



**RV College of
Engineering®**

Course: CHEMISTRY OF SMART MATERIALS AND DEVICES

Unit I

Sustainable chemistry and E-waste management:

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 using software.

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.

These are the polymers which gets decomposed by the process of biodegradation.

Biodegradation is defined as a process carried out by biological systems usually fungi or bacteria wherein a poly chain is cleaved via enzymatic activity.

They are broken down into biologically acceptable molecules that are metabolized and removed from the body via normal metabolic pathways. They slowly disappear from the site of administration in response to a chemical reaction such as hydrolysis.

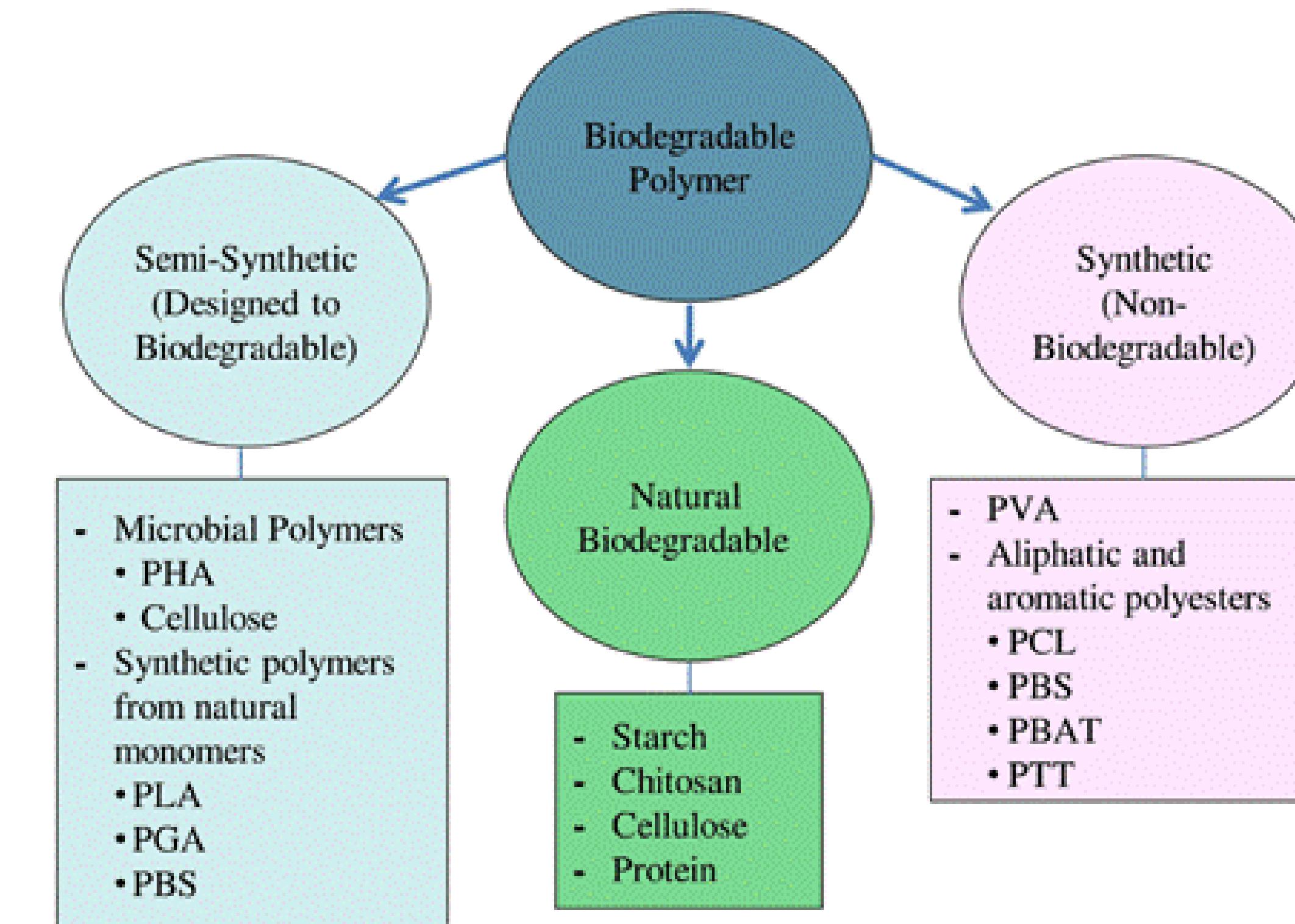


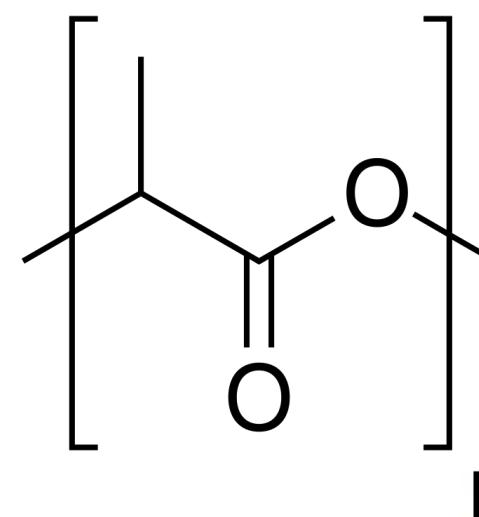
EDITABLE STROKE



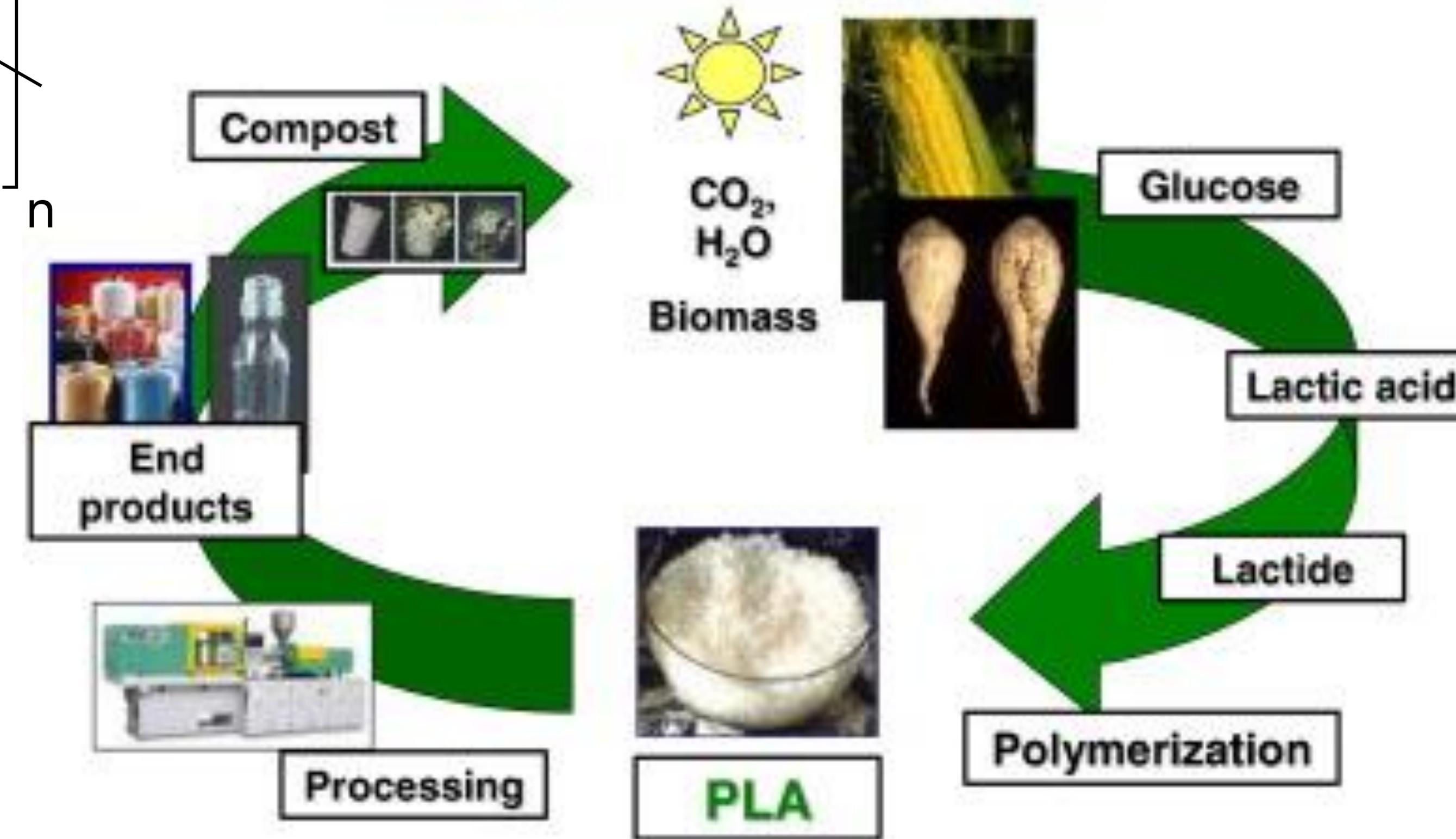
Classification of biodegradable polymers:

- The biodegradable polymers can be classified according to their chemical composition, origin and synthesis method, processing method, economic importance, application, etc.





Poly(lactic acid) cycle





Application
of Polylactic
acid (PLA)

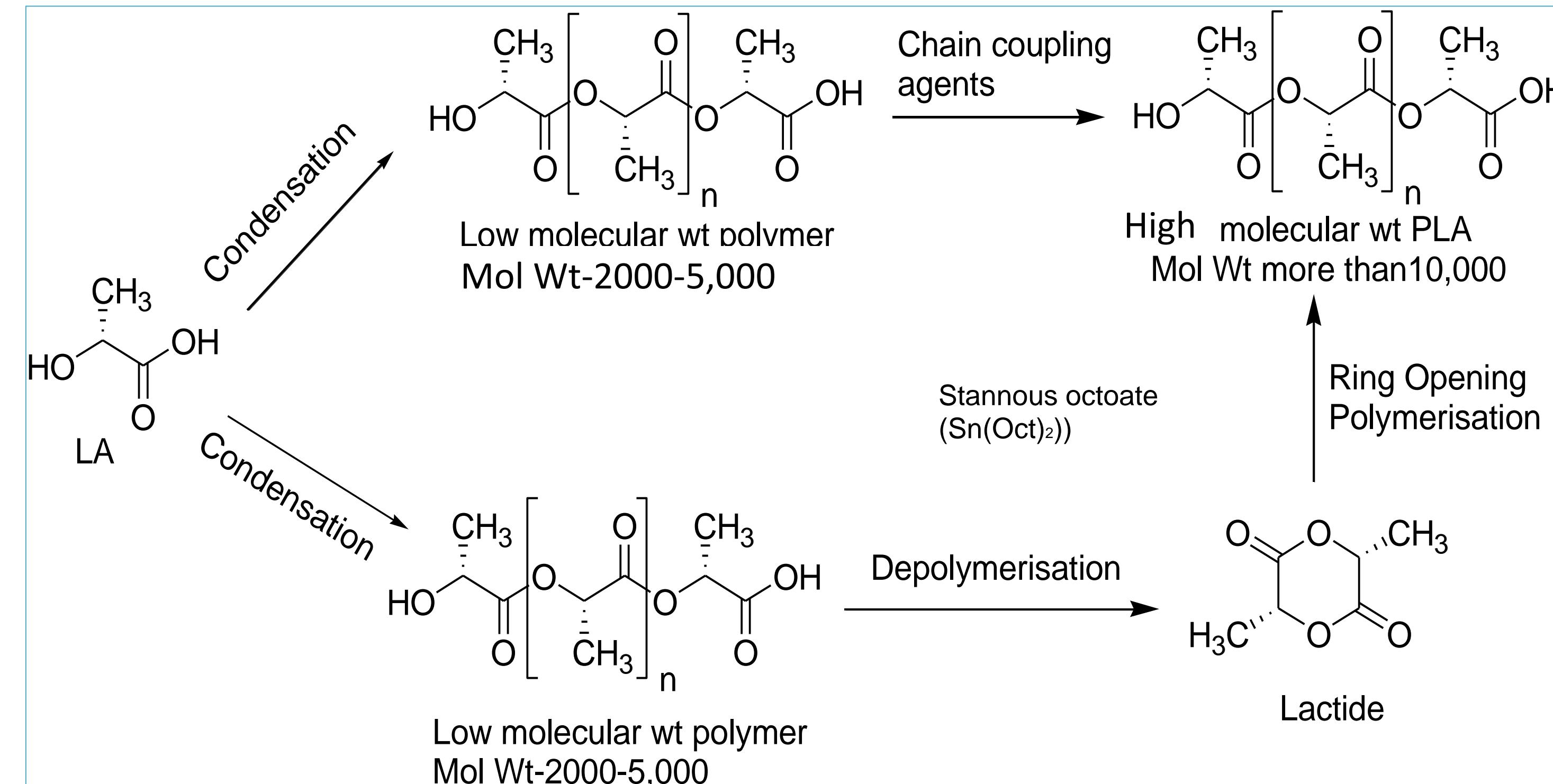
Properties:

- The PLA is a semi-crystalline polymer with glass transition temperature around 55 to 59°C and melting point 174-184 ° C.
- It shows a good mechanical strength, high Young's modulus, thermal plasticity and has good processability.
- It is unstable in wet conditions, which can undergo chain disruption in the human body and degrades into nontoxic by- products, lactic acid, carbon dioxide and water which are subsequently eliminated through the Krebs cycle and in the urine.

Synthesis of Poly Lactic Acid:

There are two important methods for PLA synthesis:

- (i) Direct polycondensation of lactic acid and
- (ii) Ring opening polymerization of lactic acid cyclic dimer, known as lactide.



Note

- In direct condensation, solvent is used and higher reaction times are required.
- Ring-opening polymerization (ROP) of the lactide needs catalyst (Stannous octoate (Sn(Oct)₂)) but results in PLA with controlled molecular weight.

- Polycaprolactum can be used as micropsheres for drug delivery systems.
- Polycaprolactum can be used as medical implants.
- Ultrahigh-strength PLA are used to make bone nails and screws
PLA are used in Fracture fixation and Ligament augmentation

Medical Applications

Wound management

Sutures

Staples

Clips

Adhesives

Surgical meshes

Orthopedic devices

Pins

Rods

Screws

Tacks

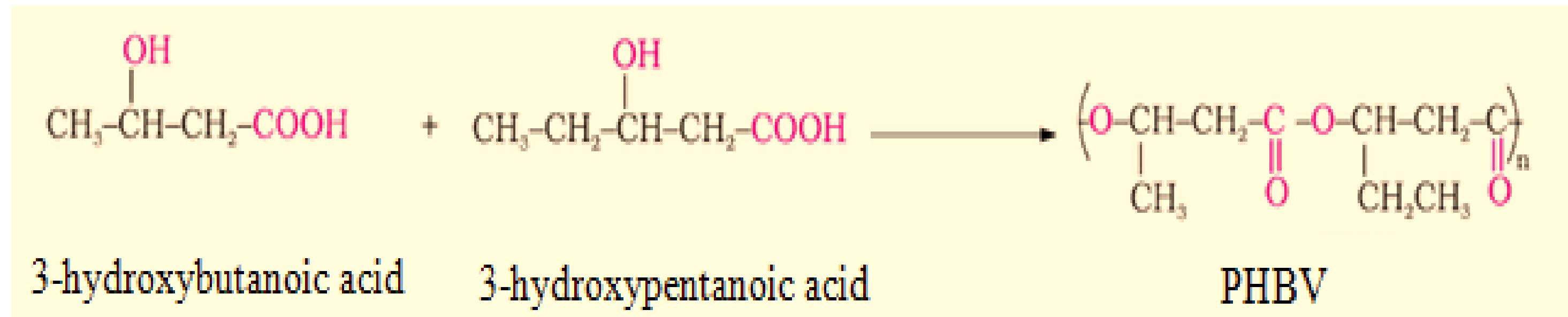
Ligaments

- Biodegradable polymers are very expensive.
- They are not easily available.
- In order to store potentially hazardous materials, landfills are built to be free of moisture and air tight. These anaerobic conditions which serve to guard against the release of hazardous chemicals from landfills also retard biodegradation.

Bio-compatible polymeric materials:

- Biocompatible polymers are both synthetic (man-made) and natural
- Helps in living system or work with living cells.
- These are used to gauge, treat, boost, or substitute any tissue, organ or function of the body.

Poly(3-hydroxybutyrate-copolymerization-3-hydroxyvalerate) OR PHBV



It is a thermoplastic linear aliphatic polyester. It is obtained by the copolymerization of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.

Properties: It may be biodegradable, nontoxic

- biocompatible plastic produced naturally/synthetic by bacteria and a good alternative for many non-biodegradable synthetic polymers.
- PHBV undergoes bacterial degradation in the environment.

Degradation

When disposed, PHBV undergo bacterial degradation to give carbon dioxide and water.

Applications:

- (1) It is used in controlled release of drugs, medical implants and repairs, specialty packaging, orthopaedic devices and manufacturing bottles for consumer goods.
- (2) It is also biodegradable which can be used as an alternative to non-biodegradable plastics

Biocompatible polymeric materials

Biocompatible polymers are both synthetic (man-made) and natural and aid in the close vicinity of a living system or work in intimacy with living cells. These are used to gauge, treat, boost, or substitute any tissue, organ or function of the body.

Hydrogel is a water-swollen, and cross-linked polymeric network produced by the simple reaction of one or more monomers.

OR

A polymeric material that exhibits the ability to swell and retain a significant fraction of water within its structure, but will not dissolve in water is known as **Hydrogel**.

