RECYCLING, METALS

1. Nonferrous Metals

1.1. Introduction. A nonferrous metal is any metal other than iron (qv) or one of the many iron alloys. For the nonferrous metals, recycling of aluminum, copper (qv), lead (qv), and zinc is of primary economic importance. Recycling of any material is dictated by economic factors and production from primary sources may be used as a reference point. The decision to recycle from secondary materials is a dynamic one and must be evaluated on an ongoing basis. The principal factors that determine recyclability include availability of both primary and secondary sources, purity, cost of energy, cost of waste generated, and regulatory environment. Several of these factors are interrelated. The emphasis on recycling has increased the availability of many materials. As natural ore bodies are depleted, the relative availability of waste materials is expected to increase. Two key advantages of recycling are the conservation of resources and protection of the environment (see ALUMINUM AND ALUMINUM ALLOYS; ZINC AND ZINC ALLOYS).

In 2003, the United States recycled 67×10^6 t of metal. Recycling is a significant factor in the supply of many metals used. It provides environmental benefits in terms of energy savings, reduced volumes of waste, and reduced emissions associated with energy savings. Table 1 gives U.S. apparent supply and recycling statistics for various metals. Recycling contributed 66.9×10^6 t to metal apparent supply (50.8% of supply). Aluminum, iron, and steel dominate the apparent supply. By weight, aluminum accounted for the second leading share of metal apparent supply, 5.98% and the second leading share of recycled metal, 4.22% iron and steel are in first place with 88.8% of metal apparent supply and 97% of recycled metal. Measured as recycled metal as a percentage of its own supply, lead was the most recycled metal (80%), the least recycled were tin (19%), and zinc (26%) (1).

Nonferrous metals are primarily used as the metal or in an alloyed form, facilitating the recycle of the metal or alloy because much of the recycling process requires only that the scrap metal be sorted, melted, and cast (pyrometallurgical processing). The scrap is classified into two general categories, new and old. New scrap derives from material that never reaches the market, such as scrap generated during the manufacture of products. Old scrap is obtained from worn out or discarded products. Often, the recycling process consumes only 5–50% of the energy needed to produce from an ore and in most cases generates only a small portion of the waste.

Concurrent with the implementation of the Resource Conservation and Recovery Act (RCRA) significant increases in the recycling of nonferrous metals from metal-bearing wastes occurred. The primary aim of RCRA was to establish hazard definitions for wastes and to maintain an accountability for all generated wastes that were classified as hazardous. The term recycling has no regulatory significance. Some recycling is regulated, some is not. Regeneration, a regulatory subset of reclamation, which itself is a subset of recycling, is regulated (see REGULATORY AGENCIES, CHEMICAL PROCESS INDUSTRY). It has been estimated that there are 222 million t of metal-bearing hazardous wastes produced annually from metal-related industries (2) (see WASTES, HAZARDOUS WASTE TREATMENT).

Metal finishing (see Metal surface treatments; Metal treatments) and plating (see Electroplating; Electroless plating) industries produce over 11 million t of wastewater treatment sludges (3). Although the metal content of these wastes has not been specified, it is expected that reclamation of metals from such sources could account for significant additional resource recovery. These wastes consist primarily of inorganic sludges and solids containing several metals, predominantly present as hydroxides and basic metal salts. A selective analytical survey of one specific waste type, ie, electroplating (qv) sludges (4), found an average metal content of 16.4% copper, 7.5% nickel, and 3.6% zinc where copper was the primary metal. For copper, nickel, and zinc electroplating sludges the metals averaged 8.4, 8.9, and 8.9%, respectively, plus having an average iron and calcium content of 4.4 and 5.4%. Not all metal-containing hazardous waste sludges contain from 8 to 16% copper.

Metal and metallic salt wastes are primarily generated by the electronic, electroplating, metal finishing, and machining industries, and as consumer waste. Significant quantities of metal-containing spent catalysts are also produced by the organic chemical industry. Much of the metal-bearing waste is classified as hazardous by the U.S. EPA under RCRA. This classification may result from characteristics such as corrosivity or toxicity. The classification, however, may also be arbitrarily assigned because of the specific nature of the waste source. The reclamation of metals from these types of wastes presents several regulatory concerns. Many of the concerns and disadvantages to recycling and reclamation of metals from hazardous waste have been presented (4). Often, wastes such as salts, basic salts, and hydroxides are more amenable to hydrometallurgical methods of reclamation.

1.2. Classification of Recycled Materials. The initial step in the recycle of metals is the physical segregation of the metals from other materials. For new scrap this process is straightforward; for old scrap it can be expensive. This classification and segregation of scrap is of importance to the producers of the metals from secondary materials. Historically, much of the classification has relied on hand sorting which can be reliable, but it is labor intensive. The recycling of automotive scrap is illustrative of the techniques that can be used to separate nonferrous metals into broad categories.

Automobile scrap generates almost 20% of old scrap copper yet only contains 10–35 kg per unit (5). The average mass of an automobile, which has a useful life expectancy of 10 years, is 1100 kg. The unit operations normally used in the recycling of automotive scrap are illustrated in Figure 1. Much of the copper, aluminum, and lead in the form of radiators, starters, generators, and batteries is removed prior to shredding. The automobile is shredded into pieces of 10 × 20 cm and air blown to remove fabric and plastic. The iron and steel are removed magnetically. The use of screening and heavy media or eddy-current (or both) separates glass, rubber, and ceramic components from the nonferrous metals. Heavy media separation (HMS) has become quite sophisticated. It relies on flotation (qv) in order to minimize hand sorting. One such HMS system has resulted in a final aluminum content of 99.5% (6). A typical analysis of aluminum isolated with less sophisticated classification techniques from automotive scrap follows. The nonferrous components are collected, baled, and shipped to recyclers.

Metal	Quantity, %
aluminum after remelting	83–97
silicon	0.3–10.0
iron	0.5–0.9
copper	1.0–3.2
magnesium	$<$ 0.05–0.5
manganese	0.1–0.3
zinc	0.1–8.0

1.3. Pyrometallurgical Methods of Recycling. Much of the technology used in the reclamation of metals from metal-bearing wastes was developed by the mining industries. The primary means of recycling metal from metal and alloyed scrap is via pyrometallurgy (see METALLURGY).

Aluminum. The recycling of aluminum scrap offers significantly reduced energy requirements when compared to refining from ore. The energy requirements to produce aluminum from bauxite ore are 222 GJ/t (53,000,000 kcal/t), whereas the analogous requirements from scrap are only 10 GJ/t (2,400,000 kcal/t) (see ALUMINUM AND ALUMINUM ALLOYS). There are several melting techniques used, each having advantages and limitations. Aluminum is very reactive and has a strong tendency to form a dross, ie, an oxide containing entrained metallics, at the surface of the metal. Up to 5% of the molten metal forms dross during processing. The dross produced from the melting and oxidation of pure metal is known as white dross, whereas the dross containing fluxes and impurity metals is called black dross. In order to recover the aluminum from the dross, salts, usually chlorides, must be added. This treatment produces a secondary dross containing alumina, some aluminum metal, salts, and impurities. Disposal of this waste, undergoing increasing restrictions, is becoming a less attractive alternative. Therefore, new technologies are being pursued such as centrifugation (7), flotation, plasma, and arc melting which require no salt addition to recover white dross. Use of these techniques allows for the production of a salable or landfillable black dross (8). Alternatively, salt recovery plants are being installed.

There are several furnaces employed in the melting of scrap aluminum (9). It is common to melt scrap in a standard reverbatory furnace using oil or gas and air/oxygen heating. The flame is applied directly to the scrap. The round-top melter is a high capacity reverbatory furnace having a removable top for ease of charging (10). Up to 100 t of material can be contained in the furnace and over 20 t can be charged at once. A variation of the dry hearth melter is the tower melter where the scrap is preheated by the exhaust gases from the melter. The charge is arranged so that it is conveyed closer and closer to the hearth. This type of arrangement is thermally efficient relative to the round-top melters but requires the use of heavy-gauge aluminum scrap. For the melting of light-gauge scrap, a flotation melter (11) has been used. The flotation melter uses a conical vertical chamber where the exhaust gases from the furnace are recirculated. Light-gauge scrap is introduced to the conical chamber where it is heated. The high velocity of the gases at the narrow exit port of the chamber suspends the scrap whereupon melting falls into the hearth. One of the primary advantages of the flotation melter is that no salts are required. Oxidation of the aluminum is minimized by low retention times at the higher temperatures and by careful control of the burner oxygen content.

Rotary-barrel or vertical cement mixer-type rotary gas- and oil-fired furnaces offer several advantages in the processing of scrap. These can be operated in batch or continuous mode. Salt, ie, a 1:1 mixture of potassium and sodium chloride containing fluoride as a wetter, is usually charged simultaneously to the scrap. The rotation of the furnace allows for the excellent mixing of the two. A broad spectrum of scrap gauge and purity can be processed. These furnaces are simple to operate, require relatively little capital and floor space, are thermally quite efficient, and the throughput can be high. The primary disadvantage to the rotary-barrel furnace is production of relatively high quantities of dross and salts.

Other technologies that attempt to minimize the formation of white dross have been developed. Plasma heating of rotary furnaces has been used since about 1990. The higher attainable temperatures associated with the plasma have resulted in lower dross and salt waste production. More recently, the development of arc heating has resulted in further improvements. It is more energy efficient than the alternative rotary furnace techniques and results in less waste. A comparison of the energy and mass requirements and by-product generation from the fuel/air/oxygen, plasma, and arc processes are given in Table 2 (8).

The processing of used beverage containers represents a significant portion of the recycled aluminum. The material is separated by the consumer and compacted into bales for shipping to the secondary recycler. The bales are crushed and shredded followed by removal of magnetic materials and gravel (see SEPARATIONS, MAGNETIC SEPARATIONS). Delacquering or decoating operations are being used to provide additional heat input into the melting process. A typical used aluminum beverage can (UBC) recycling process is illustrated in Figure 2.

Copper. Metals that cannot be separated from copper (qv) by traditional physical methods, eg, alloys of zinc, tin, and lead, can be eliminated by melting and oxidation. The following general conclusions can be made (3): zinc is removed by reduction to zinc metal followed by fume oxidation and collection; aluminum and iron are removed by air oxidation to slag; lead partitions between the alloy, slag, and vapor, as does tin (vapors are a mixture of lead(II) oxide, sulfide, and chloride, and tin(II) oxide and sulfide and tin chloride); nickel partitions between the slag and metal (outlet is the electrolyte tankhouse bleed); and precious metals are removed during electrorefining.

The common grades of scrap copper are shown in Table 3. No. 1 scrap is usually melted in a fuel-fired, tilting reverbatory furnace and cast or used in the direct production of alloys. No. 2 scrap (88–99% Cu) can be used to produce alloys but more often it is melted and fluxed in a reverbatory furnace. The scrap is also blended with blister copper in the anode furnace of secondary smelters to dilute the lead and nickel in preparation for electrowinning. Tankhouse maximums are 0.13% lead and 0.21% nickel. Before dilution the values often run upward of 0.4% lead and 0.7% nickel. The conditions in the reverbatory furnace are initially oxidizing to remove oxidizable and volatile impurities. Limestone flux is added to produce a slag. The slag is withdrawn and the flame is made reducing in character. The molten copper is poured into anodes for electrorefining. Brass and bronze (low iron) are melted in a rotary induction or gas-fired hearth. The composition is adjusted to specification, first by appropriate charge alloy selection, then by air (O_2) blowing to remove a portion of the zinc, followed by final composition adjustment by adding more alloy scrap, plus possibly tin ingot.

