3 Iron Unit Recycling

On a weight basis, steel is the most recycled material in use today (Figure 3-1). The 70 million net tons of steel recycled in 2000 were used to produce about 112 million net tons of new steel in the United States. Traditionally, the steel industry has focused on recycling steel that is either discarded during manufacturing processes or recovered from post-consumer products. Modern steelmaking now relies on recycled iron units for more than half of its production.

The by-products of iron and steelmaking processes and several categories of steel scrap are also a source of recycled iron units. This includes iron containing by-products which may also contain "low grade" energy units. Examples include oxide dusts, sludges, scales, slags and spent refractories, all of which are generated as natural adjuncts to iron and steelmaking processes. These by-products often are classified as "wastes" and are discarded in landfills at a significant cost, although they offer significant value when recycled and properly reused.

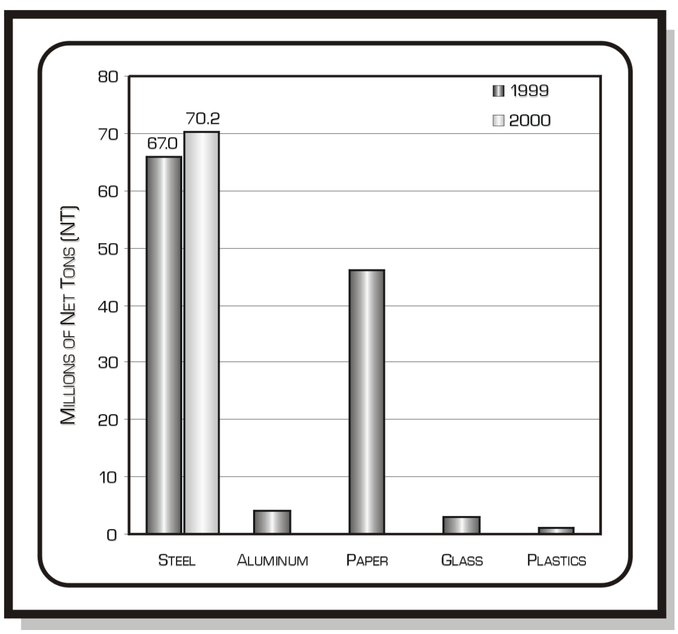

Figure 3-1. Comparison of U.S. Recycling Rate of Steel and Other Materials, 1999-2000 (SRI 2001)

R&D efforts are needed to enable the steel industry to further increase the recycling of iron units. To plan an effective strategy for this work, it is useful to examine each of the recyclable iron unit sources:

- **By-products** are the residues produced during ironmaking, steelmaking, and rolling operations. These residues include slags, dusts, sludges, and mill scale and constitute almost 7% of steel production (the individual process values are shown in Table 3-1). Currently, about 50% of this volume is recovered and recycled; limitations are set by the relatively low intrinsic monetary value of some of these chemically and/or physically complex materials.

TABLE 3-1. SLAGS, DUSTS, SLUDGES AND SCALE GENERATION

U.S. 1999 in 1,000NT Except Where Otherwise Indicated

		Annual Production*
Iron Making	Blast Furnace	51,000
Steel Making	BOF	57,700
	EAF	47,300

Process	Slag Generation**			Dusts, Sludges, & Scale Generation***			
	Rate	Annual		Rate	Annual		
		Total	Fe****	(Dry)	Total	Fe****	Zn
Blast Furnace	460 lb/NTHM	11,700	170	40 lb/NTHM	1,040	450	35
BOF	215 lb/NT Steel	6,200	1,320	50 lb/NT Steel	1,465	805	75
EAF	170 lb/NT Steel	4,000	1,010	36 lb/NT Steel	850	300	215
Ladle Treat	20 lb/NT Steel	800	30	< 1 lb/NT Steel	23	5	0.15
Casting & Rolling				70 lb/NT Steel	3,670	2,400	
TOTALS		22,700	2,530		7,048	3,960	325

* Carbon and Alloy Steels, AISI Annual Statistical Report (1999)

** Based on Data from US Geological Survey and Industry Estimates

*** Based on Data from Steel Recycling Institute and Industry Estimates

**** Contained in the Waste Product

- **Home Scrap** is generated within steelmaking plants. This category includes left-over pieces of steel from steelmaking, iron and steel recovered from slag processing, and defective or rejected products at the mill, e.g. crop ends, side trimmings, and other process related yield losses.

- **Prompt Scrap** is steel scrap generated during the manufacture of steel products. Examples of this type of scrap include punched-out pieces of steel sheet from the manufacture of appliances, turnings from the manufacture of screws and bolts, skeleton scrap from the production of can ends, and side trimming from the manufacture of hoods and bumpers at auto stamping plants.

- **Obsolete Scrap** is the steel scrap contained in post-consumer products. This category includes such diverse items as discarded cars, appliances, construction materials, containers (including steel cans), other durables, and steel scrap recovered from municipal waste.

As shown in Figure 3-2, home and prompt scrap are already being recycled at a rate close to 100%. In contrast, only slightly over half of the iron units available from by-products are currently recovered, and just over three-quarters of those available from obsolete scrap are now recycled. Figure 3-3 provides an overview of iron unit generation and recycling by source.

In absolute terms, by-products offer the potential to recycle an additional 3.5 million tons of iron units. With further research, development, and demonstration, the industry should be able to exploit this opportunity to a significant extent and recover many additional iron units.

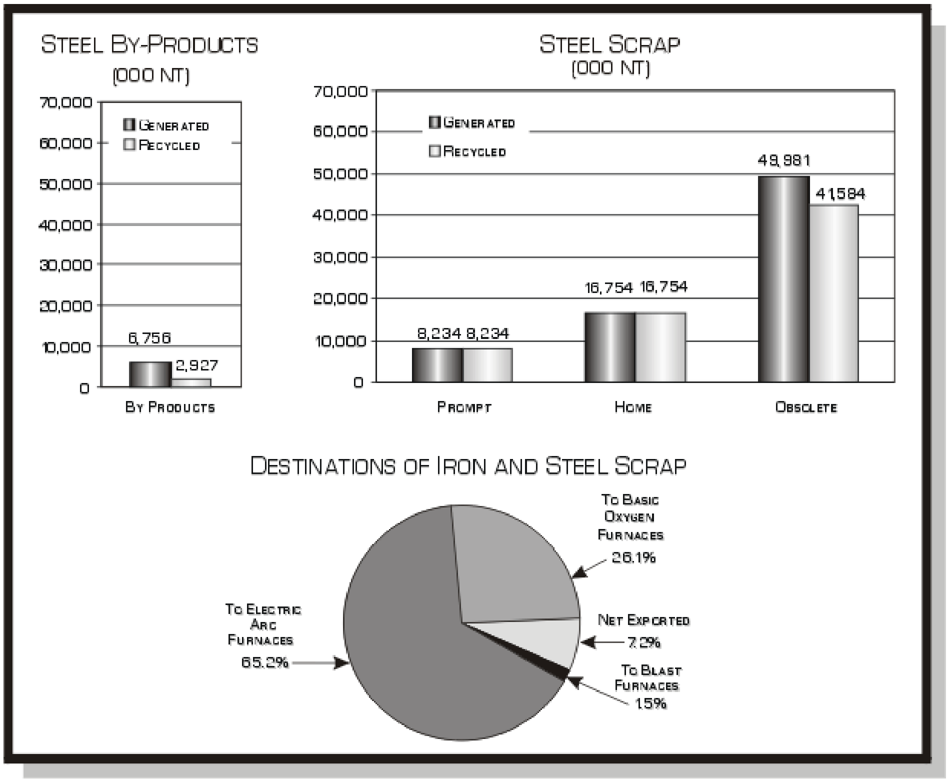

Figure 3-2. Status of Iron Unit Recycling, U.S. 2000 (SRI 2001)

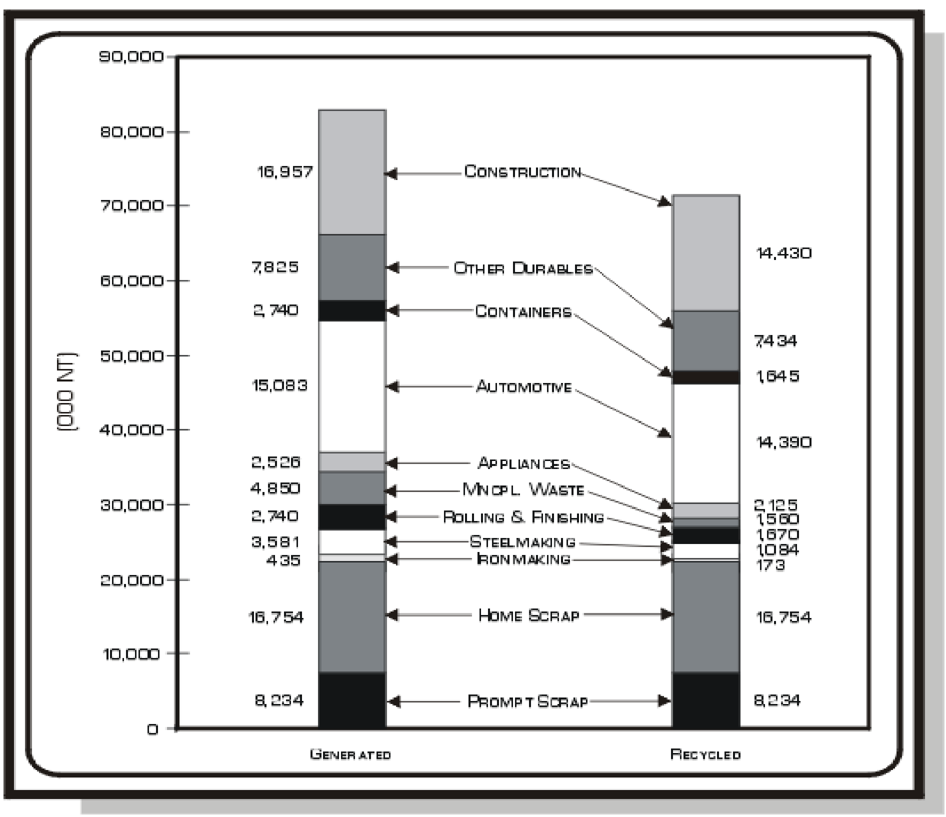

Figure 3-3. Recycling Iron Units by Source, U.S. 2000 (SRI 2001)

One advantage of focusing on this source is that most aspects of by-product generation**,** such as transportation and treatment (or storage), are under the control of the steel industry. In addition, many technologies that may assist in this effort are already under development. For these reasons, by-products are considered the best near-term, and technologically most viable opportunity to increase iron unit recovery in the steel industry.

In comparison to by-products, obsolete scrap offers an even larger opportunity in terms of volume: 8.4 million tons of iron units that have the potential to be recovered and recycled. However, the near-term prospects for exploiting this potential are less promising due to technical and economic factors. Most of the unrecovered iron units in obsolete scrap are embedded in materials from which they cannot be economically extracted using current technologies. Moreover, the design of products in which iron units are embedded is generally not under the direct control of the industry. Nevertheless, certain subcategories of obsolete scrap do offer opportunities for increased iron unit recycling.

