RV College of Engineering®

Section : SPARK

Course: CHEMISTRY OF SMART MATERIALS AND DEVICES

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Syllabus

UNIT-I	Sustainable chemistry and E-waste management:	08 Hrs

Biomaterials: Introduction, bio-degradable and bio-compatible polymeric materials: synthesis and applications (Polymers and hydrogels in drug delivery).

Green Chemistry: Introduction, 12 principles with real life examples, validation of greenness.

E-waste: Hazards and toxicity, segregation and recycling (Hydrometallurgy, pyrometallurgy and direct recycling). Extraction of valuable metals from E-waste. Battery waste management and recycling, circular economy- case studies.

E waste

E-Waste

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Sources:
a. Government and commercial sectors
b. Institutional and research organizations
c. Household
d. Manufacturing industries

Impact:
Environmental contamination (soil, air and water)

Human health effects like Lung inflammation, brain swelling, muscle weakness, kidney damage, nausea, bronchitis, etc.

Management techniques/methods:
a. Pyrometallurgical and hydrometallurgical smelters
b. Electrochemical Methods
b. Landfilling
c. Incineration
d. Reuse, recycle and recovery

Hazardous and toxicity of E waste

Persistent Organic Pollutants

soil

dust

air

water

vegetables

rice

poultry

fish

seafood

Dietary intake

Inhalation

Dermal contact

Behavioural changes

DNA damage

Mental disorders

Reduced Learning abilities

Respiratory irritation

Thyroid dysfunction

Cardiovascular diseases

Nervous diseases

Reproductive diseases

Effects on next generation?

Epidemiological evidence?

Uncontrolled e-waste recycling activities

Hazardous and toxicity of E waste

E-Waste Source	E-Waste Component	Environmental Hazard	Effects on Human
CRTs (used in TVs, Monitors, ATM, Video Camera, etc), Batteries, PVC cables, Paints	Lead, barium & other heavy metals	These metals leaching into the ground water and release of toxic phosphor	Anemia, Renal Toxicity, Insomnia
Batteries, Housing & Medical Equipment	Mercury	Air emissions as well as discharge into rivers of glass dust	Renal Toxicity, Muscle tumors, Mental retardation, Cerebral palsy
Plastics from printers, keyboards, monitors, etc	plasticizer bisephenol-A(or BPA), as well DEHP and DBP, plastic compounds known as phthalates	Chlorinated plastics release harmful chemicals into the surrounding soil, which seep into ground water or other surrounding water sources which cause serious harm to the species that drink this water.	Risk in developing heart problems, obesity, reproductive disease
PVC & polymer, Paints, Printing inks, Electrical transformers & capacitors	Polychlorinated Biphenyls (PCBs)	include extreme pollution from production, toxic chemical exposure during use, hazards from fires	Suppression of immune system; Damage to the liver, nervous and reproductive systems

Major contaminants from E waste

Compound	Location	Effect
Lead	Soldering of PCB and other electronic components	Can affect various systems in the body such as the peripheral nervous systems and central, hemopoietic system and reproductive systems.
Mercury	Batteries, switch/housing and printed wiring board.	Can causes damage to the genitourinary system, the peripheral nervous systems and fetus as well as the central.
Cadmium	SMD chip resistor, infrared detectors and semi-conductors	Toxic from cadmium compounds collects in the human body, particularly in the kidneys.
Plastics including PVC	Cabling and housing	Causes or aggravates asthma/bronchitis and DNA damage.
Brominated flame retardants (BFR)	Plastic housing of EEE and circuit board	Burning produces dioxin. It causes reproductive and developmental problem and immune system damage.

Heavy metal poisoning (Pb)

The short-term effects of lead poisoning include:

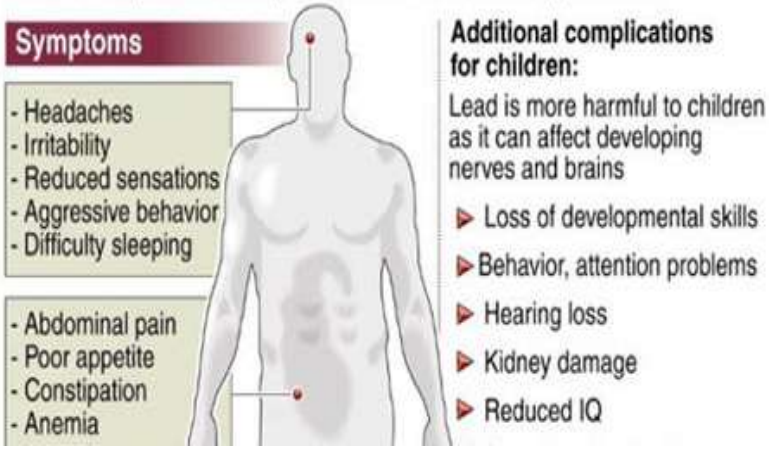
- Acute fever,
- Convulsions,
- Loss of consciousness and blindness, with anemia,
- Renal failure

Exposure to high levels of lead in a short period of time is called Acute toxicity.

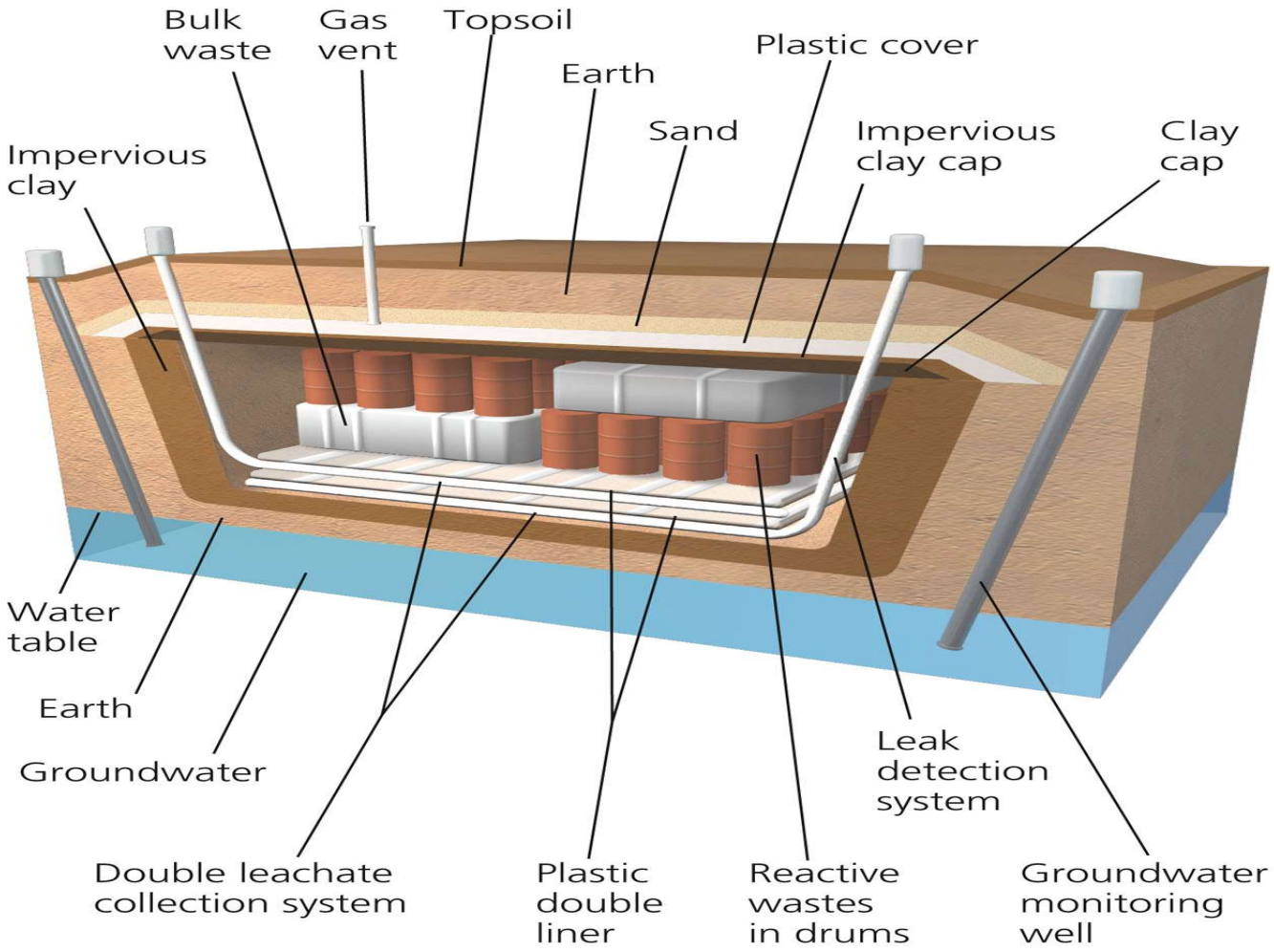
- Decreased bone and muscle growth
- Poor muscle coordination
- Damage to the nervous system, kidneys, and/or hearing and brain damage.
- Speech and language problems
- Developmental delay
- Seizures and unconsciousness (in cases of extremely high lead levels)

