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Comparative Analysis of Pyrometallurgy, Hydrometallurgy and Bio-Hydro-Metallurgy for Extraction of Metals from E-Waste.

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A B S T R A C T

Due to technological advancements and population growth, the use of electronic devices is increasing day by day. This increases e-waste generation and requires special handling, disposal and recycling methods. E-waste contains not only valuable materials but also hazardous materials. The process of recycling broken devices generates additional revenue by recovering metals from waste electronic products. Various processes have been identified to address this problem and recover metals from e-waste. pyrometallurgical, hydrometallurgical and Bio-hydro-metallurgy processes play crucial roles in the recycling of e-waste. hydrometallurgy is highly efficient for recovering precious metals, while pyrometallurgy is more versatile and can handle a broader range of materials and bio-hydro-metallurgy uses microorganisms, typically bacteria, archaea, or fungi, to extract metals from ores or waste materials. By combining these methods and tailoring them to the specific composition of e-waste, valuable metals can be efficiently recovered, hazardous materials can be safely managed, and the environmental impact of e-waste disposal can be reduced. Moreover, these processes contribute to revenue generation through the sale of recovered metals, which can help offset the costs of e-waste recycling and promote sustainability. Pyrometallurgical processes can be energy-intensive and produce air pollution, while hydrometallurgical processes can generate hazardous wastewater. Biometallurgical processes are generally environmentally friendly, but can be slow and inefficient.

Keywords: Hazardous, Hydrometallurgy, Pyrometallurgy, Bio-hydro-metallurgy, E-waste, Extraction, Technology.

Introduction :

A comparative analysis of pyrometallurgy, hydrometallurgy, and bio-hydro-metallurgy is a valuable study in the field of metallurgy and materials science. These metallurgical processes are employed to extract metals from various sources, and understanding their differences and advantages is crucial for efficient metal recovery and sustainable resource management. The extraction and recovery of metals from ores, concentrates, and waste materials are fundamental processes in the metallurgical industry. Among the various methods available, pyrometallurgy, hydrometallurgy, and bio-hydro-metallurgy stand as distinct and widely used approaches. The pyrometallurgy process is also called the dry method, the hydrometallurgy process is called the wet method, and the bio-hydro-metallurgy process is called the bioleaching process. The comparative analysis between dry, wet, and bioleaching methods aims to explore, evaluate, and contrast these methods, shedding light on their principles, applications, and environmental implications in the context of extracting metals from electronic waste (e-waste). Electronic waste, or e-waste, is a growing concern worldwide due to the proliferation of electronic devices and their relatively short lifecycles. E-waste contains a myriad of valuable metals, including but not limited to gold, silver, copper, and palladium, alongside hazardous substances, making its proper management a matter of paramount importance. The choice of extraction method plays a pivotal role in determining the efficiency of metal recovery, economic viability, and environmental impact. The primary objective of this comparative analysis is to provide a comprehensive understanding of pyrometallurgy, hydrometallurgy, and bio-hydro-metallurgy as they relate to the extraction of metals from e-waste. By examining the principles, processes, selectivity, energy requirements, environmental implications, and economic considerations of these three methods, this study aims to inform decision-makers, researchers, and industry professionals about the best practices for sustainable e-waste recycling.

Literature Survey

In 2012 Abhishek Tripathi, Manoj Kumar, and Archana Agrawal studied the metal extraction process. The rapid growth in the use of electronic equipment, combined with early obsolescence has contributed enormously to the generation of large quantities of electronic e-waste. One such e-waste, the mobile phone printed circuit boards (PCBs) contain various precious metals which can be extracted by different hydrometallurgical routes. The present work deals with the recovery of gold using ammonium thiosulfate as a leaching agent from waste mobile PCBs containing 0.021% Au, 0.1% Ag, 56.68% Cu, 1.61% Ca, 1.42% Al, 1.40% Sn, 0.24% Fe, 0.22% Zn, 0.01% Pd, etc. The cutting granules of 0.5-3.0 mm PCBs were used for leaching in a 500 mL glass beaker in an open atmosphere. The effect of various parameters viz. ammonium thiosulfate concentration, copper sulfate concentration, pH, and pulp density was studied. A leaching of 56.7% gold was obtained under the optimum condition of 0.1M ammonium thiosulfate, 40 mM copper sulfate, pH: 10-10.5, pulp density: 10 g/L at room temperature, and stirring speed of 250 rpm in 8h duration. The maximum leaching of gold in the pH range of

