



# Toxicity, Availability and Extraction of the Metals Used in Pb-Free Solders

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Pb-Free Solder for Electronic, Optical, and MEMS Packaging Manufacturing

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# Presentation Outline

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- Project Goal and Scope
- Methodology
- Results
  - Toxicity and Public Health Effects
  - Availability and Supply of Raw Materials
  - Extraction/Production Processes
  - Overall Environmental Impact
- Conclusions

The background of the slide features a large, faint watermark of the University of Ontario seal. The seal is circular and contains the text "UNIVERSITY OF ONTARIO" around the top edge and "1827" at the bottom. In the center, there is a shield with various symbols, including a book and a lamp, and the motto "VERITAS LIBERABIT VOS" is visible.

# Project Goal

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Evaluate the environmental impact of lead-tin and lead-free solders, with a focus on toxicity, availability and impact of extraction.

# Project Scope

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- Compare six alloying metals, plus lead as a baseline.
- Develop an environmental impact metric for each of the following:
  - Toxicity and public health effects
  - Raw material availability and supply
  - Extraction and production processes
- Use a scoring model principle to develop a combined metric.

# Selected Metals for Analysis

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- Baseline
  - Lead
- Alternatives
  - Antimony
  - Bismuth
  - Copper
  - Indium
  - Silver
  - Tin

# Metrics Methodology - I

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- Toxicity and Public Health Effects
  - Bioaccumulative
  - Carcinogen
  - Birth Defects
  - EPA Drinking Water Standard
  - OSHA Permissible Exposure Limit

# Lead Toxicity

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- Lead occurs naturally in the environment.
- Most lead found in the environment comes from human activities:
  - motor vehicle exhaust
  - smelting of mined ores
  - manufacturing of lead-containing products
- Lead in the dissolved phase or released into the atmosphere is bioaccumulated by plants and animals.



# Public Health Impacts of Lead

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- Effects of Acute Exposure:
  - headache, nausea, vomiting, abdominal spasms, fatigue, sleep disturbances, weight loss, anemia, kidney damage, and pain in arms, legs and joints
- Effects of Chronic Exposure:
  - impair the functions of the nervous system, kidney and brain damage, and teratogenic, mutagenic effects and slow mental development in children
- Lead follows Calcium (Ca) in the body.

# Silver Toxicity and Public Health Impacts

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- Silver is released into the environment from the manufacture of photographic materials and the mining of silver.
- Silver metal is stable and insoluble, presents minimal environmental risk.
- Silver is bioaccumulated to a moderate extent in algae, fish and invertebrates.
- Chronic exposure may cause a bluish or grayish pigmentation to the skin, eyes and mucous membranes.
- Silver is not considered to be a human carcinogen and is not known to cause birth defects.

# Antimony Toxicity and Public Health Impacts

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- Antimony is released through mining of its ores and in the production of antimony metal and alloys.
- Antimony has not been found to bioaccumulate in plants and animals.
- Effects of Acute Exposure:
  - eye irritation and hair loss
- Effects of Chronic Exposure:
  - pneumoconiosis, altered electrocardiograms, stomach pain, diarrhea, vomiting, stomach ulcers, joint and muscle pain, anemia, and kidney damage
- Because of its limited use, little is known about the effects of a high environmental loading of antimony.

# Metrics Methodology - II

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- Raw Material Availability and Supply
  - Abundance in Earth's Crust
  - World Production
  - World Reserves
  - Price per Pound

