Recycling Technologies & Considerations (Introduction to Mineral Processing & Extractive Metallurgy in Recycling)

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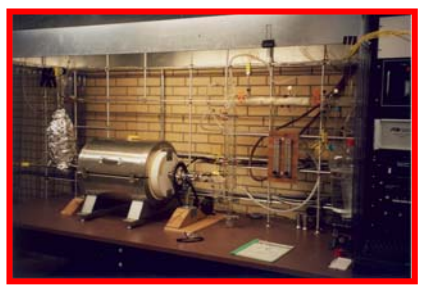


Why Should Companies Recycle?

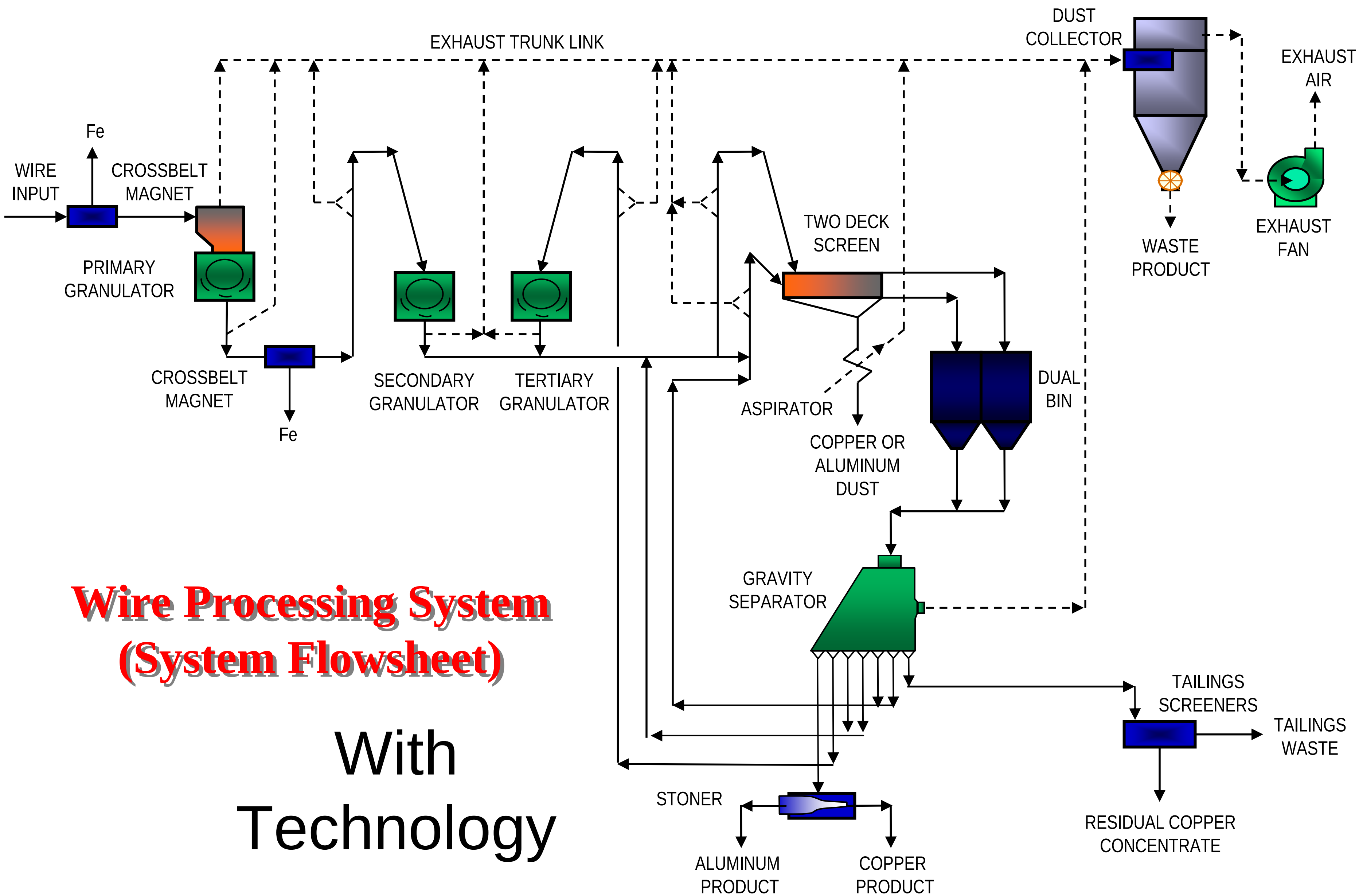
- The bottom line is **economics.**
- But in addition, companies may derive positive benefits from addressing both: **social responsibility** and **sustainable development** issues.

Computer Monitor Recycling in China – Copyright Basel Action Network

What Technology is used in Recycling?

- Most recycle technology is based upon our understanding of both **mineral processing** and **extractive metallurgy**.
- Innovative advances in both technologies have been, and are being, made to address the unique resource recovery problems associated with both **recycling** and **waste minimization**.

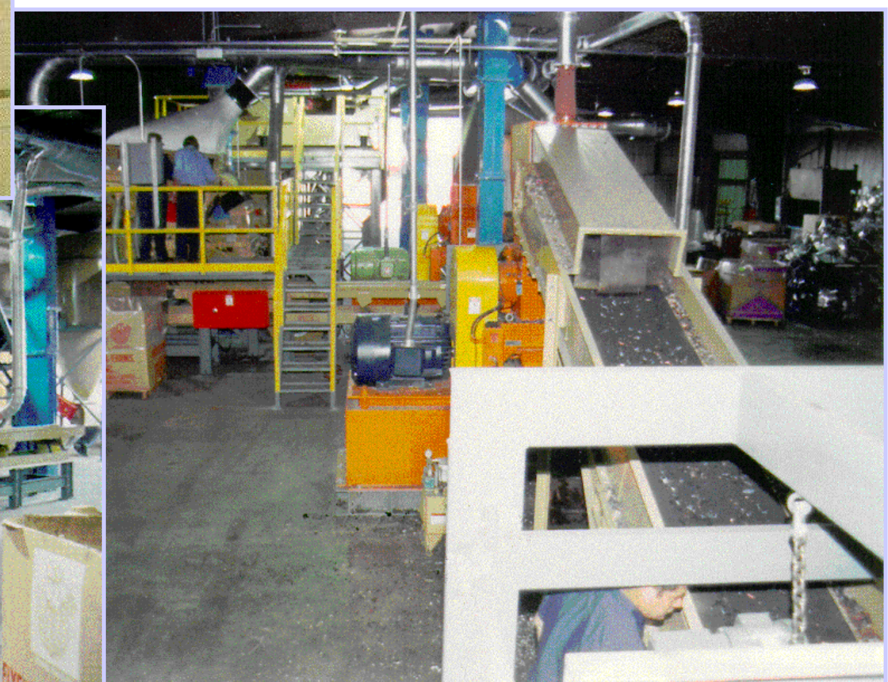
Computer Wire Recycling in China (Copyright Basel Action Network)



Wire Processing System
(System Flowsheet)

With Technology

2000 pound per hour Mechanical Wire Recovery Plant



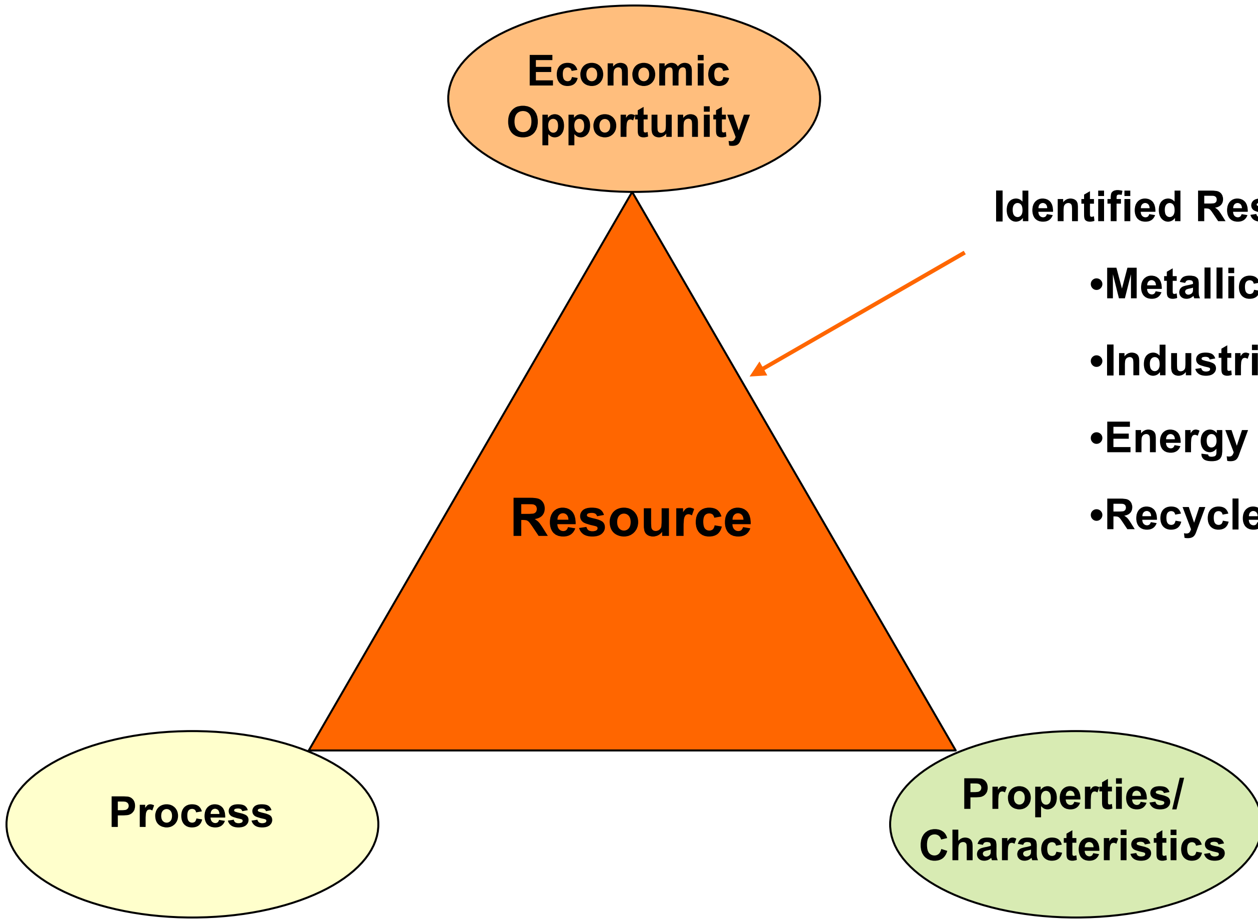
Some Questions

- What information do we need to obtain relative to a waste or recycle stream, both during the design and operational phases?
- Should we use mineral processing, hydrometallurgy, electrometallurgy and/or pyrometallurgy on a specific waste or recycle stream?

Some Questions

- What is "liberation" and why is it important?
- Some materials do not require liberation for metal recovery, in this case what is the concept of "exposure"?
- What specific qualities of a waste or recycle stream might be exploited in order to separate and/or expose it; or to selectively recover a specific metal or metals?