10-10.5 may be attributed to the higher stability of the ammonium thiosulfate. The iodometric method chemically analyzed the decomposition of ammonium thiosulfate in the different pH ranges. The ammonium thiosulfate contents in the leach liquors were in agreement with the quantity of gold leaching in the respective pH ranges. In this process, the copper sulfate worked as a catalyst. The experiment conducted with complete PCB scrap exhibited a maximum leaching of 78.8% gold at the above-optimized condition.[1]

In 2019 Ahamed Ashiq, Janhavi Kulkarni, and Meththika Vithanage studied the Hydrometallurgical techniques. this method is used for the recovery of precious metals that can be further reutilized as a secondary resource. Significant amounts of valuable metals, specifically copper, silver, gold, nickel, and lead are being recovered that are strategically important in other processes. Hydrometallurgical processing mainly involves the use of a series of acids to leach out the metals from E-waste and further separation and purification using extraction, adsorption, and ion exchange to concentrate the precious metal. Printed circuit boards that are made up of large amounts of these precious metals have proven a promising ground for hydrometallurgical recovery.[2]

In 2020 Sourav Choubey, Prerna Goswami, and Shina Gautam studied the major methods for extraction of metals from e-waste. Electrochemical, Pyrometallurgical, Hydrometallurgical, and Bioleaching are the most enhancing methods to extract metals. Among all these methods, electrochemical is one of the most efficient methods reported. (80-95) % of the metal extraction is reported in the former mentioned method by using different electrolytes. Additionally, different combinations of electrodes are used to separately extract the metals from E-Waste after the pretreatment and chemical leaching of the Waste. To identify the most efficient electrochemical methods and their challenges for extraction of metals from e-waste, this literature review has been carried out during the period between 2010 to 2019. This work will conclude the comparative analysis of all these methods for extraction of metals from e-waste based on some factors like Energy efficiency, Environment friendliness, and Economical and Efficient extraction of metals.[3]

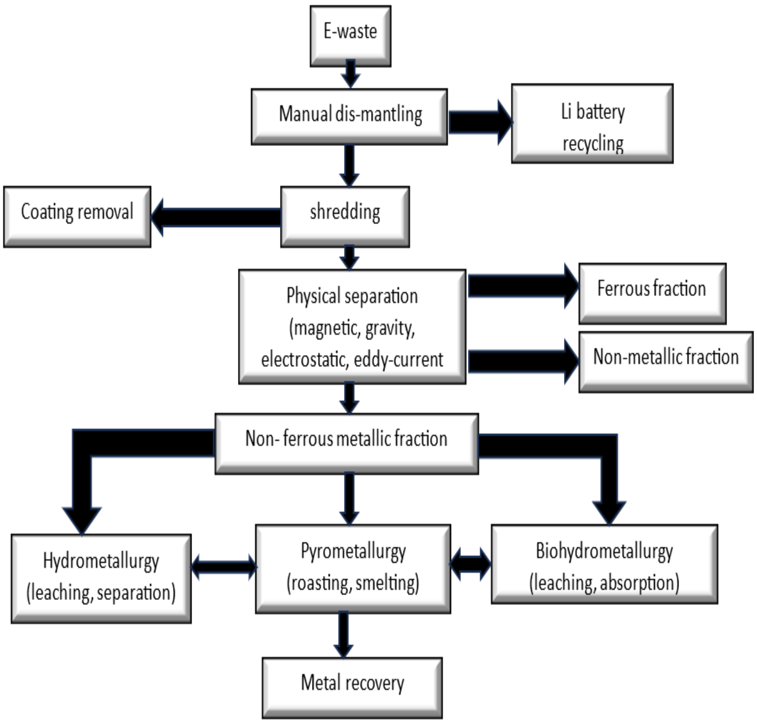

Fig 1. process involved in metal extraction

Pyrometallurgy

Pyrometallurgy is a traditional method to recover precious and non-ferrous metals from e-waste. It includes different treatments on high temperatures: incineration, melting, etc. 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. Most of the research activities on the recovery of base and precious metals from waste PCBs are focused on hydrometallurgical techniques for they are more exact, predictable, and easily controlled techniques. Recovery of plastics is not possible because plastics replace coke as a source of energy. -Iron and aluminum recovery is not easy as they end up in the slag phase as oxides. Special installations are required for hazardous

