shipping. Dehydrated batteries usually are manufactured by charging of the electrodes in open tanks (open formation) followed by rinsing and dehydration prior to assembly in the battery case. Wet-charged batteries are usually manufactured by closed formation processes, but can also be produced by open formation processes. Significant differences in manufacturing processes and subsequent process wastewater generation correspond to these product variations.

The manufacture of lead batteries includes the following steps (see Figure 2.3):

1) Grid or plate support structure manufacture
2) Leady oxide production
3) Paste preparation and application to provide the plate with a highly porous surface
4) Curing to ensure adequate paste strength and adhesion to the plate
5) Assembly of plates into groups or elements
6) Electrolyte addition as appropriate
7) Formation or charging (including plate soaking) which further binds the paste to the grid and renders the plate electrochemically active
8) Final assembly
9) Testing and repair if needed
10) Washing
11) Final shipment

Process steps (1) through (7) are anode and cathode operations while assembly, battery testing and repair, and battery washing are ancillary operations. Additional ancillary operations involved in the manufacture of lead batteries include floor and truck washing, laboratory testing, and personal hygiene activities. Personal hygiene activities include mandatory employee

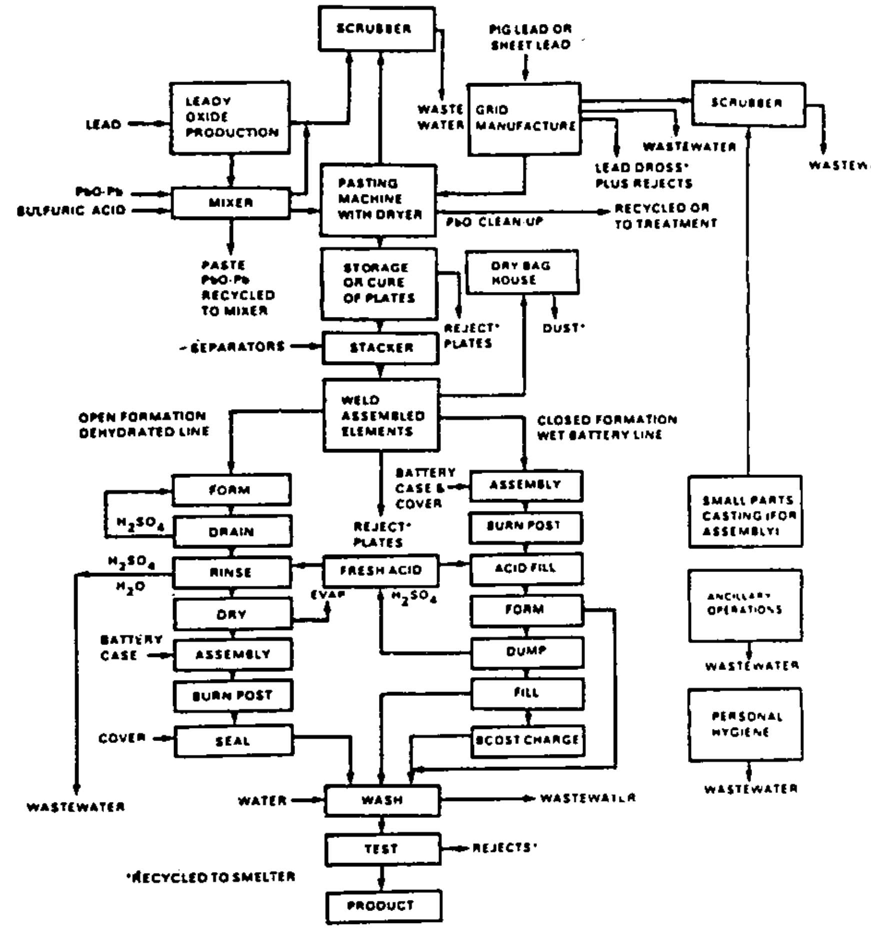

FIGURE 2.3

LEAD SUBCATEGORY GENERALIZED MANUFACTURING PROCESS handwashing, respirator washing, and laundering of employee work uniforms.

In general, process wastewater discharges result from the preparation and application of electrode active materials (steps 1-6 above), formation and charging (step 7), washing finished batteries (step 10 above), and from the various ancillary operations (floor and truck washing, laboratory testing, and personal hygiene activities). Table 2.4 is a summary of wastewater sources for each process in the lead subcategory. Wastewater from the manufacture of lead batteries is acidic as a result of contamination with sulfuric acid electrolyte and generally contains dissolved lead and suspended particulates (including lead solids).