Exposure to small amounts of lead over a long period of time is called Chronic toxicity.

Lead buildup in the body causes serious health problems

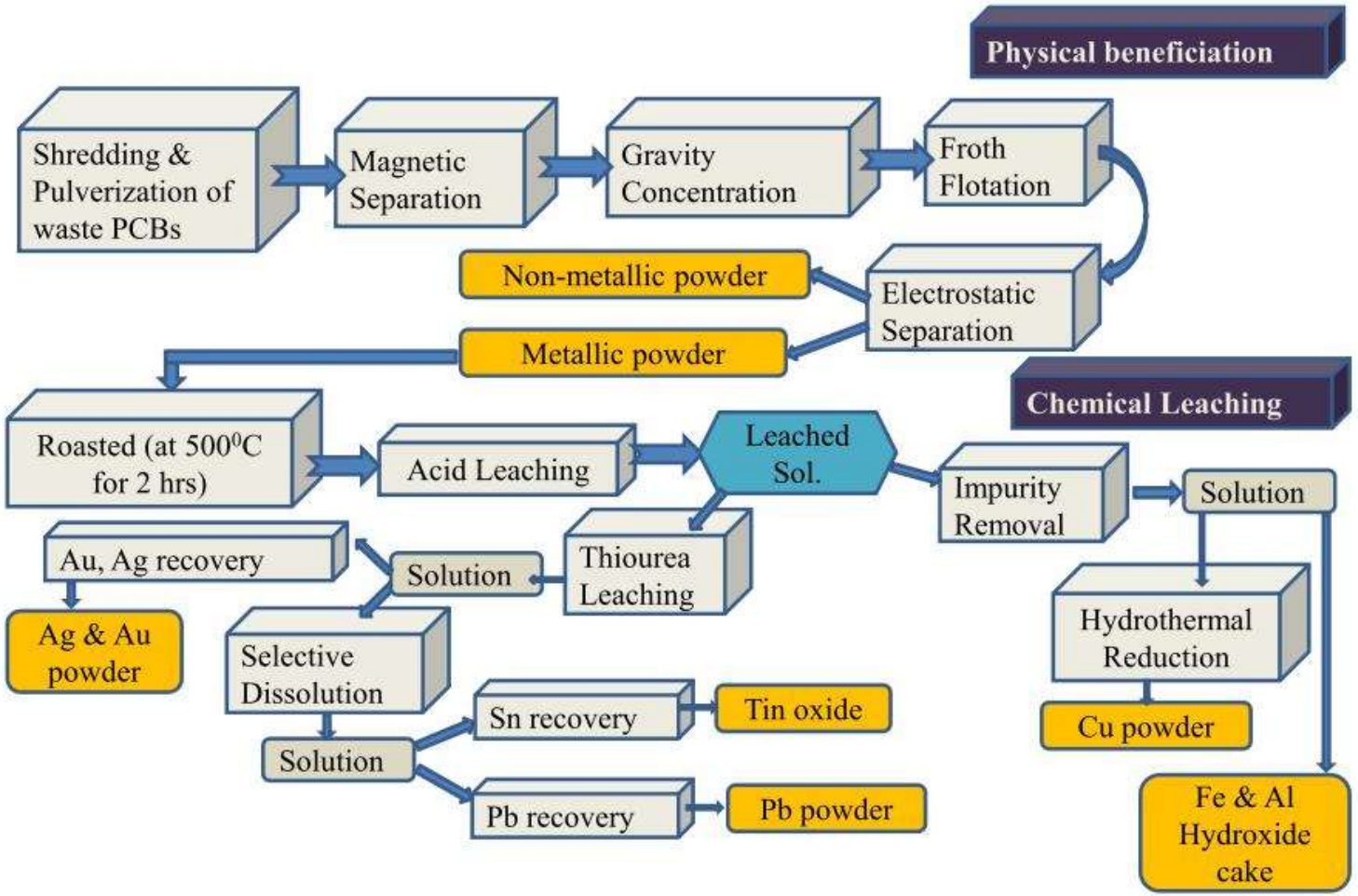


Hazardous waste management-land fill

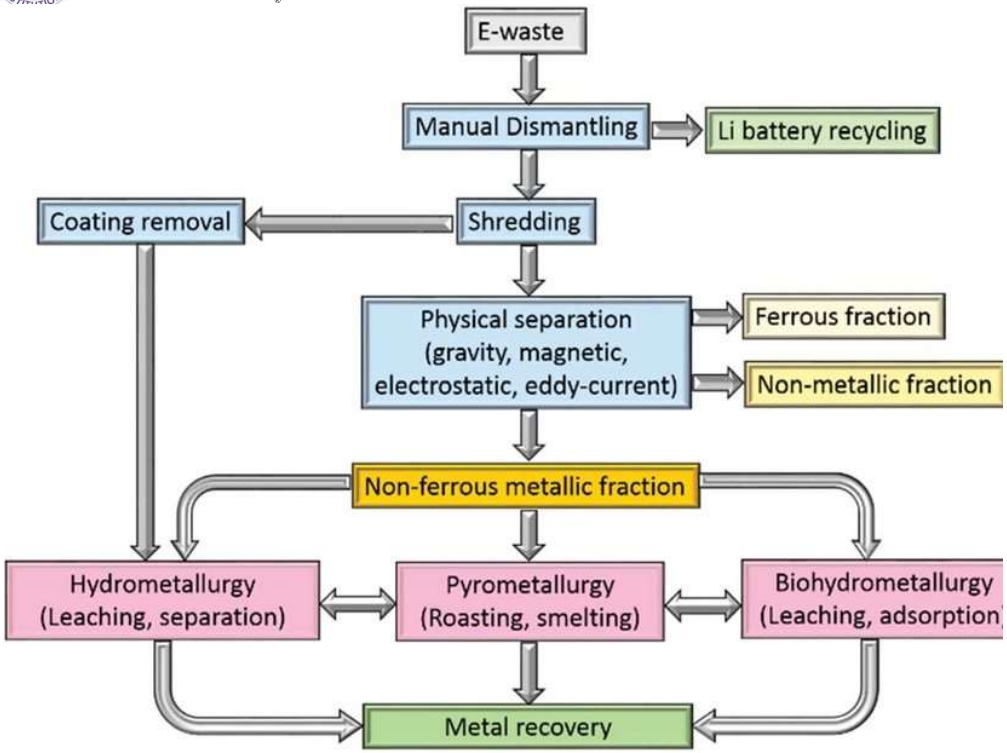


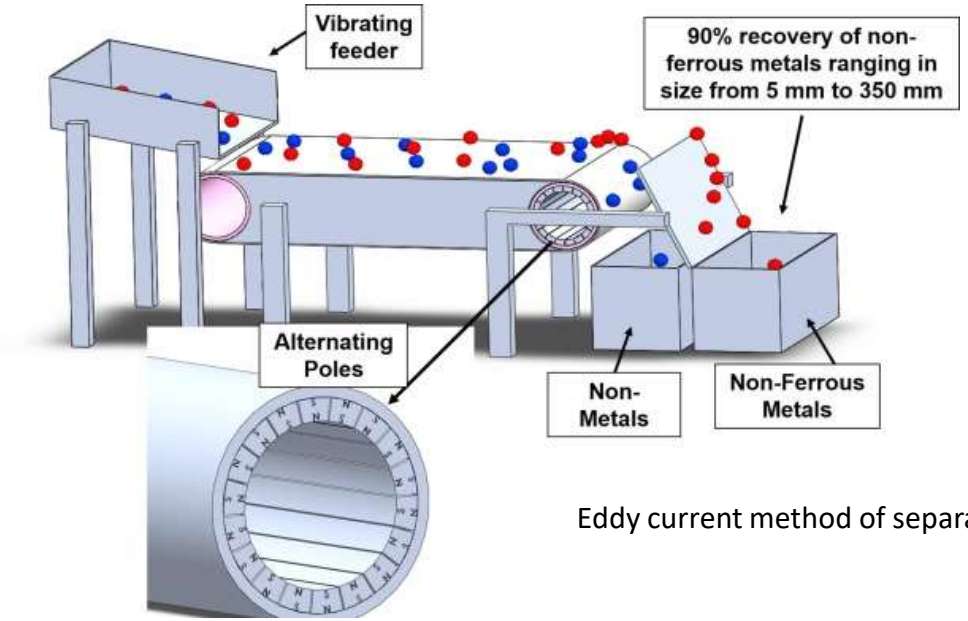
All the e-waste should be kept by this way in land filling, mostly practiced in European countries

Recovery of valuable metals from E waste



Recovery of metals from E waste





Eddy current method of separation

Eddy current is defined as the induced current in a conducting coil when a magnetic flux is allowed to flow through it or in other words, it is the induced current in a conducting body due to a change in magnetic flux. The eddy current definition can be explained as an important nature of a solid conducting body.

To understand what is eddy current it is necessary to understand Faraday's electromagnetic induction. In rapidly changing magnetic fields, due to the production of heavy emf, large eddy currents are induced. Eddy currents are capable of producing temperature as a result of this heavy temperature. Thus a coil-over a constituent metal placed in a field of the highly oscillating magnetic field will produce a high-frequency AC. The temperature produced as a result of a heavy eddy current is enough to melt the metal. This is used to extract metals from ores.

Pyro metallurgy

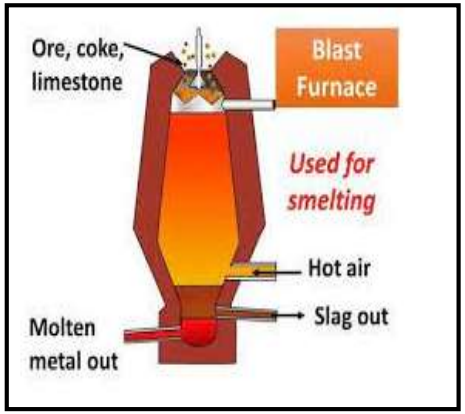
Pyrometallurgy, as traditional method to recover precious and non-ferrous metals from E-waste, includes different treatments on high temperatures: incineration, smelting etc.

Pyrometallurgy is a heat-based extraction and purification process. As with the water-based process, pyrometallurgy generally involves three steps:

Pyrometallurgy processes

