

Methods for Recycling Applications

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The recycling of metals from waste materials is important for conserving natural resources and reducing environmental issues. One of the benefits of metal recycling from scrap material is energy savings compared to the primary production of metals. For example, producing steel by remelting steel scraps saves about 74% more energy compared to producing steel from iron ores. In the case of aluminum, secondary aluminum production saves 95% more energy than primary production. For this reason, secondary aluminum production has outpaced primary production since 2001, and two nonoperating primary aluminum smelters were permanently shut down in 2015.

In general, primary metal production comprises exploration, mining, mineral processing, and extractive metallurgy as shown in Figure 1. Waste recycling follows the same general process steps, except the first two steps are (1) the identification of values in waste and (2) the collection and logistics of delivering these wastes to a central point for processing. For recycling applications, initial chemical/physical characterization of waste streams, including the use of automated mineralogy equipment such as the mineral liberation analyzer (MLA) and Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN), is required. Technologies that provide the basis of mineral processing and extractive metallurgy are fundamental to both recycling applications and primary metal production. Broadly, mineral processing utilizes physical techniques and methods, whereas extractive metallurgy processing is based on chemical separation principles. In metals and materials (waste) recycling, both mineral and extractive metallurgy processes are employed to separate and recover metals and other values, respectively.

MINERAL PROCESSING FOR ORES

The primary role of mineral processing is to concentrate (upgrade) the target material in an assembly of mixed materials (recyclable waste). When materials are intimately associated, comminution is often required to reduce the particle size for better liberation. Comminution is performed for the following reasons (Gupta 2003):

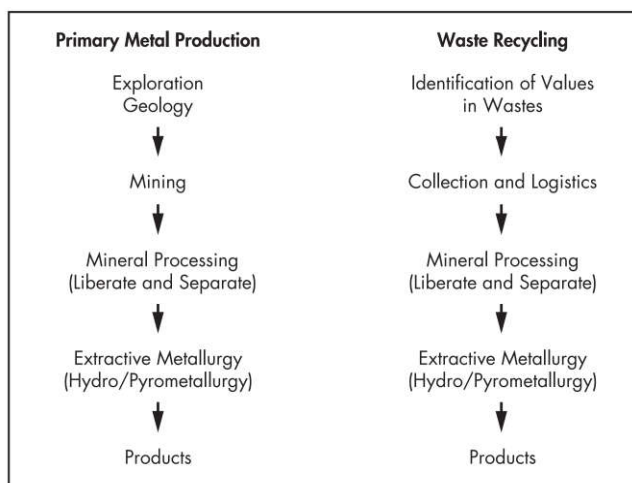


Figure 1 Flow sheets of metal production

- Liberation of one or more economically important value components from the waste components in an ore or waste assemblage
- Exposure of a large surface area per unit mass of material to facilitate some specific chemical reaction, such as leaching
- Reduction of the raw material to the desired size for subsequent processing or handling
- Satisfaction of market requirements concerning particle size specifications

Basic methods of mechanical size reduction or comminution for recyclable wastes include crushing and grinding to break apart physically attached materials or phases. After the waste is reduced in size, separation techniques are used. Liberation and separation are the two main concepts in mineral processing. In general, liberation can be achieved by the comminution processes. After that, separation processes are required to yield concentrated products from the processed ore and other materials (Fuerstenau 2003; Hayes 2003; Kelly and

Table 1 Comparison chart for pyro- and hydrometallurgical processes

Terms of Reference	Pyrometallurgy	Hydrometallurgy
High-grade ores	More economical	Less economical
Low-grade ores	Unsuitable	Suitable
Complex ores	Unsuitable	Has flexibility
Secondary resources	Unsuitable in most cases	Suitable
Reaction rate	Rapid (high temperature)	Slow (low temperature)
Environmental pollution	Waste gas, noise, dust	Mainly wastewater

Adapted from Gupta and Mukherjee 1990

Spottiswood 1982; Pryor 2012). The major purposes of separation include the following (Gupta 2003):

- A crude product is purified by removing any contaminating impurities.
- A mixture of two or more products is separated into the individual pure products.
- The stream discharged from a process step may consist of a mixture of product and unconverted raw material, which must be separated and the unchanged raw material recycled to the reaction zone for further processing.
- A valuable substance, such as a metallic ore, dispersed in a mass of inert material must be liberated for recovery and the inert material discarded.

Prominent techniques for particulate separation are based on differences in specific gravity, surface chemistry (froth flotation), magnetic susceptibility, conductivity, and a whole host of identifiable characteristics (e.g., color, reflectance, chemistry, radioactivity) for sortation. These separation techniques are very useful for separating and concentrating materials of value in a mixed recyclable waste as it is often a mixture of metallic and nonmetallic materials, magnetic and nonmagnetic materials, and/or electrically conducting and insulating materials. Different densities of materials allow the use of gravity-based separation techniques (Anderson et al. 2014; Habashi 1997; Wills and Napier-Munn 2006).

EXTRACTIVE METALLURGY FOR ORES

Extractive metallurgical processes are divided into pyrometallurgy, hydrometallurgy, and electrometallurgy and are applied to the concentrate products produced by particulate separation in mineral processing (Rosenqvist 2004). In brief, pyrometallurgical processes rely on the application of heat, whereas hydrometallurgical processes rely on the use of solvents to obtain the desired chemical reaction. Electrometallurgy is generally considered a subcategory of hydrometallurgy, and it uses electric current to produce metals from their ions in solution. Typically, the same metal can be produced by different unit processes. The selection of the unit processes mainly depends on economic and environmental considerations. Based on the ore or waste types and their complexity, different metal extraction methods can be used, and a comparison chart for pyro- and hydrometallurgical processes is shown in Table 1.

Pyrometallurgical techniques provide the separation of valuable products as a liquid phase, separating the unwanted materials through the formation of a slag. On the other hand, hydrometallurgical methods generally begin with a leaching step to selectively dissolve or un-dissolve the target material. This separation is achieved by precipitation via pH

Table 2 Metal recovery methods and their applications

Recovery Methods	Solution Types	Applications	Products
Cementation	Dilute	Au, Ag, Cu, Cd	Metal (impure)
Ionic precipitation	Dilute/ concentrated	Fe, U, Th, Be, Cu, Co	Metal compounds
Crystallization	Concentrated	Al, Cu, Ni, Mo, W	Metal compounds
Reduction with gas	Concentrated	Cu, Ni, Ag, Mo, U	Metal and metal compounds
Electrolysis	Concentrated	Au, Ag, Cu, Ni, Co, Zn	Metal (pure)

Adapted from Gupta and Mukherjee 1990

control and/or oxidation, as well as by solvent extraction and ion-exchange principles (Habashi 1999). Metal recovery from leach solution is the final stage of hydrometallurgical processes. In general, metal recovery is done using several different methods, including cementation, ionic precipitation, crystallization, reduction with gas, and electrolysis of metal. Table 2 shows how specific metals can be recovered by one of these methods.

APPLICATION OF MINERAL PROCESSING AND EXTRACTIVE METALLURGY FOR ORES TO WASTE RECYCLING

Mineral processing and extractive metallurgy techniques are used in the recycling of waste materials generated during manufacturing and use. Since the primary production involves ores that are chemically and compositionally different from the in-process or postconsumer waste forms, the process selection for treatment varies and is adjusted for the materials of interest. The environmental aspects are also different when recycling materials from industrial or postconsumer wastes. Recycling has requirements similar to those of low-energy, energy-efficient, environmentally compatible, and economically feasible processes for primary production. However, other challenges must be met to justify recycling, such as the following (Björklund and Finnveden 2005):

- The demand for materials must outstrip the supply.
- The developed recycling process must be energetically favorable.
- The process must not negatively affect the environment for air, water, and land.
- The process must be economically viable so there are economic gains for the recycler.
- Secondary resources must be available requiring high-volume collection systems.
- Separation and beneficiation (upgrading) must be technically possible.
- Feasible chemical/metallurgical processing must be available based on similar mineral processing and extraction techniques.
- A favorable market must exist for recycled products.
- The area of recycling needs to be supported politically and socially with proper policies and regulations for practical environment compatibility, economic incentives, and enforced disposal laws.
- The main sources of waste forms in metals and materials recycling come from Mine tailings and sludges;

- Materials rejected during physical concentration steps;
- Slags, baghouse dusts, and flue-dusts generated during pyrometallurgical operations;
- Fluid effluents during hydromet/electromet operations;
- Conversion of metals into alloys and engineering materials;
- Deformation and machining operations;
- Component fabrication rejects (out-of-specification components);
- Postconsumer wastes; and
- Landfill wastes.

Process Applications

Seven process application examples are presented in the following sections. They relate to (1) lithium-ion battery recycling, (2) recovery of metals and materials from red mud, (3) recycling phosphor dust for rare earth metals recovery, (4) recovery of aluminum from secondary aluminum production dust, (5) vanadium recovery from fly ash, (6) e-waste recycling, and (7) ferrous scrap recycling. All of these examples for recycling prominent waste materials exemplify the use of mineral processing and extractive metallurgy techniques.

Lithium-Ion Battery Recycling

Although many recycling processes are used industrially for lithium-ion batteries, they have some drawbacks (Al-Thyabat et al. 2013):

- Not all of them are lithium-ion battery dedicated processes.
- In most of the processes, not all of the materials are recycled.
- Usually the electrolyte, plastics, and organics are evaporated or are burned during pyrometallurgical steps and thus are not recovered.
- Hydrometallurgical processes can sometimes be questionable from an economical point of view because of the low solid-to-liquid ratio and the cost and handling of the reagents (especially if they are not recovered).
- Some battery components cannot be easily leached. An example is the strong bond between oxygen and cobalt, which makes leaching with commonly used reagents harder.

An efficient lithium-ion recycling process should adapt to the following requirements (Xu et al. 2008):

- Lithium-ion batteries can be composed of different materials, which are constantly being substituted by new ones, thus making it harder to find a process that would treat all the different compositions at the same time.
- The electrolyte (LiPF_6) should be recovered but is very hard to recover because of its high reactivity with water, moisture, and heating.
- The products produced from recycling must be pure enough to meet market needs and be competitive to new products.