The remainder of this chapter explores the opportunities for increased iron unit recycling from by-products and obsolete scrap. The quantities and characteristics of the materials and their current treatment options are described. Existing issues or barriers to recycling are discussed, and research priorities are identified as much as possible.

3.1 By-Products

Iron and steel mills in the United States presently generate approximately 30 million tons of residues each year (containing nearly 7 million tons of iron units, Figure 3-4). These residues consist of slags, dusts and sludges, mill scale, spent pickle liquor, and other iron-bearing materials. Although many additional tons of residues, mostly slags and "fixed" dusts and sludges, have been stockpiled at mills over the years, substantial progress has been made only recently in retrieving and utilizing some of these materials. As shown in Figure 3-4, the operations that produce these residues are steelmaking, rolling and finishing, and ironmaking. Recycling tonnage in Figure 3-4 refers to that recycled for iron unit recovery only. In addition, significant quantities are recycled for other applications described later in the text. Research leading to reduced generation of by-products during steelmaking operations is highly desirable.

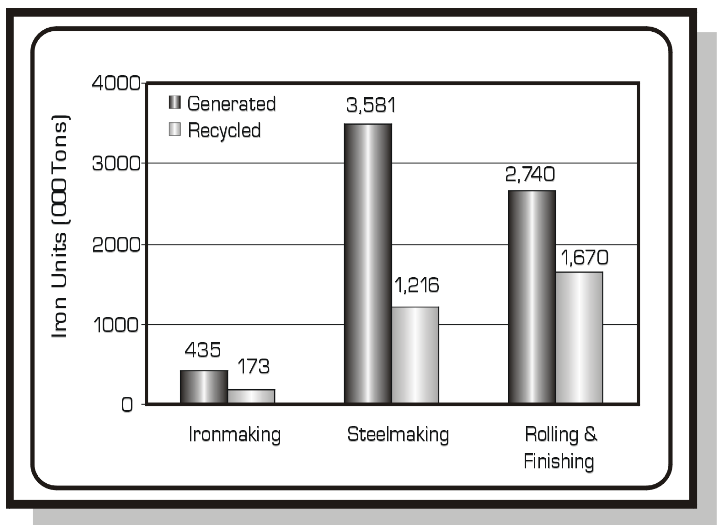

Figure 3-4. By-product Iron Units, U.S. 2000 (SRI 2001)

During the past decade, major progress has been made in the recycling and use of some of these residues, particularly blast furnace and steelmaking slags. Although significant quantities of residues are landfilled, this option has become increasingly costly. For example, the disposal of residues presently costs integrated steel producers $7 to $10/net ton of material for in-house landfilling and at least $20 to $30/net ton for non-hazardous commercial disposal. For material classified as hazardous under RCRA, charges range up to $150/net ton in addition to costs for stabilization (which further increases the volume to be placed in landfill).

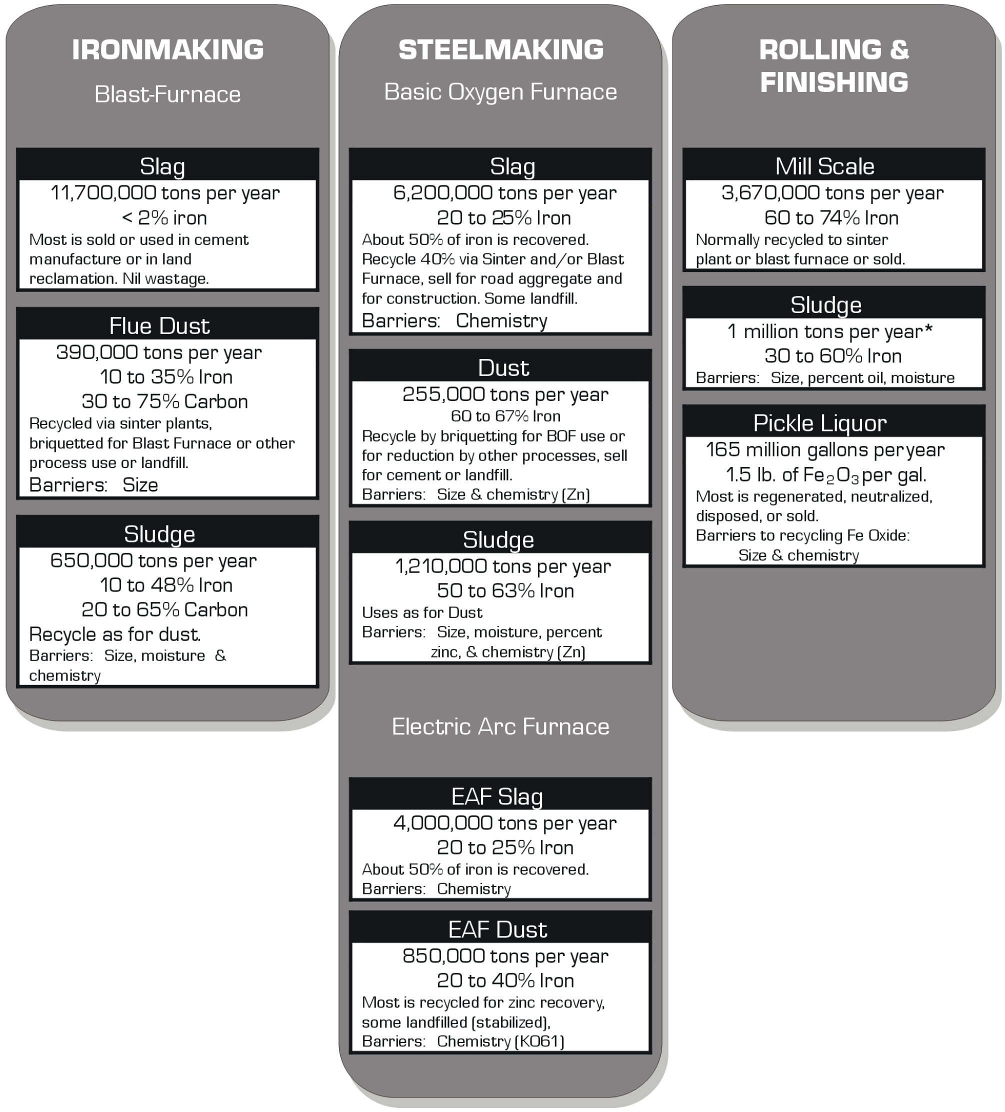

Figure 3-5. Major By-products: Generation Rates, Iron Content, and Barriers to Recycling (U.S.)

Unless creative approaches can be found to advance the utilization of these materials, tighter environmental regulations and closure of landfills will force disposal costs to escalate even further in the foreseeable future. The steel industry seeks to eliminate disposal costs and increase its primary yield by recycling internally.

Figure 3-5 provides an overview of the major by-products, including amounts generated, their approximate iron and carbon contents, and the barriers to recycling. These by-products are further described in the remainder of this section along with the major issues to be addressed through R&D efforts.

It is important to realize that several of the steel industry recycling issues are closely related to the effects of the zinc that is present in many of the process streams. The source of the zinc is galvanized scrap which is recycled through the steelmaking vessel, volatilized and carried over into the dust. The effects of this combination of the two metal systems are addressed later in the appropriate sections.

3.1.1 Ironmaking

The principal by-products produced from ironmaking operations are blast furnace slag, flue dust, sludge and top gas. Figure 3-6 shows the amount of iron recoverable from these sources. It should be noted that within every blast furnace operation there is an internal recycling loop of iron scrap (e.g., skulls, spills, entrapment in slags) corresponding to between 1 and 2% of production, or 750,000 net tons, in 1999.

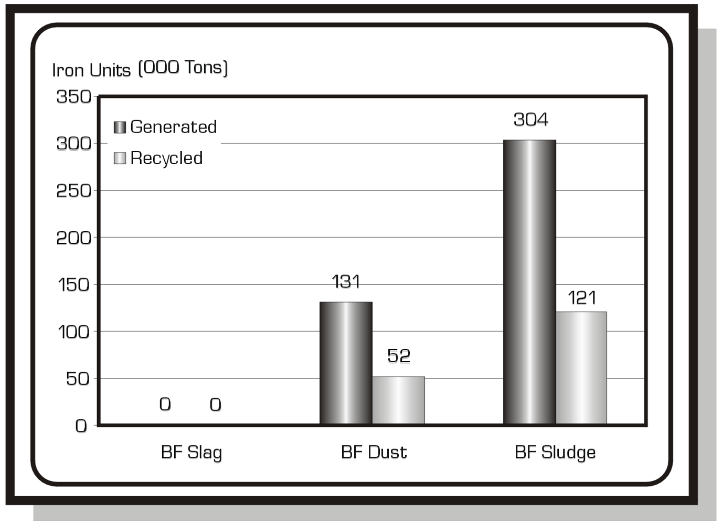

Figure 3-6. Ironmaking Iron Units, U.S. 2000 (SRI 2001)

Blast Furnace Slag

In the production of hot metal, the blast furnace is charged with iron-bearing materials (iron ore, sinter, pellets, etc.), flux (limestone and/or dolomite), and fuel (coke). Two products are obtained from the bottom of the blast furnace: molten iron and slag.

Ironmaking: Blast Furnace Slag

Composition Oxides of silica and alumina (from the iron-bearing material), and lime and magnesia (from the flux) make up 95% of the total slag produced. Typical basicity (ratio of CaO/SiO_2) is near one. Blast furnace slag also contains small quantities of oxides of manganese, iron and alkali as well as sulfur compounds. Additionally, there are trapped metallic iron globules. The latter (amounting to 1 to 2% of blast furnace output), are recovered by magnetic separation and recycled with the furnace charge.

Production Approximately 11.7 million NT (Net Tons) were produced industry-wide in the US in 1999. Slag generally constitutes 15 to 30% of hot metal production; 460 lb/NTHM (Net Tons of Hot Metal) is a typical rate for the US.

Current Treatment Options

In the United States, nearly all blast furnace slag finds commercial applications, mostly in the cement and concrete industry. Depending upon how it is cooled, slag is also used commercially as an aggregate in materials used for:

- railroad ballast
- slope protection
- anti-skid material
- roofing granules
- mineral wool
- soil conditioner
- embankments & fills
- sewage trickle-filter media

Recylability Issues/Barriers

BF slag has a low intrinsic value between $9 and $28/NT depending on the method used to cool it and therefore most cannot be transported economically for long distances; however, this has not been an impediment to almost full consumption by various industrial customers. The sulfur content is a source of concern due to risk of release of odors and/or leaching when used for road construction.

Trends and Drivers. Blast furnace slag has a relatively low iron content and finds almost complete utilization in a wide variety of commercial applications (mostly in the manufacture of cement, concrete, and road construction although there is some concern regarding its sulfur content). Therefore, it is considered a by-product, and there is little pressure to develop new applications.

New and Emerging Technologies. Reported alternative applications for blast furnace slag include use in the production of zeolite and refractories (IISI 1994 and EC Report 1988) and, as observed during the AISI team's visit to the Novolipekst Plant in Russia in 1994, for manufacture of artificial marble.