# Metrics Methodology - III

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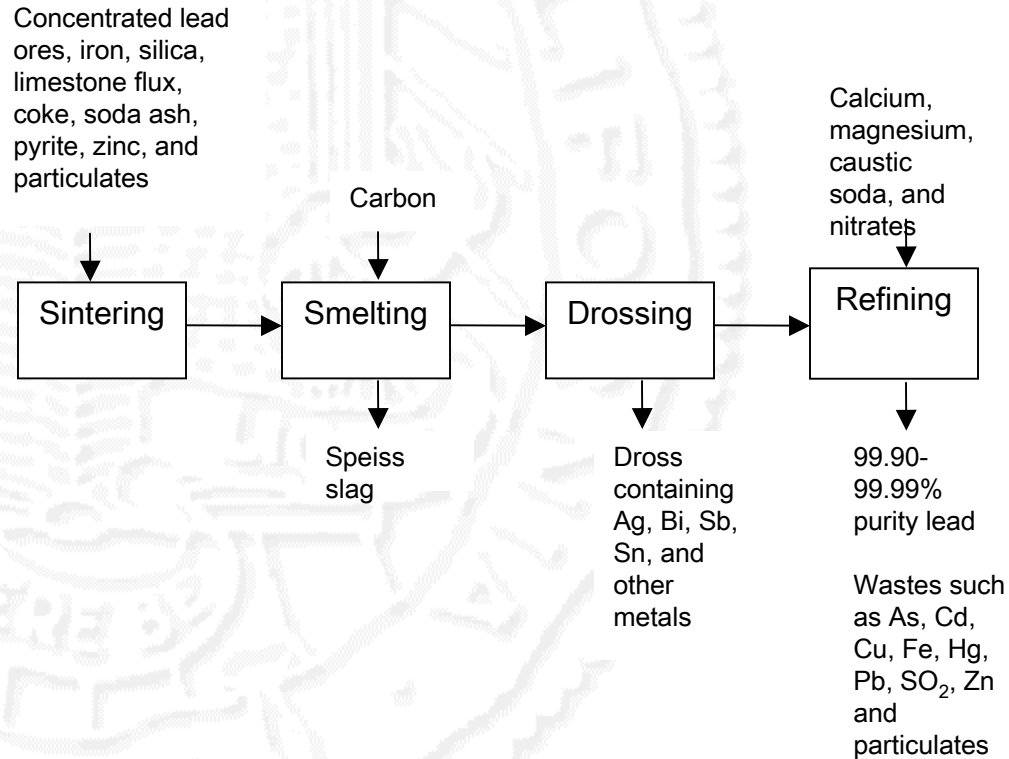
- Extraction and Production Processes
  - Energy Required for Metal Extraction
  - Hazardous Material or Strong Acid in Waste
  - Criteria Pollutants (Clean Air Act)

# Lead Production Process

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- Lead ores are sintered and sent to the smelter.
- A molten layer of lead bullion from the smelter gets sent to the dressing process.
- It is then refined with a pyrometallurgical process to lead alloys or casts.
- The speiss and matte layers from the smelter are sold off to copper smelters.
- Slags are stored or recycled.