Because of these difficulties, considerable research has been conducted over the last few years. The primary goal is to maximize recovery of the products and be environmentally friendly. A proposed approach to recycling lithium-ion batteries described by Marinos and Mishra (2015) is presented in Figure 2.

First, the material is shredded to liberate the constituents of the lithium-ion battery. This step requires a good exhaust system, such as a baghouse, to avoid dust and organic gas. Dust will be collected and all the fine material treated separately as shown in the flow sheet. Then the shredded material is passed through a low-intensity magnetic separator to remove the ferromagnetic material, which is primarily the steel battery shell.

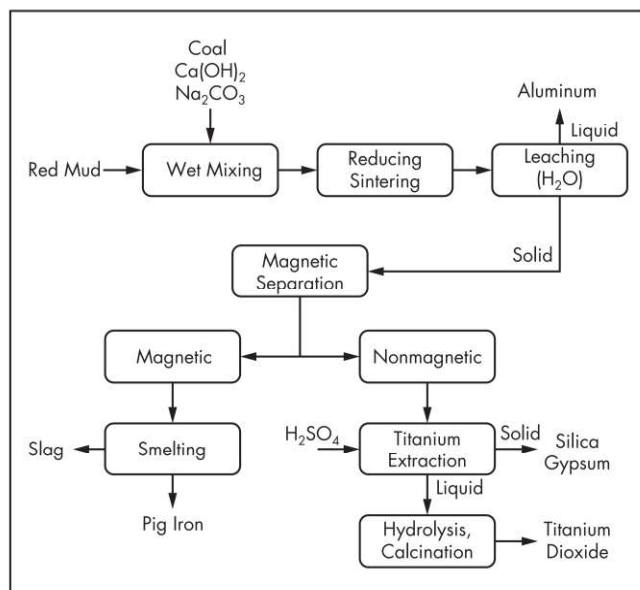
The remaining material is leached at room temperature for one hour using distilled water as the leachant. Lithium is present in the cathode, usually as LiCoO_2 (insoluble in water), and in the electrolyte as LiPF_6 . Thus, during the leaching process, lithium present in the electrolyte, as LiPF_6 , goes into solution. This leaching step can be performed in a flotation cell at ambient temperature, pressure, and pH. After leaching is complete, the air valve is opened, forming bubbles and thus helping the low-specific-gravity particles (plastic and some fine particles that are stuck on the plastic) float. In this way, plastic and some fine particles are separated from the lithium-bearing leach solution. The main advantage of this system is that both leaching and separation are conducted in one step. The floated plastics and fine particles are then wet screened into coarse and fines to wash the plastics and separate the fine particles that are stuck on the plastic material. The coarse plastics can then be recycled and the fine material will be collected to treat separately.

The remaining pulp, pregnant solution, and solids of high specific gravity are wet screened into multiple sizes. The wet screening helps to clean the particles from the fine carbon and cathode powder. Each differently sized fraction will be treated separately. The very fine will be combined with the rest of the fines and go through the hydrocyclone and/or be leached to recover carbon and cathode materials. Carbon could also be recovered from fines using pine oil to float it selectively from the rest of the fines, and the cathode materials could be recovered in multiple ways that have been researched.

The pulp that passes through the smallest sieve gets filtered, and the pregnant solution is recovered. Fine particles that are filtered are combined with the fines from previous steps. Lithium concentration in solution is low, and to precipitate lithium carbonate from the pregnant solution, according to lithium carbonate solubility at 100°C , the concentration of lithium must be at least 1.4 g/L and at room temperature at least 2.4 g/L. The concentrations are based on the fact that lithium carbonate solubility decreases with increasing temperature. Thus, if the concentration of lithium in the pregnant solution is lower than 1.4 g/L at 100°C or 2.4 g/L at room temperature, the solution is recycled back to the leaching step to increase its concentration. If the concentration of lithium is higher than that, the lithium carbonate product is recovered using carbon dioxide or hydrochloric acid, to turn LiOH to LiCl , and sodium carbonate. This process is used industrially for the recovery of lithium.

The rest of the fractions that were obtained by sieving will be dried and sent separately for high-intensity magnetic separation and then eddy-current separation. High-intensity magnetic separation and, more specifically, rare earth roll magnetic separators operate at very high magnetic field intensities and thus could separate many paramagnetic materials from diamagnetic materials.

After the high-intensity magnetic separation, each fraction will be sent separately to an eddy-current separator. Eddy-current separation, depending on particle size, is very



Adapted from Piga et al. 1993

Figure 3 Flow sheet for recovery and recycling of iron, aluminum, and titanium from red mud

by the formation of grossular hydrogarnet. In a study conducted by Zhong et al. (2009), about 87.8% of alumina was extracted from the red mud with mild hydrochemical process conditions utilizing NaOH pressure leaching, which is essentially a repeat of the Bayer process.

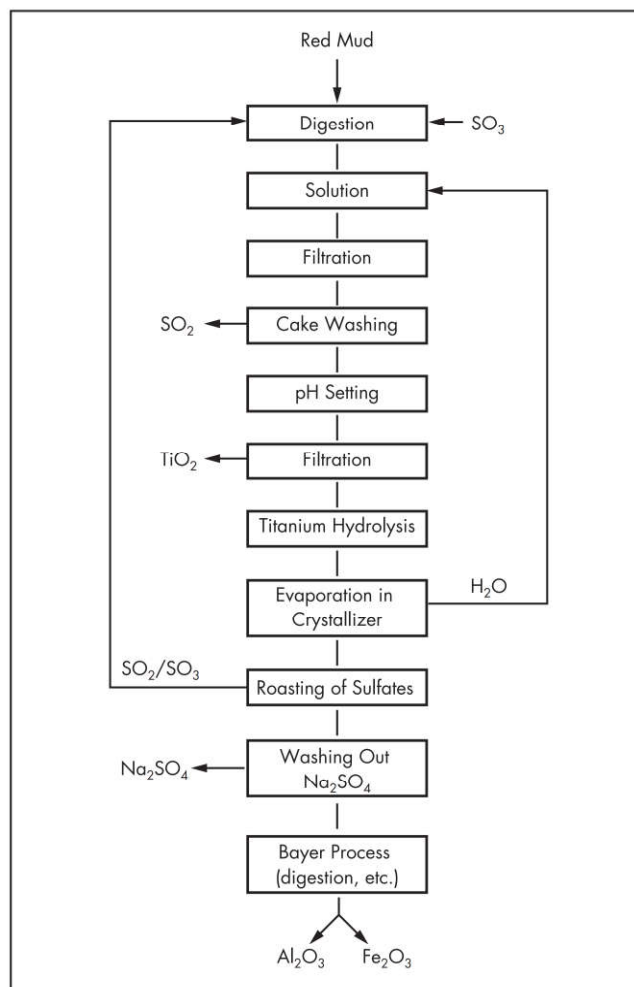
Bruckard et al. (2010) tried smelting on red mud, which was mixed with calcium carbonate at 1,400°C. The Al and Na could be easily recovered because of the phase transformation into $(\text{Na,Ca})_{2-x}(\text{Al,Fe}^{3+})_{2-x}\text{Si}_x\text{O}_4$. The slag was subjected to water leaching at 60°C, and 55% Al and 90% Na could be recovered at 50% pulp density.

Li et al. (2009) have attempted to devise a simultaneous sintering process for alumina recovery and converting hematite to magnetite. They found that the sintering temperature and amount of carbon strongly influence alumina recovery. A high recovery of 75.7% Al and 80.7% Na can also be obtained by soda lime roasting followed by water roasting of red mud.

Iron is the major constituent in red mud. The concentration of Fe in iron oxides varies between 6.8 wt % and 71.9 wt %, depending on the grade of bauxite. A prior reduction of the hematite in red mud transforms it into a magnetic product that can be separated by magnetic separation. Li's team (2009) suggested that pulsating magnetic current utilization would provide better separations than the conventional magnetic current. A high-gradient magnetic separator can separate magnetic particles less than 100 μm in size. Li et al. observed that weakly magnetized particles are attracted.

Xiangong et al. (1996) found that adding calcium, sodium, or magnesium salt can improve the efficiency of carbon-based direct reduction of iron in red mud. A team led by Jayasankar (2012) has proposed that the addition of 10%–12% dolomite would increase iron recovery to 71%. A recovery of 94.5 wt % Fe can be obtained by employing 6% Na_2SO_4 and 6% Na_2CO_3 in the mixture.

The soda ash roasting and leaching process described by Li et al. (2009) generates a leach residue consisting of magnetite,



Source: Zimmer et al. 1978

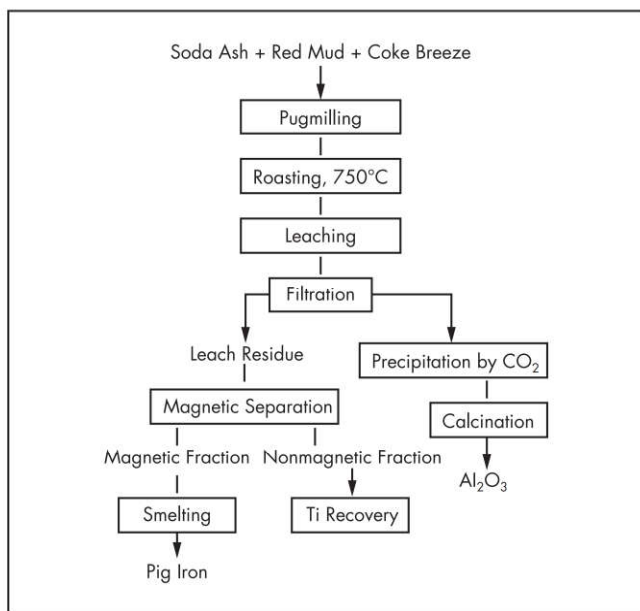
Figure 4 Alternative flow sheet proposed for value recovery from red mud based on hydrometallurgical processing

hercynite, and TiFe_2O_4 . The iron recovery decreases because of agglomeration of ferrous phases and other impurities.

Acid leaching for recovering iron was also investigated. A high recovery of 97.5% Fe can be obtained at a calcination temperature of 600°C and subsequent leaching in 6M H_2SO_4 .

