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End-of-Life Vehicle Recycling: State of the Art of Resource Recovery from Shredder Residue

Energy Systems Division

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End-of-Life Vehicle Recycling: State of the Art of Resource Recovery from Shredder Residue

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The opinions expressed in this report are those of the authors and do not necessarily reflect the opinions of the CRADA partner organizations.

NOTATION

The following is a list of the abbreviations, acronyms, and units of measure used in this document. (Some acronyms and abbreviations used only in tables may be defined only in those tables.)

GENERAL ACRONYMS AND ABBREVIATIONS

Alliance	The Alliance of Automobile Manufacturers
ACC-PD	American Chemistry Council-Plastics Division (formerly APC)
AIAG	Automotive Industry Action Group
AIAM	Association of International Automobile Manufacturers
ARD	Auto Recycling Demonstration (Project)
Argonne	Argonne National Laboratory
APC	American Plastics Council
API	American Petroleum Institute
APME	Association of Plastics Manufacturers in Europe
ARA	Automotive Recyclers Association
ARIC	Appliance Recycling Information Center
ASR	automobile shredder residue
BDAT	best demonstrated available technology
BP	British Petroleum
BSEF	Bromine Science and Environmental Forum
CAR	Certified Automotive Recyclers (Program)
CD	compact disc
CMP	Center for Materials Production
CRADA	Cooperative Research and Development Agreement
CTU	Conzepte Technik Umwelt AG
CWT	Changing World Technologies, Inc.
DM	Deutsche Mark
DOE	U.S. Department of Energy
DSD	Duales System Deutschland
ECUT	Energy Conversion and Utilization Technologies
ELV	end-of-life vehicle
ELVS	End-of-Life Vehicle Solutions Corporation
ENPA	Environment National Protection Agency
EPA	U.S. Environmental Protection Agency
EPIC	Environment and Plastics Industry Council
EU	European Union
EUCAR	European Council for Automotive R&D

EV	electric vehicle
FBP	final boiling point
FTC	Federal Trade Commission
GC-ECD	gas chromatography-electron capture detector
GC/MS	gas chromatography/mass spectroscopy
GDL	gas diffusion layer
HEV	hybrid electric vehicle
IBP	initial boiling point
IDIS	International Dismantling Information System (software)
IGEA	German abbreviation of "Syndicate for the Environmentally Compatible Disposal of Nonmetallic Waste from Vehicles"
IR	infrared
ISRI	Institute of Scrap Recycling Industries
JAMA	Japan Automobile Manufacturers Association
JCI	Johnson Controls, Inc.
KDS	kinetic energy separators
KT	Krupp/Thyssen
MEA	membrane electrode assembly
MDEC	Michigan Department of Environmental Quality
MFR	melt flow rate
MMI	Michigan Molecular Institute
MSW	municipal solid waste
NRT	National Recovery Technologies, Inc.
NVMSRP	National Vehicle Mercury Switch Recovery Program
OEM	original equipment manufacturer
ORNL	Oak Ridge National Laboratory
PCR	post-consumer recyclate
PEM	polymer electrolyte membrane
PIA	Plastics Institute of America
PMC	polymer-matrix composite
PMMA	polymethylmethacrylate
PURRC	The Polyurethane Recycle and Recovery Council
R&D	research and development
RBRC	Rechargeable Battery Recycling Corporation
RCRA	Resource Conservation and Recovery Act of 1976

REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
ROHS	Restriction of Hazardous Substances Directive
RPI	Recovery Plastics International
SAE	Society of Automotive Engineers
SARS	Stiftung Auto Recycling Schweiz
SB	Sthlwerke Bremen
SEM	scanning electron microscope
SG	specific gravity
S.N.A.M.	Société Nouvelle D'Affinage des Métaux
SOC	substances of concern
SPORT	Sustainable Polymers to Olefins Recycling Technology
SVC	Siemens Venture Capital Gmbh
TCLP	toxicity characterization leaching procedure
TCP	thermal conversion process
TOC	total organic content
TOX	total organic halogens
TRB	Transportation Research Board
USABC	United States Advanced Battery Consortium, LLC.
USAMP	United States Automotive Materials Partnership
USCAR	United States Council for Automotive Research, LLC.
USGS	U.S. Geological Survey
UV	ultraviolet
VAI	Voest-Alpine Industrieanlagenbau GmbH & Co.
VIAQ	volatile interior air quality
Vinyl Institute	The Vinyl Institute/ACC (PVC issues)
VOC	volatile organic compound
VRP	Vehicle Recycling Partnership, LLC.
WEEE	Waste Electrical and Electronic Equipment Directive
XPS	X-ray photon spectroscopy

ELEMENTS AND COMPOUNDS

ABS	acrylonitrile butadiene styrene
Al	aluminum
$CaCO_3$	calcium carbonate
Cd	cadmium
CFC	chlorofluorocarbon
CO	carbon monoxide

CO_2	carbon dioxide
Cr	chromium
Cr^{+6}	hexavalent chromium
DecaBDE	decabromodiphenyl ether
DEG	diethylene glycol
EMPP	elastomer (rubber) modified polypropylene
EPDM	ethylene propylene diene-monomer
HCl	hydrogen chloride
HDPE	high-density polyethylene
HF	hydrogen fluoride
Hg	mercury
HIPS	high-impact polystyrene
KOH	potassium hydroxide
Li $CoCO_2$	lithium cobalt dioxide
Li-ion	lithium-ion
MEK	methyl ethyl ketone
Mg	magnesium
Ni-Cd	nickel-cadmium
Ni-Fe	nickel-iron
Ni-MH	nickel-metal hydride
NO_x	nitrogen oxides
PA	polyamide
PA6	polyamide 6 (also known as nylon 6)
PA66	polyamide 6/6 (also known as nylon 66)
PAH	polycyclic aromatic hydrocarbon
PAN	polyacrylonitrile
Pb	lead
PBDE	polybrominated diphenyl ethers
PBT	polybutylene terephthalate
PC	polycarbonate
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-P-dioxins
PE	polyethylene
Perc	perchloroethylene
PET	polyethylene terephthalate
PMMA	polymethyl methacrylate
PP	polypropylene
PPO	polyphenylene oxide

PS	polystyrene
Pt	platinum
PUF	polyurethane foam
PUR	polyurethane rubber
PVC	polyvinyl chloride
Ru	ruthenium
SAN	styrene acrylonitrile
SO_x	sulfur oxides
TEO	thermoplastic elastomer olefins (also abbr. TPO)
TTEG	tetraethylene glycol
TPO	thermoplastic olefinic

UNITS OF MEASURE

bbl	barrel
Btu	British thermal unit
cc	cubic centimeters (cm^3)
cm	centimeter
cPs	centipoise
DTUL	deflection temperature under load
ft^3	cubic feet
g	gram
gal	gallon
GPa	giga Pascal (tow tensile modulus)
h	hour
Hz	Hertz
in.	inch
kg	kilogram
kJ	kilo Joule
ksi	kips per square inch (kips/in.^{2})
L	liter
lb	pound
m^2	square meter
MHz	mega Hertz
μm	micrometer
min	minute
MJ	mega Joule
MPa	mega Pascal (tow tensile strength)
mm	millimeter
ppm	parts per million
psi	pounds per square inch (lb/in.^{2})
sec	second
yr	year

SUMMARY

Each year, more than 25 million vehicles reach the end of their service life throughout the world, and this number is rising rapidly because the number of vehicles on the roads is rapidly increasing. In the United States, more than 95% of the 10–15 million scrapped vehicles annually enter a comprehensive recycling infrastructure that includes auto parts recyclers/dismantlers, remanufacturers, and material recyclers (shredders). Today, over 75% of automotive materials, primarily the metals, are profitably recycled via (1) parts reuse and parts and components remanufacturing and (2) ultimately by the scrap processing (shredding) industry. The process by which the scrap processors recover metal scrap from automobiles involves shredding the obsolete automobile hulks, along with other obsolete metal-containing products (such as white goods, industrial scrap, and demolition debris), and recovering the metals from the shredded material. The single largest source of recycled ferrous scrap for the iron and steel industry is obsolete automobiles. The non-metallic fraction that remains after the metals are recovered from the shredded materials — commonly called shredder residue — constitutes about 25% of the weight of the vehicle, and it is disposed of in landfills. This practice is not environmentally friendly, wastes valuable resources, and may become uneconomical. Therefore, it is not sustainable.

Over the past 15–20 years, a significant amount of research and development has been undertaken to enhance the recycle rate of end-of-life vehicles, including enhancing dismantling techniques and improving remanufacturing operations. However, most of the effort has been focused on developing technology to separate and recover non-metallic materials, such as polymers, from shredder residue.

To make future vehicles more energy efficient, more lightweighting materials — primarily polymers, polymer composites, high-strength steels, and aluminum — will be used in manufacturing these vehicles. Many of these materials increase the percentage of shredder residue that must be disposed of, compared with the percentage of metals that are recovered. In addition, the number of hybrid vehicles and electric vehicles on the road is rapidly increasing. This trend will also introduce new materials for disposal at the end of their useful lives, including batteries. Therefore, as the complexity of automotive materials and systems increases, new technologies will be required to sustain and maximize the ultimate recycling of these materials and systems.

Argonne National Laboratory (Argonne), the Vehicle Recycling Partnership, LLC. (VRP) of the United States Council for Automotive Research, LLC. (USCAR), and the American Chemistry Council-Plastics Division (ACC-PD) are working to develop technology for recovering materials from end-of-life vehicles, including separating and recovering polymers and residual metals from shredder residue. Several other organizations worldwide are also working on developing technology for recycling materials from shredder residue. Without a commercially viable shredder industry, our nation and the world will most likely face greater environmental challenges and a decreased supply of quality scrap, and thereby be forced to turn to primary ores for the production of finished metals. This will result in increased energy consumption and increased damage to the environment, including increased greenhouse gas emissions.

The recycling of polymers, other organics, and residual metals in shredder residue saves the equivalent of over 23 million barrels of oil annually. This results in a 12-million-ton reduction in greenhouse gas emissions.

This document presents a review of the state-of-the-art in the recycling of automotive materials.

1 INTRODUCTION

1.1 BACKGROUND

The recycling of automotive materials can have a significant impact on the conservation of materials, domestic energy use, and emissions of greenhouse gases. The automobile industry is one of the largest consumers of materials. For example, in 2001, the 217 million vehicles on the U.S. roads contained 5.3% of all steel and 13.8% of all aluminum in use in the United States (USGS 2006a, 2006b). In 2007, there were 246 million vehicles on our roads — about 21% of all registered cars and about 42.6% of all registered trucks in the world. The average weights of vehicles built in 1995, 2000, and 2007 were 3,694 lb, 3,902 lb, and 4,076 lb, respectively (Davis et al. 2009). Based on these weights, it is reasonable to estimate that the average weight of a vehicle is about 3,900 lb. This implies that 480 million tons of materials were used to build these vehicles. These materials include different types of steel, iron castings, aluminum, magnesium castings, copper and brass, lead, zinc castings, powder metal parts, plastics and composites, rubber, coatings, textiles, fluids and lubricants, glass, and other materials (Davis et al. 2009). In comparison, the average weight of vehicles in Europe was 2,125 lb in 2006, which is expected to increase to 2,260 lb by 2015 (GHK 2006).

In 1999, materials use in the domestic U.S. automotive industry exceeded 32 million tons (Table 1.1). The automotive industry's consumption of steel accounted for 20% of all domestic steel use. In the case of aluminum, the automotive industry used about one-third of the total domestic use of aluminum. The primary energy consumed in the production of the 32 million tons of material used in the automotive sector is estimated to be about 1.5 quadrillion Btu, which was roughly 20% of the domestic industrial energy use. This consumption is equivalent to about 250 million barrels of oil. In comparison, the energy consumed in 1999 to fuel the total automotive fleet, including cars, trucks, and buses, was about 3,500 million barrels of oil equivalent (Ward's 2000). In 2007, about 13% of all steel consumed in the United States was used in vehicle manufacturing (estimated on the basis of data from Davis 2009 and USGS 2008).

As one of the largest consumers of materials, vehicles also represent one of the largest sources of recycled materials. Annually, between 10 and 15 million obsolete vehicles in the United States are retired from service and enter the domestic recycling infrastructure (Table 1.2). In 1999, sales of all vehicles in the United States exceeded 17 million vehicles, and the total number of vehicles in use exceeded 200 million. Table 1.2 presents similar data for the year 2007. There are also about 18 million vehicles on Canadian roads, and about 450,000 of them are retired annually (http://autorecyclers.blogspot.com/2008_02_01_archive.html).

Over the past 15–20 years, the ways in which automotive materials are used have changed in response to the demand for improved fuel economy, safety, and performance. The average weight of domestically built vehicles has been rising lately, after it began to decrease in the years following the 1974 oil embargo. Recent increases in the cost of gasoline and heightened awareness of potential energy shortages in the future may raise the demand for lighter vehicles. Lately, the trend has been a substitution of higher-performance, lighter-weight materials to achieve improved fuel efficiency.

In the future, we can expect increased use of lighter-weight materials, such as aluminum alloys, polymers, and polymer matrix composites. Automotive systems will become more sophisticated and complex as hybrid and alternative fuel vehicles enter the market. These changes in automotive materials use and vehicular system complexity will require the development of new and advanced technologies for sustainable automotive materials recycling.

TABLE 1.1 Automotive Industry Materials Use in 1999*

Material	Automotive Consumption (tons)	Automotive as a Percentage of Total Consumption (%)
Aluminum	3,969,000	32.2
Copper	550,000	11.8
Iron	3,101,000	31.3
Lead	1,384,240	32.2
Plastic	1,778,660	4.1
Rubber	2,592,700	66.9
Steel	16,771,000	15.8
Zinc	308,200	23.0
Other materials	1,845,000	n/a
Total	32,299,800	n/a

* Includes materials for cars, trucks, buses, and replacement parts.
Source: Ward's (2000); other materials estimated by authors.

TABLE 1.2 Selected Automotive Statistics

Statistic	Number of Vehicles for 1999*	Number of Vehicles for 2007**
Motor vehicles in operation	209,508,000	246,431,000
Passenger cars	126,868,000	135,933,000
Trucks	82,640,000	110,498,000
Motor vehicle sales	17,425,000	
Domestic cars and light trucks	14,399,000	12,334,756
Import cars and light trucks	2,514,000	3,754,244
Heavy vehicles	512,000	884,200
Motor vehicles retired from use	11,663,000	
Passenger cars	7,216,000	
Light trucks	4,447,000	
Alternate fuel vehicles	322,302**	695,766

* Source: Ward's (2000).
** Davis et al. (2009); includes hydrogen and electricity, excluding military vehicles.

1.2 THE AUTOMOBILE INDUSTRY

The automobile industry has grown very rapidly in the last 100 years (see Table 1.3 and Figures 1.1 and 1.2). The number of vehicles in use is expected to triple in the next 50 years (Levizzari, Bonino, and Corrias 2002). Of these vehicles, approximately 6% reach the end of their useful life annually. Materials used in manufacturing vehicles have also been changing. More significant changes are anticipated in the near future to make vehicles lighter and more energy efficient, to increase performance, and/or to improve safety. The average useful life of a vehicle is about 10–15 years, so more than 12 million vehicles annually reach the end of their useful lives in the United States. Over 95% of these end-of-life vehicles (ELVs) are recycled for their metals content, which represents about 75% of the weight of the vehicle (Sendijarevic et al. 1997). The other 25% typically ends up in landfills, with a small percentage used as landfill cover.

In the past 10 years, significant increases in the number of vehicles on the road have also been seen in developing countries, especially in China and India (Figure 1.3). In China, the total number of cars on the road in 2008 exceeded 24 million, an increase of about 24.5% over 2007. Privately owned cars in China numbered 19.47 million, representing a 28.0% increase over 2007 (http://www.greencarcongress.com/2009/02/total-number-of.html, February 27, 2009). In India, the number of registered cars jumped from about 5.15 million in 2000 to about 8.6 million in 2007 (Davis et al. 2009).

TABLE 1.3 Growth in the Number of Motor Vehicles (cars, buses, and trucks) in the World (Elert 2001)

Year	Number of Cars	Number of Trucks and Buses	Total
1900	4,192	0	4,192
1968	169,994,128	46,614,342	216,608,470
1985	375,000,000	109,000,000	484,000,000
1996	485,954,000	185,404,000	671,358,000

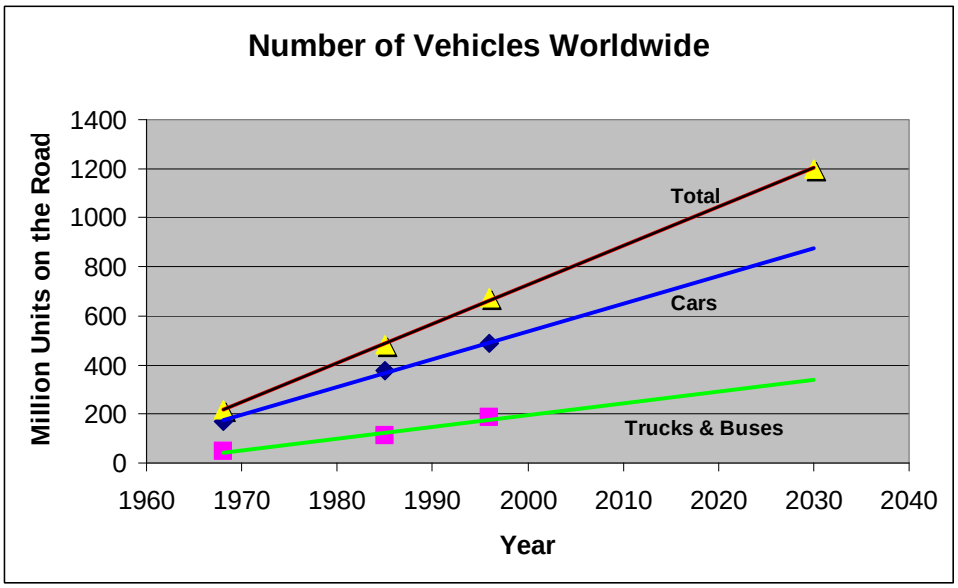

FIGURE 1.1 Historical Growth in the Number of Vehicles in the World (based on data in Elert 2001)

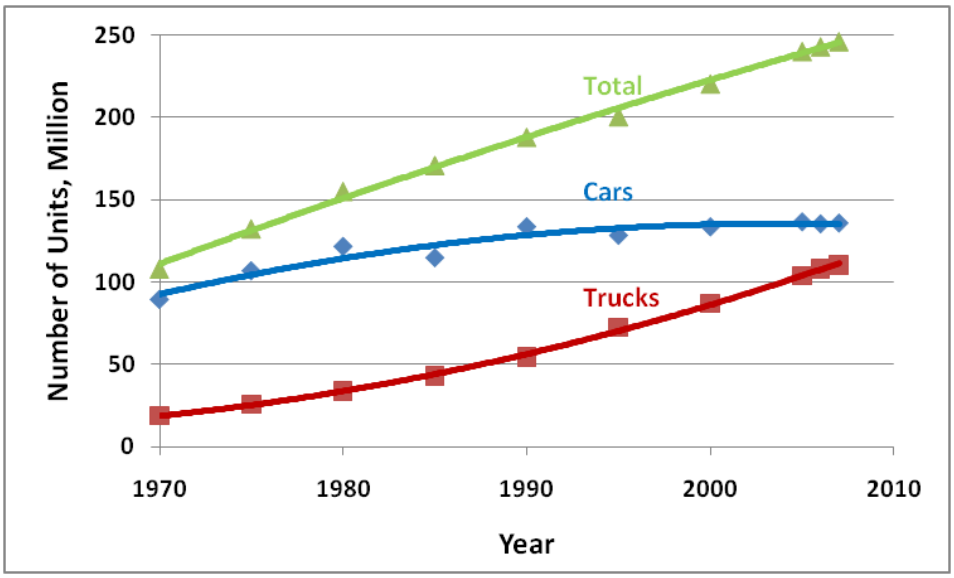

FIGURE 1.2 Historical Growth in the Number of Vehicles on the Road in the United States (Davis et al. 2009)

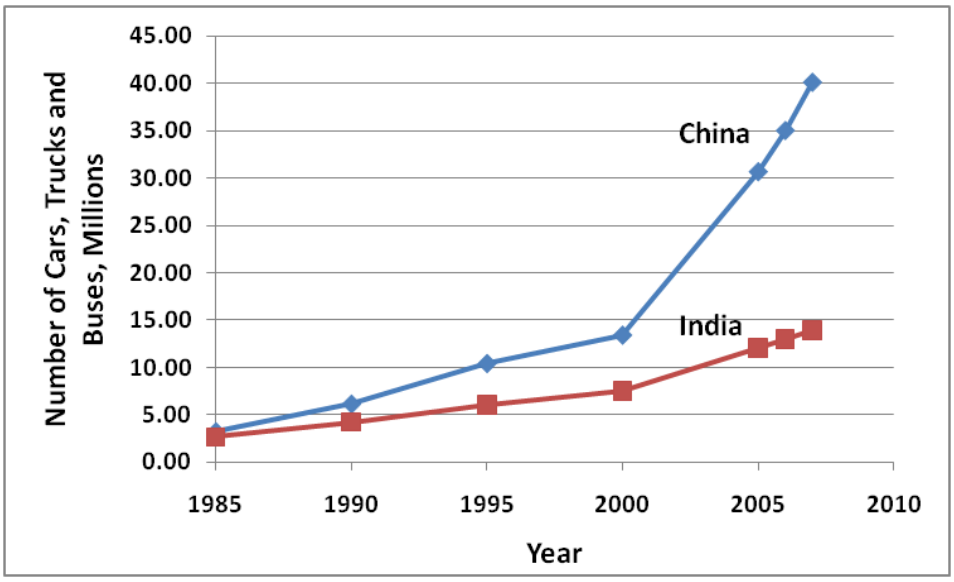

FIGURE 1.3 Growth in the Number of Registered Vehicles on the Road in China and India (Davis et al. 2009)

As new materials are introduced, as is the case with more polymers and polymer composites, the composition of shredder residue will change. Figure 1.4 shows the weight percent of plastics in North American light vehicles in the last 10 years. Polypropylene, polyurethane, and nylons are the fastest increasing polymers in vehicles (Figure 1.5). The average weight of vehicles and the weight of lightweighting materials in vehicles both continued to increase after 1995 (see Figure 1.6) and reached 4,076 lb, of which 510 lb were plastics, composites, and rubber. This results in an increase in the amount of shredder residue going to the landfill, unless these lightweighting materials are recycled along with the metals.

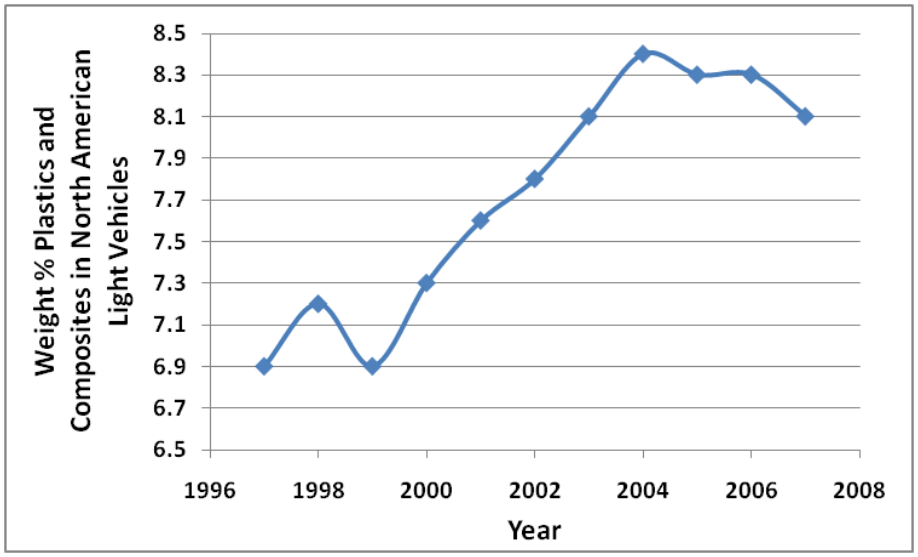

FIGURE 1.4 Weight Percent of Plastics and Composites in North American Light Vehicles (Swift 2008)

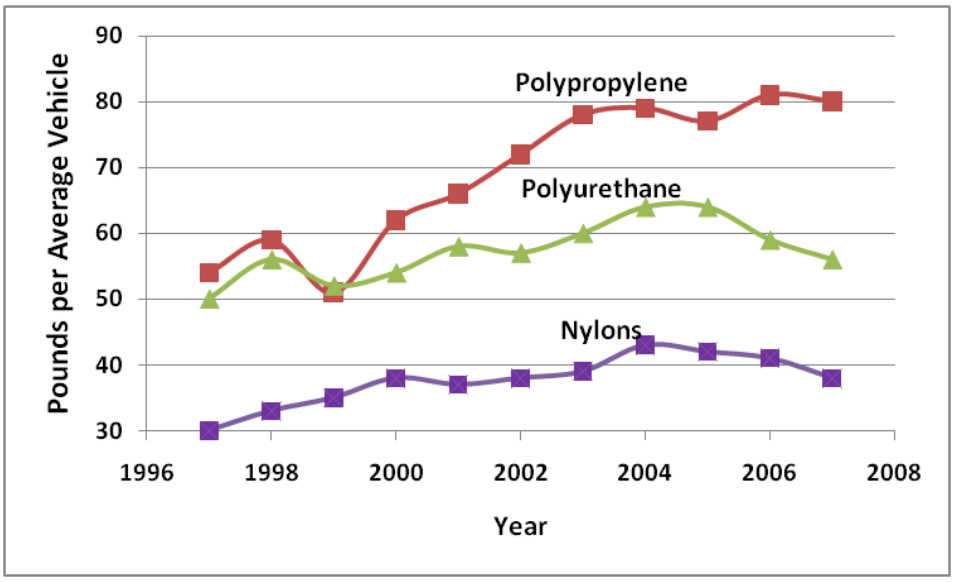

FIGURE 1.5 Weight of Polypropylene, Polyurethane, and Nylons in an Average North American Light Vehicle (Swift 2008)

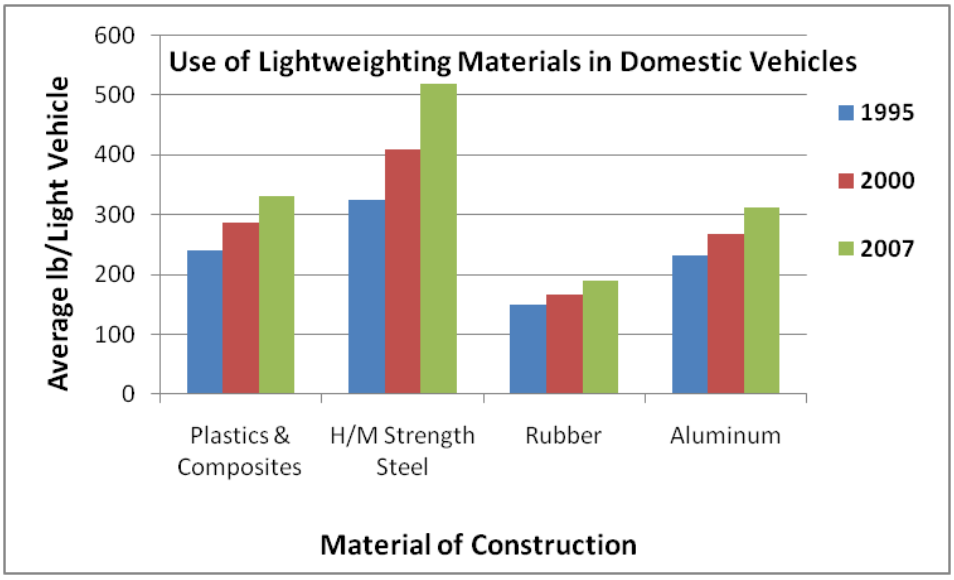

FIGURE 1.6 Steady Increase in the Use of Lightweighting Materials in Vehicles (based on data from TRB 2009 and data from Ward's Communications 2008 [and updates, 2009]) (H/M refers to high- and medium-strength steel)

1.3 AUTOMOTIVE MATERIAL RECYCLERS

Optimizing the economic recyclability of automobiles requires a comprehensive and integrated approach (Reuter et al. 2004). The various processors (auto companies and their suppliers, dismantlers, and shredders) must work together to coordinate the interaction between the process/quality control and the science behind the separation technology in order to implement an effective approach. They also must comply with governing regulations and meet market requirements.

Dismantling: Obsolete vehicles are typically received and processed first by automotive dismantlers. In the United States, there are more than 15,000 auto-dismantling facilities. At the dismantling yard, useable parts are recovered from the vehicle for resale and/or remanufacturing. The dismantling operation provides low-cost replacement parts to repair shops, parts brokers, and individual customers. Direct reuse of a part (such as a door panel or trunk lid) conserves the materials and energy that would otherwise be required to produce the replacement part from virgin materials, as well as the manufacturing energy required to stamp the part and assemble the component. It is the practice of original equipment manufacturers (OEMs) to have stockpiles of parts and components (up to 10 years) for warranty/service availability once vehicles are no longer in production.

Remanufacturing: Remanufacturing and rebuilding of certain components of dismantled vehicles by dismantlers or by repair shops is another important aspect of the existing recycle infrastructure. Many automotive components are remanufactured to supply lower-cost repair and replacement parts to maintain the domestic fleet. For example, more than 90% of the replacement starters and alternators are remanufactured. Other automotive parts that are typically remanufactured include engines, transmissions, brake systems, and water pumps. Remanufacturing entails the tear down, inspection, repair, and/or replacement of subcomponents, as well as testing of the remanufactured component to ensure that the performance specifications of the remanufactured part are met. Thermoplastic olefin (TPO) bumpers and aluminum wheels are also “remanufactured;” these are cosmetic repairs and are not required to be retested for Federal crashworthiness.

Over 95% of batteries and catalytic converters are collected. The acid is neutralized, and the lead is recovered by smelting. The batteries’ plastics casings (polypropylene and polypropylene co-polymers) are recycled into automotive fender liners. The precious metals from the catalytic converters are recovered. These are recycled into various markets and products.

Shredding: After useable and re-manufacturable parts are removed from obsolete vehicles, the final step in the recycling infrastructure is the recovery of materials for recycling. Typically, the remaining auto hulk is crushed and transported from one of the dismantling facilities to one of more than 200 shredding facilities. At the shredder, the auto hulk and other materials, including consumer durables (such as home appliances) and other scrap iron and steel, are processed. A typical shredder can process one or two car hulks per minute. A shredder is a large (3,000–8,000 hp) hammer mill that tears up the auto hulk and other metals-containing materials into fist-sized chunks of materials. Ferrous metals are recovered by using magnets, and

nonferrous metals are typically recovered by using eddy-current separators. These materials are then recycled into new products. The primary source materials for shredders are obsolete automobiles, followed by obsolete home appliances.

Perhaps the most important characteristic of the North American automotive materials recycling infrastructure is that it is economically self-supporting. More specifically, the values of the components and materials that are recovered and recycled in each stage of the infrastructure provide a profit to the operator. In North America, automotive material recycling is not subsidized by either taxpayers or car buyers.

1.4 RECYCLING SUPPORTS SUSTAINABILITY

Recycling promotes sustainability. For an activity to be sustainable it must be economically attractive and environmentally friendly and provide a beneficial service to society in a safe and responsible manner. A sustainable operation is a target that today's industries are striving to attain as the world faces material shortages, increased costs, and more stringent environmental regulations. The automotive industry and its products are major users of natural resources and a source of greenhouse emissions. In order to reduce energy consumption and greenhouse emissions, the industry is using more lightweighting materials to manufacture its products. These materials include polymers, composites, high- and medium-strength steels, aluminum, and magnesium. The increased interest in hybrid vehicles will expand the need for new materials such as lithium, cobalt, and nickel. At the same time, regulations are calling for more recycling of the obsolete vehicles and components (e.g., airbags).

Replacing conventional steel, which is recyclable, with lighter materials will result in a reduction in the recycling rate of vehicles, even if the lighter materials are recycled at the same rate. Unless the lightweighting materials are recycled, the drop in the recycling rate can be significant. Lightweighting and hybrid vehicle battery materials are expensive and, unless recycled, could become in short supply with constrained availability. Improper disposal of these materials can have adverse environmental impacts. Therefore, the recycling of these materials is essential to the sustainability of the automotive industry and its suppliers. Dismantling of the proper parts and materials from obsolete vehicles is an important step in recycling these materials and components (Duranceau 2009).

Without a commercially viable shredder industry, our nation may face greater environmental challenges and a decreased supply of quality scrap, and thereby be forced to turn to primary ores for the production of finished metals (Menken and Voigt 2002). Without a viable shredder industry, constraints on the availability of nonferrous metal quantities for lightweighting are predicted at the current projected market usage. Upcycling of recycled, nonferrous metals will be needed, especially for aluminum, magnesium, cobalt, and nickel. Replacing brominated fire retardants with non-bromine compounds will also require greater aluminum, titanium, and antimony usage.

An efficient and economical solution to recycling the current and future shredder residue is necessary to enhance the sustainability of the automotive industry and its suppliers. To

produce quality products at the lowest cost, the solution is likely to be an integrated system of many technologies.

1.5 THE METALS RECYCLING (SHREDDING) INDUSTRY

The more than 200 shredders in the United States shred 10 to 15 million vehicles annually (in addition to white goods and other source materials) (Daniels et al. 2004). As a result, based on 2000-year vehicle weight, the U.S. shredders currently supply about 17 million tons of recovered ferrous and nonferrous scrap from end-of-life vehicles for use in the metals industry (12 million cars × 3,902 lb/vehicle × 75% metal content of the car × 95% of the metals are recovered). Over 8 million passenger cars are scrapped each year in Western Europe (Costes and Monteil 2000).

By recovering the metals from obsolete materials, the U.S. shredder industry generates large amounts of shredder residue that must be disposed of. Figure 1.7 shows the materials that are presently recycled, and Figure 1.8 shows the amounts that are presently not recycled from an average 2000 light vehicle. About 73% of the weight of the vehicle is metals for which recycling technology exists (Figure 1.7). The non-metals (Figure 1.8) constitute about 20%, and they are presently not recycled. The remaining materials (Figure 1.9) are partially recycled. Overall, about 25% of the vehicle materials are not recycled. American shredders generate about 6 million tons of shredder residues from shredding vehicles alone (12 million vehicles × 3,902 lb/vehicle × 25% of the vehicle's weight end up as shredder residue). Shredder residue has a density range of about 15–25 lb/ft^3 and a moisture content that can exceed 25% of its dry weight.

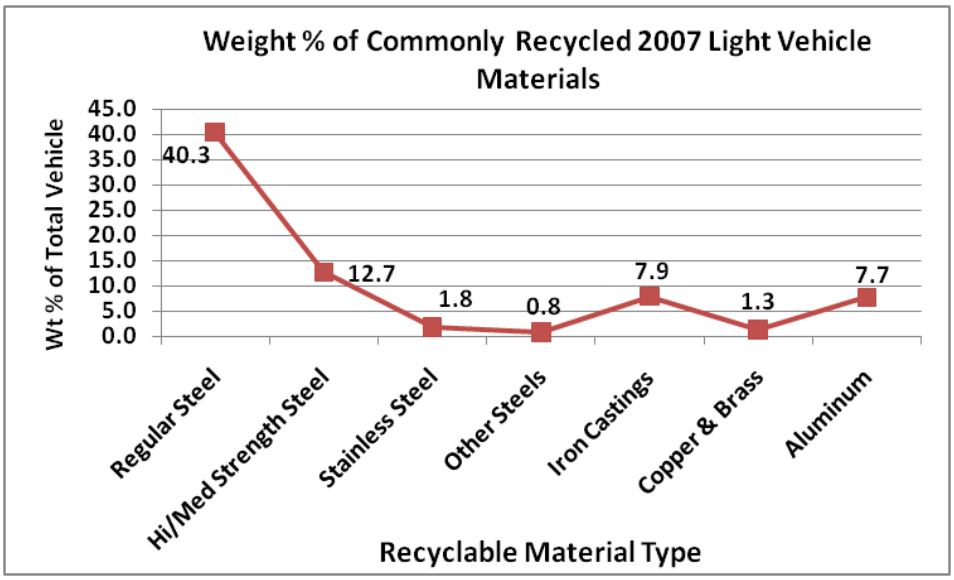

FIGURE 1.7 Recyclable Materials in an Average 2007 Light Vehicle (based on data from Davis et al. 2009 and data from Ward's Communications 2008 [and updates, 2009])

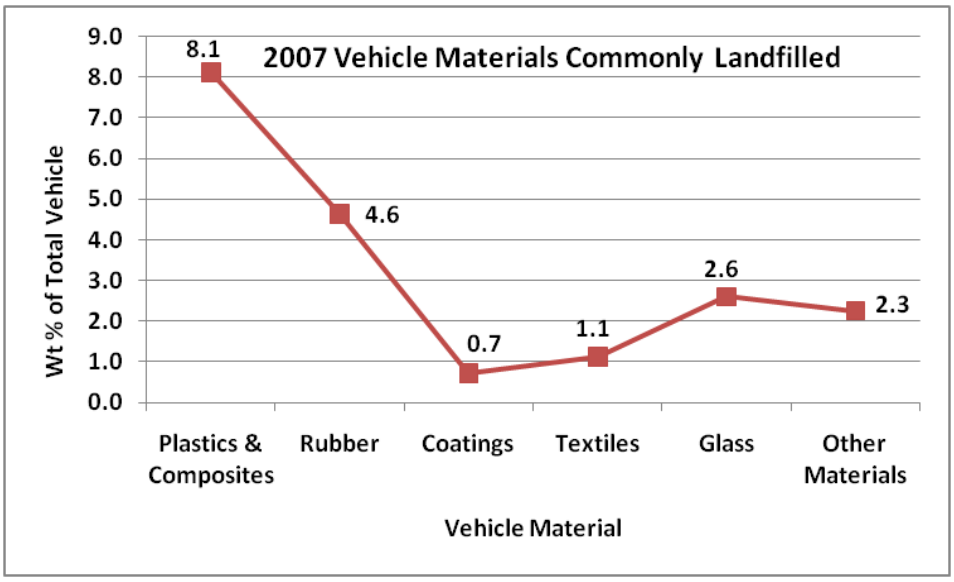

FIGURE 1.8 Commonly Landfilled Materials in an Average 2007 Light Vehicle (based on data from Davis et al. 2009 and data from Ward's Communications 2008 [and updates, 2009])

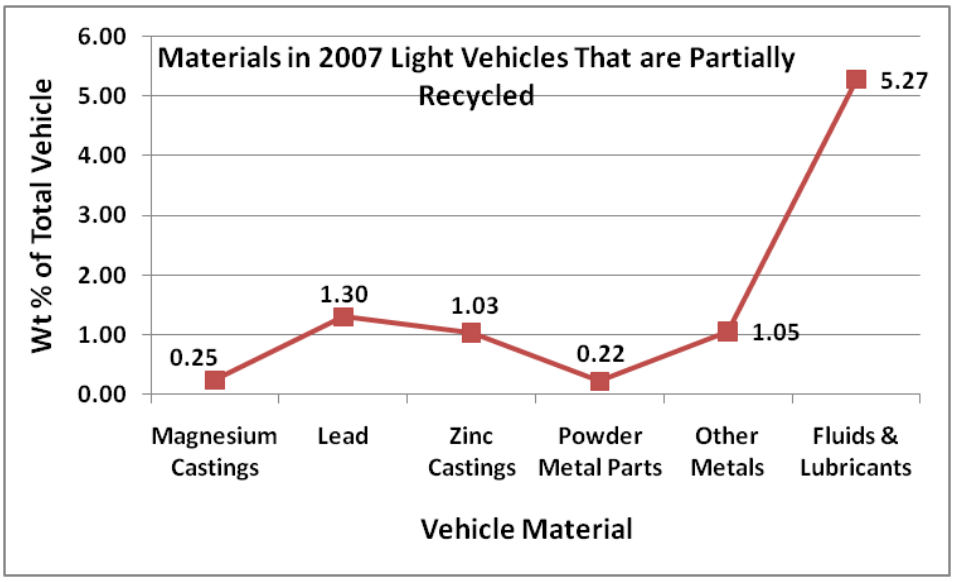

FIGURE 1.9 Partially Recycled Materials in an Average 2007 Light Vehicle (based on data from Davis et al. 2009 and data from Ward's Communications 2008 [and updates, 2009])

Of the vehicles on the road, approximately 6% reach the end of their useful life annually. The average useful life of a vehicle is about 10–15 years. Over 95% of the ELVs in the United States are recycled for their metals content, which represents about 75% of the weight of the vehicle (Sendijarevic et al. 1997; Davis et al. 2009). The other 25% typically ends up in landfills, with some used as landfill cover or incinerated. State-by-state regulations vary with specific permitting, treating, or special handling requirements. Davis et. al. (2009) reported that in 2007 there were a total of 645,286,000 registered cars and 266,236,000 registered trucks and buses on the road in the world. Assuming that the average weight is 5,000 lb per unit, that they will retire from service in the next 10 years, and that 25% of their content is non-metallic, over 50 million tons of shredder residue will be generated if these vehicles are recycled for their metals only, as is the practice today. The energy (heating value) in these 50 million tons is equivalent to about 115 million barrels of oil.

