RECYCLING LEAD, BYPRODUCT METALS, SULFATE, AND POLYPROPYLENE IN SECONDARY PB-SMELTERS

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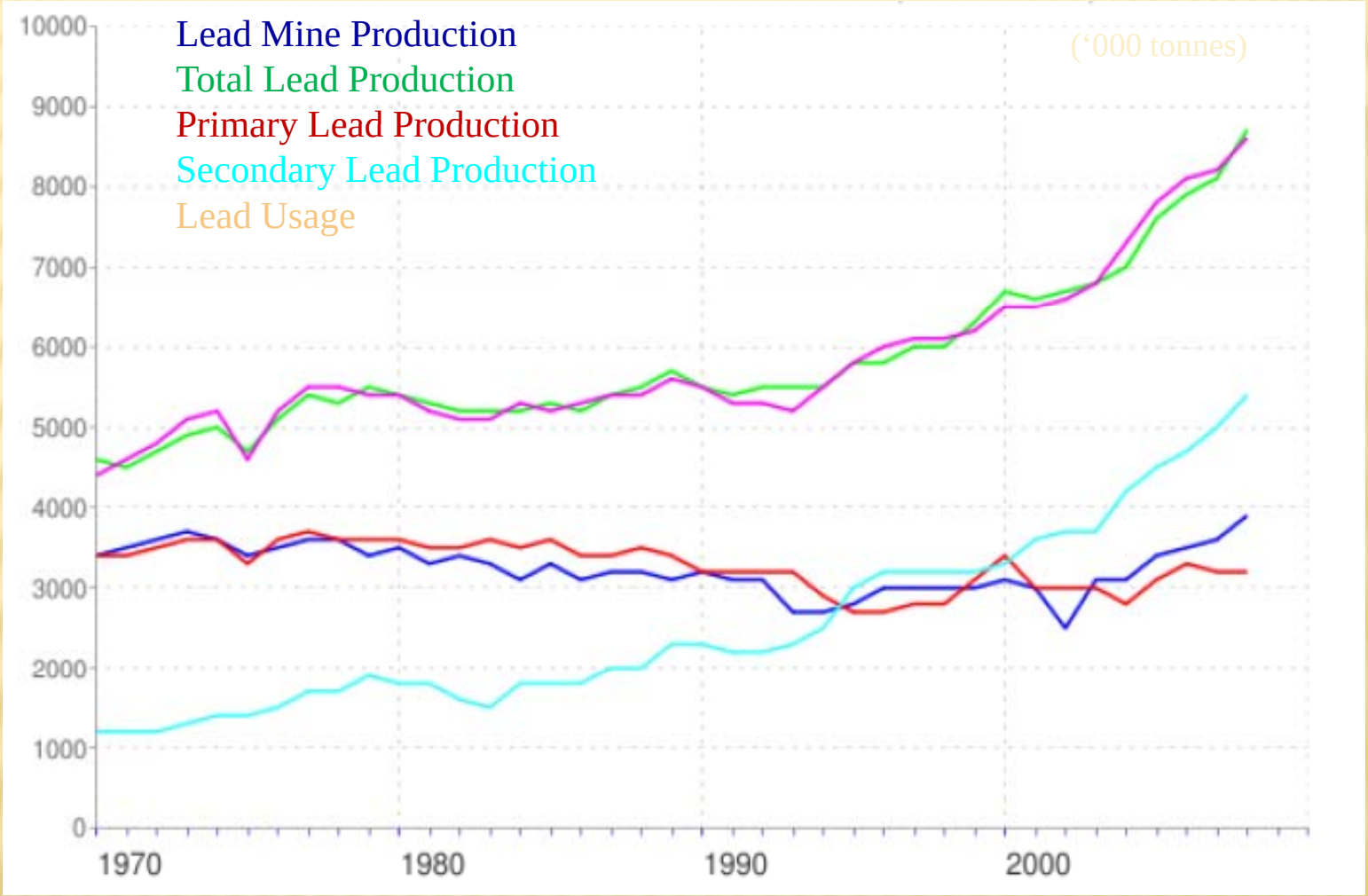
Pb Zn 2010 Short Course
Vancouver, B.C.
October 2 - 3, 2010

OVERVIEW

- Lead Production and Usage
- Secondary Lead Smelting Flowsheets
- Battery Breaking
- Paste Desulpurization
- Smelting Technologies
- Environmental and Health Protection
- Value Added Processes
- Refining

LEAD STATISTICS WORLD TOTAL 1970 - 2009



Source: ILA

REFINED LEAD PRODUCTION

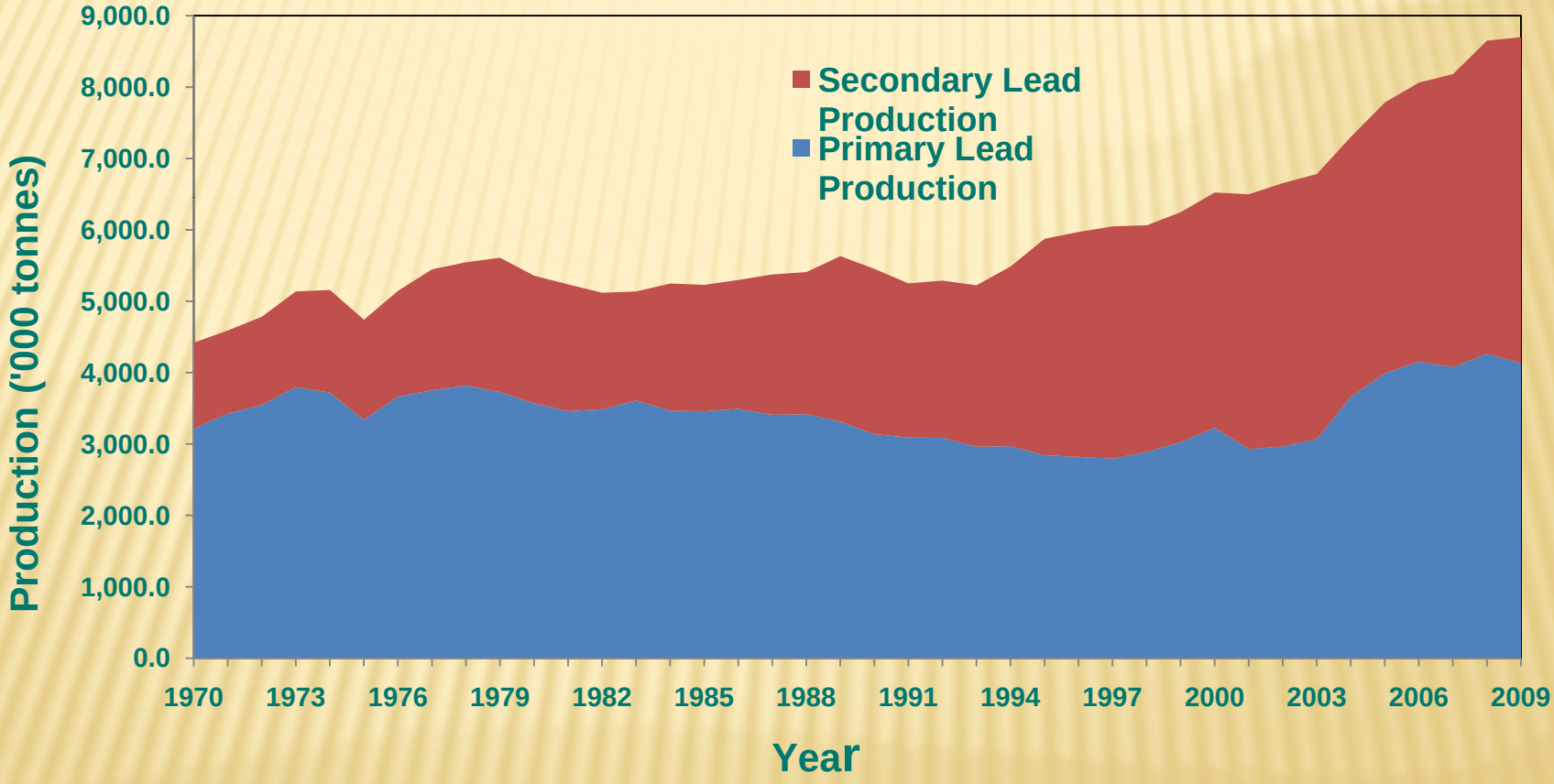
(Tons in thousands)

	2006	2007	2008	2,009	Variance '08-'09	
						%
United States	1,303	1,303	1,280	1,240	(40)	(3.1)
Europe	1,661	1,779	1,812	1,663	(149)	(8.2)
Canada	250	237	259	260	1	0.4
Mexico	253	255	255	234	(21)	(8.2)
Peru	120	117	114	26	(88)	(77.2)
China	2,715	2,788	3,206	3,708	502	15.7
Japan	280	276	279	247	(32)	(11.5)
Korea, Rep.	240	260	270	290	20	7.4
Australia	241	238	261	235	(26)	(10.0)
Other Countries	872	873	917	924	7	0.8
Total	7,935	8,126	8,653	8,827	174	2.0
Western World	4,793	4,829	4,939	4,661	(278)	(5.6)