Recycling Phosphor Dust for Rare Earth Metals Recovery

Rare earth elements (REEs), which include 15 lanthanide series plus scandium and yttrium, are important components of modern technologies, such as electronics, clean energy, national defense, and others. The unique properties of the REEs, including luminescence, magnetism, and electronic properties, promote the performance of high-tech equipment by adding a small amount of REEs. Currently, more than 95% of world rare earth production comes from China, and the U.S. Department of Energy (DOE) addressed the challenges associated with the use of REEs in energy technologies. Thus, the DOE has supported the Critical Materials Institute and updated the criticality assessments of the materials since 2010. According to its *Critical Materials Strategy* report (DOE 2011), five REEs (dysprosium, neodymium, terbium, europium, and yttrium) and indium are most critical for clean



Source: Kumar and Srivastava 1998

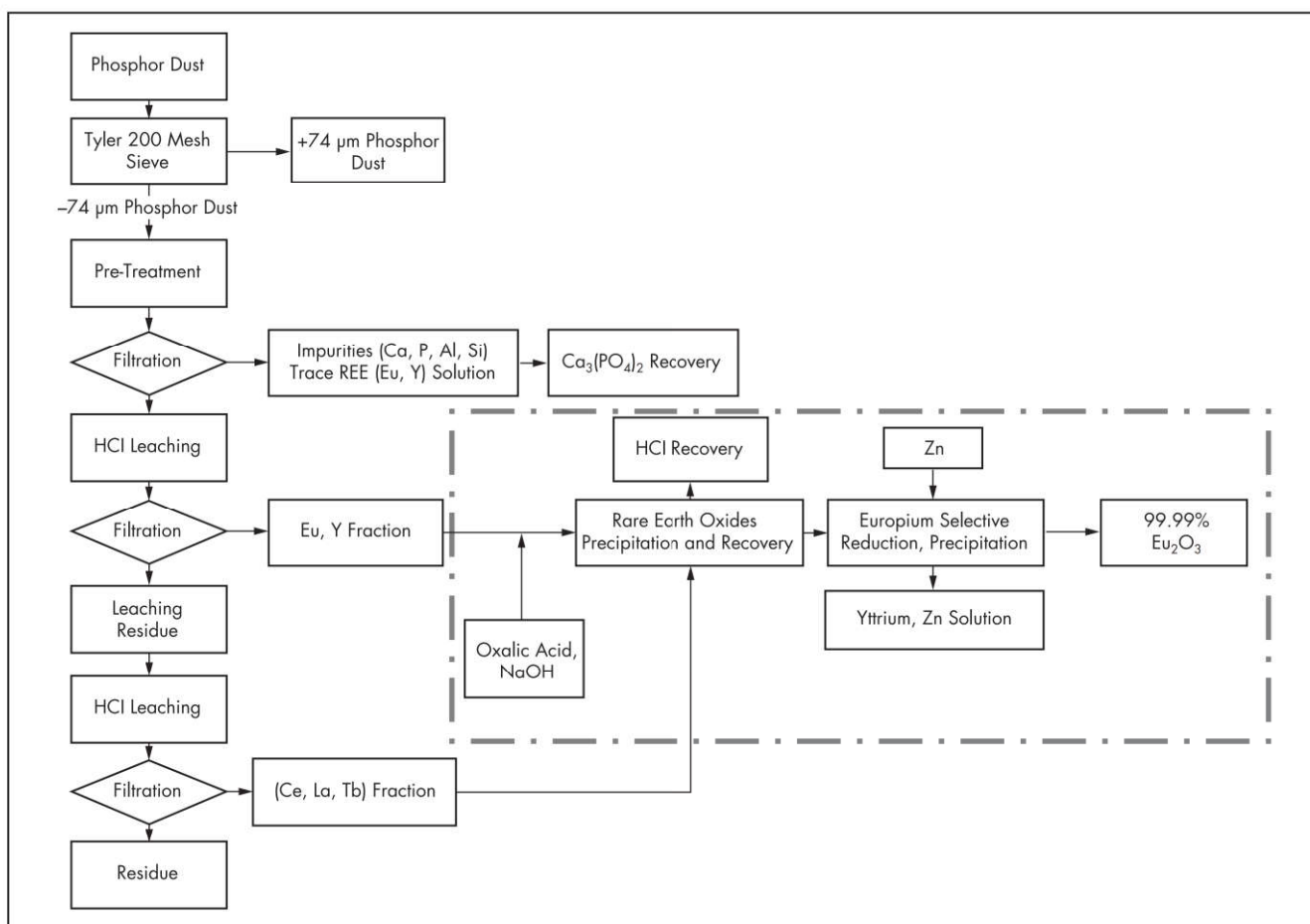
Figure 5 Hydrometallurgical and pyrometallurgical processing of red mud for separation of iron, titanium, and aluminum

energy technologies. In general, fluorescent lighting phosphors contain europium, yttrium, and terbium, which are critical materials based on the DOE's materials strategy. Strauss (2016) and Eduafo (2016) conducted the recovery of REEs from phosphor dust, and the proposed flow sheet is shown in Figure 6.

Based on the flow sheet in Figure 6, a characterization of phosphor dust was completed for waste lamp phosphor dust. Various processes were used to quantify the dust. QEMSCAN found that the majority of the powder was quartz (54.30%), followed by apatite (16.64%), yttrium-bearing minerals (14.98%), and calcite (4.75%). Monazite was also present with trace amounts of xenotime, iron oxide, barite, celestine, and europium- and terbium-bearing minerals.

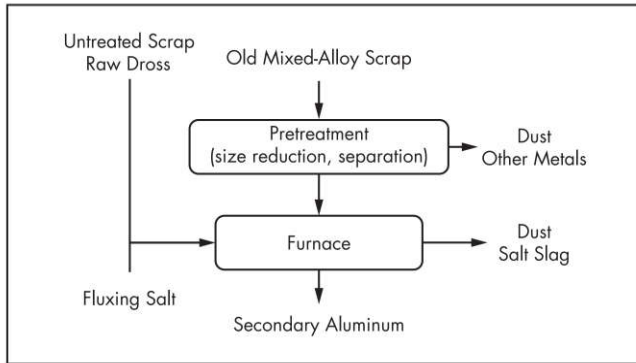
More than 60% of the rare-earth-containing minerals were smaller than 10 μm . In particular, more than 95% of the europium-containing minerals were less than 10 μm . In addition, more than 66% of the quartz was greater than 75 μm , indicating that size-based sorting could present a viable physical separation process for this approach. Future work should focus on physical separation methods, such as those using a cyclone, or magnetic separation unit operations.

Oxalic acid precipitation was optimized for the europium and yttrium leach solution. The optimized conditions were 25°C, 600 rpm agitation, pH = 0 (native pH). Neither



Source: Strauss 2016

Figure 6 Recycling of rare-earth metals from postconsumer products using low-energy hydrometallurgical processes



Adapted from Altenpohl and Kaufman 1998

Figure 7 Traditional processing of old scrap for secondary aluminum

temperature modification from room temperature nor pH modification with NaOH were necessary for optimization. More than 99% recovery and 99% purity were achieved for mixed yttrium and europium rare earth oxides (REOs). Future work should focus on conditions to decrease oxalic acid consumption to improve the economics of the process.

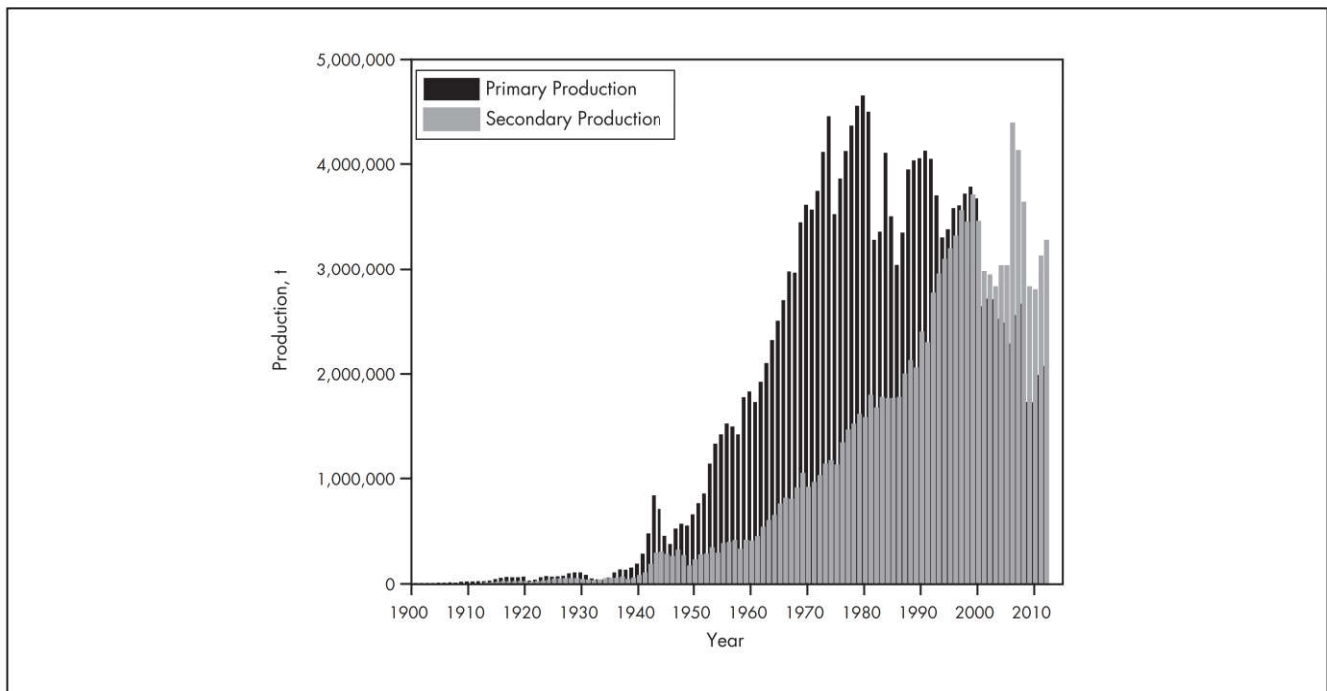
The selective reduction of europium(III) to europium(II) in solution along with precipitation of europium(II) sulfate is a successful method to separate europium from yttrium. More than 95% pure europium sulfate was created in the process at laboratory scale with more than 80% recovery. However, more research needs to be conducted to scale up this work to a larger apparatus and to verify that it can be economic. In addition, more simulations using HSC's Gibbs free energy minimization need to be conducted.