1.6 IMPACT OF USING LIGHTWEIGHTING MATERIALS ON THE RECYCLABILITY OF VEHICLES

Recyclability studies were conducted to examine the effect of using automotive lightweighting material on recyclability. A Toyota Prius hybrid was selected as a reference case. This vehicle is a second-generation hybrid with a gas/electric powertrain. Evaluating the recyclability of this vehicle and its new technology will be a step in identifying changes that will impact the end-of-life recycling of vehicles of the future. In collaboration with Johnson Controls, Inc. (JCI), the Vehicle Recycling Partnership, LLC. (VRP) dismantled the vehicle, according to VRP procedures, to single material components and entered data for each part into a database. A material list that identified the breakdown of materials into separate classifications (such as ferrous and nonferrous metals, as well as composite materials and plastics) was prepared.

The materials breakdown is summarized in Table 1.4. For comparison, the materials composition of a production Ford Taurus is summarized in Table 1.5.

TABLE 1.4 2004 Toyota Prius Materials Breakdown

Materials	Mass (lb)	%
Ferrous metals	1,713	60.6
Nonferrous metals	507	17.9
Plastics	341	12.1
Elastomers	87	3.1
Inorganic materials	77	2.7
Other	62	2.2
Organic materials	42	1.5
Vehicle mass (less fluids)	2,829	100.0

TABLE 1.5 2004 Ford Taurus Materials Breakdown

Materials	Mass (lb)	Percent
Ferrous metals	2,223	70.4
Plastics	340	10.8
Nonferrous metals	312	9.9
Elastomers	152	4.8
Inorganic materials	90	2.9
Other	38	1.2
Organic materials	4	0.1
Vehicle mass (less fluids)	3,159	100.0

Three different recyclability calculations were made (Table 1.6). The Federal Trade Commission (FTC) recyclability number is the percentage by weight of the material that is currently being recycled; it includes metals, fluids less fuel, and batteries. The European guidelines include FTC materials plus fuel at 90% of a full tank, plastics that could be recycled, and up to 10% by weight energy recovery. Note that Europe requires 95% recyclability for new vehicles. The feasibility-to-recycle number includes the FTC materials plus plastics that can be recycled. Changes to the current infrastructure would be required to increase recycling beyond the current FTC percentage.

To establish an indication of the impact of lightweight materials on the reference case recyclability calculations, the 2004 Toyota Prius is compared with a proposed aluminum-intensive lightweight vehicle and a proposed composite lightweight vehicle, both of which are also based on the 2004 Prius. The production 2004 Toyota Prius hybrid vehicle body is steel with an aluminum hood and deck lid. The suspension is of steel, except for an aluminum steering knuckle on the front suspension. This vehicle is used as the base for this study.

TABLE 1.6 Reference Case Recyclability: 2004 Toyota Prius

Calculation Method	Recyclability %
Federal Trade Commission	80.86
European	97.61
Feasibility of recycling	85.58
Ref. 2000 Ford Taurus	80.50

The aluminum alternative is for a 2004 Toyota Prius with an aluminum body and a magnesium engine cradle and a rear axle substituted for the production parts. In addition, seat frames, body brackets, and the instrument panel cross-car beam have been changed from steel to aluminum. As a result, the weight has been reduced by approximately 630 lb, or 21%. Because the weight reduction is entirely in the currently recycled portion of the vehicle, the recyclability is adversely affected and is reduced from 80.86% to 76.10%. No changes were made to the currently non-recycled portion of the vehicle. Aluminum replaced steel at 50% by weight of the original steel.

The composite alternative is for a 2004 Toyota Prius that consists of (1) a carbon-fiber body with 40% carbon fiber and 60% thermoset polyurethane/urea resin by volume, 49.72% carbon, and 50.28% thermoset polyurethane/urea resin by weight; and (2) a magnesium engine cradle and a rear axle substituted for the production parts. In addition, seat frames, body brackets, and the instrument panel cross-car beam have been changed from steel to composite. As a result, the weight has been reduced by approximately 711 lb, or 24%. Because the weight reduction is entirely in the currently recycled portion of the vehicle, the recyclability is adversely affected and is reduced from 80.86% to 57.20% if none of the composite is recycled, or to 74% if all the composite material is recycled. No changes were made to the currently non-recycled portion of the vehicle. The composite material replaced steel at 40 wt% of the original steel.

There are reductions in all three recyclability calculations for lightweighted vehicles, even though the rest of the vehicle is not changed (Table 1.7). Where the aluminum and composite material is being recycled, the same amount of material would be disposed of in landfills in each of the three scenarios. The only difference is that the recycled portion of the lightweighted vehicles would be lighter. Although the recyclability would be less, there would be no difference in the amount of material disposed of in landfills, and the lighter vehicles would use less fuel during their life. As can be seen, lightweighting presents challenges in the European market. Note that these calculations do not take into account the downsizing of related components that would accompany any lightweight vehicle, such as powertrains, brakes, and tires. Because the downsized components are high in metallic content, downsizing will further reduce recyclability and make it difficult to meet the European 95% requirement.

In conjunction with this study, additional evaluations are planned by using these data as a starting point for assessing the recyclability of cars of the future. The impact of vehicle lightweighting and material selection on recyclability will be evaluated. In addition, the impact of powertrain changes in future vehicles (including hybrid and fuel cell alternatives) on recyclability will be determined in comparison with powertrains in current vehicles. An assessment of various alternatives on recycling and the effect on the current recycling infrastructure will be produced. No downsizing of other components was included in this study. Future studies will reflect the downsizing of powertrains, brakes, tires, and other components in recyclability calculations. Items requiring further study resulting from these assessments will support future projects to determine the feasibility of various alternative vehicle configurations and choices of materials.

TABLE 1.7 2004 Toyota Prius Recyclability: Reference Case vs. Aluminum and Composite Body Materials

Calculation Method	As Produced (%)	Aluminum Body (%)	Composite Body (%)
FTC	80.9	76.1	74.0[a]
European	97.6	96.0	94.5[a]
Recycling feasibility	88.3	85.6	83.9[a]

[a] If the composite material were not recycled, then the numbers would be FTC: 57.2%, European: 78.2%, and feasibility of recycling: 67.1%. Recycling of the composite material would require significant changes in the current recycling infrastructure. In addition, a market for the recycled carbon fibers would need to be developed. Current technology for recycling carbon fibers results in a 20% loss in fiber properties and would limit their reuse to short fiber applications.

These results demonstrate the need for technology to recycle lightweighting automotive materials if recycling mandates are to be met and to ensure that lightweighting materials are not excluded because of the inability to recycle them.

It is interesting to point out that, even if the lightweighting metals that replace steel and iron are recycled at the same rate as the present rate of recycling steel and iron, the overall recyclability rate of the obsolete vehicle will decrease because the relative weight of the metals in the vehicle will decrease. Therefore, in order to maintain high vehicle recycling rates, it is important that the non-metallic materials that are presently not recycled, such as polymers, be recycled.

1.7 LIFE-CYCLE ANALYSES OF DIFFERENT RECYCLING METHODOLOGIES

The objective is to use life-cycle analysis to assess the environmental impacts of various separation and alternative end-of-life recycling technologies. This information will then be used to create a flexible, computerized life-cycle inventory model, which is process-specific and yet can be modified to include additional recycling technologies and various material inputs. Life-cycle involves assessing all the upstream burdens associated with the production of the materials and energies used in the process, including the transport of all materials to the facility.

PE Europe GmbH, a company that is experienced in conducting life-cycle assessments and in model development using its own GaBi (Ganzheitliche Bilanzerung) software, was contracted to perform these analyses. Three analyses have been completed: (1) Salyp NV's mechanical separation process, (2) Changing World Technologies (CWT) thermal conversion process (TCP), and (3) Argonne's mechanical and froth-flotation process. PE Europe has developed a flexible end-of-life model, which was used to compare the two different approaches

to recycling shredder residue. The model allows the user to run simulations on shredder-residue separation within different boundary conditions. The following boundary conditions can be modified: (1) shredder-residue composition, (2) location of the facility, (3) type and distance of transportation, (4) market values for the separated fractions, (5) new potential applications for separated fractions, and (6) utilization ratio of the facility.

Salyp's separation process combined equipment developed by Argonne and several others to create a facility that separates shredder residue into discrete fractions of metals, foam, mixed plastics, and fiber-rich and fines streams. The Argonne process separates the shredder residue by means of dry and wet processing to recover polymers and residual metal. On the other hand, the CWT process converts organic materials into hydrocarbon fuels and other potential products. These processes are described in more detail later in this report. Data were collected for each analysis, including all energy, water, and material inputs, plus data on emissions to air and water, wastes, and products produced. The four sets of data were entered into the GaBi software to create a flexible model of the process.

In the case of the Salyp separation process, three different scenarios for handling the various materials recovered from shredder residue were determined. These scenarios included using specific material fractions as fuel for cement kilns (energy recovery), as well as using mixed plastics to replace such products as wood pallets and polypropylene (PP) pellets (material substitution). The various scenarios were assessed by using a variety of impact categories, including primary energy demand and carbon dioxide (CO_2) emissions. In the case of primary energy demand, all scenarios showed a net credit in total energy use. For the three scenarios studied, substituting recovered polypropylene/polyethylene (PP/PE) in a new PP application had the greatest benefit. However, if the mixed plastic stream were used to replace wood (e.g., decking material, park benches, wood pallets, etc.), the benefits to primary energy demand were less than if the recovered materials were simply used for energy recovery. In terms of CO_2 emissions, the PP application again showed the greatest benefit. Substituting PP for wood applications was next with a lower benefit, while the energy-recovery scenario showed an increase in CO_2 emissions.

In the case of the CWT process, two basic scenarios were assessed. They involved using the light hydrocarbon oil generated by the process for fuel oil used in power plants to generate electricity and substituting light hydrocarbon oil for diesel oil (both with and without an added hot-oil processing step). While the oil product generated is more refined than an actual crude oil, it would require additional steps before it could be considered a true diesel oil. Therefore, reality is probably located somewhere between scenarios 1 and 2. In this study, the impact on primary energy demand resulted in a benefit in all cases. The benefits in the diesel-substitution case were slightly greater than in the fuel oil case. In the case of CO_2 emissions, all scenarios again showed an overall benefit. However, the diesel-substitution case had a greater benefit than the fuel-oil substitution case.

Life-cycle analysis of the Argonne process considered both the mechanical separation of the shredder residue to produce a polymer concentrate and recover residual metals, followed by froth flotation to separate plastics from the polymer concentrate for recycling as plastics (material substitution). The analysis concluded that both the mechanical and the froth-flotation

processes resulted in environmental benefits (Figure 1.10). The environmental benefits of the Argonne process were also compared with those of the Salyp (Table 1.8) and CWT processes (Table 1.9). The environmental benefits were higher for the Argonne process compared with the Salyp process, except for the acidification potential (AP), and higher for the Argonne process compared with the CWT process, except for the impact category eutrophication potential (EP) and nitrogen oxides (NO_x) emissions. Energy-wise, the Argonne process was the most advantageous. Interestingly, the analyses concluded that the best results could be obtained by combining the Argonne and CWT processes, where organic fractions separated by Argonne that do not meet the requirements for material substitution (such as mixed plastics and rubber by-products) are processed by CWT for fuel production.

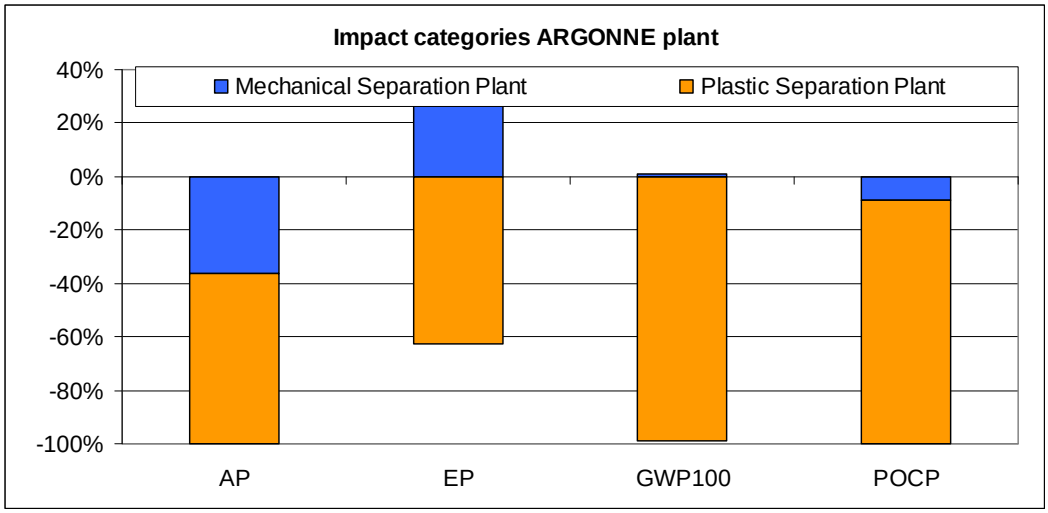

FIGURE 1.10 Impact Categories of the Argonne Plant (AP is acidification potential, EP is eutrophication [depletion of oxygen in water] potential, GWP is global-warming potential, and POCP is photochemical ozone creation potential.) (The Y axis indicates the increase (+) or decrease (-) in the impact of the different categories.)

TABLE 1.8 Comparison of the Argonne and Salyp Processes — Relative Environmental Impact (A negative value indicates a reduction in the pollution category [an environmental benefit], while a positive value indicates an increase in the pollution category.)

	Argonne Process (mechanical and froth flotation)	Salyp Process
AP [lb SO2-equivalent]	-0.0060	-0.0165
EP [lb phosphate-equivalent]	-0.00011	0.00148
GWP100 [lb CO2-equivalent]	-1.354	0.861
POCP [lb ethene-equivalent]	-0.0026	0.0126

TABLE 1.9 Comparison of the Argonne Froth-Flotation and CWT Processes — Relative Environmental Impact (Both processes require mechanical separation of the inorganic fraction. A negative value indicates a reduction in the pollution category [an environmental benefit], while a positive value indicates an increase in the pollution category.)

	Argonne Process (Froth Flotation)*	CWT Process
AP [lb SO2-equivalent]	-0.01103	-0.00662
EP [lb phosphate-equivalent]	-0.00055	-0.00079
GWP100 [lb CO2-equivalent]	-4.167	-0.309
POCP [lb ethene-equivalent]	-0.0088	-0.0044

* The comparison is done here with only the froth-flotation process, because both the Argonne froth-flotation process and the CWT process require mechanical separation of the inorganic materials.

1.8 METHODS FOR DISPOSAL OF SHREDDER RESIDUE

Before the introduction of the automobile shredder in the early 1960s, the most common method of recycling obsolete automobiles involved open-air combustion of the automobile hulk to burn off tires, plastics, and other combustibles. Open-air burning is no longer practiced because it is a gross violation of environmental (Clean Air Act) regulations. More controlled incineration techniques were explored in the late 1950s and early 1960s (Dean et al. 1985; Bilbrey, Sterner, and Valdez 1978; Ellsworth, Ballinger, and Engdahl 1957). With the introduction of the shredder and the incorporation of better separation techniques (such as multiple magnetic separation stages, air classification, screens, and wet-and-dry cyclones in the early 1960s [Dean et al. 1985] and the eddy current separators on a large scale in the 1990s), the number of obsolete automobiles processed increased dramatically — and so did the amount of recovered metals.

Several publications that appeared in the late 1960s and early 1970s addressed a variety of topics on the subject, including the production of quality scrap, improved separation methods, the impact of increasing plastics content of automobiles, process economics, and environmental concerns associated with the process (Kaiser and Tolciss 1961; Dean and Sterner 1969; Adams 1972; Luntz 1973; Dean, Sterner, and Valdez 1974; Daellenbach, Mahan, and Drost 1974; Jody and Daniels 1994; Sawyer 1974).

Public interest in the processing and recycling of plastics waste also increased (Sterner, Steele, and Shirts 1984; Warner, Parker, and Baum 1970; Mack 1971; Leidner 1981; PIA 1987). Interest was stimulated primarily by (1) increased public awareness of the magnitude of the waste problem in general and (2) increased disposal costs.

During the 1970s, two methods of shredder residue disposal were practiced: land filling and incineration. Land filling continues to be, by far, the most widely practiced technique for disposing of shredder residue. However, the disposal of shredder residue in landfills is already cost-prohibitive in parts of the world or banned altogether. In the United States, some states require that shredder residue be treated to fix and immobilize heavy metals before its disposal in landfills. The State of California is presently re-examining the regulations governing the disposal of shredder residue (Sandoval 2009). Because the disposal costs of and environmental concerns over shredder residue are expected to continue to escalate, more economical and environmentally friendly alternatives are needed. Even though shredder residue is a preferred daily landfill cover, it is still required to be mixed with calcium carbonate ($CaCO_3$) lime to decrease leaching into ground water.

Because approximately 40–55% of the shredder residue is hydrocarbon-based materials (such as plastics, rubber, fibers, wood, paper, tar, and oils), the amount that needs to be disposed of can be reduced significantly by:

- Separation and recovery of recyclable materials from the shredder residue, primarily plastics, rubber, and residual metals, including the reprocessing of the fines fraction.

- Conversion to liquid and gaseous fuels via pyrolysis or gasification of its organic content.

- Incineration with heat recovery. The heating value of shredder residue varies from about 4,000 to 6,500 Btu/lb and averages approximately 5,400 Btu/lb (Hubble, Most, and Wolman 1987).

The noncombustible fraction, which contains glass, dirt, rocks, sand, moisture, and residual metals and metal oxides, can also be reduced by separating and recovering the metals and their oxides and perhaps the glass. The approximate composition of today's shredder residue is shown in Table 1.10. All shredder residues contain essentially the same materials, including polymers and residual metals. Variations in the percentage of the different materials exist. However, these variations do not make a standard separation process design obsolete. Processing of shredder residue from a single source over a six-month period showed that the composition of shredder residue remained essentially the same. For example, the amount of polymers (polymer concentrate) recovered, shown in Table 1.11, stayed about the same.

Techniques to recover materials from shredder residue for recycling and to reduce the amounts that need to be disposed of are discussed in Sections 4–10 of this document.

Because of the organics in shredder residue, care should be exercised when storing and handling it. Horii and Iida (1999) conducted tests on shredder residue to determine its self-ignition characteristics. They found that spontaneous combustion can occur in stockpiles 2–3 m high at temperatures of about 70–80°C, while for stockpiles of about 7–8 m high, ignition could occur at 40–50°C. Because shredder residue contains some biodegradable materials, localized heating within a stockpile may occur, resulting in dangerously high temperatures.

TABLE 1.10 Variability in Quantities of Recovered Fractions from Shredder to Shredder(data generated at Argonne's mechanical separation pilot plant)

Fraction	Average wt. (%)	Range wt. (%)
Oversized heavies (metals and rocks)	5	2-8
Oversized polyurethane foam	2	0.5-5
Fines	39	24-60
Ferrous fraction	2	1-4
Nonferrous rich	4	3-7
Mixed material fraction	5	10-20
Polymer concentrate	25	20-45
Loss due to moisture and other materials	18	10-30

TABLE 1.11 Yield of Polymer Concentrate from a Given Source over a 6-Month Period (data generated at Argonne's mechanical separation pilot plant)

Run #	Polymer Concentrate (wt. %)	Run #	Polymer Concentrate (wt. %)
1	36	5	43
2	39	6	45
3	45	7	37
4	37	8	38
Average		40	

1.9 REGULATORY ISSUES

1.9.1 United States Regulations

In the United States, no stringent regulations such as those enacted in Europe exist at the federal level. In 1991, U.S. Congressman Robert Torricelli and Senator Frank Lautenberg sponsored the "Automobile Recycling Study Act," which called for an analysis of the potential for greater recycling of automotive components. This act was incorporated into a set of amendments to the Resource Conservation and Recovery Act of 1976 (RCRA), but it failed to gain approval. Since then, regulatory activities in the United States have been limited to the state level, and they addressed primarily (Orr et al. 2000):

- Labeling of liquid containers, including washer fluid and coolant fluid bottles;
- Limits on dismantler storm water runoff;

- Landfill restrictions on mercury-containing components; and
- Classification of shredder residue as hazardous waste in California.

In 2005, Ohio's House of Representatives passed a bill exempting auto shredder residue from the waste generation fee (http://www.encyclopedia.com/doc/1G1-135814029.html, August 1, 2005).

California is presently re-examining the regulations governing the disposal of shredder residue (Sandoval 2009). In California, the regulation (Bill Number: SB 524, before it was amended in 2009) authorized auto shredder waste "that is treated as required by regulations to be used as alternative daily cover if specified requirements are met." The amended rule states:

1. The Secretary for Environmental Protection is required to establish an auto shredder residue working group, comprised of representatives of the board, the department, the State Air Resources Board, the State Water Resources Control Board, members of the auto shredder industry, landfill operators, and other interested stakeholders. The working group should be established by February 1, 2010.

2. The working group is required to review "the existing practice of using treated auto shredder residue as alternative daily cover, determine the effects of the department's proposed revocation of the current regulatory classification of treated auto shredder residue and resulting prohibitions on its use as alternative daily cover, determine whether the current regulatory classification of treated auto shredder residue poses a threat to human health and the environment, identify the constituents in auto shredder residue that could pose health and safety or environmental problems when used as alternative daily cover in accordance with applicable regulations, recommend approaches to work with the auto industry to manufacture vehicles that produce less hazardous waste at end-of-life, and recommend changes to statute, regulation, or agency practice, if any, based on the working group's analysis."

3. "The bill would require the Secretary, on or before December 31, 2010, to report to the Legislature on the findings of the working group, and would prohibit the department from altering the current regulatory status of auto shredder residue without first considering the factors the working group is required to consider."

Many, however, do not consider regulations to be an effective means of encouraging the recyclability of shredder residue and do not believe that there should be mandated ELV recycling systems (Gesing 2004). Gesing pointed out that a scrap recycling system that collects scrap from various markets, processes the scrap to recover the metals, and sells the metals to consuming markets already exists. He indicated that imposing a monitoring system on this recycling system is not likely to result in an increase in recycling, but only an increase in cost. He instead recommended (1) an approach to monitor and set metal, rubber, and plastic maximum content limits on any residue streams from the recycling system and (2) that air and water monitoring systems of the recycling facilities be implemented. Air should be monitored for both toxics

(dioxins, furans, and polycyclic aromatic hydrocarbons [PAHs]) and greenhouse gas emissions. Water should be checked for contamination from liquid residue streams and by leachate from solid residue (Gesing 2004).

In 2006, the National Vehicle Mercury Switch Recovery Program (NVMSRP) was initiated as a result of a two-year collaborative effort involving the EPA, vehicle manufacturers, the American Iron and Steel Institute, the Steel Manufacturers Association, the Institute of Scrap Recycling Industries, the Automotive Recyclers Association, Environmental Defense, the Ecology Center (Ann Arbor), and representatives of the Environmental Council of the States. The EPA and these stakeholders announced a voluntary program to recover mercury switches from scrap cars and trucks before they are shredded for recycling. End-of-Life Vehicle Solutions (ELVS) (ELVS 2010a, 2010b) carried out the program responsibilities for the vehicle manufacturers. One goal of the NVMSRP was to maximize switch collection nationally. A $4 million fund was established to reward dismantlers/recyclers in the participating states over a 3-year period. As of July 2009, the NVMSRP voluntary incentive fund was depleted. Incentive payments continue in states as required by law (AR, IL, IA, MA, NJ, RI, UT, MD) or in states that have a state-funded program (NC, SC,WA), but they have ceased in voluntary states. All other aspects of the switch collection program continue as a commitment to the environment. (https//www.epa.gov/mercury/switch.htm).

Reacting to the European Registration, Evaluation, Authorization, and Restriction of Chemical Substances Directive's (REACH) list of substances of very high concern (SVHC), various states adopted regulations governing chromium (Cr), lead (Pb), and mercury (Hg). Some expressed concern about brominated flame retardants and phthalates.

1.9.2 European Regulations

In September 2000, European Union (EU) legislators issued a (draft) stringent ELV directive (Directive 2000/53/EC [September 18, 2000]) that included several provisions about the disposal of ELVs. According to the *Official Journal of the European Communities* (October 21, 2000), the directive was to be integrated into national law no later than April 21, 2002. The directive and its related provisions assigned product accountability to the manufacturers of the vehicles (Goldmann 2002; Levizzari, Bonino, and Corrias 2002; Schäper 2002; Essenpreis 2002). It also required that:

- Reuse and recovery shall be increased to a minimum of 85% by January 1, 2006, and

- Reuse and recovery shall be increased to a minimum of 95% by January 1, 2015.

To achieve 85% and 95% recyclability rates, shredder residue must be recycled at 40% and 80%, respectively (Figure 1.11). This requires development of technology to facilitate the economical separation and recovery of recyclable materials from ELVs, including from shredder residue. It also requires resources to track and document the accomplishments.

The directive also specified recycling quotas for non-metals, limited the energy recovery, and ordered that the vehicle manufacturer is responsible for the recovery cost (Schäper 2002; Essenpreis 2002). The directive also called for (Essenpreis 2002; Kamari, Pineau, and Shallari 2003) the following:

- Developing an infrastructure for the manufacturers to take back and recycle ELVs;
- Restricting the use of certain materials;
- Developing technical requirements for recycling plants;
- Marking components to facilitate recycling;
- Ensuring that ELV processing does not result in the contamination of the shredder residue with hazardous species or impair the recovery of components for reuse;
- Promoting reuse and recycling as the preferred disposal routes;
- Requiring that the ELV reuse/recover and reuse/recycle rates be 85% and 80%, respectively, by January 1, 2006;
- Requiring that ELV reuse/recover and reuse/recycle rates be 95% and 85%, respectively, by January 1, 2015;
- Addressing the dismantling, reuse, and recycling needs in the design of new vehicles;
- Limiting the amounts of lead, mercury, cadmium, and Cr(VI) in vehicles built after January 1, 2003;
- Requiring the removal of catalysts and components containing copper, aluminum, or magnesium before shredding; and
- Noting that regulations concerning polyvinyl chloride (PVC) in ELVs is still pending.

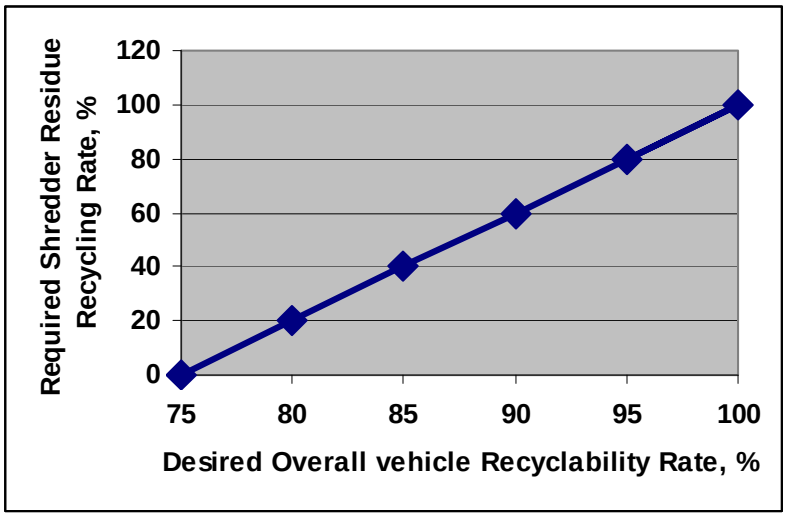

FIGURE 1.11 Shredder Residue Recycling Rates Required to Achieve High Overall Vehicle Recycling Rates

There are two other European directives that can affect the disposal of shredder residue: (1) Directive 2000/76/EC (December 4, 2000) on the incineration of waste and (2) Directive 1999/31/EC (April 26, 2000) on the disposal of waste in landfills. Directive 2000/76/EC (December 4, 2000) on the incineration of waste includes the following requirements:

- Different emission regulations for dust, nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon monoxide (CO), hydrogen fluoride (HF), total organic content (TOC), polychlorinated dibenzo-P-dioxins (PCDD), heavy metals, and mercury apply to municipal, medical, and hazardous wastes;

- Hazardous waste that contains over 1% halogenated organic materials must comply with fluorinated PCDDs (PCDD/Fs) (fluorinated) destruction regulations; and

- Hazardous waste that has a heating value of 30 MJ/kg (12,900 Btu/lb) or more is excluded from hazardous waste regulations.

Directive 1999/31/EC (April 26, 2000), which dealt with the regulation of waste disposed of in landfills, stated that:

- Whole or shredded tires cannot be disposed of in landfills and

- Only treated waste can be disposed of in landfills; this is regulated differently from state to state.

These directives can also complicate the definition and legal and economic future of shredder residue treatment and processing technologies. For example, under the Directive 1999/31/EC (April 26, 2000), waste shredder residue disposed of in landfills can be considered

the product of ELV treatment, so it could fall under "waste that has been subject to treatment." Another example is that, because of the PVC in shredder residue, Directive 2000/76/EC (December 4, 2000) on the incineration of waste may require incineration under special conditions, followed by stringent gas cleanup.

Another European regulation that may impact the recycling of automotive materials is the Registration, Evaluation, Authorisation, and Restriction of Chemical substances directive (REACH) which was enacted in June of 2007, including regulations pertaining to substances of very high concern (SVHC) (http://ec.europa.eu/enterprise/sectors/chemicals/reach/index_en.htm). It is intended to protect people and the environment from chemical hazards. It addresses chromium, lead, mercury, brominated flame retardants, and phthalates, which are present in many polymers. For example, phthalates cannot be used unless one can get authorization for their use, thus involving a costly application process. Since this cost burden is passed on to the suppliers, they may opt to not apply for authorization, which could indirectly impact the automobile industry.

Individual European countries have also set their own regulations. For example, in Switzerland, the Swiss automobile importers set up The Foundation for the Environment-Friendly Disposal of Motor Vehicles in 1992, and Switzerland became the first country in the world to dispose of all shredder residue by thermal processing (Christen 2002). Over 250,000 metric tons (275,000 tons) of shredder residue have been incinerated in municipal waste-incineration facilities. The Environment National Protection Agency (ENPA) of Italy also developed its own series of activities, including monitoring, data gathering and analysis, and reporting. In Germany, the regulation governing the polychlorinated biphenyls (PCBs) in shredder residue dictates that shredder residue be incinerated as a hazardous waste and that incineration should be the primary disposal route for shredder residue. Yet, most of this waste is still disposed of in landfills (Pasel and Wanzl 2003).

In 2005 a committee reviewed the status of the implementation of the 2000 directive (Duncan 2005). It was concluded that:

1. The reuse and recycling targets set in the EU Directive of 2000 are high. Member States are unlikely to achieve the targets by 2015, and consideration should be given to freezing the 2006 target of 80%.

2. The 2015 ambitious target of 95% for reuse and recovery should be maintained at 95%.

3. Dismantling non-metallic parts (e.g., glass, plastics) should be optional instead of mandatory.

Others (Schliessner 2002; Duncan 2005) reported that up to 2005 the implementation of the Directives was inadequate. The European Parliament's Committee on the Environment, Public Health and Food Safety requested another study (Fergusson 2007) to assess the status of the implementation of the Directives. The study reported that although the first set of reuse,

recycling, and recovery targets was to take effect on January 1, 2006, some countries are still in the process of implementing the directives. The study reported that:

- Sweden and the Netherlands reached the 85% target in 2005.
- Belgium met the 80% reuse and recycling target in 2005, but it is still unclear whether it reached the 85% reuse and recovery target.
- Other countries may have met the 80% reuse and recycling target or are close to doing so.
- Documentation in some member countries is still not up to par.

The study (Fergusson 2007) also outlined some of the reasons for the delay in implementing the Directives. These reasons include:

- Different and complex disposal regulations already existed in different member countries.
- The availability of adequate resources to implement the Directives was uncertain, including who would pay for the vehicles already in service. The Directive wanted the car companies to take back their products at their own expense, including those already on the market. This was strongly opposed by the carmakers.
- The Directive required high recycling rates that require recycling polymers and other non-metallic materials. This increased the disposal cost of ELVs.
- The Directive imposed new administration and reporting requirements and procedures, including requirements on dismantlers.

We believe that the lack of economic technology to recover and recycle the polymers and other non-metals from shredder residue is another major reason.

1.9.3 Japanese Regulations

In Japan, over 5 million vehicles reach the end of life every year. In 2002, Japan introduced a law (Automobile Recycling Act) governing the recycling of ELVs. This law requires manufacturers to recover refrigerants and airbags (Sakai 2007). A law governing the recycling of ELVs (the End-of-Life Vehicle Recycling Law [Automobile Recycling Law)]) went into effect in Japan on January 1, 2005 (Togawa 2006; also see the Honda 2005). The law dictates that:

- Automakers (domestic and foreign) will charge car buyers recycling fees.

- Automakers (domestic and foreign) must provide dismantling manuals for vehicles and airbags/ignitors.

- Vehicle owners are responsible for taking their ELVs to an authorized recycling facility.

- Manufacturers and importers are responsible for the recycling of ELVs and must accept their own vehicles.

- The manufacturers must properly collect and dispose of refrigerants, air bags, and shredder residue from scrap dealers.

- The costs for the treatment of ELVs will be borne by vehicle owners.

1.9.4 Russian Regulations

In March 2010, Russia enacted vehicle dismantling and manufacturer take-back requirements. This initiative was a decade in planning, awaiting sufficient development of the needed infrastructure.

1.9.5 Canadian Regulations

In Canada, there are federal, provincial, and municipal regulations governing the recycling of ELVs and the handling of resulting waste streams.[1] For example, a dismantler in Ontario must have an Ozone Depletion Prevention permit to remove and handle refrigerants. In addition, the recycling industry developed its own codes of practice, including, for example, the Canadian National Mercury Switch Recovery program known as "Switch out."[2] *This program* is designed for removing, collecting, and managing mercury lighting switches and mercury sensors in end-of-life vehicles before the vehicles are shredded. The Ontario Automotive Recyclers Association developed its own "Code of Practice" for its members. Similarly, Environment Québec developed a "Best Practice" guide for the ELVs industry.

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[1] "Mercury and the Environment-Switch Out: Canada – Options for a National Program for the Responsible Recovery of Automotive Mercury Switches (http://www.ec.gc.ca/Mercury/switchReport/En/regulatory.cfm#51, March 2010); see also British Columbia regulation Reg.200-2007, O.C. 447/2007, "Vehicle dismantling and recycling industry environmental planning regulation, 2007; B.C. Reg. 449/2004, 2004, Environmental Management Act-Recycling Regulation; Recycling Council of Canada, Management of End-of-Life Vehicles (ELVs) in Ontario, Report, Proceedings and Draft Recommendations of The RCO Roles and Responsibilities Forum, April 28, 1999; and Ontario regulation 189/94, Environmental Protection Act – Refrigerants (and amendments).

[2] http://switchout.ca/, accessed November 2010

1.9.6 Chinese Regulations

As stated earlier, the number of vehicles on Chinese roads is increasing rapidly. Chen (2006) reported that in February 2006 China published the "Motor Vehicle Product Recovery Technology Policy." The policy established a target by 2010 that specifies "reuse and recovery for all end-of-life automobile products shall be increased to a minimum of 85% by average weight per vehicle, and the use of lead, mercury, cadmium, and hexavalent chromium is prohibited." The policy requires that "starting in 2010, Chinese automobile manufacturers and importers will be responsible for collecting and recycling vehicles or will designate other authorized ELVs dismantlers to handle the business." It was also reported (Recycling International 2008) that China launched a pilot program to recover and reuse parts from ELVs, and that the Chinese auto makers and auto part manufacturers signed letters of commitment to the recycling program. The recycling effort initially focused on engines, transmissions, electrical generators, and a few other major items. In 2008, China was considering new regulations in view of the inadequate recycling of the 2 million vehicles scrapped in 2008 (Gasgoo 2008).

1.10 RECYCLING BARRIERS AND RECYCLING STRATEGIES

Barriers to recycling in general and to plastics recycling in particular include:

- Unavailability of adequate collection systems for certain waste materials. In the case of ELVs, the collection infrastructure is already in place.

- Lack of technology to identify, separate, and recover quality recyclables economically from the waste stream. Separation and cleaning of the desired materials at a high enough purity for recycling can be complicated and costly, depending on the characteristics and composition of the waste stream. A clear example is the separation and cleaning of plastics from shredder residue.

- Incompatibility of different materials. For example, most polymers are not compatible with each other, and the separation from each other can be challenging and costly. Compatibilizer research by the VRP and others indicates that compatibilizers (e.g., block-co-polymers) may compatibilize some mixtures of commingled plastics without the presence of PVC (e.g., municipal solid waste [MSW] mixtures (Duranceau 1996]).

- Market value of the recovered materials (i.e., available amounts, market price of the recovered material, etc.). The price of recycled plastics and foam has been fluctuating and in many cases is dependent on export of the materials overseas.

- Perceptions of inferior quality.

- Limited color (black or dark grey) and appearance surface usage (class 'A').

At present, modern recycling facilities are able to recover over 95% of the ferrous and nonferrous metals in ELVs. The less than 5% of the residual metals that remain in the shredder residue constitute about 5–15% of the weight of the shredder residue. To facilitate the recycling of non-metallic materials from shredder residue, the dismantling industry, repair shops, the shredding industry, and automobile manufacturers must work together. The shredding industry can:

- Provide expertise in the shredding and separation of shredder residue components.
- Become more selective in choosing their feedstocks and planning their shredding campaigns to prevent cross contamination of the residues and to reduce the number of species in the shredder residue that must be separated.
- Develop markets for the recycled materials.

The dismantling industry can:

- Increase the number and amount of materials and parts that can be removed by dismantling.
- Endeavor to market and use the dismantled materials, because the dismantled parts are not as contaminated as the shredded materials.

The repair shops, including dealerships, can:

- Sort, save, and ship defective and damaged parts for recycling. Some repair shops segregate TPO bumpers and sell them for recycling.
- Recover automotive fluids from defective and damaged parts and send them for recycling.

Car manufacturers can:

- Design cars for easy dismantling of potentially reusable parts, so the dismantlers can recover additional parts for reuse and recycling more efficiently and economically.
- Reduce the number of polymer species used in building vehicles.
- Eliminate or minimize the use of hazardous materials and substances of concern (SOC) that could make recycling more difficult or expensive.

Recycling strategies can be divided into four major types: (1) recovery of materials for recycling into primary products, (2) recovery of materials for recycling into secondary or lower-grade products, (3) chemical and thermochemical recycling into chemicals and fuels, and (4) recovery of the energy value. Because shredder residue is rich in polymers and other

hydrocarbons, all four types of recycling can be applied to it. In the 1970s and 1980s, the greatest emphasis on shredder residue recycling focused on the second and fourth types. Later, the emphasis shifted toward primary and chemical recycling of the organic materials.

2 RECYCLING INFRASTRUCTURE AND STRATEGIES

2.1 RECOVERY OF MATERIALS FOR RECYCLING INTO PRIMARY PRODUCTS

This type of recycling generally refers to the recycling of uncontaminated waste material within the industrial manufacturing sector. Concerning ELVs, this method could also apply to:

- Dismantling and/or remanufacturing of parts for reuse, and
- Separation of individual plastics from shredder residue at high purity and without degradation of their properties, with the intent of using them for blending with virgin material or with other regrind plastics.

2.2 RECOVERY OF MATERIALS FOR RECYCLING INTO SECONDARY PRODUCTS

This process entails the production of secondary products from shredder residue. It has been pursued for shredder residue because of the thermoplastics content of the shredder residue. The most comprehensive research regarding secondary recycling of shredder residue materials was that funded by the Energy Conversion and Utilization Technologies (ECUT) branch of the U.S. Department of Energy (DOE) (PIA 1987). Thermoplastics represent approximately 70–80% of the total plastics in shredder residue. For non-critical applications, thermoplastics can be heated and remolded into different products without the need to achieve a high degree of separation of impurities. Products such as park benches, lamp posts, road traffic furniture, shingles, and other construction materials can be made from waste rich in plastics by using state-of-the-art extrusion and molding equipment. The quality of products that can be derived from shredder residue can be upgraded by partial separation of undesired components (such as glass, metals, and gravel) and by the addition of virgin plastics and other additives (PIA 1987; PIA 1980). The appearance of the product can also be enhanced by sandwiching the recycled material between thin layers of virgin material. Sixty-four such products have been identified (PIA 1987). The presence of hard objects in the waste material (such as gravel, metals, and glass) could, however, damage the molding equipment and/or increase its maintenance cost.