Building an Economic Opportunity from a Resource



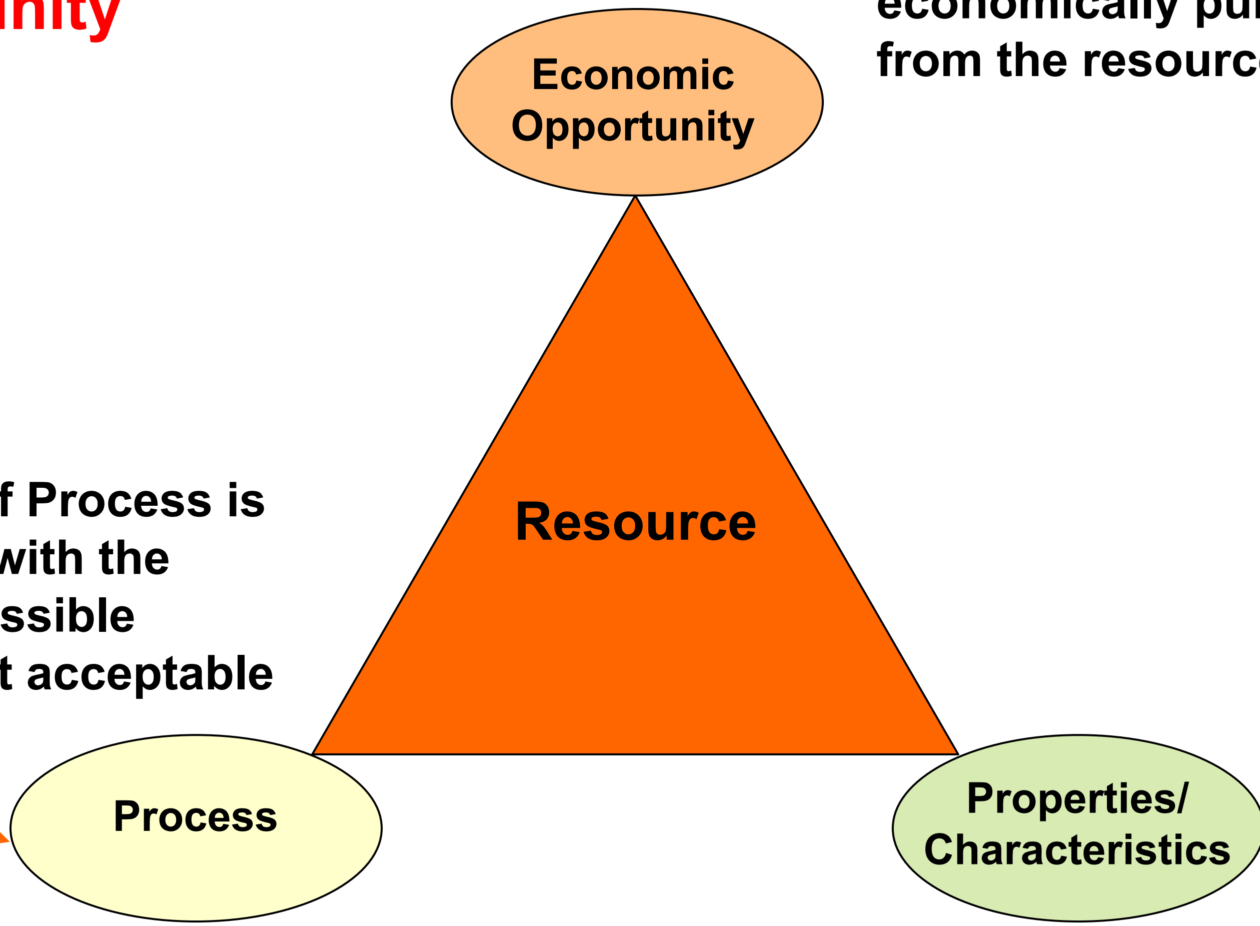
Identified Resource

- Metallic Mineral
- Industrial Mineral
- Energy Mineral
- Recycle Material

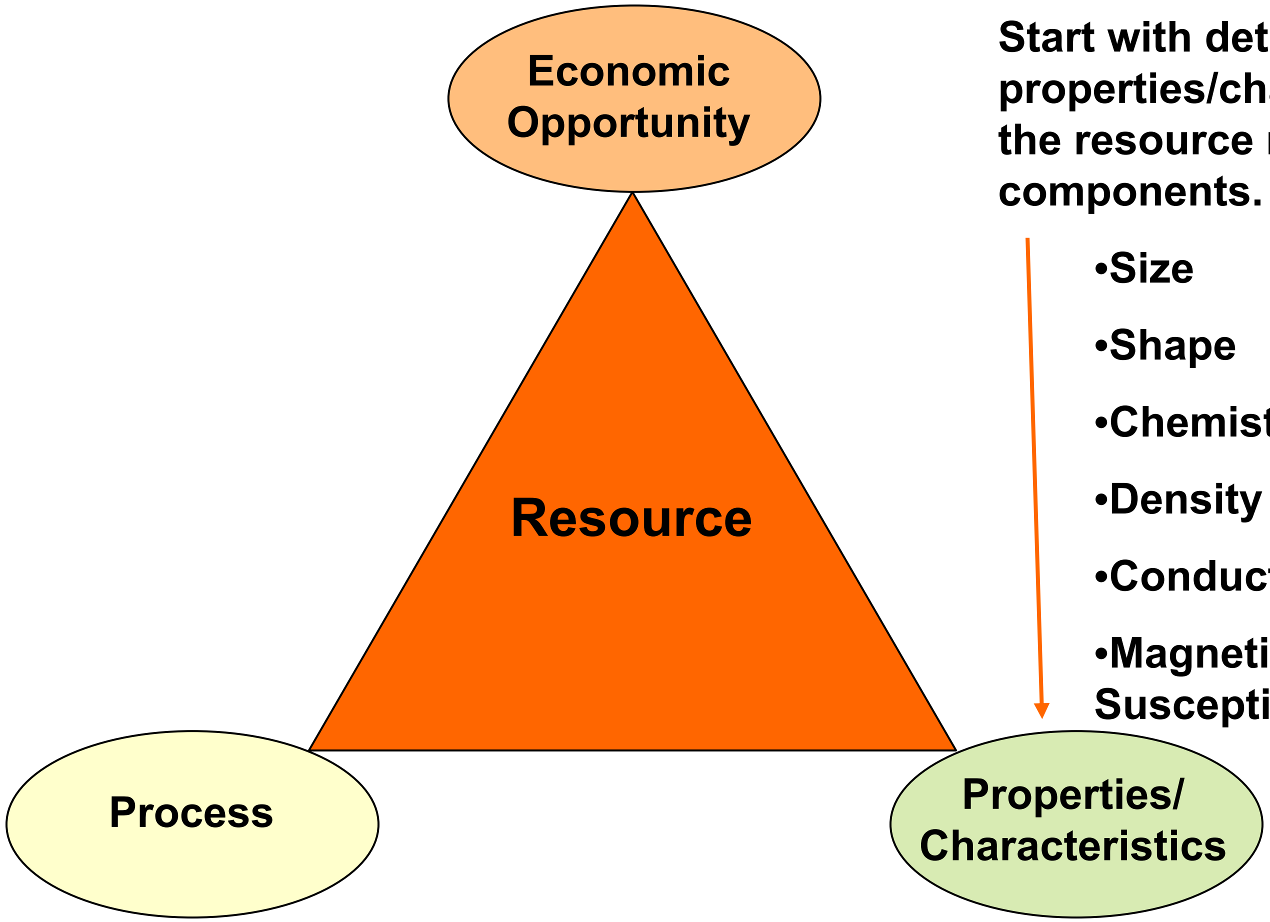
Process Supports the Economic Opportunity

The ultimate goal is production of metals and materials in their economically purest form, from the resource.

The goal of Process is a product with the highest possible recovery at acceptable grade.



Properties/Characteristics support the Process



Start with determining the properties/characteristics of the resource matrix and its components.

- **Size**
- **Shape**
- **Chemistry**
- **Density**
- **Conductivity**
- **Magnetic Susceptibility**

Characterization by Microscopic Grain Count

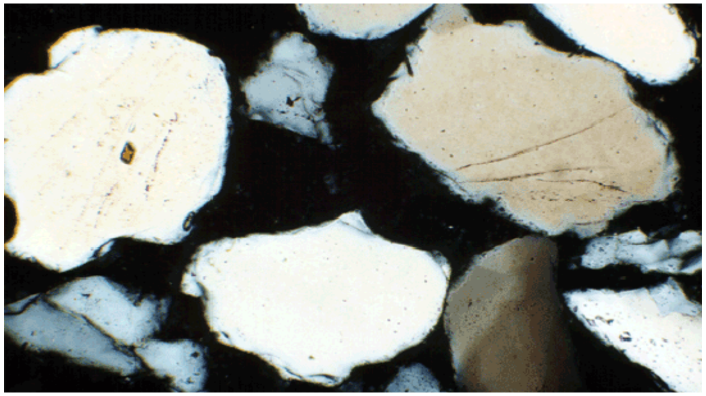
Photograph by Outotec Inc., Jacksonville FL 2007

- **Typical Heavy Mineral (beach sand) concentrate assemblage.**
- **Ilmenite, rutile, zircon, etc., (valuable HM) as well as non-value minerals.**
- **Characterization required to develop process scheme and to monitor process success.**

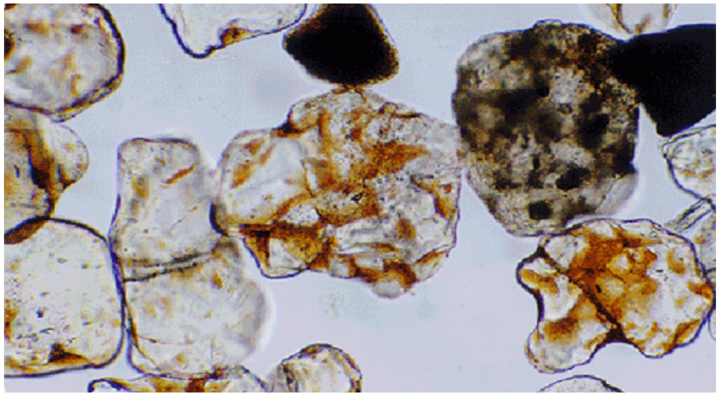
Two Quartz Sand Deposits

Optical Microscopy Characterization showing Potential Iron Inclusion Problems

Both Deposits have nearly identical Fe content



YES



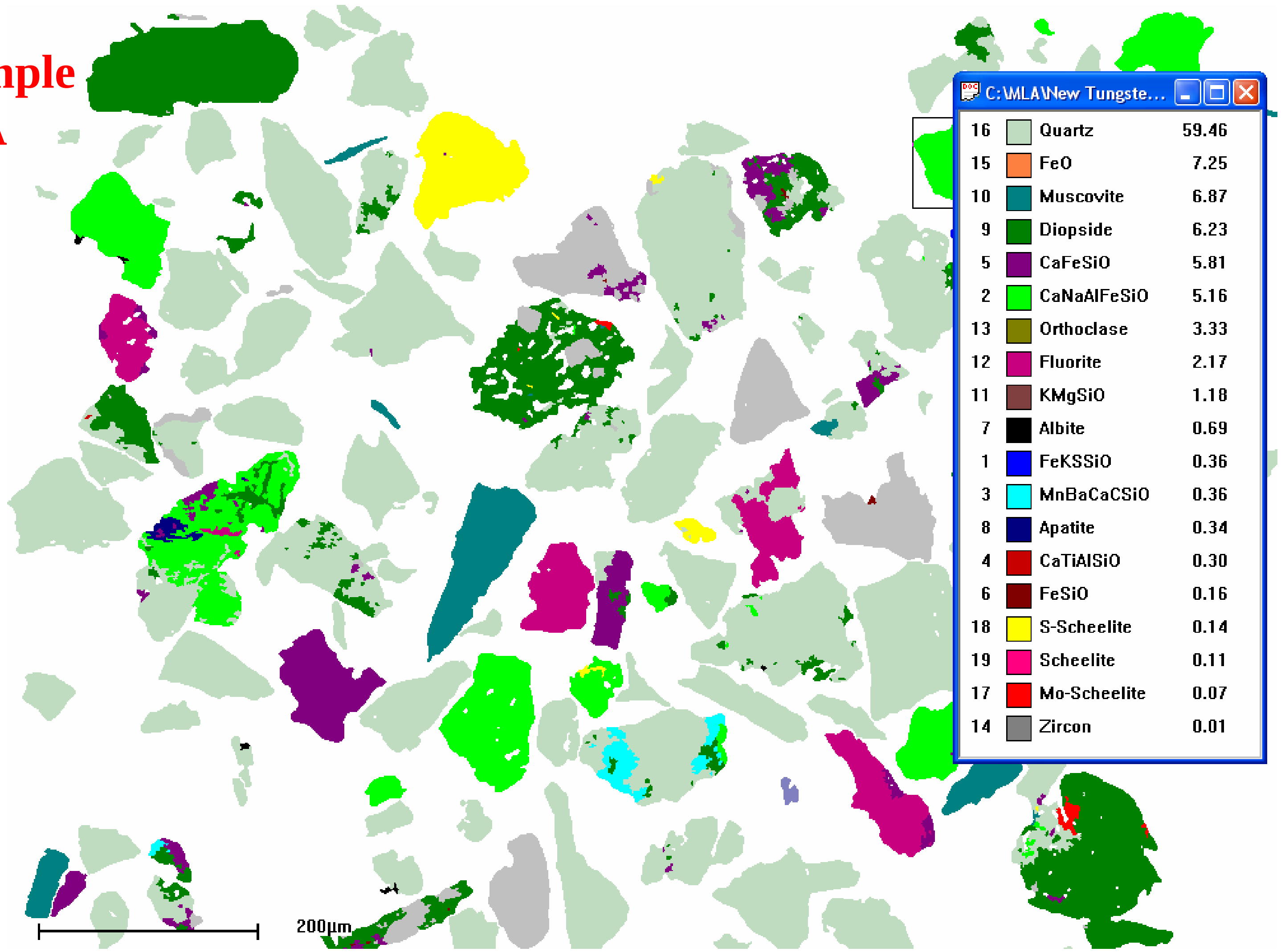
NO

Pictures Outotec Inc., Jacksonville FL, 2007

Complexity of Particles' Characterization and Liberation

- Requires sophisticated computer-controlled electron scanning. Always conducted as a (f) particle size
- Scanning electron Microscope (1 - 0.005 μm)
- QEM-Scan is commercial SEM based unit with very broad application including minerals
- Mineral Liberation Analyzer (MLS) is also SEM based
- Provides bulk mineral assemblage, a calculated bulk chemical analysis and particle-by-particle deportment of target metals