Source: ILZSG

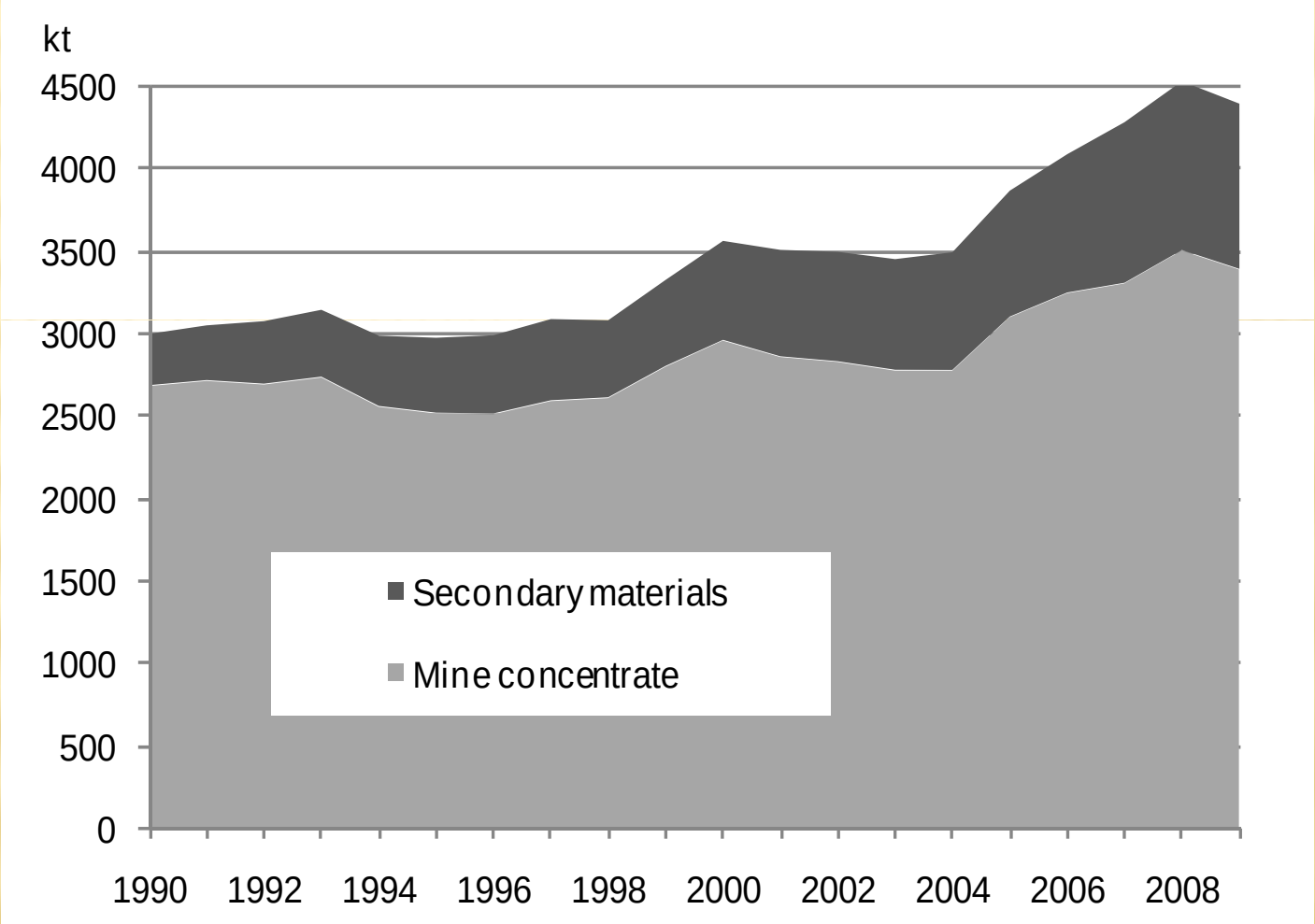
PRIMARY AND SECONDARY LEAD PRODUCTION

WORLD TOTAL 1970 - 2009



Source: David Wilson - ILA

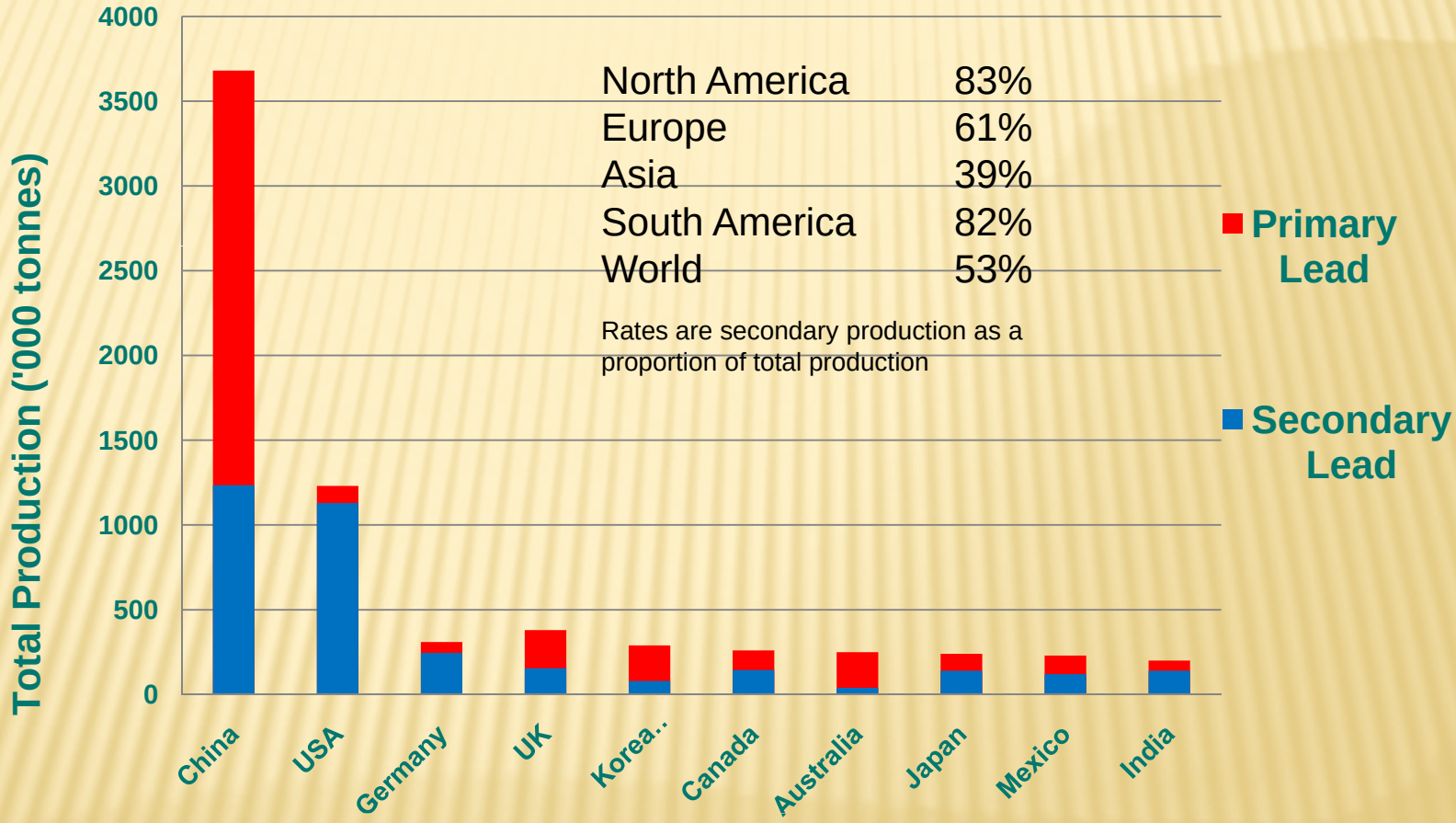
PRIMARY LEAD PRODUCTION FROM MINE CONCENTRATE AND SECONDARY LEAD-BEARING FEED*



*** WORLDWIDE LEAD SUPPLY AND DEMAND – CHR Metals Ltd. – Plenary PbZn 2010**

PRIMARY AND SECONDARY LEAD PRODUCTION

TEN LARGEST LEAD PRODUCING COUNTRIES 2009



Source: David Wilson - ILA

SECONDARY LEAD SMELTER BY REGION

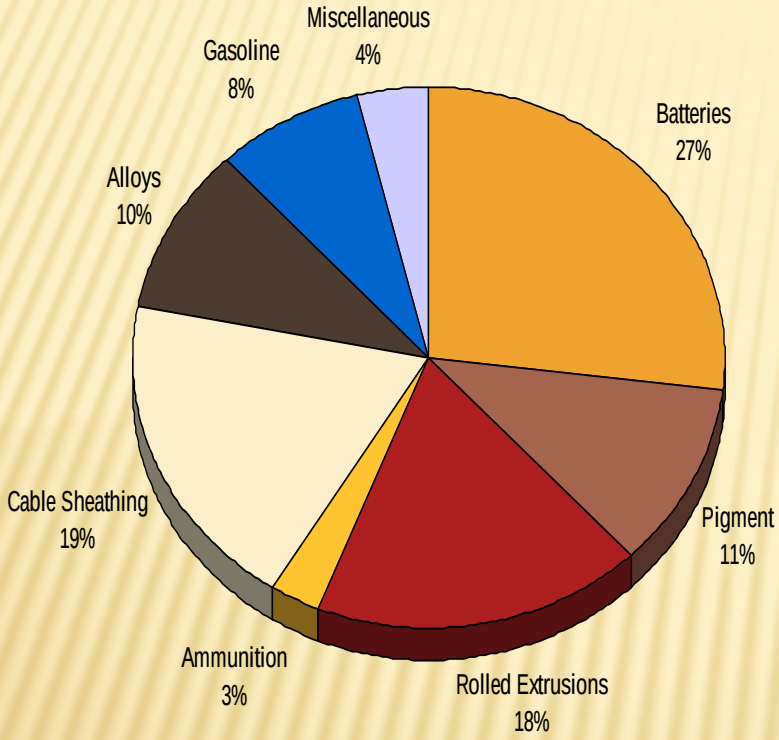
Globally ~ 170 secondary lead plants in 49 countries
listed by International Lead and Zinc Study Group

Thousands of smaller plants operate unofficially or even illegally

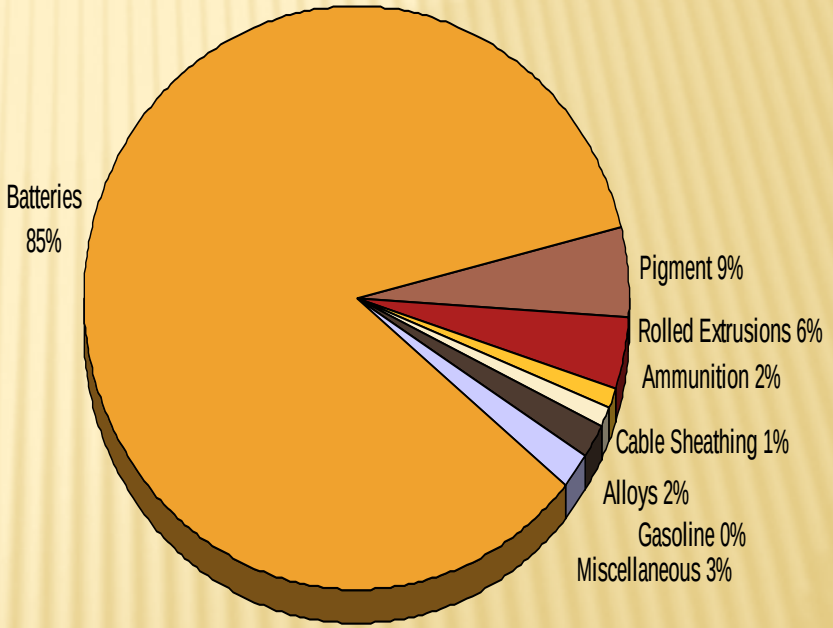
	Number of plants	Total capacity (tonnes)	Average capacity (tonnes)
North America	30	1,429,000	47,600
Europe	39	1,217,000	31,200
Asia	67	1,077,000	16,100
South America	14	187,000	13,400
Africa	16	131,000	8,200
Oceania	3	56,000	18,700

Source: David Wilson - ILA

END USES OF LEAD BETWEEN 1960 - 2009



1960



2009

CHANGING PATTERN END USES OF LEAD

	1960		2009	
	Total	of which potentially recyclable	Total	Of which potentially recyclable
Batteries	814	814	7330	7330
Cable sheathing	573	573	77	77
Rolled & extruded products	545	545	312	312
Shot/ammunition	83	-	116	-
Alloys	288	58 (1)	117	23 (1)
Pigments & compounds	348	-	480	-
Gasoline additives	235	-	11	-
Miscellaneous	114	57 (2)	181	90 (2)
Total	3000	2047	8624	7832
% Recyclable		68%		91%

(1) Estimated 20% recyclable
(2) Estimated 50% recyclable

Source: David Wilson - ILA

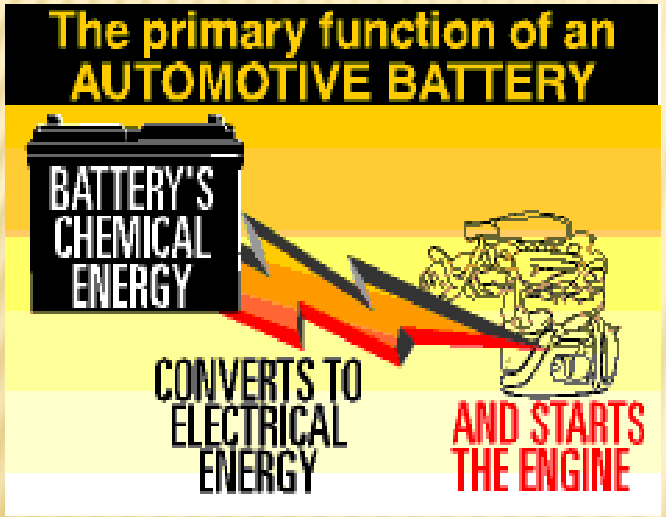
PRINCIPLE MAIN LEAD-ACID BATTERY TYPES

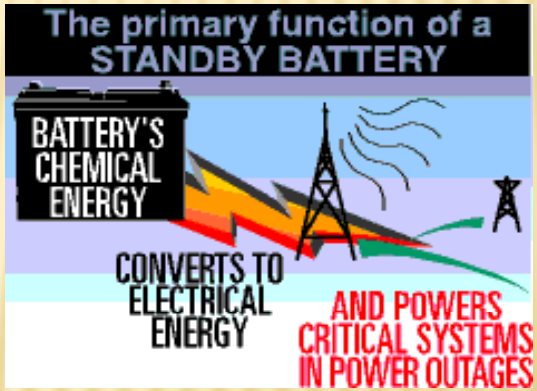
Automotive SLI Battery
≈ 60%

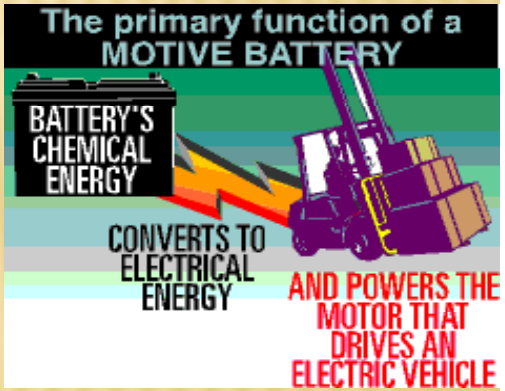
Industrial Batteries
≈ 40%

Stationary
≈ 60%

Motive
≈ 40%

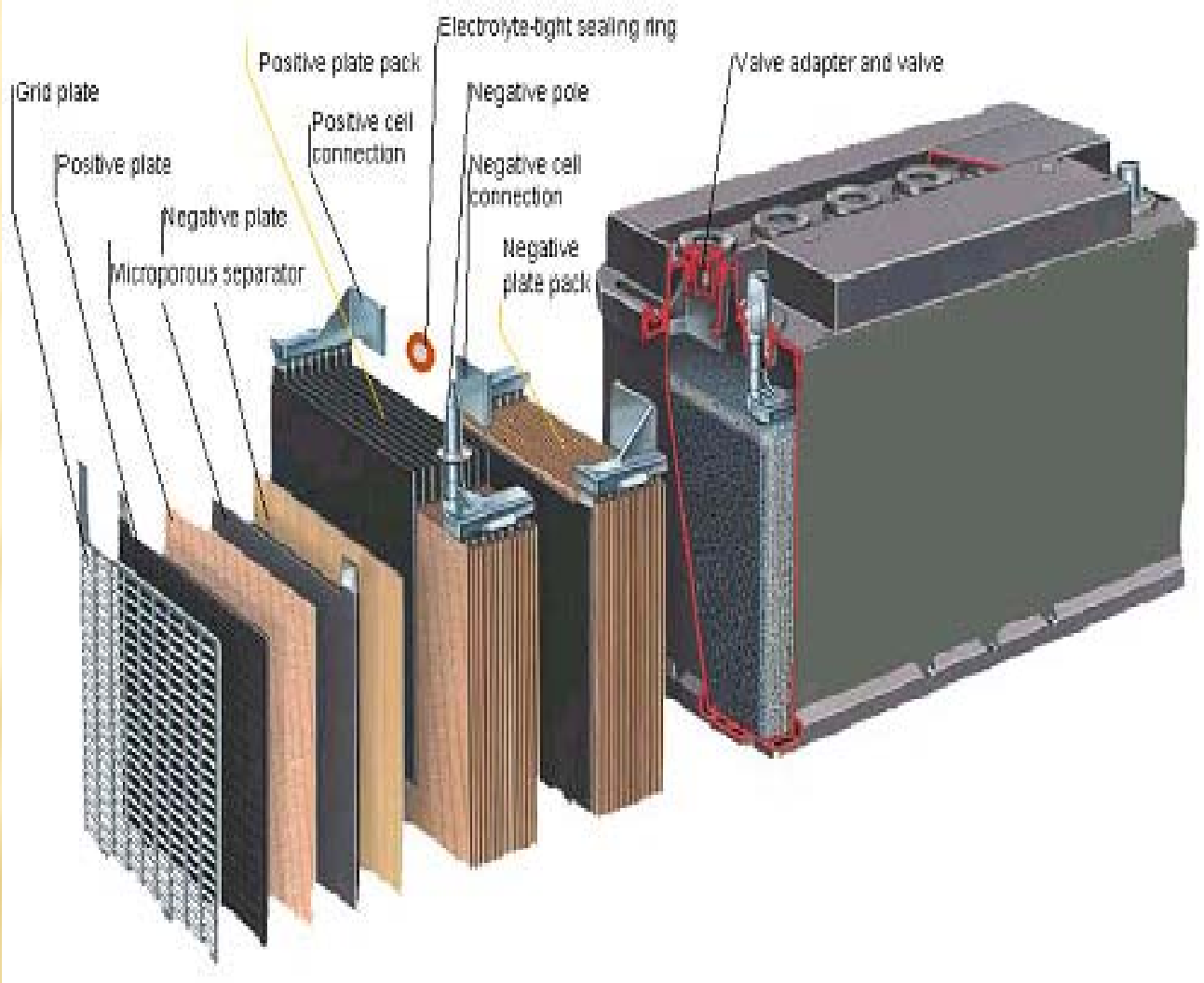






TYPICAL CONTENTS OF A LEAD-ACID AUTOMOTIVE BATTERY

1	**PP-Container**	**(≈ 5%)**
2	**Grids**	**(≈21%)**
	Paste	**(≈55%)**
3	**Separators**	**(≈ 3%)**
4	**Electrolyte**	**(≈11%)**
5	**Terminals**	**(≈ 5%)**



Recycling For A Better Environment

Transportation
The same transportation network used to distribute new batteries safely trucks spent batteries from point of exchange to recycling plants.

At the recycling facility, spent or "junk" batteries are broken apart and separated into components to begin the recycling process.

Plastic
Plastic pellets recycled from old battery cases and covers are used to manufacture new battery cases and covers.

Crush the cases and covers

Plastic pellets

New Covers and Cases
Battery covers and cases are manufactured for new batteries from recycled plastic pellets.

New cases and lids

Lead
Lead ingots recycled from battery grids and lead oxide are used to manufacture new battery grids and components.

Melt grids

Lead ingots

New Grids and Lead Oxide
Battery grids are manufactured from recycled lead for use in new batteries. Recovered lead oxide is also used in new battery manufacturing.

New grids

Lead oxide

Battery Acid-Option 1
Sodium sulfate crystals separated from old battery acid are recycled and sold for use in textile, glass and detergent manufacturing.

Neutralize battery acid

Sodium sulfate crystals

Glass, textile, detergents

Battery Acid-Option 2
At some recyclers, old battery acid is clarified and reused in remanufacturing or treatment processes.

Separate solids from battery acid

Acid is neutralized, treated, tested. Then returned to the environment.

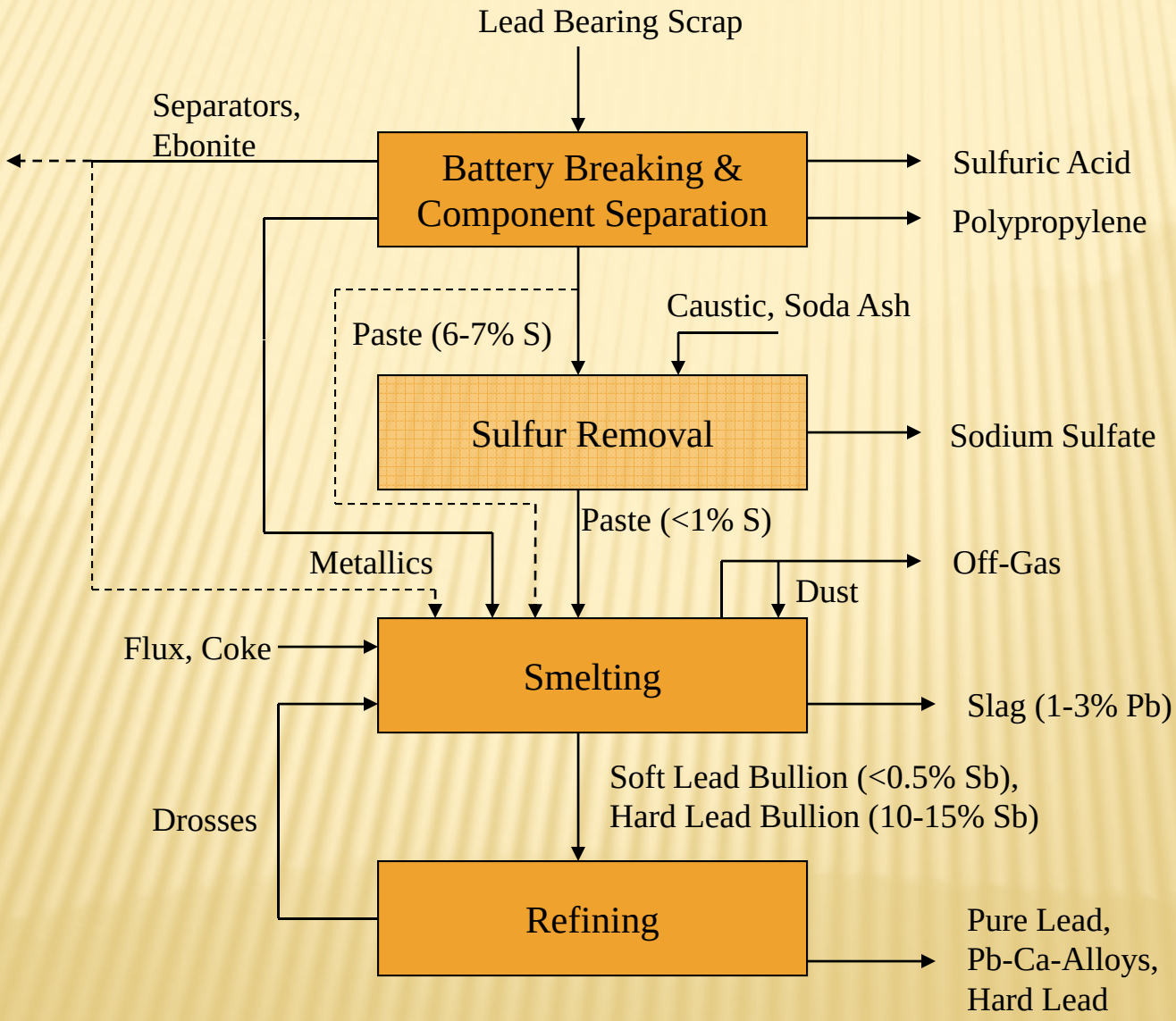
OR

Acid is chemically treated then reused or recycled.