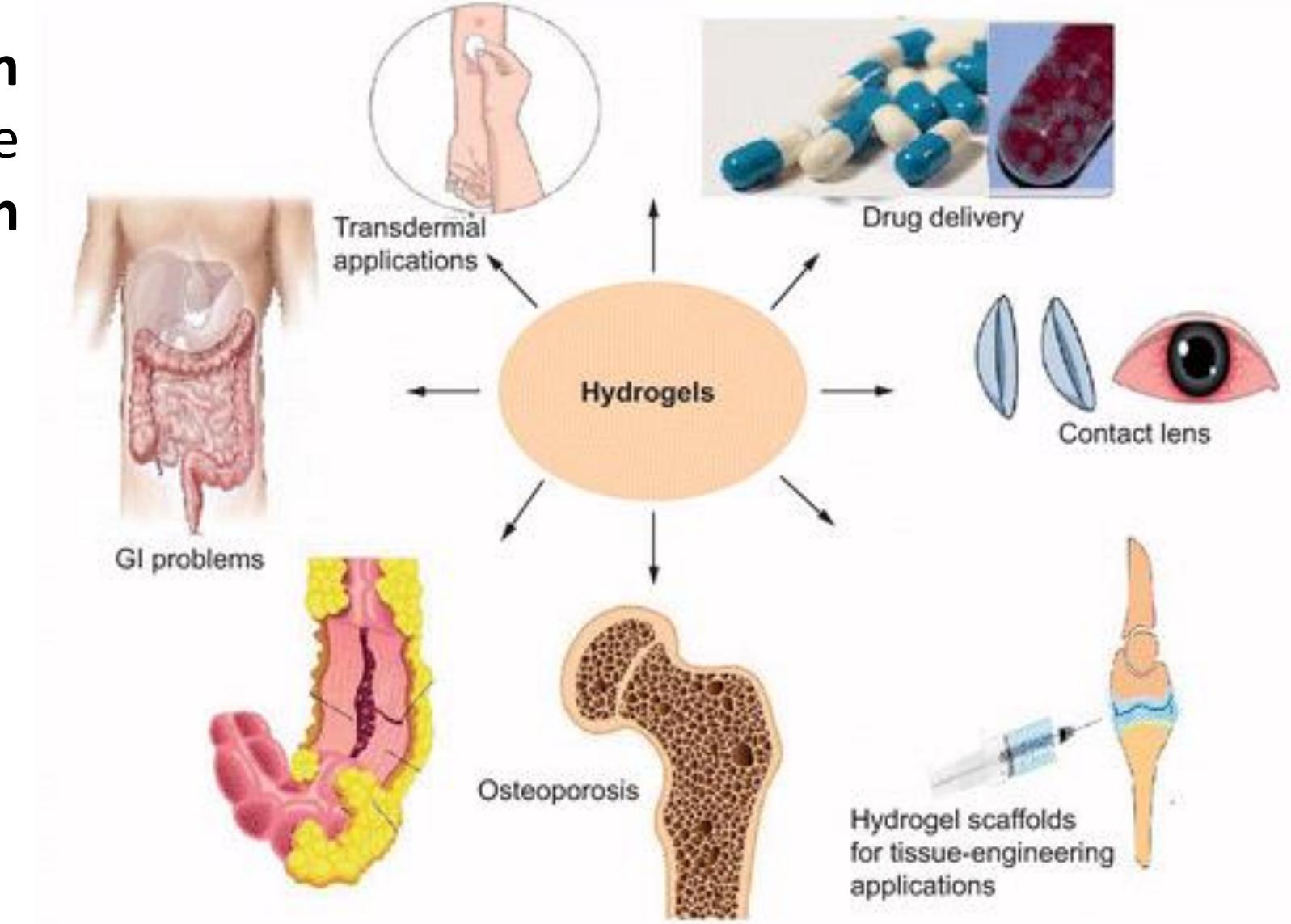
Hydrogels are **crosslinked hydrophilic polymer structures that can imbibe large amounts of water or biological fluids**. Hydrogels may be based on natural polymers, including **macromolecules extracted from animal collagen, plants, and seaweed**

Properties of Hydrogels

- mechanical strength
- biocompatibility
- biodegradability
- swellability

Mechanism

The swelling-controlled drug release from hydrogels uses drugs dispersed within a glassy polymer which when in contact with a biofluid begins swelling. The expansion during swelling occurs beyond its boundary facilitating the drug diffusion along with the polymer chain relaxation



Applications of Hydrogels

producing contact lenses, hygiene products, wound dressings, drug delivery, tissue engineering

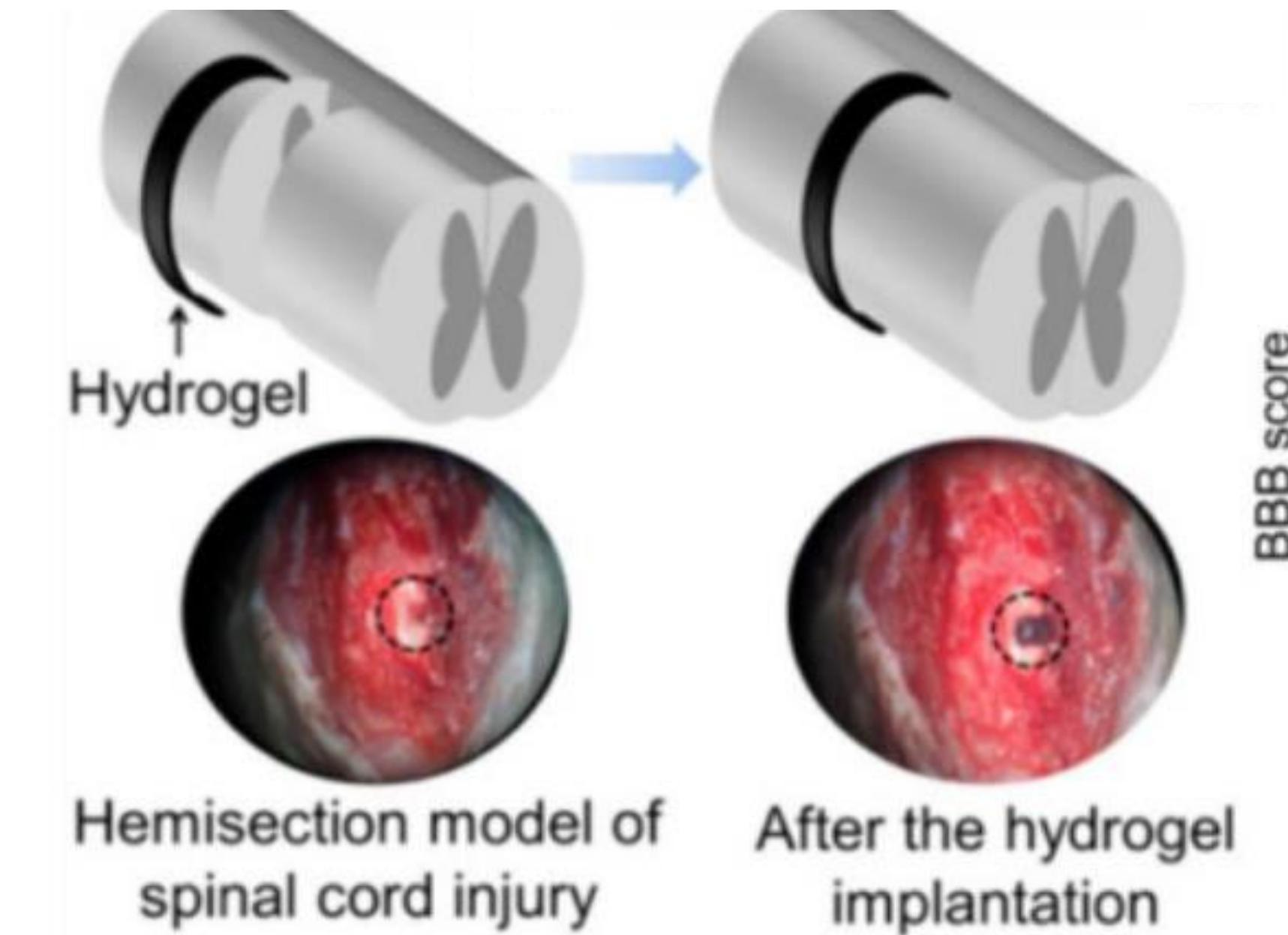
synthetic and biodegradable polymers, **aliphatic polyesters such as poly (glycolic acid), poly (lactic acid), poly (caprolactone) and polydioxanone**, are most commonly used and applied to drug delivery systems

Important features of hydrogels:

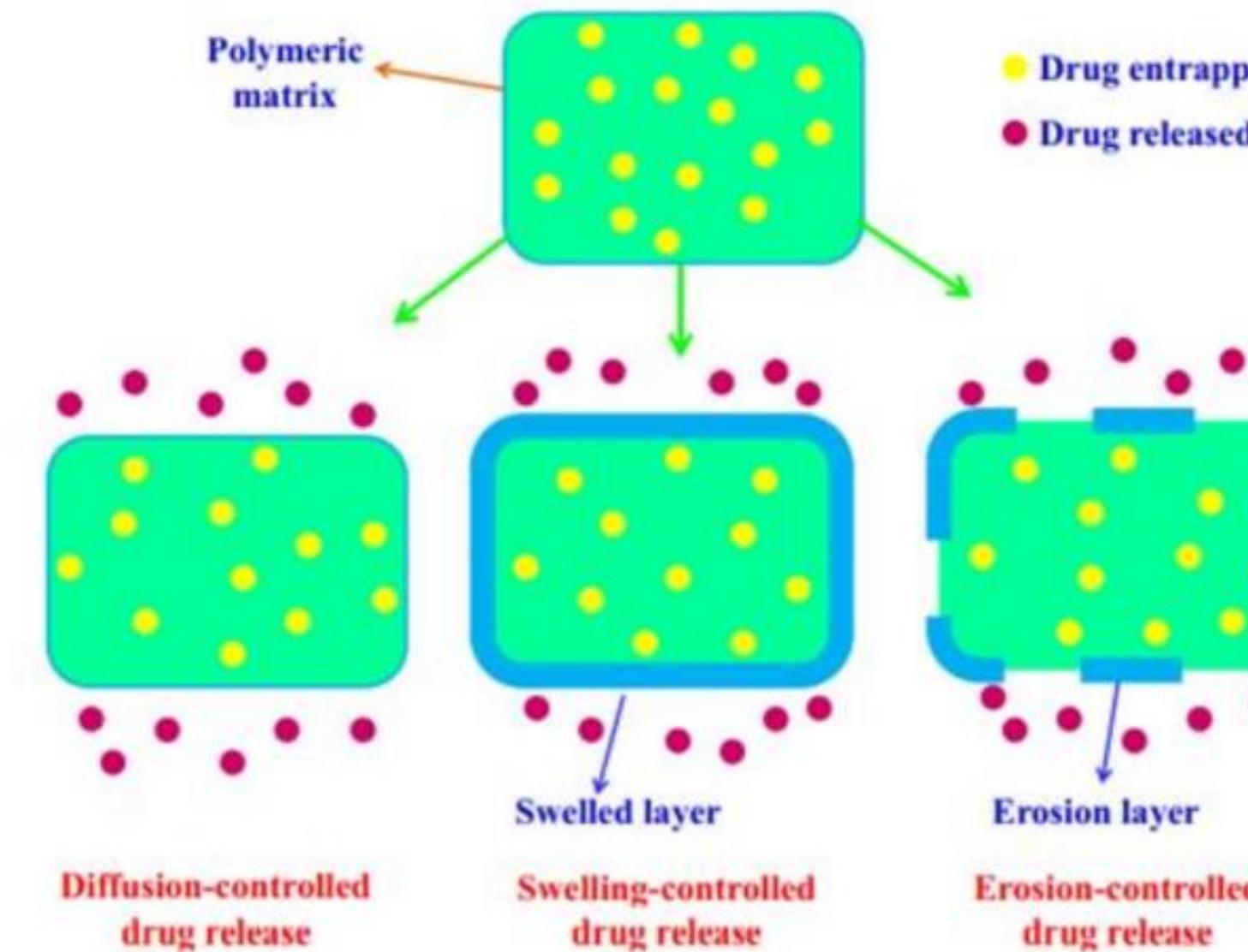
1. The ability of hydrogels to absorb water arises from hydrophilic functional groups attached to the polymeric backbone, while their resistance to dissolution arises from cross-links between network chains.
2. Hydrogels have similarities with human soft tissues in composition, structure, and properties.
3. Due to their superior biocompatibility and low toxicity, hydrogels play a significant role in the biomedical fields.
4. Hydrogels are considered to be the most prospective alternative materials for soft tissue due to their exceptional mechanical properties.

Classification of Hydrogels

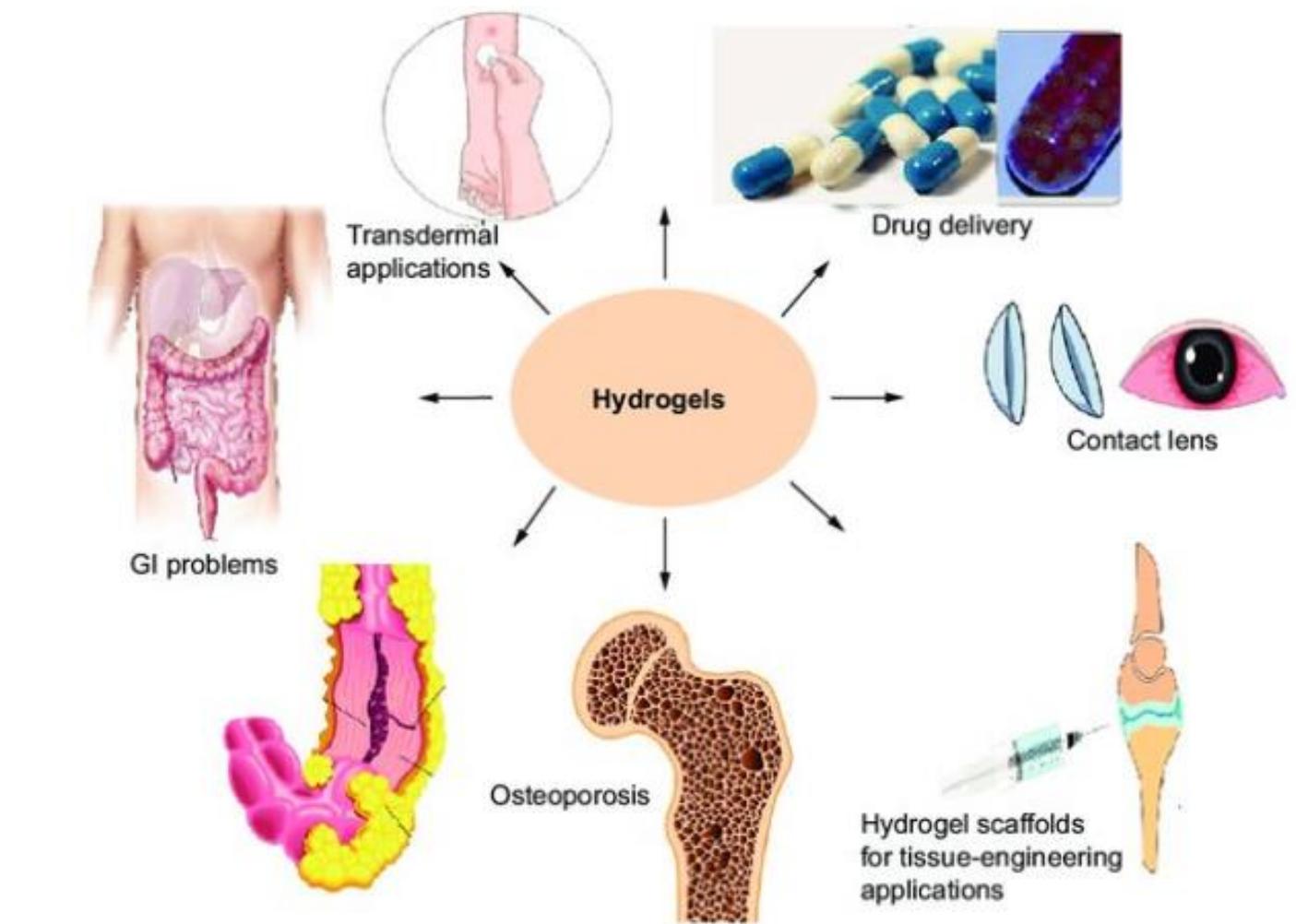
1. **Natural hydrogels:** Collagen, silk fibroin, hyaluronic acid, chitosan, alginate.
2. **Synthetic hydrogels:** Polyhydroxyethyl methacrylate (PMMA), Polyvinyl alcohol (PVA), Polyethylene glycol (PEG), etc



Application of Hydrogels



Mechanism of drug release from a polymeric matrix including diffusion, swelling, and erosion controlled methods



- (1) Producing contact lenses,
- (2) Hygiene products,
- (3) Wound dressings,
- (4) Drug delivery,
- (5) Tissue engineering

GreenChemistry

Green Chemistry is the utilisation of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products.