Low grade scrap (15–70% Cu) requires complete smelting, converting, and refining. A general flow for the refinement of low grade copper scrap is shown in Figure 3. The economic recycling of low grade copper scrap and residues requires complete smelting and converting operations. The smelting operation consists of a blast furnace operated under strongly reducing conditions. Alternatively, the top-blown rotary converter can be used to perform both the blast and converter functions to produce the blister copper. The blast furnace operation produces a slag that is low in copper and discardable. The converting furnace (Pierce-Smith, Hoboken, New Jersey) or top-blown rotary is distinctly more oxidizing, giving much lower levels of impurities by selective oxidation, but producing a high copper-containing slag (see COPPER). This slag is usually recycled to the blast furnace.

Blast furnaces are charged through the top with coke, flux (usually iron metal and silica), and scrap while air is injected through tuyeres continuously at the bottom just above the black copper. The coke (100 kg/t slag) burns to maintain furnace temperatures of 1200°C, provides the reductant, and maintains an open border. A charge of 10 t/h is typical. The furnace produces a molten black copper that contains about 80% copper. The zinc, lead, and tin oxides are collected from the off-gas of the furnace in baghouses and a silicate slag containing about 1% of the copper is discarded. Iron reports to the slag and black copper and zinc to the slag and fume.

The top-blown rotary furnace can also be used for smelting, converting, and fire refining. The charge of low grade scrap, silica, limestone, and coke are melted with a burner located above the charge. The melted charge is continuously rotated and the oxygen fuel ratio of the burner adjusted to produce the required level of impurity. The slag is removed and the oxygen ratio is again adjusted to convert the black copper followed by fire refining.

The molten black copper is converted under more oxidizing conditions. Sufficient heat is generated during the oxidation of the iron and zinc to be autothermal. The blister copper contains 96–98% copper with $< 1\%$ nickel, lead, and tin; the remainder is oxygen and sulfur. The blister is fire refined by melting in a hearth furnace under reducing conditions to produce the low oxygen-containing 99% copper. Anodes are poured followed by electrorefining of the anodes to complete the process.

An electric-arc furnace has been used melt low grade scrap and flux (13). Air is introduced for oxidation of impurities. The primary advantages of the electric-arc furnace are that it produces only about 20% of the expected off-gas from a blast furnace, and more completely reduces the charge producing a slag containing low quantities of heavy metals.

Zinc. Secondary zinc metallics are usually melted and selectively drossed or vaporized. Lead is removed from the bottom of the melt as an insoluble and iron forms the intermetallic $FeZn_3$ at the zinc-lead interface. Aluminum forms a top dross intermetallic with iron, $FeAl_3$. Further purification is obtained through distillation. A Pinto furnace is especially capable of removing iron from galvanizer grade top and bottom drosses (14). The Pinto furnace is a cylindrical vessel equipped with agitation that holds about 2 t of molten metal. The melt (650°C) is stirred for 20 minutes. Aluminum is added to form the high melting, low density intermetallic $FeAl_3$. The zinc is separated from the intermetallic by the effects of the agitation. Air is introduced to oxidize the surface of the intermetallic, further separating the zinc from the dross. The dross contains about 10% each of aluminum and iron. The zinc is advanced to a reverbatory furnace for alloying with aluminum.

The zinc retort is a large heated bottle made of silicon carbide and graphite containing about 2500 kg of material (14). One batch per day is common producing 50 t/month of zinc per retort. Oxides are usually not processed in the retorts. Zinc metal or oxide can be produced in the retorts but economics dictate that a specialty zinc dust or zinc oxide is obtained. Dust can be manufactured in a surface condenser at the rate of 1 t/m^3 of volume. For the production of French process oxide, the zinc vapor is burned in air. The residue from the retort is poured out while hot, and depending on conditions may have very little zinc remaining. Energy consumption for the retort is around 15.9 GJ/t (3,800,000 kcal/t).

Muffle furnaces are used to upgrade zinc metallics and dross. A typical muffle furnace is divided into two sections. One section is for melting and the other for vaporizing. Zinc scrap is added to the melting portion of the furnace. High melting point materials are skimmed and screened for metal recovery. Iron reacts with aluminum in the scrap to form the insoluble $FeAl_3$ which is skimmed. The recovered dross contains about 60% zinc and 2–3% lead. The melted zinc flows under a partition to the vaporizing chamber. The vaporizing chamber is usually heated in an upper chamber separated from the vaporizing metal by a muffle constructed of brick. The combustion gas exits into the melting unit. The vaporized zinc is either condensed or burned to the oxide. Aluminum and copper accumulate in the melt, the lead is tapped from under the melt, and the cadmium exits with the zinc. Up to 10 t of the 36-t melt is tapped weekly to produce a high aluminum, high zinc slab that is sold for the production of aluminum diecast alloys. The slab contains 10–30% copper, 15–50% zinc, $< 0.1\%$ chromium, and $< 1.5\%$ the remainder aluminum.

Larvik furnaces are electrically heated muffle furnaces that offer improved thermal efficiency. These are used to treat lower grade zinc residues containing significant quantities of iron such as $FeZn_3$ as bottom dross. Energy consumption is 5.4–7.9 GJ/t (1,300,000–1,900,000 kcal/t). Vapor is superheated by graphite resistors and moves countercurrent to the liquid. As the vapors cool, the melt is heated to near boiling (907°C) as both exit through a reflux column. Lead is refluxed into the melt where it falls to the bottom and is tapped. Materials that do not melt are skimmed. For the production of zinc, care is taken to avoid the addition of aluminum-containing materials which would form a $FeAl_3$ top dross containing high levels of entrained zinc. High boiling point impurities concentrate as they flow toward a tap at the far (high temperature) end of the furnace. A phosphorus-containing flux is added to lower the melting point for tapping. Most of the zinc is fumed off in this end of the furnace leaving an iron alloy containing 10% phosphorus and 2% zinc. A typical Larvik furnace treats 1800 to 2800 t/yr of zinc (14).

Sweating furnaces are used to process heavily contaminated scrap where the lead–zinc–aluminum–copper materials are not alloyed. Both reverbatory and muffle furnaces are used for this purpose. The metals are separated by melting points from organics, nonmetallic residues, and higher melting metals. Commonly, sweating furnaces are used to separate low melting point metals such as zinc, aluminum, and lead. The metals are separated sequentially by melting point, ie, lead (327°C), zinc (420°C), and aluminum (660°C). The energy requirements when sweating lead and zinc are around 753 MJ/t (180,000 kcal/t) of feed, and for aluminum, 1.3 GJ/t (300,000 kcal/t).

1.4. Hydrometallurgical Methods of Recycling. Changes in environmental regulations, notably RCRA, have brought about increased implementation of hydrometallurgical means for metals recycling. Because many of the wastes are classified as hazardous, there are economic incentives to recycle rather than discard such materials. Significant improvements have been realized in the efficiency of hydrometallurgical or aqueous solution-based processing (15). Some of the reasons (16) given by the mining industry for this shift in emphasis from pyrometallurgy to hydrometallurgy are increasing environmental legislation which has had a significant affect on the industry primarily owing to the reduced emission requirements for sulfur dioxide from the smelting of sulfide concentrates, increasing costs to produce suitable grades of concentrates for smelter purposes as the grades of ore continue to decrease, increasing costs of energy and labor, the amenability of complex sulfide ores to processing by chloride leaching, and the relative ease of separations of multimetal materials using hydrometallurgical techniques (17).

This shift in emphasis by the mining industry has led to the development and use of a variety of improved techniques, in particular the commercial availability of several metal specific extractants. These techniques are particularly useful in the separations and recycling of metals from metal sludges and metal salt solutions.

Concentrated waste solutions are obtained from spent metal plating baths and etchants. However, the majority of metal wastes are solids or sludges obtained from the hydrolysis of metal-bearing solutions and industrial process effluents. Most of these water-insoluble wastes are composed of hydroxides or basic salts of the contained metals. For processing by hydrometallurgical routes the materials must be brought into solution usually by acid or ammoniacal or alkaline digestion.

Precipitation. *Hydrolysis and Cementation.* Precipitation is one of the oldest techniques used for metal–metal and metal–solution separations. Precipitation can be illustrated by the following reactions:

$$Cu^{2+} + 2\ Fe^{3+} + 6\ OH^- \xrightarrow{H^+ \text{to pH } 3.5} Fe_2O_3\ (s) + 3\ H_2O + Cu^{2+}$$

$$Cu^{2+} + Fe^0 \longrightarrow Cu^0(s) + Fe^{2+}$$

The first equation is an example of hydrolysis and is commonly referred to as chemical precipitation. The separation is effective because of the differences in solubility products of the copper(II) and iron(III) hydroxides. The second equation is known as reductive precipitation and is an example of an electrochemical reaction. The use of more electropositive metals to effect reductive precipitation is known as cementation. Precipitation is used to separate impurities from a metal in solution such as iron from copper (eq. 1), or it can be used to remove the primary metal, copper, from solution (eq. 2). Precipitation is commonly practiced for the separation of small quantities of metals from large volumes of water, such as from industrial waste processes.

For a sparingly soluble salt, the product of the total molecular concentrations of the ions is a constant for a given temperature. Thus for the dissolution of the electrolyte,

$$\mathrm{A}_n\mathrm{B}_m \rightleftharpoons n\mathrm{A}^{m+} + m\mathrm{B}^{n-} \quad K_{\mathrm{sp}} = [\mathrm{A}^{m+}]^n[\mathrm{B}^{n-}]^m$$

where K_{sp} is the solubility product constant and the brackets denote molar concentrations of the ionic constituents. Although activities of ions should be used in the strictest sense, molar concentrations are most often substituted in dilute solutions. The effects of pH on the solubility of certain metal hydroxides and sulfides are illustrated in Figure 4.

Hydrolysis is the interaction of the ion or ions of a salt with water to produce a weak acid, weak base, or both. When a metal hydroxide is brought into equilibrium with water the following occurs:

$$\mathrm{M(OH)}_n \rightleftharpoons \mathrm{M}^{n+} + n\mathrm{OH}^-$$

From the solubility product data the thermodynamic tendency of a metal hydroxide to precipitate as a function of pH can be determined. The actual solubilities on complex samples must be determined empirically; however, general predictions can be made regarding metal–metal separations by hydrolysis.

Cementation, the removal of a metal ion from solution by reduction of the metal with a more electropositive material, is also known as reductive precipitation. For a simple case the following can be used:

$$\mathrm{M}^{x+} + \mathrm{N}^0 \rightarrow \mathrm{M}^0 + \mathrm{N}^{x+}$$

where N^0 is a more electropositive metal than M^0, and N^{x+} and M^{x+} are the hydrated ions of those metals, respectively. Because the process in water is galvanic, the driving force of the process can be gauged using the standard reduction potentials for the metals in question.