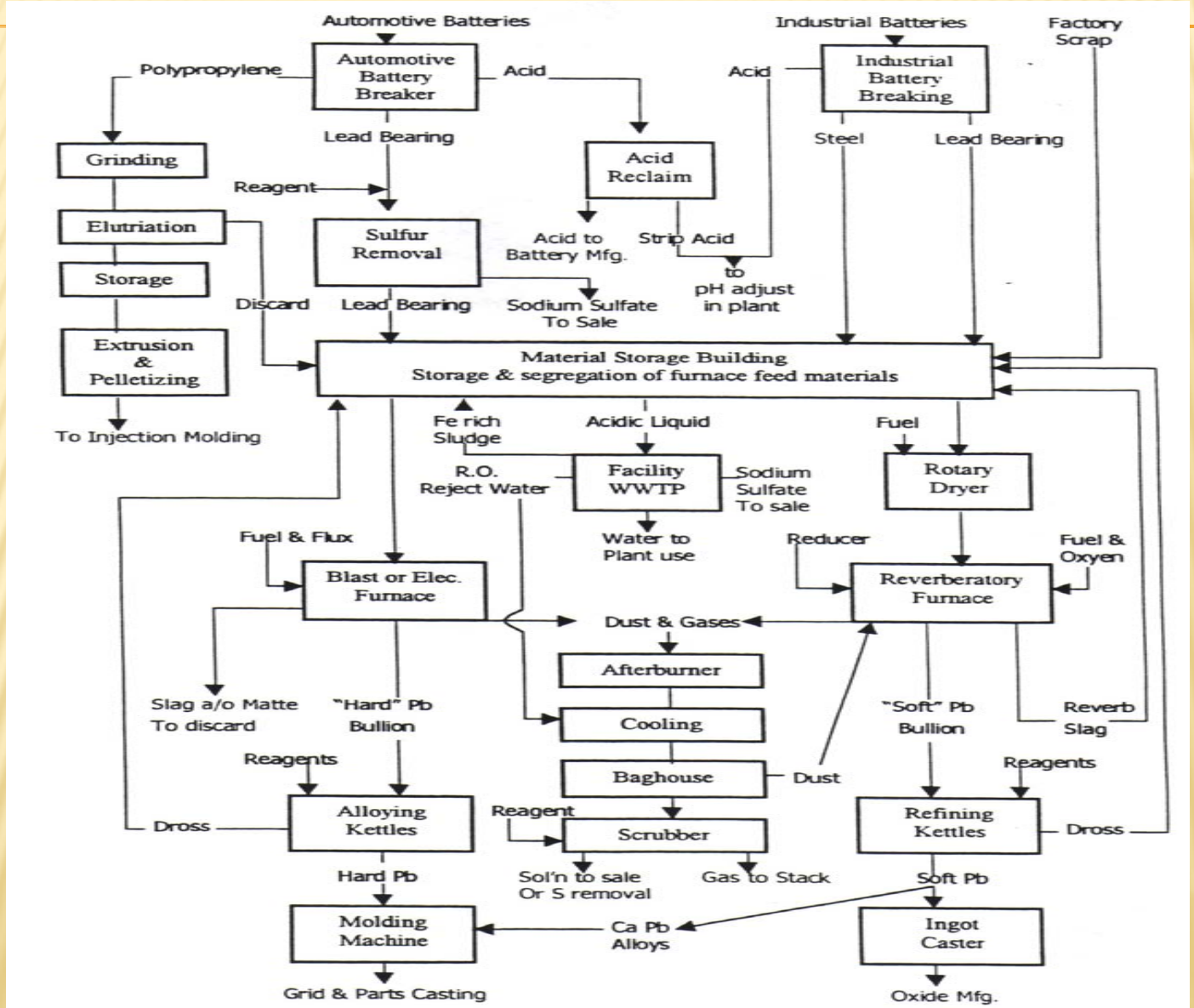
New Battery

New batteries are recyclable and comprised of previously recycled materials.

TYPICAL BLOCK DIAGRAM SECONDARY PB-SMELTER

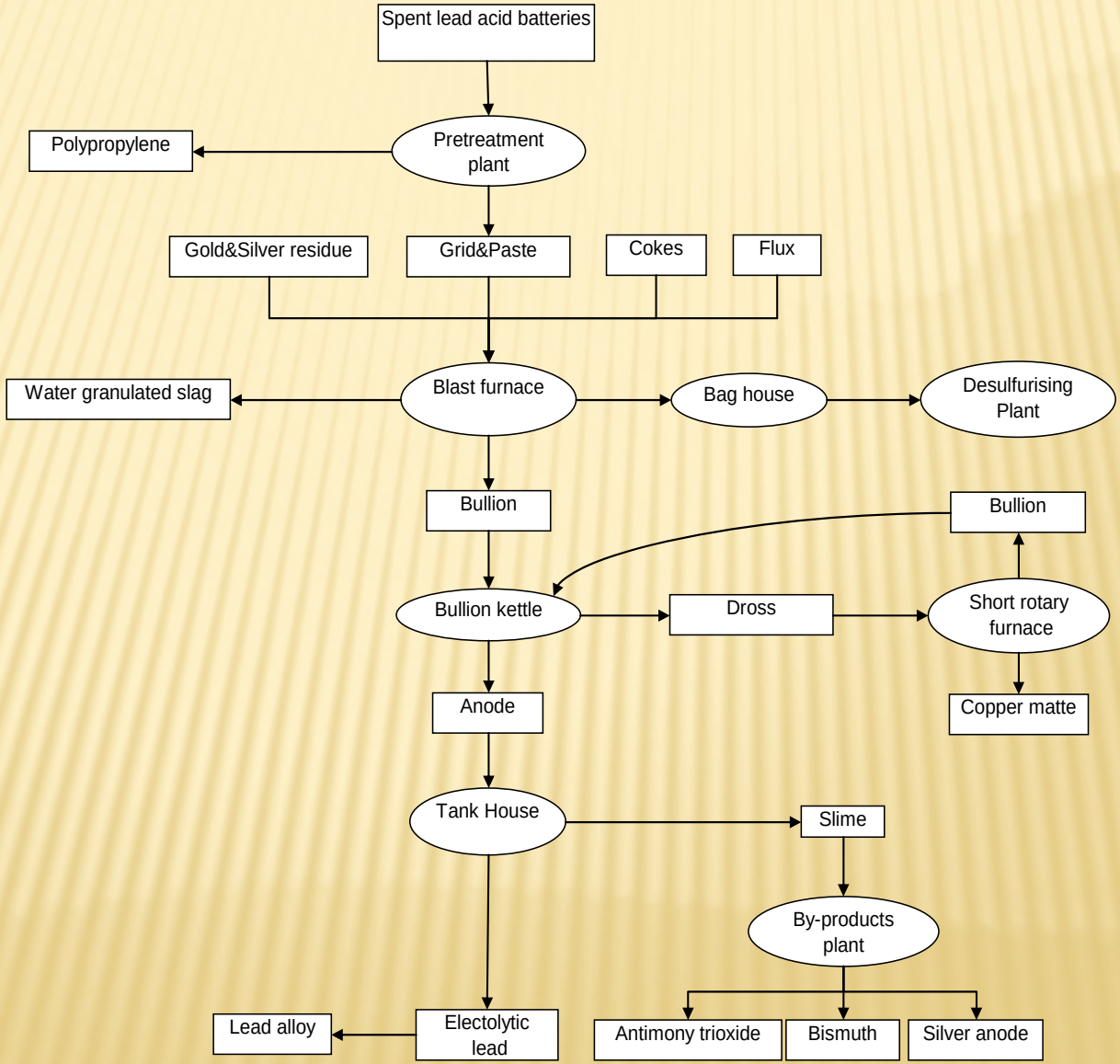


TYPICAL PROCESS FLOW REVERB / EF TECHNOLOGY



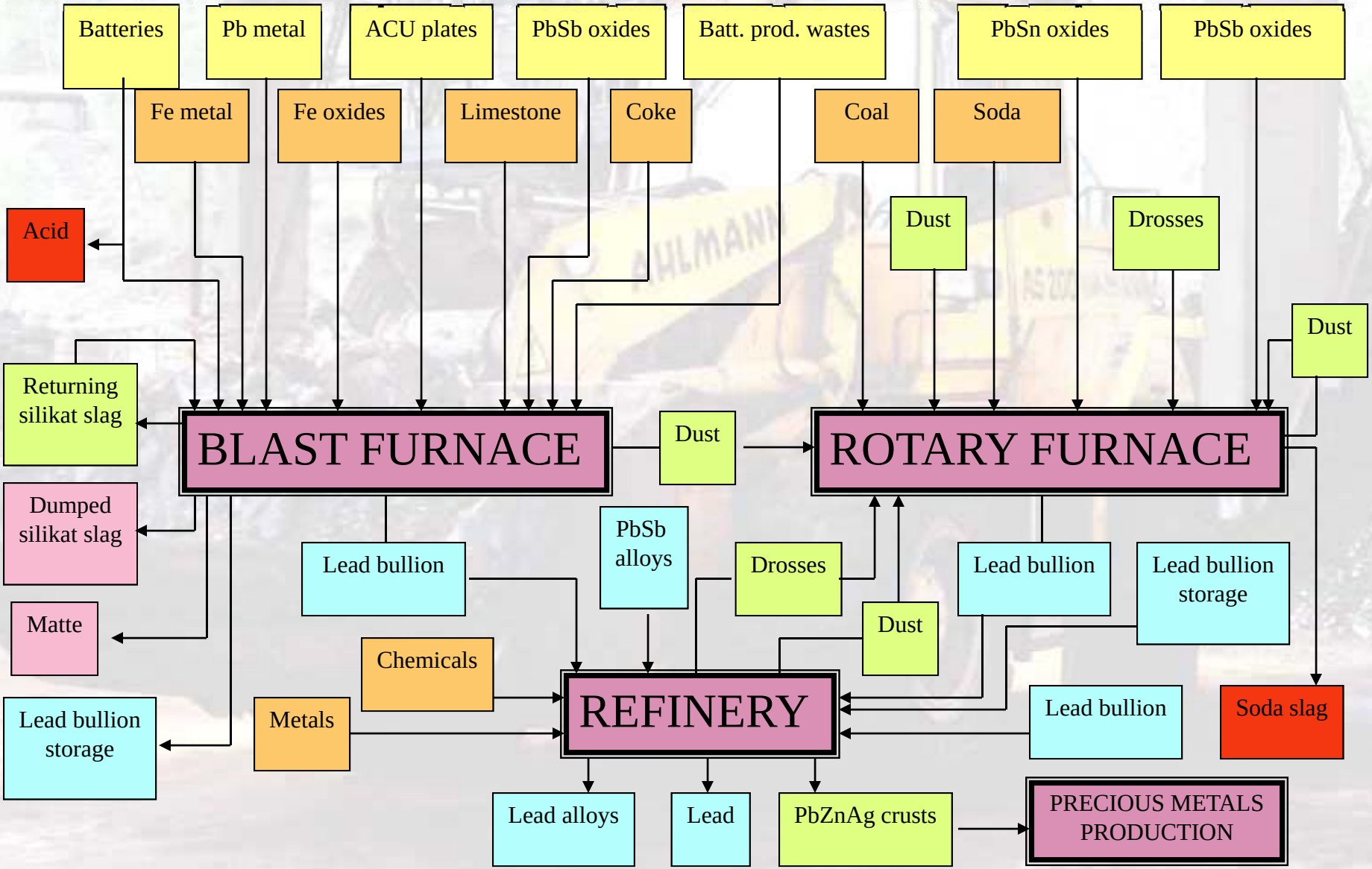
Source: Rick Leiby / East Penn – PbZn 2005