In Japan, the Institute for Advanced Materials Processing and Tohoku University have developed two technologies for granulating slag. The process granulates the slag by spraying a high pressure jet of steam and natural gas, producing CO and H_2.

Blast Furnace Flue Dust and Sludge

Blast furnace flue dust and sludge are generated as a result of scrubbing and cooling the flue gases produced during the ironmaking operation. The off gases produced in the blast furnace are exhausted through the top of the furnace. These gases are cleaned, cooled, and then burned in the stoves to preheat the incoming cold air to the furnace or are used as fuel in other parts of the plant. Generally, cleaning the flue gases involves the removal of large particulates by a dry dust collector (yielding blast furnace flue dust) followed by a wet gas cleaning system for fine particulate removal (yielding blast furnace sludge).

Trends and Drivers. Two new technologies have been implemented for utilization of the iron units contained in blast furnace dust and sludge: cold bonding (briquetting) of the fine particles to make them suitable for use as a raw material in ironmaking and reduction in a RHF (McManus 1996 and Balajee 1995). While some steel plants have been successful in recycling the briquetted blast furnace residues to the blast furnaces, degradation problems occur while the briquetted residues are heated during descent in the furnace. This causes a loss in permeability of the burden resulting in loss of production. As described below, the RHF process is able to recover these iron units while treating other materials from the plant. Additional work is needed to develop better, cheaper binders for cold briquetting these materials and to develop other lower cost technologies to process them.

Of significant concern is adherence to the limits for maximum allowable zinc concentration in materials to be charged to the blast furnace. Levels vary from steel plant to steel plant, but the control level of zinc (maximum) charged into the blast furnace is generally about 0.5 pound/net ton of hot metal. This experience-based limit is set to prevent zinc related buildups in the blast furnace stack (which have been linked to catastrophic instances of internal scaffolding and slips) as well as damage to refractories by penetration of zinc followed by condensation of zinc chlorides.

New and Emerging Technologies. Some success has been achieved using hydro-cyclones, a wet classification process to treat blast furnace sludge. Since 1984, Hoogovens in the Netherlands has operated a two-stage hydro-cyclone system capable of reducing the zinc concentration in the feed return material to between 0.1 and 0.3%, although a new stream containing up to 7% zinc is created (Balajee 1995).

Bethlehem Steel's Burns Harbor Integrated Waste Management Facility treats all blast furnace sludge, BOF sludge, and waste water treatment sludge (Lynn 1997) . The facility incorporates blast furnace hydro-cyclone slurry and oily sludge into the sinter plant. It is important to note that at this plant the BOF generated dusts and sludge are essentially free of zinc (<0.3%) by virtue of local scrap management policies.

Ironmaking: Blast Furnace Dust and Sludge	
Composition	Primarily composed of oxides of iron, calcium, silicon, magnesium, aluminum, as well as carbon in the form of coke breeze.
Production	Dust and sludge typically constitute 1 to 4% of the hot metal production. In 1999 approximately 380,000 NT of blast furnace flue dust and 650,000 NT of blast furnace sludge were produced by U.S. integrated steel plants.
Current Treatment Options	At steel plants with sintering facilities the dust and sludges are used as minor iron and carbon sources for sintering operations. At others, it maybe mixed with other residues, briquetted, and recycled back to the blast furnace. Some plants landfill the dust and sludge.
Recyclability Issues/Barriers	Key barriers to the recycling of the dust directly back to the blast furnace include its size distribution (95 to 99% minus 20 mesh) and the shutdown of many sinter plants. In comparison to the dust, blast furnace sludge is less effectively recycled and/or utilized; much of both is landfilled and/or stockpiled. Barriers to sludge recycling include its size distribution (97 to 100% minus 20 mesh), moisture (20 to 35%), and chemistry (can contain up to 5~7% zinc, which adversely affects blast furnace operation and refractory life). Recent implementation of two technologies, cold briquetting with other oxides and coke breeze for direct return to the blast furnace and/or rotary hearth furnace reduction, have shown that the iron units in blast furnace dusts and sludges can be recovered for reintroduction into the iron/steel making flow sheet. The direct use of briquettes in the blast furnace often results in loss of permeability in the stack with consequent loss of productivity. Better and lower cost briquetting methods would be beneficial in extending recovery successes.

3.1.2 Steelmaking

The principal residues produced from steelmaking vary according to the type of process. The two major types are the BOF process and the EAF process. Figure 3-7 shows the number of iron units in the major residues generated and currently recycled for recovery of iron units. Although the iron units are lost, a large portion of BOF slag and EAF slag are utilized for other applications described later in the text. EAF dust is processed for recovery of zinc and the slag generated in the process is also used.

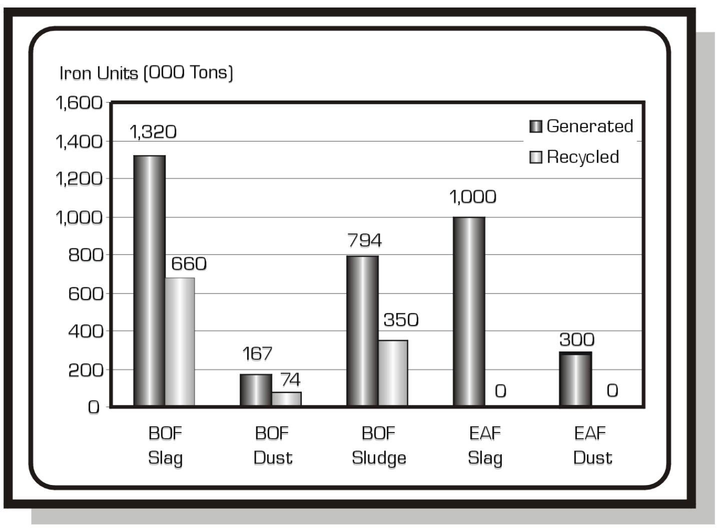

Figure 3-7. Steelmaking Iron Units, U.S. 2000 (SRI 2001)

BOF Steelmaking

In the basic oxygen steelmaking process, molten iron and scrap are converted into steel by blowing oxygen and simultaneously adding fluxes. At the end of the cycle, alloys are added. The basic oxygen furnaces used in this process generate BOF slag and BOF dust and sludge, all of which contain iron units.

BOF Slags

Different kinds of slags arise during the steelmaking process. During the oxygen blow, impurities in the metal (carbon, silicon, manganese, and phosphorus) as well as some iron are oxidized to form the largest portion of the steel slag, the so-called primary slag. Secondary slags are produced from the pretreatment processing of hot metal and from secondary steelmaking operations known as ladle treatment of molten steel.

Trends and Drivers. Disposal or utilization of steelmaking furnace slags present challenges due to their low intrinsic cash value. Significant quantities are landfilled in some plants. In integrated plants, the natural in-house customers for these slags are the sinter/blast furnace operations. However, their use is restricted by required limits of phosphorus levels in the hot metal. As a result, plants with sintering facilities consume 40% of BOF slag internally. Efforts have been made (Fruehan 1999) to develop technologies to remove phosphorous from steelmaking slags, but economics in the United States do not favor this approach. For EAF slags, the technical issues are similar although the option for in-plant utilization (i.e., use in a sinter plant) is not available.

In the past, the presence of large amounts of free lime (up to 7%) made external sale difficult. The presence of free lime necessitated hydrating by exposing the slag to the elements. Improved BOF and EAF steelmaking practices have limited the content of free lime so that current steelmaking slags have many commercial applications, with room for development of others. Presently, most slags find applications as road aggregate and in the manufacture of Portland cement. For the latter application, a portion of the MgO and FeO contained within the slag are of benefit; however, high concentrations limit its use. It is important to note that there is a significant energy credit to the steel industry from supply of the stone and dolomite which it has calcined. Other applications include anti-skid material for icy roads and landfill daily cover.

BOF slag has been used in agriculture in Western Europe and has been found to have a neutralizing value almost equivalent to that of limestone, but with added benefits attributed to the presence of P_2O_5 and some trace elements (EC Report 1988).

Ladle treatment facilities also generate a small amount of slag. The chemical and physical characteristics of these slags are unique to each facility, and their reusability usually is limited to forming the "base" or starter of slags for the same application. Some refining slag is recycled into EAFs for use of the lime units.

New and Emerging Technologies. Several new developments are underway to increase the use of steelmaking slags, and support is warranted to achieve complete usage. Developments include:

- Reuse of spent slags to expedite the dissolution of newly added fluxes
- Use of cooled slags in place of fresh magnesia in slag-splashing practices
- Reaction of free lime and sand injected with oxygen into the slag pots, a practice developed in Germany (Kuhn 1997)
- Development of faster artificial aging techniques, such as utilized in Australia and Japan, to stabilize steelmaking slags.

Alternative industrial applications, where the energy content of the pre-fused steelmaking slag would be a credit, need to be explored. One potential application uses slag as an ingredient in glassmaking.

BOF Steelmaking: Slag

Composition

Calcium silicates combined with fused oxides of iron, aluminum, manganese, calcium, and magnesium. Components in the hot metal from the blast furnaces, such as carbon, silicon, manganese, and phosphorus, as well as some of the iron are oxidized during the oxygen blow; whereas the oxidized carbon leaves as CO (to be converted to CO_2 above the slag), the other elements form oxides that enter the slag together with some of the sulfur in the hot metal and in the scrap.

BOF slag has a higher basicity than blast furnace slag (lime/silica ratio of 2.5 to 4.0), higher FeO content approximately 25 to 35%, and is far more variable in chemical composition. A major concern is the significant content of "free lime" often present in these slags.

Production

200 to 440 lbs of primary BOF slag is produced for every ton of steel made using the oxygen steelmaking process. During 1999, approximately 6.2 million NT of steelmaking primary slag were produced in the United States. A typical steelmaking slag processing operation involves recovery of the metallic iron fraction for re-use within the ironmaking and steelmaking, as well as the crushing and sizing of the non-ferrous fraction for re-use either within the steel works or for external sale.

Current Treatment Options

Steelmaking slag is crushed and sized for charging to the sinter plant (if available) and/or to the blast furnaces to utilize the fluxing compounds CaO, MgO in the slag and to recover the contained chemical energy as well as the iron and manganese units. Unfortunately, most of the phosphorous in the BOF slag reverts to the hot metal in the blast furnace. This limits the quantity of BOF slag that can be charged to the sinter plant and the blast furnace to about 25% of generation.

Some steelmaking slag can be used as a starter fluxing agent in steelmaking furnaces. It is used extensively outside the steel works, mainly for road construction, where it provides excellent anti-skid properties, and in the cement industry. Unfortunately, some is landfilled while opportunities for sale to the cement industry remain to be capitalized.

Recyclability Issues/Barriers

The practice of recycling steelmaking slag internally has declined (from 30% about ten years ago) as a result of increased demand for low-phosphorus steels.

The use of steelmaking slag in road construction has fallen into disfavor in some parts of the United States because the free lime present in steelmaking slag can subsequently hydrate, causing expansion and disintegration of the roadbed. Additionally, the free lime can lead to the formation of tufaceous calcium carbonate ("tufa"), which can plug roadbed drains; this has forced the implementation of methodologies to stabilize the "free" lime by practice changes or by aging or by steam curing. At present, about 75% of BOF steelmaking slag produced each year in the U.S. is consumed inside or outside of the steel works. This leaves 25% to be landfilled, a situation in part caused by unfavorable costs incurred in transportation of a relatively low value material. The rate of slag recycling is higher in Canada, Europe and Japan in part due to economics and environmental regulations.