The key limitations of this type of recycling are (1) the market for such products is small and (2) the cost of making such secondary products is not insignificant. As a result, secondary products are, at best, only marginally competitive in most cases with their counterparts that are made of inexpensive virgin materials (such as wood, sand, and gravel). Concerns associated with this type of recycling are:

- Shredder residue contains SOCs, including heavy metals and PCBs. Cleaning of plastics to remove these materials can be cost prohibitive in view of the relatively low market value for materials used for making secondary products.

- Changes in the composition of shredder residue require that the design of the process incorporate ample tolerances to regularly meet product specifications and to prevent obsolescence. Upgrading of the required materials may also be necessary.

In 1985, Dean et al. reported on a set of experiments conducted by the Bureau of Mines in which heavy-medium separation of the individual plastics in shredder residue was attempted. In these experiments, the float and middling fractions from a water elutriator were sent to a gravity separator that consisted of a series of brine cells, each maintained at a different specific gravity (SG). Although the process did not produce individual plastics at high concentration, the tests showed that certain plastics could be concentrated in the various fractions. Concentrating the various fractions of shredder residue is necessary to improve the viability of any recycling opportunity, although heavy-medium separation may not necessarily be the best method or best approach (economically). Many more advanced technologies have been developed and tested since then. Equipment that has been developed for the recycling of plastics from MSW streams could be adopted for this type of recycling of plastics from shredder residue. This equipment includes Mitsubishi's Revezer™, the Klobbie™, the FN™ machine, the Flita System™, the Remaker™, the Regal Converter™, and Kabor K board.

The ECUT work also evaluated the use of shredder residue as an additive for "polymer concrete" (PIA 1987). In general, the conclusions appear to indicate a lower compressive strength for the shredder-residue-polymer concrete. Boeger and Braton (1989) reported on another concept for recycling shredder residue in which it would be physically separated into three fractions: metals, mill fuel, and mill cover. The mill cover is the nonmetallic fraction under two inches, and it was tested as a landfill cover. The fraction greater than two inches is reported to have a calorific value of almost 11,000 Btu/lb (which is about the same as coal) and could be considered as a fuel. Some parts of shredder residue are being used today as landfill cover.

2.3 CHEMICAL RECYCLING

Chemical recycling could be used to produce value-added products (such as monomers, light hydrocarbons, and/or liquid and gaseous fuels) from the hydrocarbon-based fraction of shredder residue (plastics, rubber, paper, and wood) (Sawyer 1974; PIA 1987; Curlee 1986; Braslaw and Gerlock 1984; Mahoney, Weiner, and Farris 1974; Dean, Chindgren, and Valdez 1972; Banks, Lusk, and Ottinger 1971; Huang and Dalton 1975; Tukker 1999). Plastics and rubber, however, will be the main source for such products. Processes that may be employed for chemical recycling include pyrolysis, gasification, hydrolysis, selective dissolution, hydrogenation, and de-polymerization.

These techniques are discussed in Sections 7 and 9.

2.4 COMBUSTION FOR ENERGY RECOVERY

This process involves the recovery of the energy value of the waste via incineration, and the heat recovered from the combustion gases can be used to produce steam and/or electricity. The heating value of shredder residue is about 13 million Btu/ton. This is equivalent to more than the energy content of two barrels of oil. However, incineration of shredder residue that contains PVC and other chlorinated materials could result in the emission of air toxics, including dioxins. Small amounts of chlorinated materials in waste can be enough to form dioxins when burning waste. Shredder residue can be mixed with other wastes (such as MSW) and incinerated. Tests conducted in the United States and in other countries showed that shredder residue incineration is technically feasible (Mark and Fisher 1998). These tests are discussed in Section 6.

3 THE PROCESS OF RECYCLING DURABLE GOODS

3.1 RECYCLING AUTOMOBILES

Optimizing the economic recyclability of automobiles requires a comprehensive and integrated approach (Reuter et al. 2004). The various processors (auto companies and their suppliers, dismantlers, salvage yards, repair shops and shredders) must work together to understand the interaction between the process/quality control and the science behind the separation technology in order to implement an effective approach.

3.1.1 Dismantling for Direct Resale

According to the Automotive Recyclers Association (ARA), the automotive recycling industry generates $22 billion a year in sales (ARA 2009). The industry plays a major role in the recycling of automotive materials, and it provides low-cost automotive replacement parts to repair shops and remanufacturing operations. There are more than 15,000 automotive dismantlers in the United States who process over 10 million vehicles a year. Most of the dismantling operations are carried out manually. Therefore, dismantling is generally limited to high-value parts that could be sold for reuse. What remains of the vehicles is sold to shredders, where they are shredded to recover their ferrous and nonferrous metals.

Remanufacturing is an important component of the existing recycle infrastructure and can compliment dismantling. Many automotive components are remanufactured to supply lower cost replacement parts to maintain the domestic fleet. For example, the majority of replacement starters and alternators are remanufactured. Other automotive parts that are typically remanufactured include engines, transmissions, brake systems, and water pumps. Remanufacturing entails the tear down, inspection, and repair and/or replacement of subcomponents, as well as testing of the remanufactured component to ensure that the performance specifications of the remanufactured part are met.

The ELVs are typically processed first by automotive dismantlers. Over 80% of the 95% of ELVs that are recycled in the United States start their final journey at a dismantling facility, commonly called junkyards (Duranceau and Lindell 1999). The other 20%, because of their age or condition, go directly to the shredders. At the dismantling facility, useable parts (such as radios, batteries, bumpers, windshields, whole car seats, door panels, transmissions, and engines) are manually removed for direct resale and reuse. Damaged or malfunctioning components are sent to be repaired and remanufactured. Automotive parts remanufacturers rebuild old parts, including transmissions, engines, cylinder blocks, alternators, generators, starters, fuel pumps, water pumps, and windshield-wiper motors. The dismantling/remanufacturing operation provides low-cost replacement parts to repair shops, to parts brokers, and to individual customers. Direct re-use of a part, such as a door panel or trunk lid, conserves the materials and the embodied energy that would otherwise be required to produce the replacement part from virgin raw materials, as well as the manufacturing energy required to stamp the part and assemble the

component. Therefore, dismantled parts that can be reused will result in significant energy savings and environmental benefit.

Present vehicle dismantling operations include:
(http://www.a-r-a.org/content.asp?pl=505&contentid=435, June, 2009)

- Draining automotive fluids;
- Removing undamaged parts for resale or remanufacturing;
- Cleaning, testing, inventorying, and storing the recovered parts until sold;
- Removing certain items, such as the catalytic converter and batteries, for recycling by others; and
- Flattening the remaining "hulk" for sale to shredders.

Future dismantling operations are likely to include, in addition to the above items, the following:

- Hybrid vehicle batteries
- Automotive electronic gadgets.
- Aluminum and magnesium components.
- High, ultra-high, and advanced high-strength steel components. (However, if these parts are damaged, repair methodologies must developed.)
- "Smart materials," such as self-repairing materials.
- Advanced catalyst materials.

U.S. dismantlers also collect several other items for recycling by others. These include:

- Car batteries are collected for recycling of their lead, sulfuric acid, and plastics content.
- Catalytic converters are recycled for their precious metal catalysts.
- Refrigerants and fuel are extracted from the vehicles. These generally end up being reused in some applications after purification and upgrading. Other automotive fluids, such as engine and transmission oils, are also drained and recovered, especially when required for environmental reasons.

- Several dismantlers have experimented with dismantling bumpers for recycling. Among the problems encountered in recycling the bumpers are the paint on the bumpers (Schultze 2006) and the many different materials sometimes used in making an individual bumper. Bumpers made of XENOY® resin, which is a thermoplastic alloy blend of polybutylene terephthalate (PBT) and polycarbonate (PC), are valuable for recycling because of the high value of the XENOY®. However, production of XENOY® bumpers was stopped many years ago. Repair shops and some dismantlers collect polypropylene and thermoplastic olefins (TPO) bumpers for recycling. Collecting, separating, and handling old bumpers is not always economical. American Commodities, Inc., has developed a process for removing paint and other contaminants from polymeric regrind particles (Wisner 1999). Many TPO bumpers that are removed and sorted by repair shops are recycled.

- Dismantlers have tried to manually recover some plastics and seat foam from vehicles for resale. These efforts were quickly terminated because the operations were not economical. The cost was high, and plastics markets were not readily available. The storage of scrap plastics and foam also required a large amount of space that interfered with more conventional dismantling operations. In addition, the amounts collected by an average dismantler would be small and, therefore, difficult to market profitably.

In general, however, dismantling for the recovery of materials such as polyurethane foam (PUF) and plastics is not cost-effective (Christen 2002; Emblemsvag and Bras 1995; Chen, Navin-Chandra, and Prinz 1993; Coulter et al. 1996). The primarily reason is because (1) dismantling is labor-intensive and, therefore, costly; and (2) only a small amount of material can be recovered at an average dismantling yard, and, therefore, the storage and transportation costs for most such materials are generally prohibitive.

Many damaged parts are removed by repair shops, including repair shops at dealerships, in order to replace such parts. Collection and recycling of these parts could be economical, since the dismantling cost is paid for as part of the repair job. An onsite shredder can be used to reduce the size of these parts for transport to a recycling center.

The ability of U.S. automotive dismantling facilities to meet requirements equivalent to the recently legislated EU Directive on automotive recycling has been studied (Paul 2001). Criteria used to categorize the performance of these facilities include (Paul 2001):

- Number of dismantlers,
- Facility size,
- Facility locations,
- Ability to meet certification requirements,
- Environmental compliance,
- Techniques and methods in use,
- Equipment in use,

- Disposal practices, and
- Market factors.

The study led to the following conclusions:

- The U.S. infrastructure meets the recyclability targets of the EU Directive. Automotive Recyclers Association (ARA) members, in general, are likely to come very close to meeting many of the EU standards.

- Existing local, state, and federal regulations are approximately equivalent to the EU dismantler requirements applicable to ELV treatment. Additional laws are not necessary. Enforcement would improve compliance, but probably only marginally improve recycling.

- Significant improvements in recyclability are likely to come from increased glass or plastics recycling.

- ARA CAR-certified (CAR: Certified Automotive Recyclers Program) facilities handle higher volumes, pretreatment, and dismantling in an environmentally reasonable fashion.

- More information is required about the operation of the scrap vehicle processors and their levels of performance.

A strategy that may have a major impact on dismantling is "design for recycling." For example, if instrument panels can be made so that they are easy to remove, the panels would yield about 25 lb of plastics available for potential recycling (Mark 2001). The economics of the process would still depend on other costs, including those for storage and transport. If the instrument panel could be built by using a single plastic material (such as polypropylene), then polypropylene would be less expensive to separate and recover.

Another problem facing dismantlers is the ability to rapidly and accurately identify plastics used in cars. The accuracy of identification is important in order to minimize the contamination of the recovered plastics in dismantling operations. Issues related to the rapid identification of plastics were examined at the Vehicle Recycling Development Center, which was operated by the United States Council for Automotive Research (USCAR) (Garrenstroom, Coleman, and Duranaceau 1997) in the late 1990s. The study concluded that:

- Commercial specular reflectance infrared (IR) spectroscopy systems are available. Plastics can be identified in about 5 seconds by using these systems. The price range is about $34,000–50,000.

- The accuracy of identification depends on the quality and completeness of the reference library of spectra. "Nearly all incorrect identifications on smooth plastic surfaces in the study were attributed to absence of certain plastic-types in the reference library." The accuracy of identification on the American Plastics

Council 30-piece reference set was 90–100%. Most errors tend to be between closely similar polymers (acrylonitrile butadiene styrene [ABS] vs. styrene acrylonitrile [SAN]; polyamide 6 [PA6], also known as nylon 6, vs. polyamide 6/6 [PA66], also known as nylon 66; and polyethylene terephthalate [PET] vs. polybutylene terephthalate [PBT]).

- Specular-reflectance instruments are not adequate for identifying foams and elastomers because of their poor reflectance and inadequate signals.

- Improvements are needed for efficient removal of surface coatings before analysis/identification.

Other issues that may face future dismantling operations include:

- New materials of construction and parts are likely to have appreciable market value and, therefore, will be cost-effective to recover. On the other hand, removing more of the recyclable metals from the vehicle will reduce its value to the shredder, who will have less material to recover as product and a higher percentage of non-metallic materials to dispose of. The dismantlers will have to strike a balance between recovering things for resale versus selling more of the vehicle to the shredder. Integrated dismantling/remanufacturing/shredding operations are likely to flourish in the future.

- Damaged old vehicles may be leaking oils and automotive fluids. Therefore, contamination of the ground can occur. Future regulations may place constraints on the dismantlers concerning contaminated grounds and cleanup requirements. Dismantlers will also have to invest in better equipment and processes to protect the employees, the public, and the environment from potential pollution resulting from leaking automotive fluids and other automotive materials.

- The dismantlers will have to implement new controls and new safety measures to address concerns related to new materials. For example, recently a dismantler using a torch to remove a part near a magnesium piece set the magnesium on fire.

Some dismantling case studies are discussed below.

3.1.1.1 Case Study 1. The USCAR/Vehicle Recycling Partnership (USCAR/VRP)

One of the most extensive dismantling studies was conducted by the USCAR/VRP. The objective was to evaluate the feasibility and viability of collecting and recycling automotive polymers from domestic ELVs (Orr 2000; Gallmeyer et al. 2003). The project identified North American ELV recycling practices; explored scenarios for plastic material handling and local transportation; and evaluated sorting, processing, and compounding. Specifically, recovered ABS and PP plastic materials were formulated to OEM specifications and molded by using production tooling to establish the viability and economics of the pursuit of these materials as a commercial enterprise. The study also examined the way in which reuse contributes to

recyclability (Duranceau and Lindell 1999). The results of this study found that the sale of used parts played a significant role in vehicle recycling and will continue to play an essential role. The Federal Trade Commission (FTC) has now recognized reuse as recycling.

Conclusions indicate that, while the materials and parts are acceptable (the PP is clearly useful, and the ABS is potentially useful with some additives), the economic incentives and altered logistics needed to support this endeavor will not currently be borne by existing North America market economics. The study estimated that proper incentives are required to offset part of a fixed cost of about $0.48/lb (in 2001) (Gallmeyer et al. 2003).

The USCAR/VRP field study (Orr 2000; Gallmeyer et al. 2003) reported the following additional conclusions:

- Although the study began by considering the removal of PP, ABS, polyamide (PA), PC, polyurethene foam (PUF), TEOs (thermoplastics elastomer olefins — also called TPOs), PE, PVC, and ethylene propylene diene-monomer (EPDM), at the end of the study, it was decided to recover only PP and ABS. The EPDM was excluded because there was no means to separate the usable ones from the others.

- The International Dismantling Information System (IDIS) software was found to be not applicable in the North American context.

- The type of vehicle did not matter much after the dismantler gained enough experience and could work from memory.

- The USCAR field study also concluded that the basic retrieval and processing cost is in the $0.40/lb range and that "It appears that with the proper incentives post-consumer automotive plastics could be collected for a fixed cost of $0.48 per pound (in 2001).

During the USCAR field trial, purities of the recovered material were high (ABS, 99%; PE, high-impact polystyrene [HIPS], EPDM, 1%; PP, 99.2%; ABS, 0.4%; PE, 0.4%). The recovered polypropylene was found to be useful without additives, even though it is stiffer and has a lower melt flow rate than the virgin (prime) PP commonly used in automotive applications. Table 3.1 shows the properties of the recovered PP and compares them with the properties of virgin automotive PP.

The recovered ABS was considered useful for a few applications. However, for most applications, additives may be required. The flow rate was 10% higher than the "benchmark" flow rate, while the impact strength was only about two-thirds that of the "benchmark." An impact modifier and stabilizer were used in formulating the recovered ABS to compensate for heat aging and loss of stabilizer over the years. Auto parts were molded by using 100% dismantled PP and ABS. Both the PP parts and the ABS parts were usable and considered to be production quality. ABS was molded into an exterior door bump strip, and it was stated that the ABS is "potentially useful with additives." Table 3.2 shows the properties of the recovered ABS and compares them with the properties of virgin automotive ABS.

TABLE 3.1 Comparison of the Properties of Recovered Polypropylene in the USCAR Field Trial with Virgin (Control) Polypropylene (Orr et al. 2000)

Polypropylene Property	Control Sample	PCR* Extruded	PCR* Flake #1	PCR* Flake #2
MFR (melt flow rate)	36.4	19.9	17	28
IZOD	1.4	1.8	1.8	1.9
Flexural modulus (1,000 psi)	139.6	136.9	131.9	
Flexural strength	4,712	4,361	4,470	
Tensile yield	3,379	3,130	3,136	3150
Elongation at yield (%)	18	19	18	
Tensile rupture	2,326	2,388	2,384	
Elongation at rupture (%)	71	59	60	
DTUL** (°F)	131.2	129.7	136.5	

* PCR is post-consumer recyclate.
** DTUL is deflection temperature under load.

TABLE 3.2 Comparison of the Properties of Recovered ABS in the USCAR Field Trial with Virgin (Control) ABS (Orr et al. 2000)

ABS Property	Control Sample	PCR* Extruded	PCR* Flake #1	PCR* Flake #2
MFR (melt flow rate)	6.3	7.4	8.3	6.2
IZOD	3.8	2.5	2.5	2.3
Flexural modulus (1,000 psi)	258.0	299.5	295.3	
Flexural strength	8,832	10,084	10,061	
Tensile yield	5,974	5,995	5,974	5,640
Elongation at yield (%)	10	10	10	
Tensile rupture	4,504	5,156	5,178	
Elongation at rupture (%)	42	33	29	
DTUL** (°F)	167.4	170.4	169.5	

* PCR is post-consumer recyclate.
** DTUL is deflection temperature under load.

The study concluded that for ABS:

- Physical properties that replicate those of commonly used automotive-grade ABS resin are potentially achievable and

- 5–10% butadiene rubber (corresponds to 10–20% modifier) restored the impact properties of the ABS without significant degradation in heat stiffness and tensile properties.

3.1.1.2 Case Study 2. The "PRoVE" – Plastics Reprocessing Validation Exercise

This study[3] was conducted in Europe. The primary objective of this study was to provide generic specifications for 25% recycled/75% virgin automotive plastics that can be used as a basis for standards across the industry. As part of the study, independent testing validated the generic specifications. Auto parts were also made from polymers containing recycled plastics. The results of the study are summarized below for the different plastics.

Polypropylene. Work on PP involved using pieces that were handpicked from shredder residue and washed to remove most of the associated dirt. Mixtures of 25% recyclate/75% virgin PP (both with 20% talc and with 40% talc) had properties that were within the specifications, except for the elongation at yield, melt flow index, and fog number. Only a minor improvement in the fog number was possible with washing. Air filter housing units were also molded by using 25% recycled PP/75% virgin (40% talc filled). The molding process did not require any changes in tooling or processing conditions. The only problem encountered was due to the small pieces of metals from the recycled material. A sample of 100% recycled-rubber-modified PP (EMPP [elastomer (rubber) modified polypropylene] or PP+EPDM) was also extruded and pelletized and used to make auto parts. The material processed well and, except for the elongation at yield, met the criteria. The authors concluded that these materials (PP+ EPDM and EMPP) can be used for making new car parts.

ABS. The ABS-containing recycled material from ELVs and electronics was used to make auto radiator grilles. No changes in tooling or processing conditions were needed. The ABS derived from both sources gave similar results. However, the elongation at break and the notched Izod of the recycled automotive ABS was inferior in comparison with the electronics ABS. Further, the presence of the fire retardants in the electronics ABS did not affect the properties of the recycled material. The properties of the recycled and virgin materials were also compared. The tensile strength at yield was found to be greater for the recycled material, which implies that the recycled material was stiffer. However, it was stated that even with the reduced flexibility, the 25%/75% material molded well.

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[3] *PRoVE 2 — Plastics Reprocessing Validation Exercise*, T. Weatherhead, Final Report, prepared by JEMA Associates, Ltd., January 2005, and *PRoVE Recycling Works — Plastics Reprocessing Validation Exercise*, Project Summary, June 2003.

High-Density Polyethylene (HDPE). Automobile washer bottles made of HDPE were manually dismantled from ELVs before shredding. Test pieces made from the recycled material were injection molded without the use of additives without problems. Mixtures of 25% recycled/75% virgin also met the generic specifications, except for the melt flow index.

Polyamide PA66 (Nylon 66). Radiator end caps, which are made of PA66, were collected from ELVs. They were contaminated with rust, water (2.4%), and ethylene glycol (0.7–0.8%). The authors reported that the process was also labor-intensive. Processing of this material caused foaming because of the absorbed fluids, and it did not extrude well even after excessive drying.

PVC. Two types of PVC were collected from ELVs: flexible linings and body side moldings. Heavy metals were found to be a major problem for PVC. For example, of the 10 samples of the flexible lining material analyzed, two exceeded the limit for arsenic, two exceeded the limit for chromium, one exceeded the limit for mercury, and six exceeded the limit for antimony. Antimony was used as a fire retardant. However, all 10 samples were below the limits for cadmium and lead. Of the three body side moldings samples that were analyzed, one contained an elevated concentration of chromium (295 ppm), and two samples exceeded the limits on lead (1,475 ppm and 6,300 ppm). Lead was used as a stabilizer for PVC.

Overall, the key findings of the study included:

- PP and ABS collected from 1990 ELVs were of sufficient quality to meet PRoVE specifications.
- The PP and ABS required compounding with virgin material and could not be used at the 100% level.
- The 25%/75% recycled PP/virgin PP and 25%/75% recycled ABS/virgin ABS worked well.
- From the 20 vehicles sampled, the amount of plastics recovered was about 2.568 kg per vehicle. This amount of plastics could be dismantled from a car in about 10 minutes. Also, it has been reported that attaining the next 2.5 kg will take twice as long. Given that time requirement, dismantling is unlikely to be economical.
- Heavy metals are problem for PVC recycling.

For details on the properties of PP and ABS, see Tables 3.3 and 3.4 in Jody and Daniels (2006).

3.1.1.3 Case Study 3. The BMW Dismantling Center

BMW operated a dismantling center that processed about 1,100 BMW vehicles per year (Competitive Analysis Centre, Inc., and Economic Associates, Inc., 1998). The objectives were to:

- Develop methods and equipment for dismantling vehicles,
- Evaluate the economics of dismantling operations, and
- Provide information to vehicle designers to help develop designs that would be more efficient to dismantle.

Several methods and equipment designs were developed, and some were implemented by dismantlers. Examples include:

- Multiple-level auto storage racks,
- A jig for safe shattering and collection of window glass,
- A jig for elevating cars for easier dismantling,
- A procedure for removing catalysts from the catalytic converter,
- A handcart for transporting multiple tires at a time, and
- Plastics identification equipment and procedures.

However, it was determined that dismantling of plastics is a labor-intensive and costly process and does not lend itself well to automation.

3.1.1.4 Case Study 4. The MBA Polymers Study of Radiator End Caps

The VRP and the American Plastics Council (APC) sponsored an MBA Polymers study to determine the technical and economic feasibility of recovering metals and plastics from end-of-life radiator end caps (Paxton and Caron 1999). The VRP obtained samples from two metal recycling companies (Sims Metal America and Aaron Metals) through the Institute of Scrap Recycling Industries (ISRI). The radiator end caps studied in this project contained over 50% metal, most of which was nonferrous. The recycling of the radiator end cap samples used for this study generated about 40% nonferrous metal, 19% mixed ferrous and nonferrous metal, and about 20% PA flakes. MBA Polymers also indicated that:

- With minor processing changes, the yields could be improved to about 52%, 6%, and 29% for the nonferrous, ferrous, and plastic fractions, respectively.
- The polyamide from radiator end caps could be recovered in reasonably high yield and purity by using tight density separations.

- The polyamide could be blended with virgin material to create a material consisting of 25% post-consumer recycled content that exhibits between 85% and 100% of the virgin properties.

- The recovered polyamide required more extensive drying to prevent outgassing during extrusion. The extended drying period was attributed to absorbed coolant that was more difficult to evaporate.

3.1.1.5 Case Study 5. The MBA Polymers Study of Interior Trim Plastics

The APC and MBA Polymers conducted a study to evaluate the potential for the recovery of ABS and PP interior-trim plastics from disassembled car parts (Fisher, Biddle, and Ryan 2001). A combination of dry-and-wet processing of over 50,000 lb of interior trim parts obtained through selective dismantling was completed, and streams of ABS and PP were isolated. The results demonstrated that density separation can significantly upgrade both unfilled PP and ABS resins from less than 50% to greater than 90% purity. However, because of the presence of PP in the ABS, further purification of the ABS by using other separation techniques is necessary. Other projects are discussed in Rasshofer and Schomer (2003).

3.1.1.6 Case Study 6. The Honda Study

Eighteen Honda vehicles, model years ranging from 1982 to 2001, were used in a study conducted at two automotive recycling centers and a scrap metal processing facility with an automotive shredder (Paul, Chung, and Raney 2004). The dismantlers removed parts and components for reuse. The hulk was then shredded. Dismantling times and part weights were recorded, and dismantling procedures were videotaped. After the hulk was shredded, the ferrous, nonferrous, and landfill materials were separately collected and weighed. The overall recyclability rate was then calculated. The study concluded that:

- The recyclability rate of new Honda models is over 90% as a result of high parts and components reuse/resale.

- Vehicles with extensive damage have lower recyclability.

- Older vehicles have a steadily declining rate of recyclability, but it was still 84% or higher.

- The experience of the dismantler and the availability of power tools influence the speed and quality of vehicle processing.

- The efficiency and completeness of fluid collection is variable and related to the fluid type and quantity of the reservoir capacity.

- Because early model vehicles are out of warranty, the demand for their used parts is higher than it is for late-model vehicles, and they have the highest rate of return on investment.

3.1.1.7 Case Study 7. Electroplated Hubcaps

Recycling of dismantled electroplated hubcaps by using cryogenic grinding followed by metals and plastics separation resulted in the recovery of both the plastics and the metals (Dom et al. 1997). The properties of the recovered plastics compared well with those of both virgin and unplated recycled materials. The ground plastic was pelletized and molded. In comparison with the pure resin, only the elongation properties of the plated and unplated material degraded. Grinding to a smaller particle size improved plastics yield. Adhesion characteristics of replated, recycled material showed only a slight difference from those of virgin plastic. Thermal cycling tests also showed only small differences between the behavior of virgin material and the recycled samples. The testing in this study was conducted with 100% recycled material.

3.1.1.8 Case Study 8. Recycling of Plastics Diverted from Landfills

Hooper, Harder, and Potter (2002) investigated the potential use of plastics dismantled from cars to make automotive components. The results indicated that the mechanical recycling of polyethylene (PE) and polypropylene (PP) plastics, as a result of manual dismantling, could be used in “high-quality” products such as automotive parts. The economic effectiveness of this approach has yet to be established. After the dismantler is finished with the vehicle, the “hulk” is sold to a shredder for its metals value.

3.1.1.9 Case Study 9. The Automotive Glass Recycling Study

The VRP (Caron, Lange, and Snyder 1999) evaluated the current state of windshield glass recycling. This area had the most opportunity for reducing pre-consumer plant scrap and recycling post-consumer automotive glass. The main barriers to be overcome were the logistics and the cost of collection. Automotive glass repair shops were chosen for the study, and a process was developed for collection and delivery of the glass to the recycler. The process was piloted, and the result produced a standard process and contract that could be used by other glass repair shops for recycling their glass. In general, the cleaner the scrap glass was, the higher its value. Disassembling the windshield glass can make it available as a replacement part (Jones 2002). The polyvinylbutyral (PVB) windshield inner layer (Declercq 2006), while a challenge to the recyclers, had the highest value in the recycling market. In addition, post-consumer windshield glass could also be economically feasible if the collection route collected greater than 3 tons per pick up of material.

3.1.1.10 Case Study 10. The EPA Grant-Sponsored Jobs through Recycling Project (administered through the Michigan Department of Environmental Quality with a contract to the Great Lakes Institute (non-profit) in collaboration with the VRP, APC, and ARA)

The Auto Recycling Demonstration Project (ARD Project) was a collaborative effort based in Michigan to demonstrate the commercialization of automotive material recovery systems. The Michigan Department of Environmental Quality (MDEQ) participated in the ARD Project through funding provided by the U.S. Environmental Protection Agency's (EPA's) Jobs through Recycling (JTR) Program (MDEQ 1998). This project was implemented through Michigan non-profit organizations in collaboration with the VRP, APC, and the American Recyclers Association (ARA) acting in an advisory capacity. Resource Recycling Systems, Inc., acted as the technical consultant to the project. The ARD project team conducted a series of pilot projects to demonstrate and document current methods and costs of automotive non-metal material recovery. Target materials included auto glass, PUF foam, high-end plastics (such as polyethylene, polypropylene, ABS, TPO, polycarbonate), textiles, and elastomers. Recovered materials were sent to potential end-market customers for evaluation. The final report for the ARD project resides on the State of Michigan website.

3.1.2 Shredding

The shredder is a giant, 3,000–8,000-hp hammer mill that shreds vehicles and other metal-containing scrap into mostly fist-size chunks to liberate the metals from everything else. Most shredders practice dry shredding, although there are several wet shredding operations. Downstream from the dry shredding process, the processing unit operations may vary from site to site, but the basic process involves air classification of the "lights" fraction followed by one or more stages of magnetic separation to recover the ferrous metals. Trommels are then used to remove particles smaller than about 5/8 in., followed by one or more stages of eddy current separations to recover the nonferrous metals. Conveyors are used to move materials around. The rejects from the eddy currents are then combined with the "lights" fraction and disposed of in landfills. Some shredder operators conduct further separation of the nonferrous metals in their own facilities.

Recycled ferrous scrap, mainly from shredding operations, accounts for over 50% of the world's steel production. Worldwide, more than 400 million tonnes of recycled ferrous scrap were used in the steel-making process in 2002.[4] In the United States alone, the scrap metal processors handle over 62 million tons of scrap metal annually.[5] This scrap includes 56 million tons of scrap iron and steel, including 10 million tons of scrap automobiles, 1.5 million tons of scrap copper, 2.5 million tons of scrap aluminum, 1.3 million tons of scrap lead, 300,000 tons of scrap zinc, and 800,000 tons of stainless-steel scrap (see footnote 3).

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[4] See http://www.smorgonsteel.com.au/recycling/products/group.cfm?GroupID=4

[5] See Institute of Scrap Recycling Industries, Inc., 1996, "Scrap Recycling: Where Tomorrow Begins," pp. 2–3, Washington, D.C., and http://www.isri.org/iMIS15_prod/ISRI/default.aspx (accessed October 15, 2010)

A study conducted in Europe in view of the European Directive concluded "the shredder route is the only processing route allowing the full compliance of the ELV Directive and the perenniality of the economic balance of the ELV processing chain" (Feillard 2002).

3.2 RECYCLING WHITE GOODS

The manufacturers of major home appliances, commonly called "white goods," have also experienced a healthy growth in the last few decades. These appliances include refrigerators, freezers, ranges, ovens, cooktops, washers, dryers, dishwashers, microwave ovens, dehumidifiers, trash compactors, and room air-conditioners. U.S. manufacturers ship about 54 million major home appliances annually, and their average useful life is about 10–16 years (ARIC 1995). The same reference provides the following information:

- About 45 million appliances were sent for recycling or disposal in 1996.
- Nationwide, 81% of major appliances were recycled in 1997.
- The percentage of appliances recycled is higher in states with landfill bans or restrictions on the disposal of appliances.
- Major home appliances make up about 10% of the steel processed by the recycling industry, cars make up 80%, and other industrial and commercial scrap makes up the remaining 10%.

The industry has also seen changes in materials of construction over the years, and this trend is likely to continue. More plastics are used, and capacitors containing PCBs and insulation foams containing chlorofluorocarbons (CFCs) are no longer used.

Older refrigerators contain CFC-12 in the refrigeration loop and CFC-11 in the PUF insulation. The CFC-12 is fairly easy to recover, purify, and reuse. However, CFC-11 is difficult to recover from the insulation foam, and the equipment to recover it is expensive because it involves grinding the foam fine enough to open its closed cells and release the CFC-11. The amount of CFC-11 in the insulation of a typical old refrigerator is about two or three times the amount of CFC-12 in the refrigerant loop (Nelson 1993).

There are also differences in the types of materials used in the United States and overseas. For example, refrigerators built in the United States contain about three times as much shredded ABS as polystyrene (PS), while the opposite is true for units built in Europe. The American Plastics Council (2005) has estimated that, by 2007, refrigerators alone will contain 126 million lb of PUF and 203 million lb of other plastics, primarily ABS and high-impact polystyrene (HIPS).

Obsolete white goods (home appliances and related products) are collected by three main routes: (1) by people who deliver new appliances and pick up the old ones, (2) by municipal waste collectors, and (3) at the landfill. When old units are collected, they are generally

examined to select the units that can be refurbished and resold. Other units that cannot be repaired for resale are sometimes exported for parts. For example, many old refrigerators are exported to other countries, where their compressors, expansion valves, cooling coils, condensers, and/or shelves are used by repair shops.

In many parts of the world, regulations prevent the shredding of the appliances before the SOCs (pollutants) are removed. These pollutants include:

- *Refrigerants.* Refrigerants include the CFCs called Freons, and ammonia in older units and in some industrial meat-packing plants presents in the compressors of refrigeration equipment. The CFCs are also used in closed-cell-rigid foam insulation, mostly R-11 (Nelson 1993). The refrigerants, except for R-11, are generally recovered, purified, and reused.

- *PCBs.* Some old capacitors that contain PCBs may still be found in some older units.

After the units are de-polluted, components such as compressors and condensers are removed for sale as scrap. Dismantling of plastics is not a common practice, even though it could be an easy process in some cases (e.g., removing the shelves in refrigerators). The storage of such items may be a problem.

Shredding: Almost no shredders shred white goods only. Most units end up at shredders, where they are shredded along with obsolete vehicles and other source materials. The primary concern about shredding white goods is the potential release of CFCs from refrigerators, freezers, and air-conditioning units. The CFCs are normally recovered during de-pollution of the units. However, some units may escape inspection.

4 SHREDDER RESIDUE

Shredder residue is a very complex heterogeneous mixture of intermingled materials that is extremely difficult to separate and handle. It also has a large number of incompatible materials, including moisture, wood, metals, glass, sand, dirt, automotive fluids, plastics, foam, rubber, fabrics, fibers, and others. In addition, shredder residue is known to contain varying amounts of heavy metals, PCBs, and fire retardants. We estimate that over 5 million tons of shredder residue are produced annually in the United States, and about 15 million tons are produced annually worldwide.

4.1 COMPOSITION OF SHREDDER RESIDUE

Because of the complexity and possible variations in the composition of shredder residue, shredder residue data should be reported within statistical limits when used to calculate the recycling rate (van Schaik and Reuter 2004). Pineau, Kanari, and Menad (2005) estimated that a minimum sample size of 140 kg (308 lb) is required for the sample to be 90% representative of shredder residue.

Table 4.1 shows a breakdown of two shredder residues processed by Argonne's mechanical separation process. The two shredder residues exhibited significant differences in their composition. This separation was done on the basis of differences in size, shape, and weight of the pieces and particles present in the shredder residues. Table 4.2 compares the composition of the polymer concentrates produced by mechanical separation at Argonne from the two shredder residues described in Table 4.1. The data in Tables 4.1 and 4.2 are believed to be reliable because for shredder residue 1, they represent the averages from processing over 25,000 lb of shredder residue over a period of about 6 months. Data for shredder residue 2 represent the averages from processing over 75,000 lb of shredder residue over a period of about 6 months. In both cases, over 90% of the recoverable polymers present in particle sizes greater than about 6 mm were recovered in the concentrate.

TABLE 4.1 Gross Composition of Shredder Residue

Material	Weight Percent in Shredder Residue 1	Weight Percent in Shedder Residue 2
Fines (<1/4 in.)	24	60
Polymer concentrate	36	14
Oversized lights (polyurethane foam)	05	01
Oversized heavies (metals, rocks)	08	02
Lights rejects	06	02
Ferrous-metal-rich fraction	01	01
Nonferrous-metals-rich fraction	04	05
Loss (moisture, dust, sweeps)	16	15

TABLE 4.2 Composition of Polymer Concentrates Produced from the Two Shredder Residues Described in Table 4.1

Material	Weight Percent in Shredder Residue 1	Weight Percent in Shredder Residue 2
Rubber:		
Rubber (mixture of EPDM, tire rubber, and many other types)	46.8	27.8
Polyurethane (solid yellow rubber)	3.6	2.1
Polyolefins:		
Polypropylene	8.8	21.2
Polyethylene	7.6	8.7
Styrenics:		
Polystyrene	1.6	2.7
Acrylonitrile butadiene styrene (ABS)	4.5	7.8
Polycarbonate/acrylonitrile butadiene styrene (PC/ABS)	0.7	0.6
Other Thermoplastics:		
Polycarbonate	3.0	2.9
Nylon	2.1	0.8
Polyvinylchloride	1.9	3.4
Polyphenylene oxide (PPO)	0.7	0.4
Polyester	0.5	0.0
Polymethyl methacrylate (PMMA)	0.02	0.4
Unknown Polymers (rich in thermosets)	14.1	6.4
Non-Polymers:		
Metals	1.1	5.3
Other (including wood)	3.3	7.8

Data in Table 4.2 show that the same polymers appear in both shredder residues, but the ratios can be different. For example, PP was 8.8% in shredder residue 1 and 21.2% in shredder residue 2. The wood content of the two concentrates (not shown in the tables) varied widely — between 1% and 6% by weight — not only from shredder to shredder but also from load to load from the same shredder.

Several researchers have reported scattered data on elemental analysis of shredder residue (see Table 4.3), and they vary over a wide range. For example, the reported hydrogen values range between 2 and 7.

TABLE 4.3 Elemental Analysis of Organic Fraction of Shredder Residue (weight percent, dry basis)

Element	Argonne National Laboratory	Trouve, Kaufman, and Delfosse (1998)	Rausa and Pollesel (1997)	Patierno et al. (1998)	Kondoh et al. (2001)	Roy and Chaala (2001); Chaala, Ciochina, and Roy (1999)	Pasel and Wanzl (2003) Maf*
C	55	51	57	18	60	33–45	60–90
H	7	7	8	2	7	4–6	8–12
N	2	3	3	<1	2	0.6–3	1–4
O	13	–	21	17	8	–	5–30
Cl	1.82	3.7	0.2	0.05	2.5	0.1–3.4	2–5

* Moisture- and ash-free basis

4.2 RECYCLING SHREDDER RESIDUE

Recovery of materials from a complex mixture (such as shredder residue) involves several stages of separation and cleaning, including:

1. Concentration of the targeted material into a more manageable fraction,

2. Separation of the targeted material from the concentrate (this may involve more than one step), and

3. Cleaning of the recovered material to remove dirt and SOCs.

The many processes for the recycling of materials from shredder residue are discussed in a number of review articles on the subject (see Zevenhoven and Saeed 2003 and Lundqvist et al. 2004), as well as later (Sections 5–10) in this document.

4.2.1 Recyclable Materials from Shredder Residue

As stated above, shredder residue contains, among other materials, plastics, rubber, glass, and residual metals. These materials are potentially recyclable. For instance, there are over 2 billion lb of synthetic polymers (5 million tons of shredder residue × 2,000 lb/ton × >20% polymers) in the 5 million tons of shredder residue that are disposed of in landfills. The embodied energy of these polymers is about 5 trillion Btu (2 billion lb × 25,000 Btu/lb of embodied energy), and their value could exceed $400 million at an estimated price of $0.20/lb. Problems that are impeding the recovery and recycling of these materials, with the exception of metals, are:

- Lack of a cost-effective technology to separate these materials from shredder residue in sufficiently high concentrations to allow their use as value-added products and not just as fillers. These technologies include the removal of SOCs to acceptable levels.

- Lack of markets to purchase recycled materials at their fair market value.

- Generation of insufficient quantities at a given site to justify a profitable business case.

Numerous research activities are under way in the United States and abroad to develop processes for recycling the plastics and the foam. Many of these will be covered later in this document (Sections 7–10). Part of process development is to produce sufficient quantities to allow for market testing, including the determination of the properties and value of the recovered materials.

4.2.2 Separation of Materials from Shredder Residue

Separation of materials is accomplished by exploiting the differences in the properties of the materials. These properties include differences in physical properties (such as size, shape, color, porosity, density, and brittleness), magnetic properties, chemical properties (such as solubility, hydrophobicity, hydrophilicity, and reactivity), and electrical properties (such as resistivity and dielectric constant). The overlapping properties among the very large number of species in shredder residue make any separation process difficult to control and manage and place limits on the purity of materials that can be recovered from it economically. Figure 4.1 illustrates the overlapping densities of the major plastics in shredder residue. One reason, at least in part, for the overlapping densities is that each one of these polymers may exist in more than one formulation, leading to different properties. For example, PP exists as a homopolymer, copolymer, talc-filled PP, and calcium carbonate-filled PP, among other formulations. Many types and quantities of fillers, modifiers, plasticizers, and other additives are also normally added to the original resin to achieve certain desired properties.