- Green chemistry is defined as environmentally benign chemical synthesis to minimize pollution
- Usage of non toxic starting materials and prevention of hazardous byproducts
- Scientists trying for benign green synthesis for new and existing chemicals

Need for Green Chemistry

Minimata Disease * 1950 village in Japan: Disease caused by mercury poisoning (in fish) occurred in Minimata bay of Japan

Itai-Itai Disease *1912 in Japan: Disease caused due cadmium poisoning (in rice). Due to acute pain people cried “Itai-Itai”

Bhopal Gas tragedy *1984 : Union carbide in Bhopal: Methyl isocyanate (MIC) (used manufacturing of insecticide “seven”)

GREEN CHEMISTRY IS ABOUT

- **Waste Minimisation at Source**
- **Use of Catalysts in place of Reagents**
- **Using Non-Toxic Reagents**
- **Use of Renewable Resources**
- **Improved Atom Efficiency**
- **Use of Solvent Free or Recyclable Environmentally Benign Solvent systems**

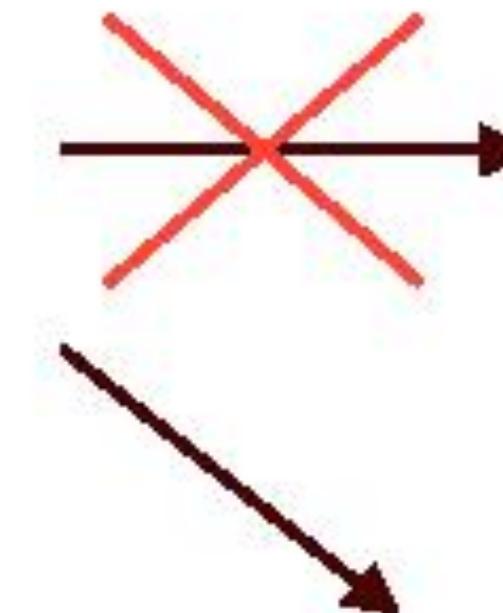
- 1. Prevention.**
- 2. Atom Economy**
- 3. Less Hazardous Chemical Synthesis**
- 4. Designing Safer Chemicals**
- 5. Safer Solvents and Auxiliaries**
- 6. Design for Energy Efficiency**
- 7. Use of Renewable Feedstocks**
- 8. Reduce Derivatives**
- 9. Catalysis**
- 10 Design for Degradation**
- 11 Real-time Analysis for Pollution Prevention**
- 12 Inherently Safer Chemistry for Accident Prevention**

Prevention is better than cure

“It is better to prevent waste than to treat or clean up waste after it is formed”

Chemical Process

WASTE PREVENTION



No waste

Synthetic methods should be designed to maximise the incorporation of all materials used in the process into the final product

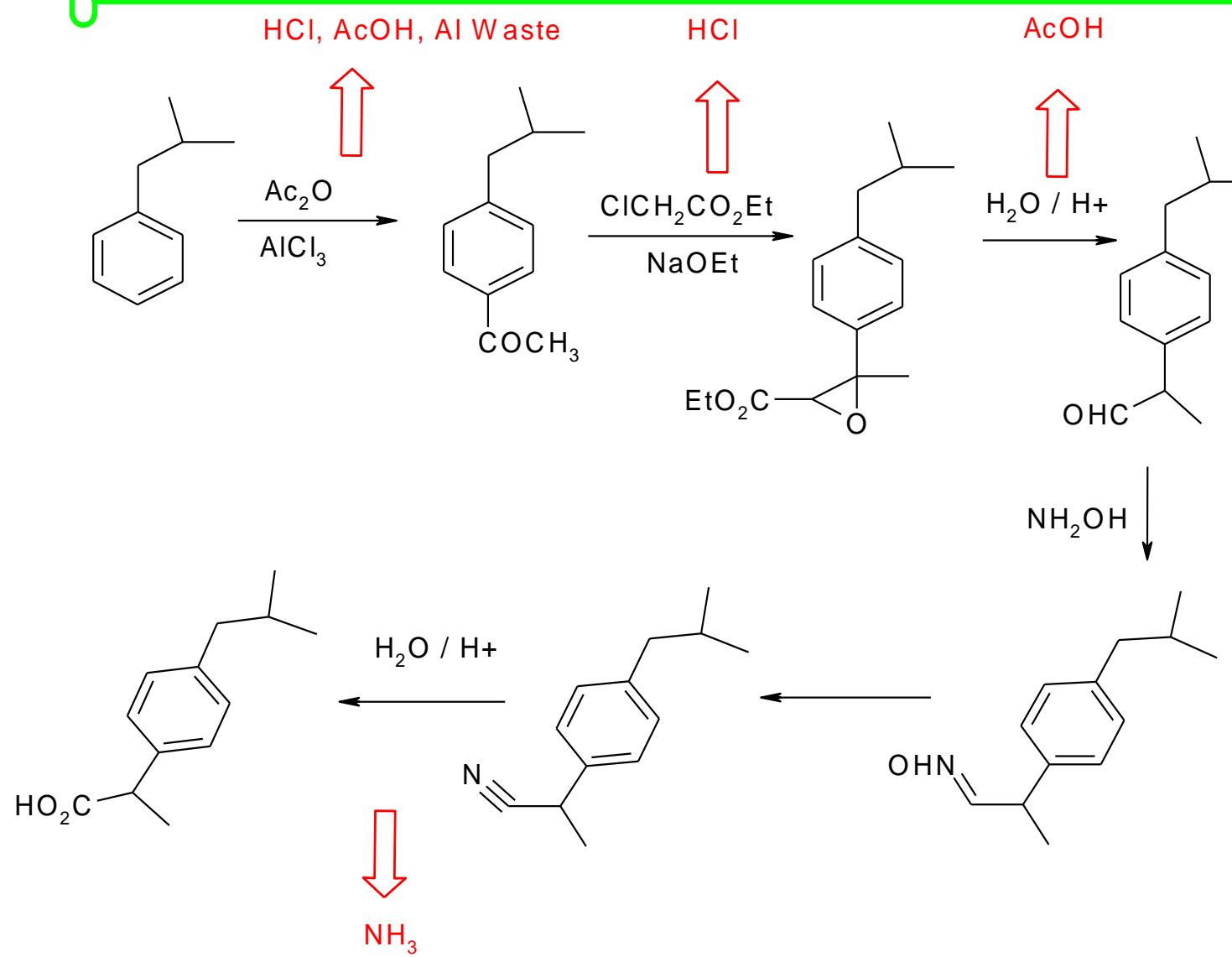
$$\% \text{ yield} = \frac{\text{Actual yield of the product}}{\text{Theoretical yield of the product}} \times 100$$

If one mole of starting material produces one mole of the product, the yield is 100%. However , such a synthesis may generate significant amount of waste or byproducts not visible in the yield calculation

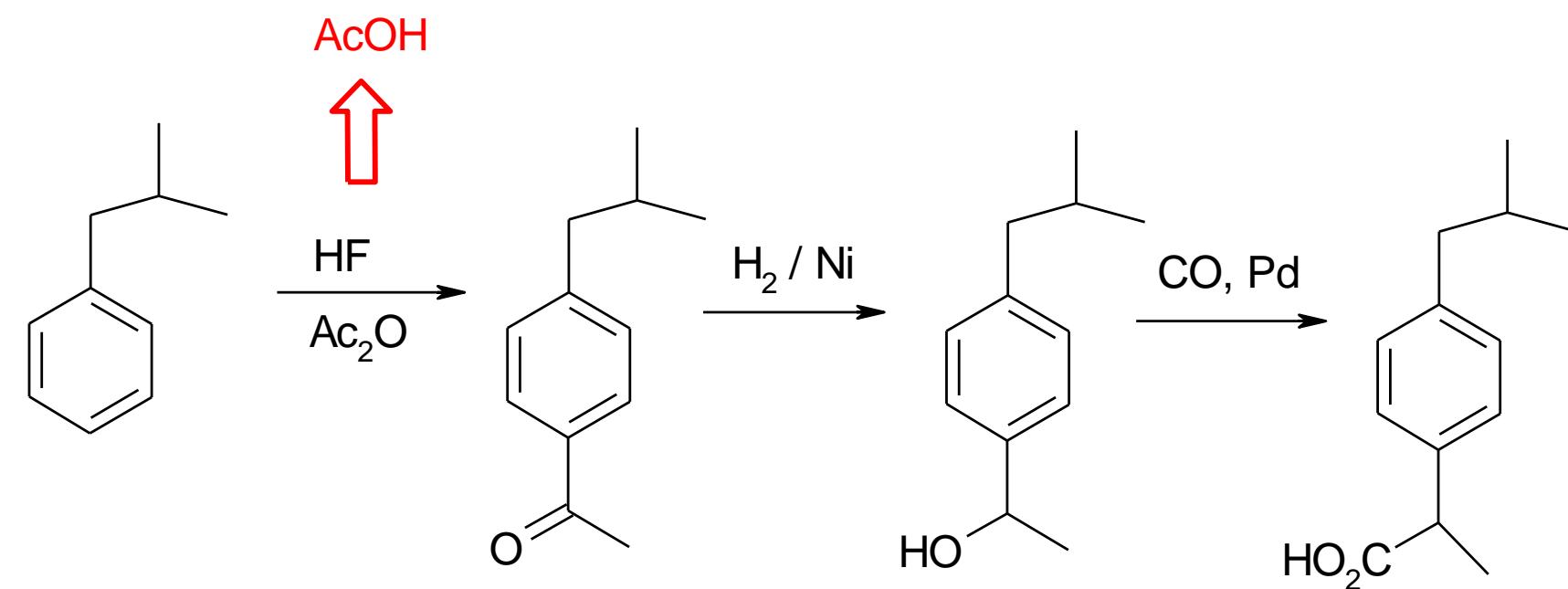
A reaction is considered to be green if there is maximum incorporation of the starting materials or reagents in the final product. One should consider % of utilization

$$\% \text{ atom economy} = \frac{\text{Formula weight of atoms utilized}}{\text{Formula weight of the reactants used in reaction}} \times 100$$

Classic Route to Ibuprofen



Hoechst Route To Ibuprofen



AcOH – Acetic acid

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to people or the environment.

One of the most important principle of green chemistry is to prevent or at least minimize the formation of hazardous products which may be toxic and or environmentally harmful. In case hazardous products are formed their effects on the workers must be minimized by the use of protective clothing, respirator etc. It will add more cost, sometimes control fails causing more risk. Green chemistry offers a scientific option to deal with such situations.

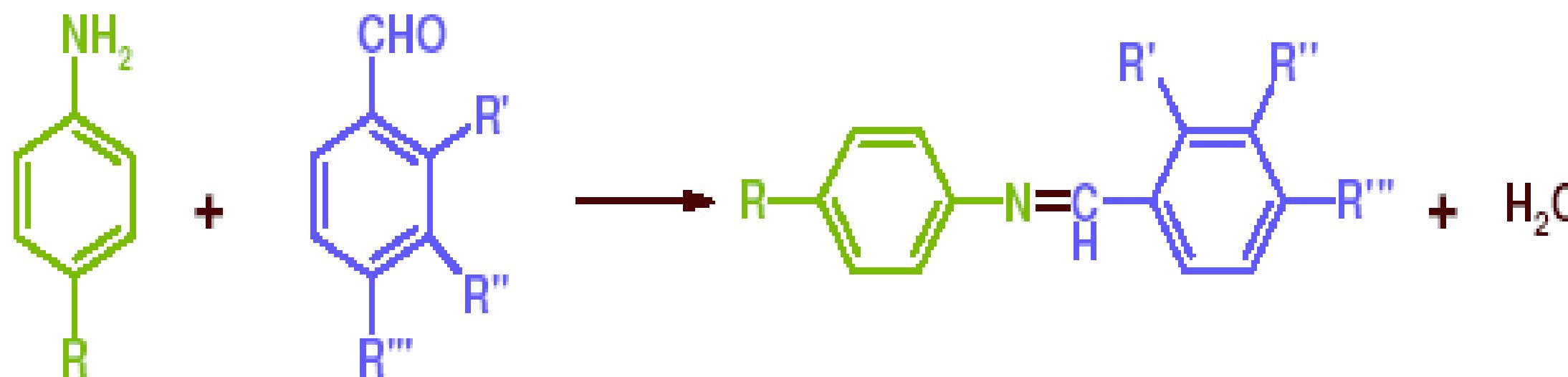
Chemical products should be designed to effect their desired function while minimising their toxicity.

It is extremely important that the chemicals synthesized (dye, paints, cosmetics etc) should be safe to use. Atypical example of an unsafe drug is thalidomide (introduced in 1961) for reducing the effects of nausea and vomiting during pregnancy (morning sickness). The children born to those women taking thalidomide suffered birth defects. Later use of thalidomide was banned. It was found thalidomide exists in enantlomesic forms. One enantiomer caused birth defect and another enantiomer was curing morning sickness. With the advancement of technology it is possible to manipulate molecular structure to produce safer chemicals.

The use of auxiliary substances (e.g., solvents or separation agents) should be made unnecessary whenever possible and innocuous when used.

“The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible, and innocuous when used”

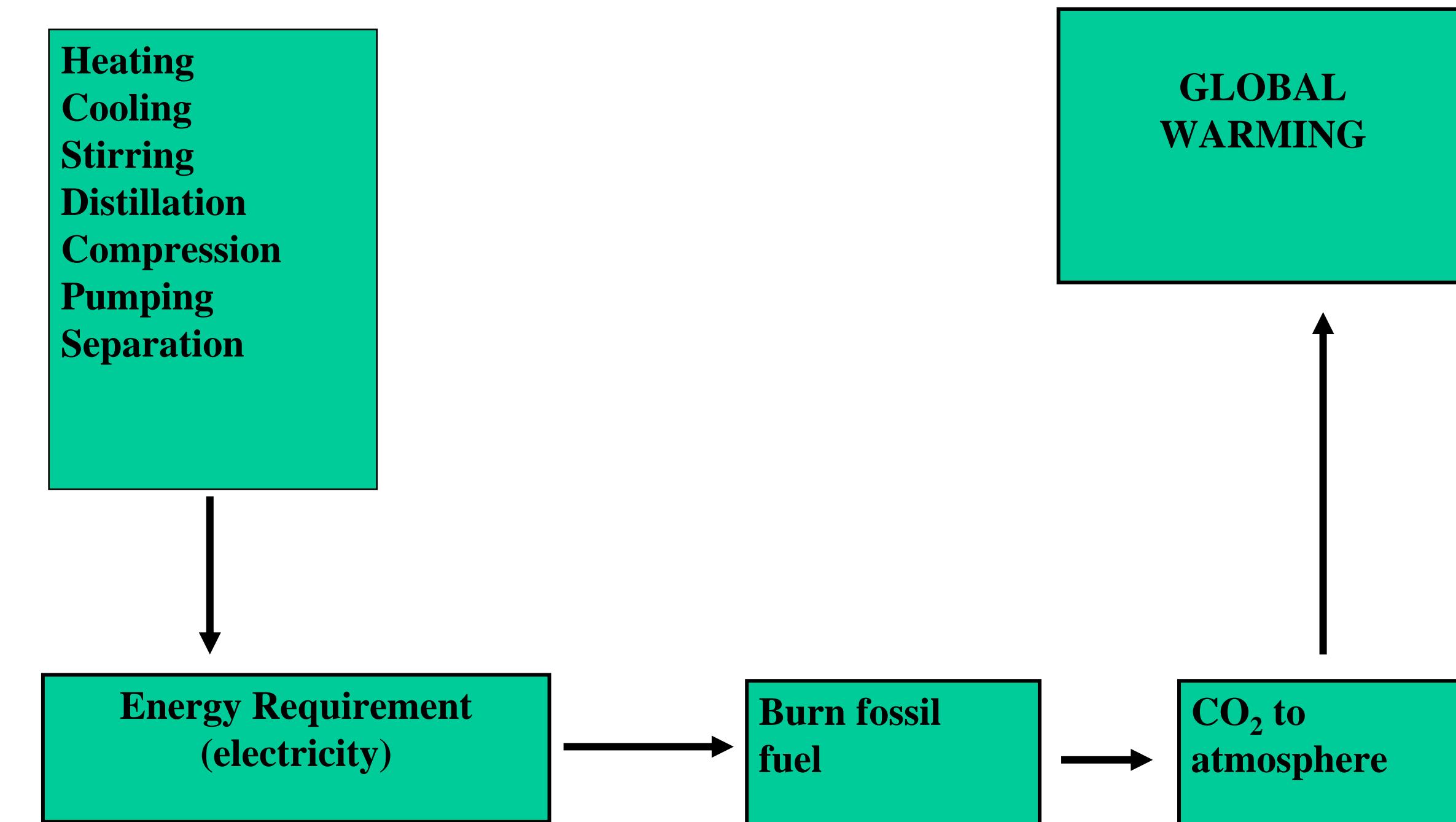
A solventless reaction:



**Mechanochemistry (above reaction as it involves grinding)
If done with alcohol it takes 12 hours

Energy requirements of chemical processes should be recognised for their environmental and economic impacts and should be minimised. If possible, synthetic methods should be conducted at ambient temperature and pressure.

“Energy requirements should be recognized for their environmental impacts and should be minimized. Synthetic methods should be conducted at ambient pressure and temperature”



A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

“A raw material or feedstock should be renewable rather than depleting wherever technically and economically practical”

Non-renewable

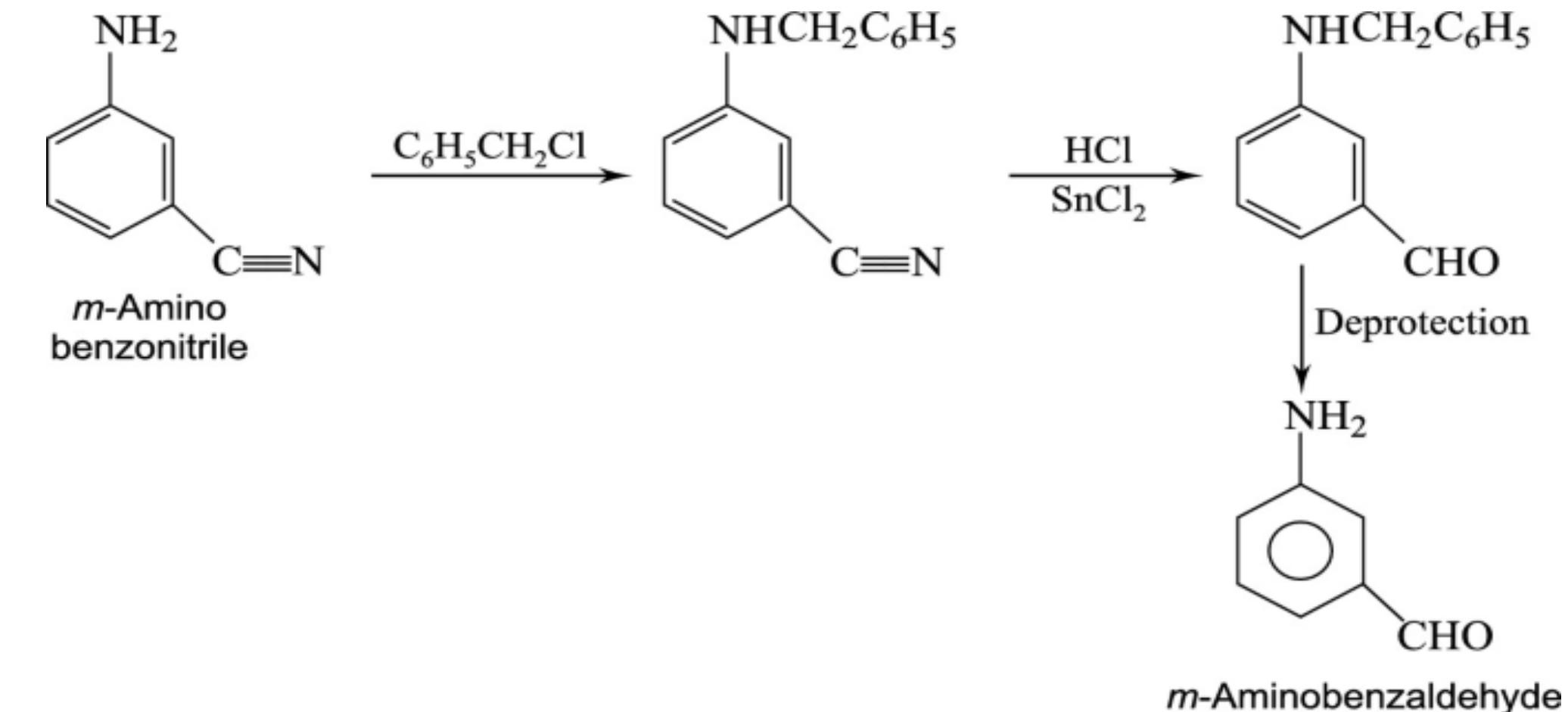


Renewable



Unnecessary derivatization (use of blocking groups, protection/de-protection, and temporary modification of physical/chemical processes) should be minimised or avoided if possible, because such steps require additional reagents and can generate waste.