# Lead Extraction Process



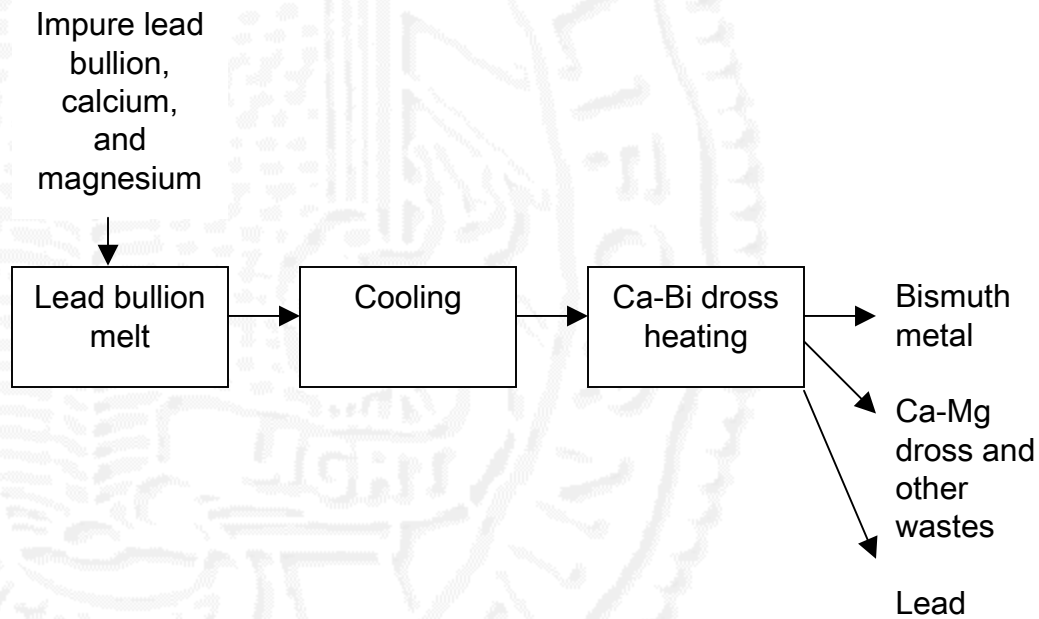
# Bismuth Production Process

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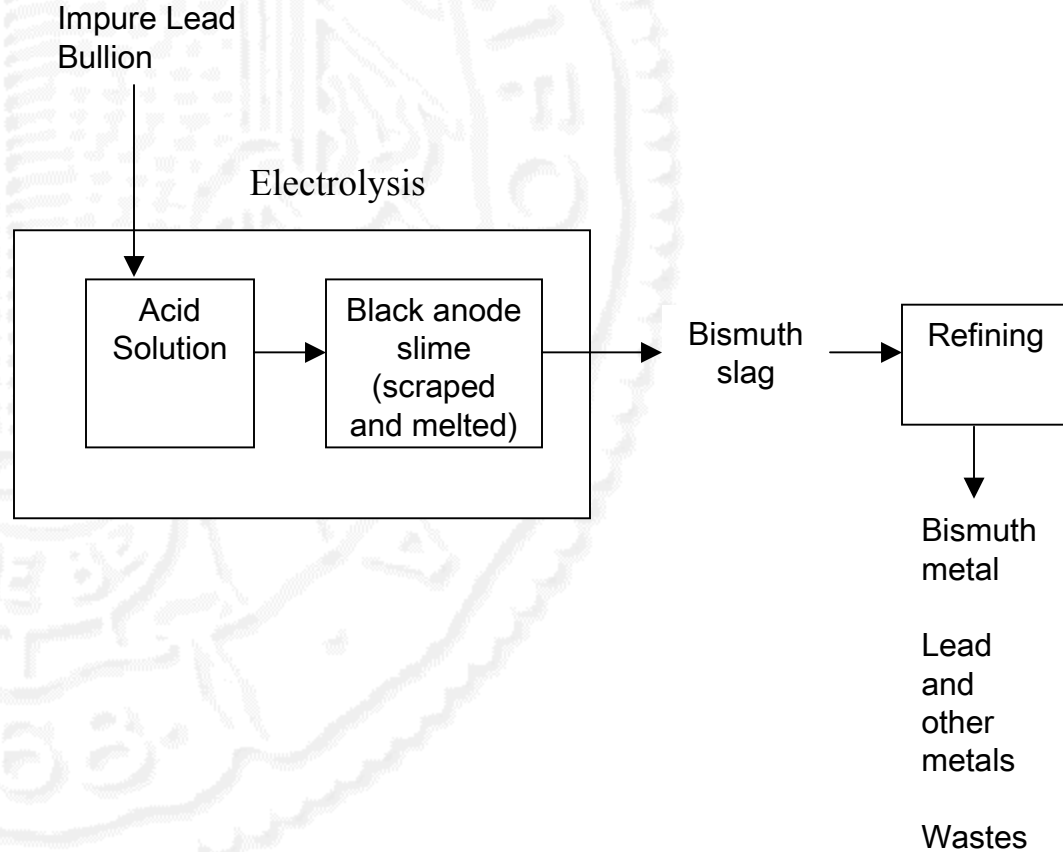
- Bismuth extraction is linked to lead and copper refining.
- Bismuth can be refined using either of the following two processes:
  - the Betterton-Kroll process
  - the Betts Electrolytic process



# Betterton-Kroll Method



# Betts Electrolysis Method



# Toxicity Metric

<b>Metal</b>	<b>Bio-accumulative</b>	<b>Carcinogen</b>	<b>Birth Defects</b>	<b>EPA Drinking Water Standard (mg/L)</b>	<b>OSHA PEL (mg/m<sup>3</sup>)</b>
<b>Lead</b>	Yes	Yes	Yes	0.015	0.05
<b>Silver</b>	Yes	No	No	0.05	0.01
<b>Antimony</b>	No	Yes (Cal EPA)	No	0.006	0.5
<b>Indium</b>	No	No	Yes (lab animals)	None	0.1
<b>Bismuth</b>	No	No	No	0.05	None
<b>Copper</b>	No	No	No	1.0	0.1
<b>Tin</b>	No	No	No	None	2.0