A classic example of cementation is the removal of copper from solution by elemental iron.

$$\mathrm{Cu}^{2+} + 2e^- \rightarrow \mathrm{Cu}^0 \quad E^0 = +0.337\mathrm{V}$$

$$\mathrm{Fe}^{2+} + 2e^- \rightarrow \mathrm{Fe}^0 \quad E^0 = -0.440\mathrm{V}$$

Iron metal preferentially dissolves; the copper does not. Therefore, the anodic and cathodic reactions are as follows, to give the solid copper.

$$\textit{Anodic}\ \mathrm{Fe}^0 \rightarrow \mathrm{Fe}^{2+} + 2\,\mathrm{e}^-$$

$$\textit{Cathodic}\ \mathrm{Cu}^{2+} + 2\,\mathrm{e}^- \rightarrow \mathrm{Cu}^0$$

The potential of the reaction is given as $E^0_{\text{cell}} = (\text{cathodic} - \text{anodic reaction}) = 0.337 - (-0.440) = +0.777\text{V}$. The positive value of the standard cell potential indicates that the reaction is spontaneous as written (see ELECTROCHEMICAL PROCESSING). In other words, at thermodynamic equilibrium the concentration of copper ion in the solution is very small. The standard cell potentials are, of course, only guides to be used in practice, as rarely are conditions sufficiently controlled to be called standard. Other factors may alter the driving force of the reaction, eg, cementation using aluminum metal is usually quite anomalous. Aluminum tends to form a relatively inert oxide coating that can reduce actual cell potential.

Because copper is a relatively unreactive metal it is much more common to remove copper from solution by cementation than it is to cement impurities from solutions of copper. In the removal of copper as an impurity from a more electropositive metal, cementation can be exceedingly useful. It is common practice to cement copper from nickel and zinc electrowinning solutions using nickel and zinc metal, respectively (18). After a chemical or group of chemicals is precipitated from solution, a physical separation must be effected. This is usually accomplished by thickening followed by filtration and washing. Often, the precipitated product (cement) is leached again for purification.

Electrolytic Precipitation. In 1800, 31 years before Faraday's fundamental laws of electrolysis, Cruikshank observed that copper metal could be precipitated from its solutions by the current generated from Volta's pile (19). This technique forms the basis for the production of most of the copper and zinc metal worldwide.

Electrowinning is the deposition of metals from a leach solution by electrolysis where the metal is produced by cathodic reduction. Cementation relies on galvanic potential differences to effect metal reduction. Electrowinning can be considered a form of reductive precipitation, but it must rely on the superimposition of a more negative potential on the system than usually found at equilibrium if the metal is to be deposited at the cathode. Oxidation occurs at the insoluble anode. Cell potentials can be carefully controlled to allow the selective separation of copper from many metals. By contrast, cementation is quite nonselective. Electrorefining differs from electrowinning in that the anodic and cathodic reactions are the reverse of one another. Impure or blister copper metal from fire refining (pyrometallurgical operations) is the soluble anode. The copper ion formed by dissolution of the anode is plated at the cathode.

For many waste streams, electrical efficiencies are compromised owing to the corrosivity of the solution toward the precipitated metals and/or the low concentrations of metals that must be removed. The presence of chloride in the solution is particularly troublesome because of the formation of elemental chlorine at the anode. Several commercial cells have become available that attempt to address certain of these problems (20).

Solvent Extraction. The selective partitioning of metals by liquid–liquid solvent extraction is one of the most powerful methods of hydrometallurgical separation. Solvent extraction can also be used to concentrate dilute metal streams to facilitate further processing. The metal extraction process can be made highly selective or exclusive either by design of the extractant or by the chemical conditions imposed during extraction. An extractant's selectivity or affinity for groups of metals is determined by its electronic and/or steric properties. Alternatively, the aqueous environment supporting the metal ions can be altered by change in pH, electrolyte content, or by the incorporation of complexing agents in the aqueous solution that either compete with the extractant, owing to compound formation in the aqueous layer, or facilitate the separation process (ion pair formation).

In practice the extractant is carried by an aqueous immiscible solvent. The aqueous layer containing the metal ions is contacted (mixed) with the solvent. Depending on conditions, typically pH, certain of the metal ions are extracted into the organic layer. The mixed organic aqueous system is allowed to separate and the metal-laden organic is then contacted by an aqueous solution that strips the metal ion from the organic. Under normal operating conditions extractants do not give absolute metal separation in one stage of contact. Several stages of solvent–aqueous contact are usually required in order to achieve the degree of separations and efficiencies desired. This requires that continuous processing be utilized in order to be economically acceptable.

One of the most common contacting schemes uses the mixer–settler contactor. The organic and aqueous streams are pumped into the mixer continuously where the streams are contacted prior to exiting by overflow into the settler stage. The two phases are given sufficient time in the settler for phase separation. The organic layer, if lighter than the aqueous, overflows a weir at the exit end of the settler and is advanced to the next stage. The heavier aqueous exits the settler, eg, prior to the weir, and is advanced to the next stage or from the system. It should be noted that, in practice, the aqueous always contacts the organic in a countercurrent flow, ie, loaded aqueous contacts lean organic and lean aqueous contacts the stripped organic. This gives optimum multistage efficiency of extraction and stripping. Several other contacting schemes are available commercially and have been detailed (21). Commonly available commercial extractants are detailed in Table 4.

Commercial Hydrometallurgical Process for Multimetal Waste Separation. Many of the wastes that lend themselves to hydrometallurgical recovery are obtained as hydroxide sludges and solutions. Most are highly complex and contain several metals of economic interest. Therefore, a general scheme of processing needs to be developed. Often a combination of technologies is employed if efficient separations are to occur. One such process (22) that has been operated at the pilot-plant level is illustrative of a multistage process scheme for mixed metal hydroxide sludges from the electroplating and metal finishing industries. The process includes recovery stages for copper, nickel, zinc, and chromium. Consideration is given for iron, aluminum, and calcium removal so that the primary metals of interest are not contaminated. No efforts have been expended to recover these secondary materials. A simplified block flow sheet of the process is given in Figure 5.

The primary steps in the process are (*1*) leaching of sludges by sulfuric acid; (*2*) rejection of high iron materials by selective precipitation as jarosite; (*3*) solid–liquid separation of the leachate from the residues and jarosite and disposal of the iron-containing residues; (*4*) separation of the copper from the leach by solvent extraction (hydroxyoxime extractants) followed by electrowinning to metal or crystallization as copper sulfate pentahydrate; (*5*) raffinate from the copper circuit is advanced to a zinc solvent extraction circuit for selective removal of zinc by di-2-ethylhexylphosphoric acid followed by crystallization of the strip liquor to give zinc sulfate; (*6*) the raffinate from the zinc circuit is advanced to an electro- or chlorine oxidation of Cr(III) to Cr(VI) followed by selective precipitation of chromate as the lead salt from lead sulfate; (*7*) the lead chromate is leached in sulfuric acid to generate a chromic acid solution and regenerate the lead sulfate; and (*8*) the nickel remaining in the filtrate from the chromium precipitation is removed by precipitation as the sulfide or hydroxide.

The process and economics are detailed (22). Owing to the complex nature of the wastes, the process becomes economical only at high production volumes. Several alternative schemes could be developed based on available technologies. Of primary importance is a thorough understanding of the types and constituents of the wastes that feed the processes. Once this is defined, the process options must be considered and tested. A knowledge of what the process cannot do, ie, its limitations, is just as important as a clear understanding of process capabilities.

1.5. Economic Aspects. The United States exported 14.2×10^6 t of scrap metal valued at $\$4.45 \times 10^9$ in 2003, while it imported 4.59×10^6 scrap metal valued at $\$1.48 \times 10^9$. Based on the total of recycled exports, iron and steel dominated at 76.6%, nickel was second at 9.96%, aluminum, chromium, and copper accounted for 4% each. Recycled metal imports were dominated by iron and steel (80%), aluminum accounted for 9.60%. See Table 5 for U.S. trade statistics.

Aluminum. In 2004, 3×10^6 t of aluminum was recovered from purchased scrap in the United States. Of this, 60% was from new manufacturing scrap and 40% was from old scrap. Aluminum recovered from old scrap was equal to 19% for consumption (23). In 2003, the rate of recycling of used beverage cans (UBCs) was 50%. The number of cans recycled was 49.9×10^9. For the past 22 of 23 years, the recycling rate was at, or exceeded, 50%. The annual average American Metals Market price for UBCs increased to 50.5 cents/lb in 2003 up from 47.4 cents per pound in 2002. Prices for secondary aluminum ingots also increased (24).

Cobalt. Cobalt-bearing scrap is generated during manufacture and/or after use in the following applications; catalysts used by the petroleum and chemical industries; cemented carbides; rechargeable batteries; superalloys; magnetic and wear-resistant alloys; and tool steels. Depending on the type of scrap, cobalt may be recycled within the industry that generated it. The products of recycled cobalt scrap include: alloys; mixed metal residues; pure cobalt metal; metal powders or chemicals; and tungsten carbide-cobalt powders (25).

In 2003, scrap consumption reported by U.S. cobalt processors and consumers was 2,140 t of contained cobalt, 24% less than the 2,800 t consumed in

2002. U.S. imports of cobalt waste and scrap more than doubled to 482 t, gross weight, valued at $\$4.0 \times 10^6$. Seven countries supplied 90% of this material—the United Kingdom (44%); Ireland (15%); Belgium (12%); Canada, France, and Germany (5% each); and Japan (4%). U.S. exports of cobalt waste and scrap nearly quadrupled to 405 t, gross weight, valued at $\$2.6 \times 10^6$. Most of this material was sent to Canada (30%), the United Kingdom (17%), China and the Netherlands (13% each), Belgium (9%), Sweden (8%), and Japan and Switzerland (5% each) (1).

Copper. Estimated world production of secondary refined copper declined in 2003 for the third consecutive year to 1.75×10^6 t, down from 2.13×10^6 in 2000. The notable exception is China whose secondary output rose by 56,000 t largely due to imports. Secondary refined production continued its downward trend, declining by 17,000 t in 2003. Copper recovered in alloys, chemicals, and powder from scrap declined by 70,000 t (7%). At brass mills, the leading consumer of direct melt scrap, scrap consumption as a total material supply declined by about 2% to 59%. Exports of copper scrap for 2003 totaled 689,000 t up from 511,000 t in 2002. China and Hong Kong were the destinations for 70% of this total. The United States remained the leading source of scrap metal. In 2004, of the total recovered scrap 71% came from brass mills, 5% from smelters, 12% from ingot makers, 12% from miscellaneous sources such as foundries and chemical plants. This scrap contributed to 30% of the U.S. copper supply (26).

Lead. About 82% of the 1.40×10^6 t of refined lead produced in the United States in 2003 was recovered from recycled scrap, of which a major source was spent lead-acid storage batteries. Lead-acid batteries account for 92% of lead produced from secondary sources, leaving 8% from other sources, including building construction materials, cable coverings, drosses, and residues (new scrap) from primary smelter refinery operations and solder.

During 2003, the U.S. exported about 92,800 t of lead-bearing scrap. Imported scrap in all forms equaled 4,970 t. The recovery of lead from spent lead-acid batteries and other lead scrap at secondary smelters was sufficient to meet about 91% of demand in 2003 (1).