2.3.4 Leclanche Subcategory

The Leclanche Subcategory includes the manufacture of batteries that consist of a zinc anode, a carbon-manganese dioxide cathode, and an acid electrolyte (zinc chloride or zinc chloride-ammonium chloride). Batteries in this subcategory contain mercury which is used to amalgamate the zinc and reduce internal corrosion. The mercury is generally added to the cell electrolyte or separator. Types of batteries include the familiar conventional carbon-zinc Leclanche cells or "dry cells" (cylindrical, rectangular and flat), silver chloride-zinc cells (less than 0.01 percent of total production in the subcategory), carbon-zinc air cells, and foliar batteries. Carbon-zinc air depolarized batteries which use alkaline electrolytes are included in the Zinc Subcategory.

TABLE 2.4

LEAD SUBCATEGORY ANALYSIS

Grouping/Element	Specific Wastewater Sources (Subelements)
Anodes and Cathodes	
Leady Oxide Production	• Ball Mill Shell Cooling • Scrubber*
Grid Manufacture	
Grid Casting Mold Release Formulation Direct Chill Casting Lead Rolling	• Scrubber • Equipment Wash • Contact Cooling • Spent Emulsion Solution
Paste Preparation and Application	• Equipment and Floor Area Cleanup • Scrubber*
Curing	• Steam Curing • Humidity Curing
Closed Formation (In Case)	
Single Fill	• Contact Cooling • Formation Area Washdown • Scrubber*
Double Fill	• Contact Cooling • Scrubber • Product Rinse • Formation Area Washdown
Fill and Dump	• Contact Cooling • Scrubber* • Product Rinse • Formation Area Washdown
Open Formation (Out of Case)	
Wet	• Plate Rinse • Spent Formation Electrolyte • Formation Area Washdown • Scrubber*

3.1 END-OF-PIPE TREATMENT TECHNOLOGIES

The major end-of-pipe technologies for treating battery manufacturing wastewaters are: oil skimming, chromium reduction, chemical precipitation of dissolved metals, settling of suspended solids, pressure filtration, and granular bed filtration. Although not considered a major treatment technology for the battery manufacturing category, membrane or polishing filtration is often used following precipitation and sedimentation for more consistent metals removal.

Skimming is used in battery manufacturing to remove free oil used as a preservative or forming lubricant for various metal battery parts and in lubricants used for drive mechanisms and other machinery. Skimming removes pollutants with a specific gravity less than water and is often found in conjunction with air flotation or clarification to increase its effectiveness. Common skimming mechanisms include the rotating drum type, a belt type skimmer (which pulls a belt vertically through the water thereby collecting oil), and API separators (which skim a floating oil layer from the surface of the wastewater).

Chemical reduction of chromium is used in battery manufacturing for treating chromium-bearing wastewater, primarily from heat paper production in the calcium, lithium and magnesium subcategories. The treatment of hexavalent chromium involves reducing the hexavalent chromium to its trivalent form and subsequent removal with a conventional precipitation-solids removal system. Reduced chromium is removed from solution in conjunction with other metallic salts by alkaline precipitation.

In most cases, gaseous sulfur dioxide is used as the reducing agent.

Chemical precipitation, followed by sedimentation, filtration, or centrifugation, is used in battery manufacturing for removal of dissolved metals. Chemical precipitation involves adding a reagent to wastewater that will transform dissolved metals to a non-dissolved state, permitting them to be removed by settling, filtration or centrifugation. Reagents commonly used are:

1) Alkaline compounds, such as lime or sodium hydroxide, precipitate metals as hydroxides;
2) Soluble sulfides, such as hydrogen sulfide or sodium sulfide, and insoluble sulfides such as ferrous sulfide, precipitate metals as sulfides;
3) Ferrous sulfate or zinc sulfate precipitate cyanide as a ferro or zinc ferricyanide complex;
4) Carbonates precipitate metals directly as carbonates, and carbon dioxide converts hydroxides to carbonates.

The performance of chemical precipitation depends on the following: maintenance of an appropriate pH (usually alkaline) throughout the precipitation reaction and subsequent settling; the addition of a sufficient excess of treatment ions to drive the precipitation reaction to completion; the addition of an adequate supply of sacrificial ions (such as aluminum or iron) to ensure precipitation and removal of specific target ions; and effective removal of the precipitated solids using appropriate solids removal technologies.