Recycling materials from shredder residue is further complicated by the SOCs (such as PCBs, fire retardants, and heavy metals) that are in the shredder residue. Further, new materials appear in shredder residue from time to time, and more new materials are expected. Except for ferrous metals, it is unlikely that a material can be recovered at sufficient purity from the shredder residue in a single step or by mechanical means only (Rasshofer and Schomer 2003). Recovery for the recycling of materials (such as individual plastics and rubber) involves at least five major operations:

1. Separation of the polymers from shredder residue, as a polymer concentrate;

2. Separation of the plastics and rubber from the polymer concentrate;

3. Separation of wood and rubber from the plastics;

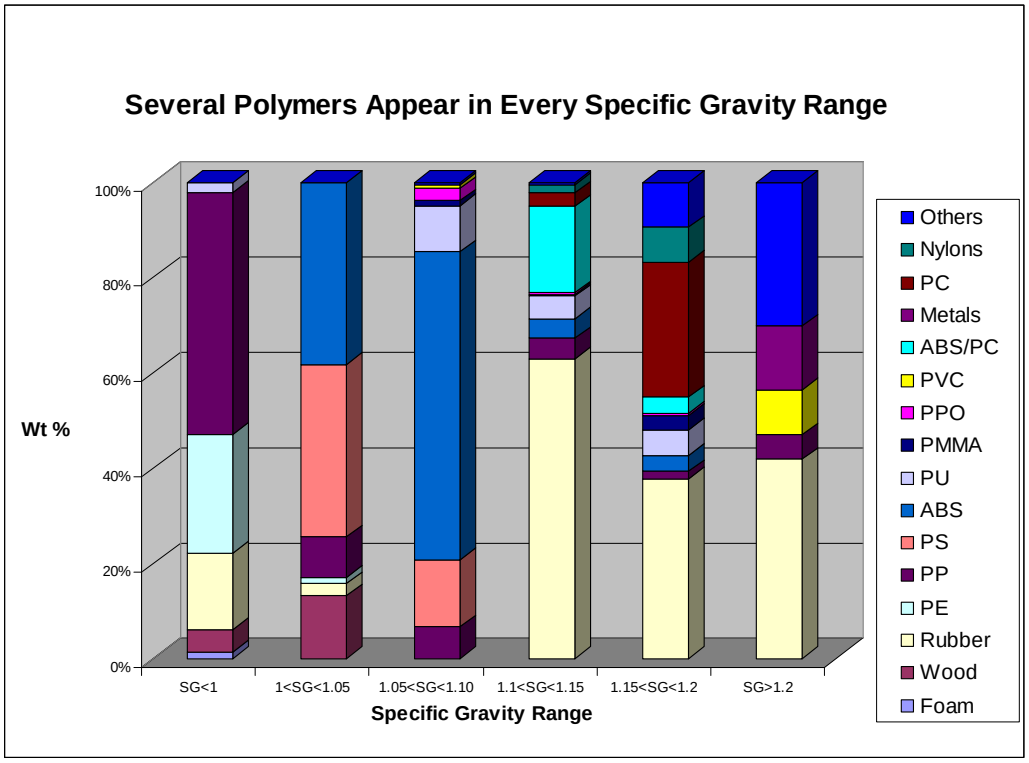

FIGURE 4.1 Flotation Characteristics of Shredder Residue Polymers Recovered by the Argonne Process (based on [1] processing of over 100,000 lb of shredder residue from five shredding facilities in the Argonne Mechanical Separation Pilot Plant and [2] on tests conducted at Argonne using plastics recovered from shredder residue)

4. Separation of the plastics from each other; and

5. Removal of the SOCs from the recovered materials.

The separation and recovery of materials (such as plastics, rubber, metals, and metal oxides) from shredder residue is discussed in Sections 7–10.

5 TECHNOLOGIES FOR CONCENTRATING RECYCLABLES FROM SHREDDER RESIDUE

Because of the complexity of shredder residue, recovery of recyclable materials in a single step from shredder residue is not practical. Therefore, pre-concentration of the targeted material is necessary.

5.1 THE ARGONNE MECHANICAL SEPARATION SYSTEM

Argonne developed and tested a dry mechanical separation system, using equipment that is commonly used by shredders, for isolating targeted materials (such as polymers and metals) in more manageable concentrates for further processing. The pilot plant, which is capable of processing up to 2 tons of shredder residue per hour, is shown in Figure 5.1. Figure 5.2 describes the unit operations used in the mechanical separation pilot plant. The plant has achieved over 90% recovery of the polymers (larger than 6 mm) in the shredder residue and over 90% recovery of the residual ferrous and nonferrous metals (larger than 6 mm).

Physical Separation Pilot Plant

FIGURE 5.1 Argonne National Laboratory Mechanical Separation Pilot Plant

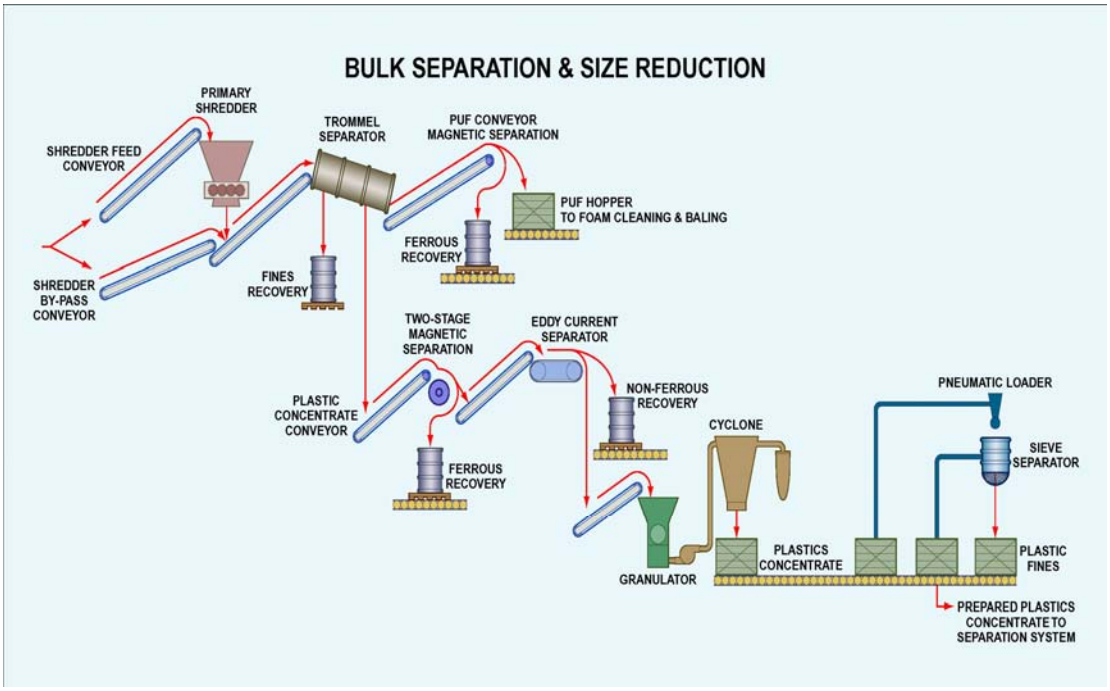

FIGURE 5.2 Major Unit Operations Used in the Argonne Mechanical Separation Plant

The mechanical separation plant's unit operations can be operated in different sequences. However, the basic sequence of operation of the plant for separating shredder residue consists of the following main steps:

1. Large metallic objects, large flexible PUF pieces, and rocks are removed manually. (In an actual full-scale operation, the large pieces of metals, rocks, and foam can be screened by a trommel and/or a de-stoner and then separated to recover the metals and the PUF. Shredders are equipped to do that as part of their metals recovery operations. The foam is then cleaned and recovered as a product (see Section 8.1).

2. The shredder residue is shredded to about 1 in. and then conveyed to a two-stage trommel. In the first stage, fines (<1/4 in.) are removed. In the second stage, thin planar and semi-planar pieces are removed through adjustable slots. This fraction consists primarily of plastics, rubber, some metals, and some small foam and fiber pieces.

3. Oversized material exits the trommel. This material consists primarily of flexible PUF, which gets squeezed in the shredder and is larger than other materials when it exits the shredder. It also contains some fabrics, fibers, and some plastics and metals that are generally larger than what can fit through the trommel's slots.

4. The oversized material is passed over a magnetic pulley to recover the ferrous metals and over an eddy current separator to recover the nonferrous metals.

5. The fraction that passes through the slots, which is the polymer-rich fraction, is also passed over a magnetic pulley to recover the ferrous metals and over an eddy current separator to recover nonferrous metals.

6. The de-metallized polymer concentrate is then granulated to an average particle size of 1/4–3/8 in. and processed on a vibrating screen to the remove fines and air classified to remove residual PUF foam pieces, dust, and other lights.

More than 180,000 lb of shredder residue have been processed by Argonne's mechanical separation plant.

5.2 THE SALYP MECHANICAL SEPARATION PROCESS

The basic Salyp process consists of the following steps:

1. The shredder residue is conveyed to a two-stage trommel. In the first stage, fines (<1/4 in.) are removed. In the second stage, thin planar and semi-planar pieces are removed through slots. This fraction consists primarily of plastics, rubber, some metals, and some small foam and fiber pieces.

2. Oversized material exits the trommel. The material consists primarily of flexible PUF and contains some fabrics, fibers, and some plastics that are generally larger than what can fit through the trommel's slots. It also contains some metals.

3. The oversized material is passed over a magnetic pulley to recover the ferrous metals and over an eddy current separator to recover the nonferrous metals.

4. Foam is then recovered from the oversized material by using a piece of equipment that was developed by Central Manufacturing in Peoria, Illinois (McLemore 2006).

5. The fraction that passes through the slots, which is the polymer-rich fraction, is also passed over a magnetic pulley to recover the ferrous metals and over an eddy current separator to recover nonferrous metals.

6. The de-metallized polymer-rich material is then granulated to an average particle size of about 5/8 in. and processed on a vibrating screen to remove fines and air classified to remove residual PUF pieces, dust, and other lights.

7. Wood is removed from the granulated material by using an optical (color) sorter.

8. The material is then washed, and in the process, some of the heavy plastics, residual metals, and glass are removed.

USCAR, under the VRP, along with Argonne, the APC, and the Association of Plastics Manufacturers in Europe (APME), conducted studies using the Salyp process for the automated recovery of plastics from shredder residue (Winslow et al. 2004). One hundred tons of shredder residue were supplied from three different shredders, including a U.S. shredder and two different European shredders. Salyp demonstrated that a clean and wood-free plastics concentrate can be produced by mechanical separation.

5.3 THE WESA-SLF PROCESS

In this process (see Sattler and Laage [2000] and Zevenhoven and Saeed [2003]), the shredder residue is separated into three size fractions: fine (<1.2 mm), middling (>1.2 mm but <7 mm), and oversized (>7 mm). The oversized material is then reduced to less than 20 mm, and a magnet is used to recover ferrous metals. The shredded material is then reduced to <7 mm and combined with the middling fraction (<7 mm) and dried to less than 2% moisture. The dried material is air classified to separate foam and fluff, screened in a multi-level sieve, and then separated into three fractions: copper, minerals and mixed metals, and organic materials. Ferrous metals are also recovered from the mixed-metals fraction by using a magnet. The estimated cost of this plant is about 60–70 Euros/ton. A 4-ton/h plant has been built in Germany.

5.4 COMPACTION AND SOLIDIFICATION TECHNOLOGY

This process (see Kusakam and Iida 2000) was developed in Japan, and it starts by passing the shredder residue over a “slanted roller separator” to separate it into three fractions: heavy-, medium-, and lightweight materials. Metals are recovered from the heavy material by using magnetic and eddy current separators. The residual material is then size-reduced and returned to the roller separator. The medium-weight material is separated, by using slanted vibratory screens, into fine, medium, and large particles. The fines are primarily sand, glass, and dirt. The medium and large particles are then mixed with the heavy material separated by the roller separator, and the resulting mixed material goes through the magnetic and eddy current separators. Dust generated by the vibratory screens goes through a cyclone, and the cyclone bottoms are mixed with the lightweight material stream. Metals are also recovered from this stream, and the remainder is compacted, slaked with lime, and extruded into wafers of about 25 cm × 10 cm × 2 cm for gasification.

5.5 THE WITTEN PROCESS FOR THE SEPARATION OF AN ORGANIC FRACTION FROM SHREDDER RESIDUE

The University of Witten in Germany (see Competitive Analysis Centre, Inc., and Economic Associates Inc., 1998) developed a mechanical separation process for producing an organic-rich fraction from shredder residue that is primarily used as a fuel in cement kilns and similar applications. The process consists of the following main steps:

1. Ferrous metals are recovered by using a magnet.

2. A hammer mill is used to size reduce the material, and a screen is used to remove fines.

3. Air classification is used to separate fibrous from non-fibrous material. The two streams are processed separately.

4. A screening jig is used to separate residual metals.

5. Fibrous material is size-reduced in a “cutting mill,” and then a screening jig is used to separate residual metals and fines.

6. A conveyor dryer is used to dry the material.

The process produces the following streams:

- 3–8% of the shredder residue is a ferrous metals fraction containing about 80–95% iron.

- 8–23% of the shredder residue is a mixed Fe/Cu/Al fraction.

- About 25% of the shredder residue is a low-density organic fraction containing between 10% and 20% ash. Its heating value is between 9,480 and 11,200 Btu/lb.

- 15–25% of the shredder residue is a higher-density organic fraction containing between 15% and 25% ash. Its heating value is between 10,770 and 13,785 Btu/lb.

- 25–35% of the shredder residue is a high-ash (75–85% ash) fraction.

A plant that has a 30,000-tonne annual capacity is expected to cost Deutsche Mark (DM) 4.75–5.00 million.

5.6 THE SORTEC PROCESS

Sortec (see Competitive Analysis Centre, Inc., and Economic Associates Inc., 1998) designed a 40,000-ton/yr (8-h/day) plant to recover metals and an organic fraction from shredder residue. The process consists of the following steps:

1. Screening to remove fines (< 0.25 in.) and to recover large metallic pieces.

2. Size reduction to less than about 1 in. (2 cm).

3. Magnetic separation of ferrous metals.

4. Size reduction to less than 0.25 in. by using fixed/rotating knife granulators.

5. Drying on a conveyor belt to <2 wt% moisture.

6. Screening into five fractions followed by air classification to remove heavies. The light fractions are the organic fraction. The heavies are the nonferrous fraction.

The ash content of the organic fraction is expected to be between 10% and 30%, and its water content is 2%. Its heating value is between 7,325 and 12,925 Btu/lb. The estimated cost of the plant is DM 6.5 million, including DM 5 million for equipment and DM 1.5 million for building and utilities.

5.7 THE NIMCO SHREDDING PROCESS

A shredder residue separation system permits the separation of ASR into many constituent components for recycling or reuse (Baker, Woodruff, and Naporano 1994). Among the products recovered are steel, stainless steel, copper, aluminum, other nonferrous metals, fine magnetic fraction (iron oxide product), clean grit, PUF, various plastics, fibers, and rubber. The ASR separation and recycling system comprises four major components. The first component is the initial size and separation of ASR into three separate fractions. The second component comprises a grit processing subsystem. The third component is a rubber and plastics recovery subsystem. The fourth component is a polyurethane foam separation and cleaning subsystem.

5.8 OTHER MECHANICAL EQUIPMENT FOR SEPARATING SOLID MIXTURES

Mechanical systems, such as gravity separators, electrostatic separators, vibrating screens, and rapid identification and sorting systems (e.g., color, infrared, X-ray, and UV-fluorescence), generally rely on differences in a single property between the materials in the mixture. Because of the large number of species in shredder residue and their overlapping properties, such equipment is not capable of separating shredder residue. However, some of this equipment could be used to purify certain fractions that are derived from shredder residue. Some of these systems are discussed below.

5.8.1 Gravity Separators

Gravity separators, such as mineral jigs, hydrocyclones, gravity sink/float tanks, and kinetic density separators, all rely on differences in density for the separation of solid particles that have different densities from a generally homogeneous mixture of solids. Because shredder residue is very heterogeneous and its contents have overlapping densities and shapes, gravity separation of shredder residue, as-is, cannot yield products from shredder residue, except for metals, as practiced in some wet shredder facilities. Such separators, whether operated by using water or a heavy media, are also not practical for the production of concentrated fractions of polymers from shredder residue directly.

However, once a somewhat homogeneous (i.e., the particles are homogeneous in shape and size, but many of their other properties are different) polymer concentrate is produced, such as the product from Argonne's and Salyp's mechanical separation systems, gravity separators can be used to fractionate the concentrate into more manageable fractions that are rich in targeted materials. Yet, each fraction will still contain a multiple of non-compatible species. Further separation will be required. Figure 4.1 shows typical fractions that can be produced by such methods. Some of the techniques are discussed in the following paragraphs.

Jigs and Kinetic Energy Separators. Delft University and Recycling Avenue in Holland have been developing jigs and Kinetic Density Separators (KDS) to fractionate mixed-plastics streams, such as the polymer concentrate produced by the Argonne mechanical separation system (Fraunholcz et al. 2002). The pre-concentrated fractions can then be upgraded by using other separation techniques to produce value-added materials. The principal concept starts with mechanical processing, including screening and magnetic separation. The resulting mixed polymers fraction can then be separated further.

Chaparral Steel Technology.[6] Automobile shredding is an integral part of Chaparral's operations. In 1990, Chaparral installed an eddy current system to recover nonferrous metals from shredder residue. In 1996, Chaparral acquired exclusive rights to a flotation separation technology to separate materials from the residue. The technology was installed in 1998. The technology allows for high throughputs while using an inexpensive flotation medium. One of the objectives was to recover non-chlorinated plastics to be used as a fuel source. The process also recovers aluminum, magnesium, and other materials. Chaparral estimated that the sale of clean plastics from its operation will generate up to $500,000 a year. Chaparral also indicated that this technology can be applied not only to shredder residue, but also to a variety of waste streams from many different processes. (The plant used for this process is no longer in operation.)

5.8.2 Electrostatic Separators

The magnitude of electrostatic charging of plastics depends on the electrical properties of the plastic material, as well as on the relative humidity of the surrounding air, degree of contact

[6] This case study was featured in "By-Product Synergy Primer" (1997), produced by the Business Council for Sustainable Development – Gulf of Mexico.

and handling, and surface roughness or frictional properties of the surface. Plastics are considered to be dielectric materials because they are poor conductors that can support an electrostatic field while dissipating a minimal amount of thermal energy (dielectric loss).

The key electrical properties that govern electrostatic behavior are dielectric constant, surface resistance, and volumetric resistivity. The dielectric constant of a material is the proportionality constant between the charge density on its surface and the field voltage. It is a measure of the extent to which a substance can concentrate the electrostatic lines of flux. The surface resistance (measured in Ohms) is the resistance of a plastic's surface to the flow of electrons over the surface. The volumetric resistivity (measured in Ohm-cm) is the resistance of the plastic material to the flow of electrons through the bulk of the material.

Materials with low dielectric-constant values (such as plastics) build up high surface charges. Materials that have low volume and/or surface resistivity help charge leakage from the material and thus reduce voltage, which, in turn, increases the dielectric constant. Plastics generally have high surface resistance (>10^{15} Ohm) at 20°C and 50% relative air humidity. These values decrease rapidly as the relative humidity increases. In addition, the dielectric constants of many of the polymers present in shredder residue are very close or even overlap. The dielectric constant also depends on the temperature and frequency (Hz). Typical values of the dielectric constant of some of these polymers are reported in Table 5.1.

TABLE 5.1 Dielectric Constant of Some Plastics*

Plastic	Dielectric Constant (MHz)
ABS	2.4–3.8
Nylon	3.2–5
PS	2.5–2.6
PVC	3
PE	2.26
PP	2.2
Rubber	3–4

* See http://www.rfcafe.com/references/electrical/dielectric_constants_strengths.htm.

Electrostatic separators have been tried for the selective separation of solids by using electric forces, which can act on charged or polarized particles. Generally, electrostatic separators are effective in separating dry binary mixtures. Because shredder residue is very non-homogeneous and many of its contents have overlapping properties, electrostatic separation of even dry shredder residue, as-is, is not practical for the recovery of products from it. However, once a homogeneous polymer concentrate is produced (such as the product from Argonne's mechanical separation system) and the particles are cleaned and dried, electrostatic separators could possibly be used to fractionate the concentrate into more manageable fractions that are rich in targeted materials for further separation and recovery. An example in which electrostatic separation can be effective is the separation of polymethyl methacrylate (PMMA) from ABS or PVC from PC.

To the best of our knowledge, separation of raw shredder residue by using electrostatic separators has never been attempted. Research has been done, however, in which electrostatic separators were used in an attempt to separate plastics concentrates generated from mixed plastics scrap. Plas Sep (London, Ontario), Carpco (Jacksonville, Florida), and other companies build such equipment.

MBA Polymers conducted electrostatic separation testing of mixed plastics by using a triboelectric separator manufactured by Plas-Sep, Ltd., Canada.[7] MBA Polymers concluded that:

1. The device did not separate rubber from plastics.

2. Process performance is dependent on particle size, film thickness, mass, and charging time.

3. Separation of an ABS/HIPS mixture from refrigerators did not work, but the separation of ABS/HIPS from electronics was more successful.

4. MBA Polymers could not get good separation of PP/PE from shredder residue, while Plas-Sep reported good separation of PP/PE from other sources.

5. PVC was easily separated from PC.

6. Separation of nylon/acetals did not work.

Hitachi Zosen Corporation[8] has reportedly commercialized a highly efficient electrostatic separator (Daiku et al. 2001). A key feature of the separator is that it can separate high-purity plastics from mixed plastics. For example, by applying this separator for separation of a PE and PP mixture, both plastics can be separated with more than 99% purity. Also, the device is claimed to be novel because the charged plastics in the separator are supplied to an electrostatic field while touching a drum electrode.

In summary, available information suggests that:

1. Electrostatic separators work well for some plastics mixtures.

2. Electrostatic separators are not capable of producing sufficiently pure individual polymers for use as polymers from mixtures containing many species, such as the plastics mixtures produced from shredder residue.

3. Even when the mixture contains two species, such as PP and PE, the literature data are conflicting. Some reported that it worked well, while others reported that it did not work. The limited testing that we conducted using commercial equipment on ABS and HIPS from refrigerators did not produce satisfactory results.

4. Electrostatic separators are very sensitive to humidity. Not only must the plastics be dry, but the environment must be at low relative humidity. A 50% room relative humidity may be too high for some of the plastics. Drying costs would have to be added.

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[7] See Xiao, C., L. Allen III, M. Biddle, and M. Fisher, "Electrostatic Separation and Recovery of Mixed Plastics;" http://plasticsresource.com/s_plasticsresource/docs/900/852.pdf.

[8] See Hitachi Zosen Corporation; http://nett21.gec.jp/JSIM_DATA/WASTE/WASTE_2/html/Doc_374.html.

6 COMBUSTION OF SHREDDER RESIDUE FOR ENERGY RECOVERY

Incineration could be a cost-effective technique to dispose of shredder residue, since its fuel value is nearly half that of coal. In fact, shredder residue will burn without the need for supplemental fuel. Because of the increased use of polymers in vehicles and other durable goods, the heating value of shredder residue is increasing. Shredder residue is also low in sulfur. Several studies have addressed this topic, and scrap processors have built a number of full-scale shredder residue incinerators (Hubble, Most, and Wolman 1987; Dean et al. 1985; Bilbrey, Sterner, and Valdez 1978; Ellsworth, Ballinger, and Engdahl 1957; Bilbrey, Dean, and Sterner 1974). Dean et al. (1985) estimated that at least 23 such units were built by the end of 1973. To the best of our knowledge, none of these units are in operation today. Although incineration can achieve reductions of more than 50% in the weight and over 75% in the volume of shredder residue, it is not widely accepted because of a combination of economic, environmental, and logistic problems, which include:

- Disposing of shredder residue in landfills is still less expensive than incineration in most U.S. locations;

- Environmental concerns persist because shredder residue contains SOCs, including chlorinated materials (PCBs and PVC) and heavy metals; and

- Shredder residue has a high ash content (~50%) and a varying moisture content (up to 25%).

Although the technology for scrubbing hydrogen chloride (HCl) exists, the scrubbing of chlorinated compounds could be expensive, especially when they are present in high concentrations, which may be the case for shredder residue. Hubble et al. (1987) reported chlorine concentrations as high as 16.9% (the average concentration was 3.4%), on the basis of samples from 12 shredding sites. Moreover, the high chlorine content, in particular, would make the flue gas corrosive, thereby increasing the materials and maintenance costs of the incinerator. Chlorine is also suspected of increasing the risk of producing dioxins and benzofurans during combustion (Hubble, Most, and Wolman 1987). Therefore, operation of shredder residue incinerators is expected to be subject to a complicated permitting process that may call for costly chemical analysis. Incineration is even more expensive if the shredder residue contains elevated levels of PCBs. Governing regulations require that PCBs be incinerated at very high temperatures (about 2,000°F), but high-temperature incinerators are costly to build and maintain. Supplementary fuel would also be required to attain such temperatures, which would increase operating costs.

The cost-effectiveness of incineration generally depends on the site and on the variability of the composition of the shredder residue, local landfill costs, heavy metal composition, and the type of incinerator. Moreover, location, installation, and operation of incineration facilities can be challenged, which further complicates the permitting process.

A study sponsored by DOE evaluated the potential of harvesting some of the energy released during the incineration of shredder residue (Hubble, Most, and Wolman 1987). During field tests, samples of shredder residue from 12 different facilities were burned in a rotary kiln incinerator. Different scenarios for the use of the released thermal energy were also analyzed. The major findings of the study are summarized and discussed below.

1. The average heating value of shredder residue is about 5,400 Btu/lb.

2. The chlorine content of the shredder residue samples varied between 0.7 and 16.9 wt%. However, we believe that the 16.9% is probably due to an unrepresentative sample.

3. The moisture content of the samples varied between 2 and 34 wt%.[9] The study demonstrated that the flue gas can be scrubbed to comply with governing environmental regulations by using state-of-the-art equipment.

4. The ash remaining after incineration is about 25–72 wt% of the starting material (average value is about 44 wt%). This proportion of ash about doubles the concentration of metals in the ash. As a result, the ash could be classified as hazardous in some localities, which would then require that the ash be fixed and/or post-processed to recover the metals. For example, according to a published report by the Center for Materials Production (CMP) (Schmitt 1990), Puremet Corporation has developed a hydrometallurgical process that would be applicable for the recovery of the metals from shredder residue incinerator ash.

5. When the heat is used to produce steam, the amount of steam generated as a result of incinerating the shredder residue material far exceeds the on-site thermal energy requirements of shredder facilities. Therefore, unless there is a customer for the heat nearby, the heat will be uneconomical to recover and transport to the customer.

[9] The water in the shredder residue will consume a substantial portion of the heat released in the incineration process, which will result in a lower flame temperature. As a result, the availability or exergy, or useful energy, is reduced. Water in the shredder residue will also increase the dew point of the flue-gas stream. As a result, condensation could occur during the heat-recovery process. Condensation will be detrimental to the duct work because of the highly corrosive nature of the flue gas.

6. On-site electricity generation was also evaluated. In general, the amount of electricity that could be produced from the shredder residue available at most shredders exceeds the on-site electricity requirements of the shredder, and this excess electricity can be sold back to the utility.[10]

A later study conducted by the EPA (EPA 1993) concluded, "The highest PCDD [polychlorinated dibenzo-P-dioxins] emissions concentrations appear to be associated with low temperature combustion processes whose function is to recover energy or other resources (e.g., metal values) by combustion of waste materials"[11] (EPA 1987). This study also reported that the highest PCDD emissions were measured at sites containing plastics in the feed, and that total organic halogens (TOX) showed stronger association with PCDD emissions than with total chloride content.

Woodruff, Mechel, and Albertson (see Appendix C of Schmitt 1990) reported, "preliminary results of one and one-half years of pilot plant test work indicate that the fluidized bed combustion process does offer an economical alternative for the disposal of automobile shredder residue."

Since the 1990s, Switzerland has experimented with co-incineration of shredder residue with MSW (Keller 1995; Disler and Keller 1997; Keller 1999a). In 1993 and 1995, extensive incineration tests were conducted on waste (with shredder residue percentages of up to 10%) in the Swiss MSW incineration plants at Horgen and Bazenheid to assess the technical feasibility and environmental impact of co-incineration of shredder residue with MSW (Keller 1995; Disler and Keller 1997; Keller 1999a, 1999b). Co-incineration of shredder residue with MSW was able to meet the regulatory limits and the short-term objective of the IGEA (German abbreviation of "Syndicate for the Environmentally Compatible Disposal of Nonmetallic Waste from Vehicles)."

Saxena et al. (1995) conducted experiments on the combustion of shredder residue in a bubbling fluidized-bed combustor. Residue particles about 6 mm were fed to the fluidized bed with alumina as the bed material at 950–1,140 K. Propane was also supplied as the fuel. They reported that the residue could be combusted. However, the CO, HCL, NO_x, and SO_x were high. For example, CO concentrations in the flue gas as high as 1.6 vol. % were observed, even when the O_2 concentration was 15 vol.%. This indicates that complete combustion was not achieved. In the presence of such high concentrations of O_2, the equilibrium CO concentration should not be that high. The authors reported that the concentration of the pollutants depended on gas velocity, bed temperature, fuel feed rate, and ratio of excess air used.

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[10] The sale of electricity depends on many factors, including compliance with regulatory requirements to qualify as a cogenerator. The economic competitiveness of such a venture will also depend on many other parameters, including the cost of electricity; the rate at which the local utility will purchase excess electricity; and the consistency of shredder residue production rates, which will affect the design of the equipment relative to its utilization. Under the assumptions of the study, a "median" plant generating 4.7 million kWh/yr of electricity from 60,000 ton/yr of shredder residue would yield a before-tax cash flow of about $105,000 per year on an investment of about $1.9 million. A large-scale plant (180,000 ton/yr of shredder residue) would produce a cash flow of $665,000 on an investment of $4.6 million (Hubble, Most, and Wolman 1987).

[11] National Dioxin Study Tier 4 — Combustion Sources, 1987, Engineering Analysis Report EPA-450/4-84-014h, prepared by Radian Corp. for the U.S. Environmental Protection Agency, Sept. 1987.

Lenoir et al. (1997) characterized shredder residue as a potential fuel. They reported that, on average, shredder residue has a lower heating value of (19 MJ/kg; 8,170 Btu/lb), ash content (38%), chlorine content (3.5%), and metals content (22%, including 13% iron). Keller (2003) reported that up to about 6% shredder residue can be co-fired with MSW without major problems and without making changes to the incinerator. The APME and the APC (Mark and Fisher 1998, 1999) also studied the co-firing of up to 8.4% shredder residue with MSW. No operational problems were encountered. It was reported that CO emissions were reduced. However, the concentrations of dioxins/furans and Cd, As, Pb, and Zn increased by up to a factor of 6, but the plant's gas cleanup system was able to handle the increase. The grate ash also showed increased levels of Zn, Cu, Sb, Ni, Pb, and Sn, but the ash still passed the governing leachability test.

Some of the processes that were tested on a large scale are discussed below.

Mutabor GmBH (Germany) Process. The inputs to this process include mixed, homogenized, and size-reduced shredder residue; packaging plastics; wire chopper plastics; and unspecified binders to produce cement kiln fuel. Commercial demonstration of the process in a 10-ton/h plant was conducted at Ueckermonde, Germany. Mutabor GmbH developed the blending and homogenizing process to produce cement kiln fuel from mixed plastics waste and shredder residue. A gate fee of 95 Euro per ton of shredder residue is estimated for process profitability (Lundqvist et al. 2004).

Voest-Alpine Industrieanlagenbau GmbH & Co. (VAI) reported that it has a "closed line" process for the complete recycling of the car. The process uses the energy of the organic plastics in melting and heating and for steam generation and binding of inorganic components in the slag (Heinz, Ramaseder, and Muller 2001).

A detailed study was conducted for the APC and the Environment and Plastics Industry Council (EPIC) of the CPIA (Competitive Analysis Centre, Inc., and Economic Associates Inc., 1997) to evaluate the potential use of the organic fraction of shredder residue as an energy source and as a source of reducing agents in blast furnaces. The process concept consisted of first isolating the organics content of the shredder residue through a series of operations that separate the organic from the inorganic materials. The following criteria were set for the desired organics fraction:

- Moisture content should be 7.5%. This target is achieved through drying in a rotary kiln.

- Particle sizes should be between 0.125 in. and 0.25 in. This target is achieved primarily through two stages of grinding by using hammer mills.

- Ash content should be less than 10%. This target is achieved through a series of vibrating screens.

The plastics and the other organics in shredder residue that are basically hydrocarbon-based materials are then used to partially replace the coke, natural gas, oil, or coal supplied to the blast furnace.

The results indicated that about 37% of the average shredder residue will be recovered as the organics fraction. The economic analysis was conducted for a plant with a design capacity of 26 tons/h of shredder residue and producing 8.91 tons/h of the organics fraction. The total cost of preparing the upgraded product was estimated to be $45.18 in 1997, of which $17.52 was the equipment cost contribution, and $27.65 was the operating cost. Distributions of the capital cost, operating cost, and overall cost are shown in Figures 6.1, 6.2, and 6.3.

The rotary dryer represented about 29% of the equipment cost, followed by vibrating screens at 15% and the exhaust system for dust control at 12%. The highest operating cost was that of the combined two size-reducing hammer mills at 36%, followed by the dryer at about 24%. Labor represented about 13% of the operating cost. Figure 6.2 shows the distribution of the overall cost for the production of the upgraded material. Overall, the most expensive process is drying, which was estimated to be about 26.3% of the overall cost, followed by the size-reducing operations at 26%. Obviously, if the shredder residue could be obtained dry (<7% moisture), the cost of processing it would be reduced. The study estimated that the price of coke is $120 per ton. The study also estimated that between 1.1 and 1.5 tons of the organic fraction would be required to replace a ton of coke in the blast furnace. Therefore, from an economics point of view, it appears to be a good potential application, if it could replace some of the coke. This application would also reduce the environmental concerns associated with coke ovens. The advantages are less obvious if it is used to replace coal, natural gas, or oil.

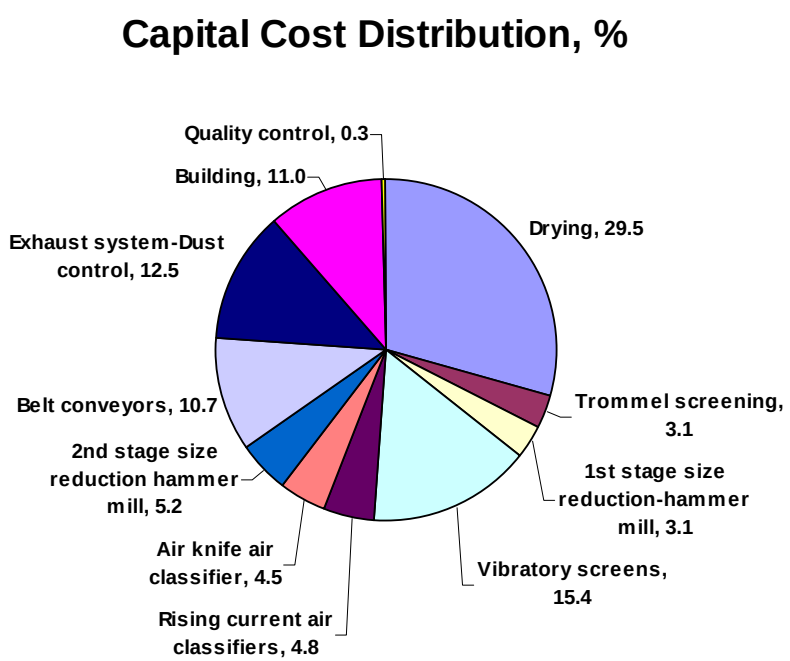

FIGURE 6.1 Distribution of the Equipment Cost for Producing the Upgraded Organics Fraction

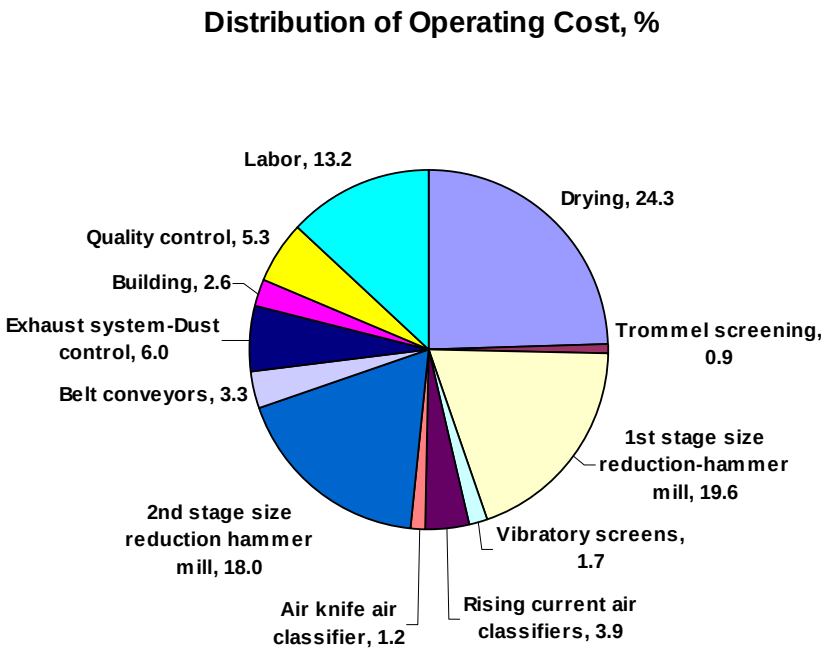

FIGURE 6.2 Distribution of the Operating Cost for Producing the Upgraded Organics Fraction

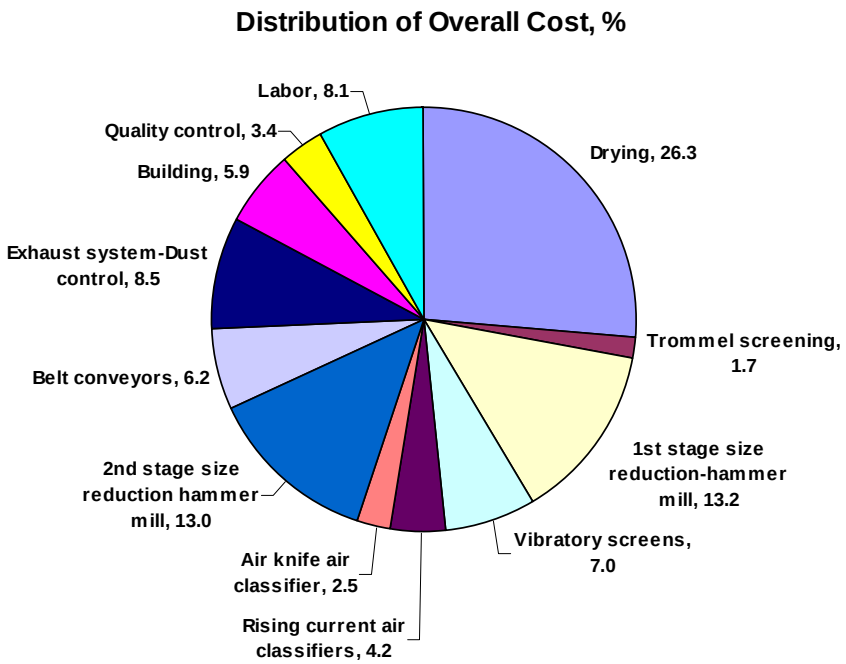

FIGURE 6.3 Distribution of the Overall Cost for Producing the Upgraded Organics Fraction

The study also raised concerns about risks associated with this application. These risks are discussed below.

- The economic and environmental advantages depend on the replacement ratio. Although mathematical modeling and calculations estimated a replacement ratio of 0.65 tons of coke per ton of upgraded material, the study mentioned an estimate of 0.90, on the basis of limited experience in Germany. The study also estimated, on the basis of published data, that an average shredder residue will have the following elemental analysis (truncated to include relevant elements only):[12]

Element	Wt%	Moles/lb ASR
C	30	0.025
O	14	0.0086
H	4	0.039

- The ability of the hammer mills to produce a product smaller than 0.25 in. and the ability of the screens and air classifiers to reduce the ash content in the organics material to less than 10% are of concern. Failure to do so could result in unacceptable metallic contamination of the steel.

- The high chlorine content of the shredder residue, because of the polyvinyl chloride and the chlorinated elastomers, may lead to unacceptable corrosion rates. The high chlorine content could also lead to the emission of chloride particulates into the air.