Example MLA



*From CAMP-Corby Anderson

Mineral Processing and Extractive Metallurgy

- ***Mineral Processing*** **– the utilization of methods to separate valuable minerals (or metals) from waste minerals based on physical or surface chemistry properties**
- ***Hydrometallurgy*** **– the utilization of aqueous environments to "leach" metals from minerals (or other sources), to separate dissolved metals from each other or dissolved impurities, and to recover metals from solution.**
- ***Pyrometallurgy*** **– the utilization of high temperatures to modify the chemistry of minerals (or other sources), to reduce minerals to metals, and to refine metals.**
- ***Electrometallurgy*** **– the utilization of electricity to recover and/or to refine metals in aqueous or molten salt solutions.**

Mineral Processing

- Mineral properties: chemistry, density, magnetic susceptibility, conductivity, surface chemistry, optical properties, etc.
- Comminution: Crushing, grinding, shredding (liberation)
- Sizing (screening, hydrocyclones, etc.)
- Gravity separation
- Flotation
- Electrostatic separation
- Dense media separation
- Magnetic separation
- Solid-liquid separation (Thickening and filtering)
- Waste treatment and minimization

Hydrometallurgy

- **Leaching – the selective dissolution of metals from minerals, ores, or other sources.**
- **Solid/liquid separation – thickening, filtering.**
- **Solution purification – solvent extraction, ion exchange, etc.**
- **Metal recovery - precipitation of metals or oxides – hydrogen reduction, cementation, pH changes, etc.**
- **Waste treatment and minimization.**

Pyrometallurgy

- **Fuel and ore preparation – reductants, drying, calcination, roasting, agglomeration, etc.**
- **Reduction of metal oxides – iron reduction, etc.**
- **Volatile metals – vaporization, zinc production, refining processes, etc.**
- **Slags and refractories – impurity removal, heat and product containment, etc.**
- **Matte smelting – Copper smelting, nickel smelting, etc.**
- **Refining Processes – desulfurization, deoxidation, etc.**
- **Rare and Reactive Metals – Ferroalloys, metallothermic reactions, pure metals, halides, etc.**

Electrometallurgy

- **Electrowinning** – the utilization of electricity to recover metals from solutions.
- **Electrorefining** – the utilization of electrical energy to purify metals.
- **Fused salt electrolysis** – the recovery of metals from molten salts through electricity (aluminum, magnesium, sodium, etc.)

Extractive Metallurgist's Toolbox

- **Characterization of chemistry and properties.**
- **Energy & Mass Balances**
- **Chemical Thermodynamics**
- **Heterogeneous Kinetics**
- **Reactor Design**
- **Transport Phenomena (Heat, Mass and Momentum Transfer)**
- **Unit Operations in Mineral Processing, Hydro - , Pyro - and Electro - metallurgy**
- **Unit Operations in Recycle and Waste Processing**

Introduction

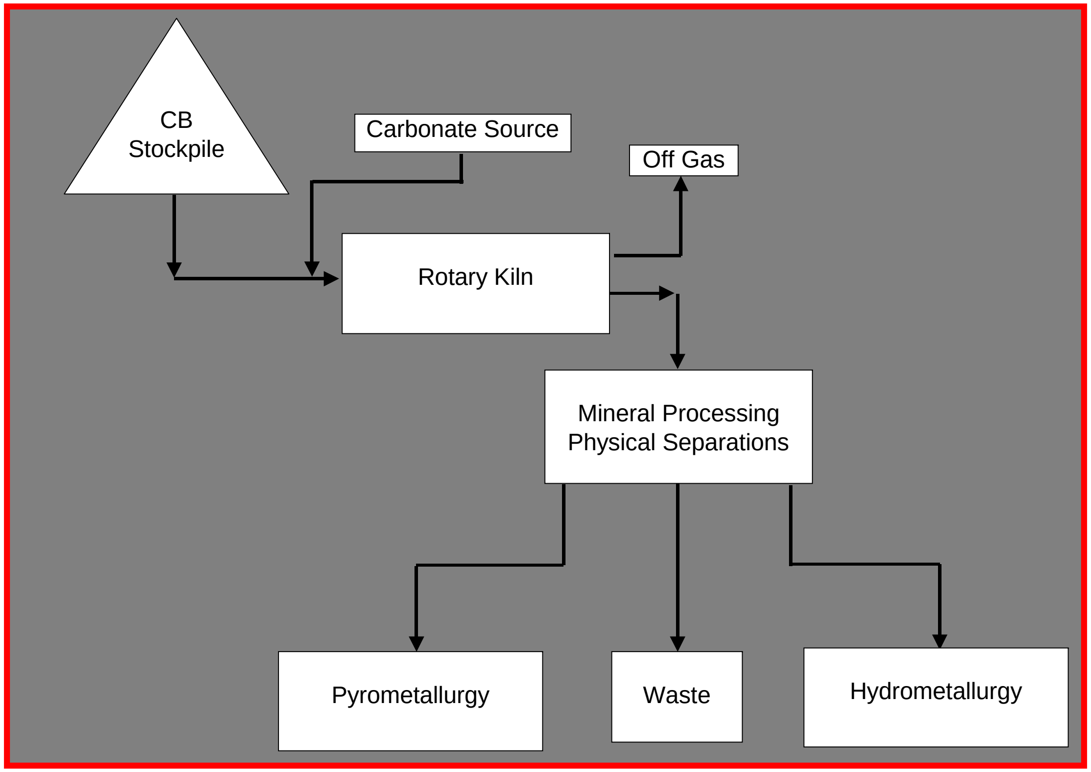
- The art of extracting metals from ores dates back to the dawn of human civilization.
- Around 4000 B.C. man learned to produce copper and bronze by the smelting of copper and tin ores in a charcoal fire.
- A visitor to a modern metallurgical plant will be struck by the large number of complex operations.
- The many different metallurgical processes may be understood as the result of a relatively small number of fundamental principles.

Ore (Resource)

- An **Ore** (or **Resource**) is a material which can be mined (or processed) economically to serve as raw material for the production of metals.
- The economic aspect is an important point, which makes the limit between what is ore and what is worthless depending on the **existing state of technology** and by the **market price for the metal** in question.
- The price of the metal or commodity is the most important driver, along with the costs (capital and operating) to treat and recover the materials.

Flow Sheets

- The combination of processes which is used in a given plant is illustrated conveniently by means of a flow sheet.
- The example illustrates the recycle of used circuit boards.

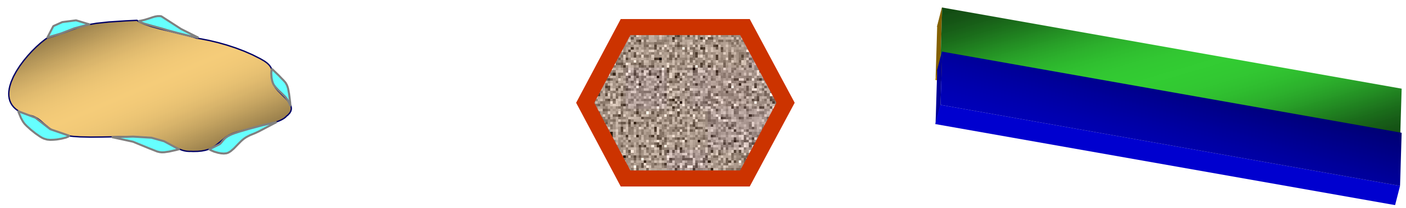


Unit Operations

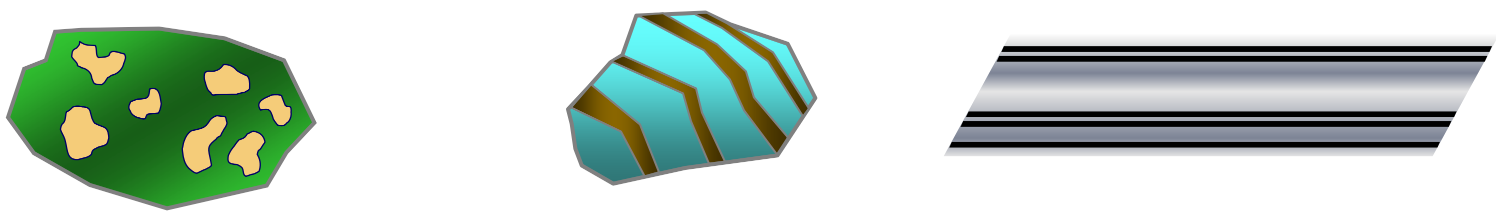
- If a flow sheet is examined more closely it is seen that they consist of combinations of steps or operations, and that some of the same steps or operations are found in the production of different metals and in different locations. Unit operations.
- For most metal resource recovery flow sheets we have the first steps that involve crushing, grinding and physical separation.
- The purpose of these steps, called mineral processing, is to separate the valuable constituents from the waste or from other valuable constituents. Liberation or Exposure.