A very preliminary economic analysis of the recovery process was conducted to study creating a recycling facility for phosphor dust. Based on the REO six-year price average and REO two-year price average, the project is viable. However, at current prices, the project is highly uneconomic. More work needs to be conducted to study the cost of wastewater treatment as well as to add the value of acid recovery and terbium oxide recovery to the process.

Recovery of Aluminum from Secondary Aluminum Production Dust

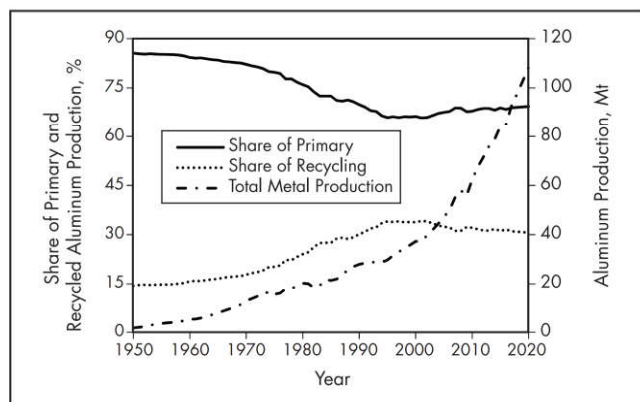
Most metal production plants utilizing pyrometallurgical processes generate air pollutants including particulate matters and harmful gases. Thus, these plants often install several dust-collecting systems such as cyclones and baghouses to control the emission of air pollutants. In general, dust collected from a metal production plant also contains metal values. Therefore, metal recycling from the collected dust can be valuable by saving metal resources as well as reducing environmental issues. One example of industrial fine wastes is aluminum smelter baghouse dust, which is generated during shredding or smelting from secondary aluminum production facilities as shown in Figure 7. Secondary aluminum production requires about 5% of energy to produce aluminum compared to primary aluminum production. Since 2001, secondary aluminum production has outpaced primary aluminum production in the United States as shown in Figure 8. Moreover, global aluminum production will increase and is projected to reach around 100 Mt/yr by 2020 as shown in Figure 9.

Typically, dust from the aluminum industry that is larger than 20 mesh in size contains a large amount of aluminum. Thus, this particular size fraction is usually remelted. However, undersize fraction (smaller than 20 mesh) is landfilled. About 1 Mt of secondary aluminum production wastes, including



Data from USGS 2014

Figure 8 U.S. aluminum production by type



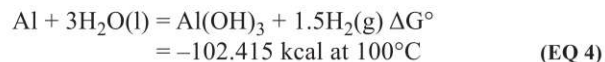
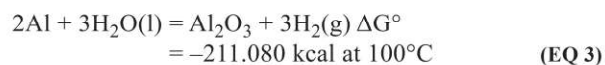
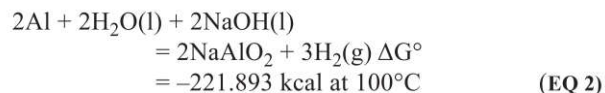
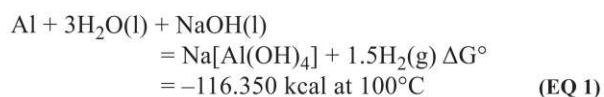
Source: International Aluminium Institute 2016

Figure 9 Forecast share of global primary and recycled metal production

salt cake and baghouse dust, are being generated annually and landfilled in the United States (DOE 1999). Therefore, disposal of aluminum industry dust will soon be an issue because of its flammable and irritant nature when the size of the dust is smaller than 420 μm (Aluminum Association, n.d.). In European Union countries, baghouse dust from aluminum production facilities is recognized as a hazardous waste.

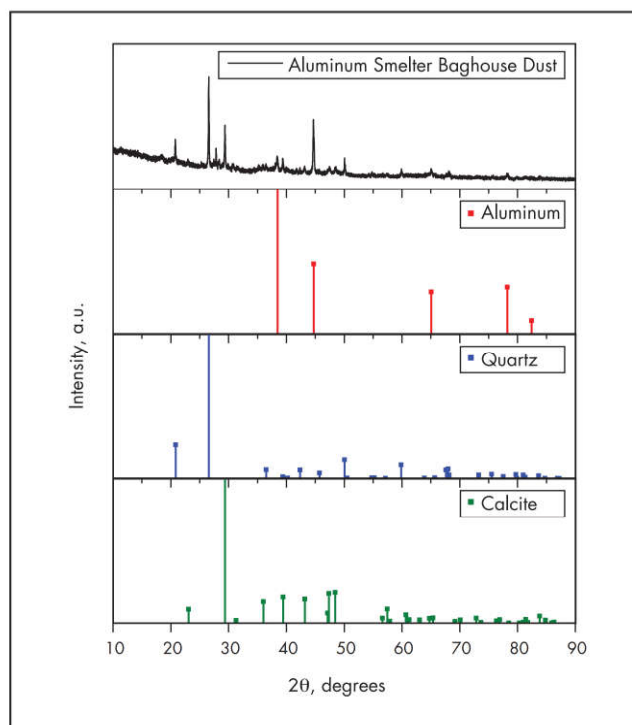
Huang et al. (2015) investigated baghouse dust samples from 13 different secondary aluminum production facilities in the United States for mineral phases and metals in baghouse dust. Based on this study, the major aluminum phases are aluminum metal, aluminum oxide, aluminum nitride, and spinel. The average aluminum content is about 18% by weight and ranges from 2.6%–60%. Therefore, aluminum recovery from aluminum smelter baghouse dust could be valuable depending on the aluminum content of the waste streams.

Jung and Mishra (2016a, 2016b) have attempted to recover aluminum from aluminum smelter baghouse dust by hydrometallurgical processes. Based on inductively coupled plasma analysis, the aluminum contents in the sample ranged from 13%–20% by weight, depending on the particle size. Similarly, samples having a larger particle size showed a relatively large amount of aluminum content. In this type of sample, aluminum metal, quartz, and calcite are the major phases of the aluminum smelter baghouse dust based on X-ray powder diffraction (XRD) analysis as shown in Figure 10. One of the main advantages of hydrometallurgical processes is the selective leaching characteristic, depending on the reagent selection. Therefore, several leaching reagents, such as sulfuric acid, nitric acid, sodium carbonate, and sodium hydroxide, are used to extract aluminum. Based on the preliminary leaching tests, alkaline leaching reagents promote the selective leaching characteristic, and sodium hydroxide is a better reagent in terms of aluminum dissolution than is sodium carbonate. Because the major phase of the aluminum smelter baghouse dust is aluminum metal, the aluminum dissolution rate is relatively fast, and more than 75% of aluminum can be dissolved within 20 minutes. Based on XRD analysis, several reaction equations between aluminum and sodium hydroxide solution are proposed:



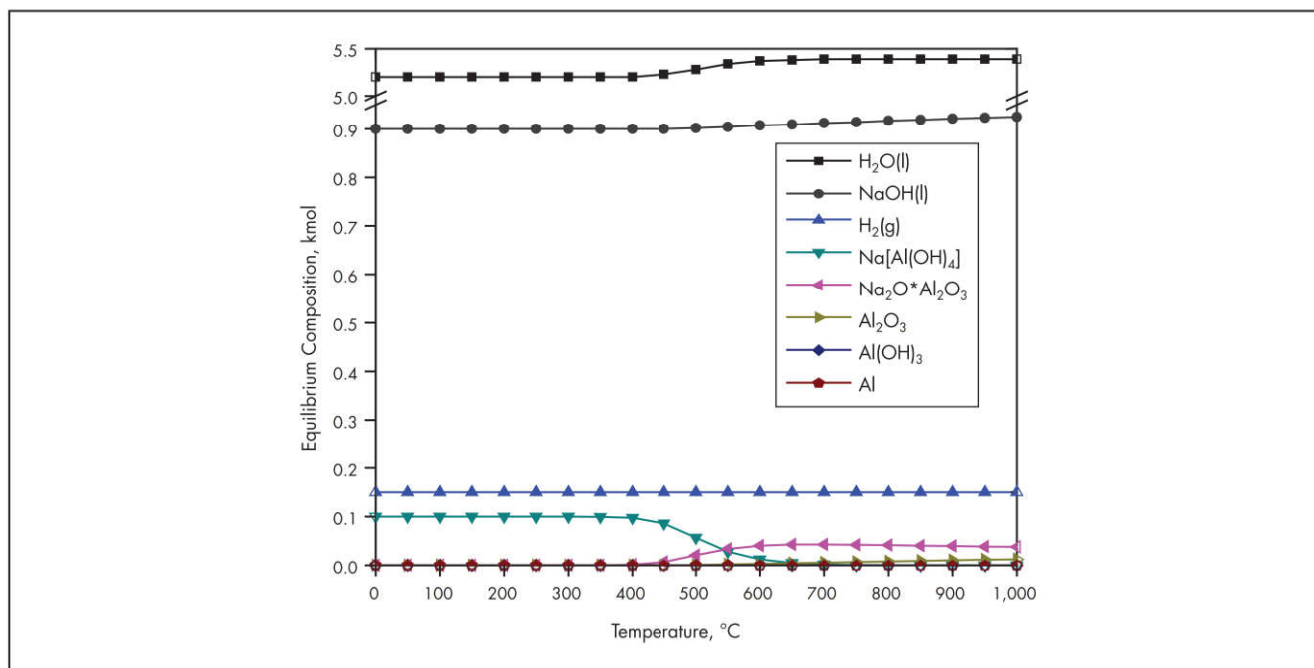
For the same molarity of aluminum, the formation of $\text{Na[Al(OH)}_4\text{]}$ is thermodynamically favorable at 100°C since it shows the largest negative value of Gibbs free energy. An equilibrium composition diagram based on the HSC chemistry shows identical results based on the Gibbs free energy minimization.