- Separating the organic material from shredder residue could leave behind a residue with nearly double the concentration of some of the heavy metals in shredder residue. As a result, this material might have to be classified as hazardous waste, which will increase its disposal cost substantially.

Another issue to consider related to this application for shredder residue is that the amount of shredder residue that is available near integrated steel plants is very small compared with the amount of coke, natural gas, and other fuels used by these plants. Therefore, these plants may be reluctant to use this material and risk impacting their operations or the quality of their products, unless they are paid for accepting it. This added cost may eliminate some of the economic benefits.

As a follow-up to this study, researchers conducted interviews with staff from two steel firms (Sthlwerke Bremen [SB] and Krupp/Thyssen [KT]), a shredder (Sortec), an automotive company (BMW), and the University of Witten, which developed a process for producing an organics fraction from shredder residue. The objectives were to gain more insight into the

[12] Note: The carbon and hydrogen in one pound of shredder residue contains approximately the reduction capacity of 0.32 lb of coke. Using the ratio of organic material to actual shredder residue leads to one lb of upgraded material, equaling the reduction capacity of about 0.9 lb of coke if it was 100% organic material. When adjusted for 10% ash and 7.5% moisture, the number is 0.74.

potential application of shredder residue in blast furnaces, evaluate their design for the production of an organic fraction from shredder residue, and issue a report (Competitive Analysis Centre, Inc., and Economic Associates Inc., 1998). The key findings are summarized below.

From the perspective of the steel mills:

- The assumed replacement ratios of coke with the organic fraction from shredder residue (0.65–0.90) were "in keeping with expectations." SB suggested the following formula for estimating the coke replacement ratio: ASR/Coke (replacement ratio) = (coal/coke replacement ratio) × (ASR energy content/coal energy content). This calculation gives a value for the upgraded material of about 0.74. Overall, on the basis of the experience of SB and KT, the replacement ratio seems to be in the range of 0.71–0.79.

- Both KT and SB had problems when trying to inject waste plastics as a replacement for some of the coke. Because of operating problems, the replacement ratio was reduced to 0.55. KT also experienced more problems when attempting to inject a mixture of organics from shredder residue and pulverized coal.

- Supplementary fuels that contain hydrogen are known to cause a cooling effect when used in blast furnaces. (The higher the H/C ratio in the fuel, the greater the effect.) SB found that the cooling effect of the plastics was about double that of the heavy oil it was using.

- Operating problems that occurred when waste plastics were used (blockages in the plastics injection system) resulted in 10% down time, which reduced the productivity of the blast furnace.

- SB suggested that a moisture content of 7.5% is high and should be reduced.

- Accommodating the higher chlorine in the upgraded material requires modifying the blast furnace.

- Metals, if not removed from the upgraded material, can cause severe problems, including abrasion in injection systems and reduction of furnace capacity for producing quality hot metal.

- Copper and lead can build up in the furnace and degrade its productivity.

- Copper could impact the quality of the steel.

- SB and KT received the waste plastics supply from Duales System Deutschland (DSD) in Germany and were paid about $124/ton for taking the plastics.

From the shredder's (Sortec's) perspective (see Section 5.6):

- The option of drying the material after granulation was suggested.
- The ash content of the organic material is most likely to be about 20%, not 10%.
- The cost to the shredder for separating the organic material from the shredder residue is about 25% more than the estimated amount.

On the basis of discussions and interviews with the various experts and developers of the Sortec and Witten processes (see also Sections 5.5 and 5.6), the following modifications to the 1997 concept were adopted:

- Replaced the rotary kiln dryer with a conveyor belt dryer, and reduced the moisture content of the organic material to 2%;
- Considered using air classification to separate fibrous materials from non-fibrous materials, but not to separate combustible from non-combustible materials;
- Considered using screening as a primary means of removing non-combustible material and magnetic separation as a secondary means;
- Considered the potential to recover copper- and aluminum-rich streams as marketable materials;
- Considered replacing the second-stage hammer mill with a granulator;
- Evaluated the impact of increased ash content and lower moisture content on the replacement ratio;
- Kept the material as fine as possible to maximize gasification rates;
- Examined approaches to minimize clogging problems in the injection system, and
- Considered abrasion-resistant designs and materials of construction.

As a result of these changes and considerations, the economics were revised. The capital cost increased to $3,278,486 (or about $23.56/ ton of organic product), and the operating cost became $34.25/ton of organic product. The total cost became $57.81/ton of product. The estimated costs for the Witten group and for the Sortec processes were reported to be $220/ton of organic product and $41/ton of organic product, respectively. The estimated capital cost for the injection system at the steel mill, including the cost of coating an existing scrubber system for the U.S. market, is between $10/ton and $17/ton.

A virtual pilot plant for the production of an organic fraction from shredder residue was developed, and interviews were conducted with North American stakeholders. This plant

consisted of the following sequence of operations: screening, first-stage size reduction, drying, screening, air classification, and second-stage size reduction. The results of the interviews were as follows (Competitive Analysis Centre, Inc., and Economic Associates, Inc., 1999):

- The primary concern of the shredders was that the ash-rich material left over after recovering the organic material may become a hazardous waste. The shredders emphasized the need to conduct actual testing to establish the performance of the proposed equipment.

- The VRP recommended that testing be done by using representative samples of shredder residue. The VRP was also concerned that the residual material could become a hazardous waste.

- A major concern of the steel mills was the zinc, copper, and chlorine content of the organic material. Some suggested trying the organic fraction in the coke oven instead of in the blast furnace, since it would be less expensive to retrofit.

- The capital cost for retrofitting the blast furnace to allow for injecting an organic fraction is estimated to be $6.6 million to $14.2 million.

More testing of shredder residue organics in blast furnaces is under way in Europe.

7 THERMOCHEMICAL CONVERSION METHODS TO PRODUCE FUELS

7.1 PYROLYSIS

Pyrolysis is the thermal decomposition of organic material in an oxygen-deficient environment. It is a well-known technique for the production of fuels and chemicals from organic feedstocks, such as wood, coal, plastics, tires, and municipal waste. The type and relative quantities of different products are generally a function of the composition of the feedstock and operating conditions, primarily temperature, pressure, and residence time. The applicability of pyrolysis to plastics has also been demonstrated. Banks, Lusk, and Ottinger (1971) reported that the major products of this process when PE was used as a feedstock were hydrogen, benzene, methane, ethylene, and propane; the major products from PVC were benzene, acetylene, styrene, and hydrogen chloride; and the major products from PS were styrene, benzene, toluene, and methylstyrene. We anticipate that pyrolysis of shredder residue would yield products similar to those produced by the pyrolysis of a mixture polyethylene, polyvinylchloride, polypropylene, and polystyrene. Some of the problems that were encountered in pyrolyzing plastics-containing materials are listed below (Leidner 1981):

- Pyrolysis of plastics requires more time than pyrolysis of other hydrocarbons because of the poor heat transfer characteristics of the plastics;
- Carbon residue produced by plastics pyrolysis has a tendency to stick to the walls of the reactor; and
- Some plastics, when heated, produce a high-viscosity material that is difficult to pump.

High-temperature pyrolysis, low-temperature pyrolysis, and pyrolysis at different pressures, including sub-atmospheric pressure, have been tried for processing shredder residue. In all cases, the pyrolysis process produces oil, gas, and a char/solid residue. Several pyrolysis tests were conducted on shredder residue in Switzerland in the 1990s (Keller 1999a). These trials led to the following observations:

- Iron makes up to a quarter of the solid product;
- Copper content in the solid product was as high as 5%, and the major part of the copper is present as fine copper filaments in elementary form;
- The concentration of polycyclic aromatic hydrocarbons (PAHs) was reduced by more than 90%, and the PCB concentration was reduced by more than 99%; and
- Because of the presence of heavy metals (i.e., cadmium, nickel, and zinc), the solid product could not be disposed of in landfills.

In 1996, Day, Cooney, and Shen (1996) described a process for pyrolyzing shredder residue at about 500°C. The process produced a mixture of oil (21%), gas (26%), water (10%), and solids (43%), including ferrous material and carbon black. The heating value of the gas was 45 MJ/kg (19,350 Btu/lb), and it contained primarily CH_4, H_2, CO, CO_2, and other hydrocarbons. The oil contained 86.2% C, 8.7% H, 2.4% N, and 2% O. It also contained 0.36% sulfur and 0.18% chlorine. Its high heating value was reported to be 41 MJ/kg (17,600 Btu/lb). The amount of sulfur reported appears to be high for shredder residue. The combined nitrogen- and sulfur-containing compounds constituted over 10% of the weight of the oil. The oil also contained a very small amount of chlorinated compounds. The high content of nitrogen-, sulfur-, and chlorine-containing compounds in the oil limits its use and reduces its value.

Rausa and Pollesel (1997) reported on heating shredder residue in helium at temperatures of up to 850°C at a rate of 20 degrees per minute and then introducing oxygen to burn some of the char. The results showed that a mass loss due to evolved gases and vapors of about 15% occurred at 200–340°C. An additional 55% of the mass was lost in the range of 340–550°C, and another 5% was lost in the range of 700–850°C. When oxygen was added at the end, an additional 5% of the mass was lost as a result of the oxidation of some of the char. About 80% of the chlorine in shredder residue evolved as HCl at about 350°C, and the other 20% evolved at about 490°C. The final ash mass was only about 13% of the starting material. The composition of the evolved gases was 60% hydrocarbons, 19% CO_2 and CO, 5% H_2O, 3.5% HCL, 2.5% NH_3, and 0.4% SO_2 and others. Part of the difference in the composition of the products of this high-temperature process and the previous one by Day, Cooney, and Shen is due to the difference in temperature. Differences in the composition of the starting shredder residue may have also contributed to this difference.

In an attempt to maximize the oil production when pyrolyzing shredder residue, pyrolysis tests were also conducted at sub-atmospheric pressures (<0.2 atm) (Roy and Chaala 2001; Chaala, Ciochina, and Roy 1999). Products from shredder residue were solids (52%), oil (28%), water (13%), gas (7%). The oil product contained <3% nitrogen, <1% sulfur, <0.15% chlorine, and <0.1% ash. The gas was consumed internally as a heat source for the process. Pyrovac International is marketing a low-pressure, patented pyrolysis technology called Pyrocycling™. Pyrolysis is performed at 450°C and 15 kPa, and it produces large quantities of pyrolytic oils and useful solids, such as charcoal and carbon black.[13]

Argonne conducted a limited investigation to determine if the thermochemical conversion of shredder residue is feasible. Specifically investigated were controlled thermal extrusion to produce a synthetic particulate coal (Jones 1994) and catalytic pyrolysis to produce gaseous and liquid fuels (Arzoumanidis et al. 1995; Brockmeier and McIntosh 1994). Again, although these processes are technically feasible, they are generally not cost-effective given the economic environment in North America (i.e., low landfill costs and low oil/energy costs relative to those costs in either Europe or Japan — countries in which this type of technology may be more cost-effective) (Arzoumanidis et al. 1995; Brockmeier and McIntosh 1994; Jones 1994).

[13] See http://www.vdq023.org/ssc/annx_039.htm.

Some of the advanced pyrolysis methods to process shredder residue are described below.

Siemens-KWU Process. Siemens-KWU (Germany) developed a pyrolysis process that is followed by combustion of the products for steam production. The process was commercialized for pyrolysis of MSW (over 160,000 tons/yr) and is operating in Furth, Germany. The plant also conducted one trial using 30 tons of shredder residue. The process pyrolizes feed material in an indirect heated rotary kiln operating at 450°C to convert the feed material to a pyrolysis gas and coke. Solids (including the char) are discharged from the kiln for recovery of metals. The pyrolysis gas and solid char are then combusted in an incinerator for steam production. Slag from the combustor meets the requirements for the Class 2 landfill in Rhine-Westphalia. Slag pH, phenol content, and residual antimony exceeded the limits for disposal in a Class 1 landfill. The process requires a tipping fee of 150 Euro per ton. The technology reportedly has been licensed to Mitsui & Co., Ltd. (Tokyo, Japan), which is marketing the technology.

Batrec Process.[14] Klammer (see footnote 13) reported on a pyrolysis process combined with mechanical separation that was developed at Batrec AG for treating shredder residue. The process involves pyrolysis of the organic fraction of the shredder residue followed by mechanical separation of the metals (iron and copper) from the residual solids. Keller (1999a, 1999b) gave more details on the pyrolysis part of the process. He conducted pyrolysis tests in a 400-kg/h (880-lb/h) reactor at 600°C (1,112°F) on shredder residue, from which big chunks of metal and foam were removed. The feed material was pressed into 10-cm × 5-cm cylinders. He reported that about one-half of the iron and copper in the solids remaining after pyrolysis can be recovered from the >2-mm fraction. Pasel and Wanzl (2003) stated that the key scale-up parameters are heating rate, residence time, and temperature.

Takuma Process.[15] Another process, known as the Takuma process, is being used in Japan. A plant with a capacity of 90 tonnes/day (99 tons/day) is operating in Kanemura, Japan. In this process, the shredder residue is first pyrolized, and then the residual solids are sorted to recover metals. About 1 tonne (1.1 tons) of copper and 8 tonnes (8.8 tons) of mixed metals are produced daily. The remaining char is then combusted in a combustion chamber (along with the gases produced by the pyrolysis process), and the heat is recovered in a steam boiler to produce electricity. The vitrified slag (18 tonne/day [19.8 tons/day]) is reported to have passed leach tests.

Citron Oxyreducer Process. This process was also developed in Europe (Brüggler 2002). A large-scale plant is in operation, and it has processed over 20,000 metric tons of shredder residue. The plant can accept pieces of up to about 7 cm (2.75 in.) and can handle materials with up to 50 ppm of PCBs and up to 100 ppm of mercury. The organic materials in the shredder residue, plastics, and other materials are pyrolized at high temperatures. The product gases, which are rich in carbon monoxide, are then used as agents to reduce some of the metal oxides and hydroxides to their elemental state. The low-boiling metals (zinc, lead, cadmium, and

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[14] See http://www.sppe.ch/kurzfassungen/pdf/waste_p2/klammer_6_43.pdf.

[15] "Introduction of Takuma Technology for Auto Shredder Residue Treatment," Takuma Co., LTD., October 2003; see http://www.ieabcc.nl/meetings/Tokyo_Joint_Meeting/03_Ayukawa.PDF.

mercury) evaporate, and then the zinc, lead, and cadmium are re-oxidized at about 1,200°C in the gas phase to produce solid oxides and destroy dioxins. The gases are then quenched at 80°C (Brüggler 2002). The mercury stays in the metallic form as a vapor in the oxyreducer reactor and is condensed during the quenching process and removed by means of a wet electrostatic precipitator and a scrubber. The high-boiling oxides (FeO_2, Al_2O_3, CaO, and SiO_2) are discharged from the oxyreducing reactor. The chlorine in the waste is converted to sodium and potassium chlorides (NaCl and KCl) (Brüggler 2002).

In addition, Environmental Waste International (www.ewmc.com) of Ajax, Ontario, Canada, through its 100% owned subsidiary, EWI Rubber, has received an order to develop a prototype tire system from Ellsin Environmental, Ltd., a private Canadian corporation.

7.2 GASIFICATION

Gasification is a high-temperature thermo-chemical process that can convert the organic content of a material, such as shredder residue, into a gaseous mixture of primarily CO, H_2, CO_2, and light hydrocarbons. In addition to the organic feed material, water and air (or oxygen) are supplied to the reactor. However, the amount of air or oxygen that is supplied is limited to achieve partial oxidation of the organic feed in order to raise the reactor temperature to the desired value, which is normally between 500°C and 1,500°C, depending on the process. Three types of gasification reactors are commonly used: (1) moving bed, (2) fluidized bed, and (3) entrained flow reactors. These processes were first developed to produce gaseous fuels from solid fuels, such as coal. Gasification of shredder residue can produce the following products, after further purification and processing:

- A gaseous mixture made of CO, H_2, and light hydrocarbons; and
- Reduced metals (e.g., iron, copper, and aluminum), as a result of the reducing environment in the reactor.

The high-temperature processes also produce vitrified ash, which is non-leachable. Kondoh et al. (2001) compared gasification with other thermal methods for processing shredder residue and discussed the variations in the product gas composition expected from different processes.

Several gasification processes were tested over the years on shredder residue. Some of these are discussed below.

VOEST-ALPINE Process. This process is a high-temperature gasification process developed by VOEST-ALPINE Industrielanlagenbau, Ges.m.b.H, of Austria (see Appendix E of Schmitt 1990). Tests were conducted in which the shredder residue was blended with mixed plastics, waste oils, and fuel oil. The net calorific value of the blended material was about 17,000 Btu/lb, which would indicate that the amount of actual shredder residue used relative to the oils and mixed plastics was approximately 25%. Analysis of the products resulting from gasification of the mixture showed that several dioxin species were present in minute quantities.

The product gas, which consisted of nitrogen (58%), hydrogen (12.7%), carbon monoxide (17%), and carbon dioxide (5%) (the balance was water vapor), had a calorific value of about 100 Btu/ft^3. This product would be considered a low-Btu industrial fuel gas. It would have to be used on-site because it is not economical to transport in pipelines.

TwinRec Process. The TwinRec process was developed by Ebara Corporation in 2000, and now over 14 process lines are in operation (Selinger, Steiner, and Shin 2003; Kummer 2003). The process is based on fluidized-bed gasification with ash melting. Ebara and Ube Industries, Ltd., developed the process further for other applications. SEINAN, a large shredder in Japan, has been operating a combined material and energy recycling "TwinRec" plant since 2000 (Ando et al. 2002). Shredder residue from five shredding plants and three nonferrous-separation plants is brought to the plant and fed to the TwinRec gasifier without any pretreatment. As of January 2002, the plant had processed 95,000 tons of shredder residue and operated for more than 11,500 hours in continuous 24-hour mode. The plant recovers ferrous and nonferrous metals (including copper and aluminum). The fine inert residue is vitrified in the process and used in road construction. Zinc and lead-rich fly ash from the process are sent to the zinc industry for further processing. The energy content of the shredder residues is used to produce steam, which is then used for power generation.

SVC Process. This gasification process, SVC (Siemens Venture Capital Gmbh) or SVZ (Sekundarrohstoff-Verwerktungs-Zentrum Schwarze Pumpe, Germany), has recycled shredder residue (along with other wastes containing organic material, such as MSW), for many years (Obermeier and Markowski 2002). Tests on shredder residue were conducted using a ratio of 30% shredder residue/70% other solid and liquid wastes. Raw shredder residue cannot be fed into the gasifier and must be preprocessed to produce a fuel puck to feed the material into the gasifier. Compacting the shredder residue to produce a fuel puck is done at the shredder's site and expense. The gate fee for the shredder residue fuel puck is reported at about 75 Euros per ton.

In a 2005 report (Buttker 2005), it was reported that a large-scale gasification test was conducted at SVC in Germany. Over 1000 tons of shredder residue were fed to the gasifier, along with other waste materials at ratios up to 25 wt% shredder residue and a total flow rate of up to 175 ton/hr. The gasification/partial oxidation process was carried out at 2,370–2,910°F and a pressure of 367 psia. Pre-processing of the shredder residue is generally required.

Several reactors, having different throughputs are in operation, and over 1 million tons of different types of waste have been gasified (Picard 2005). The mixed-waste material is processed into high-purity methanol (EPRI 2003). SVC Schwarze Pumpe is working to increase the relatively low ratio of shredder residues used in its mixed feed. This task requires removal of the fines from shredder residue before gasification. SVC reports that, even though the technology is well demonstrated, it cannot compete economically with landfills in Germany. An increase in landfill cost would be necessary for it to be economical. The SVC commercial gasification facility currently processes 450,000 tons/yr of solid waste and 50,000 tons/yr of contaminated oil and oil-water emulsions in a Lurgi moving-bed gasifier. The feed to the plant contains about 10–20 wt% shredder residue after removing the metals. It is estimated that about 211 kg (464 lb; 65

gal) of methanol is produced from every tonne of shredder residue fed to the plant (Identiplast 2001; Obermeier 2001). More information is given in an EPRI 2003 report (EPRI 2003)

Plasma Processes. Another form of gasification that has been used experimentally on shredder residue is plasma gasification (Leal-Quiros 2004; Circeo 2008; Westinghouse 2002; Sawyer 2009; Tellini et al. 2007). This process takes place at very high temperatures (~5,000–10,000°C) and atmospheric pressure. In the process, the organic material is converted to a gas rich in CO and H_2. The inorganic residue is melted into a slag that, when cooled, solidifies into a potentially useable construction material. The slag normally passes the toxicity characterization leaching procedure (TCLP) test. Many companies have built and tested plasma systems for waste treatment, including:

- StarTech Environmental Corporation
- Westinghouse Plasma Corporation
- Shinoda Plasma Corporation
- Plascon
- Peat International
- Ecochamas
- Rainbow Xuzhou Plasma Environmental Tech Company, Ltd.

PyroArc Technology. This technology, developed in Norway, was initially developed as a waste-incineration process incorporating a gasifier followed by plasma combustion of the gasifier off-gases. The temperature in the first stage (gasifier) is about 1,000°C, and in the plasma reactor, the temperature is as high as 5,000°C (Gustavson et al. 2005). The process also employs extensive gas cleanup. Quench and cooling of the combustion gases follows for removal of particulates and acid gases. It also produces steam for co-generation. The process has been commercialized for non-shredder residue wastes; 400 tons of shredder residue have been processed only in a pilot-plant. lnorganics in the feed material are recovered as molten slag and metal from the gasifier bottom. The developers report an energy recovery efficiency of 65–70%. In trials conducted with shredder residue, product gases after plasma combustion and gas cleanup met environmental standards. Slag from the gasifier meets the leach requirements (according to the Dutch standard) that would allow the slag to be used as a construction aggregate. A minimum gate fee of 50 Euro/ton is estimated by the process developers for a plant processing 50,000 tons/yr of shredder residue and producing steam from the heat. The gate fee would increase to 100 Euro/ton for an equivalent-capacity plant converting the steam to electricity. At 10,000 ton/yr, the gate fees would exceed 175 Euro/ton.

Montello Process (Italy). This process is an integrated gasification/scrap iron preheat process. Limited testing of the process was conducted (2 months in 1993 and 2 months in 1996). The process separates fine inorganic material from shredder residue and processes the balance of the shredder residue in a rotary kiln to preheat iron scrap that is to be charged to an electric arc furnace. The scrap iron is preheated to about 500–550°C by the gasification of the organic fraction of the shredder residue. The shredder residue is fed to the rotary kiln gasifier with the scrap iron at a ratio of 1 ton of shredder residue to 4 tons of iron and steel scrap. Off-gases from the gasifier are completely combusted in an afterburner/incinerator, and the resultant heat is

available for the recovery and production of steam for energy recovery or electricity generation. The process technology is designed to be co-located with the mini-mill.

RESHMENT® Process. This process, developed[16] by Conzepte Technik Umwelt AG (CTU), VAI (Sauert et al. 2001), and Babcock Borschig Power[17] in Europe (Sauert et al. 2001; Sauert 2005), is based on a smelting cyclone. Initially, large pieces of metals are recovered, and the rest of the material is size-reduced to less than 5 mm. The size-reduced material is then fed to the cyclone furnace, which is maintained at about 2,000°C — the result is the vitrification of the ash. Oxygen is also provided to the furnace to assist in oxidizing the decomposition products of the organics. In the process, the metal oxides are also reduced to their elements, and the elements are melted. The iron/copper molten material is separated by gravity to leave behind a molten mixture of minerals, glass, and some molten metals. The evolved gases are sent to an afterburner and then to heat recovery, and a cleaning-and-scrubbing system downstream of the thermal treatment module controls the emissions to comply with governing regulations. Its energy is used to produce electricity. The process recovers 98% of the cadmium, 92% of the zinc, 91.5% of the iron, 89.5% of the copper, 82% of the lead, and 35% of the aluminum from the material.[18]

The IGEA foundation selected this technology for the treatment of the shredder residue produced in Switzerland (Schaub, Christ, and Jürgen Ritter 2002; Christ 2003). In 2003, the Swiss "Stiftung Auto Recycling Schweiz" (SARS) chose the RESHMENT® technology for Europe's first plant to thermally treat shredder residue[19] (*"Swiss Auto Recycling Foundation — Annual Report 2002,"*April 29, 2003). The contract for a first engineering phase was signed between SARS and Voest-Alpine. The design capacity of the plant is 105,000 tons/yr, including 55,000 tons/yr of shredder residue, and plant start-up was scheduled for 2007 (Sauert 2005).[20] In a recent article, Daniel (2010) discussed co-incineration of shredder residue without reference to the RESHMET process. Therefore, we are not sure if the plant was built and is operational or not.

Dry Distillation/Gasification. This process, known as dry distillation/gasification, was developed in Japan (Horii and Iida 2001; Kusakam and Iida 2000). Dried and compressed wafers of the organic material in shredder residue are fed to a batch "dry distillation furnace," in which gasification occurs as the wafers are brought in contact with a gas that is at up to 1,100°C and contains up to 7% O_2. The residence time is between 30 and 60 minutes. The wafers are also doped with 1.2% of $Ca(OH)_2$ for capturing the chlorine in the feed material. The product gas from the gasification process is further refined in a secondary reactor that is heated by using an external fuel, such as liquefied petroleum gas.

Horii and Iida (2001) reported that the best results were obtained at process temperatures between 500°C and 700°C, which resulted in a gas having a heating value of about 15.5 MJ/kg

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[16] See http://www.ctu.ch/modules.php?name=reshment (accessed in 2005)

[17] See http://www.ctu.ch/modules.php?name=reshment.(accessed in 2005)

[18] Swiss Auto Recycling Foundation — Annual Report 2001

[19] Swiss Auto Recycling Foundation — Annual Report 2002, April 29, 2003

[20] See http://www.ctu.ch/modules.php?name=News&file=article&sid=8 (accessed in 2005)

(6,665 Btu/lb). The gas contained about 30% combustible gases, primarily CH_4 (93.6%) and C_2H_6 (5.5%). At temperatures above 700°C, copper in the ash started to oxidize at higher rates. The heating value was also a function of the process temperature, as shown in Figure 7.1. About 50% of the feed material was lost (converted to gas) during gasification.

Thermoselect Process. Another high-temperature process, Thermoselect, was also tested for the treatment of shredder residue (Stahlberg et al. 2002; also see Drost et al. 2004[21]). The process was proven in a large-scale demonstration facility and commercialized by the Thermoselect Company. The technology was licensed by Interstate Waste Technologies for use in the United States, Mexico and the Caribbean, and it is used mostly for processing MSW. The technology is also licensed by JFE (formerly Kawasaki and NKK), which operates seven plants in Japan. Several plants are also operating in Europe. The process has four stages: waste compaction, pyrolysis, gasification, and water and gas cleanup.

In 2002, a large trial, using over 1,000 tons of shredder residue, was conducted in which mixtures of shredder residue (up to 45% by weight) and MSW were used. In the process, mixtures of shredder residue and MSW are fed in discrete packages into a degassing channel, and the waste spends about 1–2 hours in the channel. The material is dried, and the organics are converted to gas and char. The material then enters a high-temperature fixed-bed oxygen-blown gasifier reactor in which the residence time is about 2–4 seconds. The gaseous products leave at about 1,200°C, and the mineral/metal molten slag leaves at about 1,600°C as a two-phase flow because of the difference in the density of the minerals and the metals. The molten material is then quenched by using water. Because the thermal conductivity of the minerals is different than that of the metals, the quenching process produces two products, minerals and metals, that can be

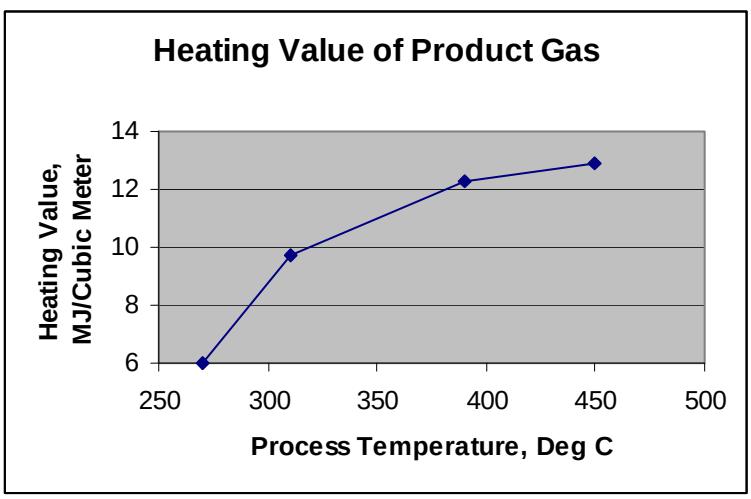


FIGURE 7.1 Heating Value of the Product Gas as a Function of Temperature (based on the data of Horii and Iida 2001)

[21] Drost, U., et al., 2004, *Report on the Operating Trial with Automotive Shredder Residue (ASR)*; http://www.assurre.org/downloads/archive/20a90150-ea41-4121-8e22-e283829abe48.pdf.

separated by a magnet. The product gas stream is cleaned by first very rapidly quenching (near instantaneous cooling) with water. The gases are scrubbed in an acidic scrubber to remove HCl, HF, and heavy metals. The gases are then scrubbed in an alkaline scrubber to remove residual acid liquid droplets. The gases are subsequently de-sulfurized and dried. No changes in the operating procedures were required to accommodate the shredder residue, and no significant changes were observed in the output streams. All emissions remained well within the limits. No refractory wear beyond that observed when processing MSW was apparent.

The inorganic components of the waste are in the molten state at 1,600–2,000°C. The molten material flows through a homogenization reactor and into a water quench bath, where the material forms mineral chips and iron-rich metal pellets that are magnetically separated for recycling outside the plant. The hot synthesis gas passes into a rapid water quench. The gas is then scrubbed and purified of chlorine, sulfur, lead, cadmium, and other contaminants. In the Karlsruhe plant, the purified synthesis gas is used as fuel to raise steam for power generation. In the Chiba plant, the gas is used as fuel for the steel production plant (Stahlberg et al. 2002). Commercial plants are in operation in Karlsruhe, Germany, and Tokyo-Chiba, Japan.

7.3 CHANGING WORLD TECHNOLOGIES PROCESS

CWT has developed a two-stage thermal conversion/depolymerization process that converts organic material into fuels, gases, and solids. CWT's first commercial facility based on this technology was commissioned in April 2003. It converts about 200 tons/day of turkey offal into fuels and fertilizers. This installation is a joint-venture partnership between ConAgra and CWT. A study focused on a select sampling of two different types of shredder residue was conducted to evaluate the applicability of the process to shredder residue treatment (CWT 2004). Results from this initial study indicated that the CWT process was able to convert the shredder residue samples to three product fractions: an oil, a gas, and a carbon char. The resultant oil product characteristics are summarized in Table 7.1.

On the basis of the results of this initial project testing, CWT conducted a test on about 1,000 lb of shredder residue to further confirm the technical and economic feasibility of this process. The results are summarized below:

- Tests demonstrated the ability of the TCP to convert shredder residue into oil and solid product streams (CWT 2004).

- PCBs in the shredder residue dissolved in the hot oil and were eventually destroyed during hydrolysis. As a result, their concentration was reduced from 35–65 ppm to less than the detection limit of 2 ppm.

- Thermal cracking of the hydrolyzed oil at about 500°C produced hydrocarbon fuels, a fuel-gas, and a solid carbon product in ratios of 84%, 10%, and 6%, respectively.

TABLE 7.1 CWT Oil Characteristics from Shredder Residue Feedstock

Method	Test	Shredder Residue Bucket 1	Shredder Residue Bucket 2
D-287	API* @60°F	37.6	40.7
D-93	Flash point (°F)	<72	<72
D-86	Distillation (°F)		
	IBP (initial boiling point)	200	119
	10%	320	234
	50%	460	451
	90%	668	652
	FBP (final boiling point)	712	691
D-4294	Sulfur (wt. %)	0.125	0.124
D-97	Pour point	–38°F/–39°C	–38°F/–39°C
D-482	Ash (wt. %)	0.004	0.003
	Carbon (%)	86.38	85.30
	Hydrogen (%)	13.47	14.54
	Nitrogen (%)	<0.1	<0.1
D-240	Heat content		
	Btu/lb	19,094	18,622
	Btu/gal	133,046	127,409

* American Petroleum Institute.

- Fractional distillation of the cracked fuel produced gasoline (12%), kerosene (38%), diesel (32%), heavy oil (15%), and gas (3%).

- Economic analysis of the process was conducted on the basis of a plant that has a design capacity of 103,800 tons/yr (300 tons/day). On the basis of these assumptions, the plant would generate annual revenues of approximately $14,000,000. The average net free cash flow for the first 3 years would be approximately $4,6000,000. The results are summarized in Table 7.2.

TABLE 7.2 Results of the Economic Analysis

Total cost of plant	$40,000,000
Start-up costs and working capital	$8,000,000
Financing	$20,000,000 (grant)
	$28,000,000 (equity)
Total investment	$28,000,000
Tipping fee	None
Number of employees	50 (average compensation, including 35% payroll cost: $40,512)
Repairs and maintenance	10% of 60% of plant cost
License fee	$10/ton (initial year)
Conversions:	
Oil	43.10% (789 barrels)
Solids/metals	22.70% (68 tons)
End product sale prices:	
Oil	$38/bbl
Metal	$150/ton

8 TECHNOLOGIES FOR SEPARATING AND RECOVERING PRODUCTS FROM SHREDDER RESIDUE

Over the last few years, major advances have been made in process development for separating and recovering materials from shredder residue. Some of these advances are discussed below.

8.1 THE ARGONNE PROCESS FOR THE SEPARATION AND RECOVERY OF FLEXIBLE POLYURETHANE FOAM

Even though the foam is only a small weight percent (~5%) of shredder residue, it may constitute over 30% of its volume. The market for recycled foam in North America is large. At present, the foam rebond industry imports millions of pounds every year of prompt scrap foam from Europe and Asia. The imported scrap supplements the more than 1.75 billion lb of virgin foam used to produce foam products, such as residential and commercial carpet padding, automotive carpet padding and headliner, car seat cushions, and other consumer and automotive products (SRI Consulting 1997). The viability of using foam recovered from shredder residue to supply the foam rebond market depends on two key factors: (1) development of a cost-effective process for recovering foam from shredder residue, and (2) confirmation that the recovered foam meets the quality requirements of the market. Mark and Kamprath (2004) stated that the highest-quality foam can be obtained by first dismantling foam seats and then washing the foam. However, manual separation of the foam is not economical. Therefore, separating the foam from shredder residue was investigated.

Argonne, in collaboration with the VRP, the APC, the ISRI, and others, has developed a continuous process for the recovery of flexible foam from shredder residue (Jody, Daniels, and Libera 1999). Argonne built a continuous foam washing and drying system that was pilot-tested at a shredder facility. Economic analysis of the process, using manufacturers' quotes and operating data from Argonne's pilot plant, indicates a potential payback of less than two years for a plant producing about 1,000 tons/yr of foam.

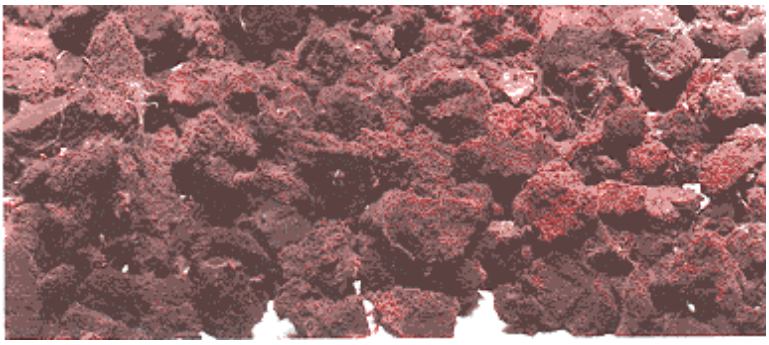
Samples of clean foam were shipped to three major foam processors; all three indicated that the quality of the recovered foam met their requirements. Tests of the recovered foam by an independent testing laboratory showed that the recycled foam met the specifications for several automotive applications, including carpet padding, headliner, and sound-suppression support materials. Annually, recovery will save about 12 trillion Btu of energy, cut the amount of solid waste being disposed of in landfills by about 150,000 tons, and eliminate the emission of about 250 tons of volatile organic compounds (VOCs) into the air that otherwise will be emitted during the making of an equivalent amount of virgin PUF.

The Argonne process consists of two parts: (1) separation of the foam from the shredder residue and (2) cleaning the foam once it was recovered. Up to 50% of the weight of the foam (approximately 30%, on average), as recovered from shredder residue, is made up of moisture,

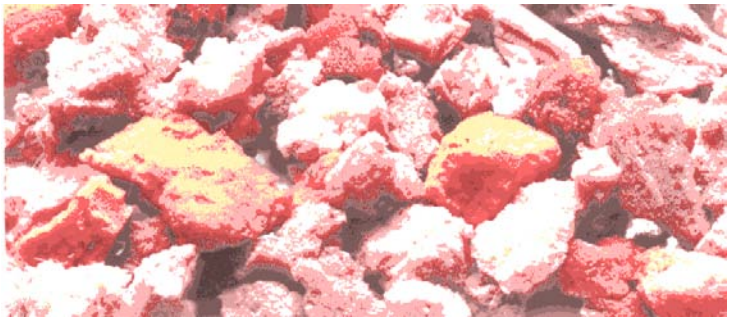
entrained dirt, sand, automotive fluids, metal dust, metal oxides, and other contaminants. Foam recovered from shredder residue before and after cleaning is shown in Figure 8.1

A continuous wash, rinse, and drying process with a design capacity of 100 lb/h was designed and tested (Figure 8.2). The overall process consisted of six basic unit operations: (1) shredder residue screening and PUF recovery, (2) sizing, (3) washing, (4) rinsing, (5) drying, and (6) baling, as shown in Figure 8.3. The heart of the system was patented linear continuous washing, rinsing, and drying equipment of unique design. The washing, rinsing, and drying equipment essentially consisted of three linear conveyors. In each of the three conveyors, the foam was compressed sequentially and released to mechanically assist in the washing, rinsing, and drying of the foam. The residence time for drying the foam in this equipment was less than 15 minutes, while in the conventional rotary drum dryer, drying time was over 3 hours. The pilot plant also included a continuous ultra-filtration unit to remove oils and fine dirt particles that may be suspended in the wash water from the wash tank. This step was necessary to keep the water in the wash tank clean.

Process economics are estimated on a design basis of 1,000 tons/yr of clean foam produced in an 8-hour shift operating 300 days/yr. This amount is equivalent to a design capacity of about 840 lb/h, which equates to the estimated amount of flexible foam that can be recovered from about 60 shredded cars per hour. The total capital investment is estimated at $700,000 for all unit-operations equipment. This investment includes the cost of the foam



Recovered Shredder Residue PUF before Cleaning



Recovered Shredder Residue PUF after Cleaning

FIGURE 8.1 Polyurethane Foam (PUF) as Recovered from Shredder Residue and after Cleaning

FIGURE 8.2 Wash, Rinse, and Dry Continuous Equipment

trommel, the foam shredder, the continuous washing and drying equipment, and the foam baler. The cost does not include the contractor's engineering fees, license fees, or taxes and permit fees. Approximately two barrels of oily wastewater would be produced each day and would have to be disposed of by a waste handler. The cost is estimated at $100/bbl, on the basis of pilot-plant data. The economic analysis is summarized in Table 8.1.

The acoustic performance of the recycled foam (6 lb/ft^3 Argonne foam) was equivalent to that of the conventional fiber pad (Figure 8.4). Large samples of foam were submitted to several scrap-foam rebonders during the project for evaluation (Figure 8.5). Cleaned foam was sent to a foam rebonder that processed it into foam logs weighing about 750 lb each; the rebonder processed the foam in exactly the same manner as it would process prompt foam scrap, using the same ratio of steam and chemicals. The foam logs were then allowed to dry, and then they were sliced into different densities. Some of the products made from these samples were tested in a number of vehicles in the United States and Canada (Blair 1998; Duranceau, Winslow, and Saha [1998]).