It is a process of extraction & purification of metals by the application of heat

Roasting | Smelting | Refining



Steps in pyrometallurgy

Roasting: This refers to the heating of compounds in air and transforming sulphide ores into oxides, creating gas.

Smelting: Smelting is used in furnaces to reduce metals and usually involves the formation of carbon dioxide, for example, reducing iron ore in a blast furnace. In addition, tin, copper, and lead ores are smelted.

Refining: In refining processes, metals are sorted by exploiting their chemical and metallurgical properties. The separation of metals is achieved by smelting in furnaces at high temperatures. Refining covers a wide range of processes involving different kinds of furnaces and electrolytic processes.

Pyrometallurgical processes could not be considered as best available recycling techniques anymore because some of the PCB components, especially plastics and flame retardants, produce toxic and carcinogenic compounds.

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Hydrometallurgical processes

It is a process of extraction of metals by dissolving compound in a suitable chemical reagent and precipitation/displacement of the metal by more reactive or electro active metal

Leaching	Solution concentration & purification	Metal recovery
Suitable solvent		Precipitation/ Cementation

- This method plays an essential role in extracting strategic (Ti) and rare metals.

Leaching is an important and first stage of Hydrometallurgical process.

It is the extraction process in which soluble substances are extracted from a solid by means of a solvent. After that the extract obtain from leaching is often subjected to concentration and purification before the metal recovery. The final step may involve precipitation or cementation process.

