Secondary Lead Smelting
Secondary Lead Smelting Objectives

- Describe the basic smelting process terms: smelting, refining, and alloying
- List key chemicals associated with secondary lead smelting
- Define volatility temperature, volatile metals, and metals partitioning
Secondary Lead Smelting Objectives (cont.)

- List major modes of release to the environment

- Identify analytical methods useful for detecting secondary lead smelting contaminants in the environment
Process Overview

- SIC: 3341; NAICS: 331492

- U.S. lead consumption: 1.8 million metric tons per year (2004)
  - 62% of which is met by secondary lead industry

- Worldwide consumption: 9.6 million metric tons per year (2010)
  - 51% of which is met by secondary lead industry
Process Overview

- SIC: 3341; NAICS: 331492

- U.S. lead consumption is 1.4 million metric tons per year (1993)

- 72% of demand is met by secondary lead industry
• Total employment: 2300 (1993)
  – 1700 by secondary smelters and refiners
• 53 active secondary lead smelters in U.S. (1991)
Process Overview (cont.)

- Largest worldwide use of lead is for batteries (80%)
  - 95% of which are recycled

- 15 active secondary lead smelters in U.S. (2011)
  - In 1991, there were 53
Smelting: Conversion of oxidized metal species into metallic (zero valence) form

Process requires:

- High temperatures (1260°C)
- Reducing agents
- Exclusion of oxygen
Refining: Separation of impurities from primary metal

Process requires:

- Melting temperatures (327.5°C)
- Refining agents
- Physical separation of insoluble layers
Alloying:

Addition of ingredients to obtain desirable product properties

Process requires:

– Melting temperatures

– Alloying agents

– May occur during refining step
<table>
<thead>
<tr>
<th>Key Chemicals</th>
<th>2011 ATSDR Rank</th>
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<tbody>
<tr>
<td>Arsenic</td>
<td>1</td>
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<tr>
<td>Lead</td>
<td>2</td>
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<tr>
<td>Cadmium</td>
<td>7</td>
</tr>
<tr>
<td>Zinc</td>
<td>75</td>
</tr>
<tr>
<td>Antimony</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Copper</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Tin</td>
<td>&gt;100</td>
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</tbody>
</table>
Standard Process Schematic

LEAD PARTICULATE
SULFUR DIOXIDE

LEAD-CONTAINING
SCRAP AND SLAGS

LIMESTONE, COKE,
SCRAP IRON, AIR,
ALLOYING AGENTS

PARTICULATE METALS,
DISSOLVED METALS

SOFT LEAD, ANTIMONIAL LEAD,
LEAD ALLOYS

SLAG, DROSS, EMISSION
CONTROL DUSTS (REUSED)

SLAG, DROSS, EMISSION
CONTROL DUSTS (K069)
Process Details

Reverberatory or blast furnace

- 1260°C
- Burnout
- Sweating
- Slagging
Reverberatory Furnace
Refining Casts
Environmental Chemistry

Metals partitioning

- Volatility temperature (VT)
- Vapor pressure $>10^{-6}$ atm
- Chlorine effect
- Volatile metals $\sim$ VT $<900^\circ$C
## Predicted Metals Volatility Temperatures

<table>
<thead>
<tr>
<th>Metal</th>
<th>With 0% Chlorine</th>
<th>With 10% Chlorine</th>
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<tbody>
<tr>
<td>Volatility Temperature (°C)</td>
<td>Principal Species</td>
<td>Volatility Temperature (°C)</td>
</tr>
<tr>
<td>Chromium</td>
<td>1613 CrO₂/CrO₃</td>
<td>1610 CrO₂/CrO₃</td>
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<tr>
<td>Nickel</td>
<td>1210 Ni(OH)₂</td>
<td>693 NiCl₂</td>
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<tr>
<td>Beryllium</td>
<td>1054 Be(OH)₂</td>
<td>1054 Be(OH)₂</td>
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<tr>
<td>Silver</td>
<td>904 Ag</td>
<td>627 AgCl</td>
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<tr>
<td>Barium</td>
<td>849 Ba(OH)₂</td>
<td>904 BaCl₂</td>
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<tr>
<td>Thallium</td>
<td>721 Tl₂O₃</td>
<td>138 TlOH</td>
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<tr>
<td>Antimony</td>
<td>660 Sb₂O₃</td>
<td>660 Sb₂O₃</td>
</tr>
<tr>
<td>Lead</td>
<td>627 PbO₂</td>
<td>B15 PbCl₄</td>
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<tr>
<td>Selenium</td>
<td>318 SeO₂</td>
<td>318 SeO₂</td>
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<tr>
<td>Cadmium</td>
<td>214 Cd</td>
<td>214 Cd</td>
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<tr>
<td>Osmium</td>
<td>41 OsO₄</td>
<td>41 OsO₄</td>
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<tr>
<td>Arsenic</td>
<td>32 As₂O₃</td>
<td>32 As₂O₃</td>
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<tr>
<td>Mercury</td>
<td>14 Hg</td>
<td>14 Hg</td>
</tr>
</tbody>
</table>

Source: EPA 1992
Modes of Release

Continuous emissions
  - Stack emissions
  - Emission control dusts/sludges
  - Slag, dross (K069)

Fugitive emissions
  - Fugitive dust
  - Seal leakage
  - Washdown dust and water
Modes of Release (cont.)

Soils

- Direct placement or burial
- Air deposition

Groundwater

- Limited migration potential

Surface water

- Mobilized particulate
- Limited solubility
### Analytical Considerations - Laboratory Methods for Lead

<table>
<thead>
<tr>
<th>Medium</th>
<th>Method</th>
<th>Detection Limit</th>
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</thead>
<tbody>
<tr>
<td>Water</td>
<td>Atomic absorption, ICP</td>
<td>0.001-0.1 mg/l</td>
</tr>
<tr>
<td>Soil</td>
<td>Atomic absorption, ICP</td>
<td>0.1-1.0 mg/kg</td>
</tr>
<tr>
<td>TCLP</td>
<td>Atomic absorption, ICP</td>
<td>0.001-0.1 mg/l</td>
</tr>
<tr>
<td>Medium</td>
<td>Method</td>
<td>Detection Limit</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Soil</td>
<td>X-ray fluorescence (XRF)</td>
<td>~10 mg/kg</td>
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<tr>
<td>Water</td>
<td>Photometric, Colorimetric test kits</td>
<td>1 ppm</td>
</tr>
</tbody>
</table>
Summary

- Secondary smelting utilizes secondary resources to convert or recover lead metal.
- Smelting furnaces and refining kettles are employed to reduce metallic species and to separate impurities.
- Air emissions of volatile metals and particulate dusts.
- Soils and surface water are primarily environmental receptors.