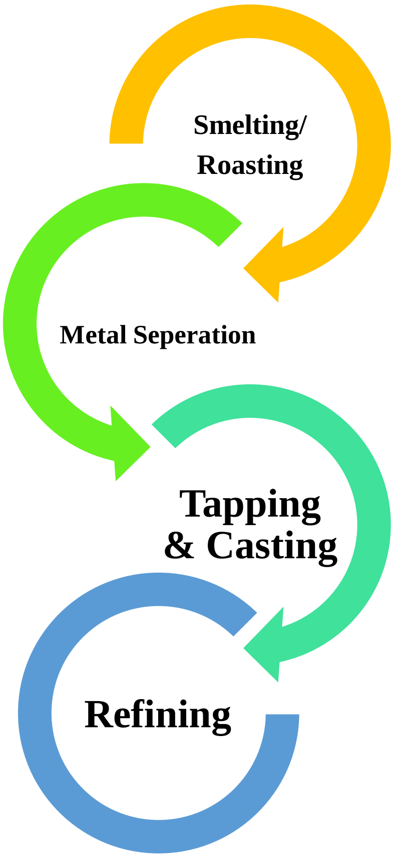

Fig 2. Processes Involved in Pyrometallurgy

emissions such as dioxins to minimize environmental pollution. Instant burning of fine dust of organic materials can occur before reaching the metal bath.

Roasting or Smelting:

The crushed and ground material is subjected to high temperatures in a furnace or smelter. The specific temperature depends on the metal being extracted and the type of source matter.

There are two primary pyrometallurgical processes:

Roasting: In roasting, the source material is heated in the presence of oxygen or air. This process is often used to remove impurities or convert metal sulfides to metal oxides.

Smelting: Smelting involves heating the source material with a reducing agent (commonly carbon, such as coke or charcoal) in a furnace. The reducing agent reacts with metal oxides to produce the desired metal.

Metal Separation:

During roasting or smelting, the desired metal(s) are separated from impurities and other elements.

The metal typically melts and collects at the bottom of the furnace due to its higher density.

Slag Formation:

As the source material is heated, impurities and non-metallic compounds often form a molten slag layer on top of the metal. The slag is less dense and floats on the metal.

Slag is typically composed of oxides and other non-metallic compounds and can be tapped off separately.

Tapping & Casting:

Once the metal has collected at the bottom of the furnace, it is tapped or poured out and cast into molds or ingots.

The casting process can be adjusted to produce different shapes and sizes of metal products.

Refining:

Additional refining steps may be required depending on the desired purity and properties of the final metal product.

Refining processes can include electrolysis, distillation, or other chemical methods to further purify the metal.

Waste & Environmental Consideration:

The pyrometallurgical process generates waste materials, including slag and emissions.

Proper management of these waste products and compliance with environmental regulations are essential to minimize the environmental impact, Pyrometallurgy is commonly used for extracting a wide range of metals, including iron, copper, lead, zinc, aluminum, and more. It is known for its versatility and ability to handle various source materials, but it can also have significant energy and environmental implications, particularly due to the high temperatures involved and the need for emission control. Efforts are made to develop more sustainable and energy-efficient pyrometallurgical processes as part of broader environmental and sustainability goals.

