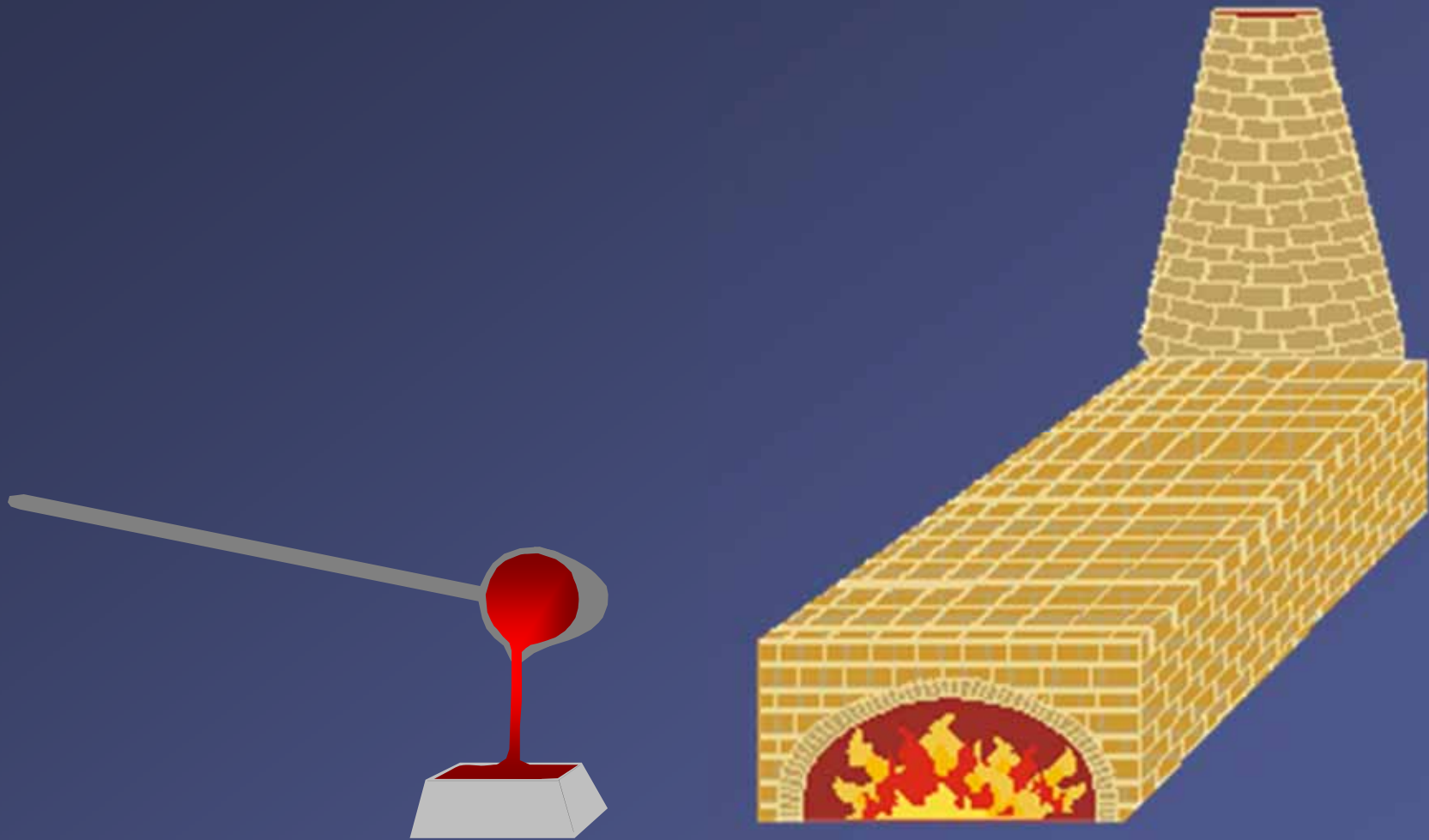


Secondary Lead Smelting



Secondary Lead Smelting Objectives

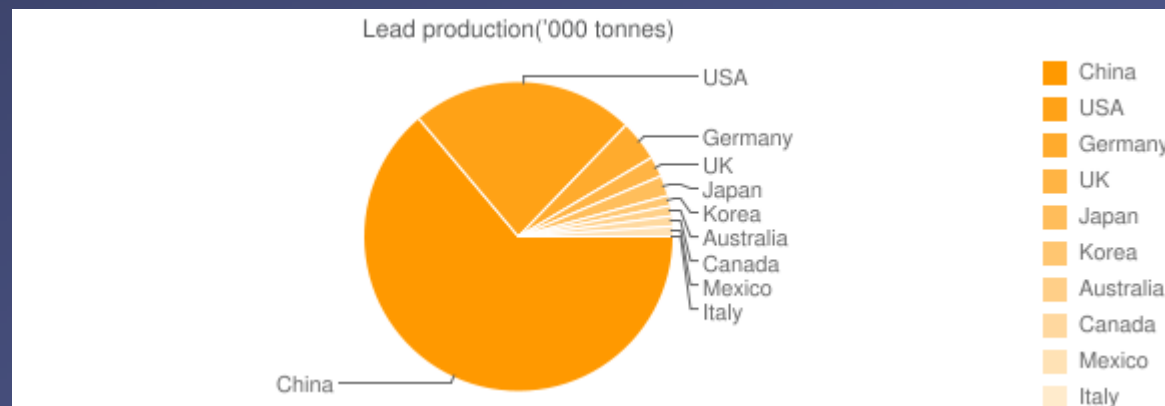
- Describe the basic smelting process terms: smelting, refining, and alloying
- List key chemicals associated with secondary lead smelting
- Define volatility temperature, volatile metals, and metals partitioning

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

Process Overview (cont.)

- 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



Process Overview (cont.)

Smelting: Conversion of oxidized metal species into metallic (zero valence) form

Process requires:

- High temperatures (1260°C)
- Reducing agents
- Exclusion of oxygen

Process Overview (cont.)

Refining: Separation of impurities from primary metal

Process requires:

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

Process Overview (cont.)

Alloying:

Addition of ingredients to obtain desirable product properties

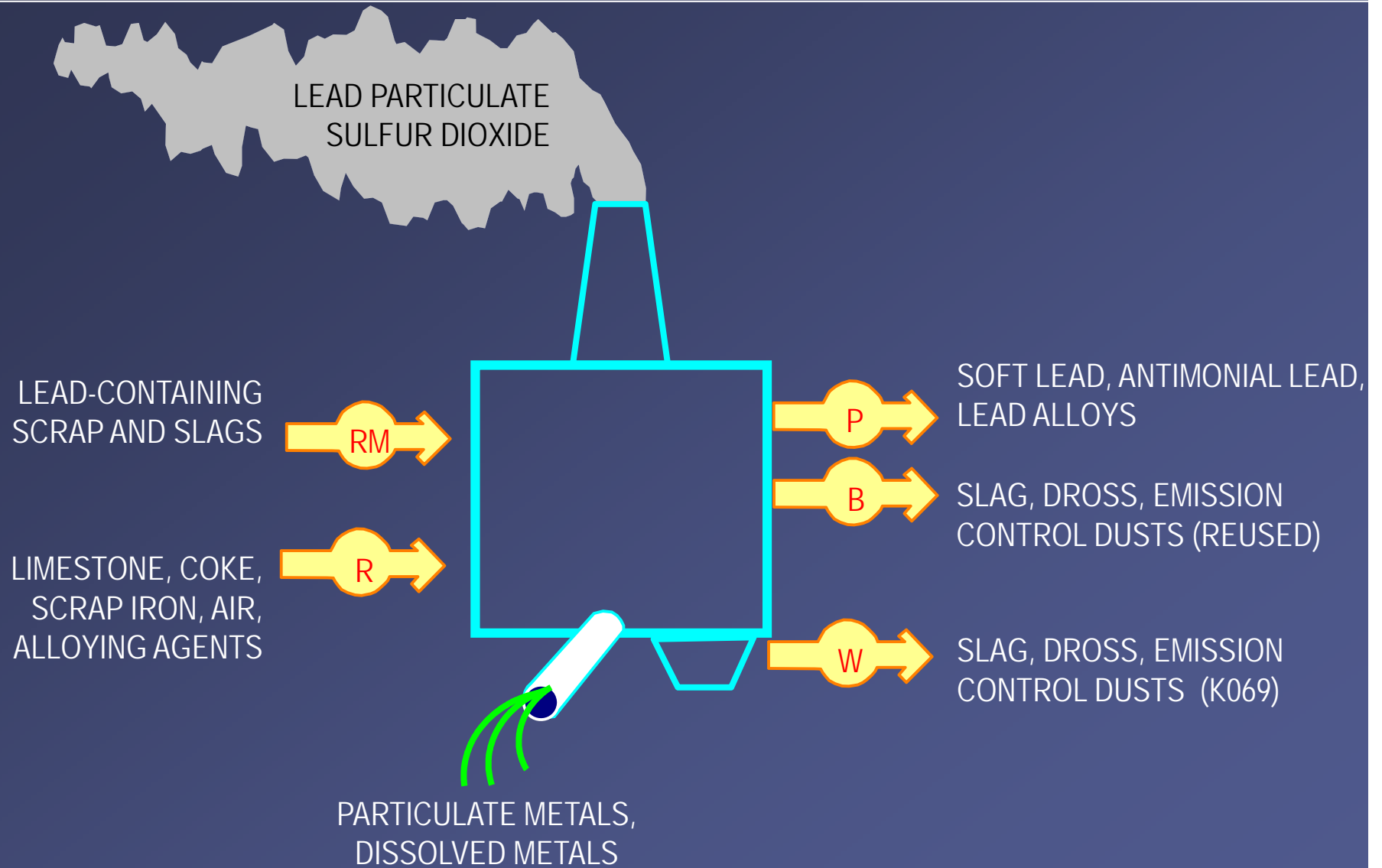
Process requires:

- Melting temperatures
- Alloying agents
- May occur during refining step

Key Chemicals

	<u>2011 ATSDR Rank</u>
Arsenic	1
Lead	2
Cadmium	7
Zinc	75
Antimony	>100
Copper	>100
Tin	>100