Composition of PCB	
Metals	**Availability (wt%)**
Copper	**30.57**
Aluminium	**11.69**
Zinc	**1.86**
Tin	**7.3**
Nickel	**1.58**
Iron	**15.21**
Lead	**6.71**

Methodology

1. Various components like RAM, ICs etc are attached on PCB were first removed manually from it.
2. Then chemical coating of epoxy resin present on PCB was removed by using NaOH because the covering of this coating does not allow the leaching agent to penetrate through it. (if organic solvent like Alcohol is used epoxy can be reused)
3. The grinded E-Waste powder contains plastic, ferrous and nonferrous metals.
4. Density separation method is used to separate the Metallic and non-metallic parts.
5. For separation of ferrous and nonferrous metals, Electromagnetic separator is used.
6. For experimental purpose 8 gm of nonferrous metal was taken.
7. The metal powder was dissolved in H_2SO_4 and stirred at 80° C, temperature for about 4 hr.
8. The solution was transferred and 40 ml of **Aquaregia** (30 ml HCl and 10 ml HNO_3) was added to the filtered solution. The resulting solution was stirred for 60 mins at a temperature 80° C,

HNO_3 (aq) + 3HCl (aq) → NOCl (g) + Cl_2(g) + 2H2O

H_2SO_4 + HCl → H_2O +Cl_2 + SO_2

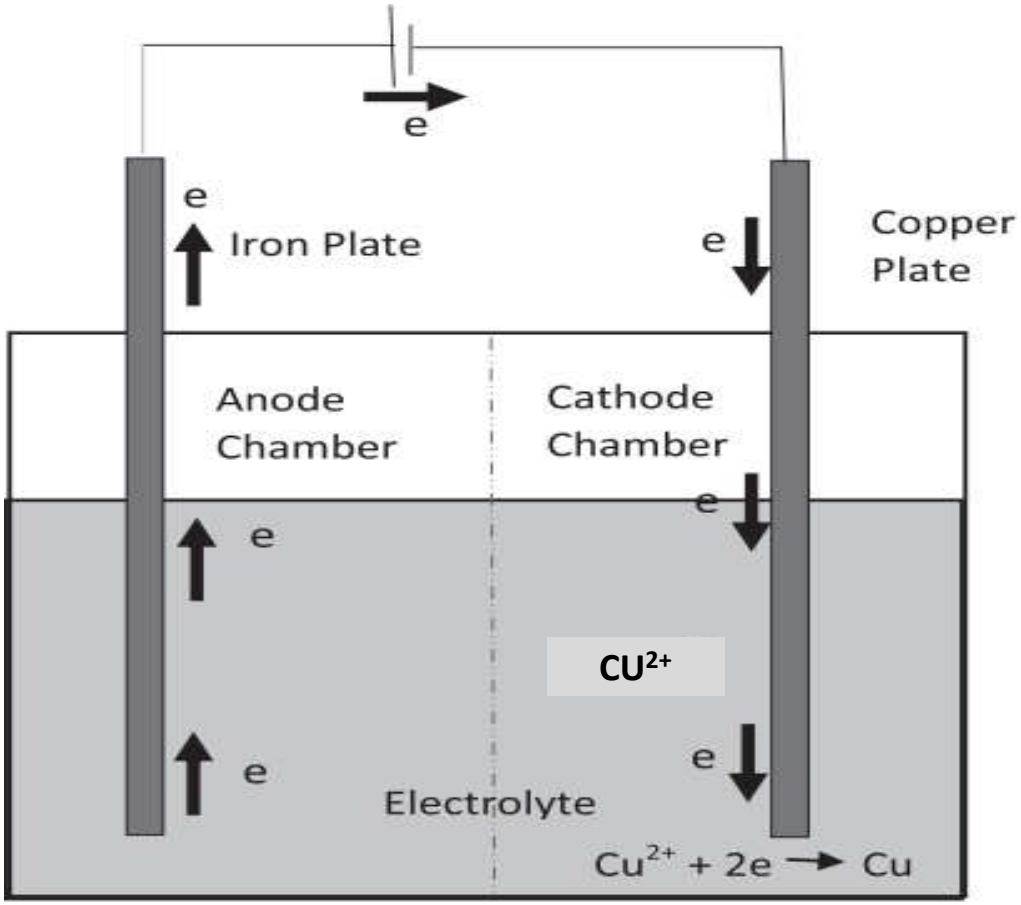
Cu + $4HNO_3$ → $Cu(NO_3)_2$ + $2NO_2$ + $2H_2O$

Cu + Cl_2 → $CuCl_2$

$CuCl_2$ + H_2SO_4 → $CuSO_4$ + HCl

9. From above solution, copper can be extracted by using suitable reducing agents like Sodiumborohydride (NaBH4).
10. **$2Cu(NO_3)_2 \cdot 3H_2O + 4NaBH_4 \rightarrow 2Cu + 4NaNO_3 + 2B(OH)_3 + 8H_2 + B_2H_6$**
11. Obtained copper metal is further purified by refining and electro refining process.

Copper is extracted by electrolysis process

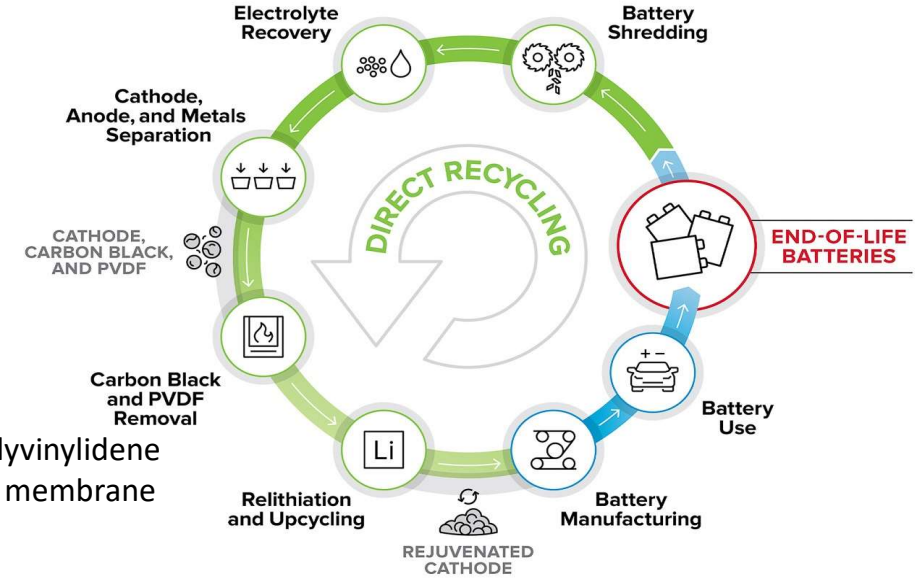


Advantages

1. Economically viable for low-grade E-waste materials.
2. Feasible for small scale applications with high metal recoveries