Nickel. Austentic stainless steel is the largest source of secondary nickel for the United States, accounting for about 88% of the 93,400 t of nickel reclaimed in 2003. An additional 2% came from the recycling of alloy steel scrap. The combined 90% represents not only scrap used in raw steel production, but lesser amounts of scrap consumed by steel and iron foundries. The remaining 10% falls into several categories, superalloys, copper-nickel alloys, aluminum-nickel alloys, and primary nickel. World demand for primary nickel set a record to 1.23×10^6 t in 2003 (27). Refinery production increased, rising to 1.20×10^6 t, but this could not keep up with the demand.

Japan and China were the leading consumers of stainless steel in 2003, followed by the United States. Russia has been exporting about 400,000 metric tons per year (t/yr) of stainless steel scrap, or about 34,000 t/yr of contained nickel, despite a 15% export duty on the material. In 2003, most of the Russian scrap went to stainless steel operations in Finland, Germany, and Sweden.

U.S. exports of stainless steel scrap rose to 37,800 t of contained nickel from 25,700 t in 2002, an increase of 47%. The increase in exports was driven by higher prices globally for ferrochromium, primary nickel, and key grades of stainless steel scrap. Taiwan was again the leading importing nation of U.S. stainless scrap, purchasing 9,630 t of contained nickel in 2003. The Republic of Korea was second with 6,360 t and was closely followed by China, with 6,210 t.

U.S. industry recycles a broad spectrum of other nickel-bearing materials in addition to stainless steel. Copper-nickel alloy scrap and aluminum scrap accounted for about 5% of the nickel reclaimed in 2003. Scrap in this category comes from a myriad of sources.

The remaining 5% of reclaimed nickel came from nickel-base superalloy scrap and pure nickel metal scrap.

Tin. In 2003, 19% of the domestic apparent supply of tin metal was recovered from scrap (Table 1). Old tin scrap was collected at hundreds of domestic scrap yards, three detinning plants, and most municipal collection-recycling centers. New tin scrap was generated mainly in the tin mills of six steel plants, scores of canmaking facilities, numerous brass and bronze plants, and many solder-making operations.

Detinning facilities are unique to the tin scrap industry in that no other major metal industry has numerous large-scale plants to remove plated metal. Detinning operations are performed on new tinplate scrap from tin mills or canmaking plants and on old tinplate scrap in the form of used tin cans. For most of the past century, the detinning process has been the only technique in the secondary tin industry by which free tin metal returns to the marketplace. The bulk of the secondary tin industry works with the various alloy forms of tin (brass, bronze, and solder); the tin is recycled within its own product-line industries, and this tin reappears in regenerated alloys.

The Steel Recycling Institute (SRI), a business unit of the American Iron and Steel Institute, continued to promote the recycling of used tin cans, which has been an important raw material for the Nation's steel industry during the past 20 years. The SRI announced that the domestic steel can recycling rate had increased slightly in 2003 to 60% compared with 59% in 2002, 56% in 1995, and 15% in 1988 (28).

Zinc. In 2003, about 30% of the world's zinc production was from secondary materials—brass, die casting scrap, flue dust, galvanizing residues, and zinc sheet. In the United States, about one-fourth of the 1.4×10^6 t consumed by domestic industries is secondary zinc. About 85% of recycled zinc was derived from new scrap, generated mainly in galvanizing and die casting plants and brass mills. The remaining 15% was obtained from brass products, flue dust, old die casts, and old rolled zinc articles.

Because of wide differences in the character and zinc content of scrap, the recycling processes of zinc-bearing scrap vary widely. Clean new scrap, mainly brass, rolled zinc clippings, and rejected die castings, usually requires only remelting. In the case of mixed nonferrous shredded metal scrap, zinc is separated from other materials by hand or magnetic separation. Most of the zinc recovered from EAF dust, produced during remelting of galvanized steel scrap, is recovered in rotary kilns by using the Waelz process. Because the most common use of zinc is for galvanizing, the latest research is aimed mainly at stripping zinc from galvanized steel scrap before remelting.

In 2003, trade in zinc scrap was small about 3% of total domestic consumption. About 79% of imported zinc scrap was supplied by Canada, and the major destination of U.S. exports was China (73%), followed by India (20%), and Taiwan (3%). Prices for scrap varied according to quality, presence of other components, geographic location, and environmental difficulties in handling, transporting, or treating.

1.6. Waste Management. Total elimination of metal-bearing wastes is not a likely occurrence owing to process and product requirements and consumer disposal tendencies. On-site waste minimization efforts have been extensive in the industrial sector, however, owing to economic and regulatory driving forces. Local and state programs have had a significant impact on the residential recycling of metal, primarily aluminum, and on glass, plastics, and paper products.

In spite of these efforts, significant quantities of metal-bearing wastes, hazardous or not, continue to be earmarked for disposal rather than reclamation. There are several reasons. Often the wastes are mixed from several process streams, contain relatively low concentrations of many recoverable metals, and may contain high concentrations of water, silicates, and secondary metals, such as calcium and iron.

Although it is generally not practical to eliminate production of the wastes, it is often possible to produce a waste that is more attractive to a reclaimer. Some factors that can be considered are segregation of waste streams, maximization of recoverable metal content and quantity, and minimization of secondary metals, leach insolubles, organics, and chelating agents (see Wastes, Industrial).

Maximization of metal content is usually achieved by removal of water, either through evaporation (qv) or drying, although dilute solutions are often concentrated by other techniques such as precipitation or ion exchange (qv). The choice of precipitant for sludge production can have a significant impact on the metal value. Sludges produced by overtreating with lime may contain very high levels of calcium and low levels of recyclable metals. The controlled addition of lime or the use of sodium carbonate or hydroxide may add significant value to the sludge. The addition of filter aids, sulfides, and carbon usually depresses sludge value and often such treatment can be accomplished in a separate stage to render all but a small portion of the waste recyclable.

Waste exchanges function as brokers for waste and often are able to match generators with recyclers of the waste. A number of public and private waste exchanges have been listed (1,19). There are several commercial operations that reclaim metals from wastes.

2. Ferrous Metals

2.1. Introduction. Recycling of ferrous scrap is a principal worldwide activity where more than 300 million metric tons are consumed annually. Numerous grades of scrap and many technical and economic complexities are involved. The term ferrous metals refers to iron (qv) and steel (qv) scrap materials of three origins: home scrap, generated within the steel mill or foundry, and being a known material of high quality; prompt industrial scrap, produced from trimmings and discards during product manufacture; and obsolete scrap, ie, old scrap from discarded or rejected items. Ferrous scrap supply is roughly estimated at about 25% home scrap, 26% prompt industrial scrap, and 49% obsolete scrap (29). See Table 1 for U.S. recycling statistics.

Primary consumers for ferrous scrap are the iron and steel mills and foundries. Minor consumers include ferroalloy producers, copper producers for use in copper precipitation (see RECYCLING, NONFERROUS METALS), and the chemical industry. The steel industry consumes about three-fourths of the total. Scrap consumption for ferroalloy production, copper precipitation, and the chemical industry total less than one million t. The United States is the leading exporter of ferrous scrap, exporting almost 10.9 million t in 2004, valued at about $1.96 billion (see also Table 5). Total value of domestic scrap purchases and exports in 2004 was $12.9 billion (29).

A comprehensive history of ferrous scrap recycling in the United States beginning in 1646 has been published (30). Some selected events of interest include the first open-hearth steel produced (1868); the first commercial direct-arc electric furnace steel produced in the United States (1906); the first large induction furnace installed in the United States (1914); the first basic oxygen steel produced in the United States (1954); the rise of continuous casters and scrap-based minimills (1965); the first thin-slab continuous caster at a minimill (1989); U.S. exports and imports of ferrous scrap at record highs (1990); and the end of production of open-hearth steel (1991).

Supply and demand of scrap is affected by a variety of factors, including technological advances in iron- and steelmaking and scrap processing, wartime effects such as price controls and export restrictions, economic depressions, and foreign trade in scrap. The open-hearth furnace, which was once a primary part of steelmaking in an integrated plant, was capable of melting up to 100% scrap or any combination of hot metal (molten pig iron) and scrap. Open-hearth steelmaking declined rapidly in the 1980s and was phased out in 1991 in the United States. The lost demand for scrap by this process has been offset by advances in electric arc furnace (EAF) and basic oxygen furnace (BOF) processes. Developments impacting scrap include minimills, continuous casting, and minimill thin-slab casting.

2.2. Sources and Types of Ferrous Scrap.

Home scrap, because it is generated within the plant during the production of steel (qv) or cast iron, has a known composition and is always recycled. Manufacturing facilities and steel service centers produce prompt industrial scrap during preparation to fabricator's specifications and during the fabrication of various industrial, commercial, or consumer products. Prompt industrial scrap is recycled because its chemical composition and physical characteristics are known or readily obtainable. Additional processing of the prompt industrial scrap may be required in some cases. For example, detinning and compacting may be required for new tin-plate scrap to be fully recyclable in the steel industry. Also, the increased use of galvanized steel in automobile manufacture and increasing environmental restrictions on EAF dust may lead to additional processing for galvanized scrap as this material becomes available in larger quantities.

The availability of prompt industrial scrap is directly related to the level of industrial activity. Producers generally do not accumulate prompt industrial scrap because of storage requirements and inventory control costs. Thus, it is rapidly available to the scrap consumer or the ferrous scrap industry. Prompt industrial scrap comes from imported steel as well as domestic steel mill products. Obsolete scrap, also known as old or post-consumer scrap, is widely used. Trends in new steelmaking capacity and the reduced proportions of premium scrap indicate that use of obsolete scrap should be expected to increase.

Descriptions of Primary Ferrous Scrap Grades. There are more than 100 distinct grades or codes for ferrous scrap listed by the ISRI (31). Some have similar grade descriptions but differ in physical size, form, unacceptable items, and certain chemical limitations. The ISRI descriptions form the basis for many detailed specifications negotiated between the scrap supplier and scrap customer. These are typically more elaborate and definitive regarding acceptable quality for a particular user's plant. Using the ISRI and other sources, descriptions and comments for some of the most commonly used grades are given herein (32,33).

Low Phosphorus Plate and Punchings. This scrap, a prompt industrial scrap consisting of punchings or stampings, plate scrap, and bar croppings, has uniform known chemical analysis, is clean, and has high furnace recovery (yield) when melted. Maximum allowable phosphorus and sulfur contents are 0.05% each. Other unwanted residual elements are also uniformly low. Size limitations are specified.

No. 1 Busheling. This scrap is a clean prompt industrial scrap limited to about 30 cm (12 in.) in any dimension. It includes new factory busheling such as sheet clippings and stampings (free of old auto body and fender stock); metals which have been coated, limed, or vitreous enameled; and electrical steel containing more than 0.5% silicon.

No. 1 and Electric Furnace Bundles. No. 1 bundles produced at the plants where scrap is generated are designated No. 1 industrial or No. 1 factory bundles. This prompt industrial scrap consists of light-gauge sheet (no coated, rusted, or incinerated steel) tightly compacted to dense bales and having a bulk density of at least 1200 kg/m^3 (75 lb/ft^3). Bundles produced in a dealer's plant from prompt scrap collected at the scrap generating plant are designated No. 1 dealer bundles. Electric furnace bundles are smaller bales suitable for foundry use.

Cut Structural and Plate. A premium scrap at least 0.6 cm (1/4 in.) thick which is prepared in different lengths, this consists of clean structural shapes, crop ends, ship scrap, and shearings having maximum phosphorus and sulfur contents of 0.05% each. It is frequently marketed as prompt scrap.