TYPICAL PROCESS FLOW BLAST FURNACE TECHNOLOGY



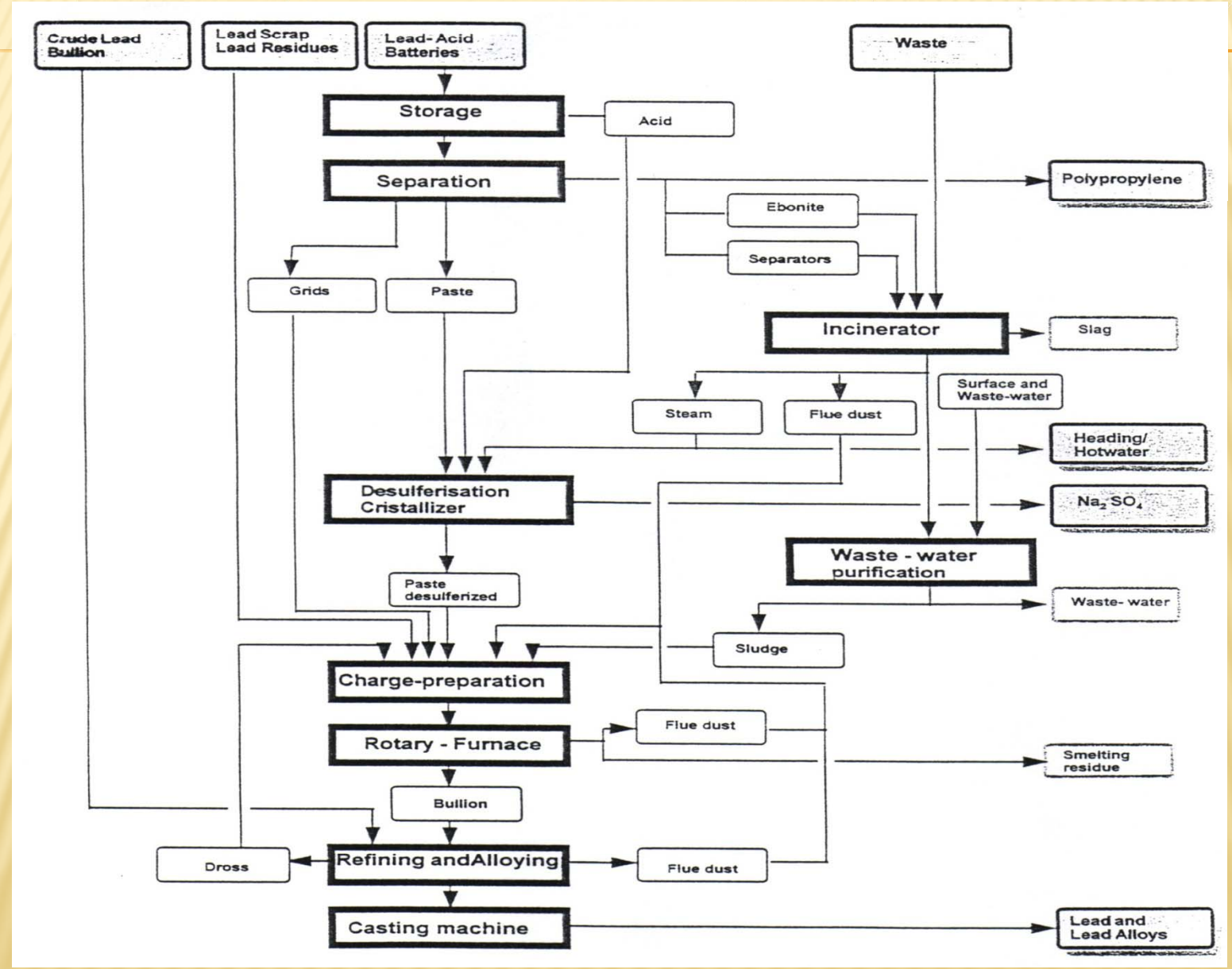
Source: K. Hayashi – PbZn 2010

TYPICAL PROCESS FLOW BLAST FURNACE TECHNOLOGY



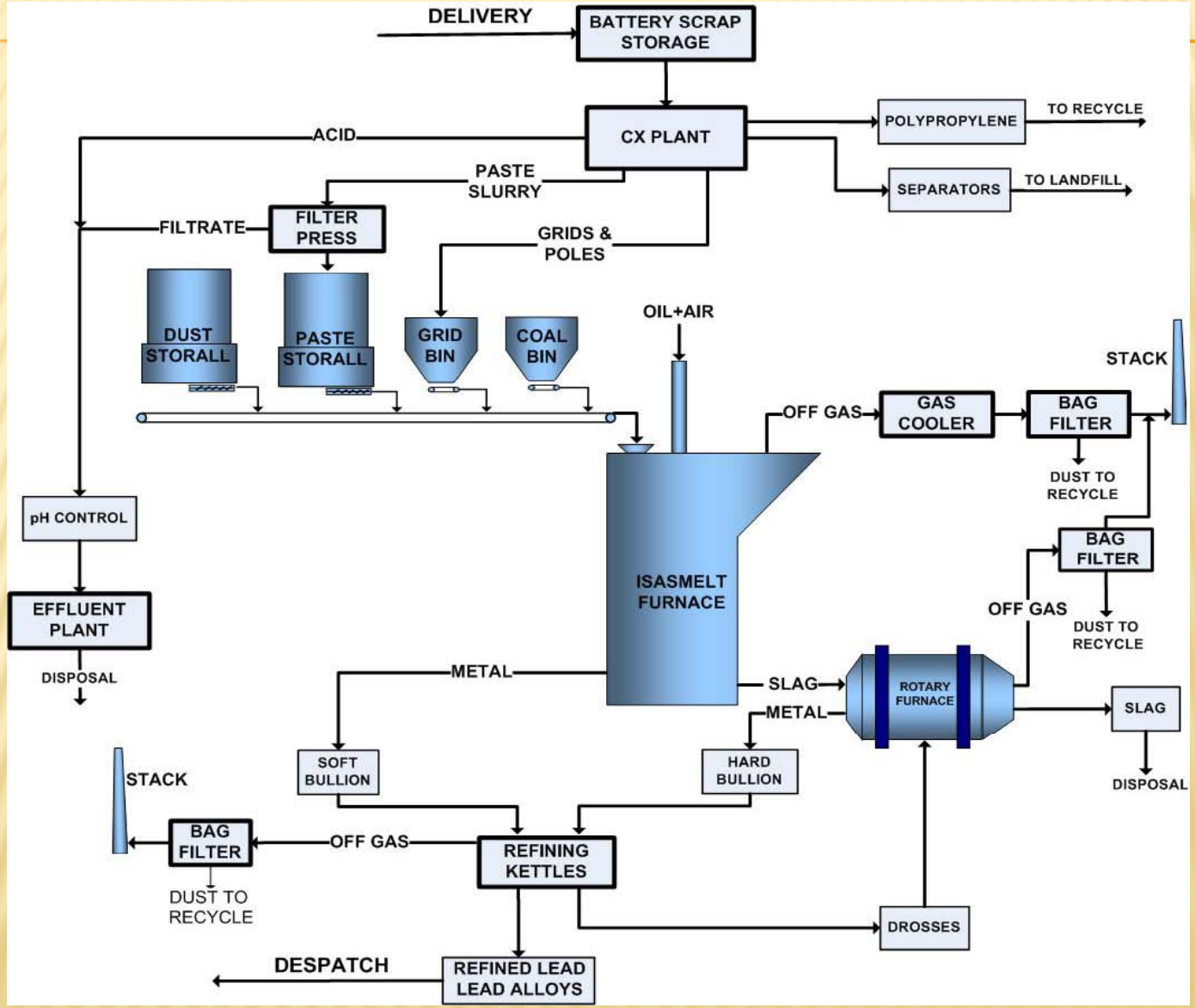
Source: Kunicky – PbZn 2000

TYPICAL PROCESS FLOW SRF TECHNOLOGY



Source: A. Siegmund – EMC 2001

TYPICAL PROCESS FLOW ISASMELT TECHNOLOGY



Source: Xstrata Technology – PbZn 2010

SECONDARY LEAD SMELTERS – BY TECHNOLOGY

Principal technology	Number of plants	Total capacity (tonnes)	Average capacity (tonnes)
Rotary furnace	79	1,686,000	21,500
Reverberatory furnace	19	766,000	40,000
Blast furnace	34	790,000	23,000
Submerged lance	4	420,000	105,000
Not specified	30	507,000	17,000

Source: David Wilson - ILA

Source: A. Siegmund – CSM 2005

BATTERY BREAKING AND COMPONENT SEPARATION

- Manual breaking is highly undesirable (health, environment, efficiency)

- Automatic breakers are generally employed
  - crusher/hammer mill
  - separation (drums, screens, flotation, filtration)
    - metallic lead
    - battery paste
    - polypropylene
    - separators (PVC, glass), ebonite, etc

BATTERY BREAKING AND COMPONENT SEPARATION

- Battery Breaking
  - Hammer Mill
  - Tooth-Studded Crusher
- Engitec - System
  - Washing off Paste,
  - Hydro-Flotation Separators
  - Sink-Float
- Density Gradient Sink-Float System

SULFUR REMOVAL FROM BATTERY PASTE

- Reduction of SO_2 - Emission
- Reduction in Matte Generation
- Minimizing the Quantity of Slag
- Disposable Slag
- Generating a Valuable Product

SULFUR REMOVAL FROM BATTERY PASTE

- Desulfurization with Caustic

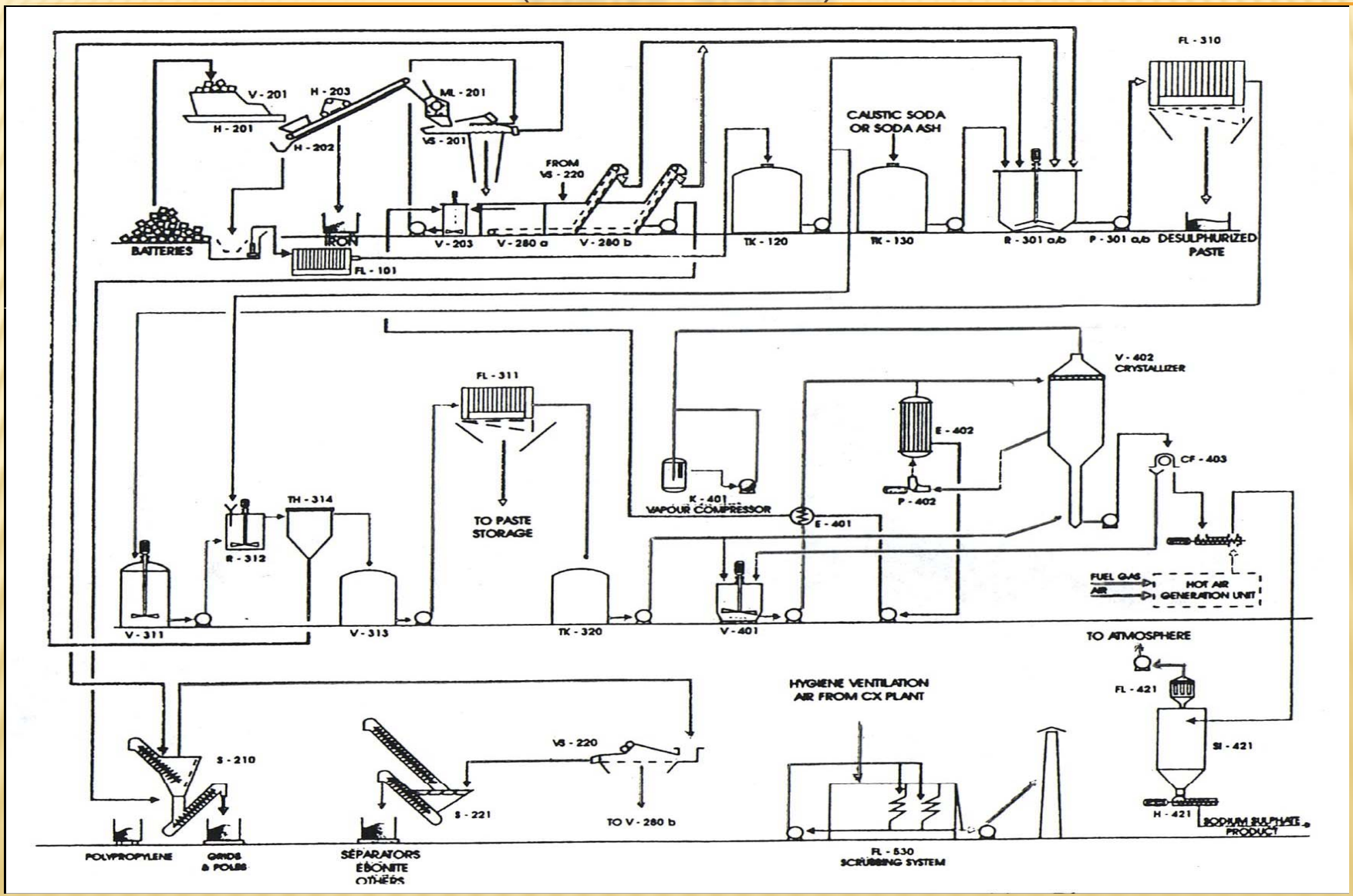
  $PbSO_4$ (paste) + 2 NaOH (aq) → PbO (paste) + Na_2SO_4 + H_2O

- Desulfurization with Soda Ash

  $PbSO_4$ (paste) + Na_2CO_3 (aq) → $PbCO_3$ (paste) + Na_2SO_4

TYPICAL FLOW SHEET BATTERY BREAKING, SEPARATION AND SULFUR REMOVAL PLANT

(ENGITEC - SYSTEM)

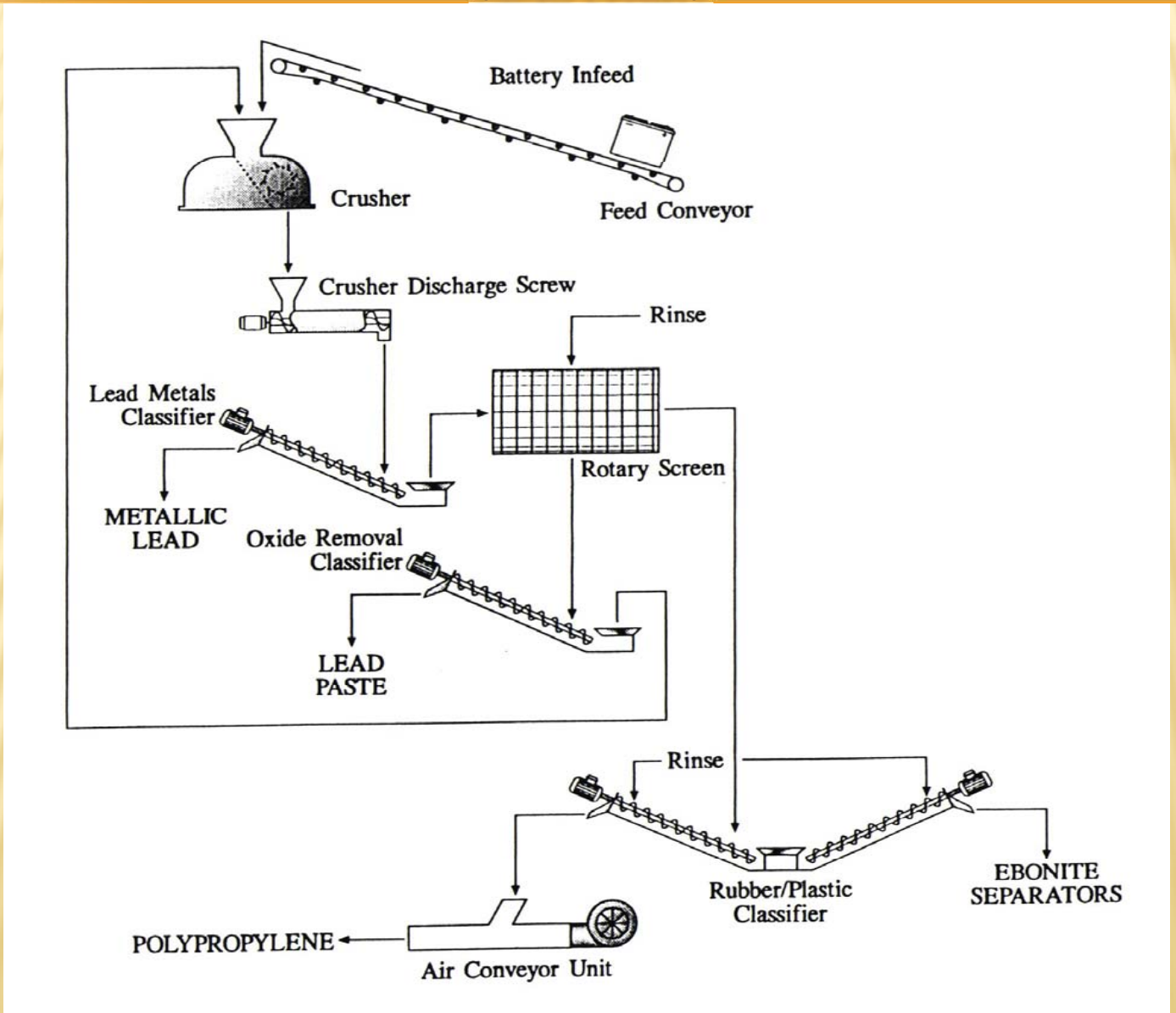


*** Andreas Siegmund – EMC 2001**

Source: A. Siegmund – CSM 2005

TYPICAL FLOW SHEET BATTERY BREAKING, SEPARATION AND SULFUR REMOVAL PLANT

(SINK FLOAT)

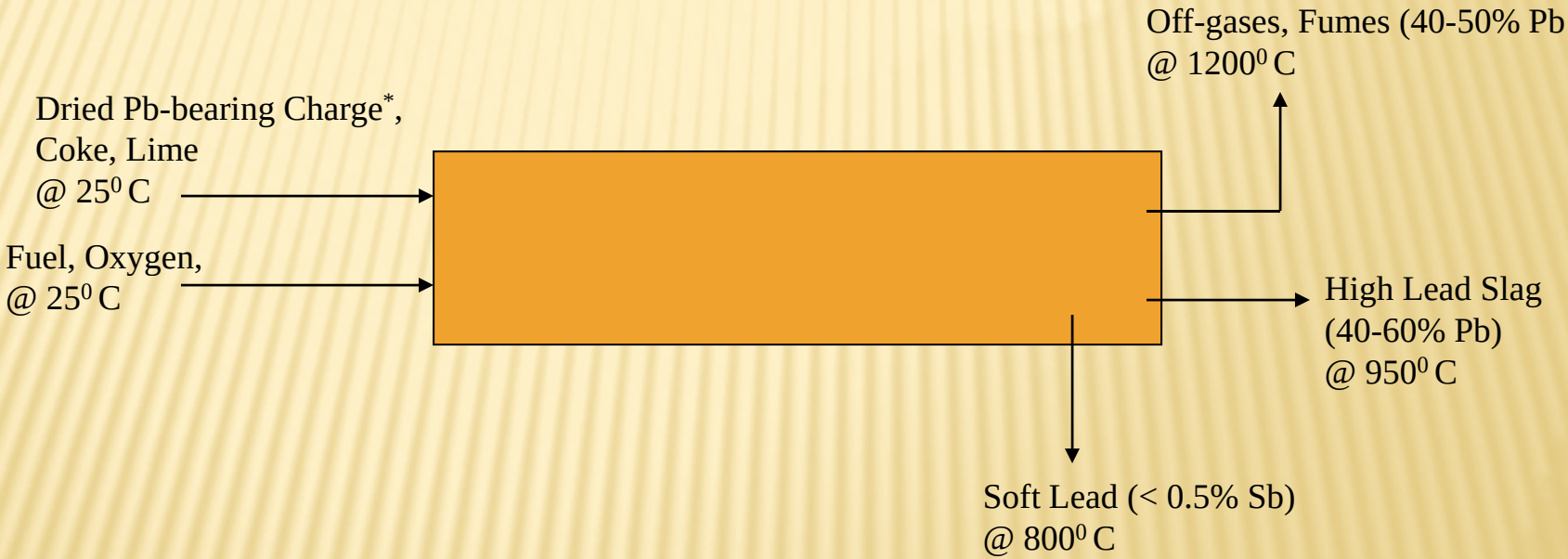



Source: A. Siegmund – CSM 2005

SMELTING OF SECONDARY LEAD MATERIAL

- Reverberatory Furnace - Blast Furnace (USA)
- Reverberatory Furnace - Electric Arc Furnace (USA)
- Short Rotary Furnace (Europe, Asia)
- Long Rotary Furnace (Canada)
- Blast Furnace (Europe, Japan)
- Isasmelt Furnace (UK, Malaysia)