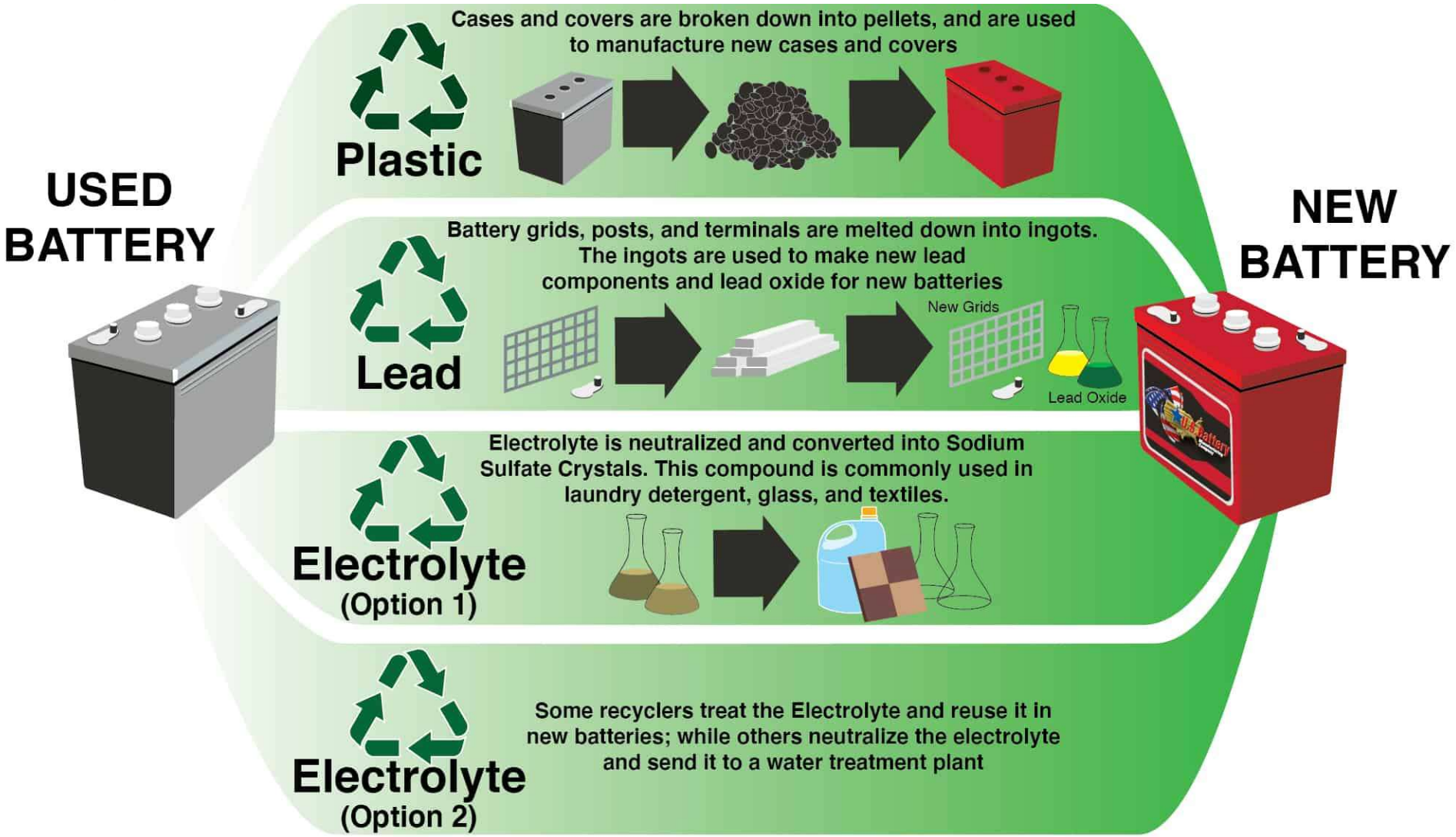
Advantages of Battery recycling

- Reduction in waste sent to landfills
- Conservation of natural resources, such as metals and minerals
- Helps prevent pollution by reducing the need to collect new, raw materials
- Saves energy spent on refining virgin materials
- Reduces greenhouse gas emissions that contribute to global climate change
- Helps sustain the environment for future generations
- Helps create new, well-paying jobs in the recycling and manufacturing industries
- Once the materials are recycled they can be reused in making new products