BOF Steelmaking Dust and Sludge

BOF steelmaking dust and sludge is generated as a result of the cleaning of the off gases emitted from the oxygen-steelmaking processes. The off gases are exhausted through the top of the furnace. In most shops, the gases, which contain nearly 90% CO, are combusted with entrained cold air, then cooled, cleaned, and released into the atmosphere through a stack. In some shops, the gases are cooled with water sprays upon leaving the furnace and vented through a flare stack. In Japan, which has much higher energy costs, some shops make use of the energy in the off gases by adding them to the plant energy grid. In either situation, the primary cleaning is normally achieved by washing the gases with water and, in a few cases, by means of a dry system (electrostatic precipitators).

The wet gas cleaning system is usually a two-stage process. In the first stage, the gases are cooled, and the coarse dust is removed. During the second stage, the fine dust fraction is washed out of the gas. After settling in a sedimentation basin or thickener, the fine slurry fraction is dewatered by means of vacuum filters or centrifuges. The coarse slurry fraction is normally treated separately in drag classifiers. Modern steel works are also equipped with secondary collection systems, which collect dry dust during vessel charging and tapping operations.

Trends and Drivers. Rising landfill costs and the increasingly stringent environmental regulations imposed in most countries highlight the need for special treatments and other applications for the material. Increased recycling of galvanized steel is increasing the zinc content in steelmaking dusts and sludges. If the zinc could be kept out of the BOF scrap charge, either by segregation or by dezincing, the resulting BOF fume would be low enough in zinc to be used in sintering in the few plants with such facilities. A broader solution to this problem may be in processes that remove the zinc, with or without reducing the iron oxide, thereby creating two separate recyclable streams.

New and Emerging Technologies. One internal recycling development is briquetting of BOF dust and sludges for recycling back to the BOF. This approach uses the BOF as a reduction vessel, reducing scrap melting and consequently steel output. In addition, vessel slopping is often encountered when using these briquetted materials, resulting in environmental problems and yield losses. Another recycling method that has been investigated extensively is the separate treatment of the low zinc-containing coarse fraction, which can be recycled directly to a sinter plant or agglomerated and recycled. Unfortunately, the coarse fraction accounts for only 10 to 30% of the total dust or sludge produced; in-plant recycling of the fine fraction has not typically been possible without further processing to remove the zinc. Wet classification processes and selective chemical leaching tend to be ineffective due to the fineness of the material and the form in which the zinc is present, zinc ferrite (oxide) particles.

BOF Steelmaking: Dust and Sludge

Composition BOF steelmaking dust and sludge generally contains 50 to 65% iron and between 0.3 and 12% zinc on a dry basis. Size consist is 97 to 100% minus 20 mesh with a significant portion finer than 0.0002 inches. For steelmaking sludge, the moisture content is 25 to 45%.

Production Combined generation rates for steelmaking dust and sludge average 35 to 40 lb/NT of liquid steel. During 1999 approximately 260,000 NT of steelmaking dust and approximately 1.25 million NT of steelmaking sludge were produced.

Current Treatment Options
Steelmaking dust and sludge have been used in the production of Portland cement and as a coloring agent for concrete. At present, less than half of the steelmaking dust and sludge generated is being re-used, very little (one plant in the U.S.) internally in sinter plants due to the deleterious effect the contained zinc would have on blast furnace operation. A few plants recover the contained iron units by incorporating the dust/sludge in cold agglomerated briquettes as a charge in the BOF but at a penalty in steel output due to the decrease in scrap melting capability. Recently, a new technology, Rotary Hearth Furnace reduction, has been introduced to recover the iron and zinc units separately for return into their respective flow sheets.

Recyclability Issues/Barriers
Barriers to the recycling of steelmaking dust and sludges directly to the blast furnace or the steelmaking furnace are size distribution, moisture, and chemistry (see Composition, above). Zinc content is the major barrier to direct recycling.

From a practical viewpoint, it appears that only pyrometallurgical processes are capable of performing this operation. Over the past 15 years, a number of pyrometallurgical processes have been developed for the treatment of residues to yield iron for recycling into the BOF and zinc for sale as a feedstock, some of which have been realized in pilot and full-scale plants. A well-known example is the rotary kiln in service for EAF baghouse dust. However, theses approaches have not been economically viable for the zinc levels in BOF by-product oxides. Thus, with the single exception of the plant at Sumitomo-Kashima, these processes are used only to treat dusts originating in EAF operations. The AISI method is a coal-based smelting process that produces molten pig iron, zinc oxide rich fume, and an off gas with fuel value, and was demonstrated in a pilot plant (Downing 1996) .

In the last few years, three new pyrometallurgical treatment processes have been studied intensively. One of these is the Inmetco process in which green pellets, made from chromium, nickel, and zinc-bearing residues are reduced in a RHF with the recovered metal units returned to the stainless steel producing industry. Recently, a related technology, the rotary hearth furnace reduction of briquetted oxides, has been demonstrated in the pilot stage (Rinker 1999, Koros 2000) and installed at Rouge Steel (Daiga 2000), Nippon Steel, and Kobe Steel (Hoffman 2000) to treat a briquetted mixture of pellet fines, oily mill scale, and blast furnace and BOF by-products for charging into hot metal transfer ladles. A high-grade zinc oxide dust catch is produced for sale to the zinc industry.

In Europe, a multiple hearth coal reduction process (PRIMUS) has been taken to the 2 NT/hour pilot plant stage at ARBED, and stepwise reduction is achieving output similar to that of the RHF. Another process, previously under development by Thyssen, USINOR and Lurgi and now abandoned due to economically insurmountable problems with materials of construction, was based on a high temperature circulating fluidized bed.

Researchers have also been looking into the possibility of reusing BOF steelmaking dusts and sludges as raw materials in the electric arc furnace. These studies are based on the idea that by recycling EAF dust into the furnace, zinc and lead can be enriched in electric arc furnace dust to a level that makes it more economically attractive to treat for recovery of these elements. However, the logic for this approach, because of high electrical energy smelting costs and economics of turning part of a non-hazardous “waste” stream into a RCRA-listed hazardous K061 material, is unclear.

An interesting opportunity exists to utilize the Fe values in BOF dusts in the cement industry to satisfy the iron oxide requirements for Portland cement. In one case in the Chicago area, payment for the iron units nearly covers the cost of transportation, and landfilling is avoided. Zinc contents typical of BOF dusts (2 to 10%) are not considered a problem for this application, but as in landfilling, the zinc values are lost.

Sumitomo Metal Industries’ process removes zinc from dusts and sludges prior to recycling through the blast furnace (Kochihira 1993). The method involves reducing the moisture content of combined BF/BOF dust/sludge slurry from 70 to 20% using filter presses and then drying the material in a Waelz Kiln. Iron (mostly as Fe_2O_3) is reduced to FeO, and the zinc is vaporized, recovered as the oxide, and sold. The coarse iron rich residue is charged directly to the blast furnace (>0.2 inch), while the fine fraction (<0.2 inch) is directed to the sinter plant. In 1991, the Sumitomo plant processed 124,000 tons of BF/BOF slurry and produced 29,000 tons of blast furnace feed material, 59,000 tons of sinter plant feed material, and 5,000 tons of zinc oxide.

The AISI and the U.S. Bureau of Mines developed a process that successfully dewaters BOF sludge from about 60 to 12% water. The process, which employs pressure filtering followed by an acetone wash, awaits full-scale pilot testing and further assessment of practical and economic feasibility.

At one location (Bethlehem Steel-Sparrows Point, Lynn 1997), a novel approach has been implemented in which part of the hot BOF slag is used to dry the sludge from the BOF shop scrubber system. The result is an iron-rich material employed as a component of the vessel charge. While this technique consumes all the sludge generated at the BOF shop, it does not yet consume dusts, sludges, scale generated elsewhere in the plant, or all of the BOF slag.

On the chemical treatment front, the Isonics-Fray Chlorination process (Fray 1999) has shown promise in the use of chlorine gas at 1475 ^{o}F to remove base metals (Zn, Pb) from dust and sludge to make clean iron units available for recycling.

In summary, the four pyrometallurgical process technologies currently most likely to succeed in recovery of the iron units in BOF generated dusts and sludges are the RHF followed by a melting step to complete reduction (from >90% metallized) to liquid pig iron; the stepwise reduction PRIMUS; the Bethlehem Steel hot slag drying referred to above; and the oxygen driven "bath" smelting HISMELT process. Other approaches under development elsewhere, including the new approach using elevated temperature chlorination, merit support.

Electric Arc Furnace

The EAF process has changed markedly during the last few years with the more intensive use of chemical energy (quantities of oxygen equivalent to the BOF), high power transformers, DC in place of AC power sources, and large portions of pig iron and of pre-reduced HBI and DRI in the charge. The result has been a dramatic shortening of heat cycle times (a 45 to 50 minute tap to tap is not uncommon), decreased total and electrical energy use, and increased volumes of furnace slag and baghouse catch. The latest trend, in Japan, Europe, and now the United States, is the charging of liquid hot metal made in a blast furnace or a smelter. This practice can reduce electrical power requirements to the 200 to 250 kWh/NT range and shorten heat cycles to less than 45 minutes.

In EAF steelmaking, specific grades of steel scrap are selected and charged into the furnace along with varying amounts of other iron-bearing materials and fluxes. Charging typically takes place through the furnace roof. During the steelmaking process, one to three large cylindrical carbon electrodes (depending on type of furnace, AC or DC) are lowered through openings in the roof to melt the charge. It is important to note that the above mentioned trends to use larger amounts of oxygen as well as charge materials other than scrap cause marked changes in the nature (i.e., amounts, composition) of the process by-products, slag and dust.

Electric Furnace Slag

For every ton of steel produced in electric arc furnaces, about 125 to 200 pounds of furnace slag are generated. In addition, ladle treatment facilities generate about 20 lb/NT of slag. In total, about 3 to 4 million tons of EAF shop slags are generated annually. These slags are somewhat different from those generated in BOF shops in terms of composition, commercial usage options, and recyclability issues. Important differences from BOF-produced slags exist due to factors related to process needs: EAF slags have lower basicity, i.e., lime/silica ratio (to permit foaming), and higher FeO and P_2O_5 contents. There is a lack of in-house reuse opportunities, and often the shipping costs to a potential industrial customer is too great to permit the sale of these low value materials for commercial consumption.

Furthermore, the newer EAF shops tend to be in rural areas with low cost access to landfills for disposal. Thus, a smaller portion of this slag actually finds industrial or construction applications. As referred to above, there are examples of use of the full output of EAF slag in an adjacent cement plant with impressive savings in energy costs and resultant increase in output of cement (Rostik 1997). Synergistic applications with other industrial operations should be explored.