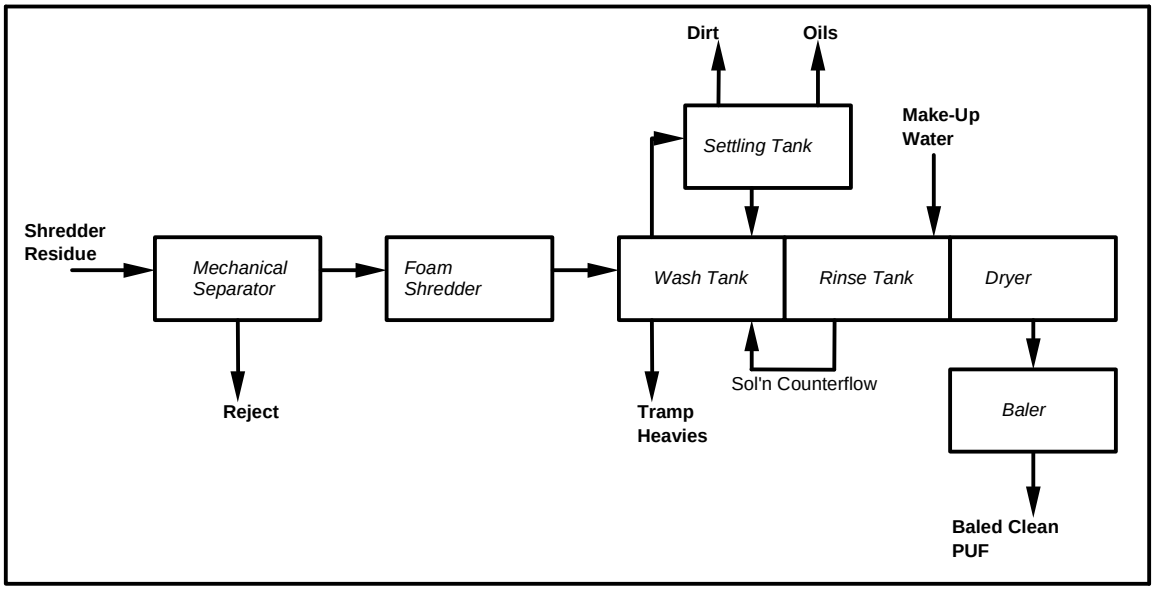


FIGURE 8.3 Block Flow Diagram of the PUF Recovery Process

TABLE 8.1 PUF Recovery Process Costs

Type of Expenditure or Earning	Expenditure or Earning ($)
Annual revenues @ $0.30/lb foam	600,000
Credit for avoided disposal @ $20.00/ton	20,000
Total Annual Revenues	**620,000**
Operating Costs:	
Labor, two operators at $18/h	86,400
Electricity, 150 kWh/h @$0.10/kWh	36,000
Natural gas, 1 million Btu/h @ $4.00/million Btu	9,600
Chemicals, 0.01 lb/lb foam @ $0.85/lb	17,000
Disposal costs for wet dirt @ $20.00/ton	8,000
Disposal costs for oils @ $100.00/barrel	63,500
Maintenance, @ 3.5% of Capital	22,750
Total Annual Operating Costs	**243,250**
Annual Earnings before Interest, Taxes, Depreciation, and Amortization	**376,750**

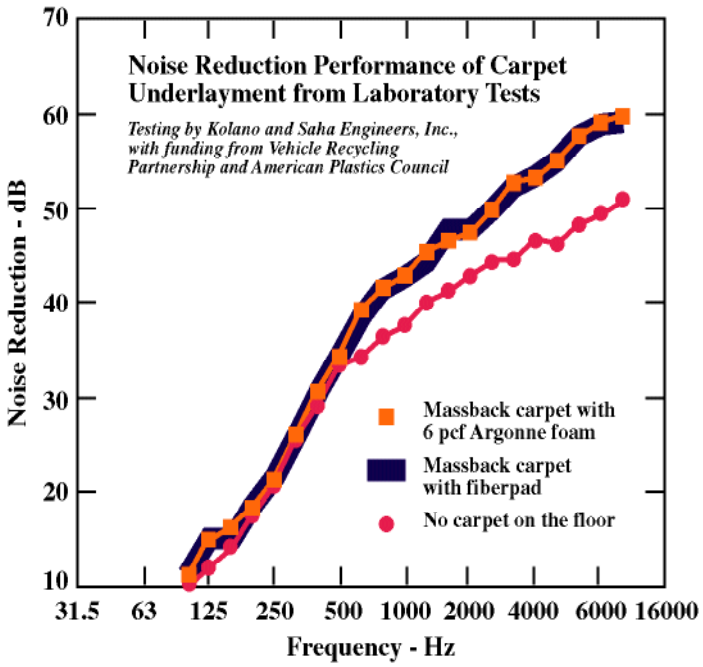


FIGURE 8.4 Noise Reduction of Automotive Carpet Underlayment (lb/ft3)

Cleaned Foam **Rebonded "Foam Logs"**

Slicing Foam "Log" **Foam Ready for Shipment**

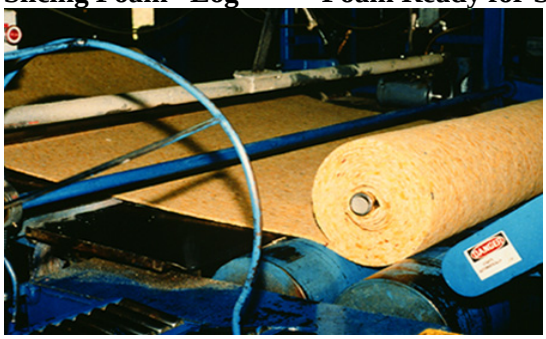


FIGURE 8.5 Recovered Foam from Shredder Residue Made into Carpet Padding

8.2 THE SALYP PROCESS FOR THE SEPARATION AND RECOVERY OF FLEXIBLE FOAM

As discussed earlier, Salyp separated flexible PUF from shredder residue in its plant in Belgium. Salyp also licensed the Argonne technology for cleaning the foam. A full-scale (500-lb/h) system for cleaning foam from shredder residue was designed by Argonne; built by Almco Industrial Finishing Systems in Albert Lee, Minnesota; and installed at Salyp's facilities in Belgium.

Salyp scaled up the pilot-scale foam recovery technology that had been pilot-demonstrated by Argonne and was able to recover a relatively clean PUF product from shredder residue. The production capability of the equipment met design throughput expectations. Although this equipment operated successfully, the equipment for washing and the treatment of rinse water solution that was included in Argonne's pilot plant was never incorporated into the Salyp operation.

8.3 THE ARGONNE PROCESS FOR THE SEPARATION AND RECOVERY OF PLASTICS

Because most plastics are not compatible with each other, they must be separated. Argonne has developed two processes for the recovery of individual plastics from shredder residue: selective dissolution and froth flotation (Jody and Daniels 1999; Karvelas et al. 1999; Jody, Pomykala, and Daniels 2003b; Jody, Daniels, and Libera 1999). The selective dissolution method is discussed in Section 9.1.2. The froth flotation process is discussed below.

The basic principle of froth flotation is to place the plastics mixture in a solution that can selectively enhance or retard the hydrophobicity or hydrophilicity of one or more of the targeted plastics, so they can be separated from the mixture. Argonne's process for recovering plastics from shredder residue consists of six main steps:

1. Separate the polymers as a concentrate from shredder residue.

2. Granulate the polymer concentrate to a particle size of 1/4–3/8 in.

3. Concentrate the plastics targeted for recovery from the polymer concentrate into more manageable fractions with a minimal number of species in each fraction.

4. Recover targeted plastics from the concentrated fractions.

5. Polish the recovered targeted species to increase purity, value, and marketability.

6. Clean the plastics products.

Steps 3 through 6 consist of the following operations after the polymer concentrate is granulated to the appropriate particle size:

1. Separation of the "light" materials, including polyolefins. The conditions in this stage of the process can also be set to force over 90% of the wood to float with "lights," so that it can be dealt with only once. This fraction contains appreciable amounts of different rubber species.

2. Separation of the "heavies," such as metals, glass, rocks, rubber, and glass-filled nylons from the sinkers of step 1.

3. Separation of the polyolefins from the "lights" produced in step 1.

4. Separation of ABS, ABS/PC, PC, PS, PVC, and other plastics from the floaters of step 2.

5. Washing of the plastics concentrate produced by the mechanical separation process to remove dirt and contaminants.

Argonne built a six-stage 1,000-lb/h pilot plant (Figures 8.6 and 8.7) to test the froth flotation process at a larger scale. The plant has been used to process about 20,000 lb of polymer concentrate from shredder residue. Argonne produced a polyolefin (PP and PE) product and a rubber-rich fraction. Solution conditions for the recovery of other plastics are being tested. The plant was also used to process scrap plastics from electronics, home appliances, and floor care equipment.

About 5,000 lb of PP/PE have been produced. This fraction contains >95% PE and PP. Samples of the recovered PP/PE fraction were analyzed to determine its physical properties. The results are summarized in Table 8.2. Table 8.2 also shows the properties of the recovered PP/PE sample after the residual impurities were removed manually. The main impurity in the recovered material is rubber. Overall, the properties of the recovered sample compare well with those of commercially available olefinic polymers. Interestingly, removing the rubbery impurities, most of which are EPDM-based, did not have a big impact on overall properties.

Larger samples of the recovered PP/PE material were mixed with recycled PP (PP regrind) copolymer (25% recovered and 75% regrind) and pelletized in standard equipment. Material output was recorded as 1,400 lb/h. The test led to the following observations:

- This initial test proved that we can make what appears to be an excellent pellet by blending the recovered material with regrind that is presently being recycled.

- The general appearance of the final pellet was excellent. The supplemental material was black, which produced an excellent black pellet (no additional colors were visible).

Plastics Recovery Facility

FIGURE 8.6 Picture of Argonne's Froth Flotation Pilot Plant

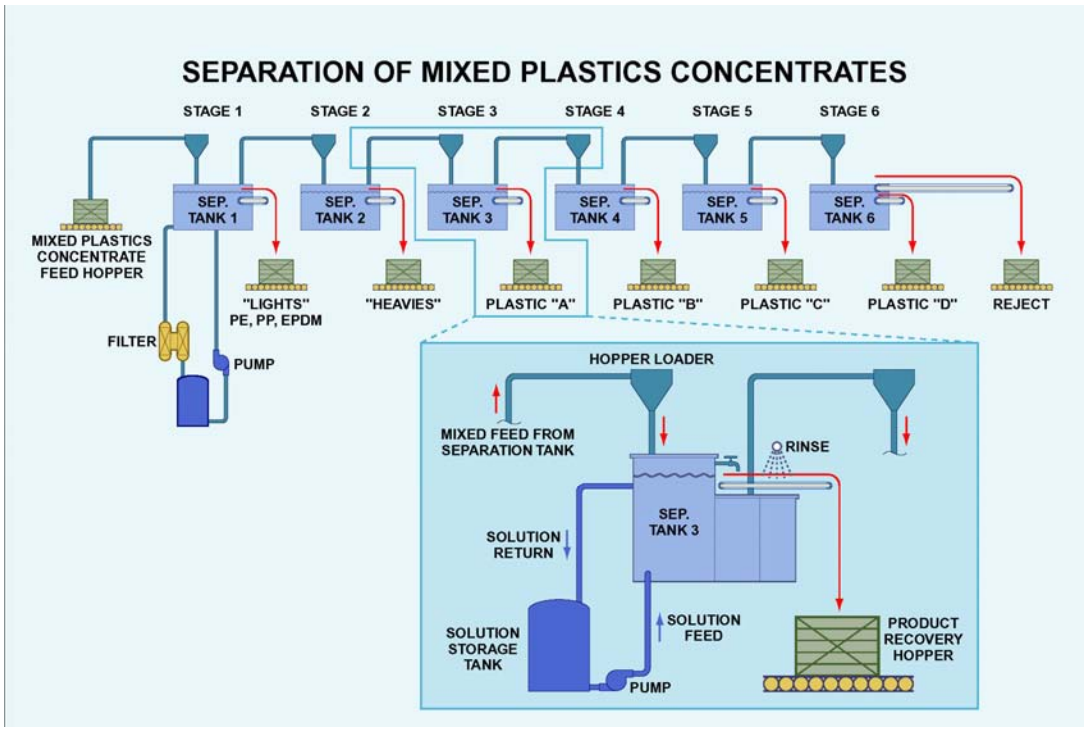


FIGURE 8.7 Schematic Diagram of Argonne's Froth Flotation Pilot Plant

TABLE 8.2 Physical Properties of the Recovered PP/PE Product from a Shredder Residue

Property	As Is (97% pure)	Impurities Removed Manually
MFR (melt flow rate) (g/10 min), 230°C	7.2	5.9
Izod impact (ft-lbf/in.) 73°F	1.7	1.8
Flexural modulus, 1%, Secant (psi)*	126,000	137,000
Tensile strength at yield (psi)	3,391	3,628
Tensile strength at rupture (psi)	3,149	3,189
Elongation at rupture (%)	12	14
Gardner impact, 73°F (in. lb)	20	68
SG (specific gravity) (g/cc)	0.94	0.93

* Pounds per square inch.

- Screen changes were required approximately every five minutes, so a second operator was needed. The screen pack used was 20/20/20/60/100/20 (these numbers denote the mesh of each individual screen in the screen pack). Screens were changed whenever the head pressure exceeded the adaptor pressure by 500 psi (that is, the pressure on the front of the screen pack exceeded the pressure behind the screen pack by 500 psi, indicating a buildup of material caught on the screen). Generally, screen changes are performed at a pressure difference from 500 to 1,000 psi.

- Un-melted plastic material was observed on the screens and in the melted material scraped from the screens. This material was primarily wood, thermoset plastics, rubber, and some dirt.

- The melted material and the final pellet both had a distinct rubber smell but no obvious shredder residue smell.

The Argonne process also recovered a filled ABS concentrate (70% ABS), an unfilled ABS/PS concentrate (60% ABS and PS), and a PC-ABS/PC concentrate (85%). Laboratory tests showed that these fractions can be upgraded to >90% purity.

The basic Argonne process also produced a rubber fraction that was over 80% mixed rubber. The remainder of that fraction was made of mixed heavier plastics and a small amount of wood. Samples of this material were sent to ADVAC Elastomers, Inc., to test and evaluate their suitability as construction materials.

A 2,000-lb/h module is under construction to demonstrate the process under full-scale operating conditions.

8.4 THE RECOVERY PLASTICS INTERNATIONAL PROCESS

RPI International (United States) developed a physical and wet "skin-flotation" process for the separation of plastics from shredder residue. RPI originally developed a "skin-flotation" technology for the separation of PVC and PET mixed plastics for plastics bottle recycling. In the mid-1990s, RPI initiated work on the development of its "skin-flotation" technology for the recovery of plastics from shredder residue. As opposed to froth-flotation technology, skin-flotation technology used a plasticizer to modify the surface of certain plastics, which would then allow the modified plastics to be selectively recovered. Large-scale pilot runs were conducted at RPI's Salt Lake facility. RPI was reportedly able to recover a polyolefin fraction that met specifications for non-appearance automotive parts used in parts of the automobile that are not visually important. Chrysler Corp. used materials supplied by RPI in the production of Chrysler's CARE cars to demonstrate the feasibility of using recycled plastics in automotive applications. RPI was reportedly able to effectively recover polyolefins from its facility with a residual PCB concentration of less than 2 ppm.

8.5 THE SALYP PROCESS FOR THE SEPARATION OF MIXED PLASTICS

The Salyp NV was a start-up Belgian company funded with private capital with the expectation of developing a complete shredder residue separation technology package that could then be sold to shredder operators. The process starts by mechanically separating shredder residue to produce a polymer concentrate, followed by (1) thermoplastics sorting for recovery of plastics from the plastics concentrate and (2) PUF cleaning for foam recovery. Salyp built a pilot plant, which operated for about a year.

Salyp acquired a license to the PUF recovery technology developed at Argonne and a thermoplastics sorting technology from a German entrepreneur company, Okütech. Using these two technologies as a base, Salyp undertook the construction of a facility for processing bulk shredder residue that incorporated multiple-unit operations. Salyp targeted a number of product fractions for recovery from shredder residue, including PUF, a plastics concentrate, a fiber-rich "fuel" fraction, and others. The complexity of Salyp's bulk separation facility resulted in operational problems and in a relatively low yield of plastics concentrate from the shredder residue.

Although somewhat complex, Salyp's bulk separation facility was able to produce a wood-free plastics concentrate. One of the unit operations incorporated into the Salyp plant was a color sorter that was able to effectively remove much of the wood that is found in shredder residue. The U.S. ELV Cooperative Research and Development Agreement (CRADA) team funded Salyp to benchmark the thermoplastics sorting technology that it had acquired from Okütech. Salyp had designed and built a full-scale two-stage thermoplastics sorting line. Although Salyp reportedly had some success in operation of this technology for the separation of

mixed electronics plastics, the technology was not able to selectively separate individual plastics from the plastics concentrate recovered from shredder residue in Salyp's bulk processing line.

The thermoplastics-sorting system uses infrared energy to heat and dry a washed stream of mixed thermoplastics. The mixed plastics are irradiated until one type of plastic in the mix is softened, but not melted. Following the heating stage, the mixed-plastic stream is fed through a set of rollers. The softened plastic sticks to the roller and is removed from the stream. The remaining plastics continue through the process and move to the second heating stage, during which another plastic is selectively softened and removed. The remaining mixture moves to the next stage and so on until, theoretically, all desired plastics are separated. However, when this process was applied to mixtures of plastics derived from shredder residue, the purity was unacceptably low. Part of the reason for low purity is that the number of species in the mixture was large and the softening temperatures of some of these species overlapped.

8.6 THE VOLKSWAGON AG-SICON RECYCLING PROCESS

Working with Volkswagen, AG-SiCon developed a process for recycling materials from shredder residue. SiCon states that its method processes over 200,000 tons of shredder residues in Europe, and it expects the amount to double by mid-2011 (http://www.sicontechnology.com/recycling-verfahren/vw-sicon-verfahren/).

Construction of the first large-scale Volkswagen-SiCon plant for recycling shredder residue was initiated in 2005 in Austria.[22] The plant has an annual design capacity of 100,000 metric tons of shredder residue. The first stage of a smaller plant based on Volkswagen-SiCon technology was commissioned in Belgium in 2005. The process involves multistage shredding in combination with sorting and segregation on the basis of physical criteria, such as density, particle shape, magnetic properties, conductivity, and optical characteristics (Guschall et al. 2005).[23] In the sink/float sections of the process, the fluid and the plastics mixture are fed to the mixing tank separately by using a metering pump and a metering screw. The tank is equipped with an agitator that keeps the plastics suspended in solution. The mixed slurry then enters the separation unit, in which some plastics sink and some float. The fluid used in the separation process is recovered and reused (see footnotes 21 and 22).

The VRP sponsored a project at SiCon in which SiCon used a five-step process to separate 4,350 lb of shredder residue. Three factions were produced: granules, fibers, and sand or fines. The metal content of the shredder residue reported by SiCon was high: 11.1% ferrous and 3.2% nonferrous. The plastics content of the shredder residue was reported to be 35%. The rubber was separated by an electrostatic separator and was purified by using an optical sorter to separate the EPDM. SiCon also recovered the polyolefins.

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[22] Volkswagen-Sicon Process for Recycling End-of-Life Vehicles Launched in Austria. Volkswagen Media Services, June 20, 2005.

[23] VW Press Release, June 2004, "ARN Plan for Separation Plant in Netherlands Will Significantly Reduce Shredder Waste from Discarded Cars" and "Smart Waste Separation with VW SiCon Process," Recycling News, Oct. 2005.

Recently, SiCon joined with Green EnviroTech and Thar to implement the technology in the United States (http://www.marketwire.com/press-release/Green-EnviroTech-Signs-Exclusive-Partnerships-With-Industry-Leaders-Agilyx-SiCon-Thar-1281219.htm).

8.7 THE GALLOO PROCESS FOR THE RECOVERY OF PLASTICS

Galloo, headquartered in France, operates a number of materials recycling facilities, including 15 shredder operations throughout France and Belgium. Galloo has developed a process that includes bulk separation of shredder residue to recover residual metals in the shredder residue from their existing operations at three of their sites. The outputs from the bulk separation of shredder residue after residual metals (residual nonferrous metals in the shredder residue are reported at 5.4%) are recovered include:

- Mineral fraction (40%) — currently disposed of in landfills, but reportedly being evaluated for road construction.

- Light fraction (30%) — primarily foam and textiles; Galloo is working with an automotive company to investigate the feasibility of using this fraction for exterior sound insulation; use of this material for interior applications would require that the material be cleaned to remove residual oils and other automotive fluids that are typically absorbed onto this material during the primary shredding operation.

- Heavy combustible fraction (15%) — primarily rubber, wood, and other polymers; this fraction has a relatively high calorific value mainly because of the rubber content; this material has been used as a cement kiln fuel, but the market is limited because of the availability of other lower cost (higher value) fuels to the cement industry, such as waste solvents.

- Plastics fraction (10%) — the plastics fraction from the three sites is apparently processed in a wet separation system located at Halluin on the France/Belgium border.

- Remaining residues (5%) — this fraction contains PVC, nonferrous metals, and stone and rock; this fraction is processed in a heavy-media separation plant to recover the nonferrous metals; stone and rock are used in road construction, and the residual is disposed of in landfills.

Process costs for the bulk separation system are reported to be 25 Euro per ton of shredder residue (including investment). The value of the recovered fractions has not been disclosed. Galloo's plastics separation line uses "static hydrodynamic" (settling) separation tanks to recover a polyolefin fraction and a polystyrene fraction from the plastics concentrate recovered from its bulk separation process. The plastics are extruded, compounded, and pelletized in-line. The extrusion system incorporates special filters to remove residual contaminants from the recovered plastics, resulting in the production of a pellet consistent with

Peugeot Citroen specifications. Galloo has stated that it plans to expand its plastics recovery process to recover other automotive plastics. Capital and operating costs for the Galloo plastics separation plant have not been disclosed. The Galloo plastics recovery plant produces an estimated 20,000 tons/year of polyolefin pellet — all of which is consumed by Peugeot Citroen. The market for the polystyrene pellet has not been disclosed. The overall recovery of the polyolefins from the Galloo process is about 50%, on the basis of controlled tests conducted using 200 Peugeot and Renault vehicles in 2002.

Galloo Plastics (a recycling unit of Galloo Group located in Halluin, France) has a commercial process that is claimed to recover polyolefins and some polystyrene and ABS from shredder residue (Shut 2004; Feraudy 2005). It is also claimed that the process can separate talc-filled PP and flame-retardant PS from other PP and PS materials (Shut 2004). Recovered PP from the Galloo process is used in making wheel wells and battery cases for Peugeot vehicles. The basic steps in Galloo's process are (Shut 2004):

1. Shredder residue is ground to an average particle size of about 25 mm (1 in.).

2. A series of mechanical separation processes (including trommels and air classifiers) are used to produce a plastics concentrate.

3. A series of density separation stages are used for further separation. These include stages at specific gravities of 1.6, 1.25, 2.2, and 3.2.

4. Proprietary gravity separation processes are used to separate plastics having specific gravity values between 0.9 and 1.5.

8.8 THE MBA POLYMERS PROCESS

MBA Polymers has developed a commercial-scale process employing physical and wet-density separation techniques that focus on the recovery of recyclates from manufacturing scrap and from post-consumer electronic and appliance plastics concentrate. MBA Polymers has conducted research and large-scale test runs on recovering post-consumer automotive plastics from shredder residue and from mixed plastics recovered in dismantling field trials. Recently, MBA Polymers conducted an 18,000-kg (40,000-lb) trial using plastics concentrates from Salyp. MBA Polymers processed the material on its pilot lines in Richmond, California. Five materials grades were recovered: (1) polyolefin "A," (2) polyolefin "B," (3) filled PP, (4) ABS, and (5) HIPS. The total yield of these products was estimated to be about 48.5% of the plastics-rich fraction. This yield is approximately 88% of the amounts of these plastics predicted from characterization of the feed material. The products were characterized and extruded on a small laboratory extruder and subsequently molded and tested. The properties of the recovered plastics were reported to be "encouraging." It is expected that most of the products could be used in some type of durable good applications without modification. The properties of the extruded pellets are given in Table 8.3.

TABLE 8.3 Properties of the Extruded Pellets from Plastics Recovered by MBA Polymers from Shredder Residue

Sample	unf-PP	f-PP	HIPS	ABS
MFR (melt flow rate) (g/10 min), 230°C, 3.8 kg	–*	–	–	5.5
MFR (melt flow rate) (g/10 min), 200°C, 5 kg	–	–	2.5	–
MFR (melt flow rate) (g/10 min), 230°C, 2.16 kg	4.6	7.9	–	–
Izod impact (ft-lb/in.) 73°F	10.3	1.6	1.8	3.4
Flexural modulus, 1%, Secant (ksi)**	130	293	315	361
Tensile strength at yield (psi)	3,029	3,779	4,319	6,291
Tensile strength at rupture (psi)	1,773	2,365	4,011	5,623
Elongation at rupture (%)	50	32	19	6
DTUL (264 psi, °F)	–	–	162	170
DTUL (66 psi, °F)	450	232	–	–
Gardner impact, 73°F (in. lb)	216	64	16	16
SG (specific gravity) (g/cc)	0.94	1.07	1.05	1.06

* A dash indicates not analyzed or not determined.

** ksi = kips per square inch.

The company has recently established two joint ventures on the basis of its plastics separation technology: one plant is operating in China, as is another one in Austria. Guangzhou GISE-MBA New Plastics Technology Co., Ltd. (GMP) was founded in China in January 2004, MBA Polymers, Inc., and Mueller-Guttenbrunn (MG) GmbH, built a 40,000-ton-per-year plant plastics recycling facility in Kematen, Austria in 2005.

8.9 THE TOYOTA PROCESS[24]

Toyota started development of technology for recycling shredder residue in 1993. In 1998, the first Toyota shredder residue recycling plant went on-line, and it had a design capacity of about 15,000 ELVs per month. In 2000, the plant demonstrated an overall vehicle recycling rate of 90% (see note 22). In 2001, Toyota established the Automobile Recycle Technical Center for the development of new dismantling technologies. In 2002, Toyota constructed a recycle/recovery pilot plant and has been conducting pilot experimentation to establish new recovery technologies for shredder residue. Processes developed by Toyota include:

- Dry separation of shredder residue.
- Production of soundproofing products from PUF and fabrics. The foam and fabric are sorted and recycled into soundproofing material.

[24] See http://www.toyota.com.cy/inside_toyota/environment/recycling_process/index.aspx. (accessed in 2005)

- Recycling of wire harnesses. Toyota developed a high-precision sorter to separate wire harnesses. The plastic shields and connectors are removed, and the remaining copper (of purity 97%) is recycled.

In addition, Toyota collaborated with industrial partners on the following:

- Toyota, with Sanei Industry Co., Ltd., developed a process for using sorted resins as an alternative fuel. This fuel has been in use since April 1999.

- Toyota worked with Aisin Takaoka Co., Ltd., to develop cupola gasification/melting furnaces. Pilot plant testing started in December 2002. The capacity of the pilot plant is approximately 10 tons/h. In the process, shredder residue is heated to 600°C or higher to allow gasification through thermal decomposition of the combustible substances. Noncombustible substances, such as glass, are then heated to about 1,600°C or more to form slag.

8.10 CENTRIFUGATION PROCESSES

Jan H. Schut, in a *Plastics Technology* article,[25] reported that Delphi and Result Technology AG have developed technologies that employ centrifugal forces to recycle polymers and other automotive materials. These technologies are discussed below.

8.10.1 The Delphi Process

Delphi has developed a process for recycling connector housings, which consist of different thermoplastics, elastomers, and metals, without shredding the housings. Working with the University of Wuppertal, Delphi developed a centrifuge-based process in which whole car parts are placed in the centrifuge, and the centrifuge is heated, under an inert environment (to prevent the oxidation and cross-linking of the plastics), to different controlled temperatures to selectively melt the plastics so that the centrifuge can separate them from the rubber and the metals. The process can also separate the different plastics one at a time, on the basis of their different melting temperatures (also see Section 1.6).

The process was tested on batches of several kilos of nylons, and it used one-fifth of the energy required to produce virgin nylon. The process also recovers PP from car interior pillar trim that consists of nylon fabric backed with PP. It can also separate PC from metallized coatings on compact discs (CDs), where the clear PC is recovered and the metal stays in the centrifuge. In addition, the process can be used to separate multilayered plastics.

[25] See “New Ways to Salvage Plastic Waste;” (http://www.plasticstechnology.com/articles/200108fa2.html).

8.10.2 The Result Technology AG Process

Result Technology AG has developed a process for de-laminating multilayered plastics and metals (see footnote 23). The process involves a rotor that rotates at 600 ft/s inside a ribbed drum, creating a 3,500-g shear force at the rotor/stator interface. This process results in the separation of flakes of multilayer plastics. According to Schut (footnote 23), "Metallic layers deform into small balls, while rigid plastic chips tend to keep their shape and flexible ones stretch and elongate." The mixture is then separated by using the different shapes of its components. Plants with outputs from 2,200 to 11,000 lb/h are in operation in Europe and the Far East and are used mostly to separate metal-plastic composites, such as aluminum-coated PP or PE film or metallized PVC blister packs. For example (see footnote 23):

- In Germany, a 5,000-lb/h plant at Retec Recycling und Umwelttechnic GmbH separates ground post-consumer computers. Another plant separates multi-material regrind from dashboards containing ABS, a polyurethane rubber (PUR) foam layer, and a PVC layer. The feed material is 15-mm chips. "After delamination in the accelerator (at a rotor-tip speed of 280 ft/sec), the PUR foam particles are 3.5 mm, the ABS chips are 1.2 mm, and PVC flakes are 0.25 mm. The user reports that these can be separated into 99%-pure ABS and 97%-pure PVC. With secondary mechanical separation, both streams reportedly can get to 100% purity. Operating cost is about 5¢/lb."

- In Sweden, a plant based on this technology recovers metals from the shredder residue.

- Tests have been conducted on flakes of PET with nylon and cellulose layers. Although the PET flakes were unchanged, the cellulose and nylon are stretched to greater than 40 mm and can be removed by air classification, leaving behind a 99%-pure PET product.

8.10.3 Recovery of Nylon from Post-Consumer Carpet Using Centrifugal Technology

Polyamid (Polyamid 2000) in Germany installed sixteen 35-in.-diameter centrifuges made by Baker Process (formerly Bird Machine Co.) in the United States (see footnote 24). The centrifuges have a combined capacity of 240 million lb/yr of waste carpet and can produce 20 million and 26 million lb of nylon 6 and nylon 66, respectively. The process starts by grinding nylon carpets to a fine particle size, and then the fine particles are centrifuged through a two-stage system. Each stage consists of eight centrifuges. The rubber backing material is separated in the first stage, and residual contaminants are removed in the second. The nylon product is then depolymerized and repolymerized into new nylon. The process is expected to produce virgin nylon at the same cost as standard nylon.

8.11 THE NISSAN PROCESS

Nissan partially modified a waste incinerator at the Oppama Plant and began energy recovery from ASR in the autumn of 2003. Full-scale operation of 400 tons per month began in January 2005. Waste from the Nissan plants and ASR from ELVs are burned together in the incinerator. Thermal energy generated during incineration is converted into steam that is effectively used for humidification and other purposes in the pre-painting processes at the plant. Since ASR generates large quantities of heat, controlling the temperature during incineration has been difficult. Another problem has been that unburned substances tend to stick to the inner walls of the incinerator and the evaporation pipes of the boiler. These problems have been resolved through optimum temperature control (Nissan 2006; http://www.nissan-global.com/EN/DOCUMENT/PDF/ENVIRONMENT/TECHNOLOGY/en_asr.pdf).

8.12 RAPID IDENTIFICATION AND SEPARATION AUTOMATED PROCESSES

8.12.1 Infrared Separators

IR separators for mixed plastics that contain black plastics that have significant amounts (>5%) of carbon black are still in the R&D stage. This technology is in widespread use for separating bottles of PET, PVC, and PE. The estimated cost for such systems (full scale; 5,000–10,000 lb/h) appears to be between $10 and $20 per lb/h. Application of this technology to chips is still limited. However, wide use may be only a few years away. The advantages of such systems are that they:

- Use no fluids, chemicals, or salts; therefore, they do not produce waste streams beyond what is in the starting material;
- Could achieve more than one separation per stage;
- Demonstrate purities greater than 90%;
- Are cost-competitive;
- Could be combined with color sorters and X-ray identification systems to achieve greater separation; and
- May be able to tolerate consistent amounts of moisture in/on the plastics.

Disadvantages of such systems include their:

- Inability, at this time, to process black plastics that contain significant amounts (>5%) of carbon black;

- Limited ability to process mixtures of plastics chips smaller than about 0.5 in.; and

- Inability to distinguish plastics alloys and multi-layered materials.

Companies that develop and build such systems include:

- MSS, Inc., based in Nashville, Tennessee. This company was acquired by CP Manufacturing in 2003.

- National Recovery Technologies, Inc. (NRT), based in Nashville, Tennessee.

- TiTech, which has a representative in Naperville, Illinois.

Work is under way to extend the applicability of these systems to the separation of black plastics. The future looks promising for these systems because, unlike flotation systems, they do not use liquids in their operation. Therefore, they do not produce liquid waste.

8.12.2 Color Sorters

Color sorters (monochromatic and full color models) are commercially available, mature equipment. Recent developments in this field made it possible for the new generations of these systems to distinguish between very close colors, such as light blue and clear, and to detect more than one color simultaneously. These systems can be used effectively to separate:

- Wood, “yellow” polyurethane, and flexible PUF from the polymer concentrate; and

- White plastics from non-white plastics.

The disadvantages of color sorters are:

- These systems cannot be used to produce pure products from a typical polymer mixture, because most plastics in plastics mixtures are present in more than one color (especially white/dark/black);

- The sorters are still expensive for the tasks they accomplish, especially when applied to plastic chips; and

- The dirt on the pieces can limit the efficiency with which the plastics can be separated.

8.12.3 X-ray Separators

This separation method, one of the earliest developed in the early 1990s, is applied mostly to the separation of PVC. The chlorine atoms in PVC generate a relatively easy to detect peak in the X-ray spectrum. Two of the companies that built X-ray systems are ASOMA Instruments, which developed the VS-2 machine, and NRT, which developed the Vinylcycle equipment. Both were used for separating bottles.

8.12.4 UV-Fluorescence for the Separation of Nylon-PC and PC-PMMA Mixtures

This separation method has been successfully applied mostly to the separation of mixtures containing nylons and PC, because these two materials fluoresce differently when exposed to an ultraviolet (UV) source. This separation technique works for the separation of clear PC and clear PMMA because PC fluoresces and PMMA does not.

8.13 RAMAN-SPECTRACODE

SpectraCode makes high-performance Raman-based instruments for chemical analysis and materials identification, including fiber-optically coupled probe-head systems for automated chemical recognition, as well as Raman microscopes for micro-chemical analysis. Success in post-consumer plastic packaging recycling relies on consistent correlations between the plastic composition of a container and easily recognizable shapes. No such shape consistencies exist for engineering plastic components. Some parts are marked by resin identification codes, but not consistently or accurately enough to serve as a basis for sorting mixed parts into pure streams. Recycling demonstration efforts, while supported by automobile and business machine manufacturers, have been limited by the methods available to identify resins.

Laboratory measurements were made with accuracy, but were too slow and expensive to be of much practical, cost-effective value, even as a means of testing the quality of reground product. Much more frequently used are informal, more intuitive at-line approaches, such as burn-and-sniff. These, however, are universally recognized as inaccurate and prohibitively hazardous (Duranceau, Grant, and Kumar 2000).

To support its recycling efforts, Ford Motor Company used a Raman-based instrument, the RP-1, co-developed with SpectraCode, Inc., to identify unknown polymeric parts. The recycling initiative involved detailed dismantling of vehicles into individual parts, calculating the percentage of recyclability, and making recommendations for the future use of recycled polymers. A large number of unmarked parts required identification. To facilitate this identification, an accurate reference library of Raman spectra for comparison with those of unknown materials was generated. The techniques were developed to specifically identify automotive polymers, especially black/dark plastics. The specific techniques included strategies for grouping of polymer types, characterization of the effect of higher laser power and exposure, binning of detected scattered light, and use of masking techniques for controlling identification

of the spectral region used. The Raman-based RP-1 is not affected by surface roughness, which is a previously noted shortcoming of specular reflectance infrared devices (e.g., Brüker).

9 CHEMICAL PROCESSES FOR RECYCLING SHREDDER RESIDUE

9.1 METHODS USING ORGANIC SOLVENTS

Selective dissolution of plastics from a mixed-plastic stream by using solvents is a technique that could be used to recover plastics in a usable form that might qualify for blending with virgin material (PIA 1980; Tesoro 1987; Lynch and Nauman 1989; Nauman and Lynch 1993; Nauman and Lynch 1994; Jody, Daniels, and Bonsignore 2003; Jody et al. 1990). Solvent specifications and operating temperatures and pressures, both for dissolution and separation, are essential to produce high-purity products that can be substituted for or mixed with virgin materials without reducing the quality of the final product (DuBois and John 1967). Two solvent waste-recovery processes are in practice at a commercial scale in Europe (see footnotes 24 and 25). The first process is the Solvay Chemicals Company's "Vinyloop" batch process.[26] The second process is the Delphi process, which was developed by Delphi Automotive Systems, in cooperation with the University of Wuppertal in Germany.

9.1.1 The Rensselaer Polytechnic Institute Process

Lynch and Nauman (Lynch and Nauman 1989; Nauman and Lynch 1993, 1994), of Rensselaer Polytechnic Institute, have developed a process in which a solvent (or solvents) was used to first dissolve plastics from a mixed stream, and then flash devolatilization was used to effect the separation of dissolved plastics from the solvent one at a time. A single solvent can be used in this process to dissolve and separate a number of plastics.

9.1.2 The Argonne Process

Argonne has applied this technique at ambient pressure for the recovery of shredder residue plastics (Jody, Daniels, and Bonsignore 2001; Bonsignore, Jody, and Daniels 1991; Jody et al. 1993, 1994a, 1994b; Daniels, Jody, and Bonsignore 1990). The approach involves using several solvents to extract individual plastics, one at a time. For instance, a mild solvent (such as hexane) can be used at ambient temperature and pressure to remove oils and clean the surface of the plastics. Treatment with acetone at ambient temperature and pressure can dissolve the ABS, and treatment with tetrahydrofuran or dichloroethane can dissolve the PVC and the ABS. Treatment with xylene at elevated temperatures can extract polyethylene and polypropylene. Using large quantities of solvents increases the processing cost and requires elaborate controls to minimize the emission of VOCs.

The process is technically feasible in that it produces ABS, PVC, and PP/PE at high purity (>98%). However, the process economics are not favorable because of the auxiliary system costs associated with the safety and environmental control equipment that is required when solvents are used. These costs are prohibitive relative to the quantity of specific

[26] See http://www.vinyloop.com/vinyloopprocess/plantsinferrara/0,,2120-2-0,00.htm.

thermoplastics that can be recovered per pound of shredder residue processed (Jody, Daniels, and Teotia 1996; Jody, Daniels, and Pomykala 1996; Jody, Daniels, and Brockmeir 1994; Daniels 1994; Jody et al. 1994a). We believe, however, that the solvent dissolution technique can be effective as a polishing step to separate residual impurities after other techniques — such as sink/float, froth flotation, and electrostatic separation — are used to purify the desired plastics when necessary.

9.1.3 The Solvay Process

The Solvay "Vinyloop" process is a batch process for recovering PVC from wire chopper fluff and other PVC-containing scrap. An electrostatic separator is used first to concentrate the PVC in the waste stream to about 85%, and then the PVC is size-reduced by grinding. The ground PVC is then fed to a reactor, where the PVC is dissolved by using methyl ethyl ketone (MEK). The undissolved impurities (such as fibers, rubber, metal, and other plastics and contaminants) are removed and dried. The solution is pumped into a recovery tank, where steam is injected into the solution to precipitate the PVC. The PVC is then dried in a spin dryer followed by an air dryer. The maximum temperature in the process is maintained below 240°F to guard against damaging the recovered PVC.

A pilot plant was started in 1999. The first commercial-scale plant was built in Italy in 2001 at a cost of $7.2 million, with a design capacity to recover 22 million lb of PVC annually. The estimated cost of PVC recovery was $0.13/lb. Another 20-million-lb/yr plant was built in Italy in 2002. In 2003, production reached a "nominal capacity" of 10,000 tons of raw material, with an 85% extractable PVC. Over 70% of the plant's raw material is post-consumer wire and cable waste (see note 24).

In 2004, Solvay and Kobelco Eco-Solutions announced that they have agreed to set up a plant based on Solvay's Vinyloop® Polyvinyl Chloride (PVC) recycling process in Japan, under the name Kobelco Vinyloop® East Co., Ltd. (http://www.solvaypress.com/pressreleases/0,,13912-2-0,00.htm).

9.1.4 The Delphi Process

The Delphi process was commercialized in 1998 by Wietek GmbH, an automotive recycler in Nohfelden-Eisen, Germany, for the removal of PVC from whole automotive wire harnesses. Schut reports (see footnote 26) that the recovered PVC will cost about 20% less than the virgin PVC. The process uses esters and ketones to swell and soften the PVC, but not dissolve it, so that it can be separated from the copper wires by centrifugation. No filtration is required in this process because the wire harnesses are not granulated. Further, because the PVC is not completely dissolved, less solvent is required. The process recovers about 500,000 lb/yr of usable PVC from Delphi's scrap wire. The copper wires are also required from the wire

harnesses as a pure product. According to a press release by Delphi Corporation,[27] about "90,000 metric tons of copper, 35,000 metric tons of polyvinyl chloride (PVC) and another 20,000 metric tons of different polymers, representing a potential value of more than $200 (U.S. $) million per year" can be recovered from the harnesses of the 9 million ELVs in Europe.