REVERBERATORY FURNACE

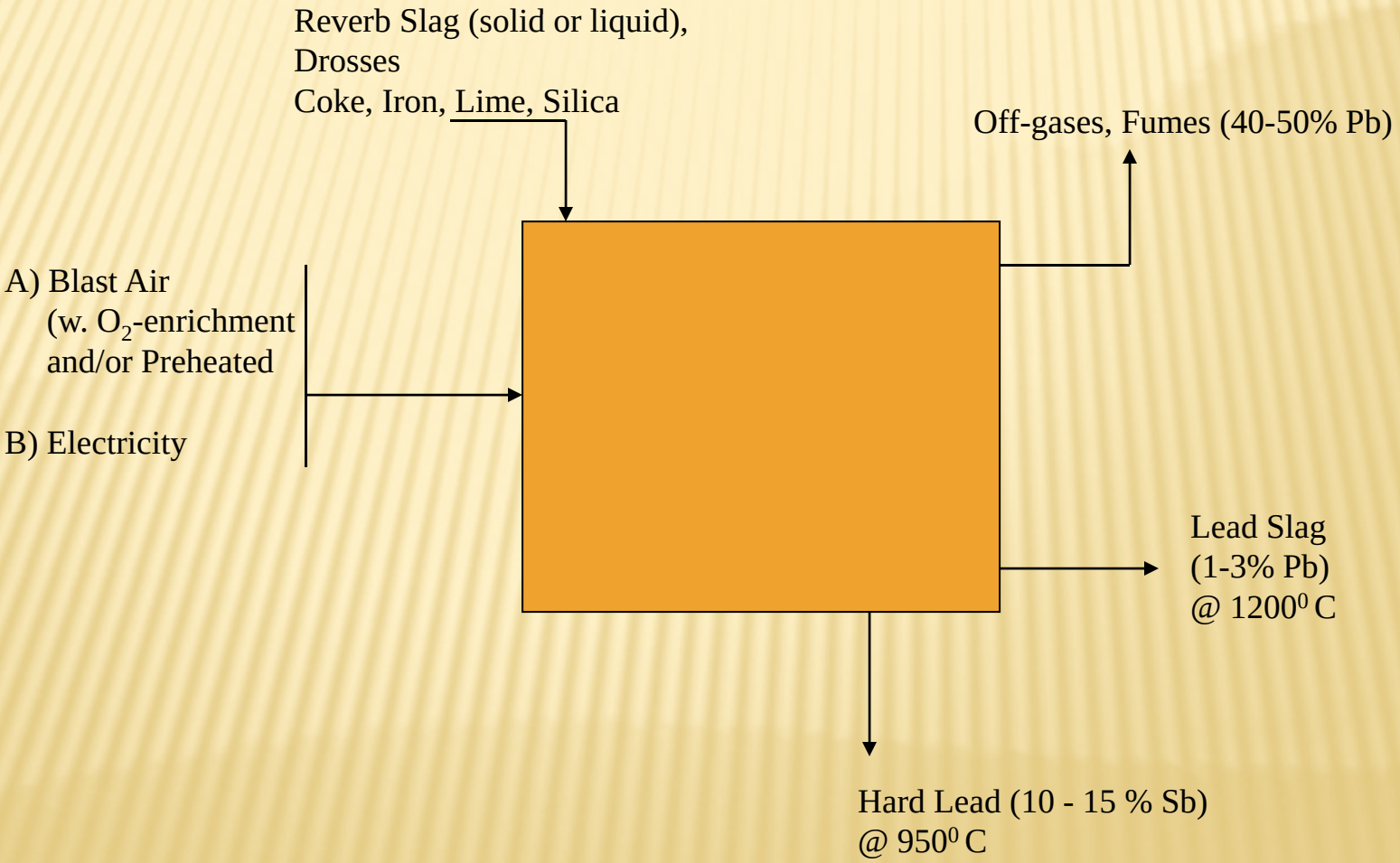


* 85 % Wrecker Material (Paste, Grids, Terminals),
  5 % Sludge from Desulfurization and ETP
  5 % Refinery Drosses
  5-10 % Factory Scrap