Electric Arc Furnace Dust

In 2000 electric furnaces produced about 50 million tons of carbon and alloy steel products in North America, generating almost one million tons of dust (Most of this is classified as K061). In the United States, this dust is collected by evacuation into a baghouse.

EAF Steelmaking: EAF Dust

Composition

EAF dust composition varies greatly depending on the makeup of the scrap charge and the furnace additives used. The primary component is iron or iron oxides; a typical EAF dust contains 30 to 40% iron by weight. EAF dust can also contain large amounts of zinc and lead (as high as 35 to 40% Zn as the oxide, sulfide or chloride and 4% Pb as the oxide) if large amounts of galvanized steel and free-machining steel turnings are used. In addition, EAF dust can contain cadmium, other metals, halides, and fluxes. The primary hazardous constituents are lead, cadmium, and chromium. Stainless steel production yields dust with high percentages of chromium and nickel oxides.

Production

The average rate of generation for EAF dust is about 25 lbs/ton of steel melted. In 1999 about 850,000 NT were generated. At a typical treatment or disposal cost of $125 to 150/NT the industry cost for 1999 was $115 million or $ 2.50/NT of EAF produced steel. (Note: due to competitive pressures, processing costs have decreased during the last few years) The amount of iron units available in the EAF dust, based on a typical analysis of 35% Fe, was 300,000 NT.

Current Treatment Options

Current alternatives are to (1) ship to an off-site processor, (2) pay for stabilization and land fill in a secure site, (3) sell to exempt markets such as fertilizer producers. Three HTMR processes are in use presently for treating EAF dust to recover zinc. The main HTMR process is the Waelz kiln; others in use are the rotary hearth furnace and the flame reactor. There are several versions of RHF processes: Inmetco, AlMet, MR&E, Redsmelt, etc. Successful pilot plant work has shown the technical viability of the AISI Direct Steelmaking smelting technology as well as of the related Hismelt process but economic issues (high capital cost) remain to be addressed.

In 1999 about 55% of EAF dust generated was treated at an HTMR facility, about 40% was landfilled and a small quantity was processed into fertilizer.

Recyclability Issues/Barriers

Emerging technologies, including new methods of HTMR, and pyrometallurgy, such as the Cl-based process (1475° F), may lead to viable options to reduce the high costs of processing EAF dust. Within process recycling, that is, return to the EAF of the baghouse catch, is a means for enrichment of the dust but at the expense of power and furnace time (=productivity).

What had appeared at first to be a lower cost alternative, hydrometallurgy, is ruled out by the combined form of Zn and Fe in the EAF dust; thus, cost remains the greatest barrier. Technologies with a low net cost to the steelmaker attained either by a lower-cost process, by generation of a high-value, marketable by-product, or through generation of a recyclable charge material are needed.

Trends and Drivers. The production of EAF dust in the United States is expected to continue to increase as more furnaces are installed. Currently, about 55% of EAF dust is processed with the most common method being the Waelz Kiln, a high-temperature metals recovery (HTMR) process for recovery of the zinc content. This method is used because of the limited number of approved process alternatives for treating K061. The Waelz Kiln process has carried an unacceptably high price tag because of limited competition and the limited credit given for the zinc recovered from the dust. Several approaches have been pursued during the last few years to lower the cost of treatment and/or disposal of EAF dust.

Although developed and emerging technologies are available to stabilize EAF dust for burial in landfills (approximately 40% of generation in 1999), the long-term interests of the industry may be better served by technologies that recover the iron units for reuse in steelmaking and take full advantage of the contained recoverable zinc. Recent EPA decisions, that increase the economic attractiveness of landfilling stabilized and delisted EAF dust, present recycling technologies with a cost challenge, particularly for EAF shops located far from the available HTMR processing facilities.

One alternative approach that has been pursued is to increase the amount of zinc recovered in order to buy down the processing cost. This approach can be accomplished by charging briquetted EAF dust into the EAF, by sub-surface injection of the baghouse dust, or by bulk addition. Furthermore, the average zinc content has increased over the past decade to the 25 to 35% range, enhancing the economics for treatment and recycling of EAF dusts. This increase is attributed to a growing use (and thus returns) of galvanized steel.

Technologies for the on-site recycling of EAF dust back into the furnace (for example, briquetting, pelletizing, or pneumatic injection as powder) have been implemented in Europe because they offer the potential to recover some of the iron oxide values while concentrating zinc values. Concentrating the zinc reduces final recycling costs because smaller quantities of dust will be shipped off site and the resulting dust has a higher zinc concentration which improves the revenue from the subsequent zinc recovery. However, the costs associated with all these practices (e.g., preparation of the powders, maintenance of the delivery equipment, increased power usage by the EAF for smelting) often outweigh the benefits. One approach (with high capital and operating costs) is in place at one shop in Germany where the zinc-rich dust generated during the scrap melting is captured in one chamber, and low zinc, iron-rich dust generated during the oxygen blowing period is captured separately and re-injected into the furnace to recover the Fe units.

Treatment processes that produce a more enriched metallized iron are particularly attractive to steelmakers. The higher metallic iron content allows processed residue to be handled in the same way as other scrap (i.e., by electromagnet), eliminating the need for special equipment.

A barrier to recycling EAF dust are the environmental laws that define EAF dust and mixtures that contain EAF dust as hazardous waste. This discourages recycling and research because non-generators are unwilling to receive the material.

New and Emerging Technologies. With support from the U.S. Department of Energy, EPRI's Center for Materials Production examined various approaches to minimizing the formation of EAF dust, such as modified scrap charge, power input level during meltdown, oxygen lancing practice, carbon dioxide for carrier gas for carbon injection, use of carbon dioxide during charging and tapping, foamy slag practice, post-combustion, and furnace draft (use of adjustable speed drives). Of these factors, the two-chamber baghouse, variable speed fans, and improved slag foaming are the most beneficial, although the capital cost for retrofits makes the first two unlikely to be implemented soon.

Hydrometallurgical and pyrometallurgical processes for treating EAF dust continue to emerge to compete with the current two commercial HTMR technologies: Waelz Kiln and rotary hearth furnace. The hydrometallurgical processes include the ZINCEX, ESINEX, and Cashman processes, while the pyrometallurgical processes include Sirosmelt (Ausmelt). It must be recognized that the hydrometallurgical processes often fall victim to the difficulty in digestion of the zinc ferrites, which, unfortunately, is the prevalent form of the zinc in EAF baghouse dust (CMP 1993). The thermal and plasma processes have the ability to break up the ferrites and thereby release all the zinc.

The biggest player worldwide in (thermal) treatment of EAF dusts are the Waelz kilns, operated in the United States by Horsehead Resource Development Company. Unfortunately, the iron units are discharged in the form of oxides in a diluted slag-like material, whereas zinc is recovered in a usable form to enter its refining flow sheet. A newer competing technology for EAF dust, based on the rotary hearth furnace, is in operation at Inmetco and one EAF shop (Sack 1999, Sloop 2000). It can produce a high purity zinc oxide catch as well as a >90% metallized Fe product ready for melting (at AmeriSteel, the iron oxide is purposely discharged at around 50% metallization for mixing into the EAF slag). The plasma furnace approach, studied by the CMP and at first marketed by Tetronics, has fallen victim to technical problems (chloride reactions with zinc and iron leading to condensation of unmanageable "hard zinc") and unfavorable process economics.

Another thermal reduction process, the AISI Waste Oxide Process, was shown in the pilot plant to successfully recycle synthetic EAF dust.

A patented high temperature metal synthesis process has reached commercialization and soon will be demonstrated with iron-bearing wastes. This PEL process will manufacture an engineered iron oxide industrial product from grinding swarf, mill scale, turnings, and eventually EAF dust. While the iron units will be lost to the industry, their use as a feedstock in the creation of another product will be beneficial through reduced landfilling.

3.1.3 Rolling and Finishing

Rolling can be categorized as hot or cold rolling operations. The principal residues produced from rolling and the related surface preparation operations are mill scale, rolling sludges, pickle liquor, grinding swarf, and other dusts. Figure 3-8 shows the estimated number of iron units in the mill scale, rolling sludge and pickle liquor.

Mill Scale

Mill scale is the product of continuous casting, reheating and hot rolling operations. It is not produced during cold rolling. The continuous casting process is used to produce semi-finished steel shapes (such as billets, blooms, and slabs[1]) directly from molten steel. The water sprays also serve to remove scale and other impurities from the steel surface. The scale is collected in scale settling basins.

[1] Although there are no strict definitions for slabs, blooms, and billets, the distinctions generally pertain to size and shape in cross-section. Billets are usually squares of up to 5 inches on a side; blooms are squares of 6 to 12 inches on a side; and slabs are rectangular, measuring 2 to 10 inches thick and 100 inches or wider.

Hot mill rolling operations consist of processes in which hot steel billets, blooms, and slabs are transformed in size and shape through a series of forming steps to ultimately produce semi-finished and finished steel products. Water is used for direct contact cooling and de-scaling. Cooling water is used to flush the mill stand work rolls and to prevent surface cracking of the steel rolls due to sudden temperature changes. Descaling sprays are also used to remove oxide scale and impurities from the surface of the material being rolled. Cooling and de-scaling water is normally discharged from the mill into scale pits where the heavier solid particles settle out (scale).

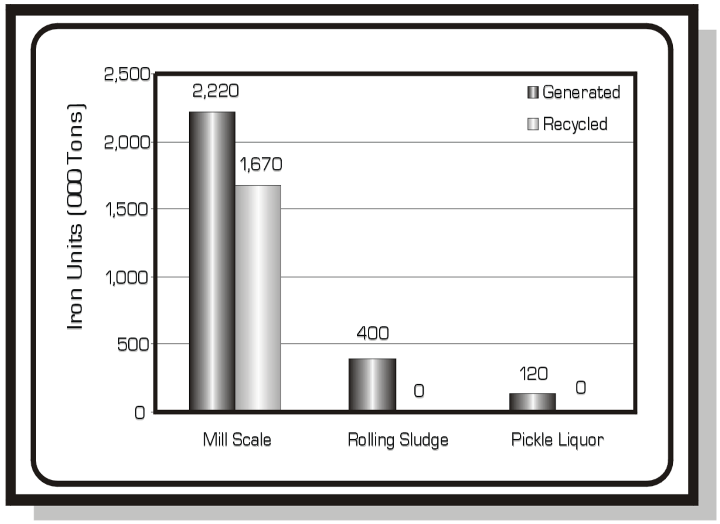

Figure 3-8. Rolling and Finishing Iron Units, U.S. 2000 (SRI 2001)

Trends and Drivers. For oily rolling scale to be recycled via a sinter plant, de-oiling of the material may be required to protect the environmental performance of the plant. Although for other applications such as cement manufacture and RHF reduction, oil is a tolerable presence, significant amounts of mill scale are landfilled.

Rolling and Finishing: Mill Scale

Composition Rolling mill scale is relatively coarse, with 85 to 90% of the constituent particles >0.006 inches. The iron content, mostly in oxide form, is about 70% (on an oil- and moisture-free basis). The oil content of rolling scale is typically in the range of 0.2 to 2%, but oil contents as high as 10% have been observed.

Production The quantities of scale generated by rolling operations vary, but tend to range between 10 and 80 lbs/ton. In 1999 approximately 4.0 million tons of rolling mill scale were produced in the United States.