In the primary production of aluminum, the Bayer process, which uses bauxite ores as an aluminum source, also uses sodium hydroxide to dissolve aluminum from the crushed and grounded bauxite ores. During pressure leaching, gibbsite, boehmite, and diaspore in bauxite ores also react with sodium hydroxide and produce $\text{Na[Al(OH)}_4\text{]}$ after leaching. The final product after leaching of bauxite ores and aluminum smelter baghouse dust is identical based on the thermodynamic modeling (Figure 11). Therefore, aluminum smelter baghouse dust can be used as an aluminum source to generate sodium aluminate and share the calcination plants to produce alumina. However, hydrogen gas generation during leaching, as shown in Equations 1 through 4, should be controlled properly because of its flammable and explosive nature. Additionally, hydrogen gas generated from aluminum recovery can be an alternative hydrogen production method, and several studies



Source: Jung and Mishra 2016a, reproduced with permission from Springer

Figure 10 XRD analysis of the aluminum smelter baghouse dust



Source: Jung and Mishra 2016a, reproduced with permission from Springer

Figure 11 Equilibrium composition diagram of aluminum smelter baghouse dust leaching with NaOH

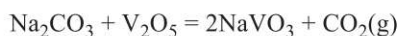
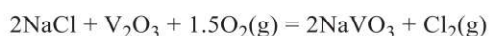
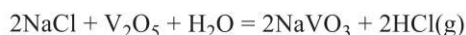
have been conducted based on the same or similar reaction equations between aluminum and sodium hydroxide.

Vanadium Recovery from Fly Ash

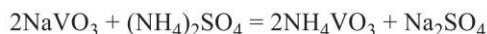
Several properties of vanadium, including its high melting point, low density, and relatively high strength, make it a valuable metal in applications in the steel, aerospace, chemical, and battery industries (Davis 2007). In 2012, about 90% of vanadium consumption came from steel applications (Figure 12) because adding less than 1% of vanadium to steel increases its tensile and high-temperature strength. In the aerospace industry, vanadium is used as an alloying element for titanium alloys because of its high strength-to-weight ratio. For example, the Ti-6Al-4V titanium alloy is widely used since it shows high strength, good toughness, and high-temperature stability. In the chemical industry, vanadium pentoxide is often used as a catalyst, such as for sulfuric acid production and selective catalytic reduction of nitrogen oxides in power plants. The vanadium redox battery is another industrial application of vanadium because vanadium can exist in solution as four oxidation states. The vanadium redox battery is a type of rechargeable battery that has an extremely large capacity and can be completely discharged without ill effects. Therefore, it is ideal for use in wind or solar energy storage.

In general, vanadium can be extracted from primary sources or secondary sources. Currently, titaniferous magnetite ores that contain about 1%–1.5% of vanadium are the most important source of the element. During the steelmaking process, vanadium-rich slag is co-produced from titaniferous magnetite and used as a source of vanadium. Additionally, certain energy-related resources containing vanadium, such as coal, oil (especially heavy fuel oil), petroleum coke, and the like, are burned and thus generate vanadium-bearing residues, such as ash, slag, spent catalysts, or residue (Moskalyk and Alfantazi 2003; Queneau et al. 1989; Tsai and Tsai 1998).

These materials can be processed for vanadium recovery. A typical flow sheet of vanadium extraction is shown in Figure 13. First, vanadium in various sources is processed to generate vanadium concentrated product. Then, vanadium from concentrates is extracted by salt roasting followed by leaching. During the salt-roasting process, vanadium oxides are roasted with sodium carbonate or sodium chloride and converted to sodium meta-vanadate. Reaction equations between sodium chloride and vanadium oxide are as follows:

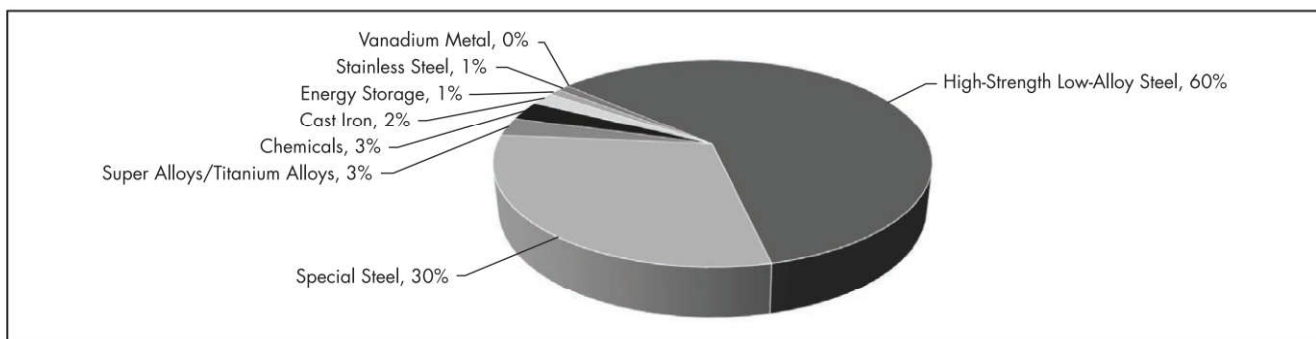


Because sodium meta-vanadate is readily water soluble, it can be separated from gangue materials by leaching. After leaching, a solution purification step, such as solvent extraction or ion exchange, could be used to purify the vanadium-bearing solution before precipitation. Finally, vanadium pentoxide is precipitated from purified vanadium solution. During precipitation, ammonium sulfate is added to precipitate ammonium meta-vanadate, and the reaction equation is as follows:



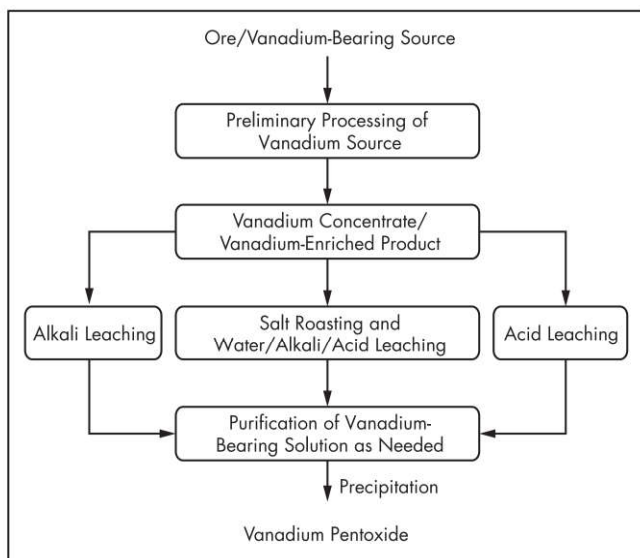
After ammonium meta-vanadate is precipitated, it is filtered, dried, and calcined to vanadium pentoxide. There is a significant body of research on the subject covering methods other than salt roasting with water leaching.

Vitolo et al. (2001) investigated vanadium recovery from a previously burned heavy oil fly ash. Vanadium recovery is performed by preliminary burning followed by acid leaching and an oxidative precipitation of vanadium pentoxide,



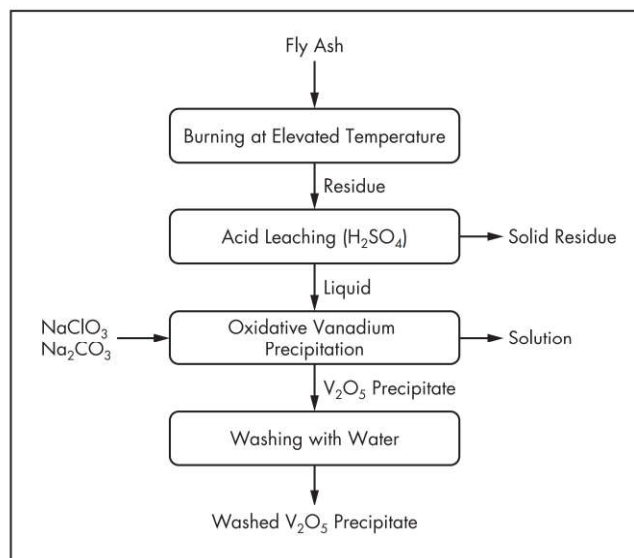
Courtesy of Terry Perles, TTP Squared, Inc.

Figure 12 Global vanadium consumption



Adapted from Gupta and Krishnamurthy 1992

Figure 13 Flow sheet of vanadium extraction



Adapted from Vitolo et al. 2001

Figure 14 Block diagram of the vanadium recovery process

as shown in Figure 14. In this method, a heavy oil fly ash containing 83.3 wt % carbon and 3.8 wt % vanadium is used for the vanadium recovery. During the preliminary burning step, the carbonaceous fraction is reduced and vanadium is concentrated from 3.8 wt % to 16–19 wt %. Then acid leaching is conducted using sulfuric acid to extract vanadium from the preliminary burned residue. The percentage of vanadium extraction is reported in the range of 91%–99% after burning at temperatures up to 950°C. However, when the burning temperature is higher than 1,050°C, formation of less leachable vanadium compounds hinders its extraction. After filtration, NaClO_3 is added to the leach solution to precipitate vanadium pentoxide at the boiling point of solution. During oxidative precipitation, typical red-brown color vanadium precipitates are observed, and the precipitation yield of vanadium is in the range of 72%–89%.

Navarro et al. (2007) also investigated vanadium recovery from oil fly ash from power plants. The researchers used a two-step process including leaching followed by solvent extraction or selective precipitation, as shown in Figure 15. The oil fly ashes collected from a thermal power plant contained 1.6% vanadium and 85% as a carbonaceous fraction.

Alkaline leaching with sodium hydroxide shows better selective vanadium extraction compared to sulfuric acid leaching. During solvent extraction, vanadium is extracted with aluminum simultaneously, and stripping vanadium from the organic solvent is difficult. Therefore, using the solvent extraction for vanadium recovery has limited possibilities. However, a selective precipitation of aluminum followed by vanadium precipitation yielded 99% vanadium recovery from the leach solution.