9.2 HYDROLYSIS

Hydrolysis involves reactions with water (generally at elevated temperatures) and is widely practiced in the chemical industry. Its applicability to shredder residue has been investigated primarily for the treatment of the PUF (Braslaw and Gerlock 1984; Mahoney, Weiner, and Farris 1974; Valdez, Dean, and Bilbrey 1975). It is also applicable to the treatment of polyesters, polycarbonates, and polyamides.

Catalyzed glycolysis of cross-member composite polyurethane parts was also studied and was found to affect partial decrosslinking of the polyurethane foam composite matrix (Kresta et al. 1999). The decrosslinked material was reacted with polymeric isocyanate to form a new composite product. Minimal amounts of glycol, catalyst, and isocyanate were used to reduce operating costs. The results of the laboratory study were confirmed by larger-scale semi-pilot tests. The results of the pilot plant work showed that (1) the cross-membering composite parts can be recycled into molding applications by using the partial decrosslinking process, and (2) the process appears economically attractive. Sendijarevic et al. (2004, 2005) have been developing a process for the hydrolysis of PUF that does not require different foam materials to be presorted.

9.2.1 The Ford Motor Company Process for Producing Very High Quality Polyols

Mahoney, Weiner, and Farris (1974) of Ford Motor Company showed that the hydrolysis of flexible PUF produces two main products: polyols and amines. Braslaw and Gerlock (1984), also of Ford, developed a process to separate and purify the product mix to produce very high quality polyols. Experiments reported by Braslaw and Gerlock used (separately) clean foam as a material input to the process and "as-received" foam from a shredder. They then tested the physical properties of their seat foam formulation by blending the recovered polyols with virgin material. A blend with up to 50% of the polyols recovered from the clean foam waste produced a foam with physical properties not "significantly different" from those of all-virgin foam. When the polyols from the "as-received" foam were blended, physical properties consistent with all-virgin foam were achieved with less than 10% of the recovered polyols. Braslaw and Gerlock (1984) estimated a $275,000 after-tax cash flow on a $1.1-million plant operating one shift per day with an annual capacity of about 1,000 tons per shift. Braslaw and Gerlock also pointed out that the technology would only be applicable for processing dirty PUF, since there is a market for clean industrial PUF waste among carpet underlayment manufacturers. When the market value of the clean foam is taken as an operating cost for the process, the positive cash

[27] See: "Delphi Recycling Efforts in Europe Benefit the Environment, 400 Metric Tons of PVC Recycled Annually."

flow becomes negative. More recent developments in the hydrolysis of shredder residue polymers are discussed below.

9.2.2 The Troy Polymers, Inc., Process for Glycolysis of Polyurethane Foam

Troy Polymers has developed a patented glycolysis process (assigned to Troy Polymers and Polyventure, Inc.) for the conversion of mixed foams into polyol initiators (Figure 9.1). In concept, the process can recycle foam collected at shredders and convert the recovered foam into polyol initiators, which can then be used to produce new urethane products (Figure 9.2). Working with the Polyurethane Recycle and Recovery Council (PURRC), Troy Polymers undertook bench tests (Table 9.1) to establish proof-of-concept. The tests demonstrated the technical feasibility of the process in converting mixed clean foams from shredder residue to polyol initiators at a yield of about 88%. Dirty foam was converted to polyol initiators at a yield of about 72%. However, the product from the dirty foam required more extensive filtration because of the solid residue contained within the foam.

Preliminary characterization of the products was also performed. The OH number, which is an indicator of molecular size (412 KOH/g) for the polyol initiator derived from clean foam and (570 KOH/g) for the polyol initiator derived from dirty foam, indicates that the foam had been broken into smaller molecules. Commercially produced initiators can have OH numbers from about 100–1,000 mg KOH/g. The OH numbers from the bench test indicate that propoxylation of these intermediate products to produce polyols with OH numbers between 42 and 56 mg KOH/g, as commonly used in industry, is feasible. Obviously, other characteristics of the polyols (such as acid number, water content, color, pH, content of terminal unsaturation, acid and alkalinity content, amount of peroxide and carbonyl groups, amount of antioxidant and residual solvent) will have to be determined and controlled. The viscosity values of the polyol initiator products are also typical of the initiators used by industry. The greater viscosity of the product recovered from dirty foam indicates that further filtration of the product is necessary.

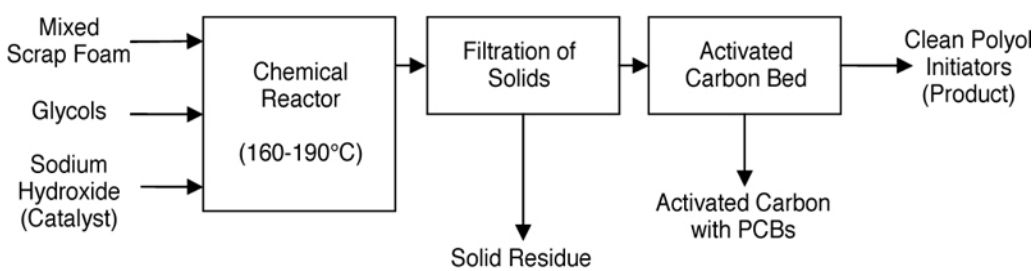

FIGURE 9.1 Glycolysis Conceptual Process Flow Sheet

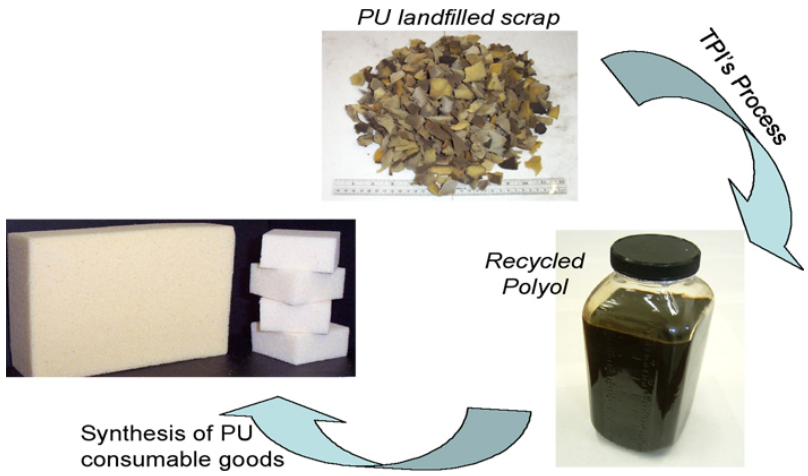

FIGURE 9.2 Glycolysis Process Concept

TABLE 9.1 Glycolysis Reaction Input Materials and Product Yield

Designation	Clean Foam	Dirty Foam
Starting Materials		
Diethylene glycol (g)	1,200	1,200
NaOH (g)	12.0	12.0
Foam scrap (g)	1,800	1,800
Product Yield		
Weight of products after glycolysis (g)	2,750	2,762
Percent of recovered materials (%)	91	92
Liquid fraction in products after filtration (%)	96	79
Solid fraction (reside) in products after filtration (%)	4	21
Yield of liquefied fraction (g)	2,640	2,182
Yield of liquefied fraction (mass of liquid product)/ (mass of total input materials) × 100	88	72
OH number (mg KOH/g)	412	570
Viscosity (centipoises, cPs)		
• @23°C	350	500
• @50°C	200	300
• @77°C	100	—

Larger-scale testing of the process was carried out in a 5-gal reactor. The filtration of solid impurities and removal of PCBs and other SOCs from the polyol initiator were also tested. Over 1,200 lb of foam separated from shredder residue, provided by Salyp and Argonne, have been processed, and over 100 gal of polyol initiator have been produced (Sendijarevic et al. 2005). The effects of temperature, glycol-to-foam ratio, and catalyst types on the reaction yields have been evaluated. Results indicate that diethylene glycol gives higher yield and allows reaction at lower temperature than dipropylene glycol. The KOH was preferred over NaOH as a catalyst. By using optimized reaction conditions with diethylene glycol (DEG) and the KOH catalyst, >90% reaction yields were consistently achieved with Salyp's and Argonne's foams.

Various filtration methods were also evaluated for the removal of unreacted solids from the polyol initiator. A nylon bag filter was installed in a recirculation loop with the 5-gal reactor to remove solids larger than 200 μm.

Treatment with activated carbon was also capable of removing PCBs from the polyol initiator to levels that were undetectable (<2 ppm). PCBs were removed more readily from the polyol initiators produced from diethylene glycol than those from dipropylene glycol. The removal of PCBs via activated carbon from the polyol initiator was demonstrated by using Aquasorb 1500. Twenty gallons of the polyol initiator that had an equivalent weight of 163.2 were also submitted for propoxylation to Pelron in Illinois, where two lots were produced. In one lot, the equivalent weight of polyol was 353.9, and in the other lot it was 172.8.

The recycled polyols produced from shredder residue foam were also tested in preparing rigid PUFs. The recycled polyols exhibited several advantages over the virgin commercial polyols. They were more reactive than the virgin polyols, requiring less or no catalyst. Furthermore, the foams based on the recycled polyols had much better flame resistance than the foams based on the virgin polyol.

Economic analysis by Troy Polymers of the process to produce polyol initiator and polyols via propoxylation indicates that the glycolysis process will be economical. Troy Polymers estimated that polyol initiator can be produced at about $0.26/lb, and the polyol (10% propoxylated) can be produced at $0.33/lb. The market value of the virgin propoxylated polyol is estimated at $0.80/lb. The process has been recently commercialized by InfiChem Polymers, LLC. Over 70% of the feedstock used in the process comes from scrap PUF. InfiChem claims that the process can produce unique polyols suitable for both rigid and flexible foam applications.

9.2.3 The Delphi Process

Delphi also developed a glycolysis process for recycling flexible printed circuit boards, which are made of a flat wire harness that consists of copper mainly laminated with polyester foils. This glycolysis process separates the copper and converts polyester to polyol.[28]

[28] See Schut, J.H., "New Ways to Salvage Plastic Waste," *PlasticsTechnology*; http://www.plasticstechnology.com/articles/200108fa2.html.

9.3 POLYMER HYDROLYSIS/DEPOLYMERIZATION TO PRODUCE MONOMERS

Depolymerization to produce monomers is another option. Several commercial processes for the depolymerization of plastics to produce monomers exist (American Plastics Council 1999). Other processes are also under development. Some plastics, such as PET, can be readily depolymerized by glycolysis, methanolysis, and hydrolysis. Polyurethanes can also be depolymerized by glycolysis or hydrolysis. Nylon 6 can be reacted with high-temperature steam in the presence of phosphoric acid to produce caprolactam, which is used for making nylon 6. Mixtures of nylon 6 and nylon 66 can be reacted with ammonia at elevated temperatures to produce the monomers of both nylons (American Plastics Council 1999). Generally, depolymerization processes are capital-intensive and, therefore, can be economical only at large scale.

One of the most recent and fairly advanced processes is one developed by British Petroleum (BP) (American Plastics Council 1999) for the depolymerization of PP, PE, and PS. The process is called "Sustainable Polymers to Olefins Recycling Technology," or SPORT.[29] The process consists of five basic sections: feed preparation, fluidized bed depolymerizer, hydrochloric acid removal section, a quench bath, and products separators.

Another process has been developed for the depolymerization of glass-fiber-reinforced nylon 6 (PA6) parts to produce caprolactam (Inoue and Miyake 2001). PA6 is used in various automotive parts, such as the air intake manifold. The waste material is first melted and filtered to separate the glass fibers. The PA is then depolymerized to produce the monomer, caprolactam. The recovered caprolactam is subsequently used to make PA6, the physical properties of which are not significantly different from those of the virgin original PA.

9.4 THE PROCESS FOR RECYCLING HEADLINER RIGID FOAM

A process to recycle headliner rigid foam was described by Rasshofer and Schomer (2004). The process can accept headliner scrap containing adhesives, glass or natural fibers, textiles, paper, and rigid foam. The process applies a modified re-bonding technique and commercially available equipment to convert the scrap foam into a large "bun" that can be sliced into new products. The acoustic properties of the products were reported to be "better than the starting headliner foams." The main steps in the process are:

1. Chopping and screening the scrap,
2. Spraying a binder (10–20% by weight) on the material while it is being agitated,
3. Curing the bonded foam by steam, and
4. Slicing the cured material into products.

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[29] Terry Knot, Managing Editor, *Frontiers*, "From Old," December 2004.

The re-bonded foam is reported to have excellent acoustic properties and met fire resistance requirements. The authors concluded that “the technology seems to have good prospects for production scrap. Recycling of end-of-life headliners is possible but favorable overall economics is doubtful due to dismantling cost.”

9.5 THE STAKE DIGESTOR PROCESS FOR HDPE FUEL TANK RECYCLING (SAE 2003-01-1371)

A research project to determine the feasibility of utilizing polyethylene post-consumer automotive fuel tanks as a source of raw material was funded by Visteon, ExxonMobil, and was conducted by Brooks Associates (Brooks 2003). Brooks Associates launched this project in the last quarter of 2000 to demonstrate the feasibility of utilizing high-density polyethylene (HDPE) post-consumer automotive fuel tanks in combination with wood fiber to create a new material suitable as an automotive substrate. The concept for the project was based on proven technology that processes wood into fiber utilizing steam explosion. The steam explosion process was commercialized to form wood fiber as a raw material for "Masonite." The product of the explosion process has also been made into a mat for further processing. This mat process is generally referred to as the "air-lay" process. The purpose of this project was to add an equal part of post-consumer, engineering-grade polyethylene from automotive fuel tanks to determine the viability of HDPE fuel tanks as a raw material source, the potential usefulness of the end products, and the limitations or consequences of the process. A trial immediately preceding this work demonstrated that plastics taken from a general post-consumer source did process successfully into a fiber mat. That mat was formed into an automotive interior door panel. This trial was designed to determine the feasibility of using post-consumer fuel tanks as the plastics source for this process.

The initial work was pursued by the VRP, and feasibility was established as an adjunct project to the U.S. field trial. At that time, the costs for further research were initially prohibitive due to high operating costs and machine purging (Duranceau et al. 2003).

9.6 AMMONOLYSIS

Shaw Industries purchased the Honeywell/DSM Technology for ammonolysis. The Evergreen plant employs patented technology that converts nylon carpet into caprolactam, the raw material used to make nylon 6. Type 6 nylon is used in such applications as residential and commercial carpet, engineering plastics, automotive parts, sporting goods, films, and packaging. The recycling system at the Evergreen plant is designed to utilize post-consumer carpets in a “cradle-to-cradle,” closed-loop process. The sustainable cradle-to-cradle process allows nylon fibers to be recycled over and over again without the loss of any aesthetic or performance properties. The DuPont Maitland plant is capable of ammonolysis. Currently, it is using postconsumer nylon from carpet recycle from a variety of sources. This recycled material is offered as a commercial post-consumer nylon 66 grade material.

9.7 MICROWAVE TECHNOLOGY FOR REVERSE POLYMERIZATION

Environmental Waste International Corporation (EWMC; http://www.ewmc.com) is a company developing and licensing waste management technologies and equipment. A patented "Emery Process" (Reverse Polymerization) uses direct microwave energy to break down organic wastes. This technology has commercial application in the reduction of medical wastes. The feasibility for processing whole scrap tires and shredder residue was demonstrated to the VRP on samples provided.

Currently, no commercial scale facility based on this tire technology exists. A demonstration facility in Ajax, Ontario, operated from 1994–1996, manually processed 330 tires per day. The basic process involved the direct application of microwave energy to whole tires/shredder residue in a nitrogen environment. Carbon black, steel, and hydrocarbon oils and gases were the anticipated principal outputs. Both waster air and wastewater were produced in the process. It was anticipated that the operational system presented by EWMC included combusting the hydrocarbon output to generate electricity for the plant.

9.8 HORIZONTAL LANDFILLS

Sustainable solutions to keeping shredder residue and plastics waste out of landfills and utilizing recovered plastic streams are being investigated for environmental and economic reasons. Lazareck's XPotential Products, Inc., has developed technologies to convert shredder residues (Lazareck 2003; 2004). Railroad ties, plastic lumber, and an entire product line have been developed. Because of the abrasive nature of the shredder residue, equipment design changes from the original pilot plant were necessary. The final plant was designed to handle the shredder residue of a medium-sized shredder (≈ 20,000 tons/yr), automated where possible to increase throughput over a manual pilot plant, and to include ancillary plastic processing equipment to produce product in a variety of sizes.

9.9 RUBBER SOLVOLYSIS

BF Goodyear and Cooper Rubber have solvolysis-based devulcanization processes (Hunt 1999 — U.S. Patent 5,891,926). Practical applications are being sought. In the laboratory, an 80% efficiency was obtained with 2-butanol (a recyclable solvent). Resource savings, especially of virgin rubber, crude oil, and power generation, were calculated. Since it can be substituted for virgin rubber at a high level in the production chain, this process is anticipated to be less expensive than virgin rubber. The economics are facility driven.

9.10 NISSAN: ENERGY RECOVERY FROM AUTOMOBILE SHREDDER RESIDUE (ASR) AT THE OPPAMA PLANT

Nissan partially modified a waste incinerator at the Oppama Plant and began energy recovery from automobile shredder residue (ASR) in the autumn of 2003. Full-scale operation of 400 tons

per month began in January 2005. Waste from Nissan plants and ASR from ELVs are burned together in the incinerator. Thermal energy generated during incineration is converted into steam that is effectively used for humidification and other purposes in the pre-painting processes at the plant. Since ASR generates large quantities of heat, controlling the temperature during incineration has been difficult. Another problem has been that unburned substrates tended to melt and stick to the inner walls of the incinerator. These problems have been resolved through optimum temperature control. (See http://www.nissan-global.com/EN/DOCUMENT/PDF/ENVIRONMENT/TECHNOLOGY/en_asr.pdf.)

9.11 MIXED PLASTICS AND WASTE PLASTICS MANAGEMENT

Chemical recycling, both compatibilized and thermal recovery, must deal with chlorine-containing compounds (e.g., PVC) (Tukker 1999). In thermal recovery, scrubbers must be added to the plant exhaust stacks. Because of compatibilization challenges, the recycling of MSW and other mixed plastic streams should eliminate or exclude PVC due to the chlorine and its polarity.

9.12 CYNTECH TECHNOLOGIES, INC.

Cyntech Technologies, Inc., was founded to research the application of existing and emerging technologies to convert used rubber, plastics, and carpet into marketable, petrochemical-based products and energy. The process, called ThermReTec™ is a patent pending, catalyst-free, closed-loop, pyrolysis/gasification system that breaks down rubber into gas oil, LPGs, process gas, methanol or diesel, and steel (Meyer and Yancy 2000). The process scaleup includes three phases. The Phase I plant would combine pyrolysis and gasification for rubber recycling. The Phase II plant would treat unsegregated plastics. The Phase III plant would process carpeting. There also is a planned phase addition for processing ASR, if it was deemed economical. (It should be noted that plastics produce more gas oils compared with tires).

9.13 FORMEX: PYROLYSIS

The FORMEX method was designed for the pyrolytic breakdown of used tires. The unique nature of the FORMEX pyrolysis process stems from the fact that the pyrolysis takes place in a liquid tin bath. The process includes pre-processing of tires from impurities (tin bath pyrolysis). The tires are chemically dissociated at a constant temperature of 480°C (tolerance of ± 2°C). During 12 minutes in the tin bath, gaseous and solid products are formed. Post-processing includes cooling the pyrolysis gas and separating it from vapor. The oil is stored in tanks, and the gas is used to heat the system. Solid components (a mixture of carbon black, fillers, steel, and tire textiles) are degassed and dried with nitrogen before further processing. Steel is magnetically separated, and a jet mill reduces the filter material (http://www.worldbid.com/showrooms/details.htm?session=&itemID=1036241).

10 SUBSTANCES OF CONCERN IN SHREDDER RESIDUE

The SOCs can impact the recyclability of automotive materials in a number of ways. Certainly, their presence in either recycled materials and/or the materials source stream impact the overall costs of recovering recyclable materials. In some cases, their presence at parts-per-million levels (such as the presence of PCBs) can prevent the reuse of the recovered materials (such as polymers and foams). The strategy that is required for the control of the SOCs may vary regionally. For example, requirements for various SOCs are different in Europe, North America, and Asia. Strategies for controlling SOCs can also depend on the technology that is being proposed for recycling the automotive material. Specific SOCs are discussed in Sections 10.1–10.3.

The presence of SOCs in current vehicles and/or in other durable goods that are presently recycled with EVLs is likely to impact the materials recycle stream for the foreseeable future. Consequently, the control of SOCs will require technology that will effectively remove the SOCs from recovered materials in a manner that is consistent with both current regulatory requirements and the market requirement for the recovered material. Shredder residue contains three basic groups of SOCs: PCBs, heavy metals, and fire retardants. Maguad and Jallon (2001) reported that a group of OEMs, chemical suppliers, and two professional organizations are working together on the development of a common database of SOCs. The database reportedly contains over 800 substances. It also contains regulatory requirements and automakers' standards and will serve as a common reference to the entire automotive supply chain.

Sendijarevic et al. (2004) measured the levels of PCBs and 10 heavy metals in shredder-residue-derived plastics and foam. They also investigated aqueous cleaning approaches by using various commercial surfactants to determine their effectiveness in removing oils, PCBs, and heavy metals. Eleven surfactants were evaluated. Triton RW-50 was identified as the most efficient surfactant (among the ones tested) for the removal of PCBs and heavy metals from both dirty plastics and PUFs. In most measurements, the total concentration of arsenic, barium, chromium, copper, selenium, silver, and mercury was low. However, the concentration of cadmium, lead, and zinc was high in several of the samples.

Mark and Picotl (2001) noted that more than 99% of heavy metals must be removed to satisfy the specifications of potential users of shredder residue, such as the power, cement, or steel industry. Other users, such as plastics processors, also require a similar or even higher stringent removal for selected metals and PCBs (Mark and Picotl 2001).

The advent of European regulations, which must be met by all imported goods, include automobiles from the United States and the rest of the world. These regulations affect the substances that can be used in the products to ensure compliance with these emerging regulations. The EU has additional Directives to facilitate compliance with the EU Directive for automobiles, the Waste Electrical and Electronic Equipment (WEEE) Directive for electronics, and the Restriction of Hazardous Substances (ROHS) Directive for hazardous substances.

REACH (Regulation on Registration, Evaluation, Authorization and Restriction of Chemicals) has been in effect since June 1, 2007. It streamlines and improves the former legislative framework on chemicals for the EU. The main goals of REACH are to ensure a high level of protection from the risks that can be posed by chemicals in relation to human health and the environment, as well as to promote alternative test methods and the free circulation of substances on the internal market, thus enhancing competitiveness and innovation. The REACH Directive, with reporting through the GADSL (www.gadsl.org), includes a list of substances of very high concern (SVHC).

REACH makes industry responsible for assessing and managing the risks posed by chemicals and providing appropriate safety information to their users. In parallel, the EU can take additional measures on highly dangerous substances, where there is a need for complementing action at the EU level (http://ec.europa.eu/enterprise/sectors/chemicals/reach/index_en.htm).

The Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment 2002/95/EC, commonly referred to as RoHS, was adopted in February 2003 by the European Union (RoHS 2002). The ROHS directive took effect on July 1, 2006, and is required to be enforced and become law in each member state. This directive restricts the use of six hazardous materials in the manufacture of various types of electronic and electrical equipment. It is closely linked with the Waste Electrical and Electronic Equipment Directive (WEEE) 2002/96/EC (WEEE 2002), which sets collection, recycling, and recovery targets for electrical goods and is part of a legislative initiative to solve the problem of huge amounts of toxic electronic-waste.

10.1 POLYCHLORINATED BIPHENYLS

Although the production of PCBs was banned in the United States in the late 1970s, PCBs, at the parts-per-million level, are still routinely found in shredder residue. The source of PCBs is still not completely understood. Historically, it has been associated with liquid PCB-containing capacitors, ballasts, and transformers that inadvertently escape the scrap inspections and control process at the shredders. However, this does not appear to be the only source. We believe that a study to identify sources of PCBs in shredder residue should be conducted to facilitate the recycling of shredder residue. Avoiding the introduction of PCBs into shredder residue is likely to be more economical than removing the PCBs from the shredder residue after the shredding process.

In a 1991 study, the EPA (EPA 1991) conducted analyses of several shredder residue samples for PCBs and other contaminants. The PCBs concentration in these samples ranged between 22 ppm and 120 ppm, with an average of 43 ppm. Other findings of the EPA study include:

- The average concentrations of PCBs in the ferrous and nonferrous metals were 0.2 ppm and 1.0 ppm, respectively.

- Soxhlet extraction using hot water over an eight-day period resulted in the extraction of only 0.0073% of the PCBs present.

- There were no statistically significant differences in measured PCBs levels between the different categories of physical components (fines; metals and wire fragments; soft and hard plastics; and rubber, glass, fabrics, paper, and wood).

Another interesting observation is that the concentration of PCBs reported by the EPA study (EPA 1991) depended on the shredder residue output stream and on the source material, as shown in Table 10.1. The data in Table 10.1 indicate that scrap sources other than automobiles and white goods could be major contributors to PCBs in shredder residue.

TABLE 10.1 Dependence of PCBs Concentration in Shredder Residue on the Sample Source and Input Material (EPA 1991)

Output Stream	Input Material to Shredder	Mean PCBs Concentration (ppm)
Fresh fluff	Auto	32
Fresh fluff	Mixed	180
Fresh fluff	White goods	80
Stored fluff	–	68
Spillover from conveyors	–	28
Ferrous	–	0.2
Nonferrous	–	1.0
Soil under fluff	–	44

10.1.1 Studies by Troy Polymers, Inc.

Troy Polymers conducted studies for VRP, Argonne, and APC to develop technology to identify and/or cost-effectively remove PCBs and other SOCs from shredder residue materials (such as plastics and foam). Experiments have also been performed to develop an understanding of the variability in PCB analytical procedures. Results are discussed in the following sections.

10.1.1.1 Bench-Scale Screening of Commercially Available Surfactants for the Removal of PCBs

Bench-scale screening of 11 surfactants and 3 organic solvents for the removal of PCBs and other contaminants from polymers derived from shredder residue has been conducted (Sendijarevic 2004). Multiple samples of mixed plastics and foam recovered from shredder residue were used in the study. The surfactant, TRITON RW 50, was found to be the most

efficient surfactant among those tried. The PCB concentrations in the plastics and foam samples that were washed with this surfactant were reduced to below 2 ppm (Table 10.2). The three organic solvents were also effective.

TABLE 10.2 Concentration of PCBs in Plastics and Foam before and after Washing, Bench-Scale Tests for Surfactant Selection

Designation	PCBs before Washing (ppm)	
Plastics	2.8 ± 1.4	
Foam	27.2	
Surfactant or Solvent Used	**PCBs in Plastics after Washing (ppm)**	**PCBs in Foam after Washing (ppm)**
Triton DF-12	<1	2.4
Triton RW-100	<1	2.7
Tergitol TMN-6	<1	4.1
Bio-Terge Pas-8S	3.2	6.0
Triton RW-50	<0.08	2.0
Triton RW-75	—	4.7
No surfactant used	—	6.2

10.1.1.2 Testing of Commercially Available Cleaning Equipment Using Aqueous Solutions

Technologies that can potentially be adapted for the cleaning/washing of plastics from shredder residue fall into three major categories:

1. Conventional methods that include the mechanical transport of material through a cleaning solution with agitation and/or scrubbing by rotating drums and/or auger systems,

2. Ultrasonic systems with and without agitation, and

3. Centrifugal systems.

Large-scale cleaning/washing tests were conducted using plastics from shredder residue by means of aqueous solutions. The objective was to identify the limitations of the various types of existing washing equipment. Testing was done by using an ALMCO rotary drum washer equipped with a dryer and SeKoN centrifuge equipment. The tests were carried out on approximately 100 lb of plastic chips each. The particles were between 0.2 in. and 0.5 in. In each of these large tests, the washed material was “visually” clean in terms of dirt and oils. However,

the PCB analyses were highly variable and indicated that, in some cases, the PCB concentration had increased. As a result, it was determined that the PCB cleaning and analysis procedures should be reexamined, as is discussed in the next section.

The results suggest that existing aqueous-based equipment, as is, is not likely to reduce the concentration of PCBs to acceptable levels. Modifications are necessary to wash small chips (1/8–1/2 in.) of plastics, such as what would be recovered from shredder residue, efficiently and economically.

10.1.2 Evaluation of the Variability of PCB Sampling and Analytical Procedures

Troy Polymers, Inc., found that there was a significant degree of inconsistency in the analytical results of residual PCB concentrations on the washed materials. In addition, two of the laboratories that conducted analyses identified Aroclor 1242 as the only PCB present, while a third laboratory identified Aroclors 1232 and 1254 as the only two present. Each of these Aroclors consists of a multiple of congeners. This variability may be due to a number of factors, including:

- Sample size,
- Plastics particle size,
- PCB extraction procedure,
- Analytical procedures, and/or
- Interference from other compounds.

To investigate the possible interference of phthalates in the PCB analysis, a sample of plastics chips derived from shredder residue was thoroughly mixed and then divided into four parts. The first part was analyzed by using (1) gas chromatography and an electron capture detector (GC-ECD) and (2) gas chromatography/mass spectroscopy (GC/MS). The other three parts were spiked with different quantities of phthalates, as shown in Table 10.3, and the spiked samples were analyzed by using the same two methods. The results show no apparent interference of the phthalates in the PCBs analysis.

TABLE 10.3 Effect of Phthalates on PCBs Analysis

Weight-Percent of Phthalates Added	PCBs Concentrations (ppm) by GC/ECD	PCBs Concentrations (ppm) by GC/MS
0	4.6+/-0.3	7.9+/-1.0
0.5	4.7+/-0.3	7.4+/-0.2
1.0	5.1+/-0.6	7.0+/-0.4
2.5	4.8+/-0.3	7.4+/-0.3

To investigate the effects of the size of plastics particles on the extraction efficiency of PCBs, a series of laboratory experiments was conducted at Troy Polymers, Inc., on 300-g samples of plastics with two different particle sizes (one was made of chips that were about 0.2 in., and the other was granulated to about 0.04 in. to 0.08 in.). Typically, in PCBs analyses, extractions are done on a few grams of material, even though the dirt, oil, and PCBs are not evenly distributed on the shredder residue plastics.

Samples of the plastics before and after washing were analyzed directly by three different laboratories by using standard PCB analytical procedures. Extracts from nine sonications of 300-g samples were also analyzed for PCBs by the three laboratories. The analyses lead to the following observations:

1. The three laboratories are fairly consistent for each set of samples.

2. Direct analysis of the samples from the three laboratories showed that the concentration of PCBs in the granulated plastics was about 5 ppm, and in the ungranulated plastics, it was 10 ppm. Obviously, the granulated samples have a larger surface area per unit mass than the other samples. Therefore, more efficient extraction of PCBs from the plastics would be expected in the case of the granulated chips. Because this was not the case, the results indicate that the particle size does not affect the extraction of PCBs.

3. Because the material of smaller particles has more of the inner surface exposed than the material of larger particles, the results indicate that the PCBs are on the surface of the plastics and are not absorbed in the plastics. After extraction, the samples all had less than 2 ppm of PCBs, except for one sample that showed 2.8 ppm.

Calculation of the concentration of PCBs in the original samples based on the determined PCBs in the hexane extracts (prepared via nine sonications of 300-g samples) showed that the concentrations of PCBs in the granulated samples were comparable with those of the ungranulated samples.

10.1.3 Evaluation and Testing of Solvent-Based Washing Systems

Troy Polymers, Inc., identified three companies with equipment and/or proprietary washing solvents and solutions that could potentially be used for non-aqueous removal of PCBs from plastics recovered from shredder residue:

- Environmental Technology Unlimited (Wilmington, North Carolina);

- Cool Clean Technologies, Inc. (Burnsville, Minnesota); and

- itec Environmental Group, Inc. (Oakdale, California).

Each company was supplied with a sample of plastics with the assigned (determined) concentration of PCBs of 11 ppm. Samples were washed at the three companies, and the washed samples were evaluated for PCB levels. The results were as follows:

- Environmental Technology Unlimited used a proprietary METHEX solvent-based system and aqueous-based systems. They performed six treatments of shredder residue plastics, and five of the six washed samples had PCB concentrations below 2 ppm. The METHEX solvent-based system was superior to the aqueous system.

- Cool Clean Technologies technology used CO_2 only. Washing failed to remove the PCBs.

- The ITEC Environmental Group reduced PCB levels in the plastics from 11 ppm to 2.8 ppm via solvent washing. No CO_2 treatment, which normally follows the basic process, was used.

On the basis of these results, Environmental Technology Unlimited and ITEC Environmental Group appear to have the technology that could remove PCBs to below 2 ppm. However, at present, only ITEC has the full-scale equipment ready to be integrated into a plastics recycling process. Initial testing using the ITEC technology did not reduce PCBs to below 2 ppm in all the samples that were cleaned.

10.1.4 The ECO2, Inc., Plastics Cleaning Process

ECO2 Plastics, Inc. selected a closed-system multi-step cleaning process using a bio-degradable solvent followed by liquid carbon dioxide treatment that was claimed to be effective for removing PCBs from a known polyolefin plastics concentrate sample provided by Argonne. This work was done under a contract funded by the Vehicle Recycling Partnership, Inc. (VRP). In the cleaning process, the reclaimed shredder residue plastics were washed with a combination of an organic solvent (environmentally friendly, biodegradable biosolvent) and liquid carbon dioxide. The recovered solvents were distilled and distillation tanks collected dirt, oils, and PCBs. Because the adaptations of ECO2's proprietary process were specifically developed for the removal of all PCBs from shredder residue plastics, the exact methodology remains confidential. The final report to the VRP claimed that the ECO2 Plastics cleaning process demonstrated the effective removal of all PCBs from shredder residue plastics.

This limited trial demonstrated the potential effectiveness of the ECO2 Plastics' process to remove PCBs from shredder residue samples. The results of this trial were analyzed by using the VRP/TPI extended soxhlet extraction method and the GC/MS Detection Method. This method is considered to be more severe than the standard EPA Method SW 846 using GC/ECD Detection Method. On the basis of the testing cited under the VRP purchase order #07-9018; Task 6 – Final Cleaning Run, no detectible PCBs were found. The ECO2 Plastics Task#6 Final Report and Presentation (ECO2 2009) states that the ECO2 cleaning process can remove PCBs from plastics. These test results were not third-party verified by Argonne. The presentation

accompanying the final report stated that this process was determined to be cost-effective when the ECO2 Plastics equipment was used at its production manufacturing site in Riverbank, CA [www.eco2plastics.com/] ECO2 2009).

10.1.5 The Thar Process

Thar Technologies has developed the Thar Process, which is a proprietary process that uses high-pressure CO_2 to clean plastics and remove PCBs.

10.1.6 Evaluation of Automobiles as a Source of PCBs

In a recent study conducted by VRP, ACC-PD, and Argonne, four categories of vehicles were shredded in a newly installed shredding facility (Garden Street Iron and Metal, in Fort Meyers, Florida) with relatively clean equipment, grounds, and surroundings. The four categories were:

- Late Model "Big 3" (2000–2005 models),
- Late Model "Transplant" (2000–2005 models),
- "Normal-aged" Domestic (pre-2000 models), and
- Late Model "Federalized Import" (2000–2005 models).

The Late Model "Big 3" and "Normal-aged" Domestic categories included Ford, GM, and Chrysler vehicles built in North America. "Transplant" vehicles were autos manufactured by foreign companies in North America for use in the United States. Late Model "Federalized Import" vehicles were built outside of North America. Before the vehicles were shredded, they were drained of their fluids. Tires, rims, and mercury switches were also removed. All vehicles were manually inspected, and all foreign "non-auto" materials were removed from the vehicles. This is an exceptional treatment compare with a normal shredding plant. In addition, the vehicles chosen for this test were only a select few. The oldest vehicle was a 1983 model year, built after the ban on PCBs. Also, because the test was limited to a small number of vehicles, many manufacturers were not included. This will have to be considered when interpreting the results.

Figure 10.1 illustrates the procedure followed in shredding the vehicles and in collecting the shredder residues. Shredder residue consisted of two fractions: a coarse fraction (between 12 mm and 6 in.) and a fine fraction (smaller than 12 mm). First, the shredder equipment was started up and ran until no residual debris was left in the system. The entire grounds were then cleaned of all materials. Swipe samples were taken from various parts of the shredding equipment, from the heavy mobile equipment, and from the floor. The swipe tests were used to check for PCB contamination. Samples of the separator material (tree limbs), were also taken to verify that they were free of PCBs. A load of tree limbs was fed into the shredder and allowed to travel through the system. The shredded wood was also sampled for PCB testing. The late Model "Transplant" vehicle category was fed to the shredder. Samples of the fine and coarse residues were obtained during the discharge of the material from the system. At the conclusion of the category, the fines and coarse residues were set aside. All the bunkers were cleaned out, and

another round of tree limbs was fed to the shredder. Again, samples were taken of the wood shred for PCB analysis. The wood shred was removed from the bunkers, and the next category of vehicles, Late Model "Big 3," was fed to the shredder. The same procedures were used for this category, as well as for the other categories. The shredder residue from each category was analyzed for TCLP (metals) and for PCBs. The results of the analysis are summarized below:

1. All the swipe tests of the vehicles to be shredded and of the dismantling area reported as non-detects, with a detection limit of 5.00 µg/wipe. Swipes that were taken on shredder plant belts and feeders reported values up to 16.6 µg/wipe.

2. Ten samples of the <12-mm fines and 10 samples of the coarse shredder residue were obtained from each of the four categories of vehicles. Of these, three from each group were randomly selected for analysis, and then an average concentration was determined. Many of the samples contained non-detectable amounts of PCBs (detection limit of 0.3 ppm). Only one fines sample from the Late Model "Big 3" category contained a detectable level of PCBs (1.77 ppm). Only one coarse sample from the Late Model "Transplant" category contained a detectable level of PCBs (2.17 ppm).

3. Samples of polymer concentrate generated from processing the shredder residues in Argonne's material separation pilot plant were sent out for PCB analysis. All returned with non-detectable levels of PCBs.

4. A sample from each category's fines and coarse shredder residue were sent for TCLP metals analysis. Three samples were taken for lead and cadmium. The results are summarized in Table 10.4. One cadmium sample was high (3.91 mg/L). The sample was retested, and the result was 0.33 mg/L. It is believed that the first analysis may not have been a representative sample. Table 10.4 shows that the average cadmium concentrations for the three late model categories ranged from 0.02 mg/L to 0.07 mg/L, while the "Normal-aged" category produced 0.22 mg/L for the fine shredder residue and 0.32 mg/L for the coarse shredder residue. Zinc was analyzed twice from the coarse shredder residue of the Late Model "Big 3" category. Both came back at 178 mg/L. One of the Late Model "Federalized Import" category lead samples contained about 10 times that of any other sample taken.