Liberation or Exposure

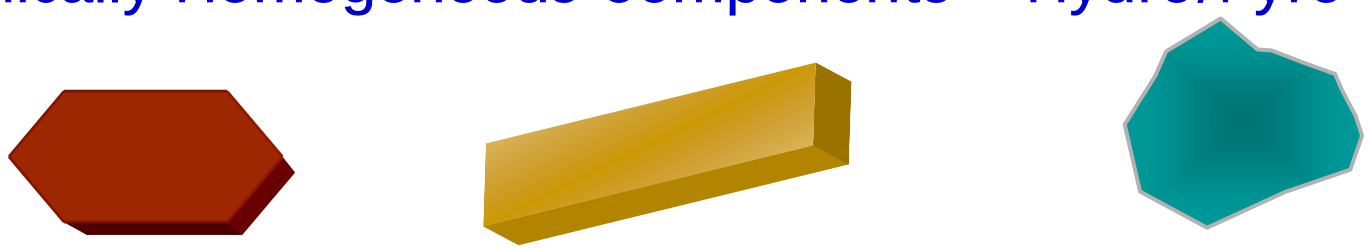
Surface Adhering Components – Physical Separation



Distributed Components – Physical Separation



Chemically Homogeneous Components – Hydro/Pyro Sep



Unit Operations

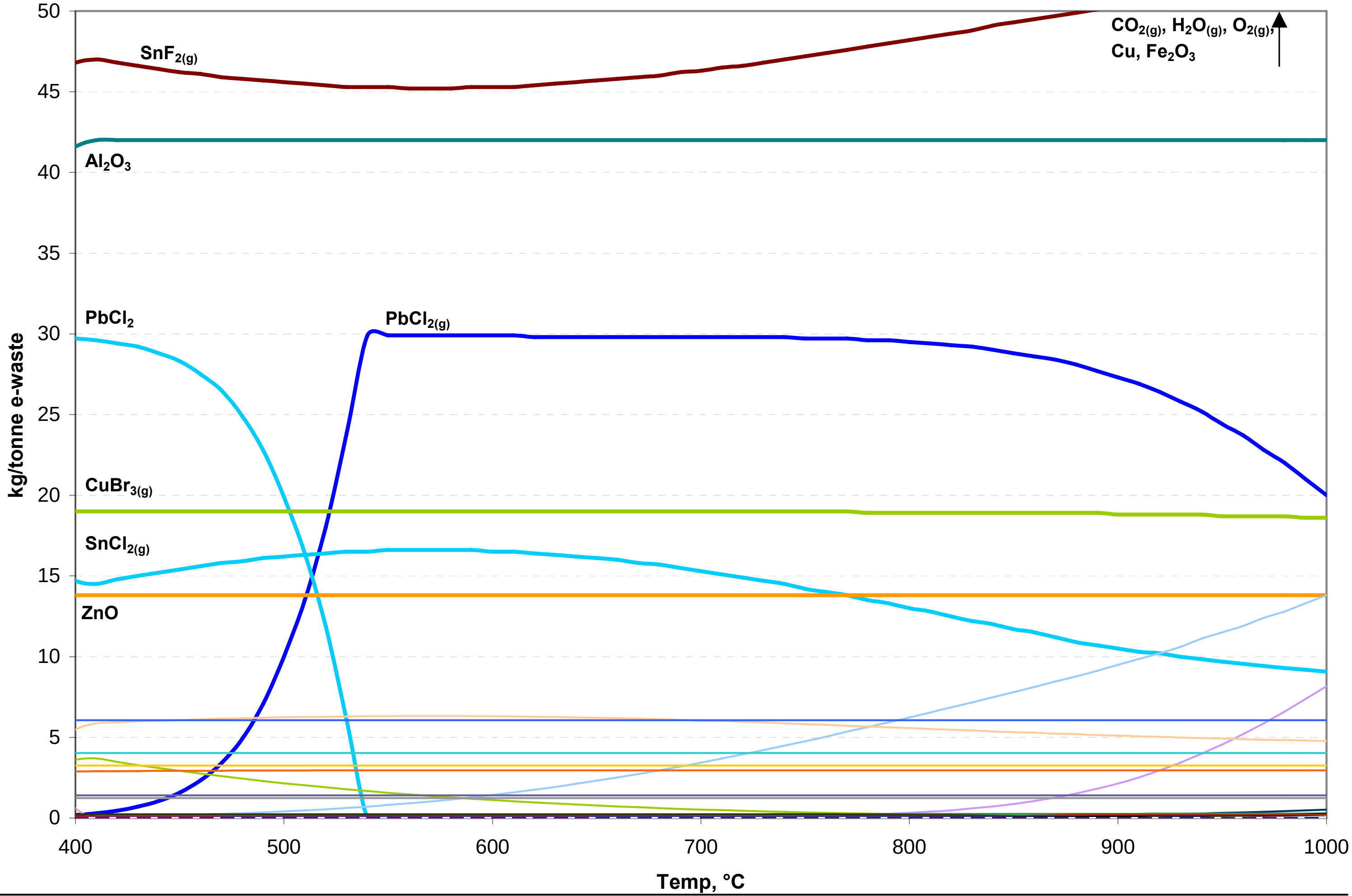
- The next steps are typically chemical in nature and allow the recovery of a product that might be refined to a more marketable form. "Extractive Metallurgy".
- Extraction and refining are typically required in order to produce marketable products.
- Thus a large variety of flow sheets are possible by combinations of a relatively small number of different single steps. "Unit Operations".
- Typically these are classified by either the physical or chemical step or both.

Chemical Unit Operation

- All flow sheets require detailed mass balances.
- A chemical unit operation has as its main purpose to carry out a given set of chemical reactions.
- It is necessary to know how to make the reaction run in the desired direction, and how to avoid unwanted side reactions.
- This is first of all a question of chemical thermodynamics and chemical kinetics.
- In some cases, a certain reaction temperature is needed.
- This requires a knowledge of heats of reaction, heat capacities and the principles of heat transfer.

Thermodynamic Model

E-Waste Composition with Excess O_2



119 kg Metal Halide @ 600°C
4.47 kg Halide Acids

Heat Transfer and Kinetics

- **From heats of reactions and heat capacities, the theoretical energy requirements may be calculated and heat balances can be performed.**
- **Finally, the process has the purpose to produce the wanted product preferably as fast as possible.**
- **An evaluation of the production capacity and of the factors which determine the size and design of reactors is obtained partly from chemical kinetics and reactor design and possibly from heat transfer and fluid flow considerations.**

Features of Metal Extraction

- **The final combination of unit operations into a complete flow sheet is to a large extent dependent on economic considerations: the cost of raw materials and market conditions.**
- **Often the same metals can be produced by several different methods.**
- **Most metals are produced from *impure* ores or recycle streams.**
- **Most commonly these are recovered to give an impure metal or solution.**

Refining of Metals

- The impure metal or solution may be refined further to remove impurities and give a product of the required purity.
- Alternatively the feed stock could be treated to give an essentially pure chemical compound of the metal, and the compound may be reduced to give a pure metal.
- This procedure, is more commonly used for the more reactive metals: titanium, niobium, and the light metals.

Recirculation

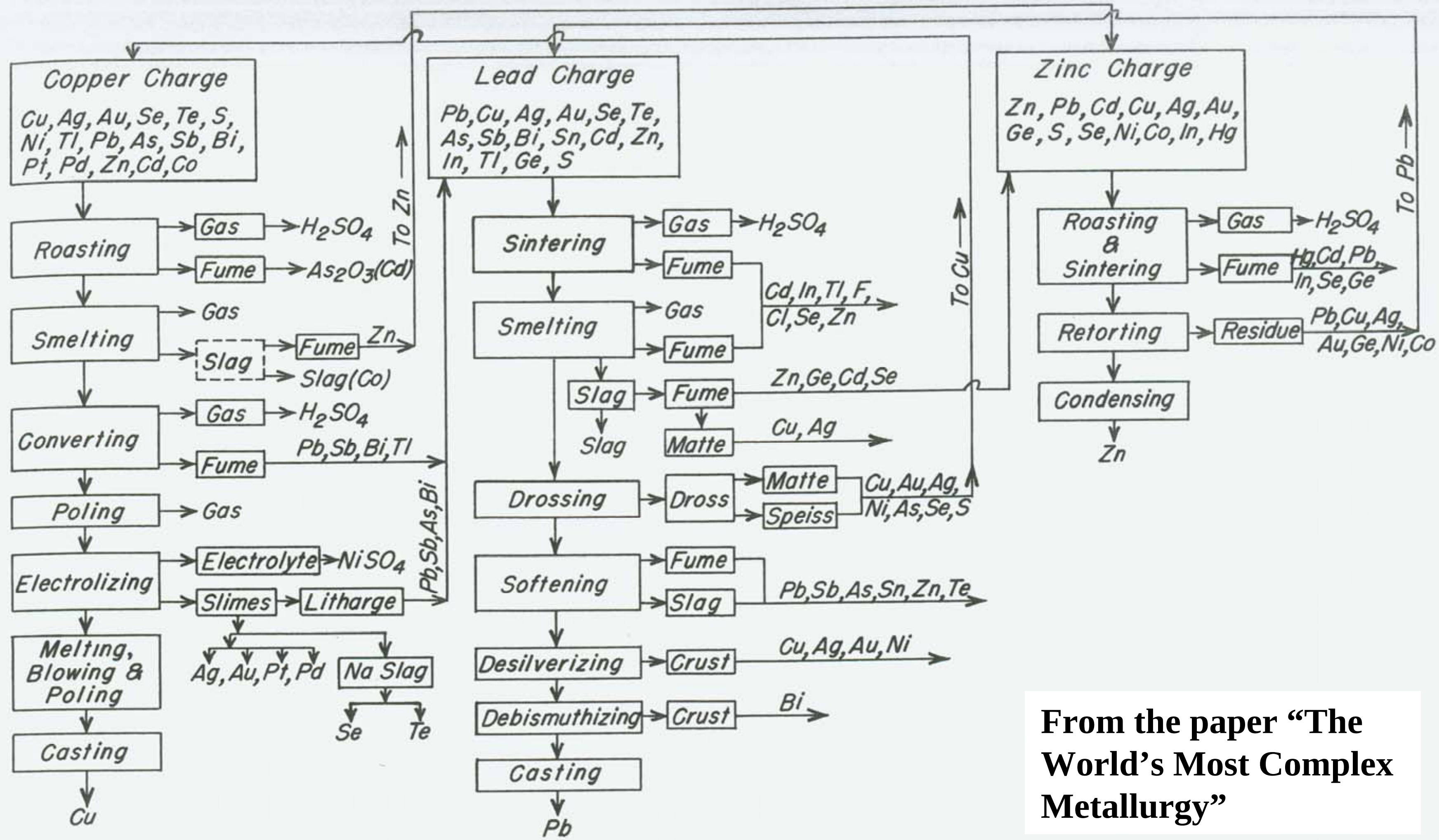
- If we examine various flow sheets, we will observe certain other common features.
- One of these is the circulation or return of intermediate products to previous steps. Recirculation.
- This is done in order to recover, as completely as possible, the valuable constituents.
- It is also done to provide methods for waste minimization.
- Recirculation cannot be used in all cases due to potential build up of unwanted species.

By-product Recovery

- In may flow sheets we observe the recovery of ***By-products.***
- Most ores (or resources) contain, in addition to the major elements, smaller or larger quantities of by-product elements.
- These may be enriched in certain phases at certain stages in the treatment.
- Also, special processes may be developed to recover valuable by-products which do not separate out during the normal refining processes.

Integrated Process

- **If the plant produces more than one main product, it is called an *Integrated process*.**
- **In an integrated plant, the by-product from one part may serve as raw material for another.**
- **The efficient utilization of by-products in an integrated plant contributes greatly to the economy of such a plant.**



From the paper "The World's Most Complex Metallurgy"

Fig. 25—Combined copper, lead, and zinc circuits.