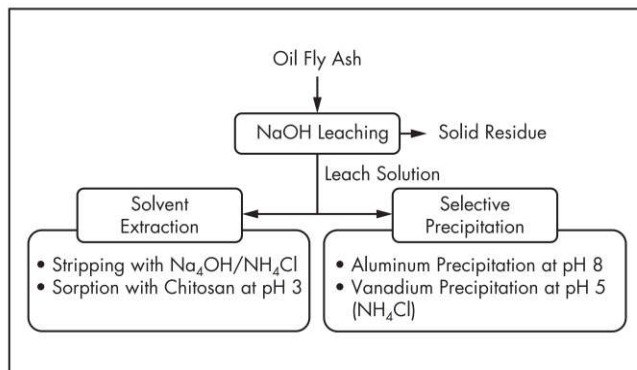
Gomez-Bueno et al. (1981) investigated vanadium recovery from petroleum coke fly ash. The recovery processes include fly ash pretreatment, fly ash roasting, and leaching of roasted ash, as shown in Figure 16. During fly ash pretreatment, carbon in the as-received sample is burned off at 500°C. Then, the carbon-free fly ash is roasted in a quartz reactor in the presence of sodium chloride and water vapor. After that, the roasted sample is leached with sodium hydroxide. These recovery processes substantially improve vanadium dissolution compared to the sodium hydroxide leaching of nonroasted fly ash. The researchers also found that satisfactory roasting is achieved at temperatures below 920°C, and hydrogen chloride generation during the salt-roasting process could be recovered and used in pH adjustment of the leaching solution.

E-Waste Recycling

Recent developments in the world of information technology (IT) devices and electronic equipment makes life more convenient. On the other hand, rapid development of these devices also decreases their useful lifetime and creates a large amount of waste streams, or so-called e-waste (Kang and Schoenung 2005). As shown in Figure 17, waste streams from various types of electronic and electrical devices, such as temperature exchange equipment, screens, lamps, small or large equipment, and IT devices, are categorized as an e-waste. In general, these waste streams are landfilled, incinerated, exported to other countries, or recycled. Based on the U.S. Environmental Protection Agency's annual estimates, in 2013, the total generation of e-waste in the United States was about 3.1 Mt/yr,

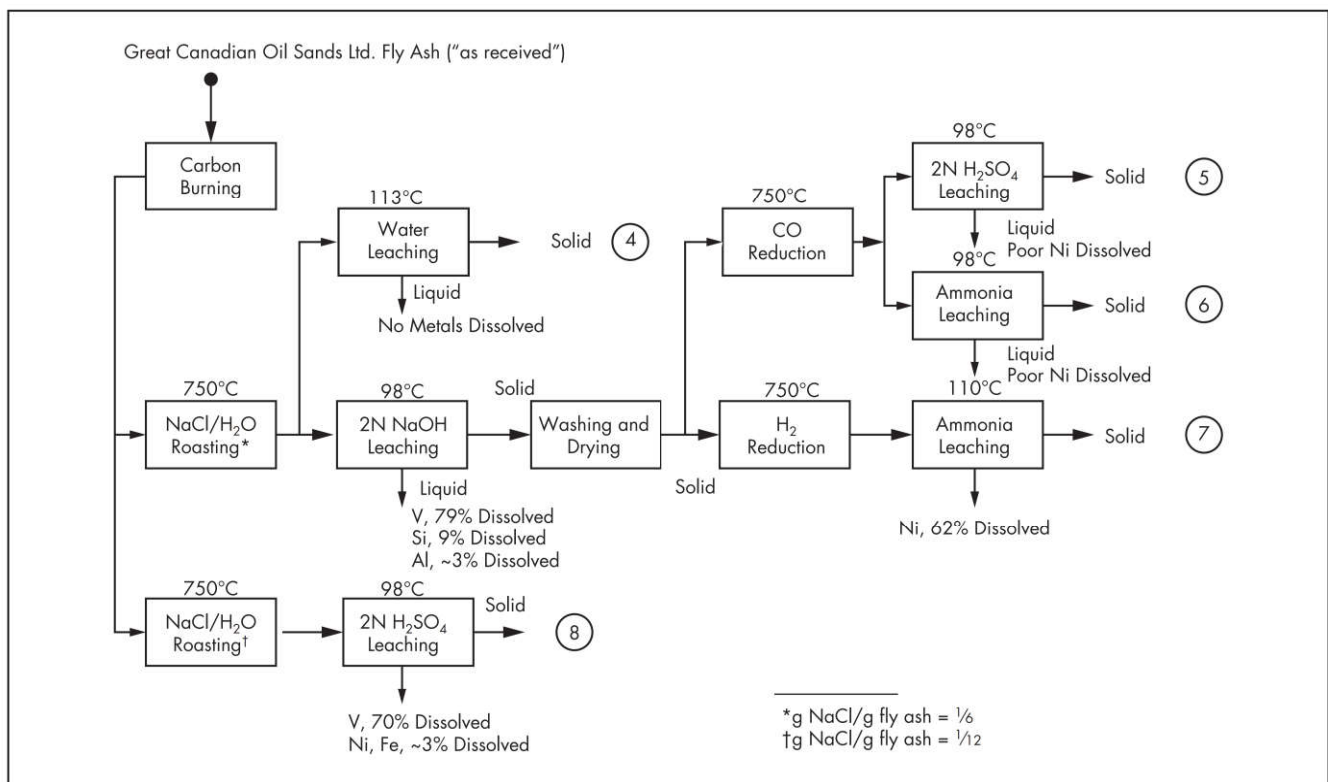
and the percentage of e-waste recycling has increased from 10%–40% since 2000 (Figure 18). Typically, e-wastes contain a relatively large amount of light/ferrous metals and plastics, as shown in Figure 19. Wires and printed circuit boards from e-waste also have a relatively large amount of gold and copper because they are very good conductors. However, e-waste includes a lot of toxic materials, such as chlorinated and brominated substances, plastic additives, and toxic metals, that must be properly separated and handled properly (Veit and Bernardes 2015). Thus, the European Union has introduced a directive to correctly manage e-waste. Today, e-waste is considered a good source of urban mining because of its high economic potential, as shown in Table 3, and many related studies, such as for dismantling, separation, and extraction, have been done.

Tuncuk et al. (2012) summarized metal recovery techniques from e-waste. As shown in Figure 20, e-waste recycling can be achieved by several different stages including dismantling, size reduction, separation, and extractive metallurgy. First, e-waste is dismantled and separated into various components, such as metals, plastics, batteries, and printed circuit boards. During these stages, valuable metals can be concentrated and hazardous materials can be removed from the recycling process. Therefore, the economic potential of e-waste recycling is closely related to the pretreatment steps. In general, mineral processing techniques are used to reduce the size of wastes and separate the materials. For example, shredders and hammer mills are often used to reduce particle size; the required particle size depends on the additional recycling processes. Physical separation utilizes different physical properties of the materials, such as specific gravity, magnetic