Settling and clarification are used in battery manufacturing to remove precipitated metals. Settling removes solid particles from a liquid matrix by gravitational force. Settling is

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• Dilute Wastestream - Boiler blowdown, noncontact accomplished by reducing the velocity of the feed stream in a large volume tank or lagoon so that gravitational settling can occur. Settling is most often preceded by chemical precipitation which converts dissolved pollutants to a solid form and by coagulation of suspended precipitates into larger, faster settling particles (using coagulants or polyelectrolytic flocculants).

Pressure filtration is used in battery manufacturing for sludge dewatering and for direct removal of precipitated and other suspended solids from wastewater. Pressure filtration works by pumping the water through a filter material which is impenetrable to the solid phase thus separating the solids from the water.

Granular bed filtration using filter media such as silica sand, anthracite coal, and garnet supported by gravel are commonly used to remove suspended solids and colloidal particles. Wastewater treatment plants often use granular bed filters for polishing after clarification, sedimentation, or similar operations. The classic granular bed filter operates by gravity flow, although pressure filters are also widely used.

3.2 IN-PROCESS CONTROL TECHNOLOGIES

In-process control technologies are intended to reduce or eliminate the amount of pollutants or the volume of wastewater requiring end-of-pipe treatment thereby improving the quality of the effluent discharge. The in-process technologies which are applicable to most battery manufacturing subcategories discussed here are waste segregation, water recycle and reuse, water use

reduction, process modification, and plant maintenance and good housekeeping. Specific application of these techniques varies among the battery manufacturing subcategories and some apply only to specific processing steps. Additional details are in Section VII of the final technical development documents for battery manufacturing.

Waste segregation of multiple process wastewater streams having significantly different chemical characteristics may lead to reductions in treatment costs and pollutant discharges. Battery manufacturing commonly produces waste streams with high concentrations of toxic metals, containing primarily suspended solids, and others that are quite dilute. Separation of these individual process wastestreams may improve the quality of the effluent discharge since treatment of more concentrated wastestreams is usually more efficient than treatment of dilute streams. Similarly, separation of noncontact cooling water from process wastewater prevents dilution of the process wastes and maintains the purity of the noncontact stream for subsequent reuse or discharge.

Wastewater recycle and reuse are frequently possible without treatment or with minimum treatment of the wastewater, and therefore are effective in reducing pollutant discharges and overall treatment costs. Recycle applies to the return of process wastewater usually after treatment to the process or processes from which it originated, and reuse applies to the use of wastewater from one process into another process. The most frequently recycled wastestreams include air pollution control scrubber discharges, and wastewater from equipment and area cleaning. In addition, wastewater from some product rinsing operations and contact cooling waters are available for recycle or reuse.

Water use reduction includes reducing the volume of wastewater discharge by simply eliminating excess flow and unnecessary water use. Often this can be accomplished by employing automatic shutoff valves or manual controls to turn off water flows when production units are inactive and by implementation of more effective water use in some process operations, particularly in rinsing operations and in equipment and area cleanup. Rinsing efficiency can be increased by the use of multi-stage and countercurrent cascade rinsing. Additional reduction in process wastewater discharge may also be achieved by the substitution of dry air pollution control devices such as baghouses for wet scrubbers where the emissions requiring control are amenable to these techniques.

Process modifications deal with process alternatives which significantly affect the quantity and quality of wastewater produced. In general, changes in electrolyte addition techniques and changes in electrode formation processes are process changes found most frequently in the battery manufacturing category. In addition, changes in amalgamation procedures and improvements in process control to reduce rework requirements are viable techniques to reduce wastewater discharges. Most process modifications to reduce pollutant discharges are specific to individual subcategories; however, one process modification applicable to several subcategories is the substitution of alternative formulations for cell wash materials containing chromate and cyanide.

This substitution reduces or eliminates these pollutants from the process wastewater.

Plant maintenance and good housekeeping practices can significantly reduce pollutant loadings at battery manufacturing plants due to the large quantities of toxic materials used as active materials in battery electrodes. These materials are handled at battery manufacturing plants and may be spilled in production areas. The water used in the cleaning of spills may contribute significantly to wastewater discharges. Good housekeeping includes floor maintenance and treatment, preventing leaks and spills, and cleaning up leaks and spills which cannot be avoided as soon as possible.