Current Treatment Options

At a few steel plants, rolling scale is recycled through the sinter plant or sold to other steel plants as sinter feed material; however, as noted below, this application is limited. Steel plants without sintering capability have attempted to directly recycle the scale through their blast furnaces but with limited success. Others have had success in briquetting the mill scale along with other residues and have used this product in their ironmaking furnaces and/or steelmaking furnaces. In addition, several other industries are using mill scale as a raw material, including the cement industry. Generally, almost all rolling scale is either recycled or sold. Rolling scale containing more than 3% oil is generally landfilled or sold for manufacture of Portland cement. New technologies such as reduction in rotary hearth furnaces have been shown to have the capability for return of the iron units to the steelmaking flow sheet. Similarly, in Belgium, a blast furnace is consuming, by tuyere injection, all the oily mill scale generated at the plant.

Recyclability Issues/Barriers

The oil/grease that is bonded to mill scale is difficult to remove and is the major impediment to the direct recycling of this by-product residue within the steel plant. The scarcity of sinter plants is also a growing barrier as many have shut down. New technologies have demonstrated the ability to make a product suitable for recycling in the steel mill. The relative newness and significant capital cost of RHF systems presently are barriers to its application.

New and Emerging Technologies. A patented de-oiling process for rolling scale was used at a steel plant in the United States for several years and was capable of processing 550 tons of material a day to less than 1% oil but the process owners have decided to abandon their technology. As discussed later, biological de-oiling of rolling scale also has been studied (IISI 1994). An economical process that reduces the oil to less than 1% is needed.

Rolling Sludge

Rolling sludge is generated during hot rolling and cold rolling operations. After the mill scale is removed from the cooling and descaling water used in the hot rolling operation, the semi-cleaned water is then normally sent on to a treatment plant where the fine particulates (sludge) are removed. Process water is then either recycled back to the mill and/or discharged.

In cold rolling operations, flat steel products are reduced in thickness without preheating. An oil-water solution is applied to dissipate heat from both the work rolls and the product as it is mechanically processed and to flush impurities from the surface of the steel. The rolling solution is recovered and recycled within the mill, then periodically discharged to an oil recovery plant. There, the rolling oil is recovered and typically returned to a refiner. The processed solution from the recovery plant is discharged to a treatment plant where the fine particulates (sludge) are removed.

Trends and Drivers. As with mill scale, sludges are bonded to oil/grease that is difficult to remove and impedes the recycling of this by-product residue within the steel plant.

Rolling and Finishing: Sludge

Composition Rolling sludge consists of oils, greases, and fine-grained solids. The iron content of rolling mill sludge typically varies from about 30 to 60 % iron. Generally rolling sludge is 100% minus 20 mesh, moisture content can range from 20 to 50%, and oil content can range from 1.5 to 30%.

Production Approximately one million NT of rolling sludges were produced in 1999. Containing 30 to 60% Fe, this represents a significant volume of iron units.

Current Treatment Options

Sludges from hot and cold rolling operations (treatment plants) often are landfilled. Limited amounts of rolling sludge have been used as sinter plant feed. Solvent extraction processes have been marketed for the deoiling of rolling and wastewater-treatment sludges. Incineration of oily sludges is also technically, if not economically, feasible. The AISI is trying to arrange sponsorship for a pilot/demonstration test of a new technology for deoiling and dewatering sludges.

Recyclability Issues/Barriers

Barriers to the recycling of rolling sludge include size distribution, moisture, and oil content. The sludge cannot typically be added to the sinter plant feed because the contained oil causes emissions. However, recent experience has shown that these materials can be processed in rotary hearth furnaces without impairment of environmental performance. The possibility of using the spent rolling oils in blast furnaces, as done in one BF in Europe, merits examination.

New and Emerging Technologies. The following processes (one in use and two under development) address the recyclability issues.

- Two Belgian ironmaking furnaces experimented with injection of an oily rolling sludge composed of 35 to 60% water, 20 to 55% oil, and 10 to 20% solids (IISI 1994). Currently, spent rolling oil is used as a tuyere injectant for one blast furnace.

- Biological de-oiling of rolling sludge has been studied; however, the process rates appear too slow for practical industrial utilization. Results to date indicate naturally occurring microorganisms with mechanical aeration could be used to achieve a 50% reduction in the oil content of rolling sludges over a seven-month period. Another study indicates that the oil content of rolling sludge can be halved in one month and reduced to 3% of the original amount in 15 months when proper biodegradation conditions are maintained (IISI 1994).

- The Carnegie Mellon Research Institute, in cooperation with the AISI and the EPRI Center for Materials Production (CMP), has developed a microwave de-oiling process for rolling sludges. The single-stage microwave de-oiling process has been proven at the laboratory scale. The products of this process are dry scale containing less than 1% oil and clean oil. A pilot demonstration of the process is in the planning stages under the auspices of the AISI.

Development work and recent commercial implementation have shown that the rotary hearth furnace process, through closely controlled time at peak temperatures and the control of the furnace atmosphere, has the capability of reducing oil laden scales incorporated in the charge oxide briquettes without deleterious effects on the gaseous effluents. These results are similar to those in cement manufacturing operations, except in the latter the iron units are lost.

Spent Pickle Liquor

Acid pickling is a finishing process used to clean the surface of hot-rolled steel products prior to cold rolling and/or coating operations. Acid pickling generates an iron-rich by-product called spent pickle liquor, which is considered a hazardous waste (K062). It generally contains considerable residual acidity and high concentrations of dissolved iron salts. There are four types of spent pickle liquor, each of which produces different types of dissolved iron salts when recycled.

Trends and Drivers. Over the last decade, the trend in treating pickle liquor has been away from deep wells and towards acid regeneration facilities. Some companies are electing to build spent pickle liquor recycling facilities on site, thereby minimizing corporate liability for transfer off site and generating revenue through sale of the by-product ferrous chloride. Most facilities have moved from sulfuric to hydrochloric acid pickling.

New and Emerging Technologies. On-site recycling processes for hydrochloric acid pickling liquor are available.

Rolling and Finishing: Spent Pickle Liquor

Composition (1) Hydrochloric acid spent pickle liquor consists primarily of water, but contains approximately 25 to 30% ferrous chloride and 1% hydrochloric acid, which is formed when the iron oxides on the steel's surface react with the acid during the pickling process. The liquor may contain traces of chromium, lead, nickel (all three of which are considered hazardous), arsenic, cyanide, and cadmium. (2) Sulfuric acid spent pickle liquor contains iron sulfate salts, which crystallize when the material is concentrated. The resulting iron sulfate has been used for agricultural applications and stabilization of EAF dust, but is mainly discarded. (3) Hydrofluoric and (4) Nitric Acids used in the pickling of stainless steel are subsequently separated from the iron salts using special membranes. This separation process produces a sludge that is classified as a hazardous waste. Bailey Engineers has developed a system that regenerates the pickle acid and recovers the iron for recycling.

Production A total of approximately 165 million gallons of spent pickle liquor are produced in U.S. integrated mills and by outside processors. This liquor contains nearly one pound of iron/ gallon. Over 90% is from HCl acid pickling lines.

Current Treatment Options

While the majority of the spent pickle liquor generated each year is recycled through acid regeneration plants or used in water treatment (in both of these cases the iron is recovered), over 50 million gallons is still disposed of each year via deep well injection. While hydrochloric acid is the main product of the acid regeneration process, a fine iron oxide by-product is also produced. If the quality of the iron oxide by-product is sufficient, opportunities exist for using this by-product in the magnetics industry. However, at times this product cannot be sold and must be discarded.

Recyclability Issues/Barriers

Barriers to the recycling of this iron oxide by-product back to the steel plant are its size and chemistry. Since the water treatment market is very limited, the greatest opportunity for using this by-product exists in the regeneration of the acid and production of iron oxide for the magnetics industry.

3.1.4 Other By-Products

A number of other by-product wastes and residues are associated with BOF and EAF steelmaking. These include:

- Grinding swarf
- Grinding flue dust
- Metal fines
- Metal machining wastes
- Hot metal/desulfurization baghouse dusts
- Other dusts
- Other sludges

Two of these waste streams are discussed briefly as follows.

Grinding Swarf

Grinding swarf is the product of cutting and conditioning (scarfing) operations. This material, generated at a rate of about 0.7% of overall steel production, is difficult to dispose of because it is typically wet and oily. Landfilling costs about $70/ton.

The iron content of swarf is about 60%. Assuming that approximately 700,000 tons were generated in 1999, some 400,000 tons of iron units would be available. Some on-site recycling of swarf is being conducted by charging it into the EAF or mixing into sinter plant feed. This is becoming less desirable, however, because of concern over contamination by tramp metals.

Other Dusts

Other dusts are collected from the steelmaking plant during maintenance and clean-up operations. At the dust generation rate of 0.13% per ton of steel, about 140,000 NT of dusts were collected throughout the industry in 1999. Despite containing about 50% iron as the oxide, these dusts are landfilled because they are generated in small amounts in disparate locations; and they may contain a broad range of contaminants. Thus, recovery of the contained 70,000 NT of iron units is economically impractical at this time.

3.1.5 By-Products Research and Development Needs

While the specific impediments to improvement of the recycling and utilization of steel plant residues vary from company to company and from plant to plant, the following problems have been identified as generic.

Ironmaking and Steelmaking Slags

While nearly all ironmaking slag is used commercially, such as in the manufacture of cement and concrete, land reclamation, landfill construction, road repair, and civil engineering projects, there is room for concern about the quantity of steelmaking slag not finding commercial markets outside the steel works.

R & D Needs

Iron & Steel Making Slags

- Develop economic process to reduce or stablize free lime in steelmaking slag
- Investigate partial reuse or steam curing free lime in BOF slag
- Identify alternative uses for slag
- Investigate Japanese method of minimizing production of BOF slag (capital & operating costs)

Potential Impact: 1.6 Million NT Iron Units

Means for minimizing the quantity of BOF slag produced during steelmaking should be investigated, calling for the use of more reactive but physically stronger lime, the recycle of slags to aid in slag formation, and the reduction of silicon and phosphorous contents of hot metal. Yield and energy use benefits would be realized.

The presence of free lime and magnesia in steelmaking slag is detrimental to its volume stability and limits its use in construction and as asphalt aggregate for roadmaking. Use of steelmaking slags as replacement for raw stone in the manufacture of cement needs to be expanded; a major energy credit arises from such use. Nonetheless, there is room for development of new economical processes to resolve the problems that limit wider use of steelmaking slags.

Alternative uses for steelmaking slag need to be identified, such as in manufacture of refractories or ceramics. The benefits from agricultural uses of steelmaking slag need to be evaluated further as has been done in Western Europe. Alternative steelmaking slag practices also need to be considered.