Standard Process Schematic





Process Details

Reverberatory or blast furnace

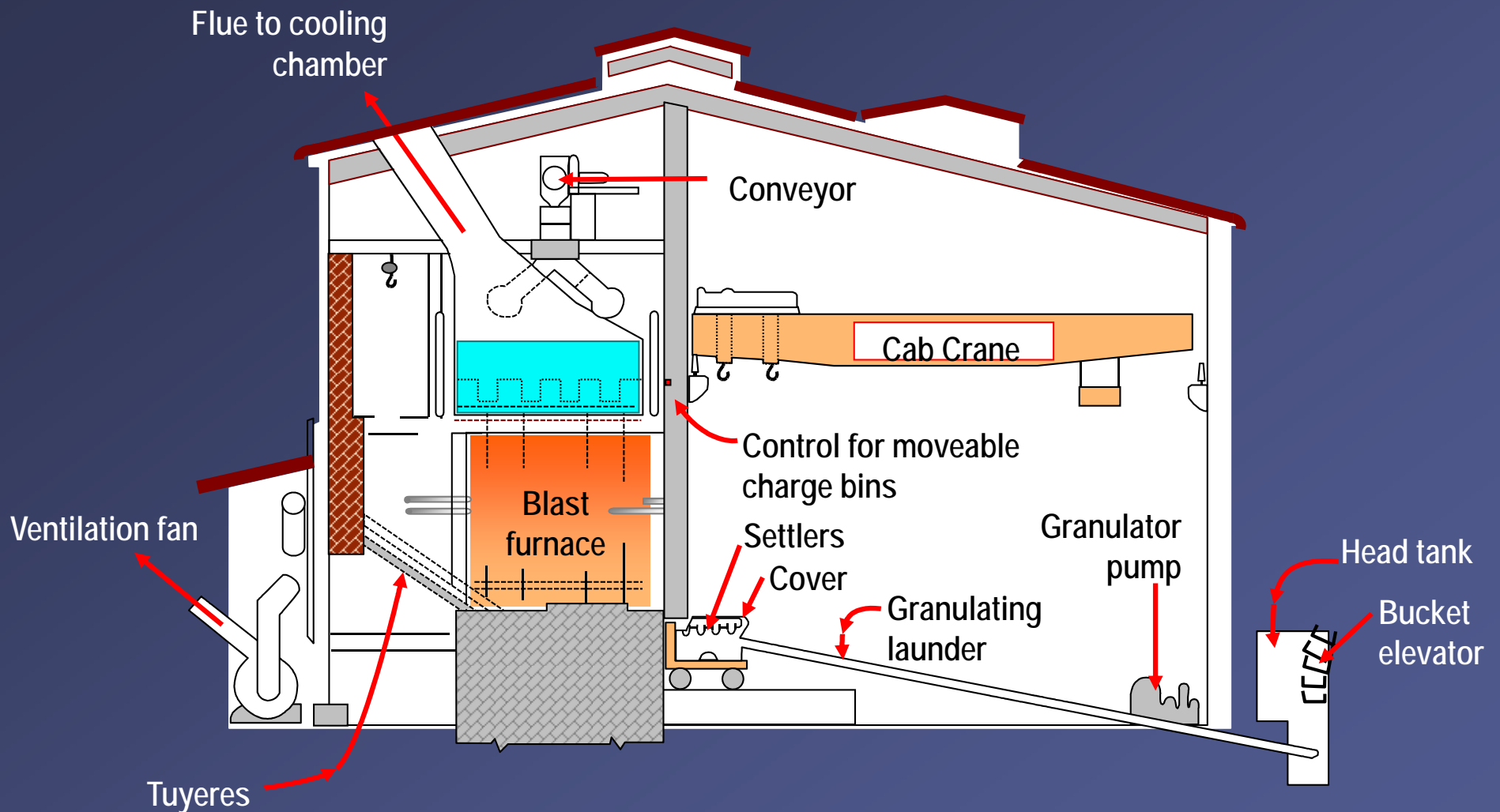
- 1260°C

- Burnout

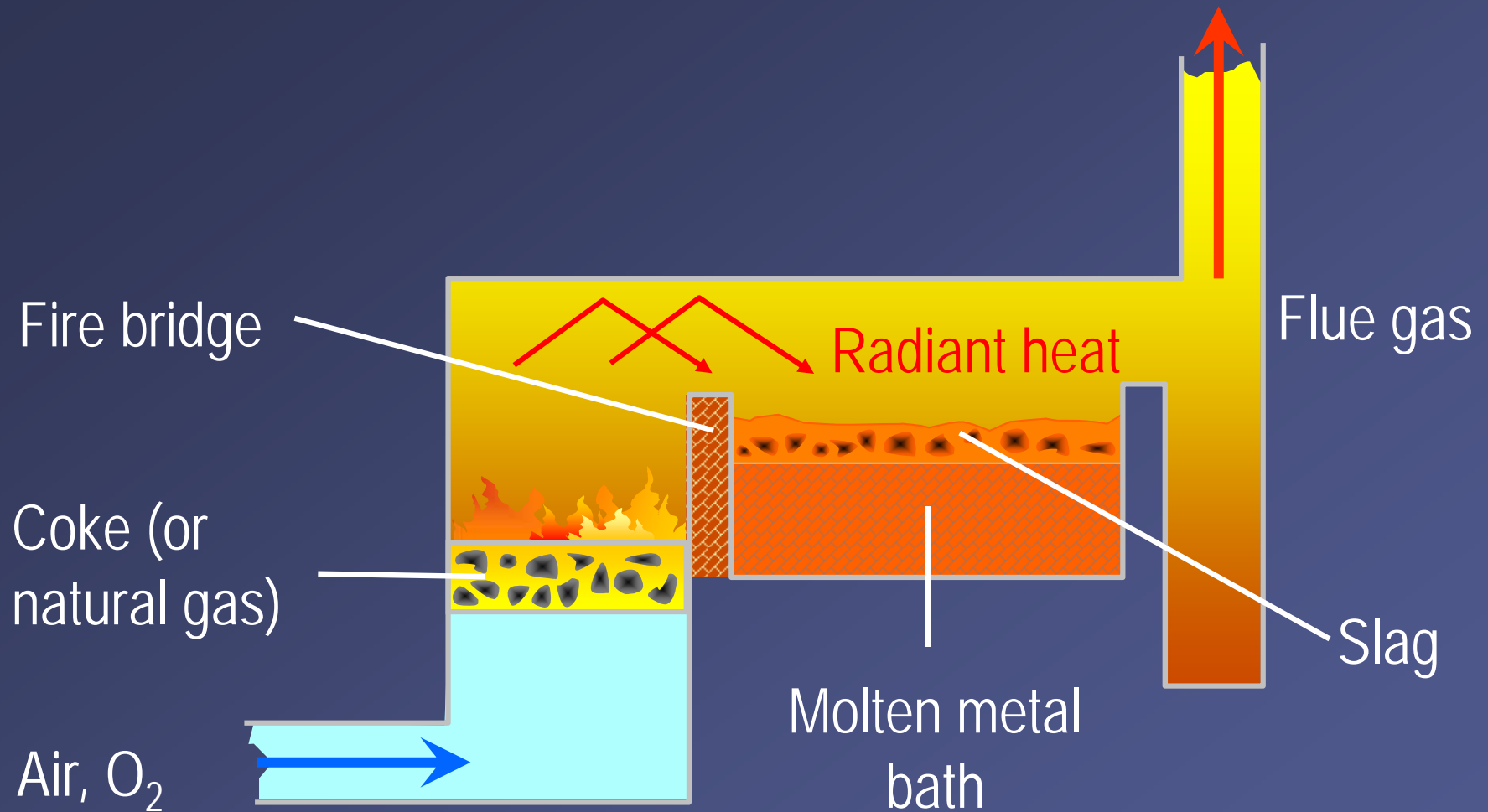
- Sweating

- Slagging

Process Details (cont.) Blast Furnace Schematic



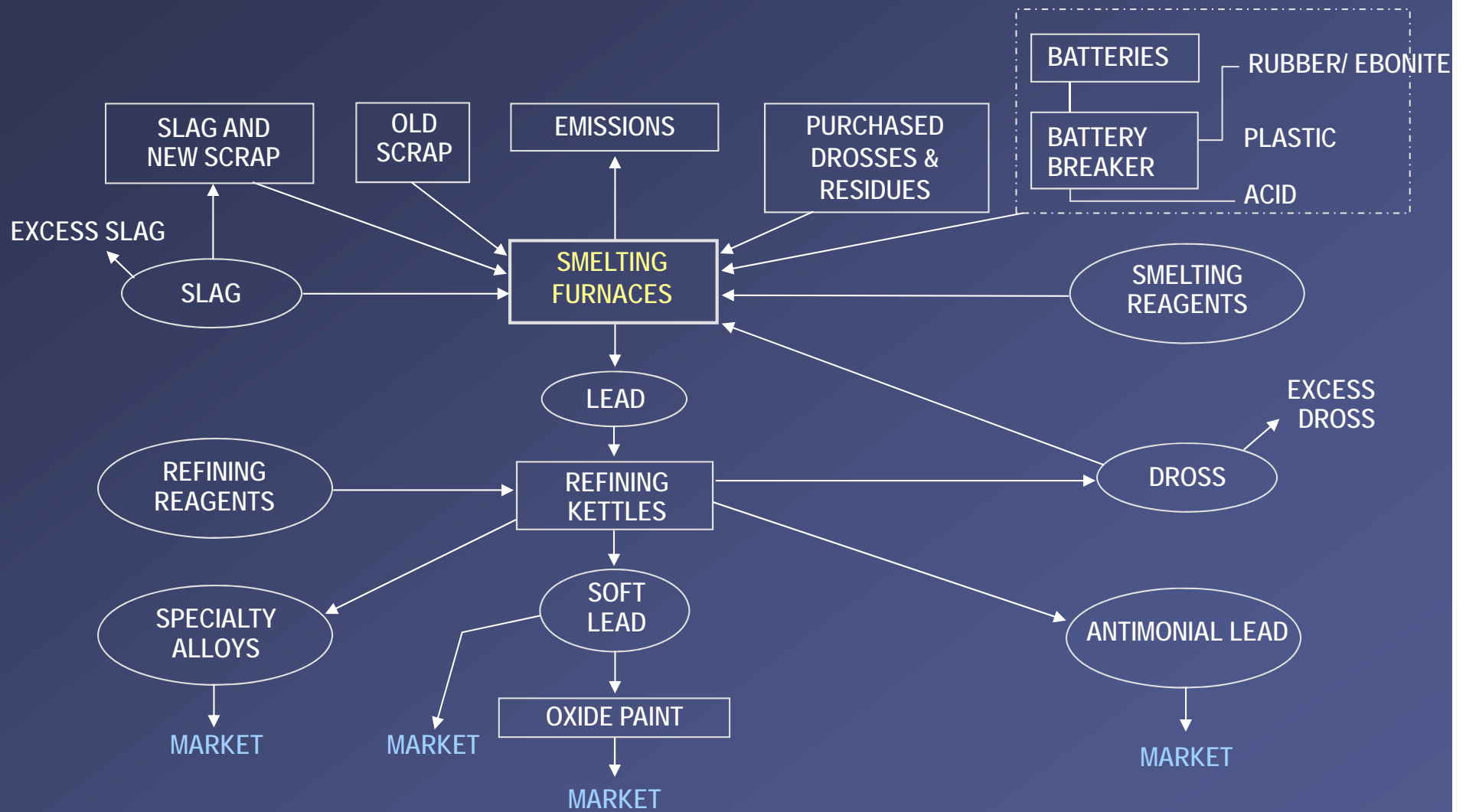
Process Details (cont.) Reverberatory Furnace Schematic



Reverberatory Furnace



Generalized Secondary Lead Refining Process



Refining Casts





Environmental Chemistry

Metals partitioning

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