No. 1 Heavy Melting Steel. Wrought iron and/or steel scrap ≥ 0.6 cm (1/4 in.) in thickness is available in three grades according to size limitations. Although not usually considered a premium grade, it is available in all primary scrap markets. Because of its wide use over many years, No. 1 heavy melting scrap is commonly used as a bellwether or reference grade for pricing purposes and various analyses of scrap use, price, and availability.

No. 2 Heavy Melting Steel. Supplied in more than one grade form based on length and width requirements and a minimum thickness of about 0.3 cm (1/8 in.), this scrap is lower quality than No. 1 heavy melting. There is the possible inclusion of a wide variety of items such as alloy steels and coated materials.

No. 2 Bundles and Other Bundles. This scrap is officially described as old black (uncoated) and galvanized steel. It is hydraulically compressed to a suitable size for furnace charging and weighs at least 1200 kg/m^3 (75 lb/ft^3). It is free of tin or lead coated or vitreous enameled material and may include household appliances and other obsolete light-gauge items. It may be designated as No. 3 bundles if a significant amount of coated materials are present. Steel can scrap obtained from a municipal waste incinerator and compressed into dense bales is referred to as an incinerator bundle. Other bundle designations include Terne plate bundles, bundled No. 2 steel, and silicon bundles, depending on the specific items contained.

Railroad Rails. A relatively high quality scrap is generated by railroad rails. There are some variations in chemical analysis, however, depending on when the rail was produced.

Turnings and Borings. This scrap grade is a broad description for the fragments generated when machining steel (turnings) and cast iron (borings). There are several distinct grades that include only steel turnings in the loose, crushed, or briquetted form; similar forms from mixtures of turnings and borings; and loose or briquetted borings. Turnings and borings are generated as prompt industrial scrap, but are commonly unsegregated and nonuniform in quality. Uniform higher quality turnings and borings are available at a higher price. Possible contaminants include elements from alloy steels; machinability additives such as bismuth, tellurium, lead, and sulfur; nonferrous machining fragments; and water and oil.

Slag Scrap. Steelmaking slag scrap consists of irregular-sized nuggets of steel recovered magnetically from crushed steelmaking slag. Depending on the steels produced and scrap used during the steelmaking process, this scrap may have various alloying or tramp residuals. Ironmaking slag scrap is a high carbon iron magnetically recovered from crushed blast furnace slag. The metallic portion of this scrap has a uniform chemical analysis and is desirable for iron foundries.

Shredded or Fragmentized. This scrap is predominantly shredded automobiles and light trucks. It may include scrap from other products such as appliances. The Institute of Scrap Recycling Industries, Inc. (ISRI) specifications describe two grades, one having a higher average density resulting from more effective shredding. This also allows the magnetic separators and air classifiers to achieve a better separation of the ferrous material from the nonmagnetic fractions. Shredded scrap is widely used in steel mills and iron foundries.

Machinery and Cupola Cast Iron. This designation combines two cast-iron grades known as drop broken machinery cast and cupola cast. The former consists of clean, heavy machined cast iron that has been broken into pieces suitable for cupola charging. Cupola cast consists of a wide variety of cast-iron scrap, including automobile blocks and parts from agricultural and other machinery, in sizes suitable for the cupola. Machinery and cupola cast-iron scrap are primary sources of scrap for the iron foundries.

Cast-Iron Borings. Several grades of cast-iron borings and drillings that are free of steel turnings, lumps, and rusted material are called cast-iron borings. Some are supplied in hot or cold briquetted form to specified densities. Oil and water limits may be specified also.

Motor Blocks. Automobile and truck motors prepared to varying degrees of quality constitute a grade of scrap called motor blocks. The higher quality grades are stripped blocks from which most of the steel and nonferrous and nonmetallic parts are removed and the blocks are broken to cupola size. Degreasing the scrap further improves its quality.

Scrap Sources and Processing. More than 5000 scrap processing facilities in the United States purchase scrap from individuals and businesses and prepare it to specification for delivery to the mills, foundries, and other consumers of scrap (34). Most of the scrap preparation facilities are small, but there are also large, corporate-owned plants having numerous employees and the capability to collect and process large amounts of scrap. Processing of scrap involves sizing as required by the consumer and sorting to take advantage of alloy content and control residual elements.

The primary types of equipment used in scrap preparation are shredders, shears, and balers. Shredders capable of reducing automobiles, appliances, and other scrap to small fragments (fist-size) are common. Shears are used to cut large pieces of scrap into sizes as needed for convenient handling by the mill, foundry, or other scrap consumer. Balers are used to compact light-gauge material into rectangular bundles for easy handling and furnace charging. Some large automotive and appliance stamping plants have their own equipment to prepare scrap for direct shipment to steel mills. Others collect the scrap for removal by the scrap facility that buys the scrap. Considerable coordination is required to assure proper scrap segregation so that the highest scrap value and consistent supply is maintained.

During 2003, steel recycling rates were 103% for automobiles (over 100% indicates more steel recovered than is used for a new vehicle), 96% for construction structural beams and plates, 90% for appliances, and 60% for steel cans, nearly 71% overall (36).

Automobiles are the largest source of obsolete scrap. Other important sources of obsolete scrap include the demolition of steel structures and railroad companies. The latter provide a steady flow of scrap from their fabricating shops and from the recovery of worn out or abandoned track and railroad cars. All iron and steel products are recyclable if economically retrieved when scrapped.

Modern shredding and upgrading techniques are factors in the widespread acceptability of automobile scrap. Each vehicle contains about 70% or one ton of recoverable iron and steel scrap (35). Most scrap autos go through dismantling operations to remove discrete salvageable items such as the battery, radiator, alternator, and catalytic converter. The dismantled autos are typically flattened to increase bulk density and the number of units per shipment to the shredding plant. Shredding has become the primary auto scrap recycling process. The scrap industry in the United States operates more than 200 shredders having a total annual shredded scrap output of over 14 million t (1). Shredders reduce the autos to several centimeters or fist-size fragments. The shredded material is processed through air classifiers, magnetic separators, liquid media operations, and sometimes manual sorting to upgrade scrap quality. Quality improvements have led to wide acceptance of shredded scrap by domestic and overseas consumers, which is reflected in its price. The price is consistently higher than No. 1 heavy melting steel scrap, the bellwether grade used in large quantities. ISRI estimates that more scrap automobiles are recycled each year than were produced by the three principal U.S. automobile producers in that year. Nearly 14 million t of ferrous scrap were recovered from automobiles and light trucks in 2004 (1).

Shredding operations may also include appliances (white goods) which are being recycled in increasing quantities at least partly because of the banning of appliances from landfills in many states.

Municipal solid waste (MSW) provides some forms of recyclable ferrous scrap, but the quality and markets are limited. The need to maximize recycling and minimize landfill disposal is forcing increased recovery of combustibles for energy and mixed ferrous scrap for recycling. This includes municipal source separation and curbside pickup programs, materials recovery facilities (MRFs), waste-to-energy (WTE) incinerators, and landfill mining. The industry and recovery of materials for recycling have been growing steadily in terms of the amount of MSW diverted from landfills for recycling and composting. The trend is expected to continue as many states and municipalities establish recycling laws and goals for recycling and waste reduction (qv) (37). The ferrous metal content in MSW ranges from about 5 to 10% (38) and consists mostly of steel beverage and food cans. Steel cans are recovered in increasing quantities in curbside programs, MRFs, and WTE operations. The recovery rate of steel cans has increased steadily to 34% in 1991 to 60% in 2003 (1).

Construction and demolition (C&D) debris is a large source of recyclables. Ferrous materials in C&D debris are typically reinforcing bars, wire mesh, and structural steel. Some of the scrap is sold for recycling once concrete is effectively removed and the scrap is sized to specification (39).

2.3. Primary Uses of Ferrous Scrap. All wrought steel is produced by basic oxygen furnace (BOF) and electric-arc furnace (EAF) processes. The steel industry consists of two principal types of steelmaking facilities: integrated plants, which use blast furnaces, BOFs, and EAFs, and specialty plants and minimills, which use EAFs exclusively. The integrated steel plants begin the steelmaking process with iron ore, which is reduced in blast furnaces and converted to molten pig iron, also known as hot metal. Hot metal is transferred to a BOF where scrap is added and refining takes place. Final refining and alloy additions to produce the desired grade of steel follow. The proportion of scrap added to the BOF is typically 10–30% of the total metal charge and averaged about 26% in 2003 (34,40). Some integrated plants also have electric-arc furnaces for converting scrap to certain specialized grades of steel.

EAF-based plants were once used primarily to produce highly specialized grades of steel, such as stainless and tool steels. The EAF-based minimill steel industry has assumed a principal role in production of a variety of carbon-steel grades, once the exclusive domain of integrated steel producers. EAFs are used as rapid scrap melting devices producing steel from nearly 100% scrap charges. Refining is limited and obtaining the desired grade of steel product depends on the quality of scrap and other charge materials. Addition of pig iron or direct reduced iron (DRI) (see IRON BY DIRECT REDUCTION) during EAF steelmaking may be required to obtain the desired chemical compositions and limit residual elements. Pig iron is a high carbon metal produced in blast furnaces and, for a given plant, has uniform chemical composition. Carbon content is about 4% or higher and residual metal concentrations are low. DRI is produced from iron ore and is about 86–88% metallic iron. Unreduced iron oxides and other oxides from the original ore remain as a gangue which may require special slagmaking additions in some furnace processes. DRI and the hot briquetted form of DRI (HBI) is very uniform in quality with only trace levels of undesirable metal residual elements making it useful for blending with lower grade, lower priced scrap.

Ferrous foundries consist of two types: steel foundries in which electric furnaces (EAF and induction) are used, and iron foundries in which hot-blast cupolas and/or electric furnaces are used. Electric furnaces use virtually 100% scrap charges. Cupolas are shaft furnaces which use preheated air, coke, fluxes, and metallic charges. Scrap is over 90% of the metallic charge.

In 2003, BOFs were used to produce 49% of total steel in the U.S. while using only 26% of total scrap consumed. During the same period, EAFs produced 51% of total steel while using 72% of total scrap consumed. Scrap was also melted in blast furnaces and other types of furnaces (40).

Residual Elements. Residual elements, a principal concern to scrap users, have been the subject of many studies to identify sources, effects on product properties, and means of elimination or control. Steelmakers need to control several elements associated with scrap in order to meet the quality requirements of their final products. Copper and tin are of particular concern because these are not volatile, oxidizable, or otherwise refinable by normal furnace practice. Dilution using virgin materials or prime quality scrap may be required to obtain the desired chemical composition. These elements, in relatively small concentrations, degrade the hot workability and deep drawing quality of many steels. Other elements such as chromium, nickel, and molybdenum affect various mechanical properties. Cast irons are produced in several classes, such as gray iron, malleable iron, and ductile iron, each having specific microstructural characteristics that are critical for meeting product specifications. Low concentrations of lead, tin, or arsenic, for example, inhibit desirable graphite structure in ductile iron. Copper, which is useful in promoting a desirable pearlitic structure in gray iron, also promotes pearlite formation in ferritic ductile irons, causing serious loss of product ductility. Whereas the effects of individual elements may be known, interactions of two or more elements are difficult to determine. Volatile elements such as zinc and cadmium are of concern because these may significantly increase the costs of particulate control and disposal. Relatively large samples of scrap (eg, $\geq 20\,t$ lots) have been melted to obtain homogenized melt analysis for the presence and concentrations of residual elements. Some mills have also devised back-calculation methods to determine scrap quality in use and as a means of monitoring scrap sources. Analyses of scrap have been published by various investigators over many years. These can be misleading, however, if used to indicate the expected analysis of a given grade of scrap from all suppliers and at different periods of time. Although these data can be useful in indicating the general level of some of the residual elements found in various types of scrap, in practice the actual compositions can vary widely, particularly in obsolete scrap. Table 6 shows concentrations for some residual elements obtained for scrap samples (32,33).