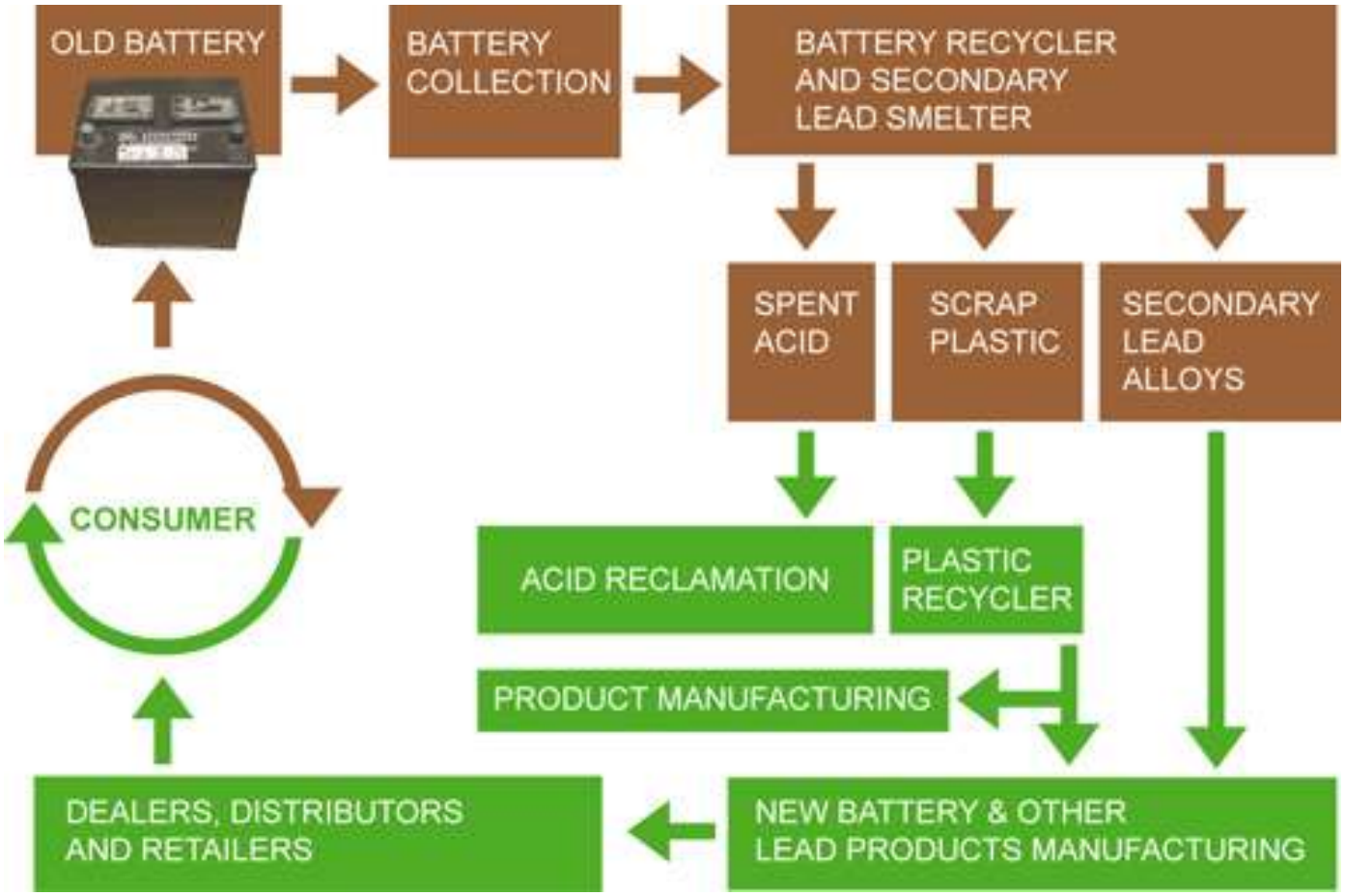


PVDF - Polyvinylidene difluoride membrane

Battery recycling

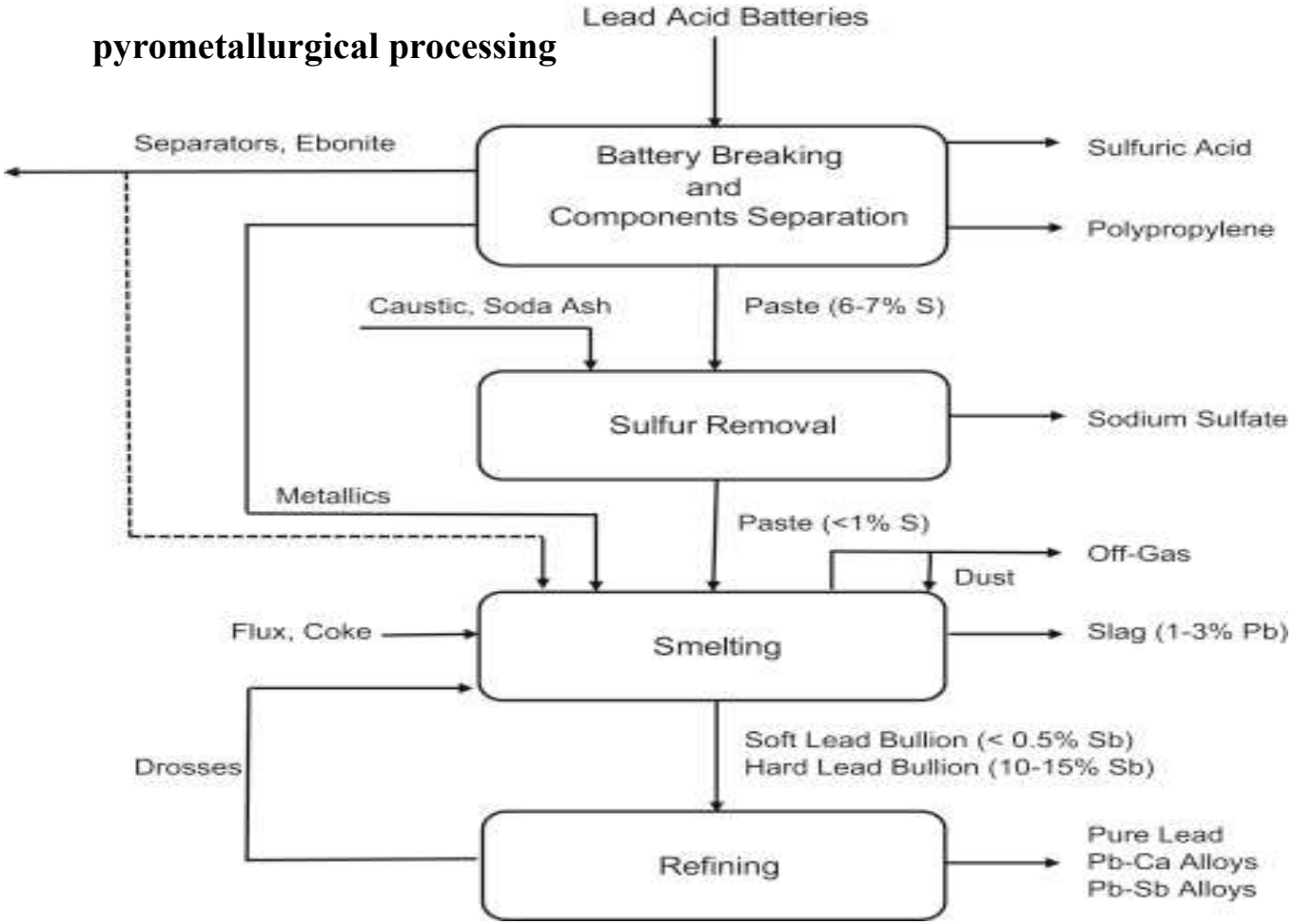


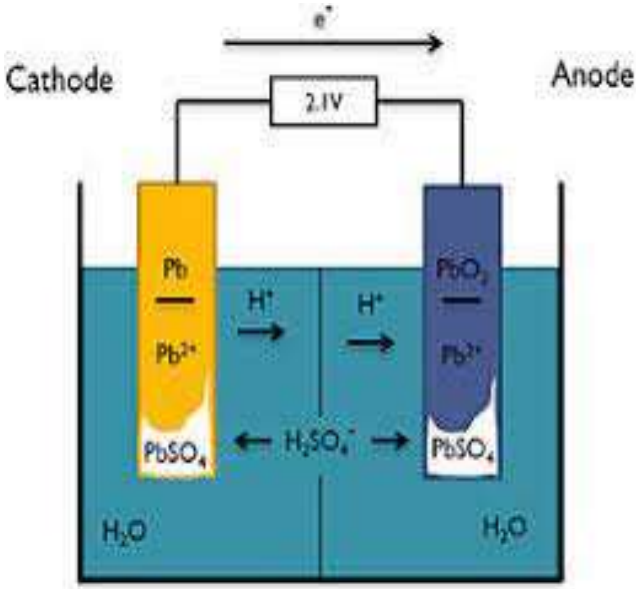
General steps involved in recycling of lead acid battery



Recycling of Lead acid battery

pyrometallurgical processing





Smelting process

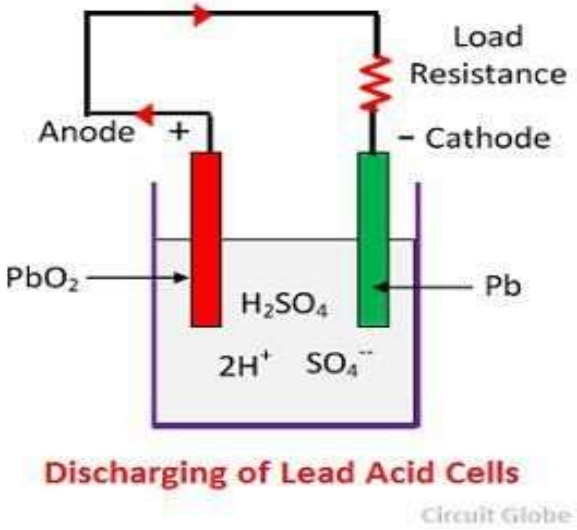
General steps involved in recycling of lead acid battery

The electro-chemical reactions of lead acid battery are:

Charging: $2PbSO_4 + 2H_2O \rightarrow PbO_2 + Pb + H_2SO_4$

Discharging: $PbO_2 + H^+ \text{ -> } PbO + H_2O,\ PbO + H_2SO_4 \text{ -> } PbSO_4 + H_2O$

Net : $PbO_2 + Pb + H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$



The first type of chemical reaction converts PbO2 into Pb through a reduction process: $PbO_2 + C \rightarrow Pb + CO_2$