# Availability and Supply Metric

<b>Metal</b>	<b>Abundance in Earth's Crust (ppm)</b>	<b>World Production (metric tons)</b>	<b>World Reserves (metric tons)</b>	<b>Price per Pound (\$)</b>
<b>Copper</b>	60-70	37.9 million	>340 million	\$0.70
<b>Lead</b>	12	8.9 million	1.4 billion	\$0.05
<b>Tin</b>	2	431,500	10,700	\$3.10
<b>Antimony</b>	0.2-0.5	140,000	2.1 million	\$0.72
<b>Silver</b>	0.1	16,400	4,372*	\$80.79
<b>Bismuth</b>	0.1	7,800	0	\$3.60
<b>Indium</b>	0.1	240	0	\$136.35

*\*U.S. Reserves*

# Extraction Metric

Metal	Energy Required for Metal Extraction (MJ/kg)	Hazardous Material or Strong Acid in Waste	Criteria Pollutants
Silver	3024	Arsenic, cadmium, lead, mercury, sulfuric acid, possibly cyanide	Carbon monoxide, lead, nitrogen oxides, particulates, sulfur dioxide
Tin	240	Strong acid	Carbon monoxide, nitrogen oxides, particulates, sulfur dioxide
Indium*	>73.7*	Arsenic, cadmium, lead, mercury, sulfuric acid, hydrochloric acid	Carbon monoxide, lead, nitrogen oxides, particulates sulfur dioxide
Antimony*	>73.7*	Arsenic, cadmium, lead, mercury, sulfuric acid	Carbon monoxide, lead, nitrogen oxides, particulates sulfur dioxide
Bismuth*	>73.7*	Arsenic, cadmium, lead, mercury, sulfuric acid	Carbon monoxide, lead, nitrogen oxides, particulates sulfur dioxide
Lead	73.7	Arsenic, cadmium, lead, mercury, sulfuric acid	Carbon monoxide, lead, nitrogen oxides, particulates sulfur dioxide
Copper	69.0	Strong acid	Carbon monoxide, nitrogen oxides, particulates, sulfur dioxide

*\*Antimony, bismuth, and indium refining is a by-product of lead production, values for these metals are estimated.*

# Combined Metric Methodology & Assumptions

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- Methodology:
  - Scoring Model as used in decision analysis.
- Assumptions:
  - Each metric is of equal weight.
  - The metals are ranked with an equal spacing for each metric.
  - Ranking values are summed to generate an overall score and rank.

# Combined Metric

Metal	Toxicity Metric Ranking	Availability and Supply Metric Ranking	Environmental Impact of Extraction Metric Ranking	Sum of the Metric Rankings	Final Rank of Metal
Lead	1	6	6	13	<b>5</b>
Antimony	3	4	4	11	<b>3</b>
Bismuth	5	2	5	12	<b>4</b>
Copper	6	7	7	20	<b>7</b>
Indium	4	1	3	8	<b>2</b>
Silver	2	3	1	6	<b>1</b>
Tin	7	5	2	14	<b>6</b>

*1 = Least Desirable; 7 = Most Desirable*

# Conclusions

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- Metrics were developed to compare the toxicity and public health impact, the availability and supply of raw materials, and the impact of the extraction processes for lead and its alternatives.
- Although lead is the worst metal in terms of toxicity and public health, several of the alternatives have limited availability, high prices and significant environmental impact during extraction.
- Metals used in lead-free solders should be further evaluated not only for materials properties, but also with respect to their toxicity and environmental impact.



# Future Work Needed

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- The long-term and high-loading environmental impacts of several alternative lead-free alloys need to be better understood.
- Waste management considerations such as reuse, recycling, and disposal also need to be analyzed in depth.

A large, faint watermark of the University of California seal is visible in the background. The seal features a central shield with a book and a sun, surrounded by the text "UNIVERSITY OF CALIFORNIA" and the year "1868".

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Thank you for your attention.

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