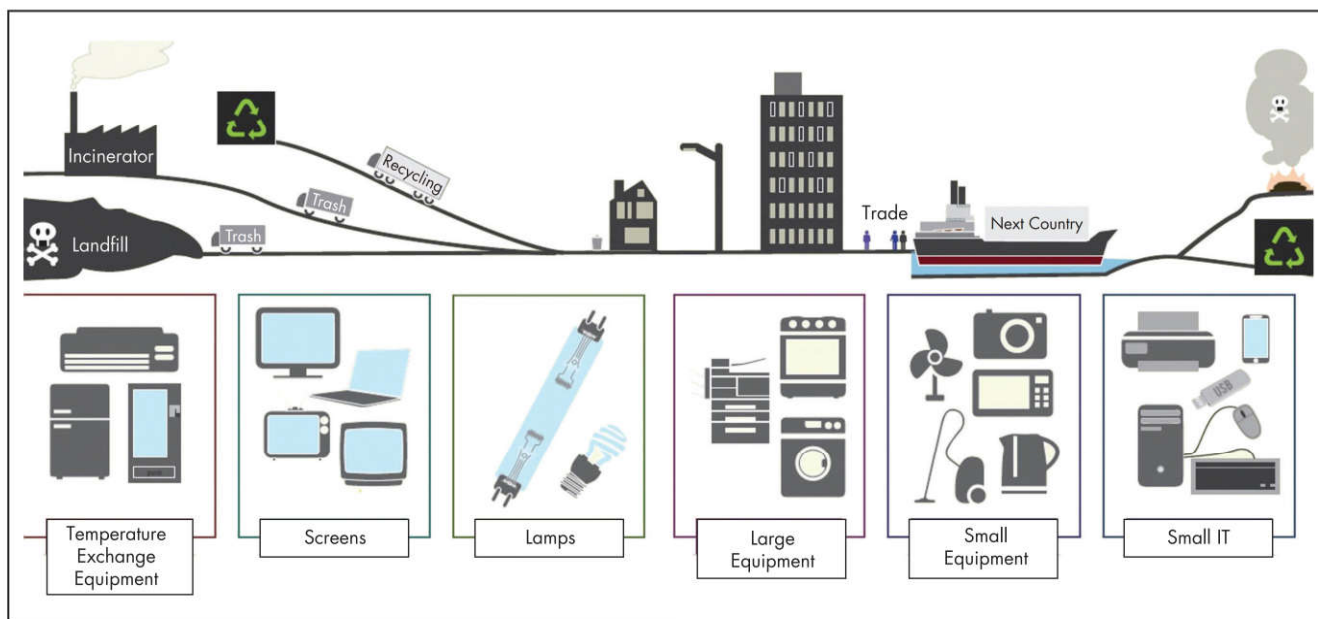
Adapted from Navarro et al. 2007

Figure 15 Integrated process for oil fly ash treatment



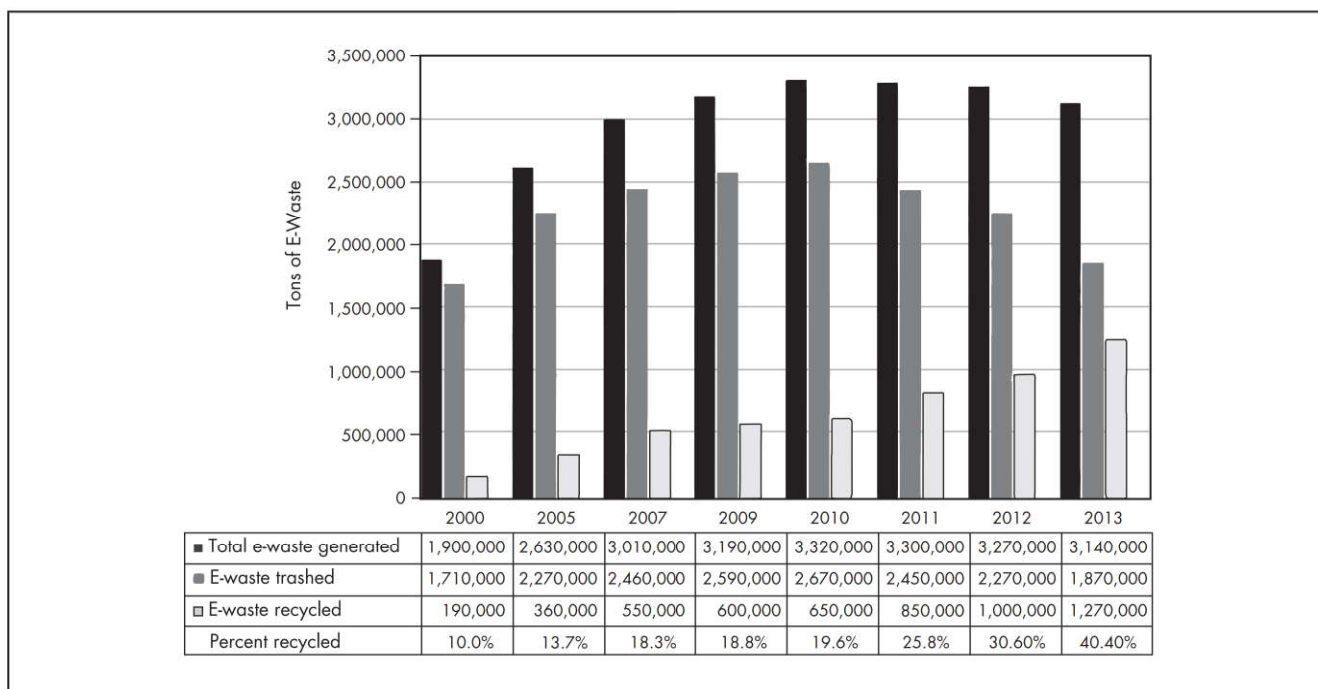
Source: Gomez-Bueno et al. 1981

Figure 16 Several treatments on carbon-free fly ash



Source: Baldé et al. 2015

Figure 17 Various types of e-waste and their flows



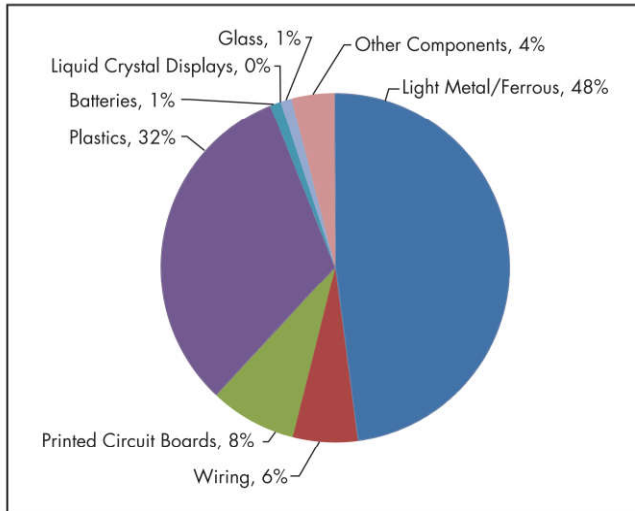
Source: Electronics TakeBack Coalition 2015

Figure 18 E-waste generation and recycling 2000–2013

susceptibility, color, and electrical conductivity. The main purpose of physical separation in e-waste recycling is separating metals from nonmetal components. Then, hydrometallurgical or pyrometallurgical processes are used to extract metals from the preconcentrated materials, and valuable metals are recovered during reduction processes, as shown in Figure 20.

Bennett et al. (2009) demonstrated several separation techniques for e-waste recycling. The researchers mainly focused

on plastics separation from e-waste based on 10 current techniques. Four different separation modes (sensor-based separation, shape/density separation, separation by impact milling, and separation by particle size distribution) were studied, and two—sensor-based and shape/density—generated acceptable plastic separation. Based on the report, near-infrared sortation can separate a mixture of acrylonitrile butadiene styrene and polystyrene into distinct polymer types; however, multiple



Source: Bennett et al. 2009

Figure 19 Typical composition of e-waste

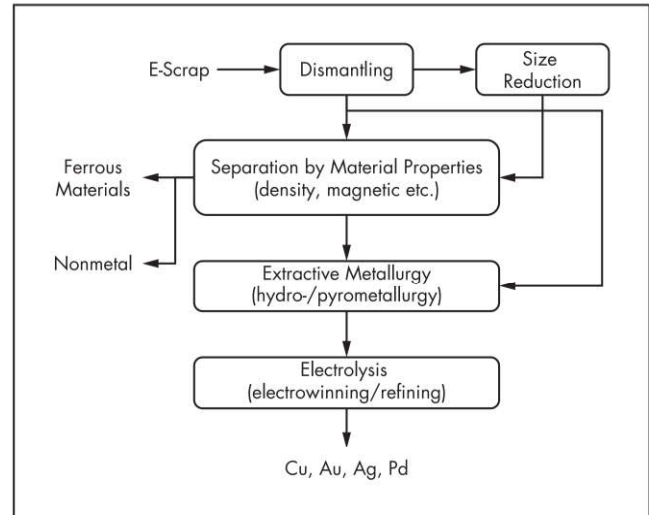
Table 3 Opportunities for e-waste

Material	Kilotons	Million Euros
Fe	16,283	3,582
Cu	2,164	9,524
Al	2,472	3,585
Au	0.5	18,840
Ag	1.6	884
Pd	0.2	3,369
Plastics	12,230	15,043

Source: Baldé et al. 2017

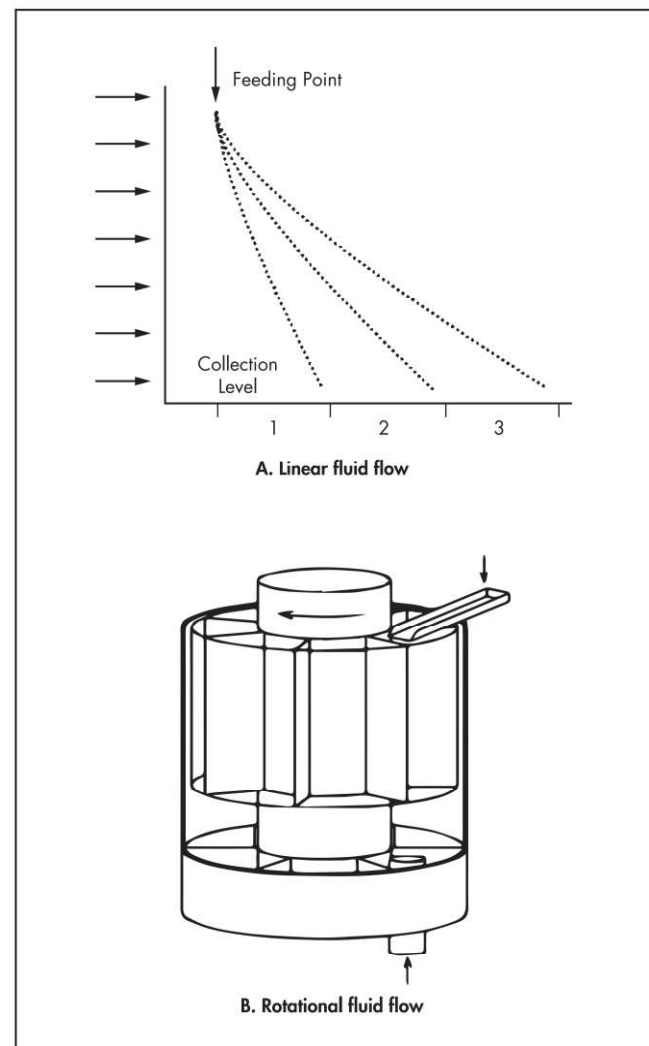
passes are required for a better product purity. Wet shaking tables and upflow separators are also used to recover copper from copper-rich plastic. The wet shaking table can produce a very high-purity copper fraction (95% copper) when the sample size is reduced smaller than 2.3 mm. Upflow separators that utilize the principles of a fluidized bed can separate light, middle, and heavy fractions. When the sample size is reduced smaller than 2 mm by a hammer mill, the percentage of copper recovery is about 94% in the heavy fraction.

Van Kooy et al. (2004) invented a prototype kinetic gravity separator that can separate particles by differences in terminal velocity depending on the particle shape, size, and density. As shown in Figure 21A, the particles with different physical properties can be separated by a horizontal fluid motion. For example, particles that have a high vertical speed will be collected near the feeding point; however, particles settling at a lower speed will be collected far from the feeding point. The researchers reported that nonferrous scrap with particle sizes between 2 and 10 mm can be separated into light and heavy alloys by the kinetic gravity separator. Bennett et al. (2009) also demonstrated that the kinetic gravity separator can be used for copper recovery from plastics, obtaining good metal recovery from the e-waste plastics. The kinetic gravity separator has the advantage of being able to perform a separation using water. Therefore, this method is relatively simple and cheap compared to heavy medium gravity separation, and it is also suitable for separating metals from e-waste plastics.