Sulphur removal: The second type converts $PbSO_4$ into PbS, again through a reduction process:

$$PbSO_4 + 2C \rightarrow PbS + 2CO_2$$

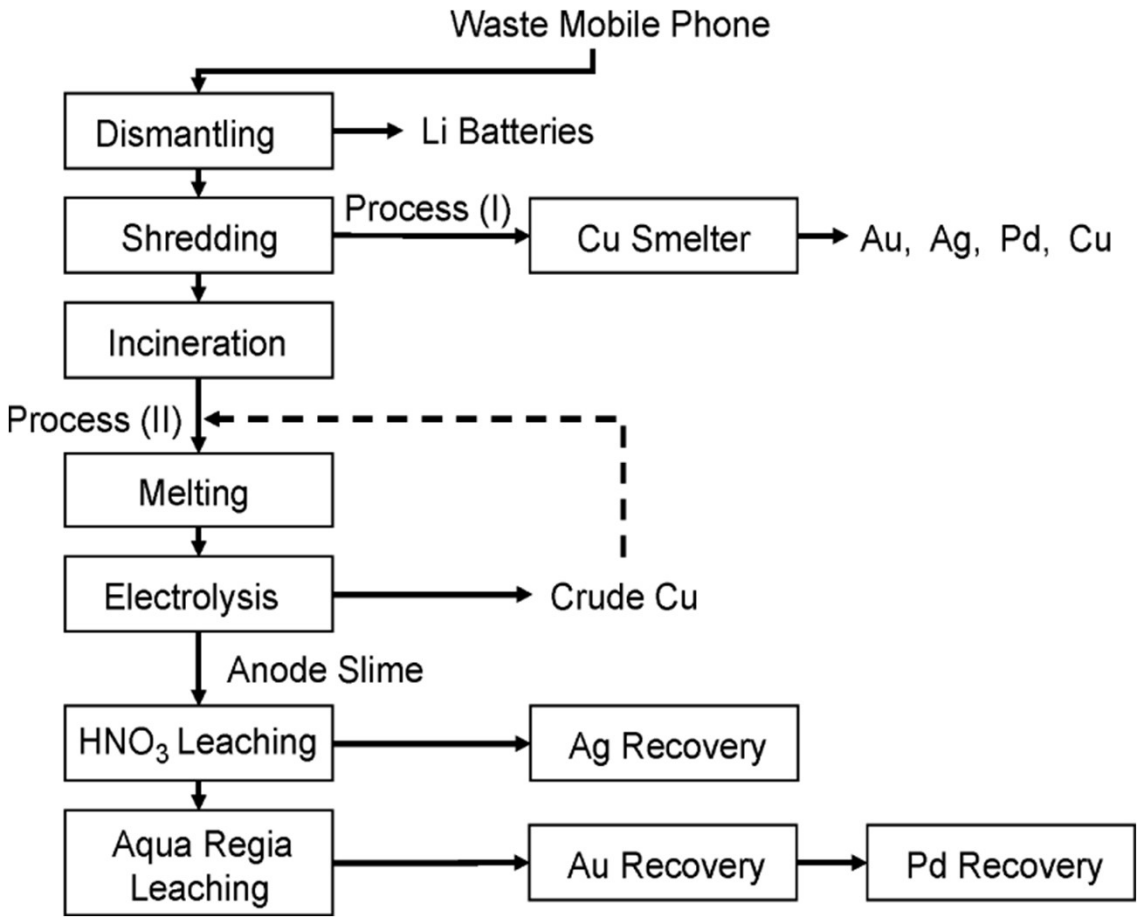
Finally PbS is converted into Pb through the following reaction

$$PbS + Fe \rightarrow Pb + FeS$$

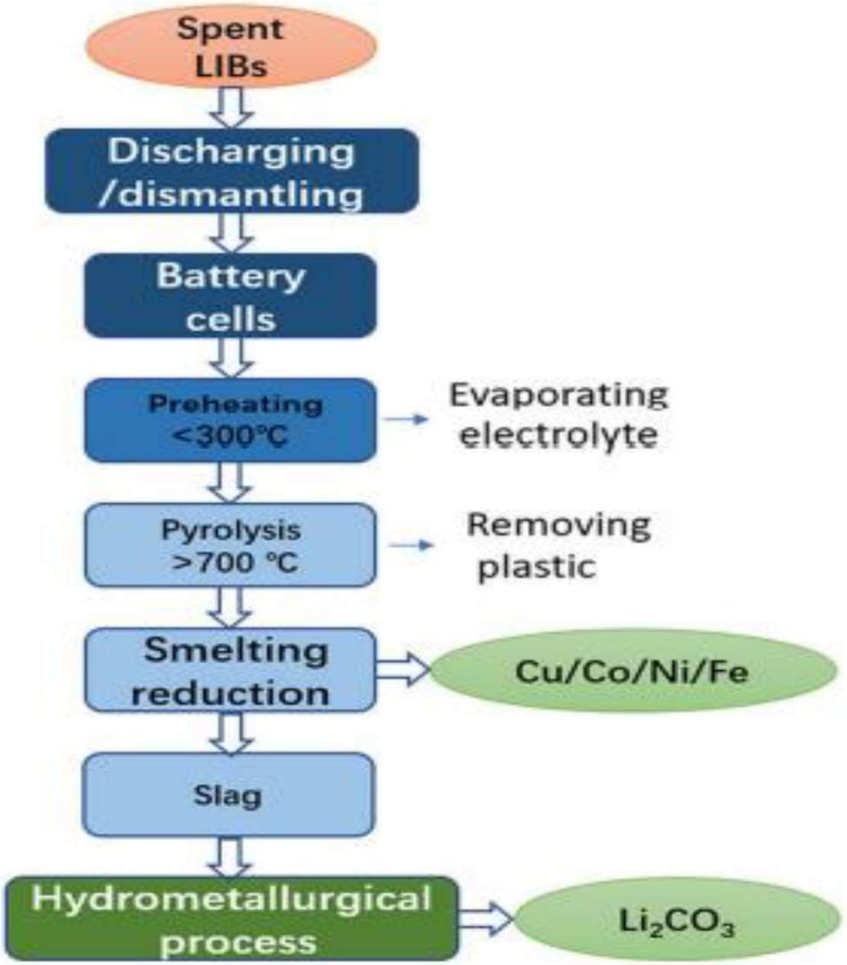
Removal of Sulphuric acid can be done by neutralizing with soda ash or caustic soda

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

General steps involved in recycling of Mobile Phones



Pyrometallurgical extraction of cobalt from spent LIBs



Steps involved in the recycling of Lithium battery

- Before the smelting process, LIBs are first disassembled into separate cells and then fed into a heating furnace.

- **Preheating:** Temperature should be lower than 300 °C to ensure complete evaporation of the electrolyte without explosion.

