

US EPA ARCHIVE DOCUMENT

**CADMIUM**

**A. Commodity Summary**

Four companies are responsible for producing all of the domestic primary cadmium. According to the U.S. Bureau of Mines, cadmium is used in batteries, 71%; pigments, 10%; coating and plating, 8%; stabilizers for engineering plastics and similar synthetic products, 5%; and alloys and other miscellaneous uses, 6%.<sup>1</sup>

Cadmium is produced mainly as a byproduct of refining zinc metal from sulfide ore concentrates. It is also produced as a byproduct of beneficiating and refining lead ores or complex copper-zinc ores. Cadmium minerals are not found alone in commercially viable deposits. Greenockite (CdS) is the only cadmium mineral of importance. It is not found in any isolated deposits, but is nearly always associated with sphalerite (ZnS).<sup>2</sup>

Exhibit 1 shows the names and locations of the four primary cadmium producers. Three of the four companies (Big River Zinc Corporation, ZCA, and Jersey Miniere Zinc Company) recover cadmium as a byproduct of smelting domestic and imported zinc concentrates. The fourth company (ASARCO) recovered cadmium from other sources such as lead smelter baghouse dust.<sup>3</sup>

**EXHIBIT 1**

**SUMMARY OF CADMIUM PRODUCING FACILITIES**

Facility Name	Location
ASARCO	Denver, CO
Big River Zinc Corporation	Sauget, IL
Jersey Miniere Zinc Company	Clarksville, TN
ZCA	Bartlesville, OK

**B. Generalized Process Description**

**1. Discussion of Typical Production Processes**

Cadmium is mainly a byproduct of the production of zinc metal from sulfide ore concentrates. The mined zinc ores are crushed and ground to liberate the zinc sulfide particles from the waste host rock. The ground ore is usually treated by a differential flotation process to separate the zinc-bearing particles from the waste rock, yielding a high-grade zinc concentrate and waste tailings. About 90% to 98% of the cadmium present in zinc ores is recovered in the mining and beneficiating stages of the extraction process. Zinc concentrate is converted from zinc sulfide to zinc oxide by roasting, and at the same time most of the sulfur is removed as sulfur dioxide. The sulfur dioxide offgas is stripped of all entrapped dust and other impurities and then converted to sulfuric acid in an acid plant.<sup>4</sup> Cadmium is recovered from zinc and zinc lead concentrates as precipitates from solution (hydrometallurgical process) or as cadmium-lead fume (pyrometallurgical process), respectively, as shown in Exhibit 2. Cadmium may also be recovered as a byproduct of beneficiating and refining lead ores or complex copper-zinc ores.

**2. Generalized Process Flow**

<sup>1</sup> Peter Kuck, "Cadmium," from Mineral Commodity Summaries, U.S. Bureau of Mines, 1995, pp. 36-37.

<sup>2</sup> Thomas O. Llewellyn, "Cadmium," from Minerals Yearbook Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, pp. 271-276.

<sup>3</sup> Ibid.

<sup>4</sup> U.S. Environmental Protection Agency, "Cadmium," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-64 - 3-71.

## **Cadmium from Zinc**

### Hydrometallurgical Process

The hydrometallurgical process is used to recover cadmium as a precipitate. In this process, cadmium, copper, and zinc are dissolved in the sulfuric acid leach of the roasted zinc ore. Copper and cadmium are among the most common interfering impurities that are removed before the purified solution is subjected to electrolysis for zinc recovery. Most of the cadmium is precipitated using a zinc dust addition. The purified zinc sulfate solution is sent to the cellroom, and metallic zinc is recovered from the solution by electrowinning. The cadmium precipitate is sent to the cadmium plant where it is filtered and pressed into a cake containing cadmium, zinc, and minor amounts of copper and lead. Impurities are separated and a sufficiently pure cadmium sponge is dissolved in sulfuric acid. Metallic cadmium is recovered by electrolysis of this solution where cadmium is deposited on cathodes. After deposition, the cathodes are removed from the cells and stripped and the cadmium metal is melted and cast into shapes. Exhibit 3 presents a process flow diagram of the production of cadmium from zinc.<sup>5</sup>