The steel mills and foundries consume many different grades of scrap. Scrap grade and price must be balanced with overall economics of use. Such factors as metal yield during melting and uniformity of quality regarding desired physical form and chemical analysis are important. The primary users' products must meet strict chemical and physical quality requirements and, although scrap generally offers the most economical form of iron units, proper selection and blending is essential to assure acceptable final product quality. Prompt industrial scrap has historically been very uniform having known or obtainable chemical analysis and is thus in high demand. Obsolete scrap is typically very heterogeneous. Chemical analysis of this scrap is not practical on a routine basis. Chemical acceptability of many grades of obsolete scrap are based on user experience and relationship with scrap suppliers.

Four scrap grades dominate purchases by steelmakers. These are No. 1 and No. 2 heavy melting steel, No. 1 and electric furnace bundles, and shredded scrap. Three grades having a combined average of more than 50% represented the principal purchases by steel foundries: low phosphorus plate and punchings, cut structural and plate, and No. 1 heavy melting steel. Iron foundries made significant purchases of four grades averaging about 50% of the total: low phosphorus plate and punchings, cut structural and plate, shredded, and No. 1 busheling. All three industries purchased many other grades in smaller quantities. The primary obsolete grades such as No. 1 heavy melting steel and shredded have higher residual content than prompt industrial scrap, but tend to be relatively predictable in uniformity and productivity in the users' plants.

2.4. Economic Aspects. Total value of domestic purchases (receipts of ferrous scrap by all domestic consumers from brokers, dealers, and other outside sources) and exports was estimated to be $\$12.9 \times 10^9$ in 2004, up about 35% from that of 2003. Manufacturers of pig iron, raw steel, and steel castings accounted for 89% of scrap consumption by the domestic steel industry, using scrap together with pig iron and direct-reduced iron to produce steel products for the construction, transportation, oil and gas, machinery, container, appliance, and various other consumer industries. The ferrous castings industry consumed most of the remaining 11% to produce cast iron and steel products, such as motor blocks, pipe, and machinery parts. Relatively small quantities of scrap were used for producing ferroalloys, for the precipitation of copper, and by the chemical industry; these uses totaled collectively less than 1 million tons.

Raw steel production in 2004 was an estimated 99.2×10^6 tons, almost 6% more than that of 2003; capacity utilization was up by 10% from that of 2003. Net shipments of steelmill products were estimated to be about 104×10^6 tons compared with 96.1×10^6 tons for 2003. The domestic ferrous castings industry shipped 8.3×10^6 tons of all types of iron castings in 2003 and an estimated 1.1×10^6 tons of steel castings, including investment castings, according to the latest available information (29).

The third quarter of 2003 displayed near-record levels of real economic growth, about 8% annualized. Growth continued with strength through 2004. U.S. apparent steel consumption, an indicator of economic growth, remained at about 107×10^6 tons from 2001 through 2003 the lowest amount since 1995, from a peak of 120×10^6 tons in 2000. However, it rose to an estimated 125×10^6 tons in 2004. Scrap prices increased steadily through 2003 and the first quarter of 2004, but moderated in the second and third quarters. Hot-rolled steel prices and the producer price index for steelmill products rose during 2003 and the first three quarters of 2004. Steelmill capacity utilization also increased steadily during 2003 and through 2004 to a peak of 97.3% in September 2004. This record performance supported forecasts of a steadily improving domestic economic recovery (29).

Ferrous scrap prices were significantly higher, on average, during 2004 than in 2003. Composite prices published by averaged about \$219 per metric ton in 2004. The average price for nickel-bearing stainless steel scrap delivered to purchasers in Pittsburgh was about \$1,450/ton in 2004, which was significantly higher than the 2003 average price of \$881/ton. Exports of ferrous scrap increased from 11×10^6 tons during 2003 to about 12×10^6 tons in 2004. Export scrap value increased from $\$2.0 \times 10^9$ in 2003 to an estimated $\$2.8 \times 10^9$ in 2004 (29).

The main trade flows of scrap are from the heavily industrialized and developed countries of North America and Europe to lesser developed steelmaking countries. The United States was the leading exporting country of iron and steel scrap in 2003, as reported by the International Iron and Steel Institute (41), followed by Germany, Japan, Russia, the United Kingdom, France, Ukraine, and the Netherlands. The most significant importing nations were, in decreasing order of importance, China, the Republic of Korea, Belgium and Luxembourg, Spain, Germany, France, and Taiwan (42). See Table 5 for recycling trade statistics.

The U.S. trade surplus for all classes of ferrous scrap was 7.2×10^6 t in 2003. Total U.S. exports of carbon steel and cast-iron scrap went to 64 countries and totaled 9.4×10^6 t. The largest tonnages went to China, the Republic of Korea, Mexico, and Canada. Total U.S. exports of stainless steel scrap went to 44 countries and consisted of 505,000 t. The largest tonnages went to Taiwan, the Republic of Korea, and Finland. U.S. exports of alloy steel scrap (excluding stainless steel) were shipped to 50 countries and consisted of 892,000 t. The largest tonnages went to China, Mexico, and Canada.

2.5. Standards. The most comprehensive set of descriptions of ferrous scrap are published by ISRI. Individual steel mill and foundry consumers usually follow the ISRI specifications, although many also incorporate specific requirements tailored to the needs of the consuming facility.

Scrap from municipal refuse may be in the form of source-separated steel cans, a mixed ferrous fraction, metal magnetically separated from mixed waste or incinerator ash, and C&D debris. An ASTM specification (E1134-86) was developed in 1991 for source-separated steel cans. The Steel Recycling Institute has a descriptive steel can specification entitled “Steel Can Scrap Specifications.” Published standards for municipal ferrous scrap also include ASTM E701-80, which defines chemical and physical test methods, and ASTM E702-85 which covers the chemical and physical requirements of ferrous scrap for several scrap-consuming industries.

Iron and steel products must meet increasingly strict quality standards, requiring the steel and foundry industries to have strict control over their raw materials. Iron and steel producers continually seek scrap of uniform consistent quality. Because most forms of obsolete scrap are heterogeneous, scrap consumers rely on scrap origin, reliability of the scrap supplier, and specifications tailored to their particular plants to assure acceptable quality.

2.6. Environmental and Regulatory Aspects. Ferrous scrap recycling provides many well-documented environmental benefits including reduced roadside litter, landfill requirements, and pollution and energy consumption compared to use of virgin materials. Use of scrap for steelmaking results in large reductions in air pollution, water use and pollution, mining wastes, and energy consumption while also conserving iron ore, coal, and limestone. The savings in landfill space is also considerable. Recycling operations do, however, generate certain emissions and waste streams that are being subjected to increasingly stricter environmental controls, thus increasing the cost of recycling in many cases.

Regulations affecting metal recycling are numerous, including comprehensive regulations resulting from the Clean Air Act Amendments of 1990 (CAA), the Clean Water Act, the Resource Conservation and Recovery Act (RCRA), and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA/"Superfund"). RCRA and CERCLA have the most impact on metals recycling (43). Under RCRA, solid wastes are regulated separately as hazardous (Subtitle C) or nonhazardous waste (Subtitle D). One source of controversy is the disincentives to recycling that result when recyclable scrap is designated as waste. Such a designation results in higher costs for transportation, processing, storage, and disposal. Definition of waste is an issue also in international agreements on export and import of scrap and wastes. An example is the Basel Convention which was designed to prevent international shipments and improper management of hazardous wastes and prevent developing countries from becoming waste depositories for developed countries. The Basel Convention, negotiated under the auspices of the United Nations Environmental Program (UNEP), was signed by more than 100 international states and has been in force since May 5, 1992 (44). The main concern to recyclers is that hazardous waste is not well defined. The criteria for waste used may not be realistic, and there is a lack of distinction between recyclables and waste for disposal. Ferrous scrap metals may fall outside Basel Convention rules. Considerable dialogue is in progress to assure proper understanding and definition of waste and recyclables and avoid unnecessary prohibition of scrap shipments.

EAF dust is regulated as hazardous waste because of the presence of unacceptable levels of contaminants such as lead, cadmium, and chromium. Furnaces that use large amounts of galvanized scrap generate dust from which zinc can be recovered and recycled. Regulations require that the dust be processed for recovery if it contains $\geq 15\%$ zinc. Dust containing $<15\%$ zinc must either be processed for recovery or be stabilized for disposal. Dusts from BOF operations fall into the low zinc category and recovery economics for zinc from these dusts are not as favorable as for the higher zinc contents in EAF dusts. EAF furnaces in the United States generate about 16.5–18 kg of dust per ton of steel produced, or about 600,000 t/yr. The average zinc content is 19%. About 86% of the dust is processed for zinc recovery, 2–3% is used in fertilizers, and the balance is landfilled (45). An international assessment reported that ~30% of the dust generated worldwide is processed for the extraction of heavy metals and recovery of zinc. The estimated cost of treating the dust is more than $200/t, and various research projects are underway to develop more cost-effective technologies for treating furnace dust and for dezincing scrap before melting (46,47) (see ZINC AND ZINC ALLOYS).

The recycling of automobiles has eliminated a former blight and is a significant source of scrap. However, new regulations are requiring adjustments at scrap processing facilities. In order to control smoke from shredders, for example, costly filters and scrubbers have been installed. The shredder residue, or fluff, produced during shredding operations has received special attention. There is concern about contaminants such as PCBs, lead, and cadmium. Studies on fluff material and scrap industry interaction with the United States EPA have indicated that fluff does not warrant regulation (43) but it represents another cost to shredder operators. Another problem is the presence of as many as 30 different types of plastics that are nonrecyclable in the mixed state. The amount of fluff has been increasing owing to increased use of nonmetallics in automobile manufacturing. Without recovery and recycling the only viable disposition is disposal. Alternative methods of disposal are being researched, including recovery of recyclable materials, chemical fixation, and energy generation (see Fuels from waste). The amount of fluff generated per vehicle is about 250–340 kg (500–750 lbs) (45, 48,49).

Radioactive scrap has the potential to become a serious problem domestically and internationally. Several accidental meltings of ferrous scrap containing discrete radioactive sources have occurred in the United States. Clean-up costs have averaged over $1 million per incident. The problem has been formally addressed by ISRI and by the United States Nuclear Regulatory Commission (50). Irradiated scrap has also received attention by the United States Department of Energy (DOE), which sponsored tests to develop technologies for decontaminating and recycling scrap metal from commercial and DOE nuclear facilities (see Nuclear reactors) (51).