Hydrometallurgy

Hydrometallurgy, uses the aqueous solutions for the recovery of metals from ores, concentrates, and recycled or residual material, plays an integral role in the multi-billion dollar minerals processing industry. It involves either the selective separation of various metals in solution on the basis of thermodynamic preferences, or the recovery of metals from solution through electrochemical reductive processes or through crystallization of salts. There are numerous hydrometallurgical process technologies used for recovering metals, such as agglomeration; leaching; solvent extraction/ion exchange; metal recovery; and remediation of tailings/waste. Hydrometallurgical processes are integral across various stages in a typical mining recovery and mineral processing circuits be it in situ leaching (where the solution is pumped through rock matrices); heap leaching (of the ROM or crushed ore); tank/autoclave leaching (of the concentrate/matter obtained from floatation); electro-refining (of the blister product from smelting routes); and the treatment of waste tailings/slags from the aforementioned processes. Modern hydrometallurgical routes to extract metals from their ores are faced with a number of issues related to the chemistry, geology, and engineering aspects of the processes involved. These issues include reductions in ore grade, differences in deposit mineralogy, and geomagnetic location of the ore site. This will have implications for the hydrometallurgical route chosen. Developing technologies to improve energy efficiency, water/resource consumption and waste recovery (particularly acid rock drainage) across the circuit are also important factors to consider. Therefore, new solutions to these existing problems are continuously being developed at both baseline and pilot levels to implement environmentally sustainable methods for extracting valuable metals.

Leaching: Leaching is the core step in hydrometallurgy. It is a process of dissolving metals from ores, concentrates, and recycled or residual material into a liquid solution. This is typically done using acids or bases. The type of leaching agent used depends on the composition of the feed material and the metals that need to be extracted.

The leaching process typically involves the following steps:

1. **Pretreatment:** The feed material is prepared for leaching by crushing and grinding it to a fine powder. This increases the surface area of the material and makes it easier for the leaching agent to dissolve the metals.
2. **Leaching:** The feed material is mixed with the leaching agent in a leaching tank. The temperature and pressure of the leaching process are controlled to optimize the dissolution of the metals.
3. **Separation:** The solid residue from the leaching process is separated from the liquid solution. This can be done using filtration, sedimentation, or centrifugation.
4. **Recovery:** The metals in the liquid solution are recovered using a variety of methods, such as solvent extraction, ion exchange, and electrowinning.

The leaching process is a complex process that is influenced by a number of factors, including the type of feed material, the leaching agent, the temperature, and the pressure. The optimization of the leaching process is essential for maximizing metal recovery and minimizing environmental impact.

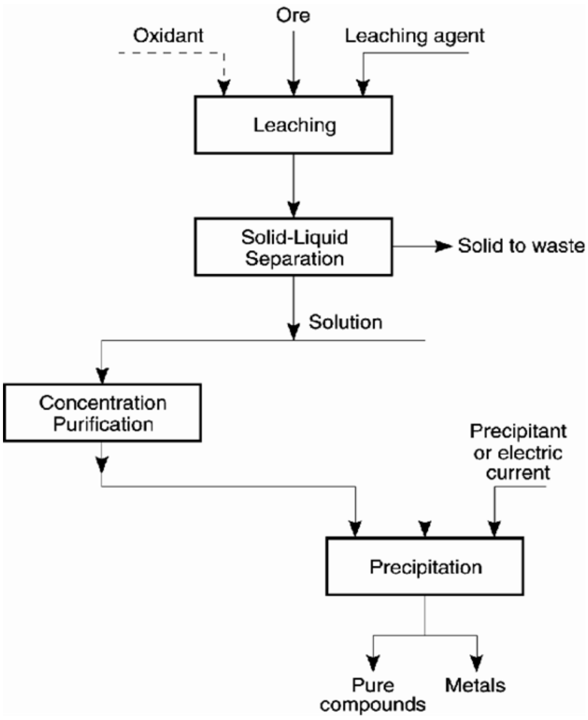

Fig 3. Processes Involved in hydrometallurgy.

Here are some examples of leaching agents used in hydrometallurgy:

- **Acidic leaching agents:** Sulfuric acid, hydrochloric acid, and nitric acid are commonly used acidic leaching agents. They are effective at dissolving a wide range of metals, including copper, zinc, and nickel.
- **Basic leaching agents:** Sodium hydroxide and potassium hydroxide are commonly used basic leaching agents. They are effective at dissolving metals such as aluminum and gold.
- **Oxidative leaching agents:** Ferric chloride and sodium hypochlorite are commonly used oxidative leaching agents. They are effective at dissolving metals such as copper and manganese.