A commonly used technique in organic synthesis is the use of protecting or blocking group. These groups are used to protect a sensitive moiety from the conditions of the reaction, which may make the reaction to go in an unwanted way if it is left unprotected. A typical example is protection of amine by making benzyl ether in order to carry out a transformation of another group present in the molecule. After the reaction is complete, the NH₂ group can be regenerated through cleavage of the benzyl ether



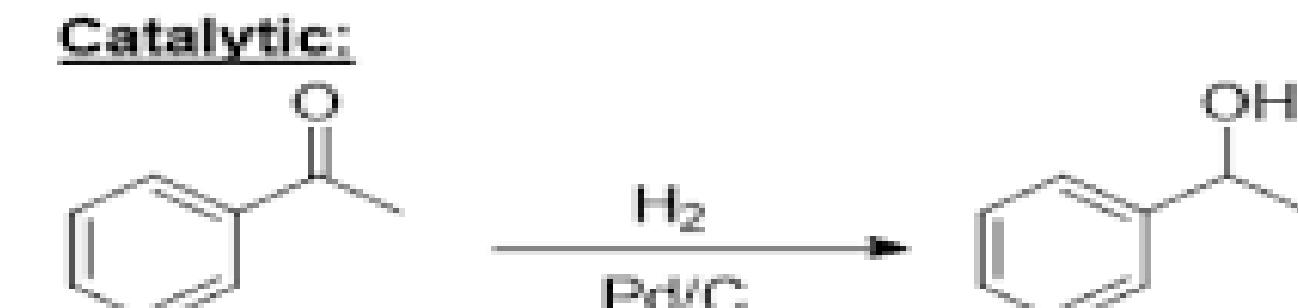
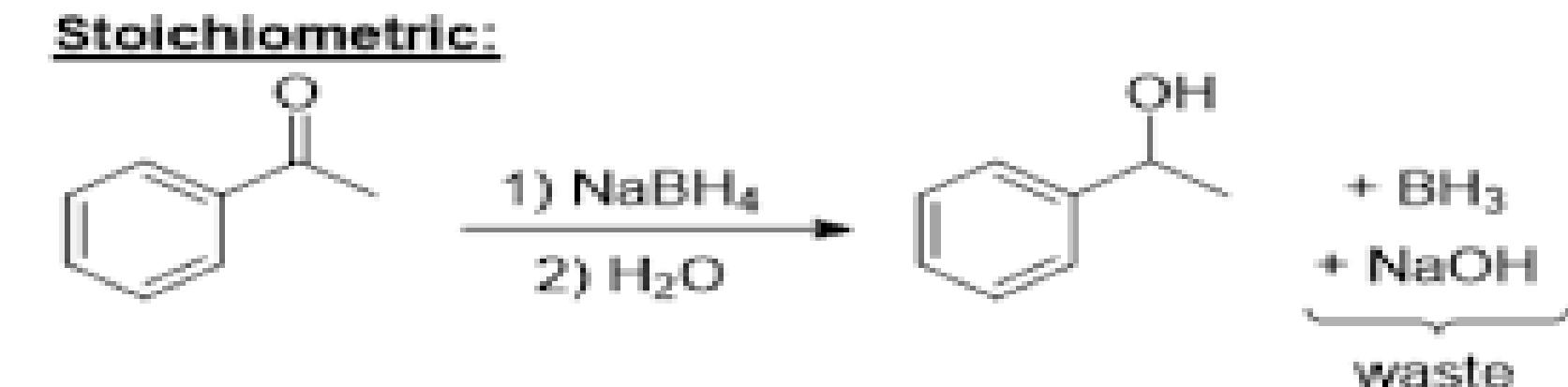
Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

Even if the yield is 100% some unreacted starting material will be left over as waste. In some cases if reagents A and B do not give 100 % of the product both excess of unreacted reagents will form part of waste. Catalyst wherever available offer distinct advantages over typical stoichiometric reagents. The catalyst facilitates the transformations without being consumed or without being incorporated into the final product.

Hydrogenation of olefins (propene to propane) in presence of nickel catalyst gives much better yields.

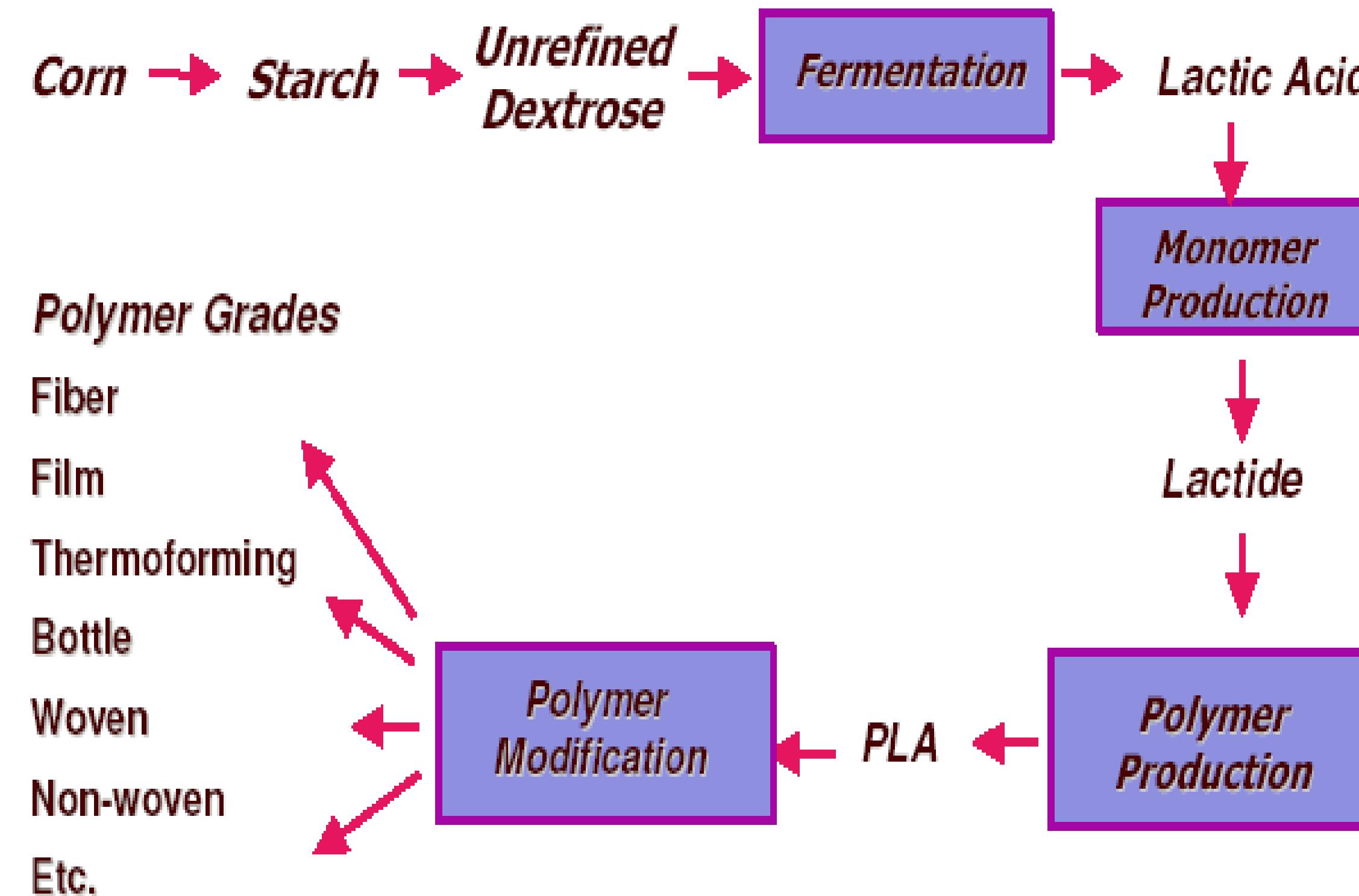


As Pd/C is used highly unsafe



Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

Poly lactic acid (PLA) for plastics production



Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

- **Need for accurate and reliable sensors, monitors and analytical techniques to assess the hazards that are present in the process**
- **Analytical methodologies and technology can prevent accidents which may occur in chemical plants**

Substances and the form of a substance used in a chemical process should be chosen to minimise the potential for chemical accidents, including releases, explosions, and fires.

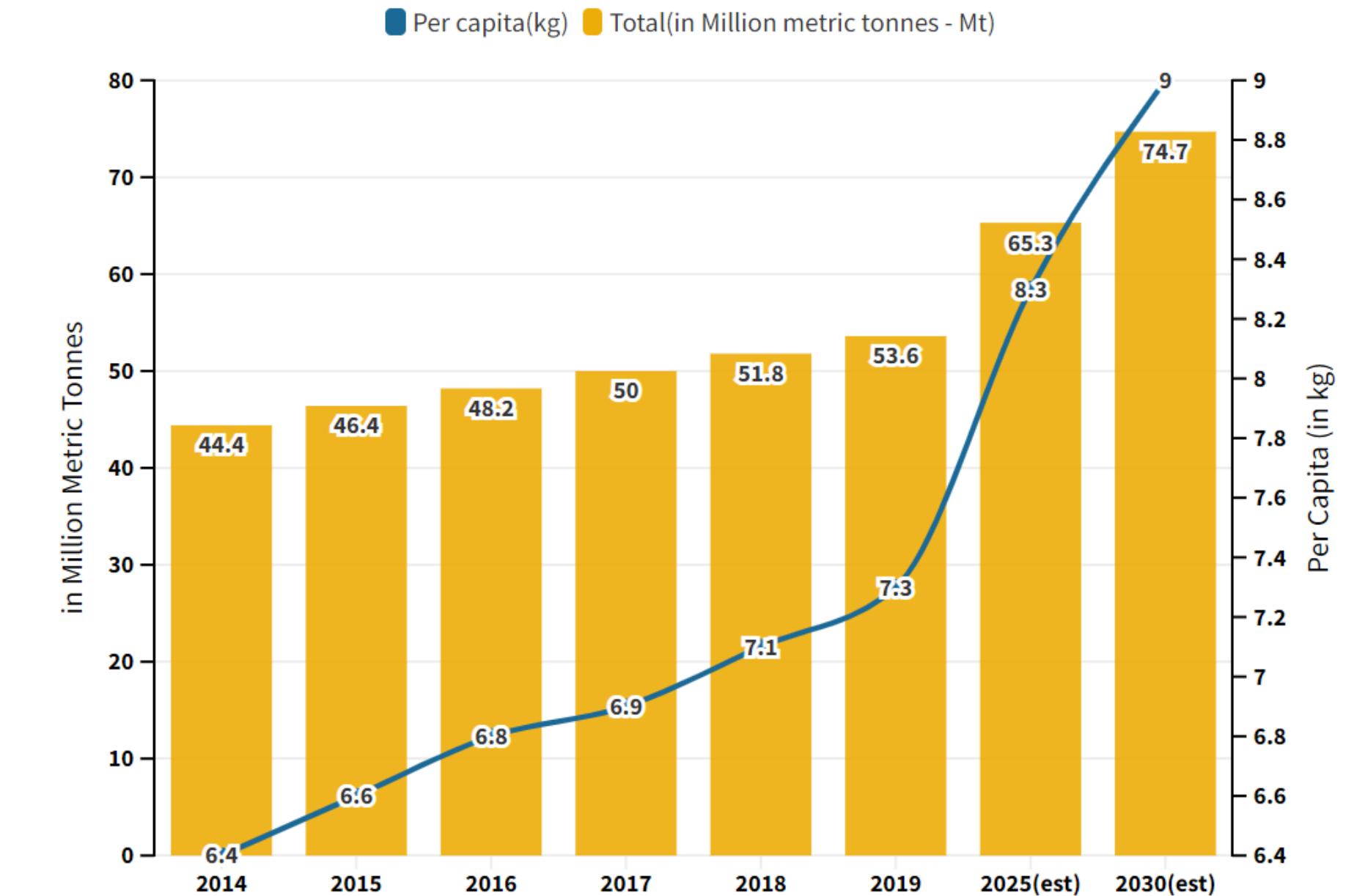
- The occurrence of accidents in chemical industry must be avoided. The accidents in Bhopal and many others have resulted in the loss of thousands of life
- Possibility in increasing no of accidents, while attempting to minimize waste generation or attempt to recycle solvents
- A process must balance the accident prevention with a desire for preventing pollution
- A possible solution not to use volatile substance, instead solids or low vapour pressure substance can be used

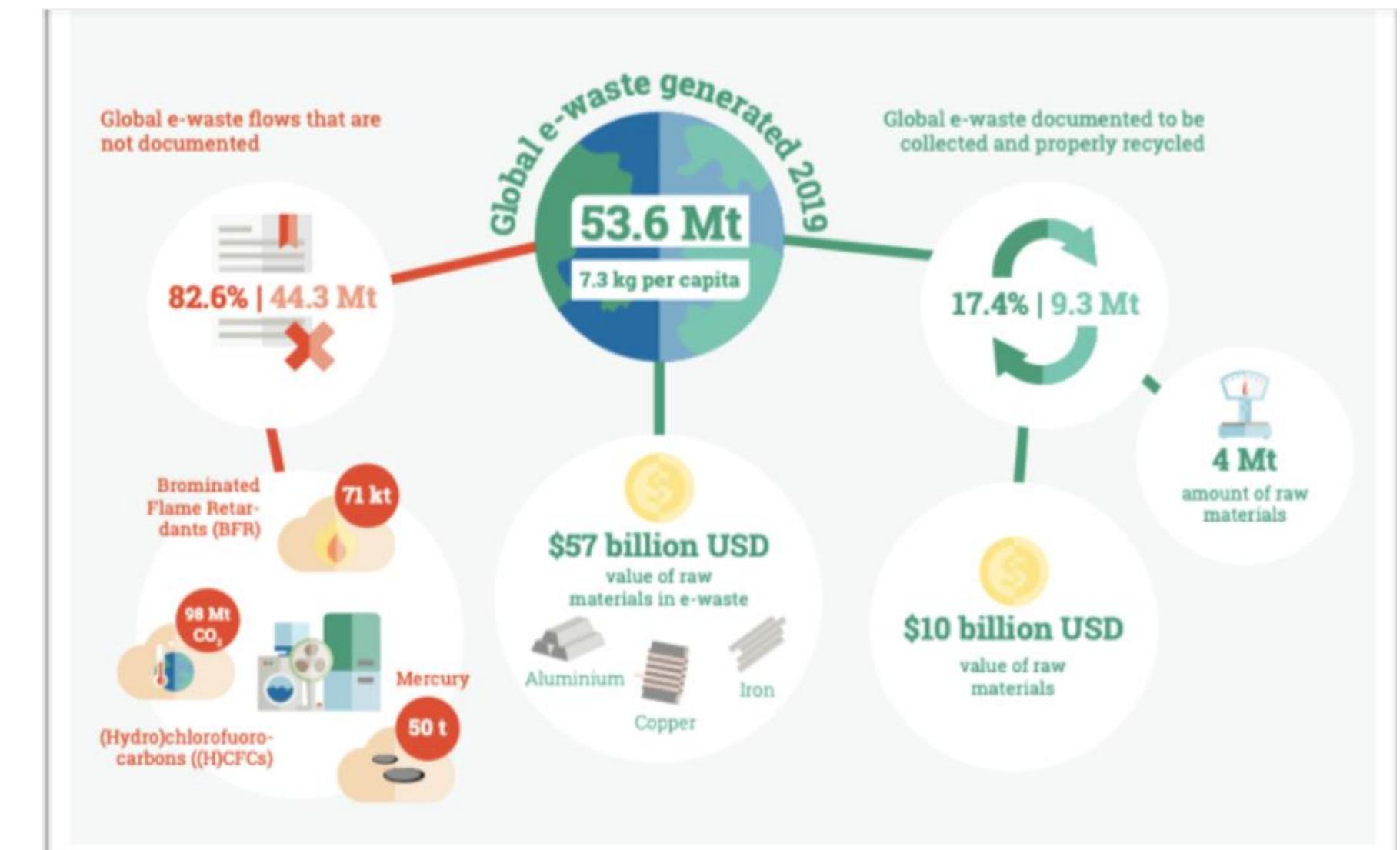
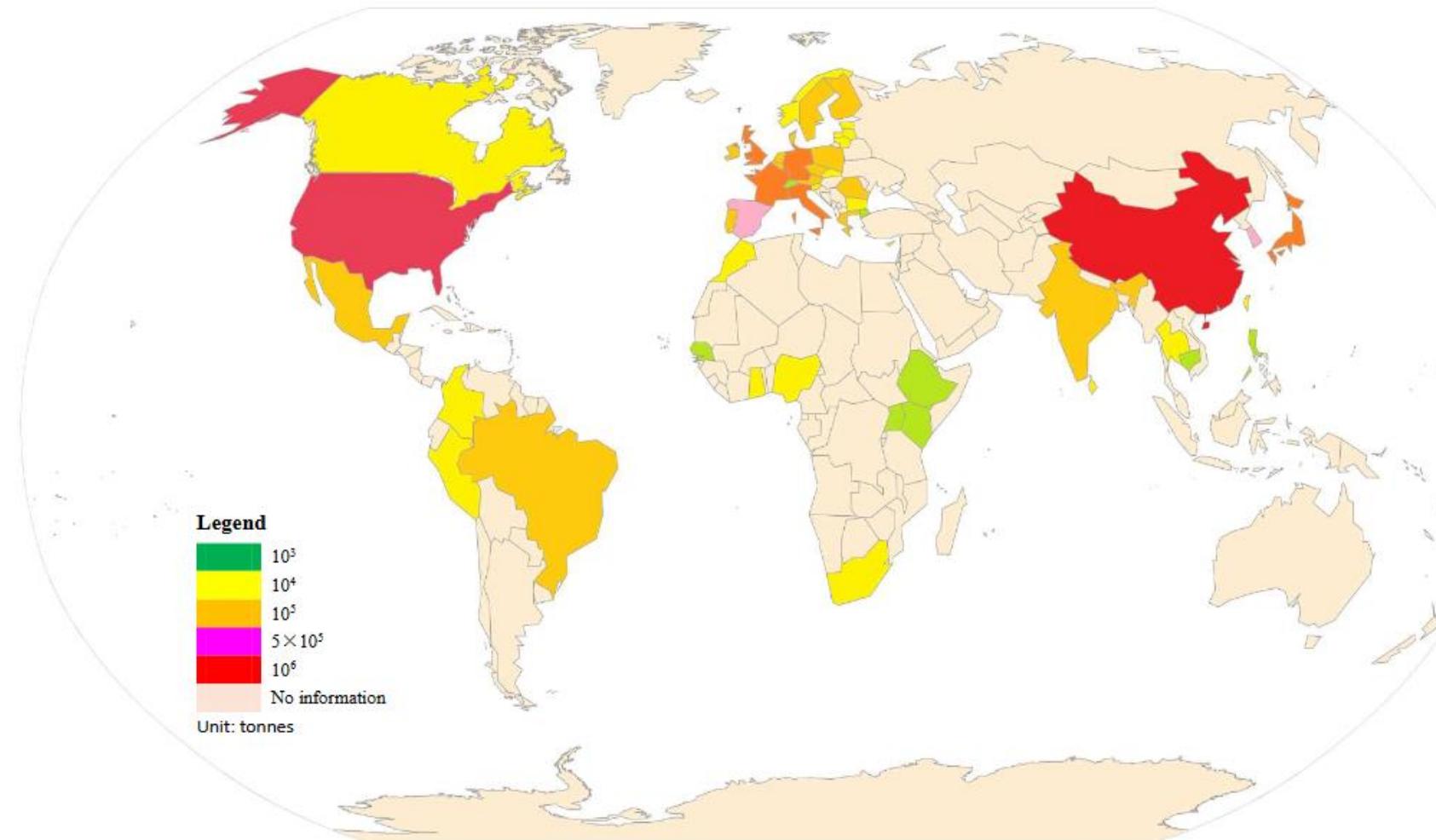
E-Waste is short form for Electronic-Waste and the term is used to describe old, end-of-life or discarded electronic appliances.