Ironmaking and Steelmaking Dusts & Sludges and Rolling Scale & Sludges

R & D Needs

Iron & Steel Making Dusts and Sludges

- Economical gas cleaning system to separate zinc-rich fraction from steelmaking gas stream
- Better and cheaper binders for cold briquetting
- Dewatering method which reduces sludge moisture to 10%
- New applications for the iron oxide by-product
- New pyrometallurgical processes to smelt dusts and sludges
- Demonstration plant for microwave de-oiling process (sludges)

Potential Impact: 1.1 Million NT Iron Units

Dusts and sludges from ironmaking and steelmaking as well as scale and sludges from rolling operations are mainly composed of oxides, primarily iron oxide. The obvious place to recycle these residues is through the blast furnace via sinter plant (if available). As discussed earlier, the main limits to recycling the ironmaking and steelmaking residues are their zinc content, the presence of oil, water, and other contaminants and the large content of fine particles. Specifically, sludges suffer from the disadvantage of too much moisture, and some rolling scale and sludges are hampered by the amount of oil they contain. Therefore, processes need to be developed to economically address these problems.

Zinc. From a practical viewpoint, currently only pyrometallurgical processes are capable of separating the zinc from the iron to create a separate marketable stream. As described earlier, HTMR processes are in place and new technologies have reached the pilot stage to accomplish this function (keeping in mind that the zinc-rich fraction of the off-gas stream from BOF and some EAF operations is not concentrated enough for purchase by an outside processor), and further support of such efforts is warranted. The alternate approach, to remove the zinc from the scrap prior to melting, is addressed later in the section on Galvanized Scrap.

Imaginative new methods are needed to better separate the zinc-rich fraction from the rest of the materials in the gas stream.

Binders. Generally, most pyrometallurgical recycling processes will require that the dusts and sludges be agglomerated. Recycling agglomerates through the blast furnace and steelmaking vessels requires that they be strong enough to withstand abrasive and thermal shock. Although RHFs are much less demanding, breakage can still occur, resulting in hearth problems and carryover of iron bearing materials to the gas cleaning system.

Better and cheaper binders for cold briquetting by-product oxides are needed. Work is also needed in understanding how binders react in a pyrometallurgical process.

Moisture. Most agglomeration processes require the moisture content of mixed incoming materials to be in the 5 to 10% range. The moisture content of a mixture can be controlled by adjustment of the proportions and sequencing of incoming wet and dry materials so as to obtain the desired moisture level. However, the quantity of wet by-products generated at a steel plant normally far outweighs the quantity of dry by-products generated.

Dewatering methods are needed that are capable of economically reducing sludge moisture to levels approaching 10%. The study addressed by the AISI should help in this endeavor.

Oil. Oily materials generally do not agglomerate well and may cause problems with the opacity of the gaseous stream emitted from the sinter plant stack. In some recycling processes, high levels of oil in the incoming materials could increase the potential for fires in the gas cleaning system of thermal dryers. In addition, due to the size distribution and nature of most dusts and sludges, binder costs can play a significant role in the economics of an agglomeration process. It is important to note that while the sintering process does not tolerate significant quantities of oil in the burden (due to the very short time in the high temperature flame zone and the risk of fires with dry stack cleaning systems), the rotary hearth furnace process offers sufficient time and completion of combustion to provide the ability for safe usage of oil and coal containing charges. The same effect prevails in cement kilns used for the manufacture of Portland cement which requires small amounts (approximately 5%) of iron.

Economical de-oiling processes that will allow material to be de-oiled to levels approaching 1% or less are needed. Experimentation with the microwave technology developed under DOE (at the CMP) and AISI sponsorship merits support. Processes to recycle the oil as a fuel and/or lubricant may be attractive. These may include the tuyere injection of spent rolling oil implemented for a blast furnace in Belgium, which merits investigation. Technologies such as the rotary hearth furnace with the capability to manage full combustion of the oil and grease on oxide materials should be also further investigated.

Pickle Liquor

Spray roasting is the most common regeneration technology used for pickle liquor. This technology produces hydrochloric acid that is directly recyclable and iron oxide that is about 98 to 99% pure. This quality of iron oxide has been found to be acceptable for most hard ferrite applications such as small motors. With the drive toward highly energy-efficient motors, however, higher-quality iron oxide is needed. In addition to the magnetics industry, the iron oxide could be recycled to the sinter plant, but the size of the material makes this difficult.

R & D Needs

Rolling and Finishing

- Decreased residual chlorides and other impurities in Pickle Liquor
- Improved quality of Pickle Liquor iron oxide by-product
- Economical agglomeration process to handle fine particles of iron oxide

Potential Impact: 1.1 Million NT Iron Units

Work is needed to reduce the residual chloride content and other impurities such as silica, calcium, and sodium. In addition, improvements in iron oxide quality are needed to make this by-product more attractive to the soft ferrite industry for use in TV cores and other electronic components.

Since the moisture content of the iron oxide is very low, it is very dusty, rendering open blending environmentally unacceptable. Work is needed in development of economical agglomeration processes capable of handling fine materials.

3.2 Obsolete Scrap

Obsolete scrap is any steel item recovered after it has reached the end of its useful life. Examples include the steel recovered through the shredding of used cars and appliances, cans collected through curbside pickup or recycling centers, and structural beams or plates recovered from the construction or demolition of buildings and bridges.

Obsolete scrap is an extremely diverse category and presents a wide variety of challenges to recycling. Figure 3-9 shows the six main subcategories of obsolete scrap along with the volumes of iron units currently available and recycled.

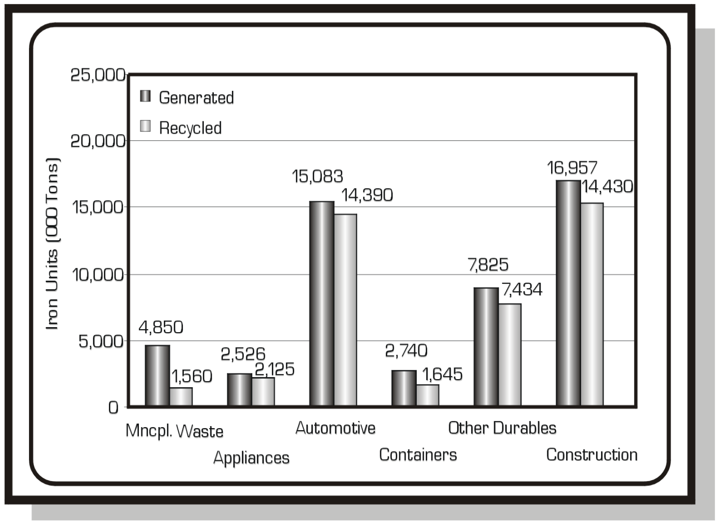

Figure 3-9. Obsolete Scrap Iron Units, U.S. 2000 (SRI 2001)

3.2.1 Municipal Waste Stream

The municipal waste stream contains a large amount of steel scrap that is not currently widely recycled, but the iron units contained in that scrap cannot be recovered economically using current technologies. The vast majority of this steel is attached to other materials from which it cannot be separated easily. Examples include steel box springs and the hinges or guide rails of old wooden furniture.

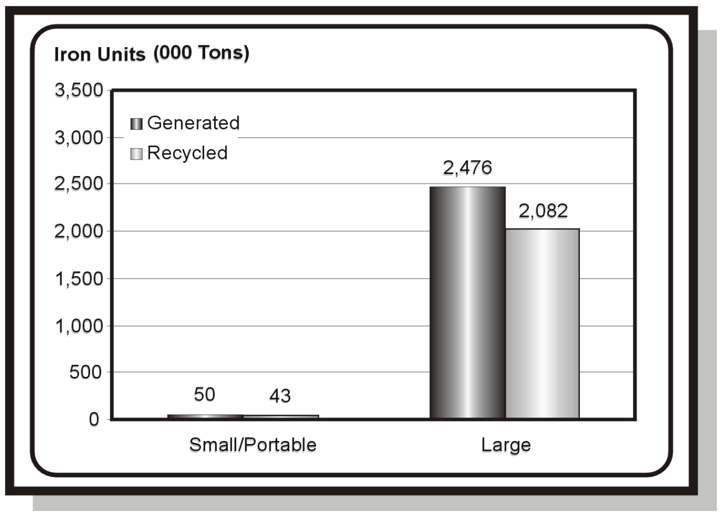

Figure 3-10. Appliance Scrap Iron Units, U.S. 2000 (SRI 2001)

Some form of magnetic separation is the most desirable way to recover the highest quality scrap from the municipal waste stream. Mass burning of municipal solid waste in waste-to-energy plants has been suggested as an alternative solution to the problem. Proponents maintain that ferrous metals could easily be recovered from the bottom ash using magnetic separation (Power 1995). This waste treatment approach, however, still must clear several technological and societal hurdles. Unfortunately, ferrous materials recovered from bottom ash are generally undesirable and unacceptable for melting high-quality steels because contaminants from the surrounding materials become alloyed into the steel scrap.

3.2.2 Appliances

All appliances contain recycled steel that can be further recycled at the end of product usefulness. As shown in Figure 3-10, however, the majority of iron units available for recovery from this source are in large appliances.

Appliances	
Composition	70% of the shredded appliance material is ferrous metal (ISRI 1999).
Production	U.S. manufacturers ship about 50 million major household appliances each year or roughly 137,000/day (ISRI 1994). In 2000, Americans discarded an estimated 3.5 million tons of appliances.
Current Treatment Options	Landfill or recycle for iron units.
Recyclability Issues/Barriers	State bans are helping to discourage landfilling of appliances. Infrastructure for collection and markets for the recycled product continues to need development. However, currently there are over 11,800 locations throughout the U.S. and Canada that accept appliances for recycling (SRI 2000.)

Trends and Drivers. To extend the life of landfills and encourage appliance recycling, several states have enacted landfill bans for large appliances (known as "white goods") thereby forcing the contained steel into the post consumer scrap stream.

3.2.3 Automotive

In 2000, the steel industry recovered and recycled more than 14 million tons of shredded steel scrap from automobiles (SRI 2001). Altogether, the scrap industry recycles about 80% of the weight of a car (Figure 3-11). The goal of the steel industry is to see that recycling of the ferrous portion of automobiles is 100%.

The biggest potential for increased recycling in the automotive sector is in the area of miscellaneous automotive scrap. More specifically, as shown in Figure 3-12, substantial opportunities exist in the recycling of used oil filters and in processes for galvanized scrap.

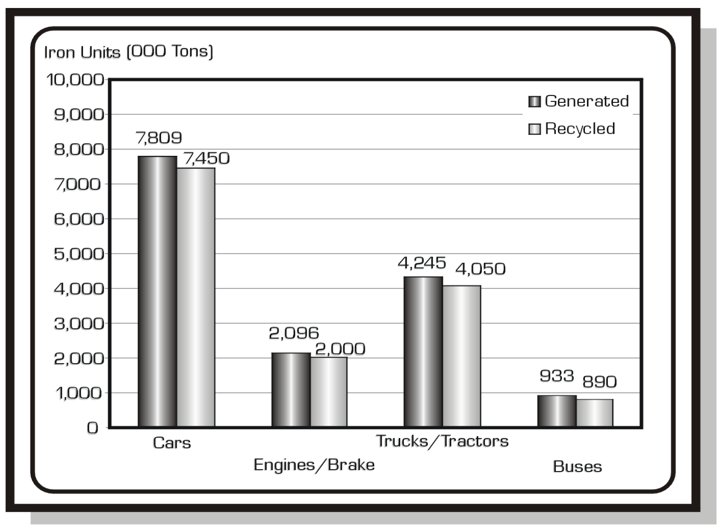

Figure 3-11. Iron Units by Vehicle Type, U.S. 2000 (SRI 2001)

Used Oil Filters

Oil filters are generated by convenience oil/lube and fleet service shops or by home do-it-yourselfer's. Historically, the do-it-yourselfer has thrown filters in the trash.