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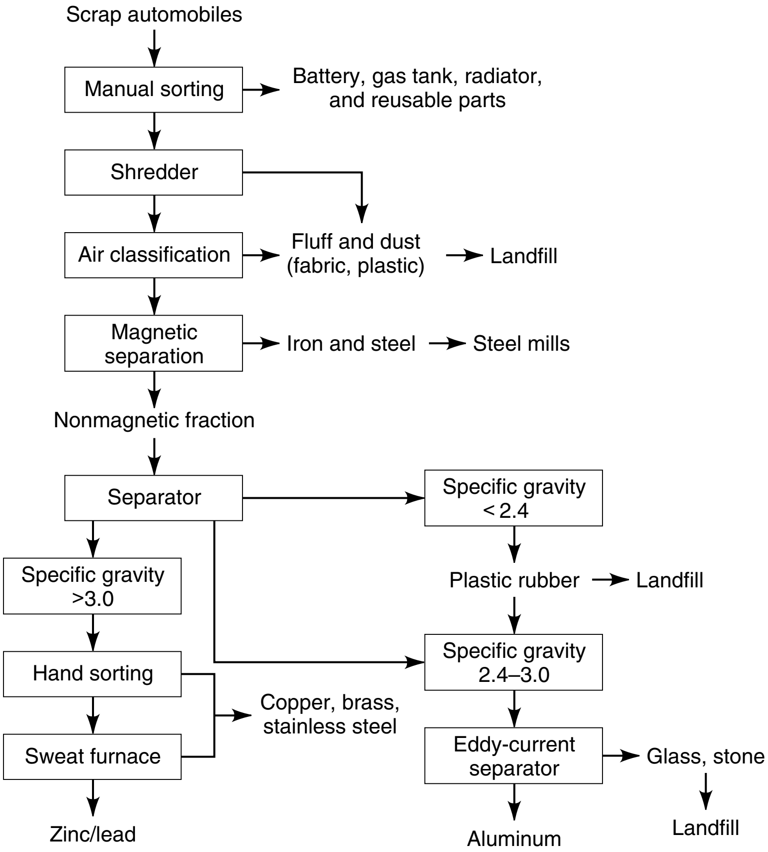

Fig. 1. Unit operations and industrial usage for the recycling of automotive scrap.

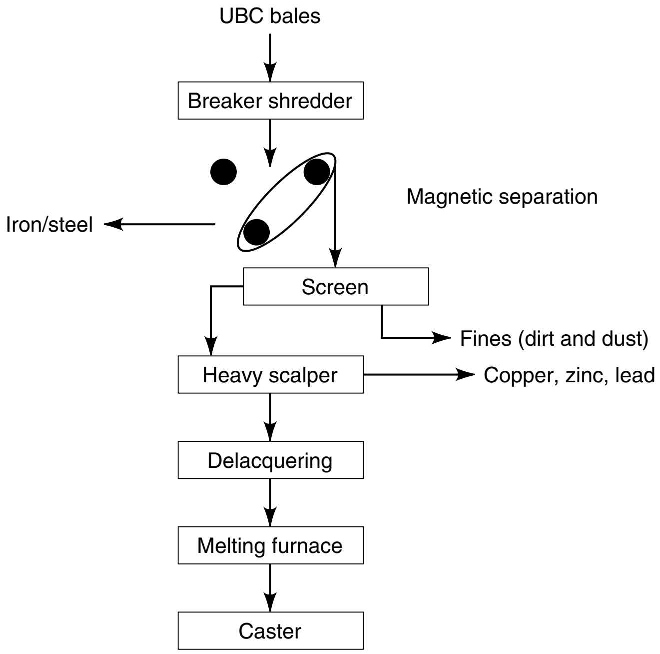

Fig. 2. Used aluminum beverage cans (UBC) recycling process.

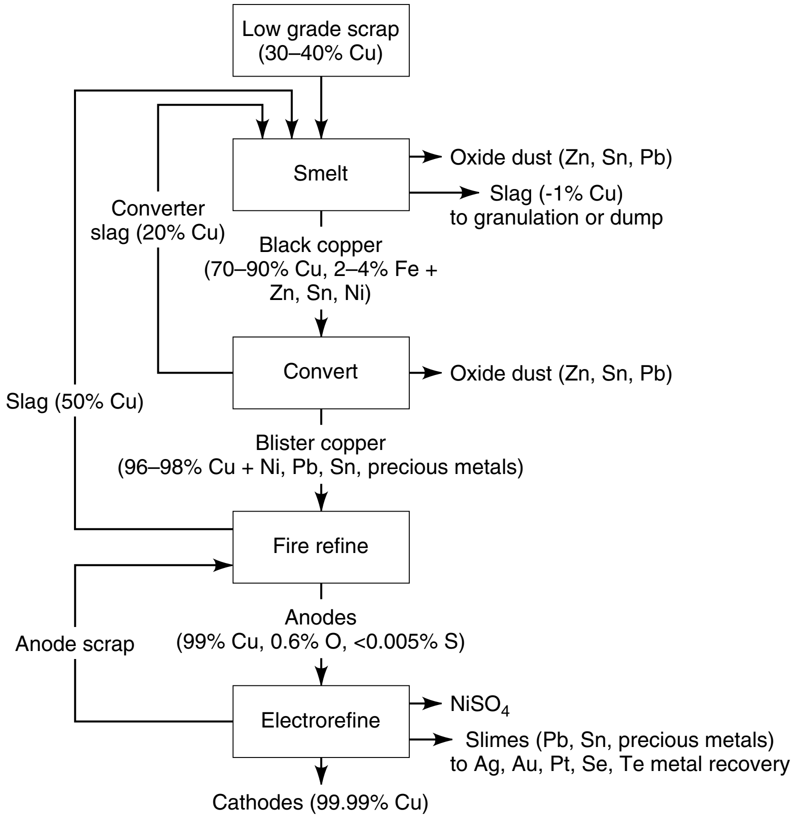

Fig. 3. General flow for the refinement of low grade copper scrap.

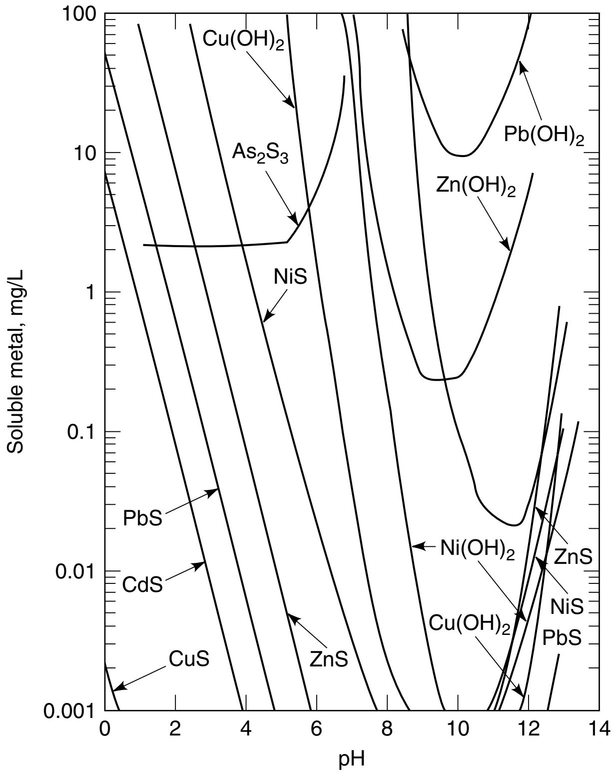

Fig. 4. Effects of pH on the solubility of metal hydroxides and sulfides.

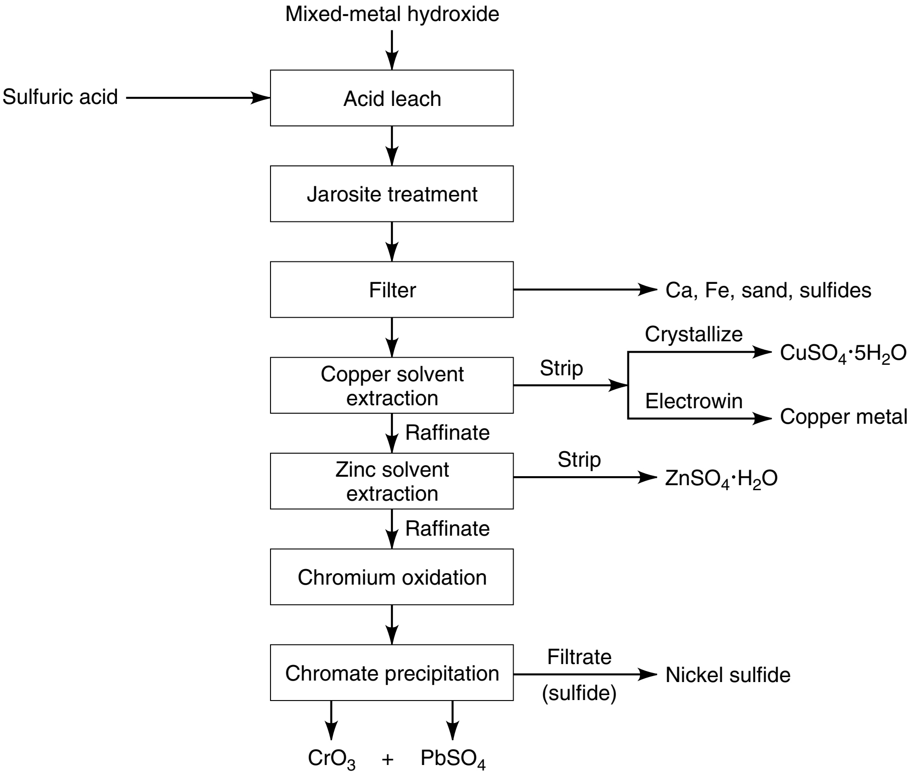

Fig. 5. Diagram showing a suggested commercial process for the separation of metal values from a multimetallic waste.