The choice of leaching agent depends on the composition of the feed material and the metals that need to be extracted. It is also important to consider the environmental impact of the leaching agent when selecting a process. Leaching is a versatile process that can be used to extract metals from a wide range of feed materials. It is a key process in the hydrometallurgical industry and is used to produce a variety of metals, including copper, zinc, nickel, aluminum, and gold.

Solid-Liquid Separation: After leaching, the solid residue (which contains the unreacted source material and impurities) must be separated from the metal-containing solution. This separation is typically achieved through filtration or sedimentation processes, allowing the clear metal-rich solution to be separated from the solids.

Metal Recovery Process: Once the metal ions are in solution, they can be selectively recovered using various techniques depending on the metal and the solution chemistry:

- **Precipitation:** Addition of specific chemicals to the metal-containing solution can cause the metals to precipitate out as solid compounds. The precipitated metals can then be separated from the solution.
- **Solvent Extraction:** This method involves the use of organic solvents that selectively extract the metal ions from the aqueous solution, followed by stripping the metal ions from the organic phase.
- **Electrolysis:** In cases where high-purity metal is required, electrolysis may be used to plate the metal onto electrodes.
- **Cementation:** This method involves the use of a more reactive metal to displace the desired metal ions from the solution. The displaced metal forms a solid precipitate that can be separated.
- **Purification:** Depending on the desired final product and its intended use, further purification steps may be required. These steps can involve additional chemical treatments or processes to remove impurities and achieve the desired metal purity.
- **Final Product:** The recovered metal, now in a usable form, can be further processed, refined, or cast into ingots for various industrial applications.

- Hydrometallurgy offers several advantages, including its ability to selectively target specific metals, its relatively low environmental impact compared to some pyrometallurgical methods, and its versatility in processing a wide range of source materials. However, it requires careful management of chemicals, waste disposal, and environmental considerations to ensure sustainability and minimize environmental footprint.

Bio-hydro-metallurgy

This is an area where biology and hydrometallurgy intersect in the various natural connections between esters and minerals and the use of microorganisms to restore essential oils. Briefly, microorganisms are used to study the birth of essences by processing them in an anhydrous environment. Sulfide minerals are stripped of their essence through a biological leaching process in which microorganisms play an important role in this process. Biohydrometallurgy, commonly known as bioleaching, is the most promising technology to obtain essential oils from waste. It can be performed in a straight or circular form, and is greatly utilized in that it roots down precious essence. It's generally understood that direct bioleaching refers to a process by which solid essences are converted to water-answerable forms through the action of microorganisms. Bobby, for illustration, is oxidized by microorganisms to bobby sulfate and essence values appear in the waterless phase, while the solid remains are discarded. circular bioleaching of sulfide minerals is eased by the force of oxidizing oxidants from microorganisms. The quantum of essential sulfuric acid produced by circular bioleaching can be controlled. In some cases, this process of bioleaching is also called bio-oxidation in which essence sulfides that contain no value are oxidized and removed from ores bearing value in the form of a dissolving medium. For example, in the case of arsenicite bioleaching, the iron and arsenic sulfide are dissolved and the remaining valuable gold essence is recovered through cyanidation. Biohydrometallurgy is a branch of hydrometallurgy that uses microorganisms similar to bacteria and archaea to extract the essence from ores and concentrates. This process uses metabolic regulation of these microorganisms to dissolve and extract essences from colorful raw materials. Biohydrorefining is considered an environmentally friendly and economically viable solution to traditional chemical methods for obtaining the essence.

Selection of Microorganisms: The first step in bio-hydro-metallurgy is the selection of suitable microorganisms that have the ability to oxidize and solubilize the target metal. Microorganisms such as Acidithiobacillus ferro-oxidans and Acidithiobacillus thio-oxidans are commonly used for this purpose.

Ore Preparation: The raw material, typically a metal-containing ore or concentrate, is crushed and ground to expose a larger surface area for microbial action. The ore is then often stacked or agitated in tanks to optimize contact with the microbial culture.

Bioleaching: In the bioleaching process, microorganisms are introduced into the ore or concentrate along with a nutrient solution. These microorganisms oxidize the metal sulfides or other compounds in the ore, releasing soluble metal ions into the solution. The chemical reactions involved are often oxidative in nature, and they generate acid as a byproduct, which further aids in metal solubilization.