### Pyrometallurgical Process

During the pyrometallurgical extraction of zinc, calcine from a roaster can be sintered with coke in a sintering machine to give a dense desulfurized product. The sintering operation results in considerable volatilization of cadmium and lead compounds, enhanced by the presence of chloride, leading to a 90-99% recovery of cadmium. The fume and dust from the sintering machine are collected in a baghouse. Cadmium not removed during sintering and subsequent operations follows the zinc metal and often is recovered during zinc metal purification by distillation.<sup>6</sup>

The cadmium content in the feed to lead and copper smelters is lower than that generally encountered in zinc plants, and this necessitates upgrading the initial cadmium level in the fume by one or more refuming steps in a kiln or reverberatory furnace. The final fume may contain as much as 45% cadmium. Fumes usually require more processing and purification steps for cadmium recovery than do purification residues from electrolytic zinc plants. Galvanic precipitation is the most frequently adopted method for the final recovery of cadmium in pyrometallurgical plants, but electrolysis may also be used.<sup>7</sup>

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<sup>5</sup> Ibid.

<sup>6</sup> "Cadmium and Cadmium Alloys," Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. IV, 1993, pp. 749- 754.

<sup>7</sup> Ibid.

**EXHIBIT 2**  
**PRELIMINARY CADMIUM ROASTING PROCESSES**

Graphic Not Available.

Source: Kirk-Othmer Encyclopedia of Chemical Technology, 1992, Vol. IV, pp. 749-754.

**EXHIBIT 3**  
**HYDROMETALLURGICAL PROCESS**

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-64 - 3-71.

**EXHIBIT 4**  
**PYROMETALLURGICAL PROCESS**

Graphic Not Available.

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-64 - 3-71.

Exhibit 4 presents a process flow diagram of cadmium recovery from cadmium bearing fumes. Depending on composition, the fume may have to be roasted with or without sulfuric acid or oxidized using sodium chlorate or chlorine in order to convert cadmium into a water- or acid-soluble form and to eliminate volatile constituents. However the leach solution is obtained, it must generally be purified to remove arsenic, iron, copper, thallium, and lead. The cadmium may also be galvanically precipitated from the leach solution and then redissolved (see Exhibit 5).<sup>8</sup>

Alternative 2 in Exhibit 5 indicates the most common method for the recovery of cadmium from purified leach solution by galvanic displacement with zinc in the form of dust, sheets, or even rods or rectangular anodes. The final processing depends on the grade of zinc. In most cases, the pH for galvanic precipitation is below 2, although one plant operates at pH 6.2. In most plants, the final cadmium sponge is washed to remove soluble impurities, and then compacted by briquetting. The briquettes may be melted under a flux of sodium hydroxide or ammonium chloride or be distilled for final purification.<sup>9</sup>

Electrolysis is the third alternative for cadmium recovery. Exhibit 6 presents a process flow diagram of this operation. The electrolysis may be operated on a semi-continuous basis with the cadmium eventually being stripped completely from the electrolyte, which is then discarded after suitable treatment. Instead of the usual silver-lead anodes, high silicon-iron anodes, such as Duriron, are commonly used.<sup>10</sup>

### **Cadmium from Lead**

Cadmium may also be obtained from flue dust collected at lead or copper smelters. Concentrates of copper, and especially lead, contain considerable amounts of cadmium. In copper smelters, the flue dusts are collected and recycled through the smelter system to upgrade the cadmium content. At the lead smelters the cadmium is fumed off and collected in the blast furnace baghouses. The baghouse dust is recycled to upgrade the cadmium content and is later used as feed material for the cadmium refinery plant.<sup>11</sup>

The cadmium upgraded dusts are charged into a tank and dissolved with sulfuric acid. The resultant solution is filtered to remove impurities and to obtain a purified cadmium sulfate solution. Next, metallic cadmium, called sponge because of its appearance, is precipitated from the solution using zinc dust. The sponge is usually briquetted, remelted, and cast into ingots.