Trends and Drivers. The recycling infrastructure for filters is developing quickly, and end-market consumption by steel mills and foundries should accelerate. Do-it-yourselfer oil and filters are beginning to be recycled through pilot programs in retail stores, such as Wal-Mart or NAPA Auto Parts. Retailers with on-site oil or lube service shops are well suited for this activity; those without a shop may offer recycling as a marketing strategy.

Melters need specialized holding areas for used oil filters to contain incidental run-off. Filters are routinely blended with other scrap, at the rate of one or two tons/melt. This limit helps ensure that air emission permit limits are not exceeded and that no flame or smoke problems are created.

New and Emerging Technologies. Recycling oil filters through the blast furnace is being studied. A demonstration may follow.

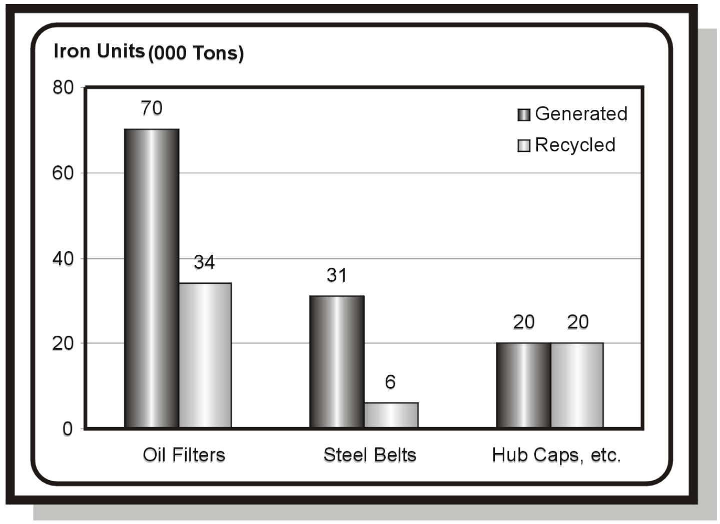

Figure 3-12. Iron Units by Vehicle Component, U.S. 2000 (SRI 2001)

Galvanized Steel Scrap

The low-carbon galvanized steels normally used in automotive bodies and appliances are a source of high-quality scrap feed for both BOF and EAF steel production. Although the steel industry and the DOE, through Argonne National Laboratory, invested heavily in support of the development of technology for removal of the galvanized coatings, the protracted delays in achievement of an economically viable solution forced most BOF operators to implement alternative methodologies to maintain environmental compliance (EAF operations, with higher dust disposal cost, benefit to some extent from the value of the contained zinc units). Thus, future process development toward dezincing scrap must be focused on approaches that can fit into the economic realities of the costs incurred presently (i.e., loss of yield, inability to recycle the iron units in the dusts/sludges, increasing costs to meet new tighter limits for water treatment, furnace delays to manage charging emissions).

Trends and Drivers. The amount of galvanized steel produced and used, and therefore the zinc content of the scrap charges, continues to rise (Koros 1998).

New and Emerging Technologies. A pilot plant using an electrochemical dezincing process for prompt scrap was in operation for about two years. Although the process could remove zinc under certain conditions, it was not demonstrated in the requisite closed loop mode.

Future work in this area will need new entrants, preferably with new concepts likely to result in a lower cost process. One such approach, based on use of air and of regenerated chlorine (Fray 1999), has been taken to the pilot stage although more work is needed particularly to diminish the amount of surface oxidation of the dezinced scrap product (the latter effect is considered undesirable by the potential customers in the foundry industry).

3.2.4 Containers

Recycling of the iron units in steel cans shows substantial room for improvement, as shown in Figure 3-13. The overall industry goal for can recycling is to recover 60% of the available iron units as soon as possible. The majority of steel cans and some pails are made from tin-coated material. It is feasible to recover the high-value tin from these containers (as well as from tin-coated home and prompt steel scrap) by detinning prior to remelting the base steel - in 1999 approximately 10% of cans were returned for detinning in 1999 (SRI 1999). The low value of tin has hindered the use of this recovery method.

Tinplated Steel Scrap

Tinplate is often used for food, general line cans, and closures to provide corrosion protection and serve as a substrate for decorative and protective lacquers. The tin coating is very thin, typically three hundred-thousandths of an inch. Detinning is practiced for two reasons: recovery of valuable tin for reuse and production of clean scrap suitable for remelting. With respect to the latter, steelmakers prefer to minimize the amount of tin in scrap because tin can be detrimental to the properties of certain deep-drawing steels and electrical steels and can contribute to embrittlement in susceptible alloy steels.

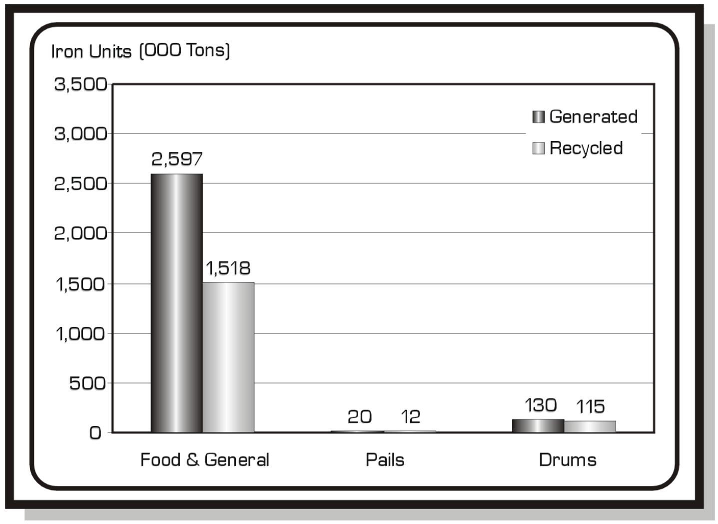

Figure 3-13. Container Scrap Iron Units, U.S. 2000 (SRI 2001)

Containers: Tinplated Steel Scrap

Composition The weight of tin on tinplate has been reduced to 0.20% from the range of 0.25% prevalent even 5 years ago. Furthermore, nearly one third of production in tin mills currently is "Tin Free Steel", which is really a chromium based coating. These factors, and the removal of tin in some can making operations, has resulted in a relatively low content of tin in post consumer can scrap.

Production Detinning technology is of interest in the US only for prompt scrap, that is, the material generated by the tin plate producer or at the can making plants.

Current Treatment Options

Industrial-scale detinning is performed by passing shredded tinplate through a warm, dilute solution of sodium hydroxide containing an oxidant. This process removes the tin and the iron-tin alloy layer in about an hour. The tin is subsequently recovered from the solution and the process sludge. Highest productivity is achieved by careful preparation of the scrap with respect to size, bulk density, and freedom from tramp material (particularly aluminum).

Recyclability Issues/Barriers

There are several problems currently facing detinning plants

- Less tin is available for recovery as the thickness of tin coatings has declined, and some modern canmaking technologies remove tin during manufacture.
- The use of TFS for food cans is increasing (tin is replaced with a chromium coating).
- The value of detinned scrap plus the amount and value of the recovered tin is reportedly too low to support an adequate financial return.
- Transport costs are high for moving recycled cans to the few detinning operations in North America. (Many integrated plants are distant from detinners.)
- As a matter of practical policy, integrated steel producers and some EAF operations melt baled post consumer can scrap with a resultant small gradual increase in tin residual levels in steel.

Trends and Drivers. Some steelmakers are using increased volumes of post consumer cans directly in the steelmaking process, especially in the production of steels for which a small amount of residual tin is less important. The average food can in 1999 was coated with only 0.20 lb/BB tin, thus with the modern low volume of internal scrap generation in the integrated steel plants the rate of residual tin build up remains relatively low (SRI 1999).

New and Emerging Technologies. None have been identified.

3.2.5 Other Durables

Approximately 90% of other durable scrap items are currently being recycled. This category includes oil rigs, pipelines, aircraft, railway spikes and tie plates, lathes and machine housings, cranes, lifts, boxcars, ships, and manhole covers. The steel industry has not yet identified this category as a priority area for expanded recycling.

3.2.6 Construction

A highly sophisticated infrastructure exists in this country for the collection and processing of steel from the construction and demolition category of obsolete scrap. The steel present in construction scrap primarily consists of steel reinforcement bars (known as rebars). In 1999 approximately 45% of recovered rebars were recycled (SRI 1999).

3.2.7 Obsolete Scrap Research and Development Needs and Opportunities

Automotive

Used Oil Filters. Further work is needed to expand the base of steel mills and foundries that accept used oil filters for scrap. Such work should include investigating the scrap value of oil filters as well as their potential energy value in blast furnaces.

Improvements are needed for the systems and equipment employed in the processing, transportation, and storage of used oil filters so as to reduce or eliminate the entrapment, spillage, or migration of used oil.

R & D Needs

Automotive and Scrap Appliances

- Determined scrap and energy value of oil filters
- Improved design of oil filter handling systems
- New dezincing process concepts
- Technology for treating galvanized obsolete scrap
- Improved method for separating out copper, aluminum, and CFC's

Potential Gain: 1.1 Million NT Iron Units

Galvanized Steel Scrap. Continued development is needed for a technology to remove zinc from shredded post consumer scrap. Current potential candidates are electrochemically aided caustic leaching and gaseous chlorination with air enhancement (removal of zinc with minimal surface oxidation.) to increase recycling by the foundry industry. A technology to treat obsolete scrap containing galvanized steel needs to be developed.

Appliances

Improved methods are required for separating copper, aluminum, and chlorinated fluorocarbons (CFC's). The applicability of sorting technology developed in Japan should be investigated. The target is approximately 600,000 NT of iron units from appliances.

Containers

Curbside recycling options for steel containers should continue to be developed.

R & D Needs	*Containers and Construction*
	‣ Assessed sensitivity of modern steels to tin residual levels ‣ Methods for reducing levels of tin in the melt ‣ Economical process for removing concrete from rebar Potential Gain: 3.7 Million NT Iron Units

Tinplated Steel Scrap. Given the economic issues surrounding detinning, a better approach to managing tin scrap is required. Research is needed to assess the sensitivity of modern steels (e.g., those containing ppm levels of sulfur, phosphorous, and copper) to increasing levels of tin residuals, especially with regard to low temperature mechanical properties. Methods to reduce the content of tin to even lower levels in the melt or in subsequent treatment processes is desired. The target is approximately 1,129,000 NT of iron units from scrap containers.

Construction

An economically sound process is needed to remove concrete from reinforcement bars ("rebars") so that the steel can be recycled easily. Currently, rebars are recovered only if they are exposed or become exposed during demolition; the exposed portions are cut from the concrete with a torch and sent as scrap for recycling. Rebar that remains in the concrete is generally landfilled.

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