Some Examples from KIEM

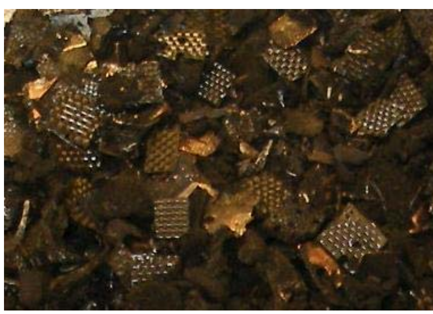
Recent or Current Projects

- **Electronic Scrap as feed to a Copper Smelter**
- **Metal and Energy Recovery from Fluff (Automobile Shredder Residue)**
- **Titanium Recovery from Investment Casting Chemical Milling Solutions.**
- **Molybdenum Recovery from a Ferro-nickel Alloy**

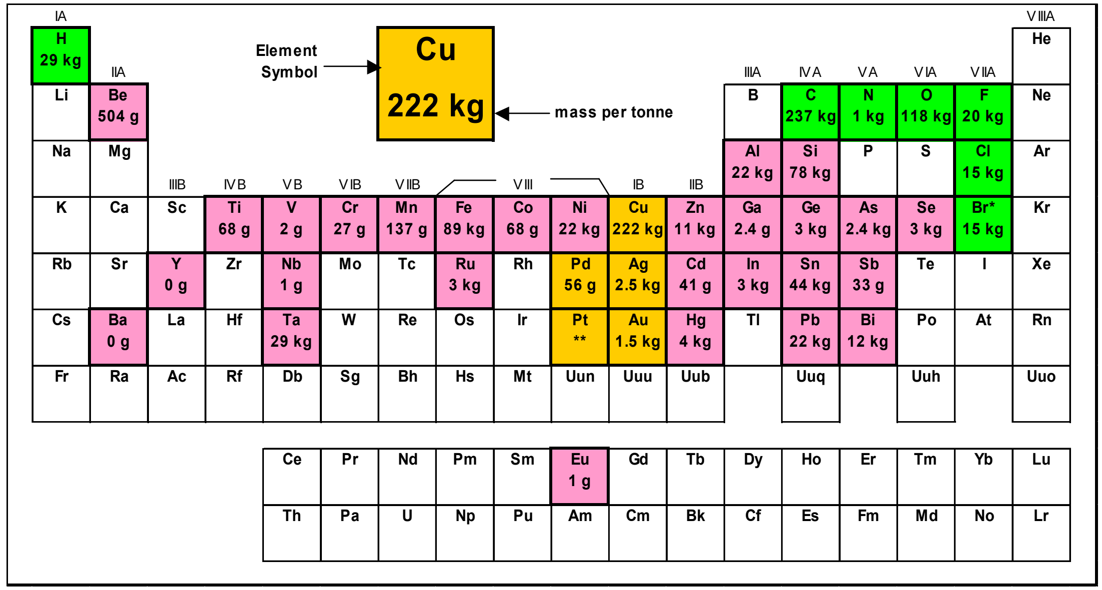
Low Temperature Pre-processing with Halide Control

Raw E-Waste

Shredded E-Waste



Low Temp Process



Energy Recovery

Metal Recovery

Ag

Au

Cu

Electronic Scrap Processing

Fundamentals:

- Chemical Thermodynamics
- Heat and Mass Balances
- Chemical Kinetics
- Reactor Design
- Chemical analysis
- Gas analysis
- Partitioning (metal/slag/vapor)

Unit Operations:

- Crushing, grinding and/or shredding.
- Rotary kiln pyrolysis
- Gas scrubbing
- Mineral Processing
- Crucible reduction
- Slag behavior and chemistry
- Refining

Composition of E-Waste

Element Symbol → **Cu** / **222 kg** ← mass per tonne

IA	IIA	IIIB	IVB	VB	VIB	VIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
H 29 kg																	He
Li	Be 504 g											B	C 237 kg	N 1 kg	O 118 kg	F 20 kg	Ne
Na	Mg											Al 22 kg	Si 78 kg	P	S	Cl 15 kg	Ar
K	Ca	Sc	Ti 68 g	V 0 g	Cr 27 g	Mn 137 g	Fe 89 kg	Co 68 g	Ni 22 kg	Cu 222 kg	Zn 11 kg	Ga 2.4 kg	Ge 3 kg	As 2.4 kg	Se 3 kg	Br* 15 kg	Kr
Rb	Sr	Y 0 g	Zr	Nb 1 g	Mo	Tc	Ru 3 kg	Rh	Pd 56 g	Ag 3.5 kg	Cd 41 g	In 3 kg	Sn 44 kg	Sb 33 g	Te	I	Xe
Cs	Ba 0 g	La	Hf	Ta 29 kg	W	Re	Os	Ir	Pt **	Au 1.5 kg	Hg 4 kg	Tl	Pb 22 kg	Bi 12 kg	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq		Uuo		Uuo

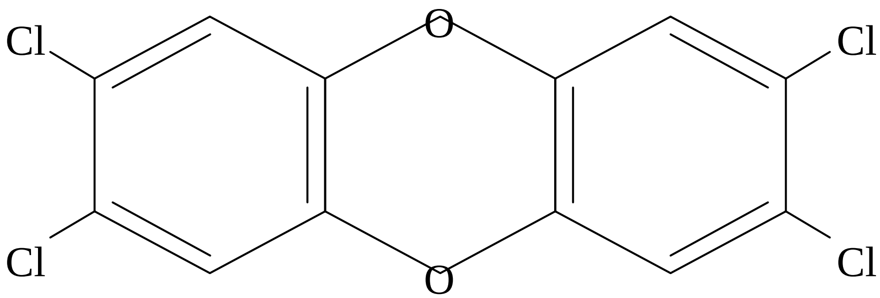
Ce	Pr	Nd	Pm	Sm	Eu 1 g	Gd	Tb	Dy	Ho	Er	Lu	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Lr	No	Lw

* Brominated hydrocarbons estimated value.
** Pt and Pd interchangeable depending on age of material.

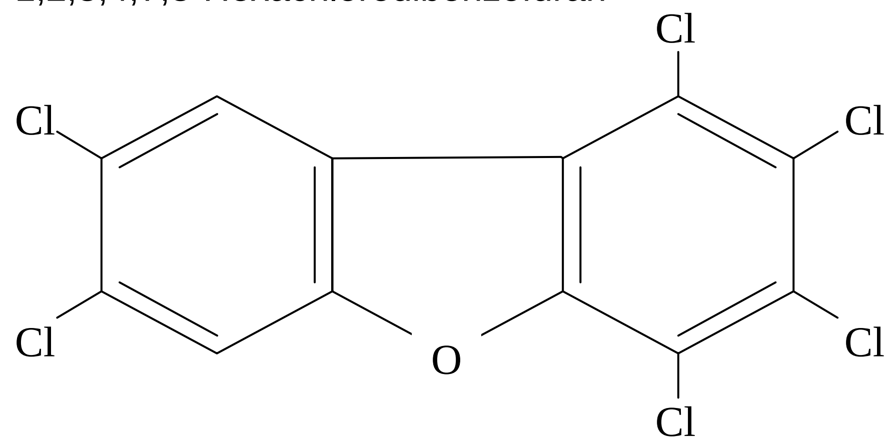
Pyrolysis of Electronic Scrap

- **Thermal decomposition of polymers in absence of oxygen**
- **Drive off Hydrogen and Methane gas**
- **Remaining material carbon black**
- **Chlorine and Fluorine = Dioxin - Furan**

2,3,7,8-Tetrachloro-dibenzo-p-dioxin



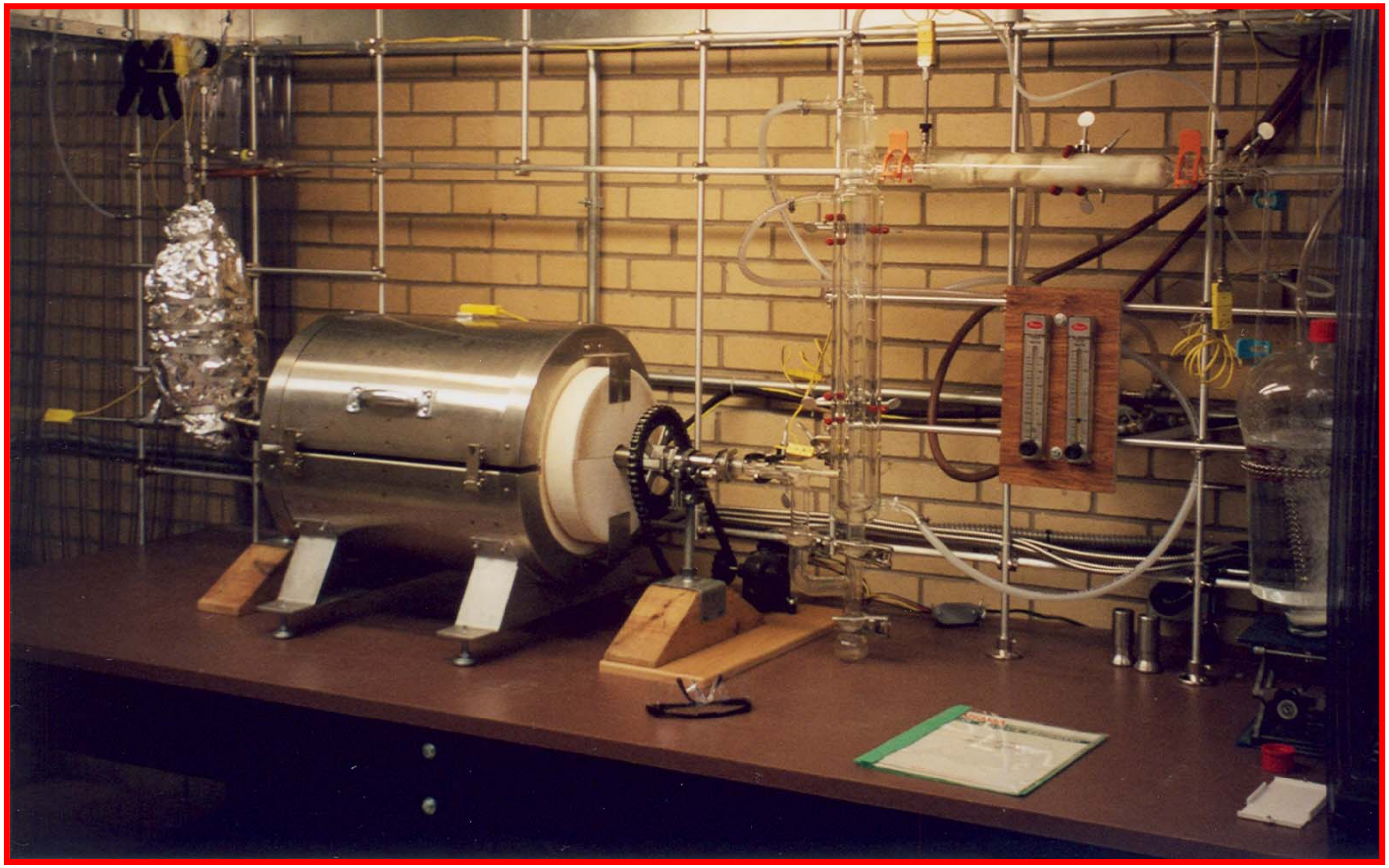
1,2,3,4,7,8-Hexachlorodibenzofuran



Pyrolysis of Electronic Scrap

- Sequestering of chlorine and fluorine was demonstrated using various carbonates (Shuey, 2006)
- Sodium Bicarbonate demonstrated the highest level of bromine, chlorine and fluorine sequestration
- Temperature range 550 to 600 C
- Potential generation of significant energy value