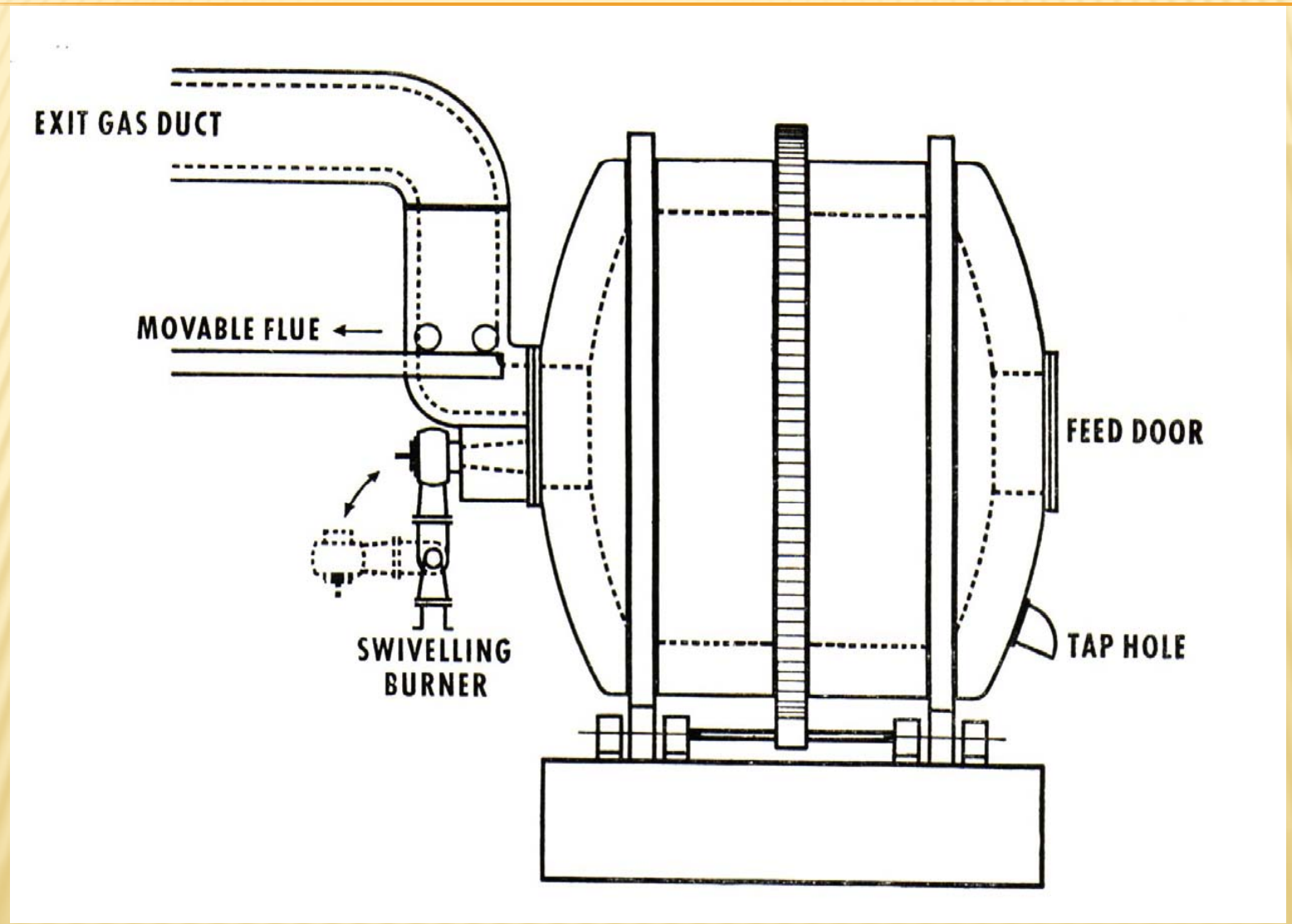
REVERBERATORY FURNACE

Source: R. Leiby – PbZn 2000

BLAST FURNACE OR ELECTRIC ARC FURNACE



SHORT ROTARY FURNACE



*** Andreas Siegmund – EMC 2001**

SHORT ROTARY FURNACES

Source: A. Siegmund – CSM 2005

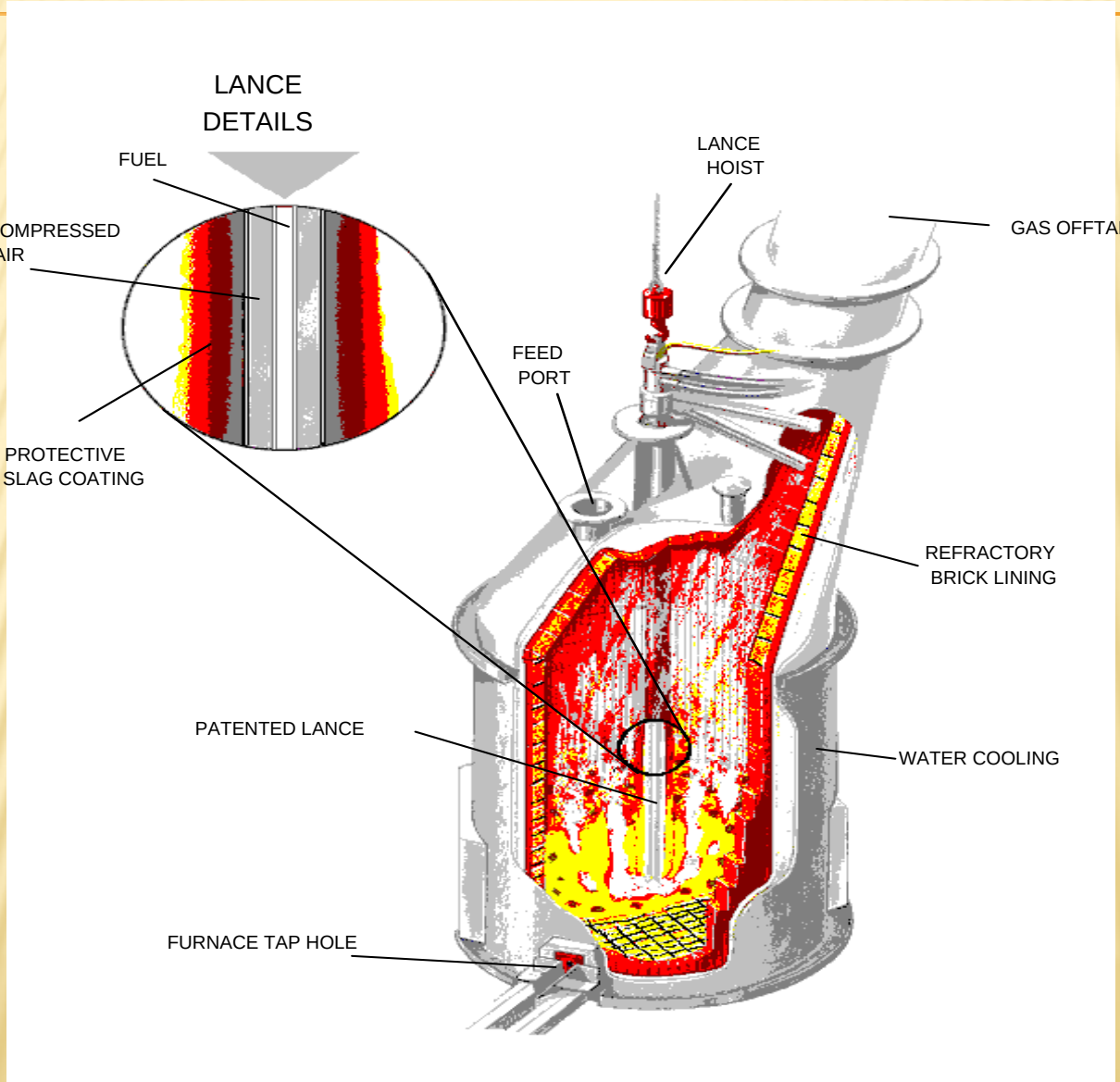
SHORT ROTARY FURNACE FEED SYSTEM

Source: A. Siegmund – CSM 2005

SHORT ROTARY FURNACE FEED SYSTEM

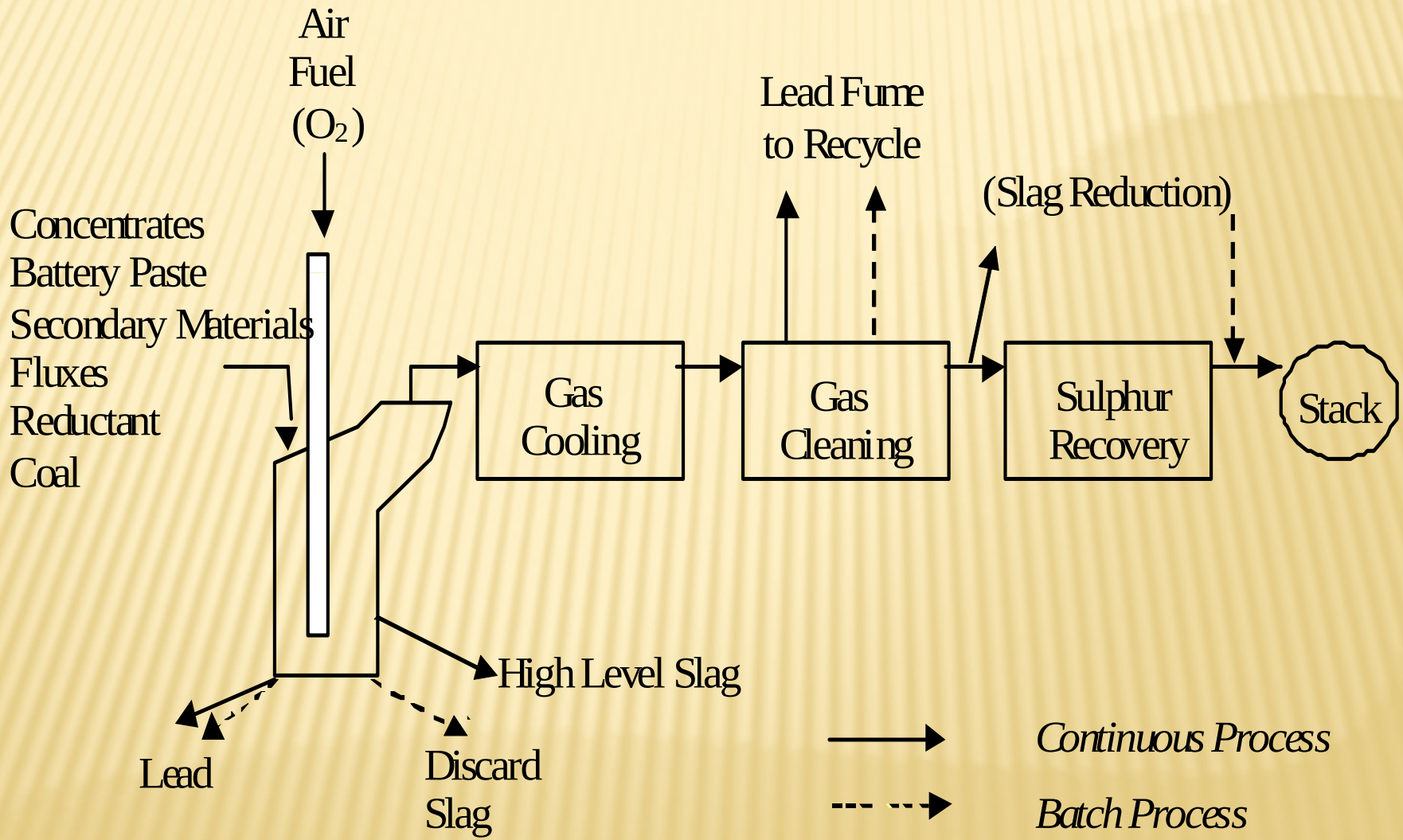
Source: A. Siegmund – CSM 2005

TOP SUBMERGED LANCE FURNACE

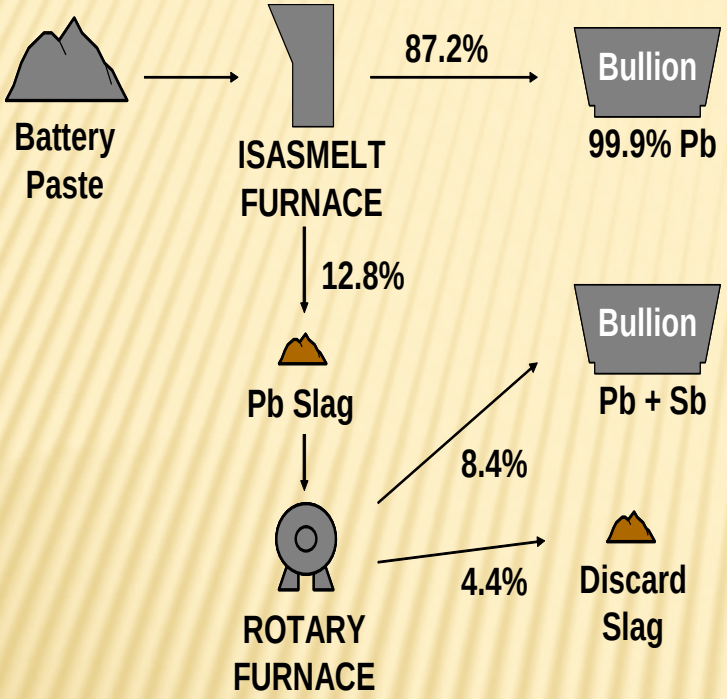


Source: A. Siegmund – Yazawa 2005

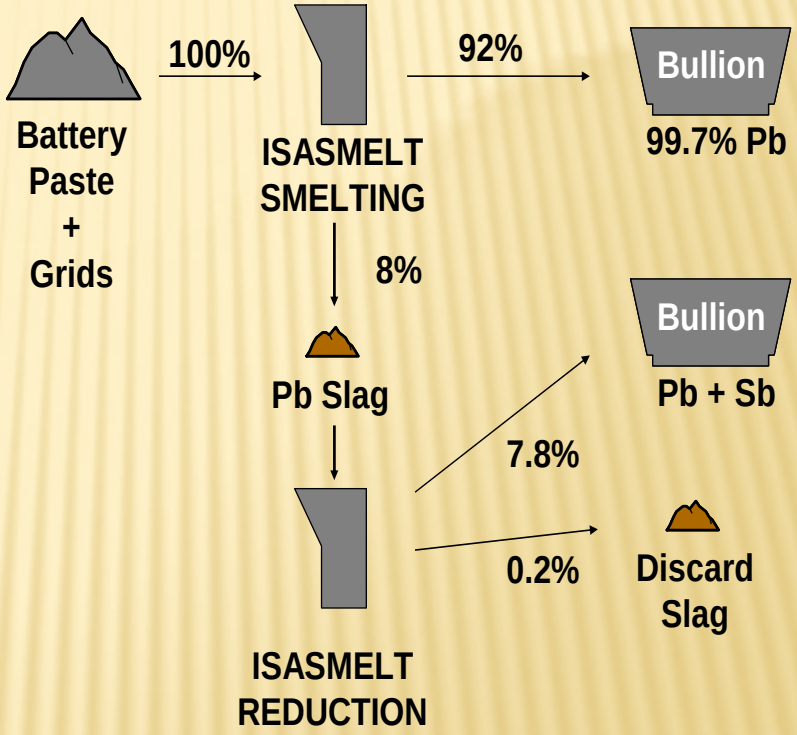
TOP SUBMERGED LANCE SINGLE FURNACE BATCH PROCESS



ISASMELT SINGLE FURNACE BATCH PROCESSES



Lead Distribution in the BRM Process



Lead Distribution in the MRI Process

Source: Xstrata Technology – PbZn 2010

ENVIRONMENTAL AND HEALTH PROTECTION

- Lead classified as toxic element
- Capture of other toxic elements/compounds in process
- No water discharge without treatment
- Control of TDS in water
- Close control of fugitive and process emissions through comprehensive ventilation and gas cleaning
- Removal of controlled compounds like NO_x and VOC
- Permanent monitoring of emission
- Close monitoring of bloodleads in employees
- Wearing of PPE mandatory
- Shower mandatory
- Daily provision of new uniform

SRF FURNACE HYGENIC AIR VENTILATION EXAMPLE

Source: A. Siegmund – CSM 2005

SULFUR REMOVAL FROM FURNACES

- Desulfurization with Lime and/or Caustic

  $SO_2 + CaCO_3\,(aq) + 1/2\ O_2 \rightarrow CaSO_4 + CO_2$

  $SO_2 + CaO\,(aq) + 1/2\ O_2 \rightarrow CaSO_4$

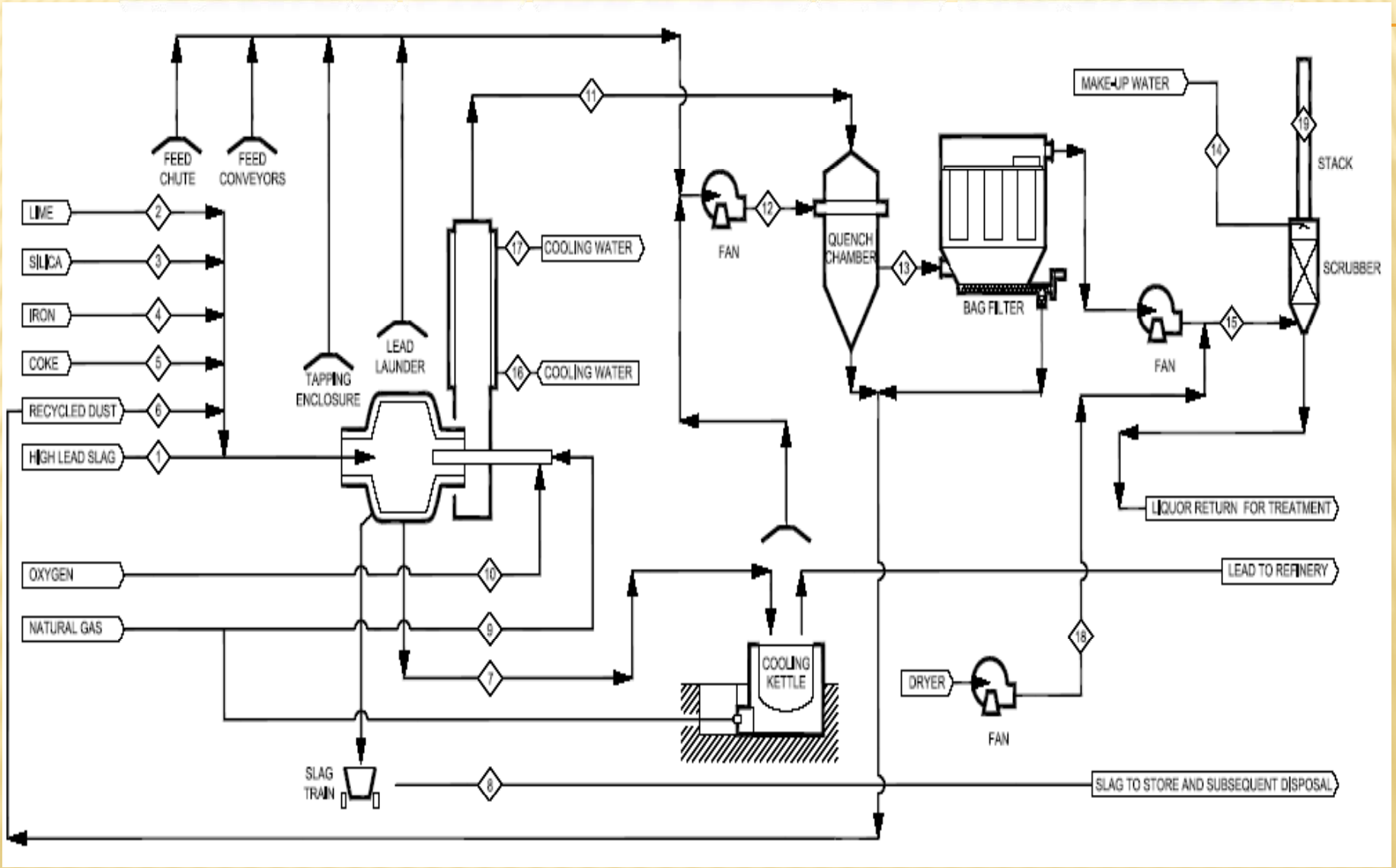
- Desulfurization with Soda Ash

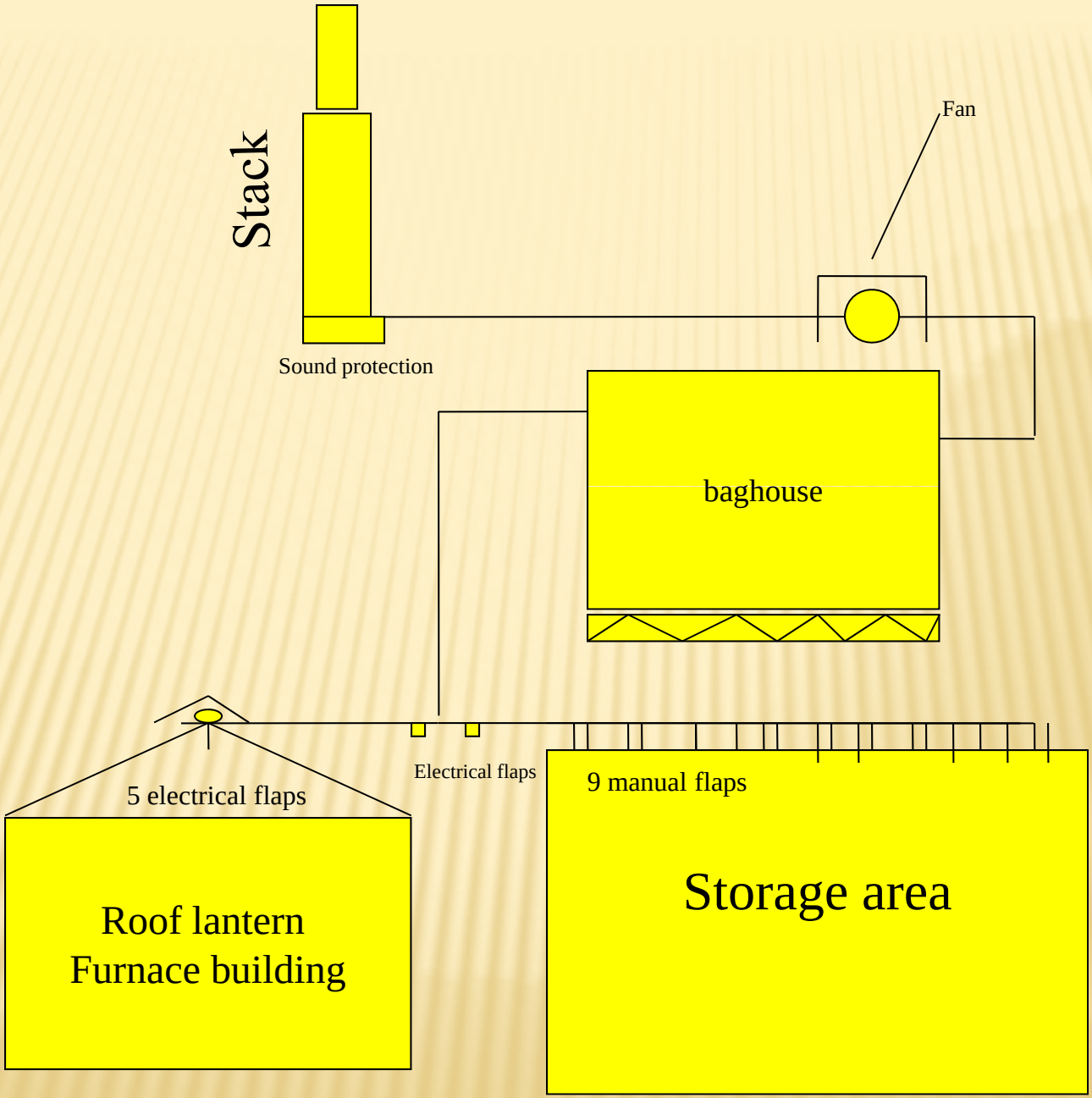
  $SO_2 + Na_2CO_3\,(aq) + 1/2\ O_2 \rightarrow Na_2SO_4\,(aq) + CO_2$