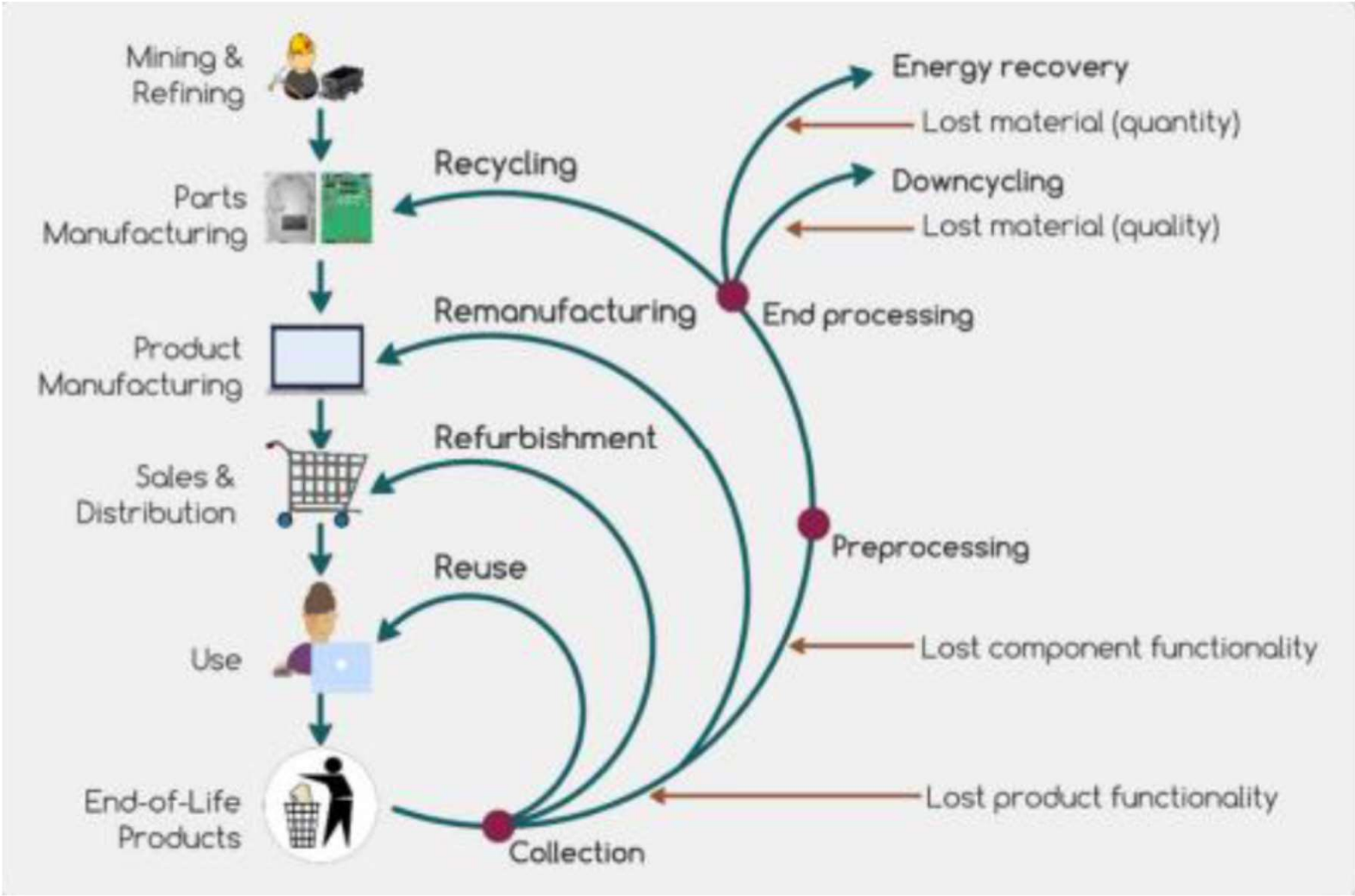
- **Pyrolysis:** The furnace temperature is controlled above 700^{o} C to remove the plastic from the battery.

- **Smelting:** The material is smelted into alloys of Cu, Co, Ni, and Fe, with the aid of carbon reductant, along with Li, Al, Si, Ca, and some Fe slag.

Since Co plays an irreplaceable role in commercial LIBs, and thermal metallurgy has a high efficiency in recovering Co rather than Li, the economy of this recovery method depends largely on the amount of Co contained in spent LIBs and the fluctuation of market value of cobalt.

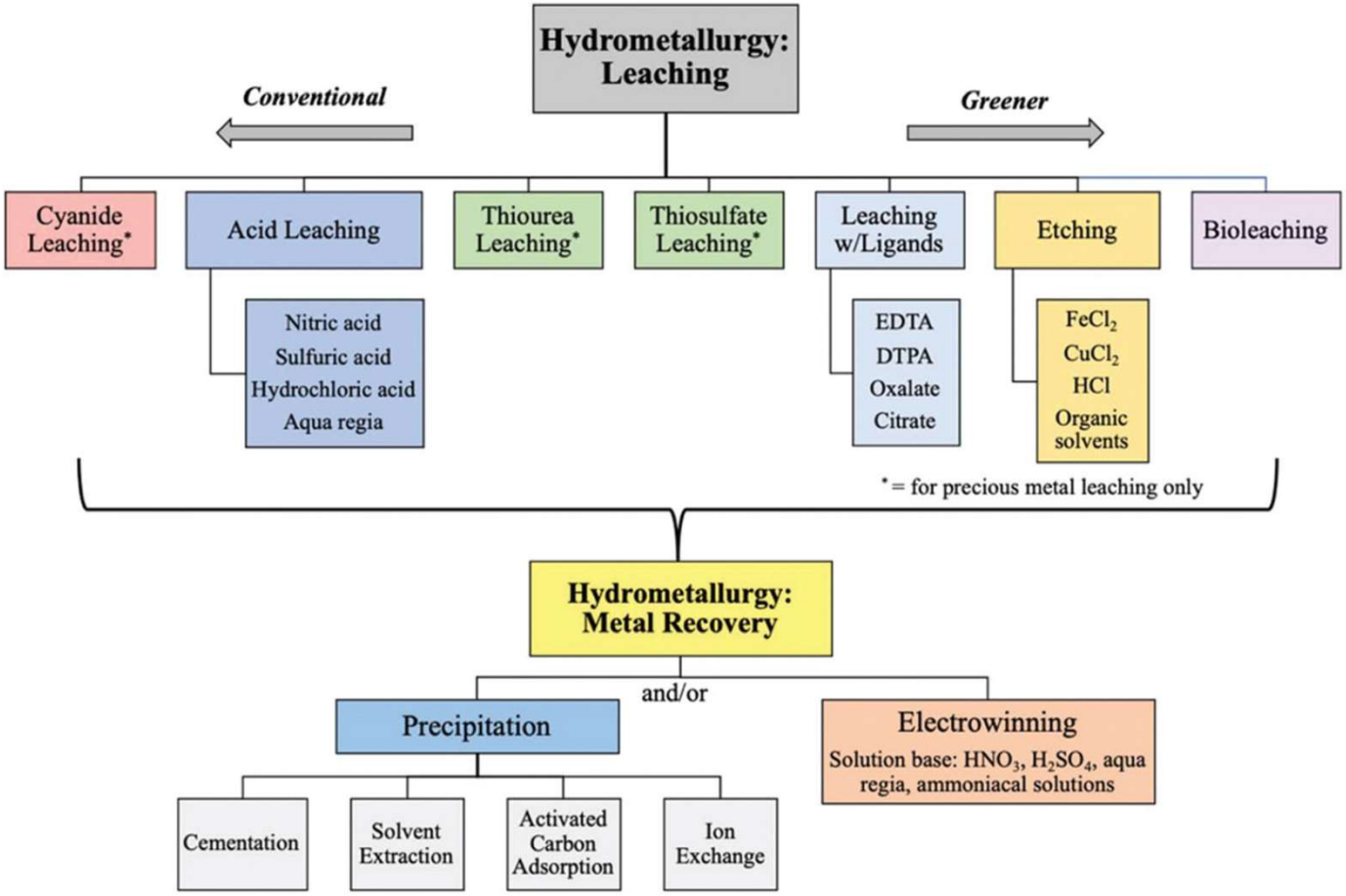
In order to recover Li from the spent LIBs, the **selective pyrolysis** method of an arc furnace can be used to convert some electrode materials into Co alloys and Li concentrate. After that, the Li is extracted by hydrometallurgy, and then it is transshipped and stored through the form of Li_2CO_3. And other components can be extracted further.

Circular Economy



Thank You

Hydro metallurgy



Extraction of valuable metals