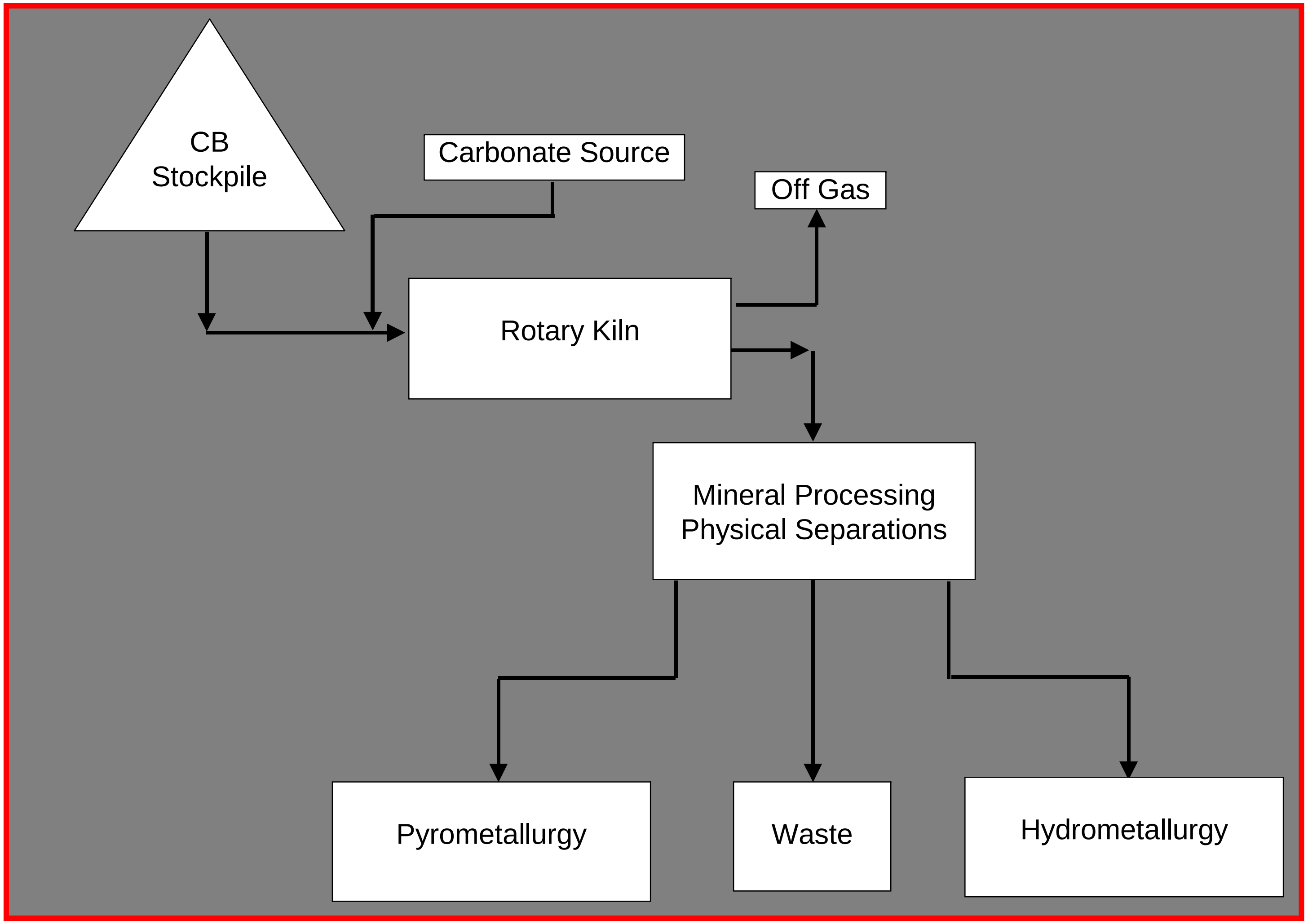
Sequestration



Sequestration

- Variables
  - Temperature
  - Carbonate Source
    - Trona, $Na_3CO_3(HCO_3)\cdot 2H_2O$
    - Sodium Bicarbonate, $NaHCO_3$
  - Gas phase Retention Time (Feed Rate)
- Responses
  - Maximize Br, Cl and F retention
  - Minimize Dioxin/Furan formation

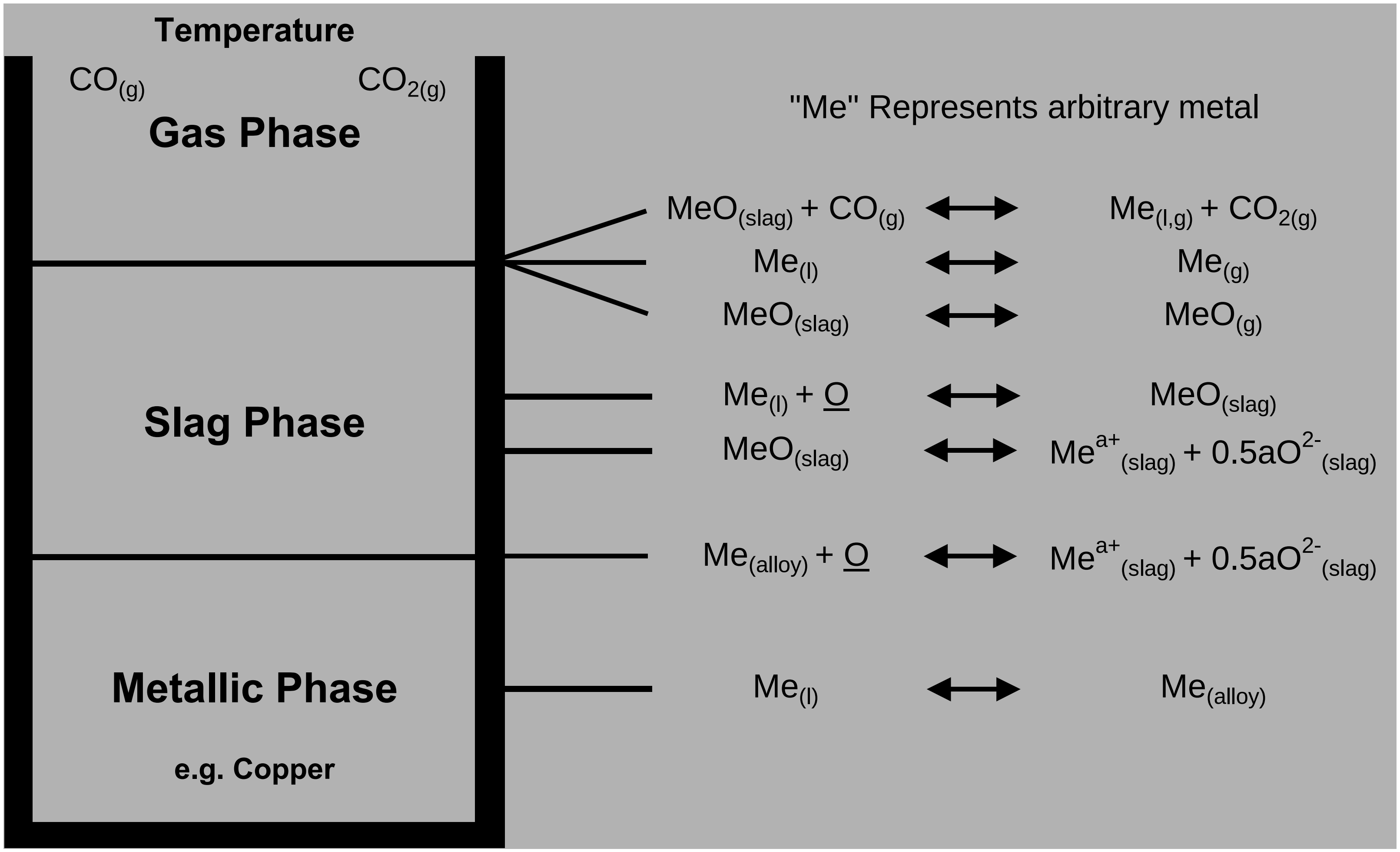
Process Routes



Pyrometallurgical Approach

- Pyrolyzed products are subjected to mineral processing to remove carbon and salts
- The material is then subjected crucible metal reduction
- Carbon provides both a heat source and a reductant
- Copper provides the collector for precious metals.

Pyrometallurgy Fundamentals



Products

- Copper Anodes for Electrolytic Refining
  - Precious metals recovered in anode slimes
- Slag
  - Disposal
  - Secondary Processing
- Baghouse Dust
  - Stabilization/Disposal
  - Secondary Processing

Low Temperature Waste Processing for Energy Recovery

Waste Lumber

Wood Chips

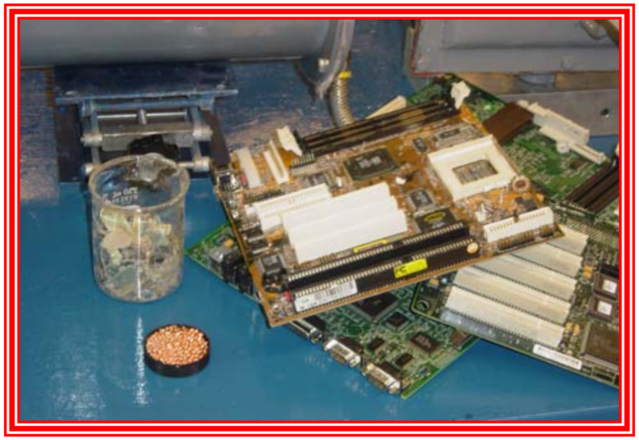
Energy Recovery
Carbon-rich Solid Fuel
CH_4/H_2-rich Gas Fuel

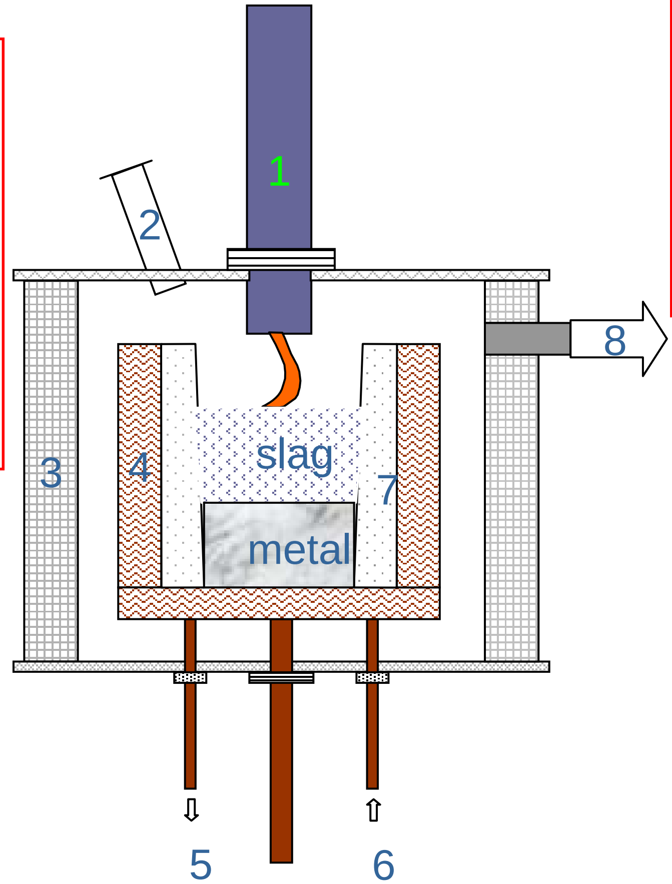
Junked Cars

Auto Shredder Residue, MSW

Metal Recovery

Transferred Arc Electro-Reduction of Electronic Waste





Mineral Processing

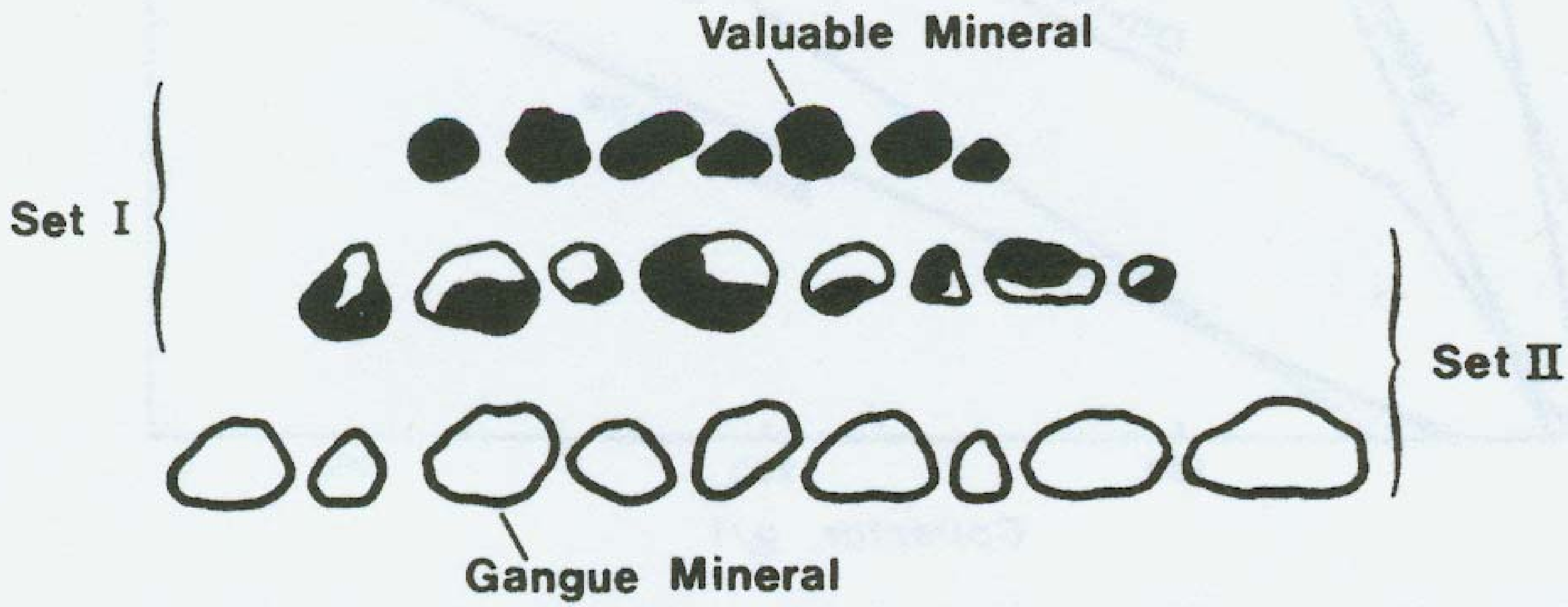


Figure 3.2. Representation of particles as sets: set I is comprised of all particles that contain some valuable mineral; set II is comprised of all particles that contain some gangue mineral. On this basis the middling particles are common to both sets.