OR

E-waste refers to any electronic devices that have reached the end of life.

- Global e-waste production is estimated to be 35 million tonnes per year.
- According to the UN, in 2021 each person on the planet will produce on average 7.6 kg of e-waste, meaning that a massive 57.4 million tons will be generated worldwide.
- The world generated 53.6 Mt of e-waste in 2019, only 9.3 Mt (17%) of which was recorded as being collected and recycled.



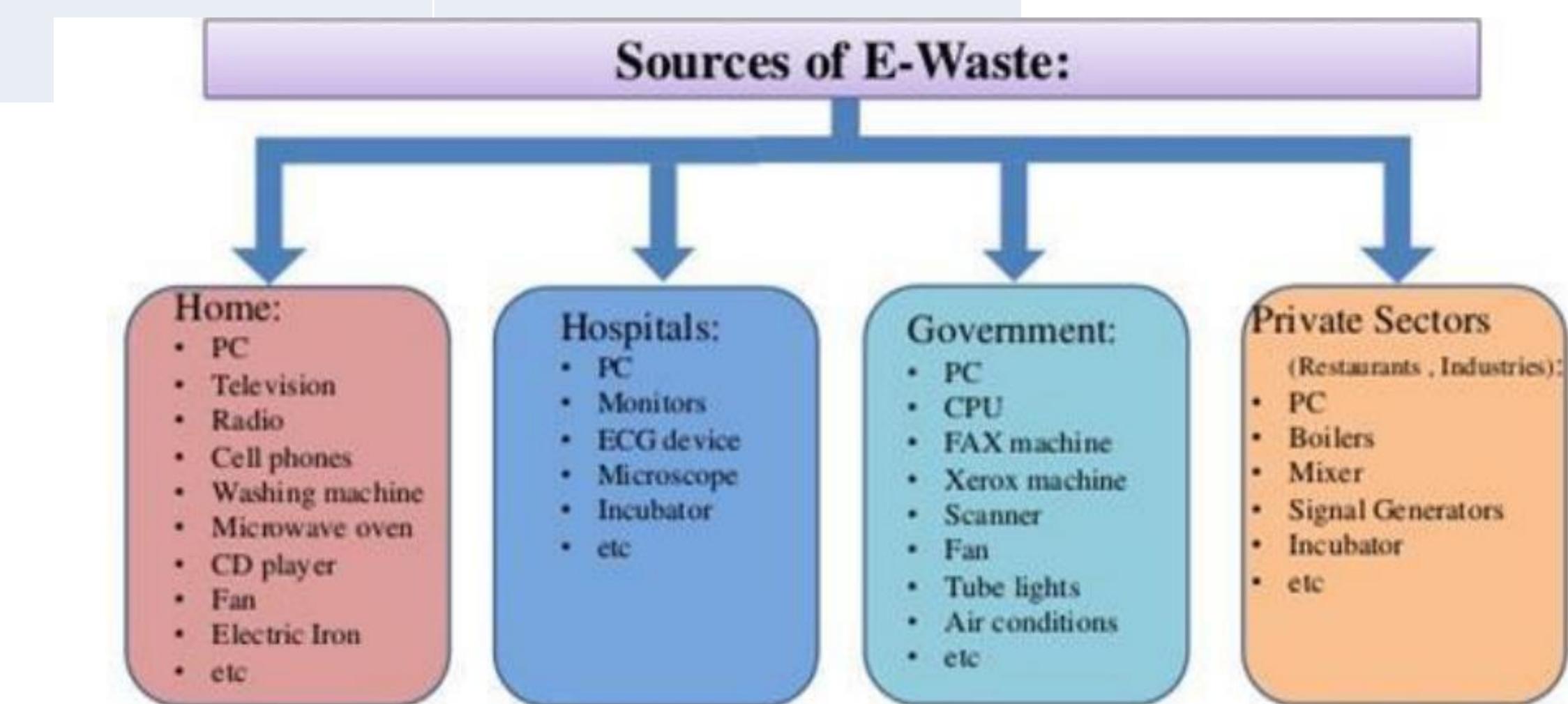
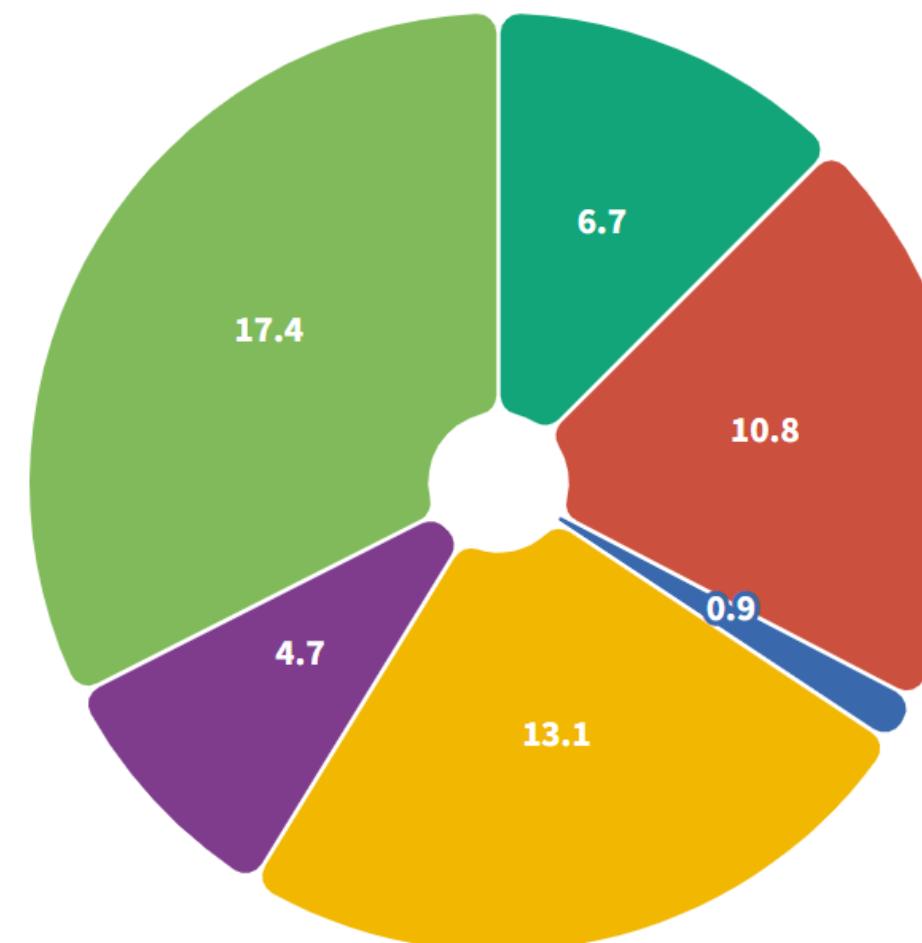


Global volume of e-waste (2019) by category

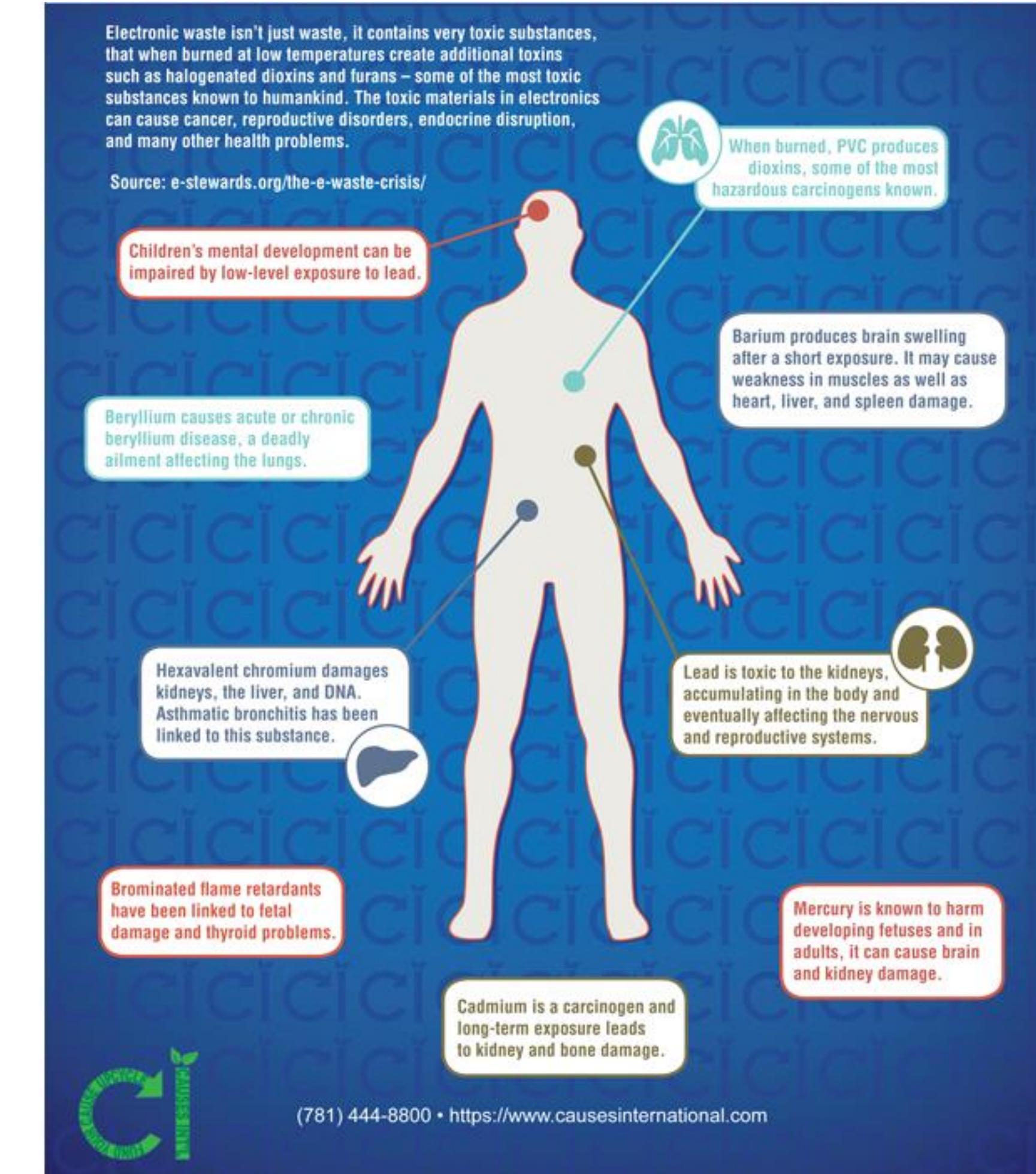
Documented and undocumented e-waste

Small Equipment's	Large Equipment	Temperature Exchange Equipment
<input type="checkbox"/> Vacuum cleaners <input type="checkbox"/> Microwaves <input type="checkbox"/> Ventilation equipment <input type="checkbox"/> Toasters <input type="checkbox"/> Electric kettles, shavers <input type="checkbox"/> Video cameras, Calculators <input type="checkbox"/> Electrical and electronic toys	<input type="checkbox"/> Washing machines <input type="checkbox"/> Clothes dryers <input type="checkbox"/> Dish-washing machines <input type="checkbox"/> Electric stoves <input type="checkbox"/> Large printing machines <input type="checkbox"/> Solar panels	<ul style="list-style-type: none"> ● Refrigerators ● freezers ● Air conditioners ● Heat pumps

█ Screens and Monitors
 █ Temperature exchange Equipment
 █ Lamps
 █ Large Equipment
█ Small IT and Telecom- munication Equipment
 █ Small Equipment



E-waste sources	Constituents	Health effects
Solder in printed circuit boards, glass panels, and gaskets in computer monitors	Lead	<ul style="list-style-type: none"> Damage to central and peripheral nervous systems, blood systems, and kidney damage Adverse effects on brain development of children; causes damage to the circulatory system and kidney
Chip resistors and semi-conductors	Cadmium	<ul style="list-style-type: none"> Toxic irreversible effects on human health Accumulates in kidney and liver Causes neural damage
Relays and switches, and printed circuit boards	Mercury	<ul style="list-style-type: none"> Chronic damage to the brain Respiratory and skin disorders due to bioaccumulation in fishes
Galvanized steel plates and decorator or hardener for steel housing	Chromium	<ul style="list-style-type: none"> Causes bronchitis
Cabling and computer housing	Plastics and PVC	<ul style="list-style-type: none"> Burning produces dioxin that causes reproductive and developmental problems
Electronic equipment and circuit boards	Brominated flame-retardants	<ul style="list-style-type: none"> Disrupt endocrine system functions
Front panels of CRTs	Barium, phosphorus, and heavy metals	<ul style="list-style-type: none"> Cause muscle weakness and damage to heart, liver, and spleen
Copper wires, Printed circuit board tracks.	Copper	<ul style="list-style-type: none"> Stomach cramps, nausea, liver damage, or Wilson's disease
Nickel–cadmium rechargeable batteries.	Nickel	<ul style="list-style-type: none"> Allergy of the skin to nickel results in dermatitis while allergy of the lung to nickel results in asthma
Lithium-ion battery	Lithium	<ul style="list-style-type: none"> Lithium can pass into breast milk and may harm a nursing baby Inhalation of the substance may cause lung edema
Motherboard	Beryllium	<ul style="list-style-type: none"> Carcinogenic (lung cancer) Inhalation of fumes and dust causes chronic beryllium disease or berylliosis

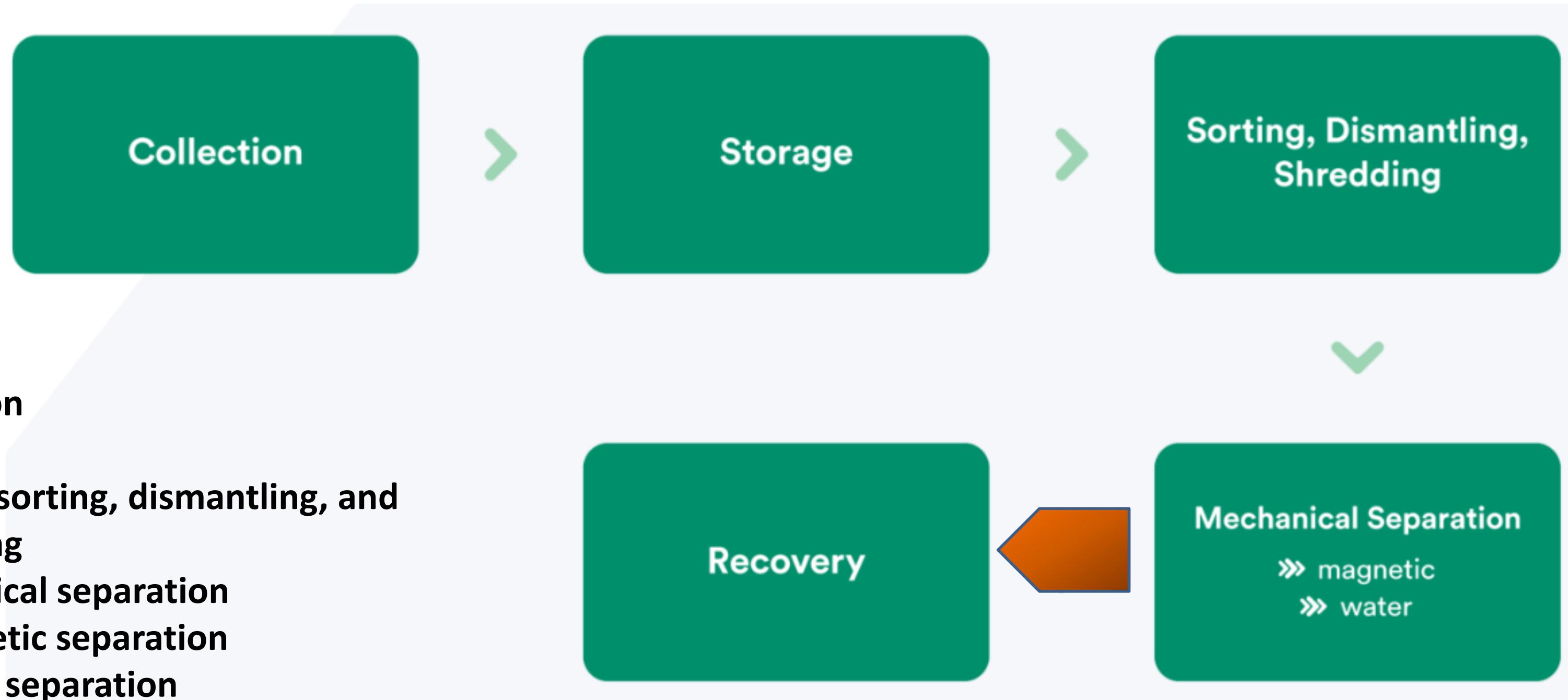


- **Conserve Natural Resources**
- **Protects the Environment**
- **Create Jobs**
- **Reduces Global Warming and Saves Landfills**
- **Makes things more Affordable**
- **Reduces Business Costs**
- **Supports Non-Renewable Recycling**
- **Conserve both Land and Energy**