Table 1. **Salient U.S. Recycling Statistics for Selected Metals**^{a,b}

	Quantity of metal, ×10^3 t					Value of metal, ×10^6\$			
Year	Recycled from new scrap^c	Recycled from old scrap^d	Recycled^e	Apparent supply^f	Percentage recycled	Recycled from new scrap^c	Recycled from old scrap^d	Recycled^e	Apparent supply^g
					Aluminum				
1999	2,120	1,570	3,700	9,890	37	3,070	2,280	5,350	14,300
2000	2,080	1,370	3,450	9,610	36	3,420	2,260	5,670	15,800
2001	1,760	1,210	2,970	7,990	37	2,670	1,830	4,500	12,100
2002	1,750	1,170	2,930	8,070	36	2,510	1,680	4,190	11,500
2003	1,750	1,070	2,820	7,880	36	2,620	1,610	4,230	11,800
					Chromium				
1999	na	na	118	437	27	na	na	77.70	377
2000	na	na	139	589	24	na	na	98.60	423
2001	na	na	122	437	28	na	na	70.90	272
2002	na	na	137	481	29	na	na	75.00	284
2003	na	na	129	468	27	na	na	99.20	391
					Copper				
1999	949	381	1,330	4,080	32.5	1,590	637	2,220	6,820
2000	955	358	1,310	4,050	32.5	1,860	697	2,550	7,860
2001	833	317	1,150	3,340	34.4	1,410	536	1,950	5,660
2002	842	208	1,050	3,450	30.4	1,410	348	1,760	5,770
2003	738	206	944	3,170	29.8	1,390	387	1,770	5,950
					Iron and steel				
1999	na	na	71,000	130,000	55	na	na	6,680	12,300
2000	na	na	74,000	134,000	55	na	na	7,100	12,800
2001	na	na	71,000	118,000	60	na	na	5,320	8,880
2002	na	na	69,000	119,000	58	na	na	6,390	10,200
2003	na	na	61,300	117,000	52	na	na	10,500	25,000
					Lead				
1999	42.7	1,050	1,090	1,790	60.9	41.20	1,010	1,050	1,730
2000	35.5	1,080	1,120	1,790	62.6	34.10	1,040	1,080	1,720
2001	47.3	1,040	1,090	1,700	64.1	45.50	1,000	1,050	1,640
2002	34.8	1,070	1,100	1,540	71.4	33.40	1,030	1,060	1,480
2003	33.9	1,100	1,140	1,430	79.7	32.70	1,060	1,100	1,380
					Magnesium				
1999	52	34.2	86.1	224	38	178	117.00	294	766
2000	52.2	30.1	82.3	199	41	158	90.80	248	601

2001	38.6	27.2	65.8	151	44	106	75.00	181	416
2002	47.1	26.4	73.6	148	50	126	70.50	196	395
2003	44.7	25.1	69.8	152	46	107	60.20	168	366
					Nickel				
1999	na	na	71	211	34	na	na	427	1,270
2000	na	na	84	231	36	na	na	725	1,990
2001	na	na	102	230	44	na	na	604	1,370
2002	na	na	106	227	47	na	na	720	1,540
2003	na	na	93	211	44	na	na	899	2,030
					Tin				
1999	8.65	7.72	16.40	57.30	29	70.40	62.80	133	466
2000	9.14	6.56	15.70	54.50	29	74.40	53.50	128	443
2001	7.21	6.70	13.90	46.30	30	24.40	29.90	54.3	316
2002	3.79	6.76	10.60	49.10	22	18.40	40.60	59	307
2003	2.46	5.42	7.88	40.90	19	na	na	na	na
					Titanium				
1999	na	na	21.90	w	55	na	na	28.9	na
2000	na	na	18.50	w	50	na	na	38.2	na
2001	na	na	17.00	w	39	na	na	35.2	na
2002	na	na	11.60	w	40	na	na	25.6	na
2003	na	na	14.30	w	46	na	na	48.0	na
					Zinc				
1999	321	78	399	1,610	24.8	379	92.20	471	1,900
2000	369	70	439	1,630	26.9	454	90.00	544	2,020
2001	317	57	375	1,420	26.4	307	55.20	362	1,380
2002	319	47	366	1,420	25.8	272	40.30	312	1,210
2003	295	50	345	1,340	25.8	264	45.10	309	1,200

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[a] Ref. 1.

[b] Estimated. na = Not available, w = Withheld to avoid disclosing company proprietary data.

[c] Scrap that results from the manufacturing process, including metal and alloy production. New scrap of aluminum, copper, lead, tin, and zinc excludes home scrap. Home scrap is scrap generated and recycled in the metal producing plant.

[d] Scrap that results from consumer products.

[e] Metal recovered from new plus old scrap.

[f] Apparent supply is production plus net imports plus stock changes. Production is primary production plus recycled metal. Net imports are imports minus exports. Apparent supply is calculated on a contained-weight basis.

[g] Same as apparent supply defined in footnote *f* above but calculated based on a monetary value.

Table 2. **Aluminum Dross Treatment Using Three Rotary Furnace Technologies**[a,b]

	Rotary furnace type			
Treatment	Air/$O_{2/fuel}$	Plasma	Arc	Centrifuge
energy, kWh				
input	630	475	473	350
loss	294	341	160	180
by-product residues, kg	625	566	525	520
recovered aluminum, kg (%)	475 (95)	453 (90.5)	475 (95)	480 (96)

[a] Refs. 7 and 8.

[b] For production from 1000 kg of 50 wt % free aluminum.

Table 3. **Purchased Scrap Categories and Treatment Methods**[a]

Scrap type	Composition, %	Most common recycle treatment
No. 1 copper wire and heavy scrap	99+ Cu	melted and fire refined, cast in shapes for rolling or extrusion or as ingots for sale
No. 2 wire, heavy and light scrap	88–99 Cu	melted, fire refined, and electrorefined; electrorefined cathodes used for all applications
leaded yellow brass scrap	~65Cu, ~35Zn, ~1Pb	melted to form new brass, alloy composition adjusted with copper or zinc and lead
yellow and low brass including cartridges	65–80 Cu, 35–20 Zn	melted to form new brass, alloy composition adjusted with copper or zinc
low grade scrap and residues	10–88 Cu	smelted and converted to remove Al, Fe, Sn, and Zn then fire and electrorefined
automobile radiators		same as No. 2 scrap
red brass scrap	80–85 Cu, 10 Zn, 7 Pb, 3 Sn	melted and cast as ingot for subsequent alloymaking
bronze scrap, nickel-copper scrap, and other alloy scrap		melted to form similar alloy

[a] Ref. 12.

Table 4. **Commercially Available Extractants**

Type	Examples	Uses
	Acid complexes and chelating extractants	
alkylaryl sulfonamide	LIX34	copper extraction from acidic leach liquors
alkyl phosphoric acids	di-2-ethylhexyl phosphoric acid (DEHPA)	uranium and europium extraction, nickel–cobalt separation
alkyl phosphonic acids	2-ethylhexylphosphonic acid mono-2-ethylhexylester	nickel–cobalt separation
alkyl phosphinic acids	Cyanex 272	nickel–cobalt separation
alkyl thiophosphinic acids	Cyanex 301, 302	nickel–cobalt separation
aryl sulfonic acids	dinonyl naphthalene sulfonic acid	magnesium extraction
carboxylic acids	naphthenic and versatic acids	copper–nickel separation, yttrium recovery
β-diketones	Hostarex DK16, LIX54	copper extraction from ammoniacal solution
hydroxyloximes	LIX63, 84, 860	copper and nickel extraction
	P5000 series	copper extraction
	MOC-45, -55TD, -100TD	copper extraction
oxines	Kelex 100, 120	copper extraction
	Ion-pair extractants	
oxines	Kelex 100, 120	copper extraction
secondary amines	LA-1 and LA-2 Adogen 283	uranium extraction proposed for vanadium and tungsten extraction
tertiary amines	various alamines, in particular Alamine 336	widely used, uranium cobalt extraction, tungsten, vanadium, cobalt–nickel separation
quaternary amines	various adogens, in particular Adogen 381	various uses, uranium cobalt, etc
	Aliquat 336	vanadium, possibly chromium, tungsten, and uranium
	Adogen 464	similar to Aliquat 336
phosphine oxides, alkyl	Cyanex 921, 923, 925	recovery of uranium, tin, arsenic from copper
pyridine dicarboxylate	CLX50	copper extraction from chloride leach liquors

Table 5. **Salient U.S. Recycling Trade Statistics for Selected Metals**[a,b]

	Exports			Imports for consumption		
	Quantity, $\times 10^3$ t			Quantity		
Year	Gross weight, t	Contained weight, t	Value, $\times 10^6$\$	Gross weight	Contained weight	Value, $\times 10^6$\$
Aluminum						
1999	419	na	445	615	na	666
2000	576	na	648	625	na	744
2001	580	na	588	497	na	552
2002	613	na	603	466	na	502
2003	577	na	633	440	na	496
Chromium						
1999	262	46.5	168	75.2	20.3	84.3
2000	469	80.8	323	66.1	19.5	94.9
2001	439	75.6	281	50.5	15.4	74.1
2002	343	59.0	259	88.5	21.2	92.2
2003	505	86.7	394	97.7	23.7	115
Copper						
1999	315	250	366	136	108.0	167
2000	485	395	537	144	112.0	186
2001	534	439	538	115	91.10	144
2002	511	407	509	100	80.3	128
2003	689	558	664	90.6	70.7	124
Iron and steel						
1999	5,560	5,560	755	4,020	4,020	427
2000	5,810	5,810	1,020	3,630	3,630	419
2001	7,530	7,530	1,150	2,810	2,810	298
2002	9,000	9,000	1,300	3,320	3,320	403
2003	10,900	10,900	1,960	3,690	3,690	556
Lead						
1999	117.0	117.0	22.0	13.20	10.90	6.10
2000	71.6	71.6	13.2	13.40	12.10	5.14
2001	108.0	108.0	24.9	10.70	10.00	4.26
2002	106.0	106.0	23.3	2.88	2.57	1.74
2003	92.80	92.80	23.3	4.97	4.60	2.46
Magnesium						
1999	16.50	16.50	46.50	6.78	6.78	7.69
2000	6.40	6.40	17.50	9.89	9.89	16.40
2001	6.95	6.95	18.60	11.00	11.00	19.20
2002	5.85	5.85	14.70	14.10	14.10	20.90
2003	5.04	5.04	11.80	16.20	16.20	22.00
Nickel						
1999	842	33.7	306	285	10.30	84.5
2000	1,310	53.1	538	446	12.30	137.0
2001	1,070	51.0	533	252	9.65	95.0
2002	1,070	42.2	506	358	10.20	107.0
2003	1,410	50.9	704	230	12.00	138.0
Tin						
1999	8.61	8.61	8.80	2.730	2.730	2.530
2000	5.91	5.91	5.29	2.340	2.340	4.460
2001	3.23	3.23	4.64	3.700	3.700	1.860
2002	5.94	5.94	9.74	0.561	0.561	0.736
2003	5.04	5.04	8.63	0.921	0.921	0.686

Table 5. (*Continued*)

Year	Exports			Imports for consumption		
	Quantity, $\times 10^3$ t			Quantity		
	Gross weight, t	Contained weight, t	Value, $\times 10^6$\$	Gross weight	Contained weight	Value, $\times 10^6$\$
			Titanium			
1999	8.13	8.13	11.70	6.870	6.870	19.5
2000	5.06	5.06	12.70	7.550	7.550	24.1
2001	7.50	7.50	18.30	11.600	11.600	41.2
2002	6.00	6.00	14.20	6.270	6.270	17.8
2003	5.32	5.32	29.20	5.550	5.550	19.7
			Zinc			
1999	23.500	na	18.6	26.6	na	13.1
2000	21.900	na	12.8	36.5	na	16.2
2001	26.800	na	14.2	39.3	na	11.6
2002	19.800	na	11.2	31.2	na	9.5
2003	32.800	na	23.3	10.3	na	5.7

[a] Ref. 1.

[b] Revised. na = Not available.

Table 6. **Residual Elements in Samples of Scrap, wt %**

Scrap grade	Chromium	Copper	Nickel	Molybdenum	Tin
ironmaking slag scrap	0.05	0.05	0.02	0.01	0.005
No. 1 busheling	0.04	0.07	0.03	0.01	0.008
electric furnace bundles	0.10	0.07	0.07	0.02	0.010
plate and punchings	0.06	0.09	0.06	0.01	0.015
railroad, rails, etc	0.07	0.09	0.07	0.01	0.015
cut plate and structural	0.09	0.13	0.09	0.02	0.025
No. 1 heavy melting steel	0.10	0.25	0.09	0.03	0.025
shredded scrap	0.14	0.22	0.11	0.02	0.02
No. 2 heavy melting	0.18	0.55	0.20	0.04	0.04
No. 2 bundles	0.18	0.50	0.10	0.03	0.10
turnings and borings	0.40	0.20	0.40	0.15	0.015