Analysis of Separation

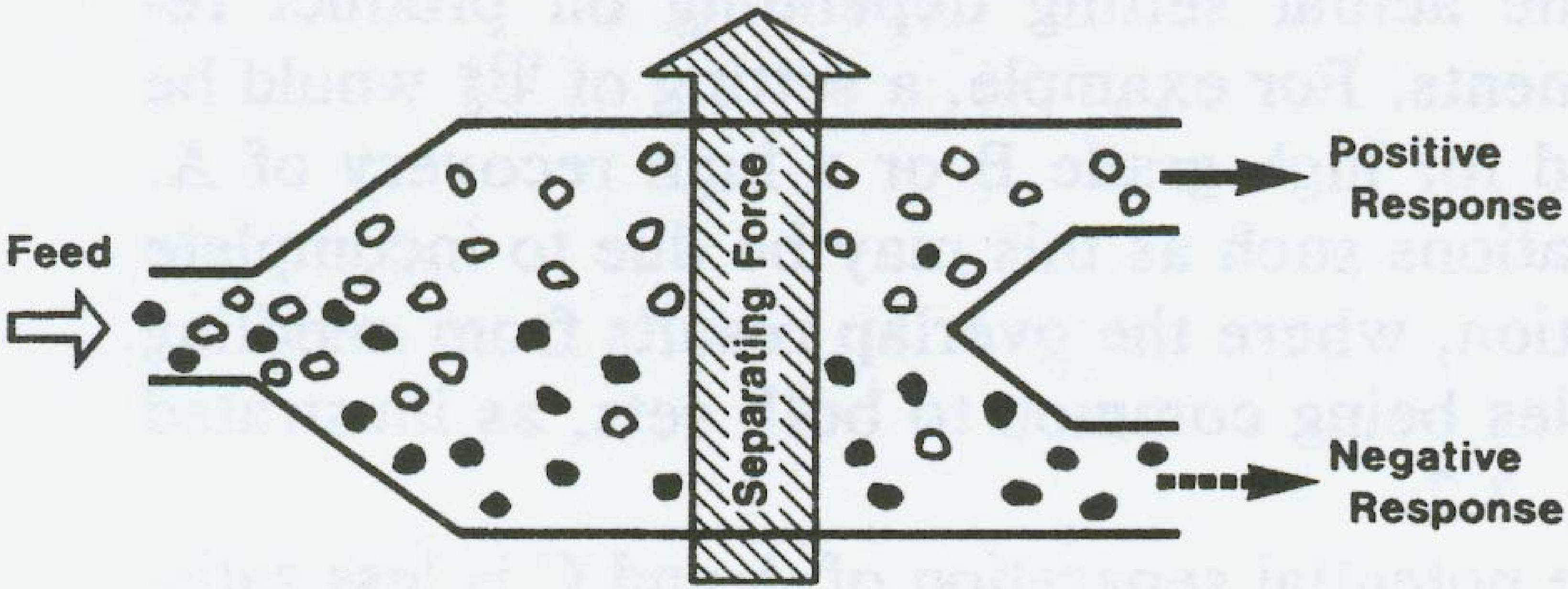


Figure 3.1. The basic principle of a separator.

Separability Curves

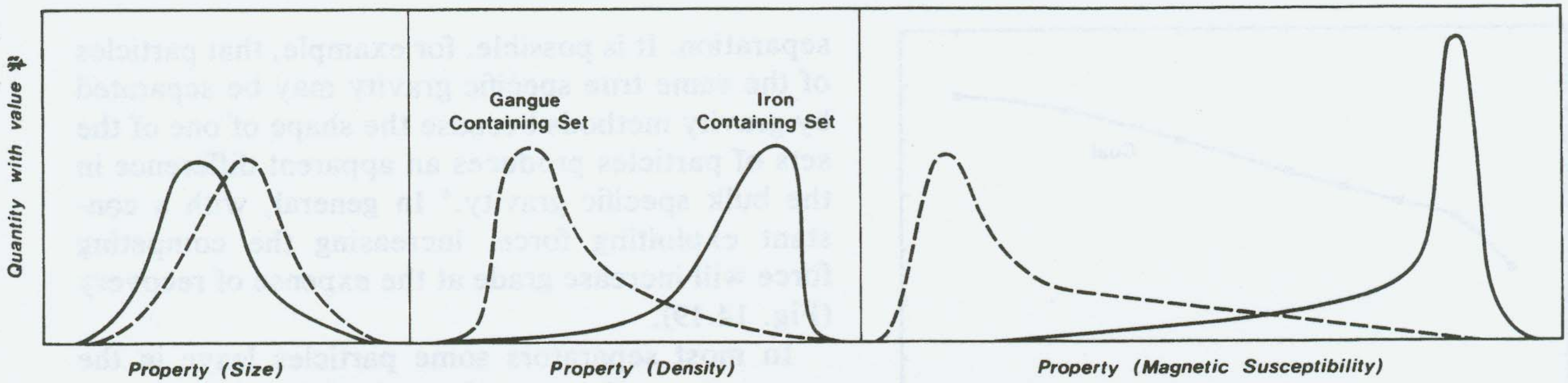


Figure 3.7. Separability curves of an iron-containing beach sand, which essentially consists of two sets: light gangue minerals and dense iron-containing minerals. Depending on the property exploited, the separation can be difficult or easy.

Example Separability Curve

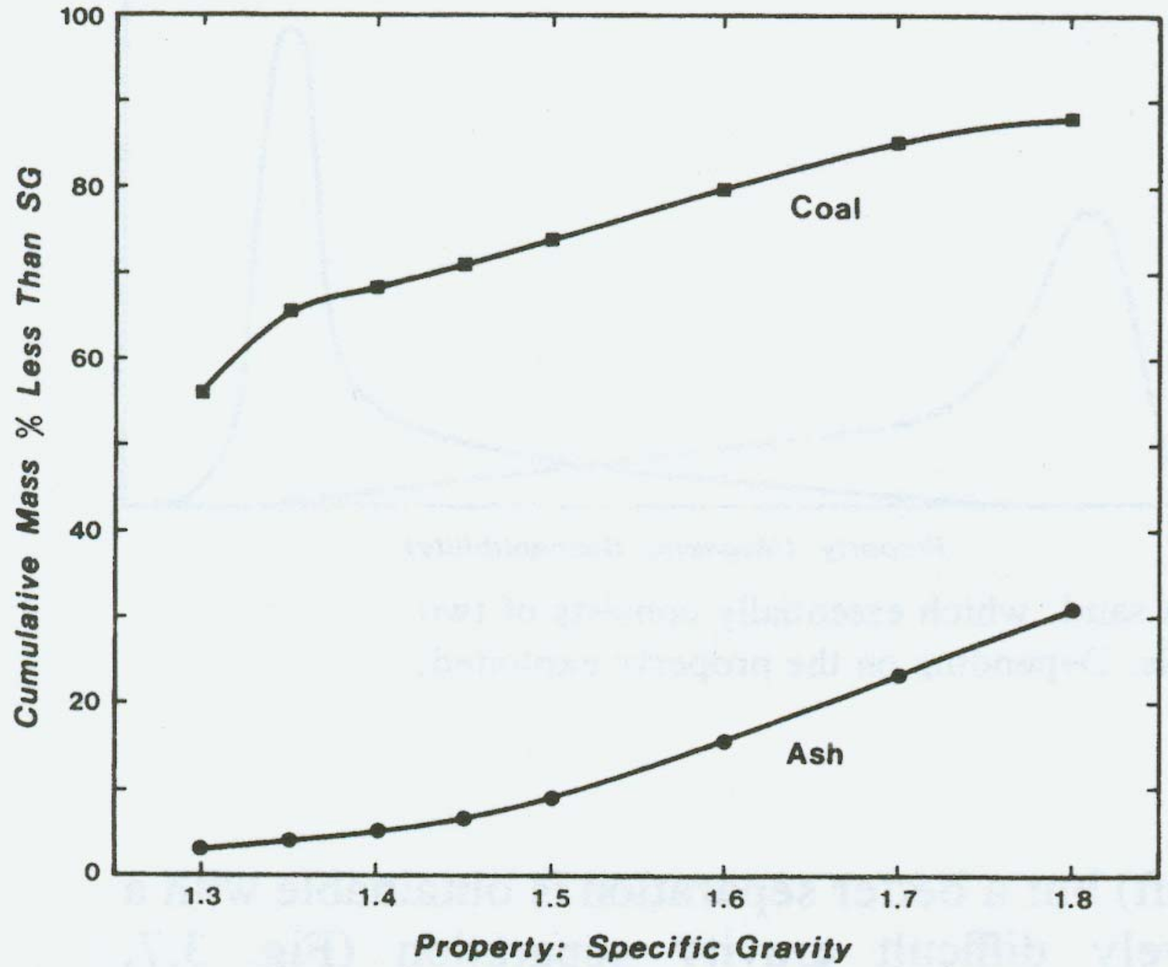


Figure E3.1.1. Cumulative separability curves of coal and ash, from Example 3.1.

The concept of recovery and grade.

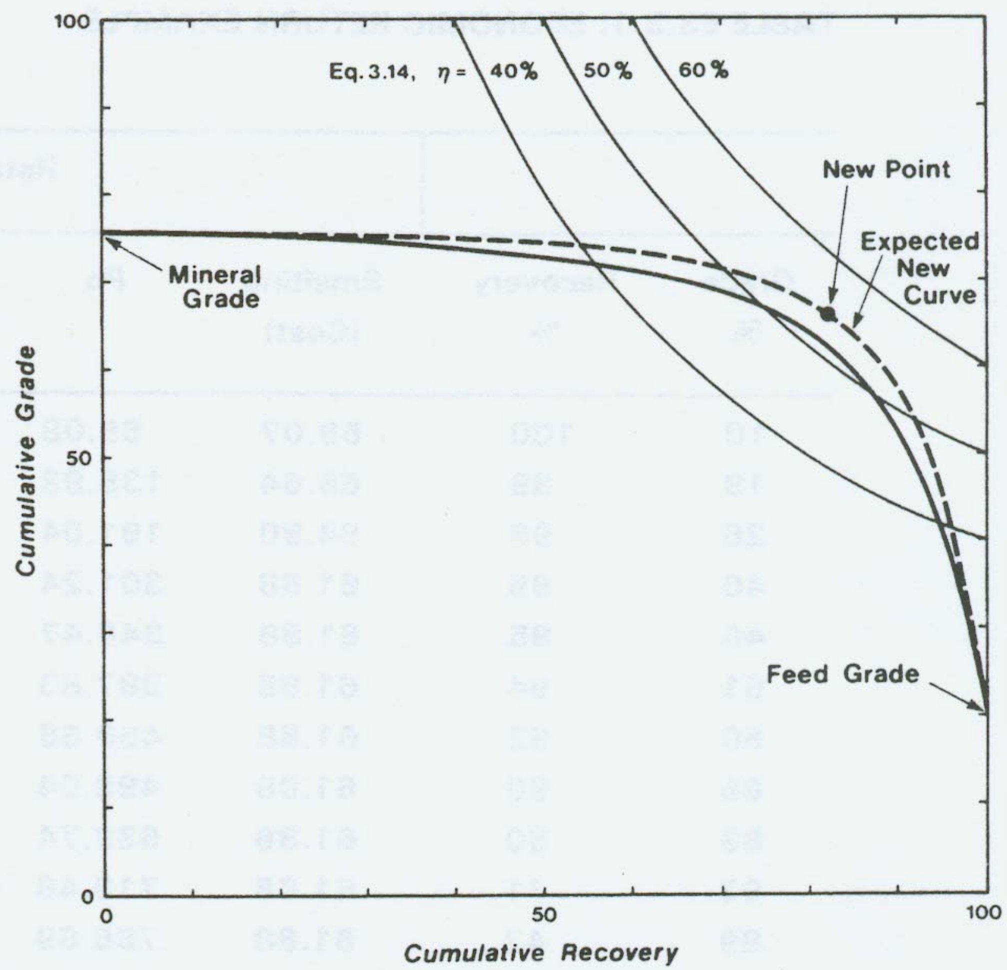


Figure 3.13. The cumulative grade versus cumulative recovery curve.