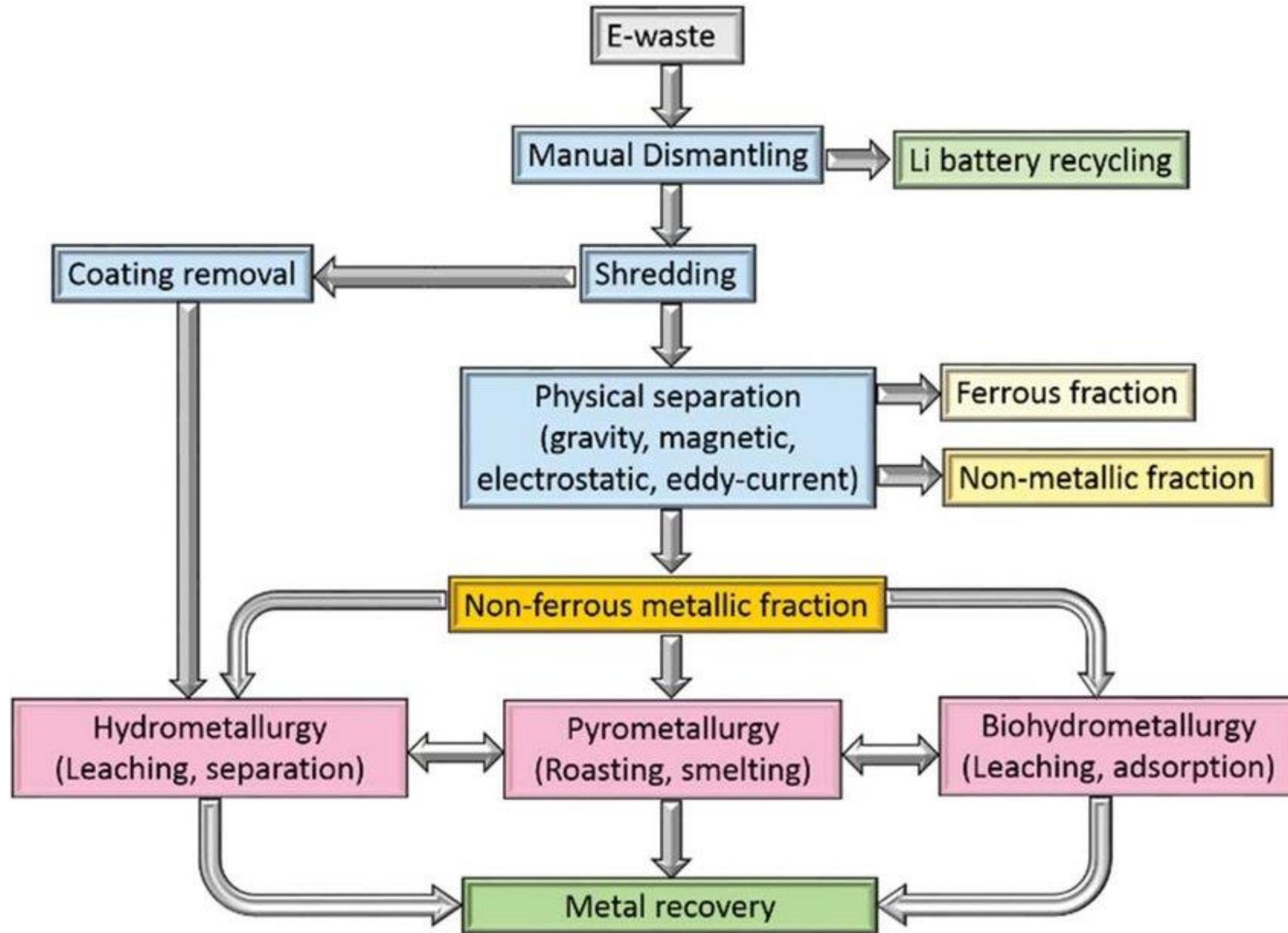


E-waste recycling process

General Steps



- Collection**
- Storage**
- Manual sorting, dismantling, and shredding**
- Mechanical separation**
 - Magnetic separation**
 - Water separation**
- Recovery**



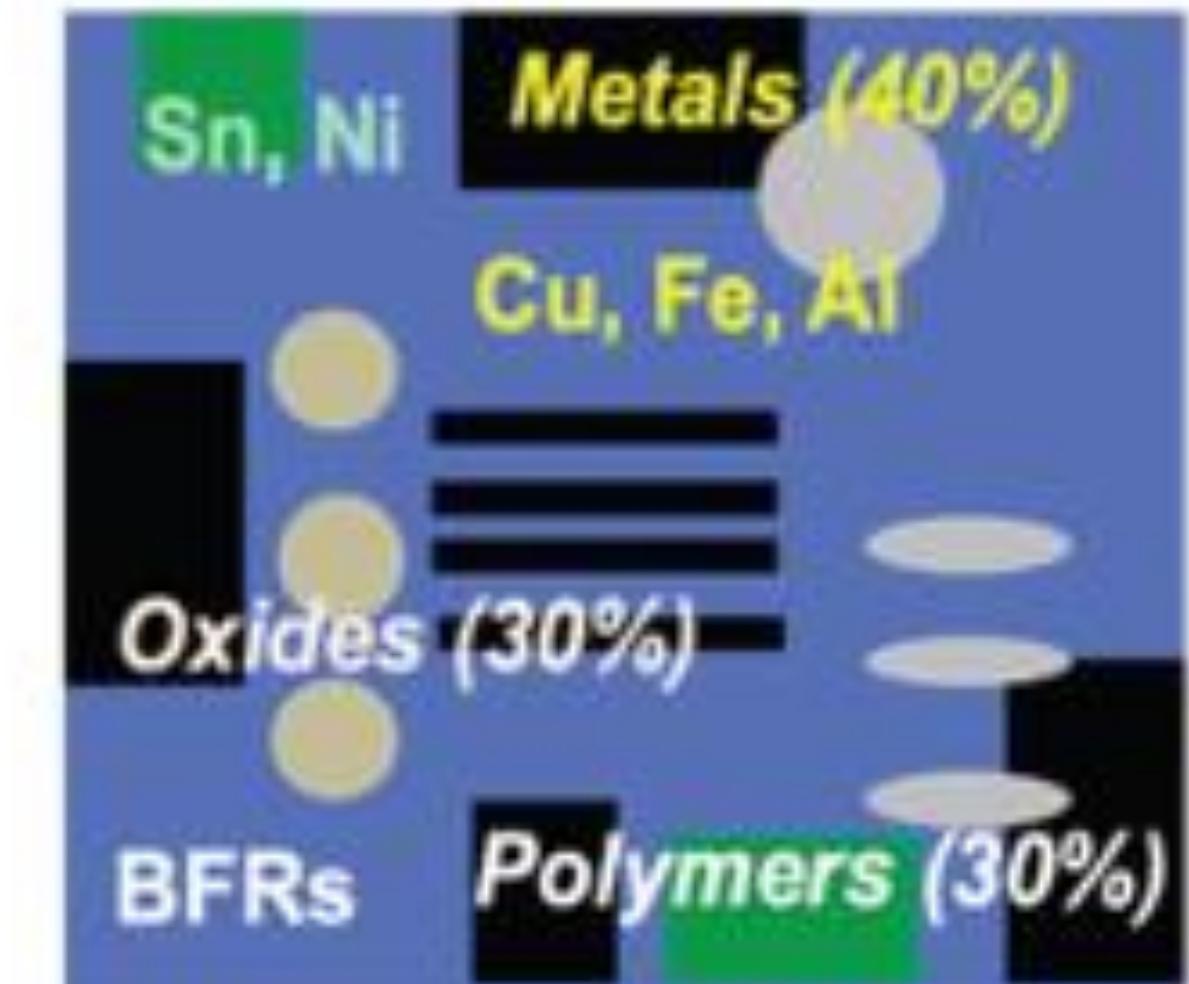
End-processing technologies

- Hydrometallurgy
- Pyrometallurgy
- Biohydrometallurgy

- a) Leaching
- b) Solution concentration and purification
- c) Metal recovery

Composition of PCB

Metals	Availability (wt%)
Copper	20.00
Aluminium	11.69
Zinc	1.86
Tin	7.3
Nickel	1.58
Iron	15.21
Lead	6.71



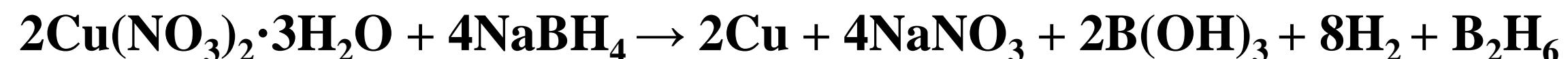
Methodology

1. Various components like RAM, ICs etc are attached on PCB were first removed manually from it.
2. 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.
3. About 10 g of small PCB sample was allowed to react with the 100 ml of leach solution of 3N HCl/HNO₃ (leaching agent) and kept for agitation.

At this concentration of an acid, the Cu reacts with nitric acid to form cupric nitrate



4. From above solution, copper can be extracted by using suitable reducing agents like Sodiumborohydride (NaBH₄).

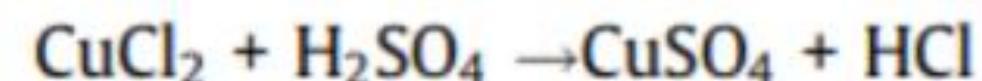
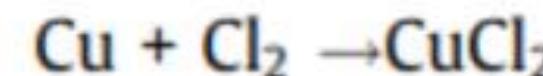
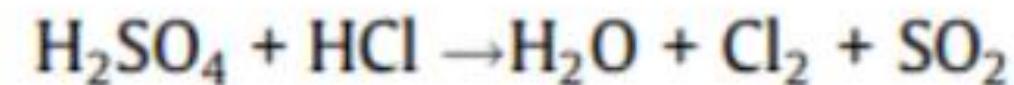
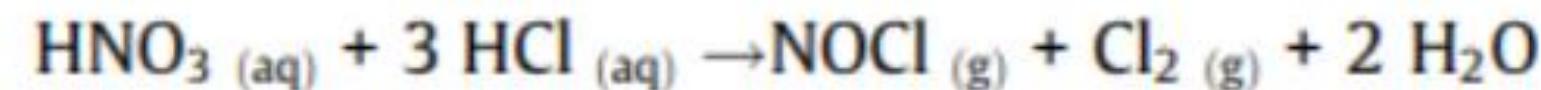


5. Obtained copper metal is further purified by refining and electro refining process.

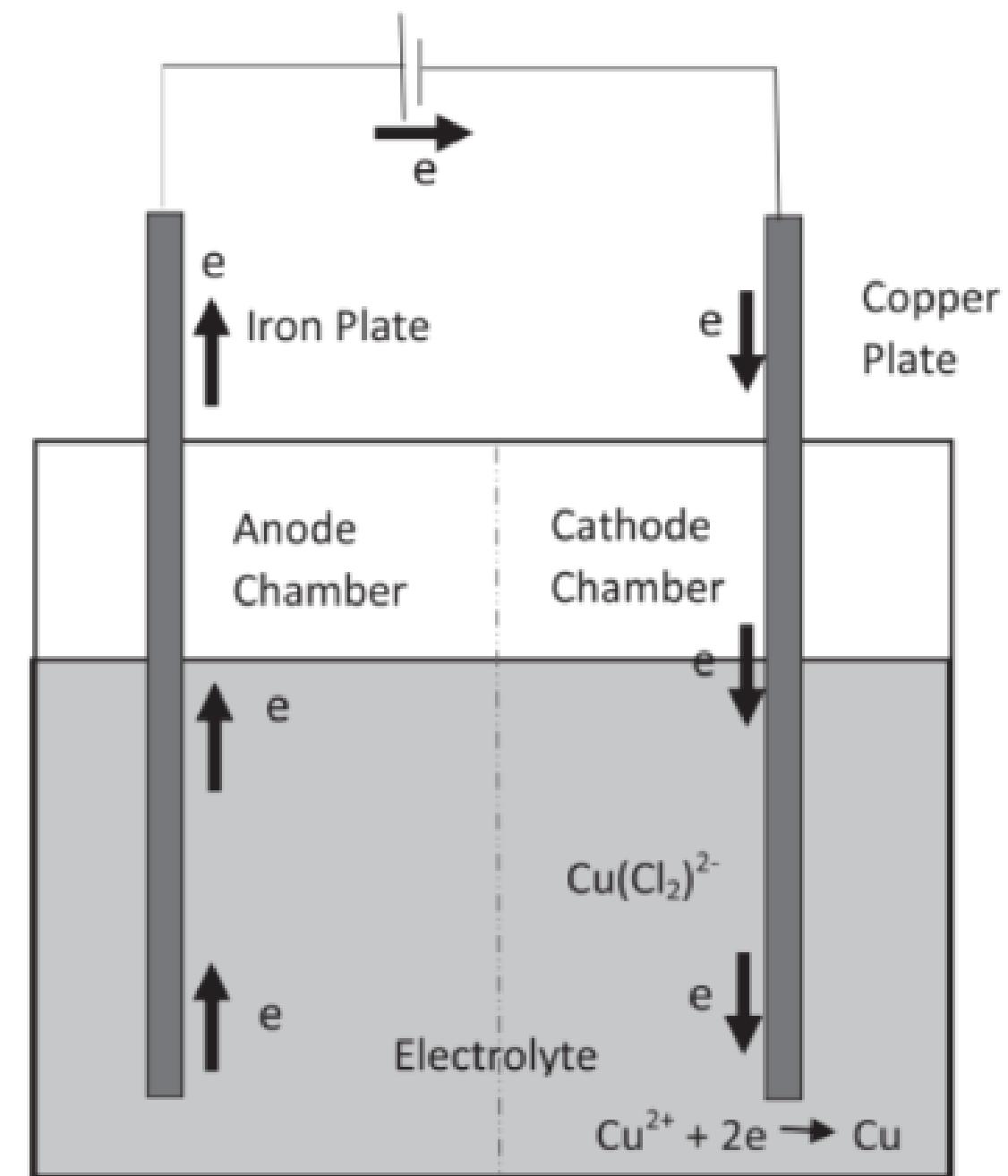
Methodology

- (1) The grinded E-Waste powder contains plastic, ferrous and nonferrous metals.
- (2) Density separation method is used to separate the Metallic and non-metallic parts.
- (3) For separation of ferrous and nonferrous metals, Electromagnetic separator is used.
- (4) For experimental purpose 8 gm of nonferrous metal was taken.
- (5) The metal powder was dissolved into H_2SO_4 and stirred at $80^\circ C$, temperature for about 4 hr.
- (6) The solution was filtered 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 $80^\circ C$,

The following reactions took place:



Electrolysis for Copper recovery



1. Pyrometallurgy is a conventional technology wherein non-ferrous and precious metals are leached from E-Waste.
2. Pretreatment in pyrometallurgy ;
 - a. Roasting
 - b. Smelting
3. Pyrometallurgical techniques employ higher temperatures to volatilize specific metals.
4. Most the metals (base and precious metals) present in the e-waste can be recycled using this technology. However, it requires hydrometallurgy for further processing.

Advantages of battery recycling

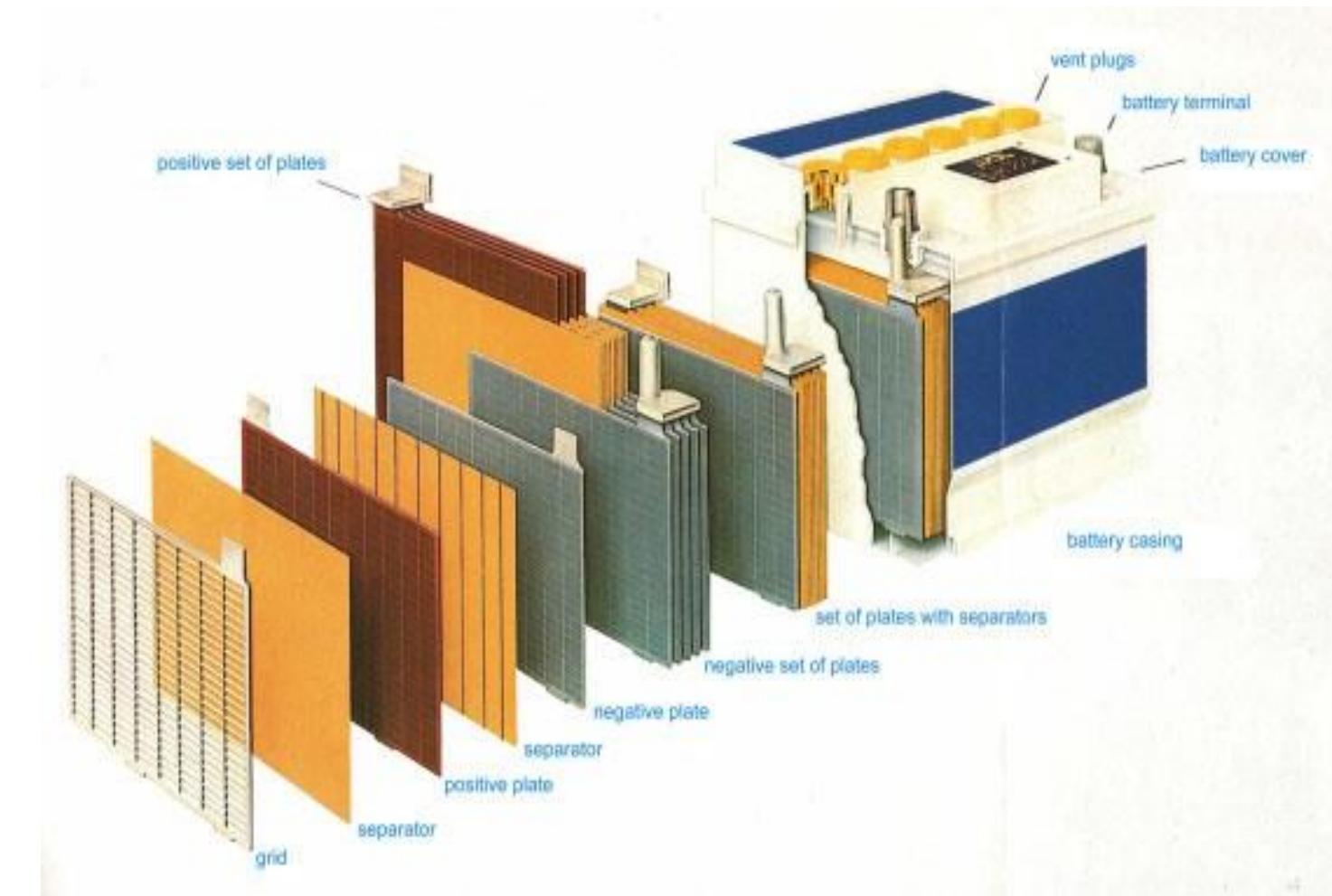
1. Reduces landfills
2. Saving of resources
3. Pollution is minimized
4. Job opportunities
5. Environment becomes clean
6. Reduces global warming