Solution Collection: The metal-rich solution, known as the leachate, is collected from the ore or concentrate. It contains dissolved metal ions, which can be further processed to recover the target metal.

Metal Recovery: Once the metal is in solution, various techniques can be used to recover it from the leachate. Common methods include precipitation, solvent extraction, ion exchange, and electrowinning, depending on the specific metal and the desired product.

Microorganism Management: The microorganisms used in bio-hydro-metallurgy require careful management, including maintaining optimal temperature, pH, and nutrient conditions to ensure their continued activity. They may also require periodic inoculation with fresh cultures to maintain their effectiveness.

Environmental Considerations: Bio-hydro-metallurgy is generally considered more environmentally friendly than traditional mining and metallurgical processes because it produces fewer harmful byproducts and reduces the need for harsh chemicals. However, the generation of acidic wastewater and the management of microbial populations are still important environmental considerations.

Percentage of metals extracted from e-waste

1. **Copper (Cu):** Bio-hydro-metallurgical processes can achieve copper recovery rates ranging from 50% to over 90%, depending on the ore type and the efficiency of the microbial culture used. In some cases, near-complete copper recovery is possible.
2. **Gold (Au):** The recovery of gold through bio-hydro-metallurgy can vary significantly, typically ranging from 60% to 90%. The efficiency depends on factors like the presence of refractory gold ores and the specific microbial strains employed.
3. **Uranium (U):** Uranium recovery rates from bio-hydro-metallurgy can be quite high, often exceeding 90%. This is especially true for low-grade uranium ores.
4. **Cobalt (Co):** Cobalt extraction using bio-hydro-metallurgy can achieve recovery rates between 60% and 80% in certain cases.
5. **Nickel (Ni):** Nickel recovery rates can range from 50% to 80% or more, depending on the ore and microbial culture used.
6. **Zinc (Zn):** Bio-hydro-metallurgical processes for zinc can achieve recovery rates ranging from 70% to 90%.
7. **Silver (Ag):** Recovery rates for silver through bio-hydro-metallurgy can vary but are often in the range of 50% to 90%.

It's important to note that these percentages are approximate and can vary significantly based on the specific conditions and technologies used in each biohydrometallurgical operation. The choice of microbial strains, the composition of the ore, the duration of the bioleaching process, and other factors all play a role in determining the final metal recovery rate. Additionally, ongoing research and advancements in bio-hydro-metallurgy may lead to improvements in metal recovery efficiencies in the future.