- Desulfurization with Ammonia

- Capturing in Soda Slag with/without Silica Matrix

EXAMPLE SRF PROCESS GAS TREATMENT





Source: A. Siegmund – CSM 2005

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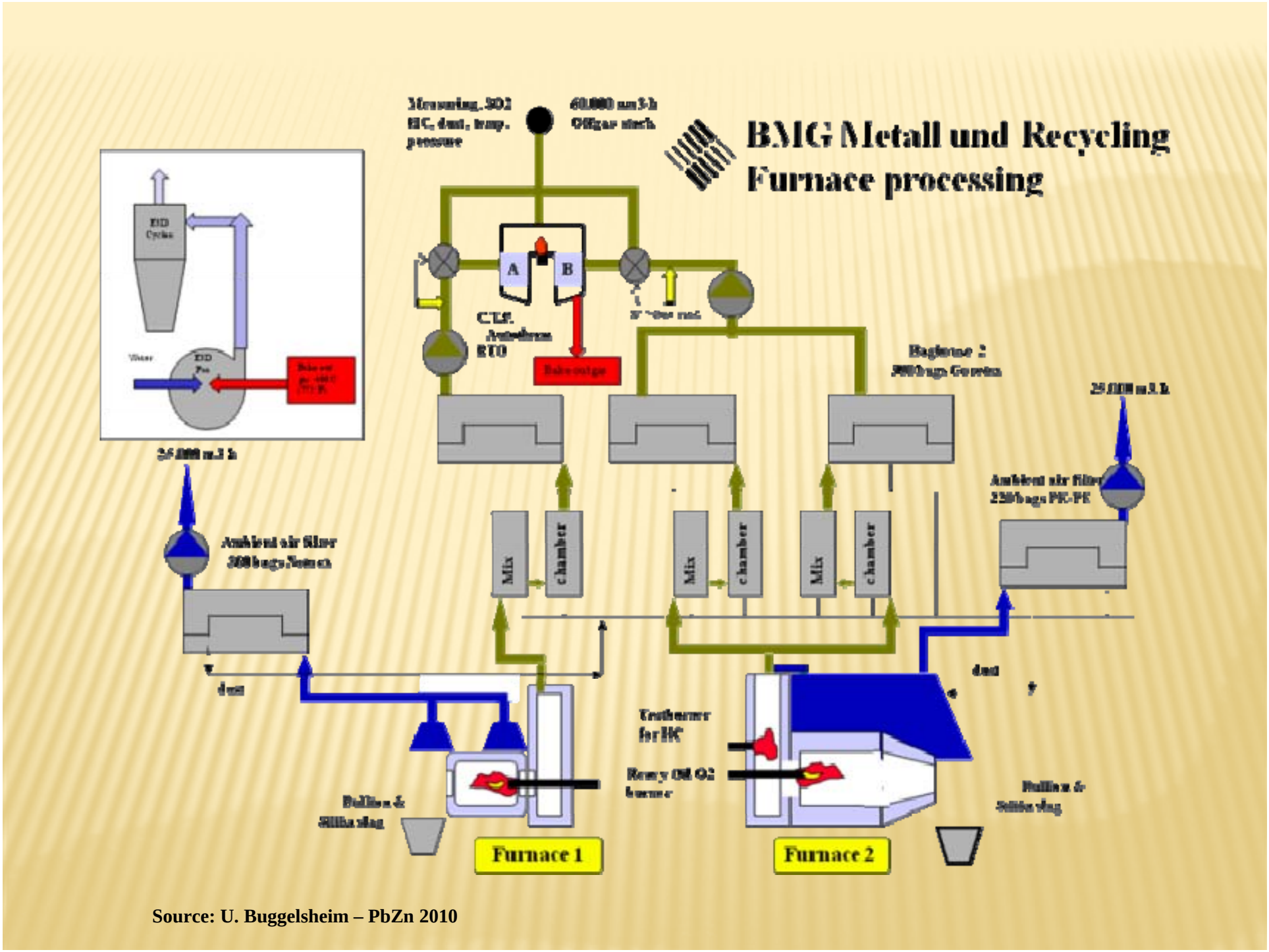
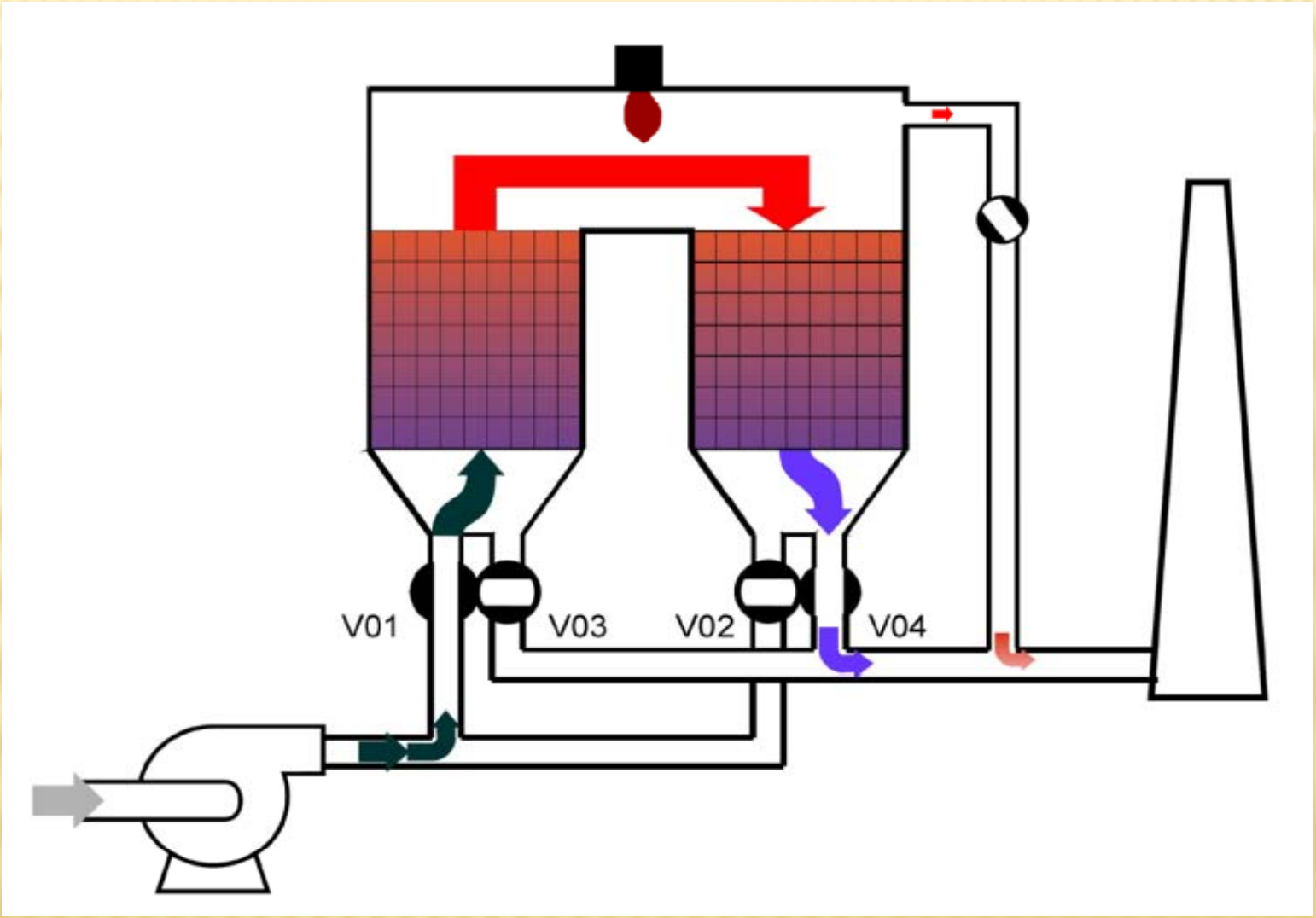


Source: U. Buggelsheim – PbZn 2010

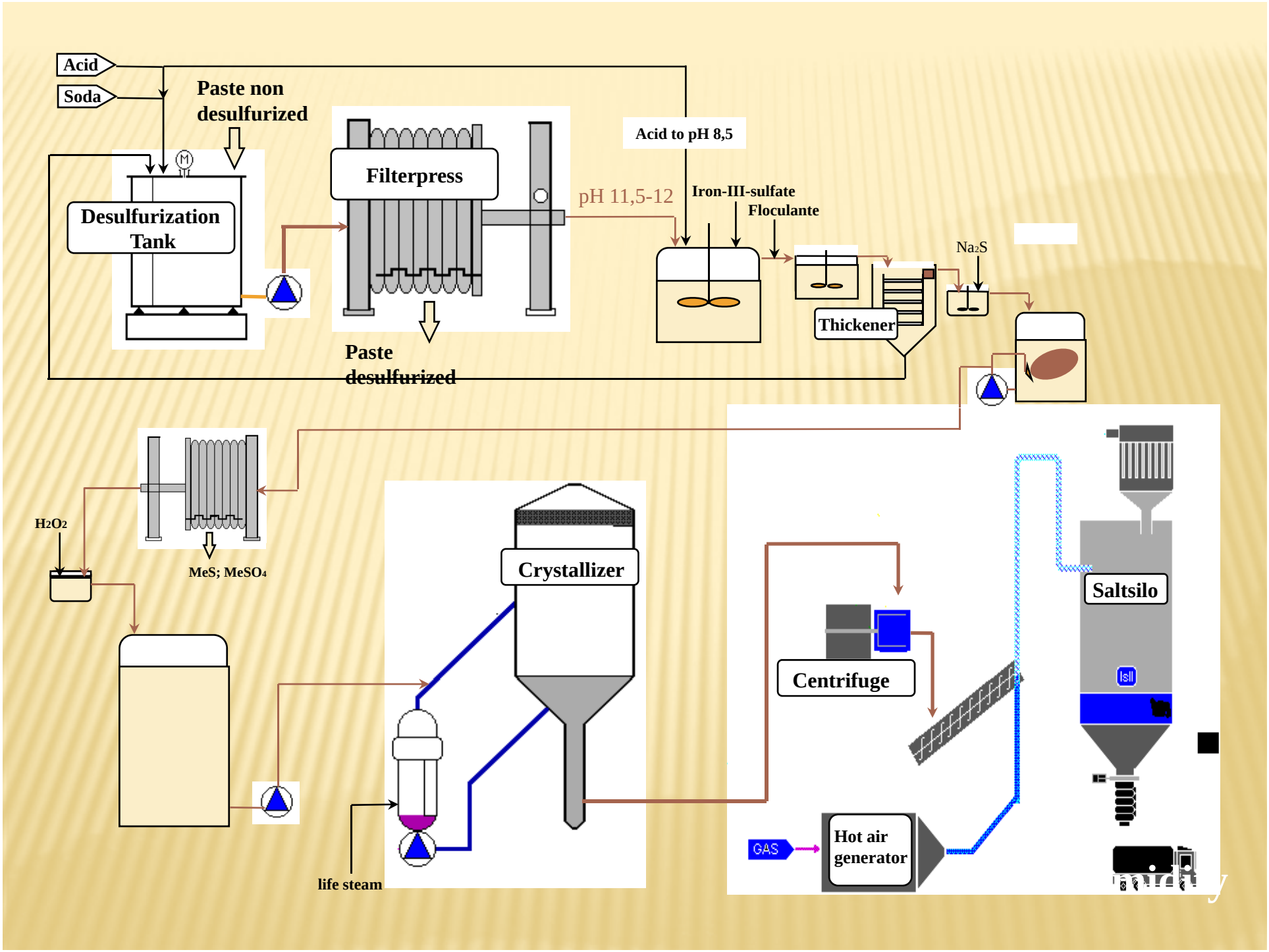
REGENERATIVE THERMO OXIDIZER SYSTEM

REDUCTION OF HYDROCARBONS

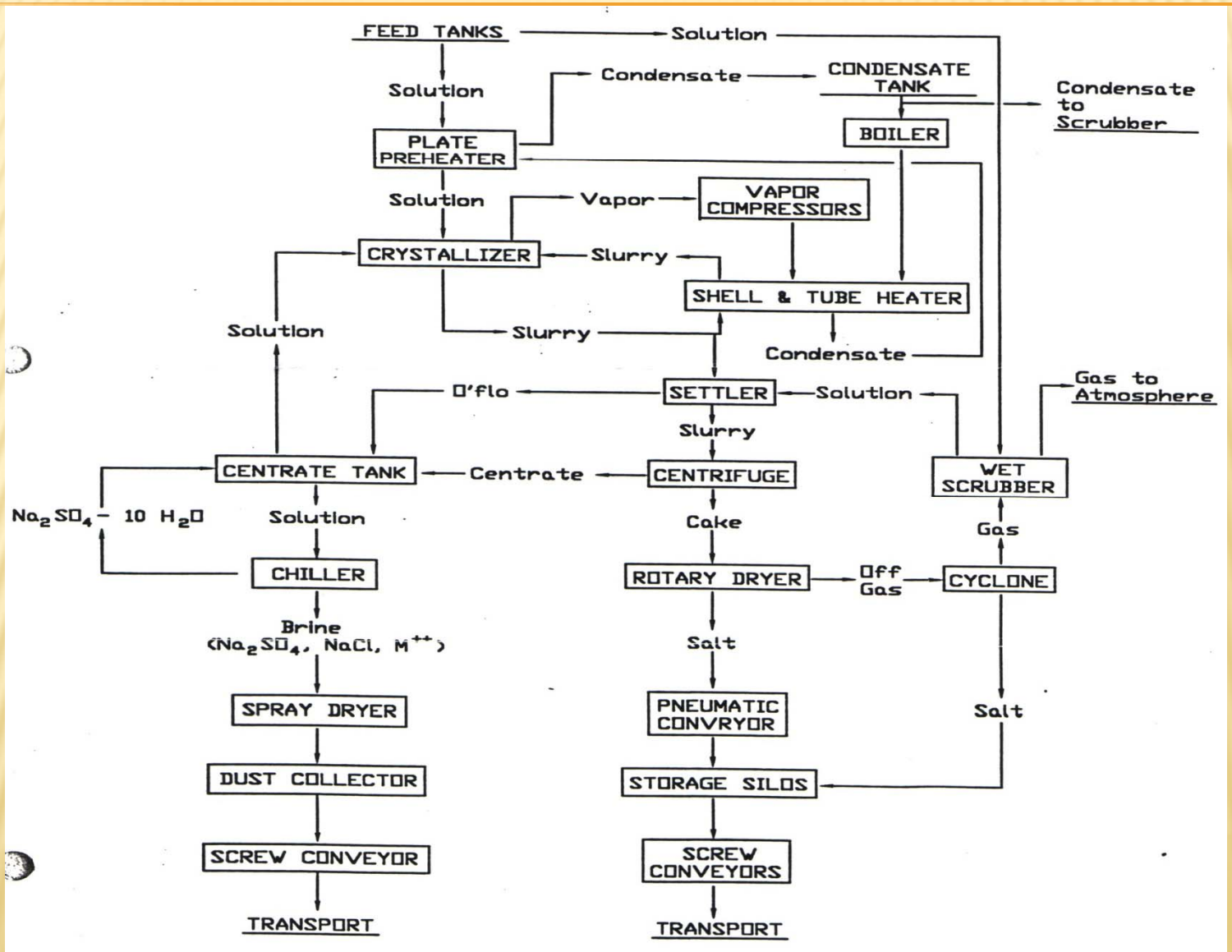


GENERATION OF VALUE-ADDED PROCESSES

- Recovery of Sodium Sulfate from Paste or Off-gas
- Recovery of Polypropylene (High for injection moulding and Low Quality)
- Strip Production on Site
- Purification of Battery Acid
- Incineration of Non-Recycable Components with Other Combustible Waste Materials


Acid
Soda
Paste non desulfurized
Desulfurization Tank
Filterpress
Paste desulfurized
Acid to pH 8,5
pH 11,5-12
Iron-III-sulfate
Floculante
Na2S
Thickener
H2O2
MeS; MeSO4
Crystallizer
life steam
Centrifuge
Saltsilo
GAS
Hot air generator