Disadvantages of battery recycling

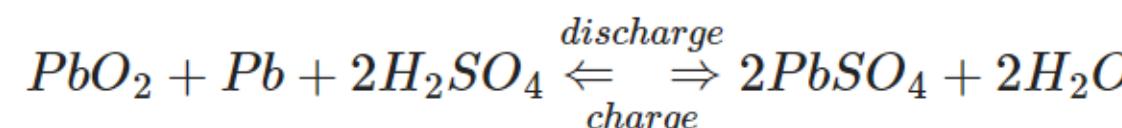
1. The value of the recycled products is comparatively low as compared to newer products.
2. Recycling is not a cost effective method as huge investment is required in setting up of industries.
3. Recycling does not guarantee good quality products.
4. The breakdown of batteries in the recycling process causes emission of toxins that are harmful and thus polluting the environment

Composition of a 12V-44Ah-210 A-starter battery in a hard rubber casing	
lead containing components	58,8%
hard rubber	17,7%
sulphuric acid	26,2%
separators (PVC)	2,3%

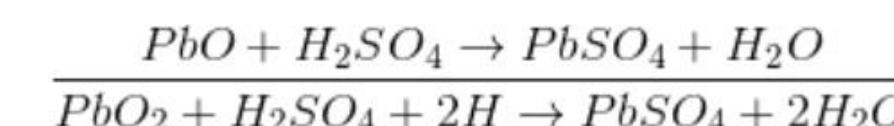
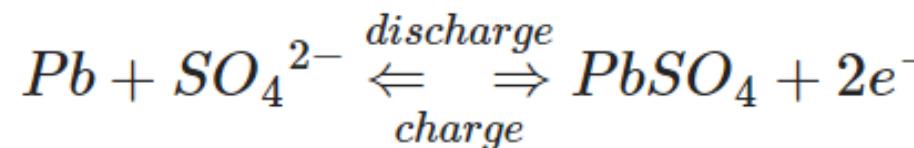
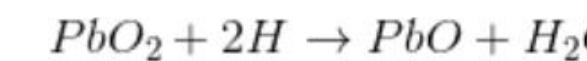
	100,0%
total weight	approximately 15 kg



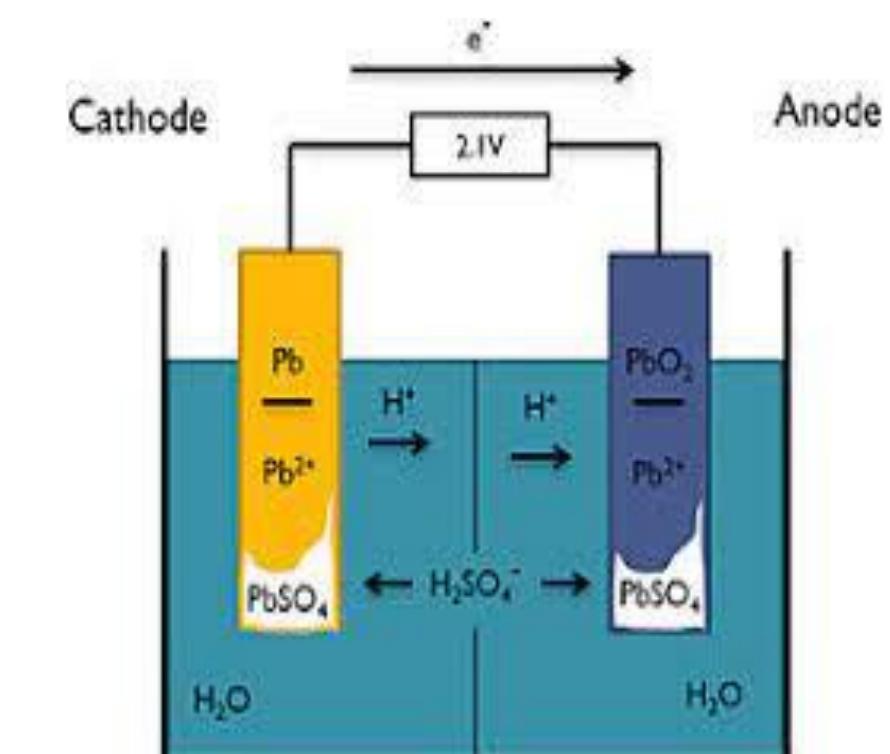
The electro-chemical reactions which take place during charge and discharge of a lead acid battery are:

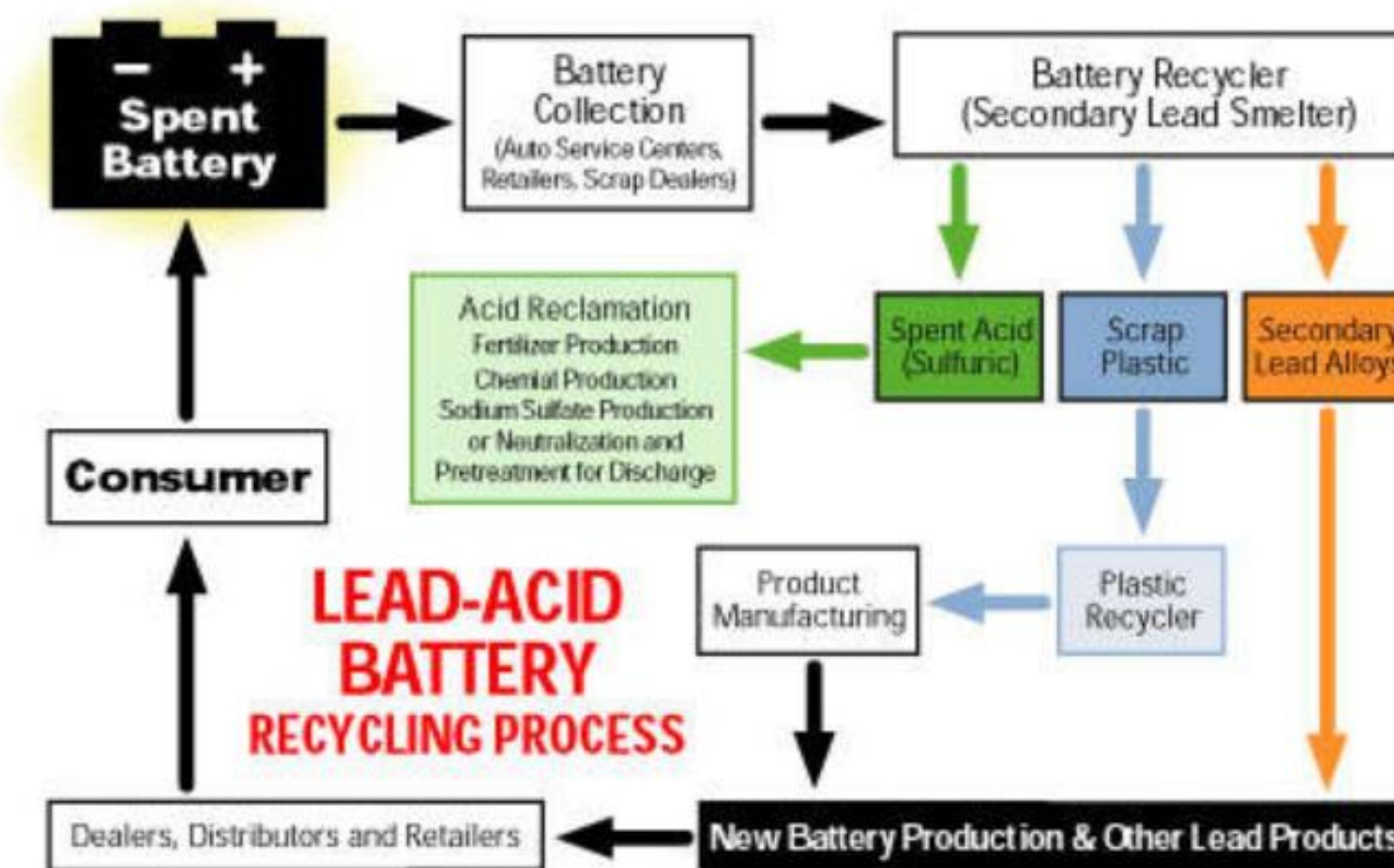


At Cathode



At Anode

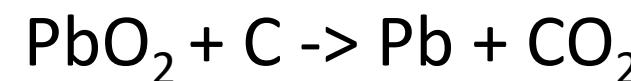
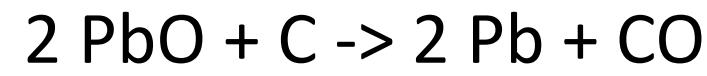




The lead bearing raw materials extracted from lead-acid battery scrap are:

1. Pb(Sb) Metal from grids, terminals
2. PbO (PbO_2) lead oxides, part of the paste
3. $PbSO_4$ lead sulphate

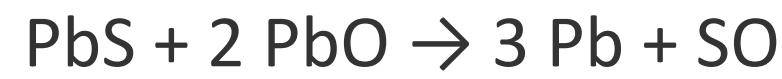
The first type of chemical reaction converts PbO (PbO_2) into Pb through a reduction process:

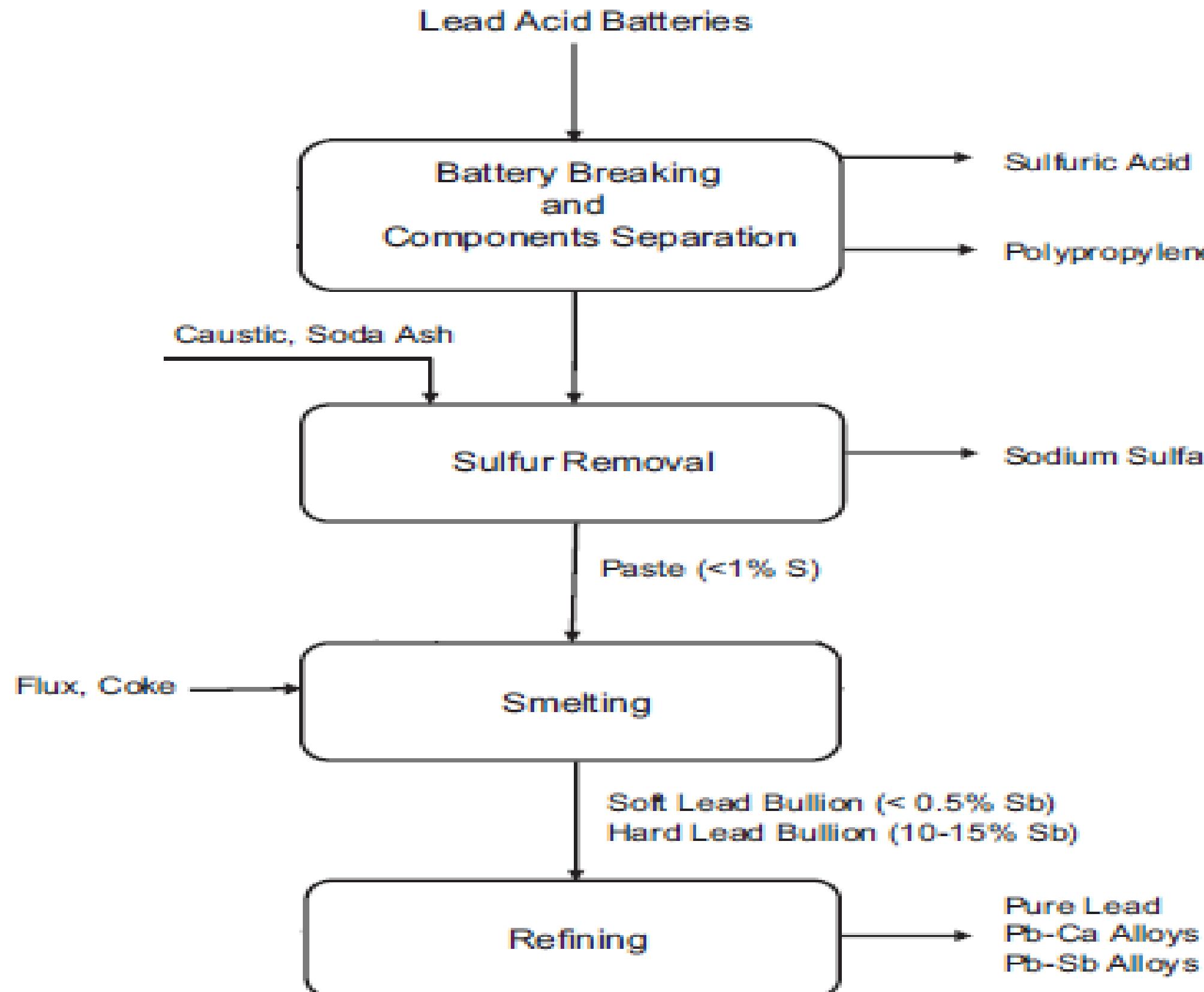


The second type converts $PbSO_4$ into PbS, again through a reduction process:



Finally PbS is converted into Pb through the following reactions:





Smelting

Hazardous elements/materials:

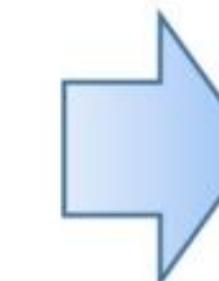
**Lead, cadmium, mercury, PVC,
and halogenated flame
retardants**