Some plants produce cadmium oxide and/or metallic cadmium powder. Cadmium oxide is produced by melting the ingots and keeping a controlled oxidizing atmosphere in the retort. To produce metal powder, the melted ingots in the retort are kept under an inert atmosphere while cadmium is distilled into a condenser as metallic powder.<sup>12</sup>

### **3. Identification/Discussion of Novel (or otherwise distinct) Process(es)**

None identified.

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<sup>8</sup> Ibid.

<sup>9</sup> Ibid.

<sup>10</sup> Ibid.

<sup>11</sup> Thomas Llewellyn, 1992, Op. Cit., pp. 271-276.

<sup>12</sup> Ibid.

**EXHIBIT 5**  
**GALVANIC PRECIPITATION WITH ZINC**  
**(Alternatives 1 & 2)**

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-64 - 3-71.



**EXHIBIT 6**  
**ELECTROLYSIS**  
**(Alternative 3)**

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-64 - 3-71.

#### 4. Beneficiation/Processing Boundaries

Since cadmium is recovered as a by-product of other metals, all of the wastes generated during cadmium recovery are mineral processing wastes. For a description of where the beneficiation/processing boundary occurs for this mineral commodity, see the reports for zinc and lead presented elsewhere in this document.

#### C. Process Waste Streams

##### 1. Extraction/Beneficiation Wastes

###### Waste tailings.

##### 2. Mineral Processing Wastes

Since cadmium is toxic to humans and certain other living organisms, care must be taken during the production, use, and disposal of cadmium and its compounds to avoid the dispersal of cadmium fumes and dusts or the release of cadmium-bearing effluents into the environment so that exposure is minimized.<sup>13</sup> Listed below are possible waste streams from cadmium production. Generally, all wastes are recycled or treated with other refinery wastes.

#### Hydrometallurgical Process

**Copper removal filter cake.** Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for cadmium. This waste may be recycled and is classified as a byproduct.

**Post-leach filter cake.** Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for cadmium. This waste may be recycled to extraction/beneficiation units and is classified as a byproduct.

**Spent electrolyte** may contain thallic sulfate. Information regarding thallium removal from the spent electrolyte remains unclear. However, according to the U.S. Bureau of Mines, there was no domestic production of thallium metal in 1993; suggesting that thallium is not recovered domestically from cadmium production operations. However, sludges from cadmium processing which are used for recovery of metals such as germanium may contain thallium. Since there is no domestic production of germanium, the thallium contained in these sludges may be recovered in other countries.<sup>14</sup> Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity for cadmium and corrosivity.

#### Pyrometallurgical Process

**Copper sulfide and lead sulfate filter cakes.** Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for cadmium and lead. This waste may be recycled and is classified as a byproduct.

**Iron containing impurities.** Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for cadmium.

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<sup>13</sup> Patricia A. Plunkert, "Cadmium," from Mineral Facts and Problems, U.S. Bureau of Mines, 1985, pp. 111-119.

<sup>14</sup> Personal communication between Peter Kuck, U.S. Bureau of Mines and ICF Incorporated, October 12, 1994.

**Lead sulfate waste (solid).** Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for cadmium and lead. This waste may be recycled and is classified as a byproduct.

**Spent leach solution.** Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristics of toxicity for arsenic, cadmium, and lead and corrosivity. This waste may be recycled and is classified as a spent material.

**Spent purification solution.** Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristics of toxicity for cadmium and corrosivity.

**Scrubber wastewater.** Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristics of toxicity for cadmium and corrosivity. This waste may be recycled and is classified as a spent material.

#### **Galvanic Precipitation**

**Caustic washwater solution.** Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristics of toxicity for cadmium and corrosivity. This waste may be recycled and is classified as a spent material.

**Zinc precipitate.** Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for cadmium. This waste may be recycled and is classified as a byproduct.

#### **D. Ancillary Hazardous Wastes**

Ancillary hazardous wastes may be generated at on-site laboratories, and may include used chemicals and liquid samples. Other hazardous wastes may include spent solvents (e.g., petroleum naphtha), acidic tank cleaning wastes, and polychlorinated biphenyls from electrical transformers and capacitors. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, waste oil (which may or may not be hazardous), and other lubricants.

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