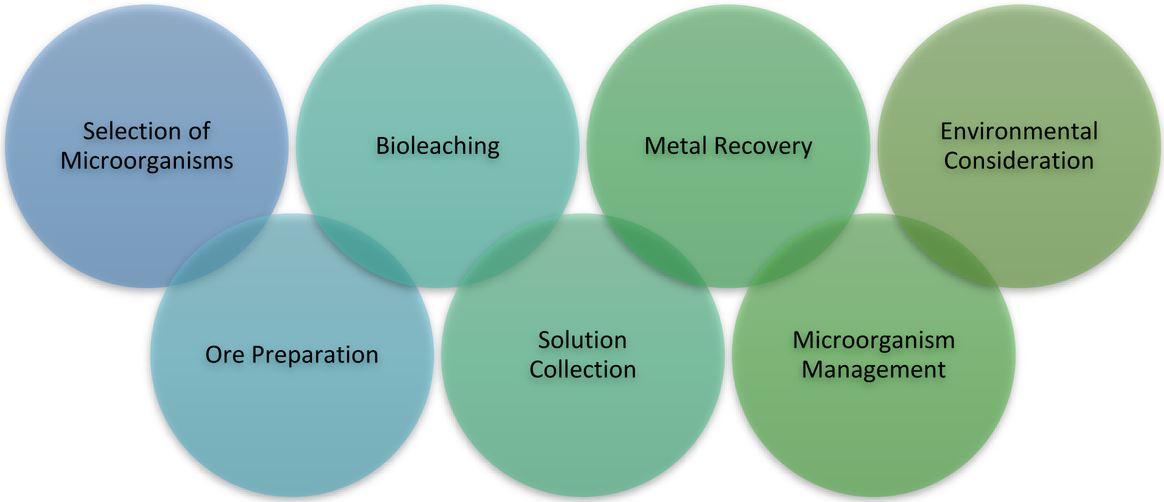

Fig 4. Processes Involved in Bio-hydro-metallurgy

COMPARISON

Factors	Pyrometallurgy	Hydrometallurgy	Bio-hydro-metallurgy
Process	Processes use heat and chemical reactions to separate metals from the gangue.	Processes use aqueous solutions, typically acids or bases, to leach metals from ores or concentrates	Bio-hydro-metallurgy employs microorganisms, such as bacteria or archaea, to catalyze the dissolution of metal ores.
Metal Extracted	Pyrometallurgical processes are suitable for a wide range of metals, including copper, iron, lead, zinc, and precious metals like gold and silver.	Hydrometallurgy is versatile and can be used for a broad spectrum of metals, including copper, nickel, cobalt, uranium, and rare earth elements.	Bio-hydro-metallurgy is primarily employed for the extraction of metals like copper, gold, and uranium.
Processing Time	Pyrometallurgical processes are often faster than hydrometallurgy and bio-hydro-metallurgy but can be less selective	Hydrometallurgical processes can be slower than pyrometallurgy but offer better selectivity for specific metals.	Bio-hydro-metallurgy processes may be slower compared to traditional hydrometallurgy but can provide high selectivity for certain metals
Residue & Waste Management	Pyrometallurgical processes often produce slag and other solid residues, which may require disposal and can sometimes contain hazardous materials.	Hydrometallurgical processes produce liquid waste streams that need to be treated or managed properly to prevent environmental contamination.	processes typically generate fewer solid and liquid wastes compared to pyrometallurgy and some hydrometallurgical methods.
Cost	Pyrometallurgical processes need around \$100-\$200 per ton of ore processed	Hydrometallurgical processes need around \$50-\$100 per ton of ore processed	Bio-hydro-metallurgy has the lowest cost around \$20-\$50 per ton of ore processed

CONCLUSION

Pyrometallurgy, hydrometallurgy, and bio-hydro-metallurgy are all viable methods for extracting metals from e-waste. However, each method has its own advantages and disadvantages, which must be carefully considered when choosing the most appropriate method for a particular application. Pyrometallurgy is the most versatile method, but it can also be the most energy-intensive and environmentally damaging. Pyrometallurgical processes typically involve high temperatures and the use of strong chemicals, which can release pollutants into the air and water. However, pyrometallurgy is also the only method that can recover all of the metals from e-waste, including precious metals such as gold and silver. Hydrometallurgy is more efficient for recovering precious metals than pyrometallurgy, but it can generate hazardous wastewater. Hydrometallurgical processes typically involve leaching the metals from e-waste using acids or other chemicals. The leachate is then treated to recover the metals and dispose of the wastewater. Hydrometallurgy is a less energy-intensive method than pyrometallurgy, but it is still important to carefully manage the wastewater to prevent environmental contamination. Bio-hydro-metallurgy is the most environmentally friendly method for extracting metals from e-waste, but it can be slower and less efficient than pyrometallurgy or hydrometallurgy. Bio-hydro-metallurgical processes use microorganisms, such as bacteria or fungi, to leach the metals from e-waste. The microorganisms produce acids and other chemicals that dissolve the metals. Bio-hydro-metallurgy is a relatively new technology, and there is still much research needed to improve its efficiency and scalability. The best choice of method for extracting metals from e-waste will depend on the specific composition of the e-waste and the desired recovery efficiency. For example, if the e-waste contains a high concentration of precious metals, then hydrometallurgy may be the best option. If the e-waste contains a variety of different metals, then pyrometallurgy may be the best option. And if environmental impact is the primary concern, then bio-hydro-metallurgy may be the best option. In the future, it is likely that a combination of these methods will be used to extract metals from e-waste. For example, pyrometallurgy can be used to pre-treat the e-waste, break it down into smaller pieces, and remove hazardous materials. Hydrometallurgy or bio-hydro-metallurgy can then be used to extract the metals from the pre-treated e-waste. This approach could help to maximize metal recovery and minimize environmental impact.

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