PROCESS FLOW SODIUM SULFATE CRYSTALLIZER

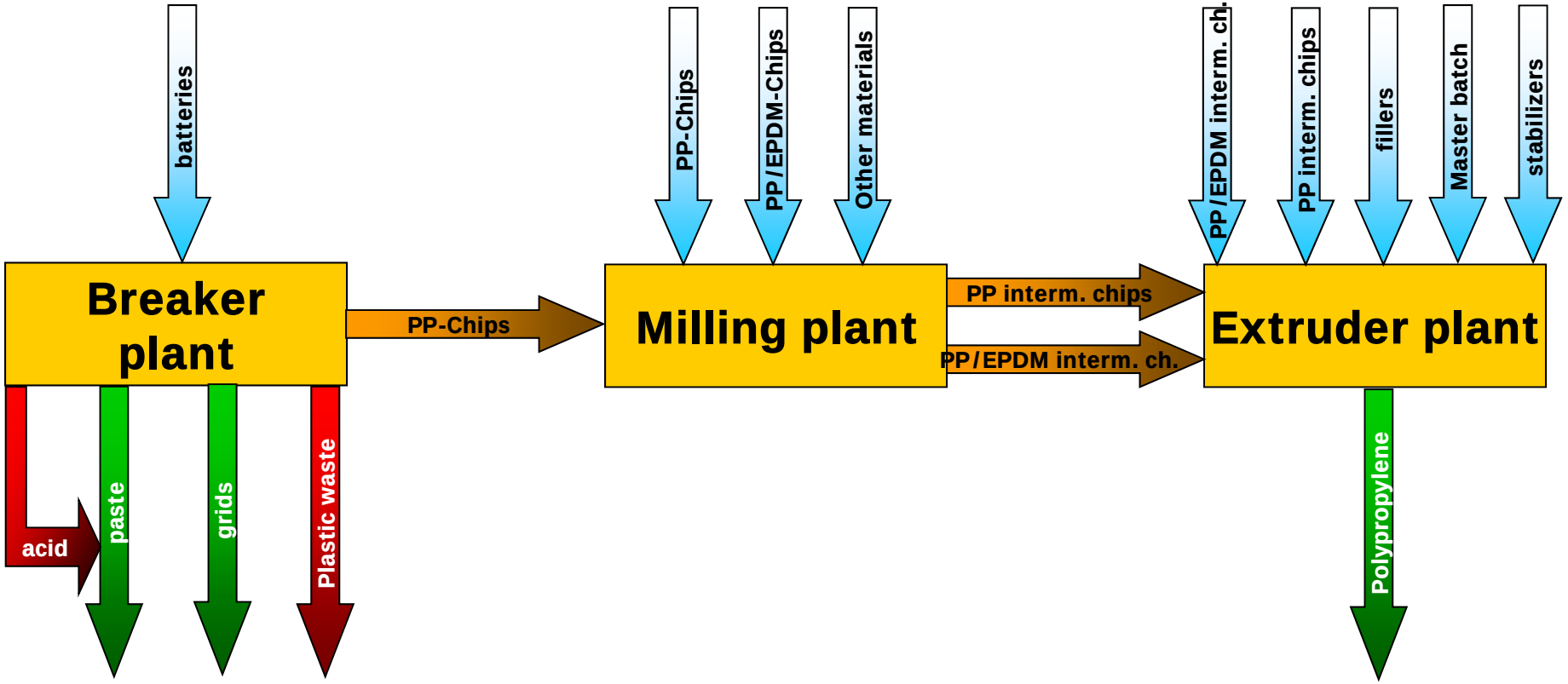


Source: A. Siegmund – CSM 2005

EVAPORATION & CRYSTALLIZER EQUIPMENT FOR SODIUM SULFATE

Source: Rick Leiby / East Penn – PbZn 2005

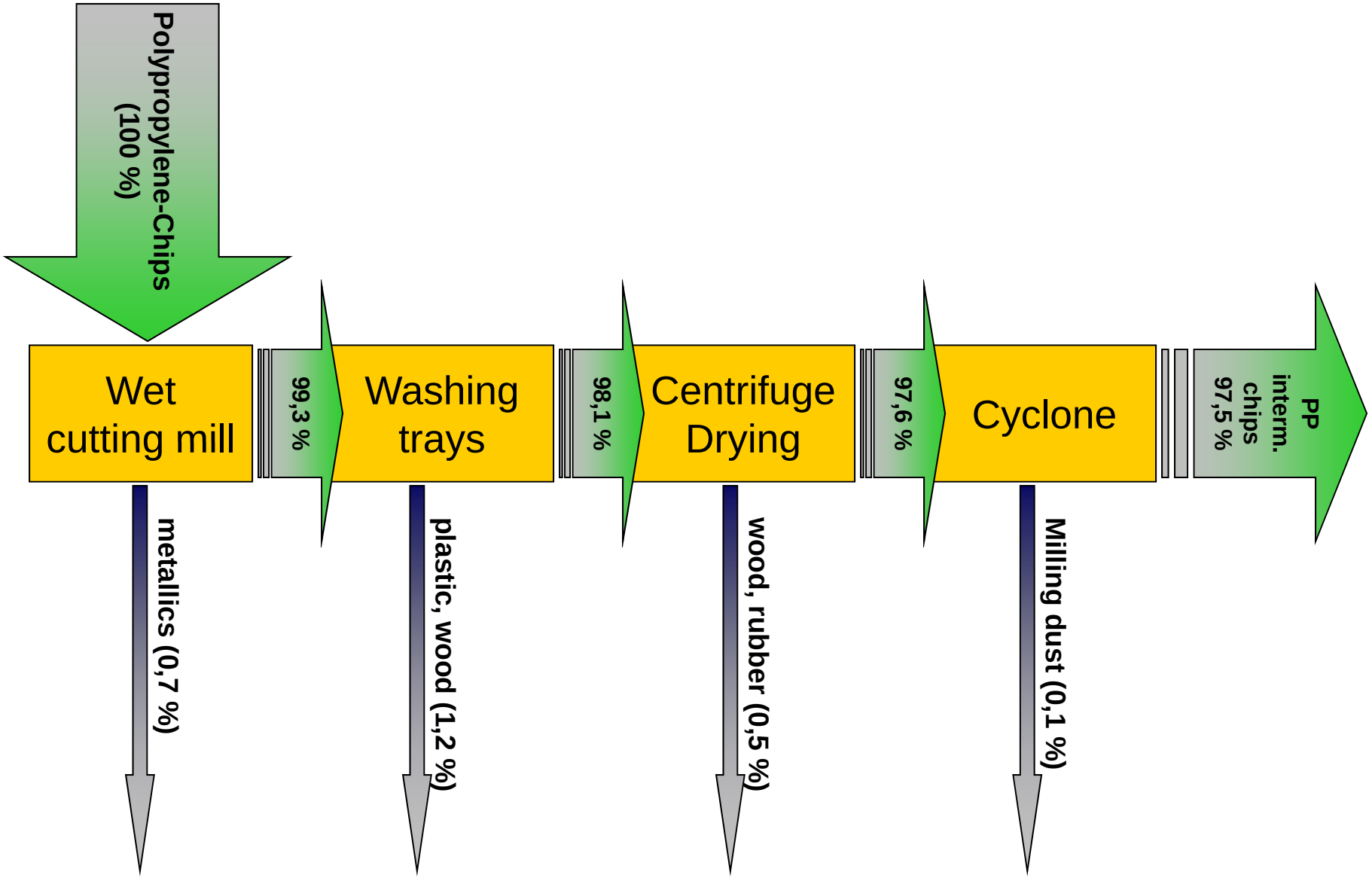
Process Polypropylene Recovery



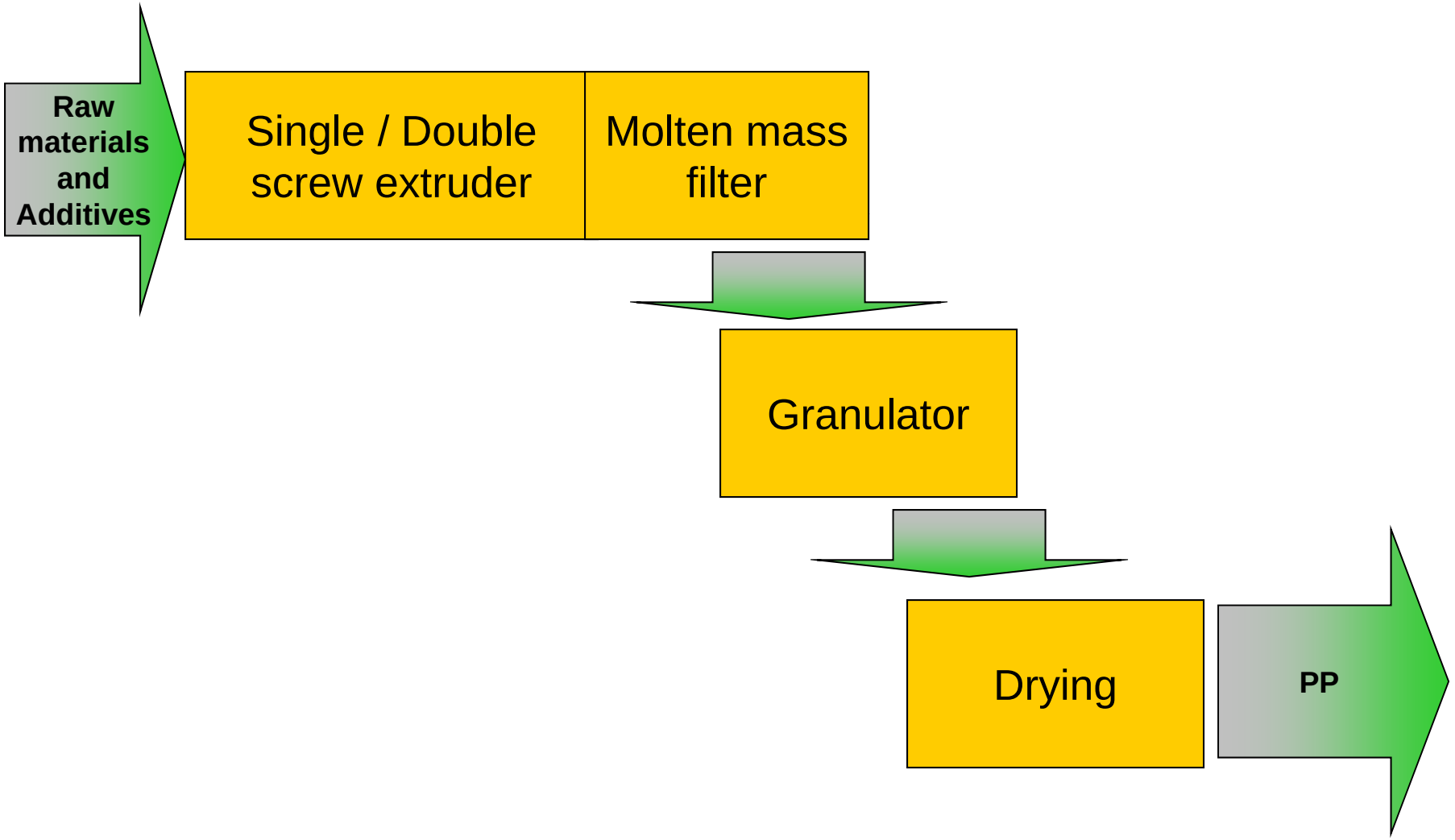
Raw materials for Plastic Recovery

- PP (origin: battery cases and other sources)

Process Flow Milling & Purification Process



Process Flow Extrusion



EXTRUDER FOR PLASTIC RECOVERY

Source: A. Siegmund - CSM 2005

RECOVERY OF POLYPROPYLENE

Source: G. Martin / A. Siegmund – PbZn 2000

BATTERY ACID PURIFICATION BY SOLVENT EXTRACTION

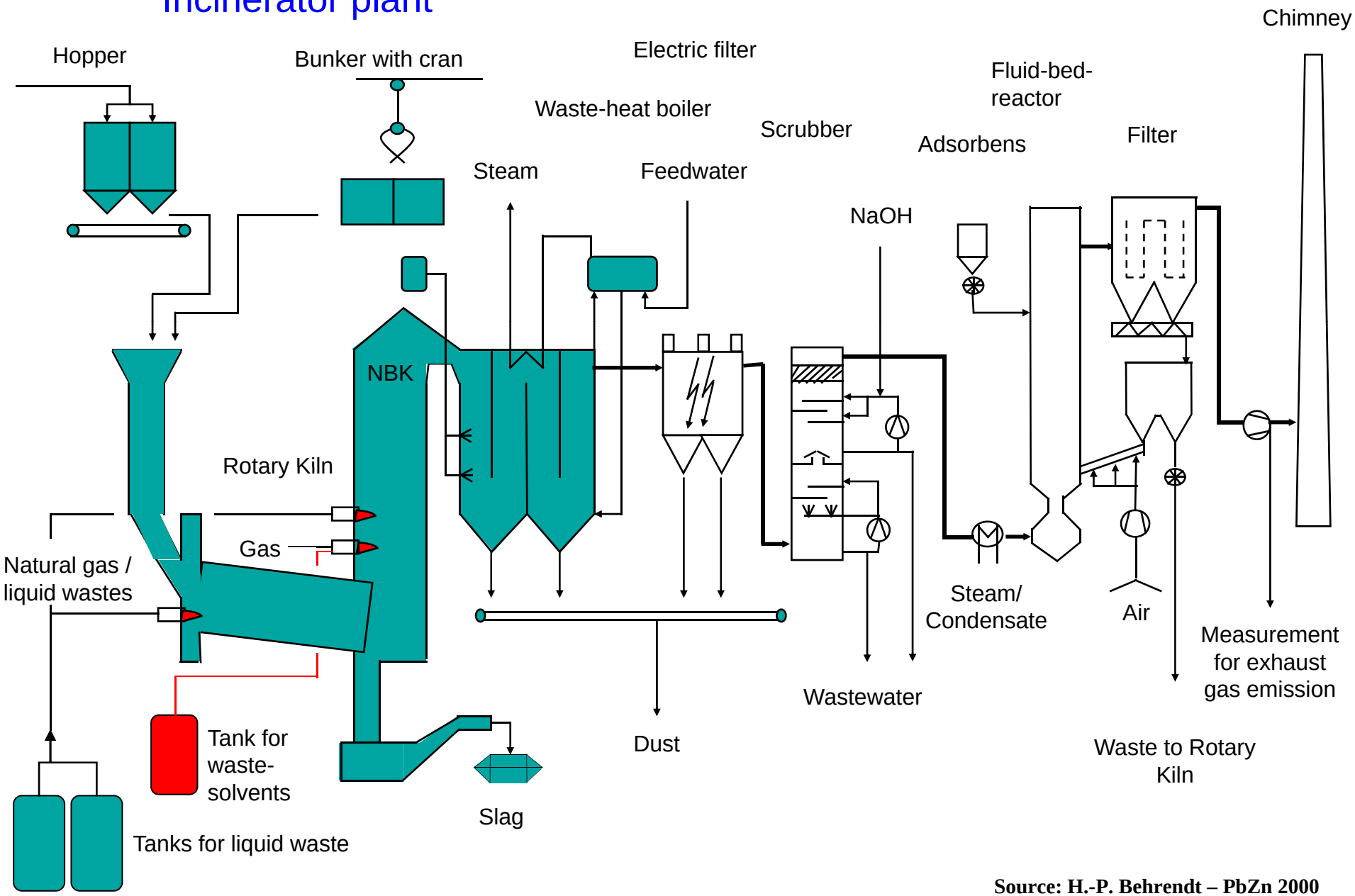
- 180 ppm Fe ➔ ≤ 20 ppm Fe
- 20 ppm Sb ➔ ≤ 6 ppm Sb

- Conventional PP-Filter to remove Particulates
- Dilute the Battery Acid to 15 - 18 % H_2SO_4
- Oxidize the Iron with Air or H_2O_2 to Ferric

Kelex 100	7%
DEPHA	12%
Tridecanol	11%
Mineral Spirits	70%

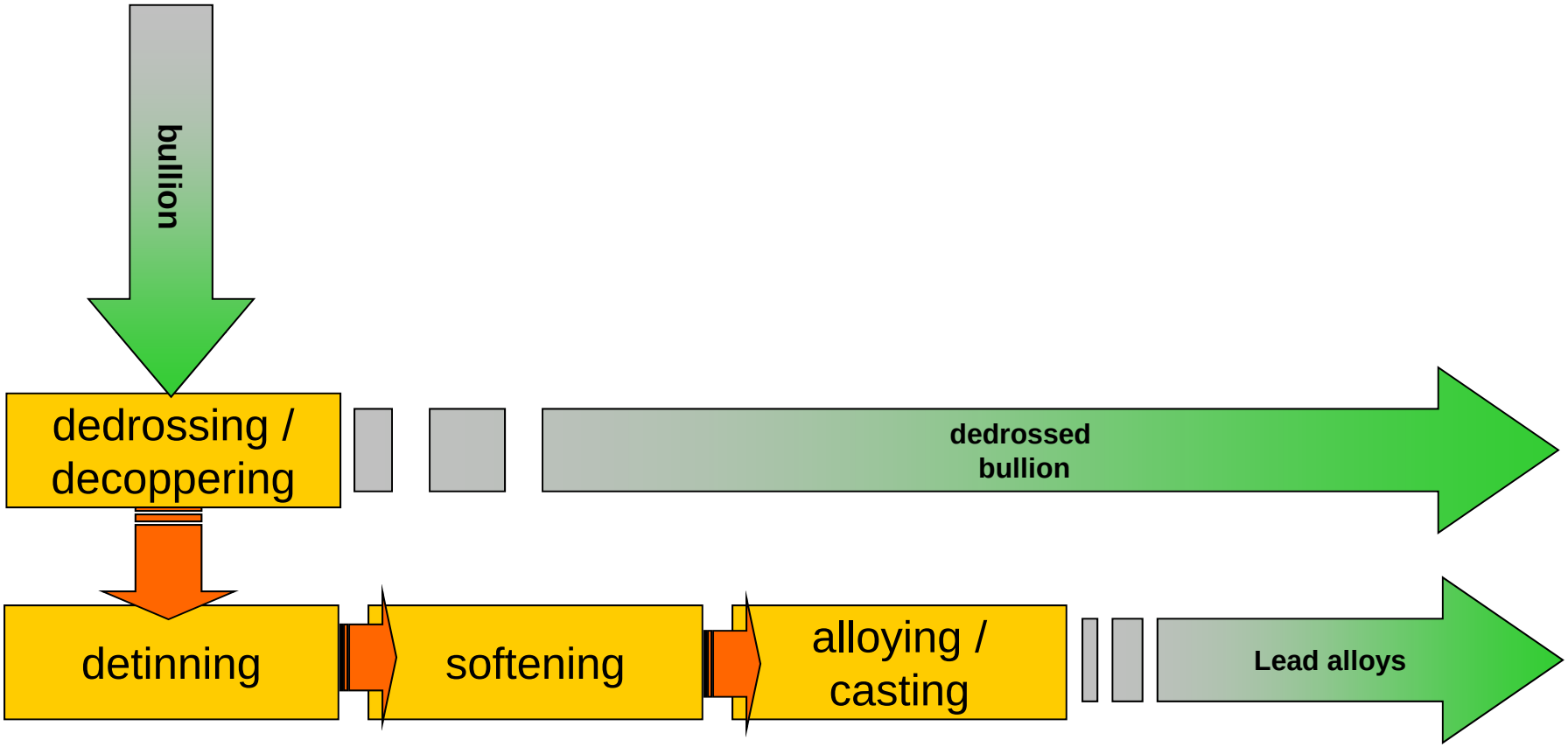
- Raffinate through Carbon Filter removing Organics
- Multiple Stripping of Solvent with 35% H_2SO_4
- Electrolytic Ferric reduction to Ferrous
- Concentration Waste Strip Acid about 2600 ppm Fe

Incinerator plant



Source: H.-P. Behrendt – PbZn 2000

Main Process Steps of Lead Refining



REFINING KETTLES

Source: Rick Leiby / East Penn – PbZn 2005


Thank you for Your Attention