- a. Pyrolysis
- b. Physical treatment
- c. Pyrometallurgical processing



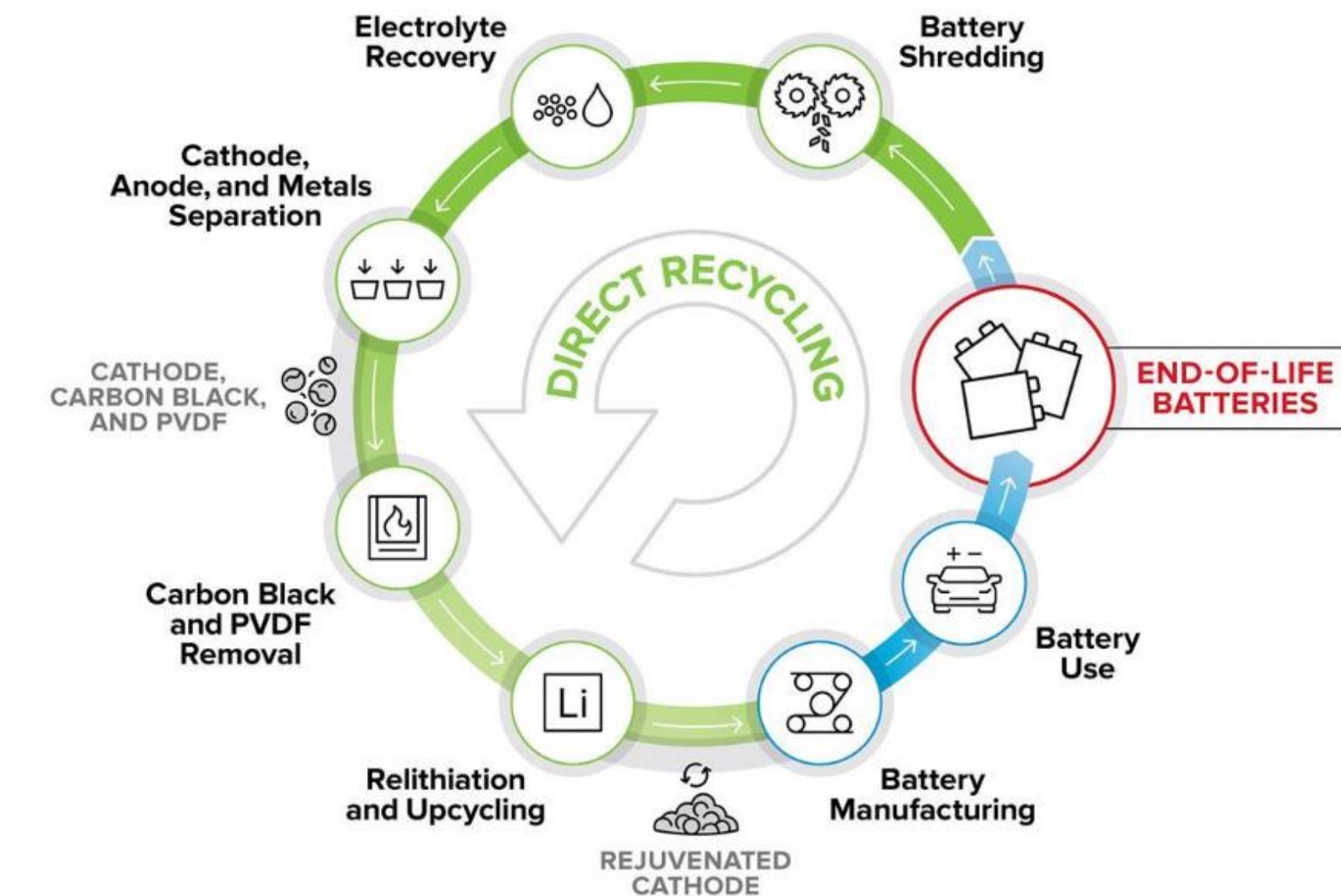
Waste mobile phone
after pyrolysis

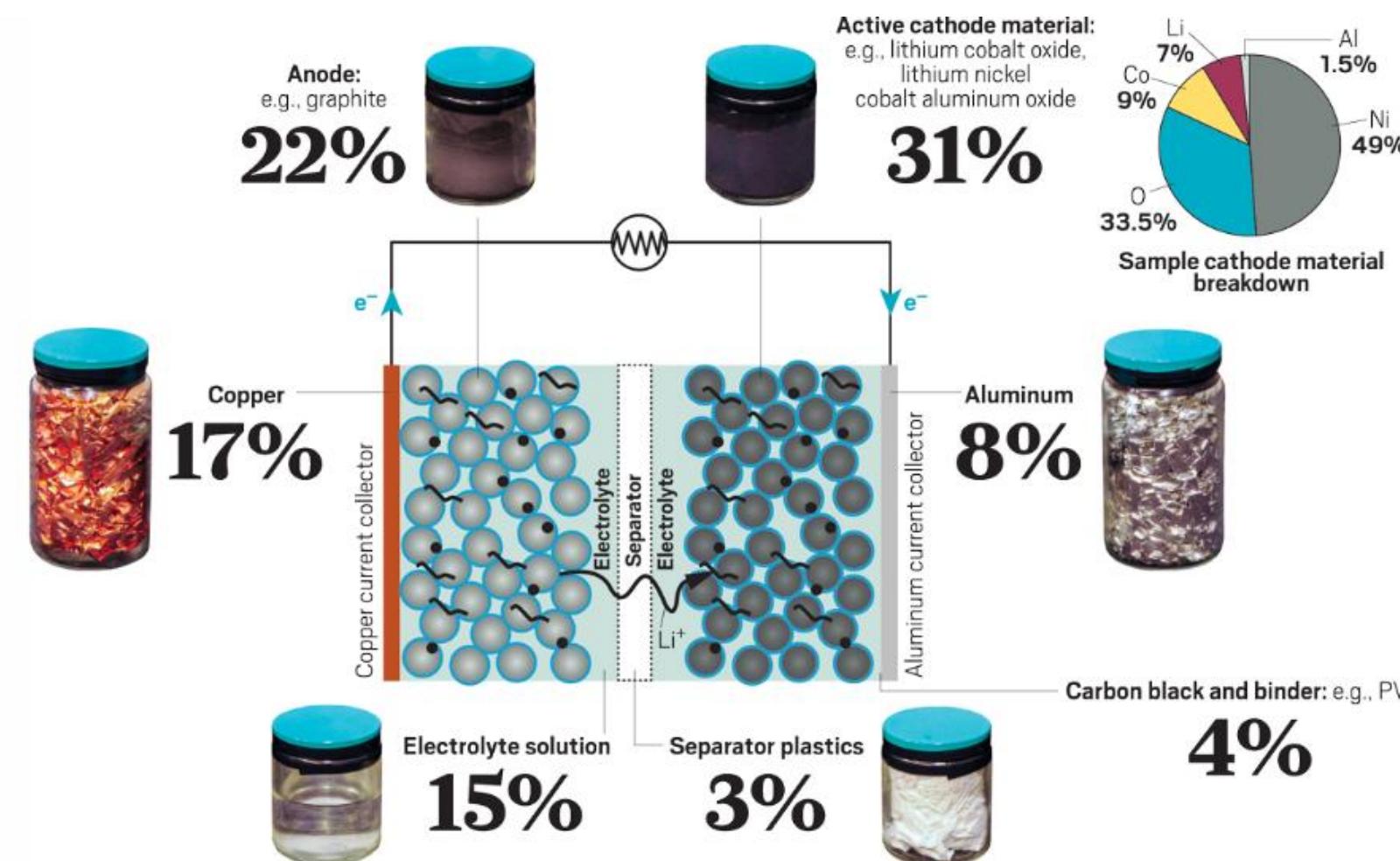
Physical
separation



Insoluble residues

Recycling of Lithium ion batteries

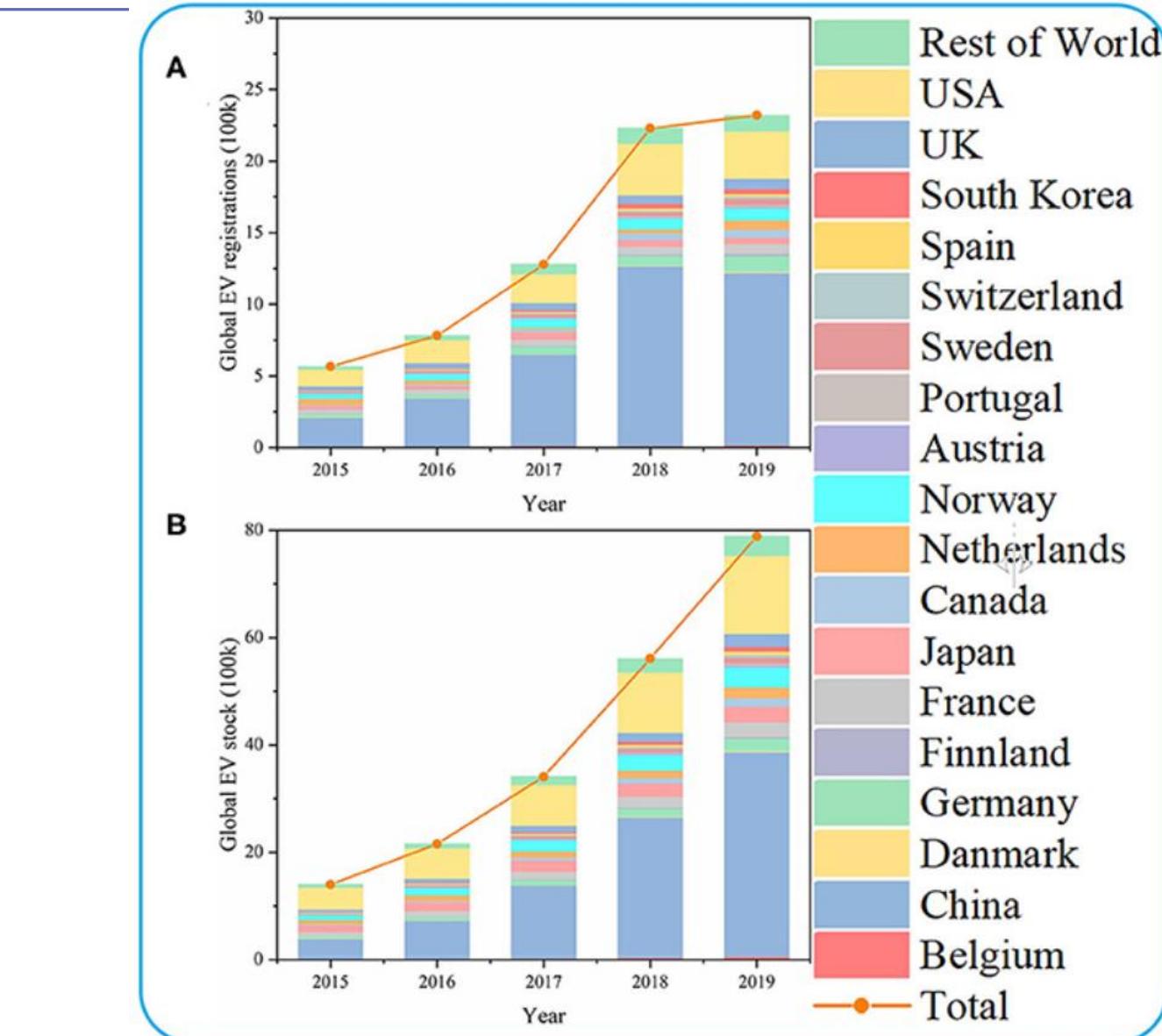




Credit: Mitch Jacoby/C&EN

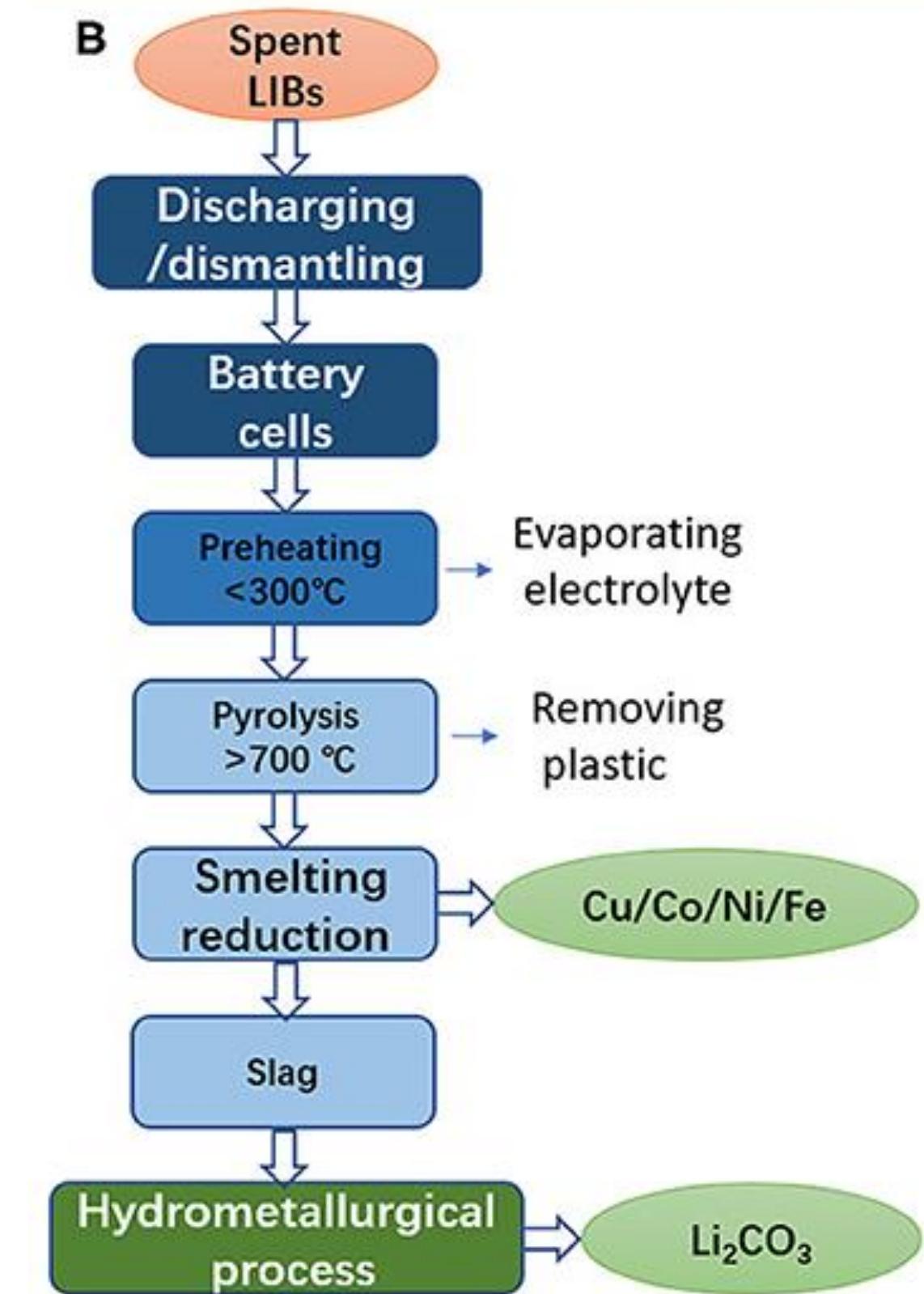
Cathode active materials:

- LiCoO₂ (LCO),
- LiNiO₂ (LNO),
- LiMn₂O₄ (LMO),
- LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ (NMC)



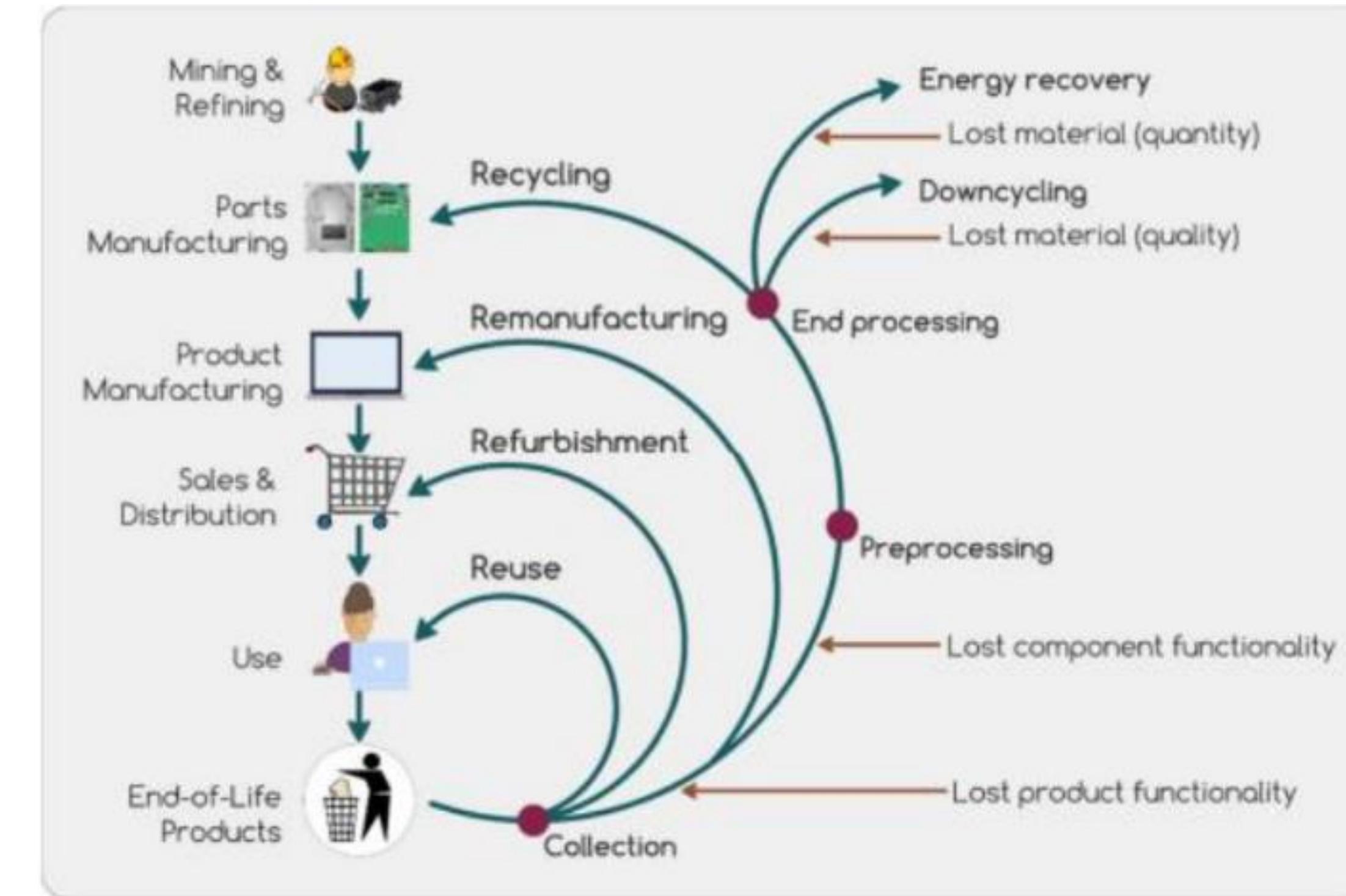
➤ LIB recycling market will reach \$23.72 billion by 2030

Recycling of valuable metals: Co, Li, Ni, Mn



Pyrometallurgical process.

Process	Advantages	Disadvantages	Challenge
Hydrometallurgical process	High recovery rate High purity product Low energy consumption Less waste gas High Selectivity	More wastewater Long process	Wastewater treatment Optimize the process
Pyrometallurgical process	Simple operation and short flow No requirement for categories and the size of inputs High efficiency	Li and Mn are not recovered High energy consumption Low recovery efficiency More waste gas and the cost of waste gas treatment	Reduce energy consumption and pollution emissions Reduce environmental hazards Combine hydrometallurgy well





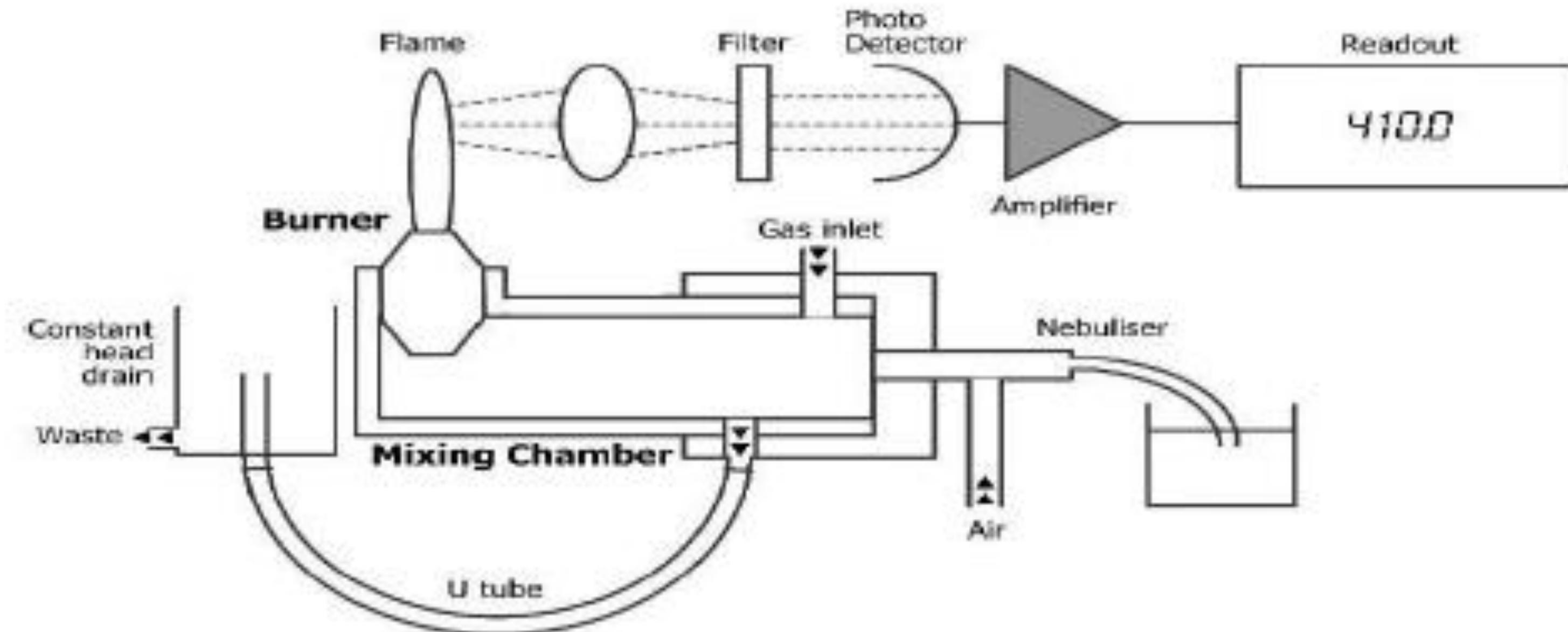
Before Equivalence point

$$E = E^{\circ} + \frac{0.0591}{n} \log \frac{[\text{Oxidized form}]}{[\text{Reduced form}]}$$

$$E = E^{\circ} + \frac{0.0591}{n} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

After Equivalence point

$$E = E^{\circ} + \frac{0.0591}{n} \log \frac{[\text{Cr}^{6+}]}{[\text{Cr}^{3+}]}$$



When a monochromatic light is passed through a colored solution, part of it will be absorbed (I_a), transmitted (I_t) and reflected (I_r). Thus,

$$I_0 = I_a + I_t + I_r \quad (1)$$

The ' I_r ' is negligible if the light propagates through glass medium.

$$I_0 = I_a + I_t \quad (2)$$