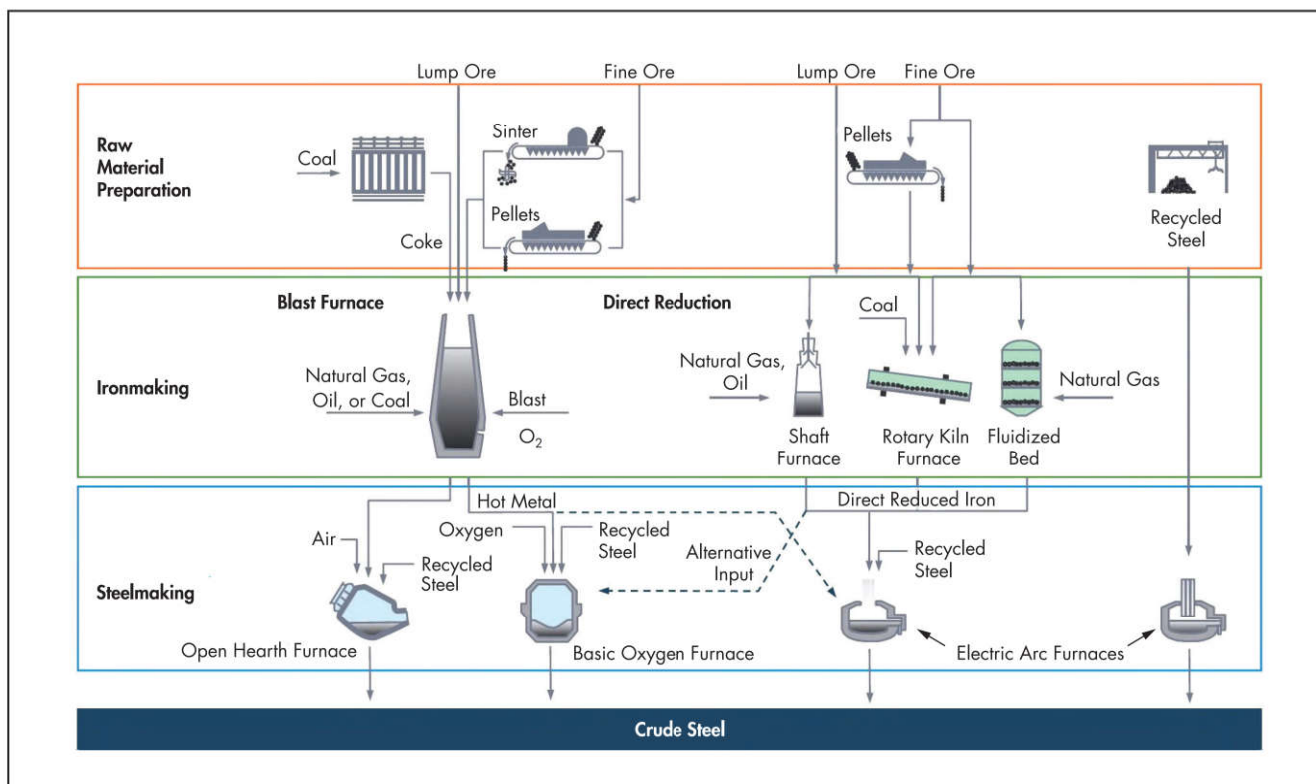
Adapted from Tuncuk et al. 2012

Figure 20 Flow sheet showing the potential process options for recovery of metals from e-scrap



Source: Van Kooy et al. 2004

Figure 21 Principle of kinetic gravity separation



Source: World Steel Association 2015

Figure 22 Steel production routes

Ferrous Scrap Recycling

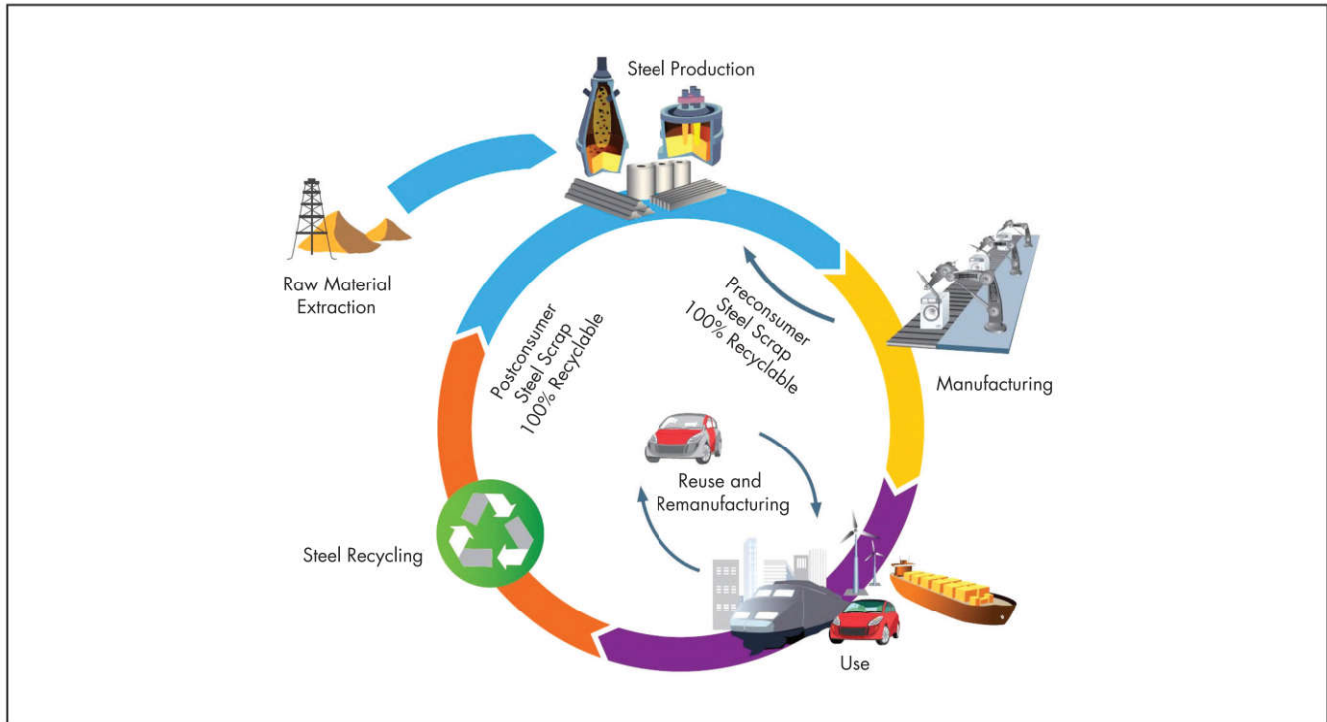
Properties such as formability, durability, and strength make steel the most important engineering and construction material. Additionally, its relatively low price attracts industries related to construction, transportation, energy, packaging, and appliances. Therefore, steel is widely used in many industrial applications. According to the World Steel Association (2015), since 1950, world crude steel production has increased from 189 to 1,621 Mt/yr to meet demand. Steel can be produced from various raw materials including lump ore, fine ore, and recycled steel. Based on the raw materials used, crude steel is produced in many ways. Energy-intensive processes are required for production of steel from ore resources; however, recycled steel is simply remelted in an electric arc furnace during secondary production of steel, as shown in Figure 22. The main advantages of using recycled steel are energy savings and resource conservation. In general, recycling steel saves 74% more energy compared to the primary production of steel and a large amount of iron ore, coal, and limestone. Moreover, steel does not lose its inherent physical properties during recycling processes. For these reasons, steel is the most recycled material worldwide. The overall recycling rate for steel in the United States was 88% in 2012 (World Steel Association 2015). As shown in Figure 23, preconsumer and postconsumer steel scraps are 100% recyclable, and about 650 Mt of steel are recycled annually. The reuse and remanufacturing of steel also contribute to its sustainability.

Bever (1976) summarized ferrous metals recycling, and Fenton (2003) investigated iron and steel recycling in the

United States. Based on their work, ferrous scrap can be categorized as old, new, or home scrap, depending on its generation. In general, old scrap, also known as postconsumer scrap, is generated from automobiles, structures, household appliances, railroads, ships, and other sources at the end of their useful life. Because of the wide range of scrap sources, old scrap has a wide variety of physical and chemical properties. Therefore, old scrap processing often requires shredding and sorting, as shown in Figure 24. During these pretreatment steps, automobiles and other scraps are reduced to fist-size pieces by a shredder. The shredded scrap contains various metals, glass, and plastics. Next, these materials are separated by magnetic separation, eddy-current separation, heavy medium separation, or flotation. For scrap materials that are galvanized or tin coated, a de-zincing or de-tinning step is also required to separate zinc and tin from the steel.

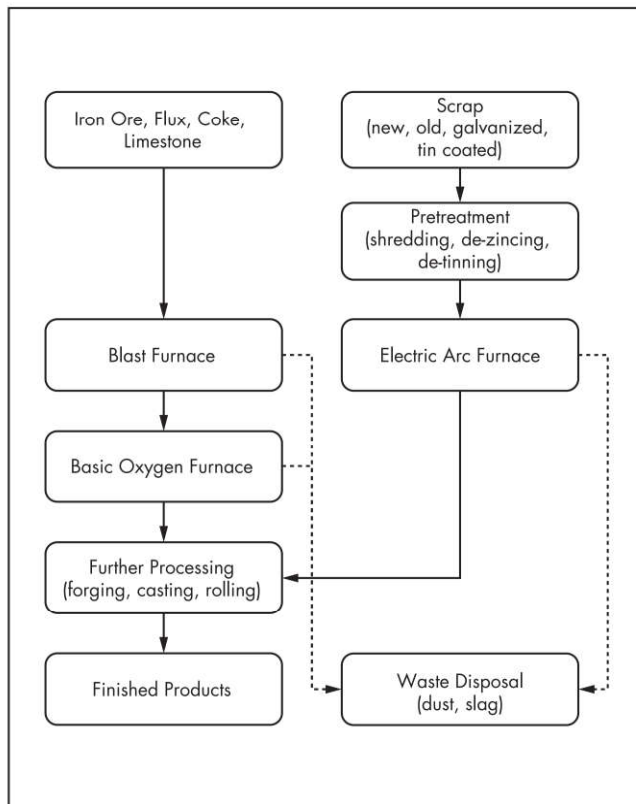
New scrap, also known as prompt scrap, is generated from manufacturing steps such as cutting, drawing, and machining. Typically, the chemical and physical properties of new scrap are already known, and therefore the scrap is transported back to the steel plant for remelting, predominantly at electric arc furnaces, as shown in Figure 24. General Motors (GM) developed a similar process to recycle the clippings generated during automobile body production. GM simply remelts the clippings in an electric furnace and solidifies the molten steel by continuous casting to make gears.

Home scrap, also known as revert scrap, is generated from steel mills and foundries during the production of steel and cast iron. This type of scrap is always recycled by



Source: World Steel Association 2015

Figure 23 Steel's life cycle



Adapted from Rao 2006

Figure 24 Schematic process flow sheet of steel recycling

remelting since the composition of the home scrap is already known. These recycling efforts are critically important from economic and environmental sustainability perspectives in industrial development.

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Flotation