Predicted Metals Volatility Temperatures

With 0% Chlorine			With 10% Chlorine	
Metal	Volatility Temperature (°C)	Principal Species	Volatility Temperature (°C)	Principal Species
Chromium	1613	CrO ₂ /CrO ₃	1610	CrO ₂ /CrO ₃
Nickel	1210	Ni(OH) ₂	693	NiCl ₂
Beryllium	1054	Be(OH) ₂	1054	Be(OH) ₂
Silver	904	Ag	627	AgCl
Barium	849	Ba(OH) ₂	904	BaCl ₂
Thallium	721	Tl ₂ O ₃	138	TlOH
Antimony	660	Sb ₂ O ₃	660	Sb ₂ O ₃
Lead	627	PbO ₂	615	PbCl ₄
Selenium	318	SeO ₂	318	SeO ₂
Cadmium	214	Cd	214	Cd
Osmium	41	OsO ₄	41	OsO ₄
Arsenic	32	As ₂ O ₃	32	As ₂ O ₃
Mercury	14	Hg	14	Hg

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

<u>Medium</u>	<u>Method</u>	<u>Detection Limit</u>
Water	Atomic absorption, ICP	0.001-0.1 mg/l
Soil	Atomic absorption, ICP	0.1-1.0 mg/kg
TCLP	Atomic absorption, ICP	0.001-0.1 mg/l

Analytical Considerations - Field Screening Methods for Lead

<u>Medium</u>	<u>Method</u>	<u>Detection Limit</u>
Soil	X-ray fluorescence (XRF)	~10 mg/kg
Water	Photometric, Colorimetric test kits	1 ppm

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