Example Process – Mineral Processing

- **Recycling A Glass Resource**

D. Erik Spiller
Principal
Spiller Consultants LLC
Research Professor, KIEM

Physical Separation in Recycling

Liberate	THEN →	Separate
Scrubbing		Size
Shearing		Shape
Shredding		Density
Impacting		Magnetic Susceptibility
Cutting		Electrical Conductivity
Ripping		Color / Reflectance
Grinding		Surface Chemistry
Thermal		

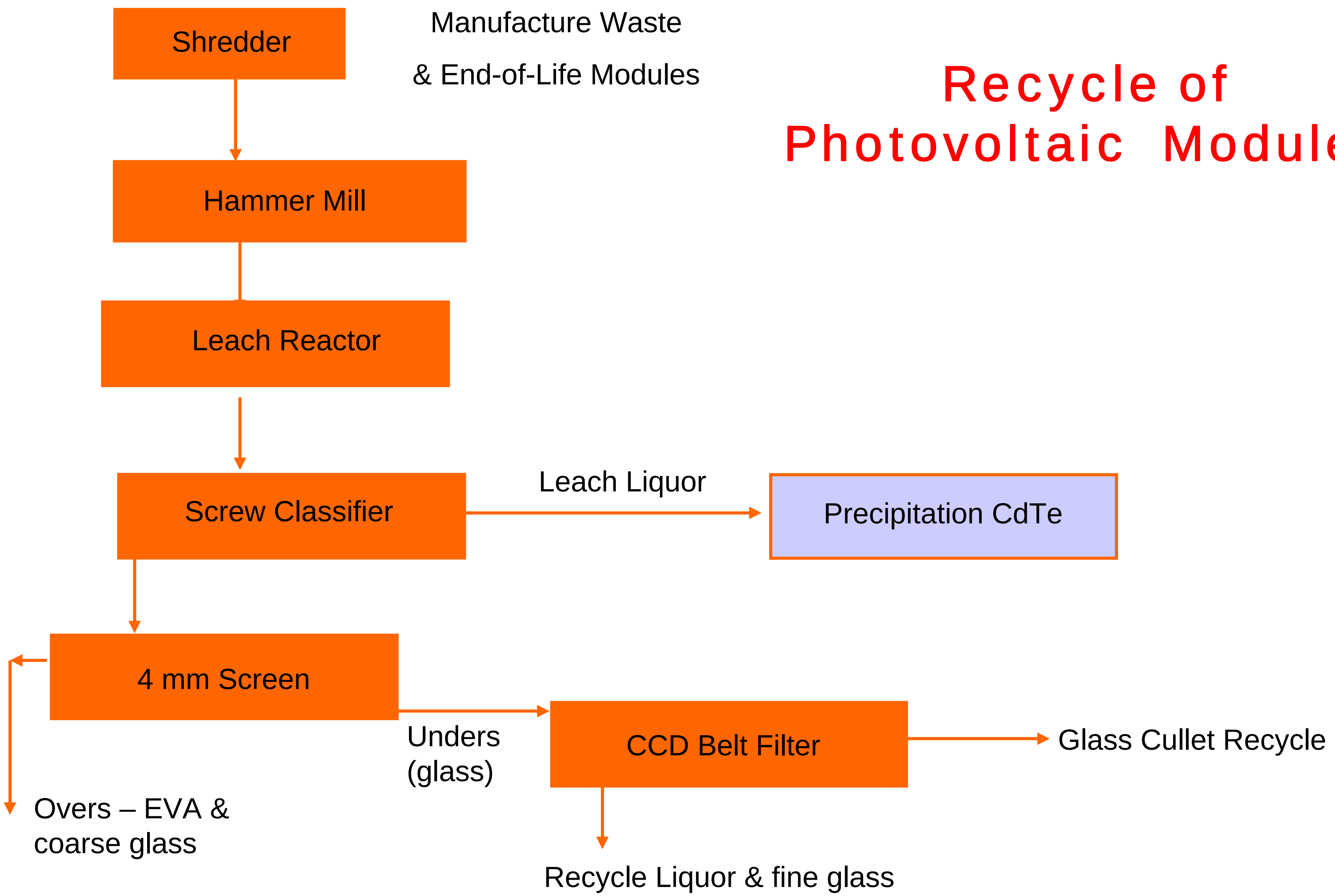
Recycling a Glass Resource

- Drivers are social responsibility and marketing
- Secondary driver is economics
- Straight Forward Physical Separation – with leaching
- Physical Separation Issues Recognized and Solved
  - Wear on equipment surfaces
  - Dewatering/draining related to Materials Handling
- Photovoltaic CdTe Modules – the resource
  - Overlaid by another glass plate – thus making laminated module
  - Semiconductor films (primarily CdTe) on glass substrate
  - Includes various plastic and wire components

Module Product

- Front: Substrate glass
- Semiconductor
- Metal conductor
- Ethylene vinyl acetate (EVA)
- Back: Cover glass

Recycle of Photovoltaic Modules




Shredded Modules
2 x 40 hp motors (>75 t/h)

Hammer Mill

25 hp


Drag Conveyor & Reactor

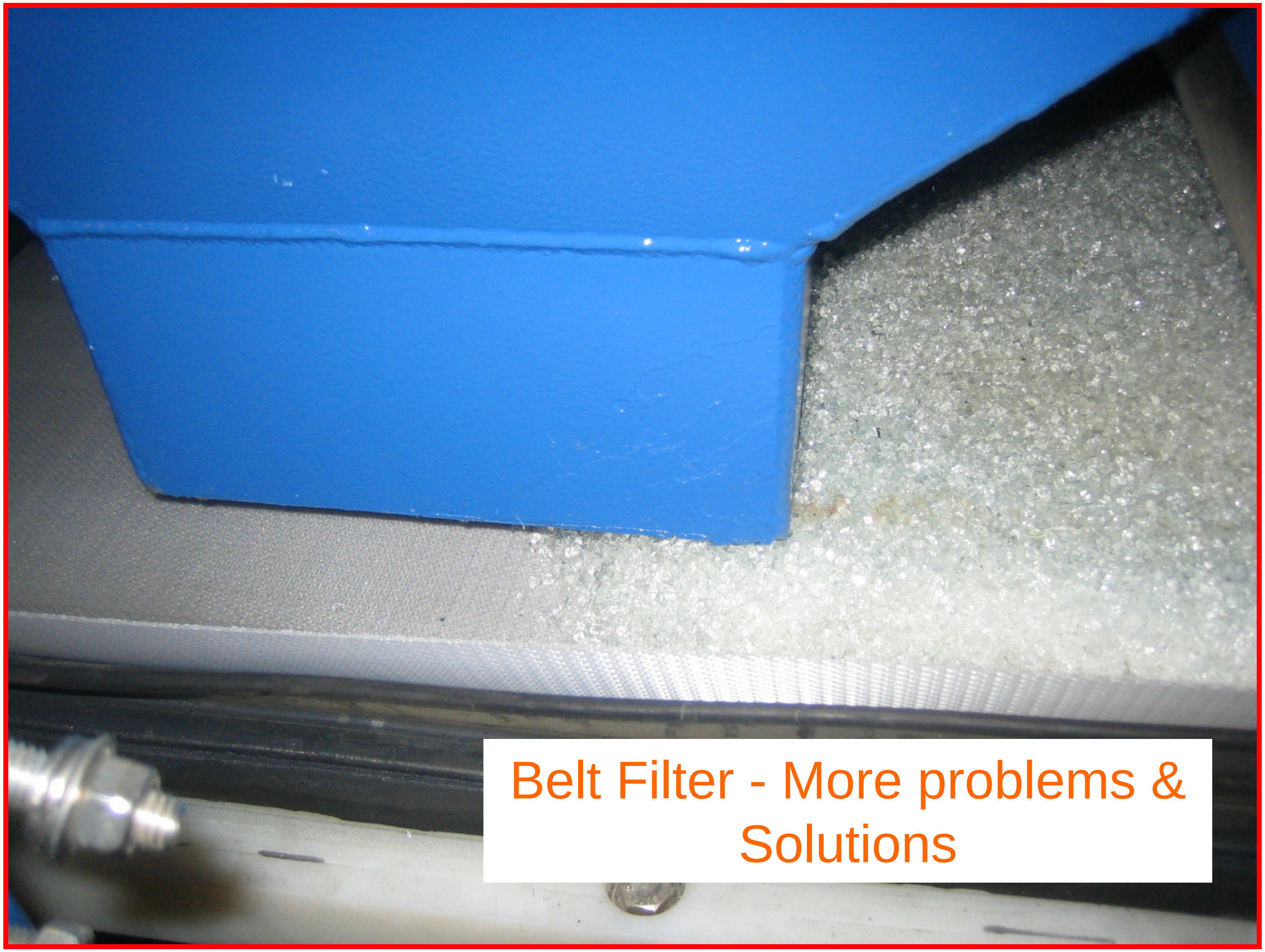

Discharging Reactor

Screw Classifier

36 - inch diameter

The Problem - Physical Characteristic

Screen


Belt Filter - More problems & Solutions


Cullet for Recycle

Conclusions

Why should companies recycle?

- **The bottom line is economics.**
- **But in addition, companies may derive positive benefits from addressing both: social responsibility and sustainable development issues.**

What technology is used in recycling?

- **Most recycle technology is based upon our understanding of both mineral processing and extractive metallurgy.**
- **Innovative advances in both technologies have been, and are being, made to address the unique resource recovery problems associated with both recycle and waste minimization.**

Kroll Institute for Extractive Metallurgy

The goal of the Kroll Institute is to provide research expertise, well-trained engineers to industry, and research and educational opportunities to students, in the areas of minerals, metals and materials processing; extractive and chemical metallurgy; chemical processing of materials; and recycling and waste treatment and minimization.

Mission:

The mission of the KIEM is to support the minerals, metals and materials industries through the following activities:

- **Maintain expertise and research capabilities important to the minerals, metals and materials industries**
- **Perform cutting edge research**
- **Train process engineers for industry**
- **Develop short courses**
- **Develop specialty conferences**

Kroll Institute for Extractive Metallurgy
KIEM

Patrick R. Taylor
Director
G.S. Ansell Distinguished Professor of Chemical Metallurgy

EXPERTISE
- Mineral Processing
- Extractive Metallurgy
- Recycling
- Waste Treatment & Minimization
- Thermal Plasma Processing of Advanced Materials
- Thermal Plasma Processing of Wastes

Gerard P. Martins
Professor of Metallurgical and Materials Engineering

EXPERTISE
- Process and extraction metallurgy
- Engineered ceramic and metal powders
- Electrochemical systems
- Corrosion
- Transport phenomena
- Reactor Design & kinetics

Brajendra Mishra
Associate Director
Professor of Metallurgical and Materials Engineering

EXPERTISE
- Pyrometallurgy
- Electrochemistry
- Materials synthesis
- Waste Processing
- Recycling
- Molten Salt Processing
- Oxidation
- Reactive & radioactive metals
- Glove box processing

Edgar E. Vidal
Assistant Professor, Metallurgical and Materials Engineering

EXPERTISE
- Extractive Metallurgy
- Thermal Processing of Materials
- Thermodynamic Modeling/Analysis of Systems
- Synthesis of Advanced Materials
- Mineral Processing

D. Erik Spiller
Research Professor, Mineral Processing and Extractive Metallurgy

EXPERTISE
- Mineral Processing Comminution, physical separation, recycling, flotation, leaching, liquid-solid separation
- Project management: feasibility, engineering, construction management, operations


Visit us in Golden, Colorado
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The Kroll Institute for Extractive Metallurgy
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