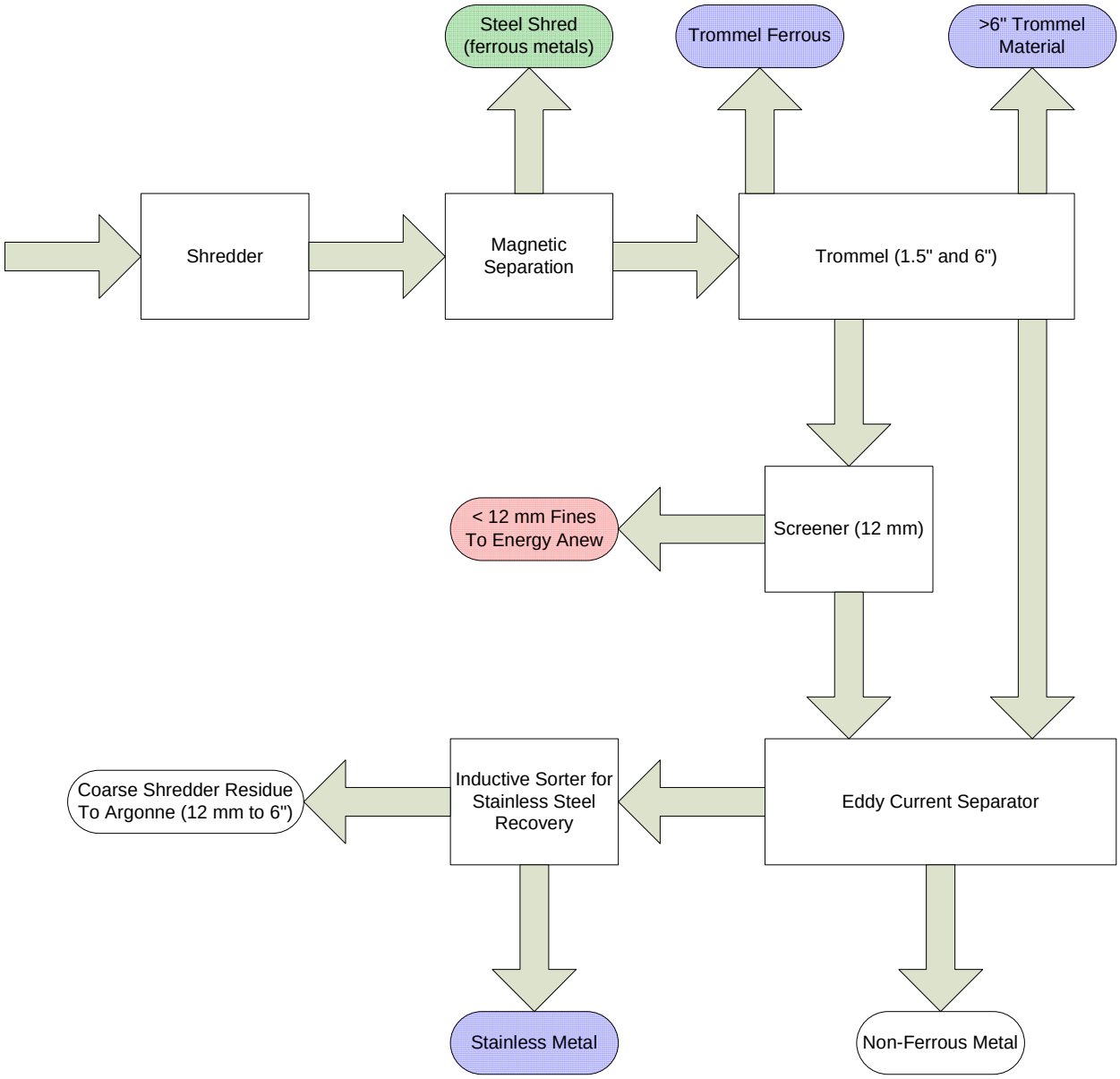

FIGURE 10.1 Process Used in the Shredding of the Four Categories of Vehicles

TABLE 10.4 Results of the TCLP Analysis

		Late Model Big 3		Late Model Transplant		Normal ELV		Late Model Import	
Units = mg/L	EPA Limit	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine
Arsenic	5	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Barium	100	0.6	0.6	1.0	1.2	0.8	0.7	1.0	1.2
Cadmium	1	0.03	0.08	0.04	0.06	0.34	0.33*	0.04	0.01
		0.03	0.05	0.04	0.03	0.36	0.14	<0.01	0.02
		0.02	0.07	0.05	0.03	0.27	0.20	0.02	0.02
Average		0.03	0.07	0.04	0.04	0.32	0.22	0.02	0.02
Chromium (T)	5	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Copper		0.12	<0.10	0.38	<0.10	0.31	<0.10	0.16	<0.10
Lead	5	0.23	0.66	0.10	0.15	0.84	0.61	6.01	0.19
		0.39	0.56	0.37	0.08	0.29	0.06	0.21	0.58
		0.82	0.42	0.16	0.22	0.59	0.12	0.70	0.97
Average		0.48	0.55	0.21	0.15	0.58	0.26	2.3	0.58
Nickel		0.89	1.28	0.45	0.54	0.71	0.65	1.26	1.10
Mercury	0.2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Selenium	1	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Silver	5	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Zinc		173	178**	145	99	201	71	53	133

* Initial result was 3.91 mg/L; uncharacteristic and unconfirmed.

** Two samples were tested. Both came back at 178 mg/L.

The PCB and TCLP results are indeed very encouraging. The only PCB concentrations detected were 2.17 ppm for one sample and 1.77 ppm for another. The other samples were below the detection limit. Therefore, it appears that automotive feed material is not a major source of PCBs in the shredder residue, bearing in mind that the oldest vehicle in the test was manufactured in 1983, after the ban on PCBs in the United States. Most of the TCLP metals were non-detectable. As mentioned earlier, one sample tested high in cadmium. Also, a sample tested high on lead. The high concentration could be due to an analytical error, or the sample could have contained a small sliver of lead.

The results and conclusions drawn based on these results are based on processing a small number of vehicles and models that were very carefully de-polluted and inspected, and all non-auto materials were removed from them prior to shredding in a newly installed shredder. These issues will have to be considered when interpreting the results. With this in mind, this limited study leads to several interesting observations and conclusions. These are discussed below:

1. Shredder residue generated by shredding only autos contained very low levels of PCBs. This demonstrates that autos, at least those newer than the 1983 model year, are not the major source of PCBs seen in shredder residue.

2. Shedder residue generated by shredding only autos contained low levels of TCLP metals. The cadmium concentration in the "Normal-aged" category was considerably higher than all the late model categories.

It is recommended that a larger study be conducted, where a few hundred vehicles, as-received by the shredder, would be shredded in a typical shredder that has been in service for awhile. Such a study would determine if the resulting shredder residue contains very low levels of PCBs and TCLP metals, as observed in this test.

10.2 HEAVY METALS

Shredder residue is also known to contain heavy metals, such as lead, cadmium, and mercury (EPA 1991; Hans-Ulrich 2002; Mark and Picotl 2001; Maguad and Jallon 2001; Sendijarevic et al. 2004). The 1991 EPA study found that lead concentration in shredder residue was high (Table 10.5). The Troy Polymers, Inc. (Sendijarevic 2004), study determined the concentrations of 10 metals in the shredder residue plastics and foam before washing (Table 10.6). The results indicated that the concentration of lead was the highest. Washing was effective in reducing the concentration of all heavy metals (Table 10.7), except for mercury, which was initially low. The concentration of chromium on plastics did not appear to change upon washing, although it was reduced to below-detectable levels in the foam.

TABLE 10.5 Heavy Metals in Shredder Residue (EPA 1991)

Analytes	Mean Concentration (ppm*)	95% Confidence Interval (ppm)
Total lead	2,800	1,800–4,100
Total cadmium	47	31–65

* ppm = parts per million.

TABLE 10.6 Concentration of Heavy Metals in Plastics and Foam from Shredder Residue before Washing (Troy Polymers, Inc., study)

Heavy Metal	Dirty Foam (ppm*)	Dirty Plastics (ppm)
Arsenic	<0.2	<0.36
Barium	38.9	28
Cadmium	1.34	0.89
Chromium	5.54	4.8
Copper	37.9	17
Lead	200	61
Selenium	<0.2	1.3
Silver	<0.05	<0.26
Zinc	618	380
Mercury	0.15	0.05

* ppm = parts per million.

10.2.1 Lead-Free Solder

Due to the EU Directive's Annex II and environmental regulatory pressures, the usage of leaded solder is being phased out. The leading replacement technology is SAC (Sn-Ag-Cu; tin-silver-copper) solder. Testing is under way. The USCAR/VRP members recommend a testing protocol for the substitution and requalification of these materials in automotive applications. The SAC solder does not perform in high-temperature applications, and no known lead substitute is available. One major failure mode for SAC solders is fatigue damage, which causes the generation of whiskers. These whiskers can cause electrical shorts and arcing, which produce field failures of electrical circuits.

10.3 FLAME RETARDANTS

Flame retardants are chemicals that are added to polymers and other materials to suppress the combustion of such materials and to slow down the spread of flames (Edenburn 2001). Many types of fire retardants have been used in plastics and foam, as well as in other materials used in automobiles and white goods. These include:

- Inorganic flame retardants,
- Nitrogen-containing flame retardants,
- Chlorinated and brominated fire retardants, and
- Phosphorous-based fire retardants.

TABLE 10.7 Concentration of Heavy Metals in Plastics and Foam after Washing (Troy Polymers, Inc., study)

Heavy Metal	Clean Foam (ppm*)	Clean Plastics (ppm)
Arsenic	<0.2	<0.35
Barium	0.74	28
Cadmium	<0.2	0.52
Chromium	<0.2.	4.6
Copper	1.24	9.6
Lead	6.32	26
Selenium	<0.2	3.6
Silver	<0.05	<0.25
Zinc	20.5	280
Mercury	0.14	0.02

* ppm = parts per million.

The brominated group, or polybrominated diphenyl ethers (PBDEs), appears to have gained an increased share of the market in the last decade. The PBDEs are used in plastics, foams, circuit boards, rubber, carpets, textiles, and other products. Also, PBDEs are used in some plastics and foams at concentrations as high as 18% by weight. For example, polyolefins can contain about 5–8% PBDEs, while some polyurethanes can have as much as 18% by weight. Studies have found rising levels of PBDEs in breast tissue and in sport fish and bird eggs from the San Francisco Bay (Kay 2003; Madsen, Lee, and Olle 2003). They are also suspected of interfering with thyroid hormone balance and brain development, and they tend to concentrate in the fatty tissues of living organisms (Kay 2003; Madsen, Lee, and Olle 2003). In 1999, about 74 million lb of PBDEs were used in North America alone, which is about half the world market (Madsen, Lee, and Olle 2003). In early 2003, the EU officially banned the use of PBDEs in electronics after mid-2006 (Madsen, Lee, and Olle 2003). Today, DecaBDE (decabromodiphenyl ether) is probably the only brominated fire retardant used in North American vehicles. A recent fact sheet published by the Bromine Science and Environmental Forum (BSEF) and USCAR-VRP, entitled "DecaBDE Flame Retardant — Automotive Facts" (April 2006), stated that DecaBDE is the best-available fire retardant for the automotive industry, and studies show that it does not present any significant risk to humans or the environment.

Bromine Science Environmental Forum. The three major producers of Deca-BDE entered into a "partnership" with the EPA to phase out production and importation of Deca-BDE. As part of the phase-out, the producers will realize year-over-year reductions in DecaBDE manufacturing and sales levels and submit annual progress reports to the EPA.

The final date for the import, sale, or manufacture of DecaBDE is set for the end 2012 for most applications. However, certain military and transportation applications could be extended

until the end of 2013 (with written permission). After the phase-out period, the EPA intends to impose additional DecaBDE testing requirements on the remaining producers/importers and implement a "significant new use rule," or SNUR, on DecaBDE and articles that contain DecaBDE.

11 RECYCLING OF FUTURE VEHICLES

Designers of new vehicles are targeting lighter weight for higher fuel efficiency. Safety is also a major driver for new designs and materials of construction. They are expected to continue to use new materials of construction that will start to show up in the shredder residue (Das and Curlee 1999). These materials include more aluminum, more magnesium, more plastics and composites, more catalysts (such as for the fuel cells), and probably less steel. Therefore, dismantling and shredding operations are likely to require modification, and the recycling of materials from shredder residue is likely to contribute more to the shredder's bottom line.

11.1 RECYCLING OF FUEL CELL VEHICLES

Hydrogen-fueled fuel cells promise to provide a cleaner, more efficient way to generate power. Automakers forecast that fuel-cell-powered vehicles will be ready during the 2010 decade.[30] The barriers facing the large-scale use of fuel cells in vehicles include the availability of hydrogen. The growth of a hydrogen economy in the United States is part of DOE's vision (National Hydrogen Energy Roadmap, U.S. Department of Energy, November 2002).

The fuel cell system has three basic subsystems: (1) the fuel supply (onboard fuel storage and reformers), (2) the fuel cell stack, and (3) the balance of the plant. The fuel cell stack consists of a multitude of repeated unit assemblies of dissimilar materials. In a typical stack design, each unit consists of a membrane electrode assembly (MEA) and bipolar (active) plates. In addition to these repeat units, there are cooling plates at certain locations along the length of the stack. The stack is usually enclosed by insulating plates, end plates with tie bars, compression springs, metallic strapping, and/or other similar arrangements to hold the stack together. The stack is fitted with operating system hardware components, such as cell voltage monitoring devices (SAE 2003). The MEA consists of multiple materials in a layered construction. These layers may include a gas diffusion layer (GDL), an anode catalyst, a proton conduction membrane, a cathode catalyst, and a second GDL. The two GDLs are typically based on carbon-based cloth that has been treated with a polymeric coating (such as Teflon™) to promote diffusion of reactants and water. The anode and cathode catalysts are typically platinum (Pt), platinum/ruthenium (Pt/Ru), or a combination of these and other metals supported on carbon within a solid ionomer solution similar to the membrane material. The bipolar plates and cooling plates are typically made from a conductive molded thermoset (such as phenolic resins and vinyl esters) and thermoplastic resin materials (such as PP and PE, and usually highly filled with graphite) or a corrosion-resistant metal (Papasavva et al. 2003).

Recommendations on how to address the end-of-life fate of a fuel cell system are provided in the SAE J2594 recommended practice document (SAE 2003). The purpose of this document is to provide fuel-cell-system designers and engineers with a tool so they can incorporate recyclability into the process of designing polymer electrolyte membrane (PEM) fuel

[30] See http://www.fueleconomy.gov/feg/fuelcell.shtml (accessed in 2005)

cells. This recommended practice defines a PEM fuel-cell-rating system that assesses the ease of removal of the PEM fuel cell system and/or components from a vehicle, and then upon the removal of that material from the vehicle, it assesses the ease of recycling. Reuse of parts is the primary objective, and it depends on the ease and cost of disassembly (Papasavva et al. 2003). Reusing components saves energy, natural resources, landfill space, and cost.

Material recycling from fuel cell vehicles is limited by many factors, among which are the technology available to process the material and separate it, the existence of a supporting infrastructure, hazardous materials content, and the cost-effectiveness of the materials recovery operations.

Some work has been done on recycling fuel cell vehicles, but it is still preliminary (Cooper 2004). Cooper (2004) suggested that many options exist and highlighted some of the changes in materials that the fuel cell vehicles will have. These include:

- Fuel cell powertrains will have a substantial (80%) reduction in the amount of iron used, in comparison with conventional vehicles. This will, of course, reduce the amounts of iron available to shredders for recycling.

- For fuel cell powertrains, the disposition of the majority of stainless steel (in the supporting equipment) is unknown.

- The mass of the graphite plates is about 20% of the powertrain, and therefore the economic recycling of the graphite may not be practical.

- Bipolar plates make up 70–80% of the mass of the stack and contain phenolic-resin, which represents an increase of up to 18 times the phenolic-resin content of current vehicles. Recycling of this resin is not state-of-the-art technology.

- The precious metal catalyst content in fuel cells is about 15 times to over 200 times that of the catalytic converter of conventional cars. Catalysts in fuel cells can probably be recycled by using the technology used at present for recycling the catalysts in the catalytic converter.

11.2 RECYCLING OF ELECTRIC AND HYBRID ELECTRIC VEHICLES

The number of electric vehicles (EVs) and hybrid electric vehicles (HEVs) is rapidly increasing. Although only 9,600 hybrids were sold in 2000, an estimated 250,000 were sold in 2008.[31] Rising oil prices will most likely accelerate the production and sales of such vehicles. The EVs are normally limited to short-distance travel, and they come in various designs and serve different needs. Their range is relatively low (under 100 miles). The HEVs are powered by a combination of an internal combustion engine and a battery. Therefore, HEVs can get higher

[31] Dr. Ken Heitner, Advanced Battery Readiness ad hoc working group meeting, Feb. 28–Mar 1, 2001, Hyatt Arlington Hotel, Washington, D.C.

miles per gallon than similar conventional vehicles. These vehicles are generally downsized to meet the average power (as opposed to peak power) requirement of conventional vehicles. The energy stored in the battery is used to drive an electric motor to meet extra demand when needed, such as for passing another vehicle. Some HEVs also have a regenerative braking mechanism to capture some of the energy lost during braking.[32]

Since the 1980s, several battery chemistries were studied for EV and HEV applications, including sodium beta, nickel-cadmium (Ni-Cd), nickel-metal hydride (Ni-MH), lead-acid, lithium-ion (Li-ion), lithium polymer, Li-ion with polymer electrolyte, and lithium nickel manganese batteries. Today, Ni-MH and lithium batteries are the leading candidates. The batteries used or considered for use in such vehicles include Li-ion, lithium polymer, magnesium-lithium, Ni-MH, sodium nickel chloride, lead acid, and nickel zinc batteries.[33] The HEVs generally recharge themselves during operation. All of these batteries, as their names imply, use chemicals that are not environmentally friendly and would require special handling when they reach the end of their useful lives. Lead-acid batteries are the most common battery in use in vehicles today, and they are readily recyclable. Nickel-iron (Edison Cells) and Ni-Cd pocket and sintered plate batteries have been in use for many years. Both of these batteries are recyclable. Sodium sulfur batteries are high-temperature batteries, and there are safety issues concerning the sodium. Lithium-ion batteries have a molten-salt electrolyte. Zinc and aluminum air batteries use either aluminum or zinc as a sacrificial anode. As the battery produces electricity, the anode dissolves into the electrolyte. When the anode is completely dissolved, a new anode is placed in the vehicle. The aluminum and/or zinc and the electrolyte are removed and sent to a recycling facility.

11.2.1 Materials for Construction of the Leading Batteries and Their Values

11.2.1.1 Nickel-Metal Hydride Cells for Electric Vehicles

Figure 11.1 shows the approximate weight percent of materials that make up the Ni-MH cells for EVs, and Figure 11.2 shows their relative costs. These batteries can be disassembled to recover some of their components, such as the stainless steel.

Nickel (as nickel and nickel hydroxide) is the dominant material (41% by weight) and accounts for about 40% of the material cost. Processes to recover and recycle the nickel (e.g., the Inmetco process) do exist and are in practice for, at least, small cells. The technology should be able to handle vehicle-size units. The nickel is normally recovered along with iron for use in making stainless steel. Similarly, processes for the recovery of other metals, particularly the expensive cobalt, do exist. Metal-hydride electrodes, which represent about 23% of the weight and cost of the materials, are not recycled as value-added products at present. For example,

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[32] See http://www.futuretruck.org/technologies/what-hev.html

[33] See http://www.madkatz.com/ev/battery.html and http://www.eere.energy.gov/consumerinfo/factsheets/fa1.html (accessed in 2005)

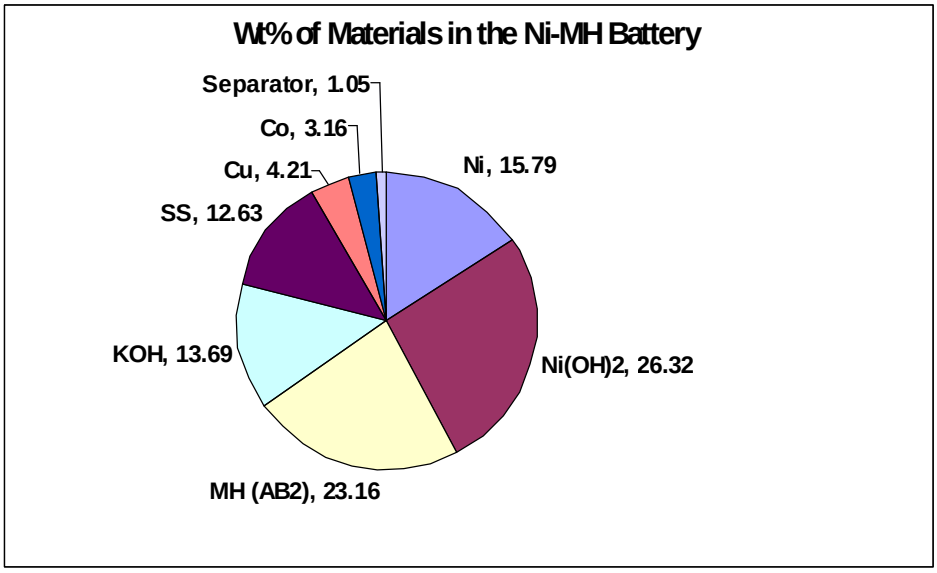

FIGURE 11.1 Materials of Construction of the Ni-MH Battery for EVs (Gaines 2000; Gaines, Elcock, and Singh 2002)

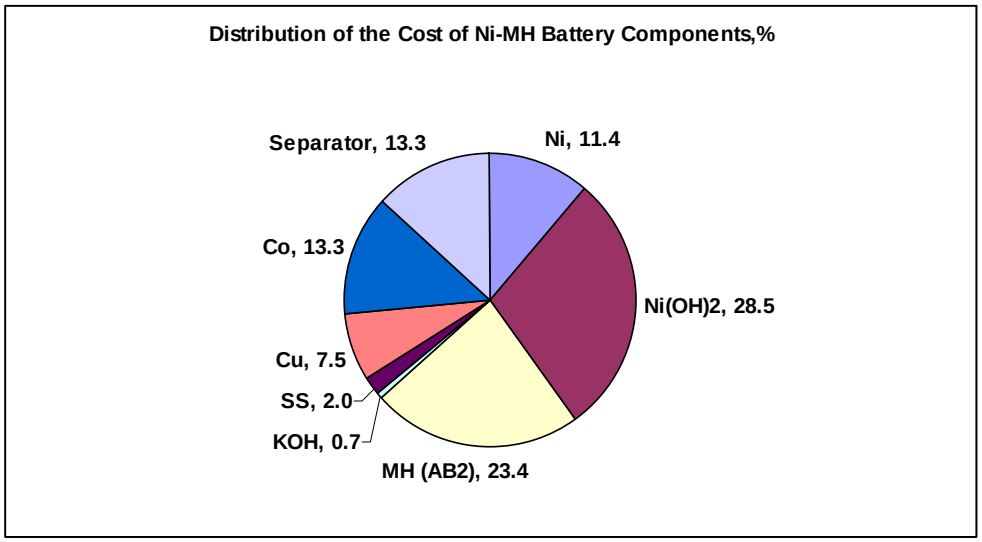

FIGURE 11.2 Cost of Materials Used in Building the Ni-MH Battery for EVs (Gaines 2000; Gaines, Elcock, and Singh 2002)

in the Inmetco process, they go to low-value use as road aggregate. These contain rare earth metals — zirconium and titanium — that are expensive, so their production and purification are energy-intensive. Therefore, a process to recover and recycle the nickel hydrides is necessary. The separator, which represents about 13% of the cost of the materials but only 1% of the weight, is also worthy of recovery as a fabricated "separator," since most of the cost occurs in making it from its materials of construction.

11.2.1.2 Lithium-Ion Electric Vehicle Battery

Figure 11.3 shows the approximate weight percent of materials that make up the Li-ion battery cells for EVs. Figure 11.4 shows the relative cost of these materials.

These cells are more difficult, if not impossible, to disassemble. For example, the cathode materials (50% of the weight) are laminated together. In addition, because lithium is extremely reactive, these cells must be processed in an inert atmosphere or at cryogenic temperatures (Sony and Toxco processes) and, even under such conditions, they can be a safety hazard.

The cathode and the electrolyte are primary targets for recycling. Graphite may also be a target, although it is a relatively lower-value material. Still, it may be used for other applications.

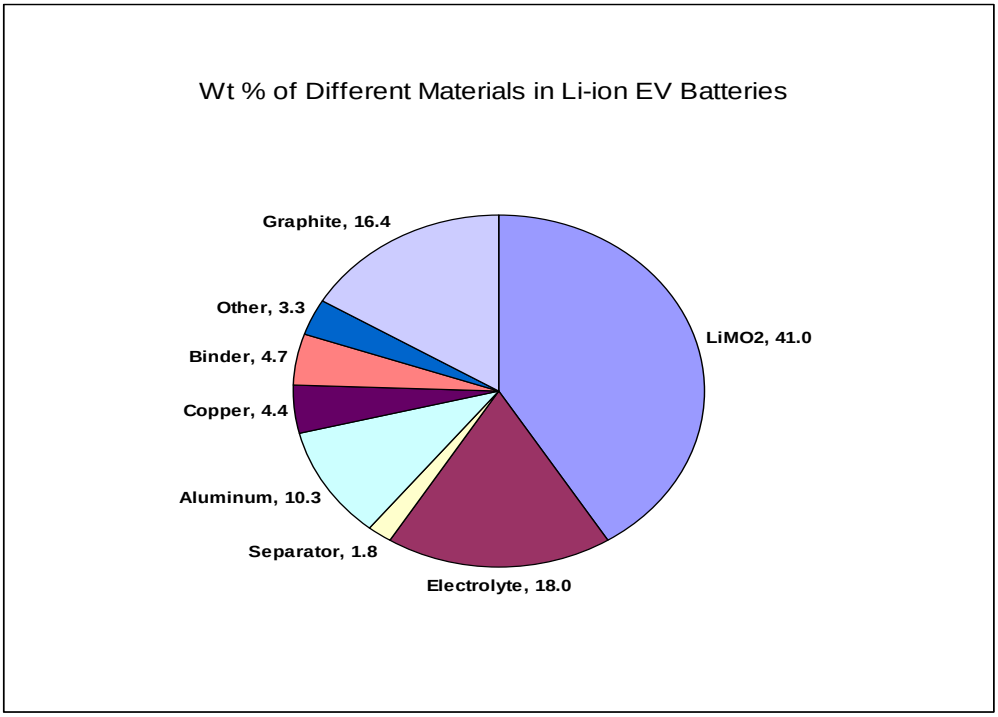

FIGURE 11.3 Materials of Construction of the Li-Ion Battery for EVs (Gaines 2000; Gaines, Elcock, and Singh 2002)

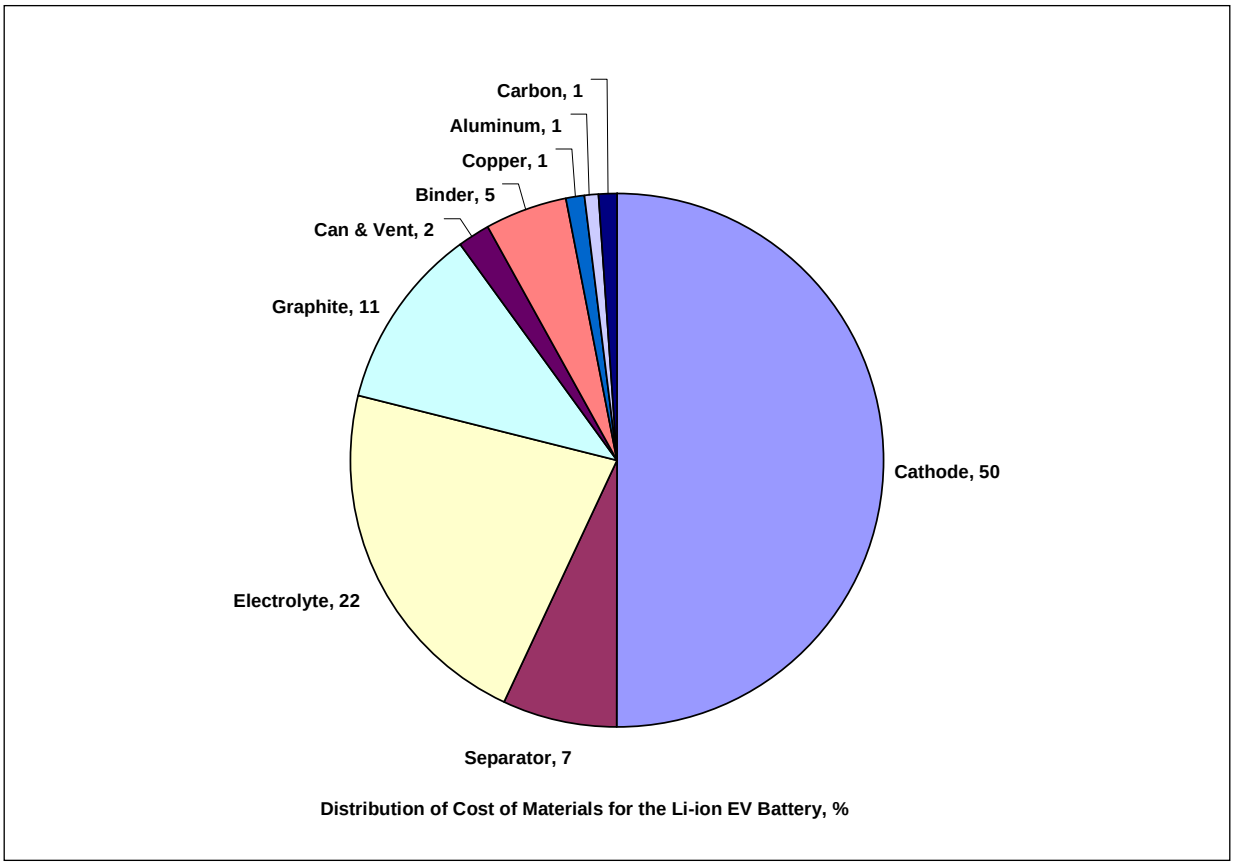

FIGURE 11.4 Cost of Materials Used in Building the Li-Ion Battery for EVs (Gaines 2000; Gaines, Elcock, and Singh 2002)

11.2.1.3 Lithium-Ion Hybrid Electric Vehicle Battery

These batteries are similar to the Li-ion EV batteries, and they use the same materials. However, the HEV Li-ion batteries use thinner coatings of electrode materials and more layers to produce more power than the Li-ion EV batteries. Figure 11.5 shows the approximate weight percent of materials that make up the Li-ion HEV Battery. Figure 11.6 shows the relative cost of these materials.

11.2.2 Processes for Recycling Batteries

The following companies have processes that are available for recycling parts of some batteries:

- Inmetco,
- Toxco,
- Sony, and
- Société Nouvelle D'Affinage des Métaux (S.N.A.M).

These processes are described below.

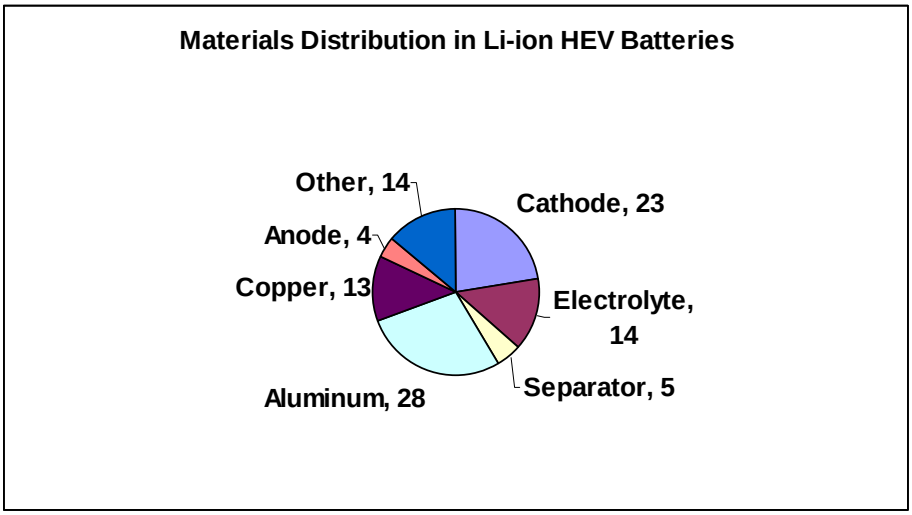

FIGURE 11.5 Materials of Construction of the Li-Ion Battery for HEVs (Gaines 2000; Gaines, Elcock, and Singh 2002)

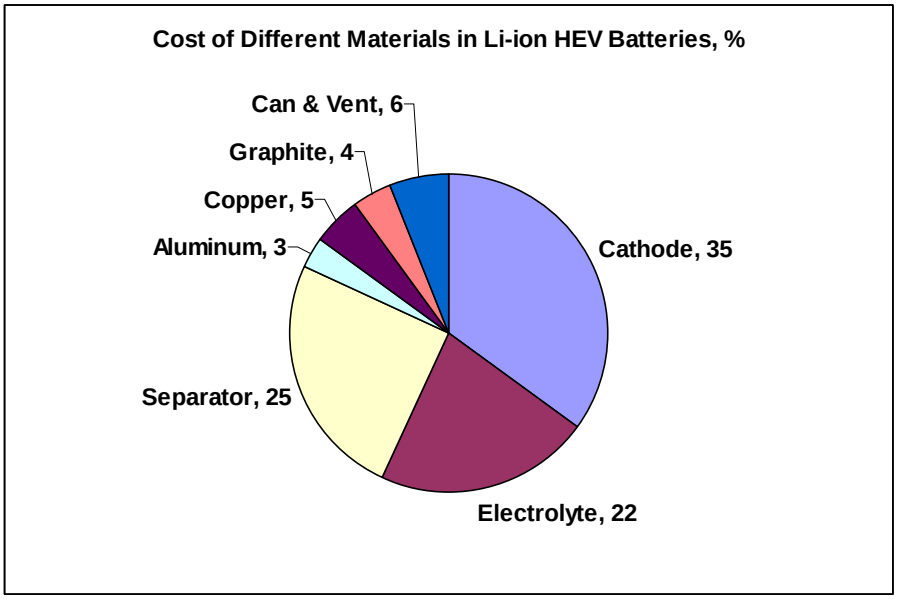

FIGURE 11.6 Cost of Materials Used in Building the Li-Ion Battery for HEVs (Gaines 2000; Gaines, Elcock, and Singh 2002)

Inmetco. Inmetco's process for recycling Ni-MH batteries consists of the following main steps:

1. Burn off plastics,
2. Melt and refine metals,
3. Recover nickel and iron for use in stainless steel, and
4. Send the metal hydride elements to slag (low value; use as road aggregate).

Inmetco also recycles Ni-Cd, alkaline, sealed lead acid, and Li-ion batteries.

Toxco. Toxco's process for recycling lithium batteries consists of the following main steps:

1. Discharge large batteries of any residual energy;
2. Cool batteries to -325°F by using liquid nitrogen;
3. Thin shear and shred the batteries;
4. Separate the shredded material;
5. Convert the lithium to lithium carbonate;
6. Neutralize electrolytes; and
7. Recover cobalt, when it is present.

Toxco also recycles alkaline batteries and prismatic non-lithium batteries.

Sony. Sony Magnetic Products, Inc., of America (Dothan, Alabama) recycles Li-ion batteries.

S.N.A.M. S.N.A.M. has a seven-stage recycling process for batteries:

1. Sorting,
2. Breaking of the battery packs,
3. Pyrolysis to destroy the organics,
4. Distillation,
5. Oxidation of cadmium at 760°C,

6. Distillation at 900°C for 24 hours, and

7. Refining and preparation of Ni-Fe residues.

Rechargeable Battery Recycling Corporation (RBRC) operates the *Call2Recycle*™ national program to help recycle used portable rechargeable batteries commonly found in cordless power tools, cellular and cordless phones, laptop computers, camcorders, digital cameras, and remote-control toys. The batteries are sent to recyclers that work with RBRC, which recycles Ni-Cd, Ni-MH, Li-ion, and small sealed-lead batteries.

Areas that require additional process development because they are not addressed by existing processes include:

- Recovery and recycling of the nickel hydrides in the Ni-MH battery,
- The cathode and the electrolyte in the Li-ion battery,
- Separation and recovery of the separators,
- Remanufacturing opportunities to use the batteries for other applications (such as storage for stationary power sources), and
- Design modifications to facilitate disassembly and recycling.

11.3 RECYCLING OF LIGHTWEIGHTING METALS FROM FUTURE VEHICLES

To build lighter-weight vehicles, automakers will likely replace some conventional steels with high- and medium-strength steel, aluminum, and magnesium. Antrekowitsch, Hanko, and Paschen (2001) stated that engine, running gear, and set frames, among other components, have been increasingly made of lightweight metals. Therefore, future shredder residue will contain increasing amounts of light metal scrap, which must be recycled. However, there are some obstacles to overcome in order to maximize the value of the recovered light metals. One of the obstacles is the need for cost-effective technologies to separate the different aluminum types (between wrought vs. cast alloys) (Das and Curlee 1999). Das and Curlee (1999) stated that, "development of cost-effective aluminum scrap sorting technologies will be crucial to: (i) separate sheet or extrusion from castings; (ii) enhance the value of each alloy separated; (iii) allow for continued use of the current infrastructure, i.e., shredding followed by separation; (iv) achieve >80% recycling goal, since the market for mixed scrap is limited to the automotive market," and finally (v) upcycling and the development of recycled aluminum alloys will be crucial and could perhaps limit the utilization of mixed aluminum scrap.

The DOE, together with the VRP of the USCAR and Argonne, sponsored a one-day workshop on issues related to automotive lightweighting metals recycling technology on September 24, 2008, at the USCAR offices in Southfield, Michigan (Workshop 2009; Green 2008). The objective of the workshop was to identify and prioritize R&D technology needs

related to automotive lightweighting metals recycling that would enable and further promote the future use of lightweighting metals in automotive applications.

The workshop facilitated a technology interaction and exchange among automotive companies, metals suppliers and recyclers, DOE National Laboratories, and academia, which resulted in the development of a technical roadmap to guide future R&D. The meeting was to cover the following automotive lightweighting metals in decreasing order of priority: aluminum, magnesium, titanium, and metal-matrix composites. Although the initial objective of the workshop was to explore issues with a future time horizon of 25 years, the workshop focused almost exclusively on near-term (less than 10 years) issues and R&D needs. The workshop evaluated and identified the expected significant losses in the life cycle of these lightweighting metals, primarily in the automotive sector, as well as the technology and R&D needs and priorities that could cost-effectively minimize these losses to ensure optimal materials use and recycling.

The workshop identified the following priority R&D needs.

Top Priority

- Encourage auto industry collaboration. Domestic auto companies should collaborate with “transplant” companies (e.g., Nissan, Honda, Toyota, and other stakeholders, such as AUTO21, and CANMET, among others) to facilitate the development of complex designs and propulsion systems and mitigate financial risk (see the presentation by Baron [Workshop 2009]).

High Priority

- Develop technology to remove detrimental impurities. Detrimental impurities must be removed from recycled metal. Specifically, in aluminum, the iron must be removed to meet a traditional melt specification of ~ 0.4 weight percent.

- Develop an alternative process to chlorine fluxing for magnesium and lithium removal.

- Separate the aluminum and magnesium process streams in scrap sorting processes and help to grow a secondary magnesium industry. In this way, eliminate both aluminum and magnesium losses during subsequent fluxing. Also, improve the separation of shredded aluminum scrap (e.g., wrought vs. cast, high iron vs. low iron, and segregation of small sizes and organics [oils/plastics]).

- Develop more recycling-compatible aluminum alloys and urge automotive designers to use fewer overall alloys; that is, different heat treatments of the same alloy for inner and outer closure panels.

- Improve aluminum recovery through (1) improved furnace designs, (2) improved de-coating/de-lacquering processes, (3) rapid submergence technologies, and (4) improved fluxing practice.

- Develop an improved process for handling by-products (salt cake) for the recovery of constituents (e.g., aluminum, salt flux, and oxides and non-metallics).

- Decrease aluminum melting costs through better energy utilization by using improved burners (see Peterson presentation [Workshop 2009]) and improve delivery of molten metal (better energy efficiency).

- Adopt life-cycle analysis as a methodology to harmonize industry practices and adopt the lowest-energy processes for recycling.

Medium Priority

- Develop a process to recover non-Class 1 scrap.

- Improve alloy methods of magnesium to reduce energy consumption.

- Develop a process to minimize or eliminate salt flux use in magnesium melting.

- Develop processes to remove copper, nickel, and iron for higher-quality magnesium. In the case of molten magnesium, processes must be developed to remove copper, nickel, and iron to extremely low values to ensure good corrosion resistance properties of the resultant magnesium. (see Powell and Davis presentations [Workshop 2009]). Also, conduct a process demonstration to establish that the rare earth (RE) elements needed for creep resistance can be economically recycled and reused.

- Demonstrate an alternative (non-SF6) cover gas for melt processing of magnesium (see Davis presentation [Workshop 2009]), Also, encourage “best practice” processing in the application of SF6 cover gas in magnesium melting and, in the longer term, develop an alternative for SF6.

- Evaluate scrap separation procedures for co-cast aluminum alloys (from a discussion in relation to the Novelis co-casting technology [Workshop 2009]). Regarding joining technologies, evaluate optimum sorting procedures for friction stir welded materials and assess procedures for adhesively bonded materials.

- Investigate magnesium scrap consolidation and semi-solid processing (rheocasting and thixocasting) as a way to minimize scrap generation and flux use.

- Develop information on the composition of future light-metal recycle streams to enable dismantlers and recycle processors to anticipate potential processing

issues. This has safety ramifications (request from processors during discussion [Workshop 2009]).

Low Priority

- Enhance current titanium recycling by developing more rapid scrap sorting techniques. Quantification of interstitial elements is an issue (see Lavender presentation [Workshop 2009]).

- Conduct a cost-benefit analysis of MMC design, including recycling, to select the best MMC composition. For example, while silicon carbide may be the best reinforcement for an aluminum matrix, what is the trade-off with an aluminum oxide reinforcement from a recycling viewpoint? Silicon carbide particulate will adversely impact the quality of an aluminum melt; an alumina particle less so.

11.4 THE ARGONNE THERMAL TREATMENT PROCESS FOR THE RECYCLING OF COMPOSITES

Because of their high strength-to-weight ratios, carbon-fiber-reinforced polymer-matrix composite (PMC) materials are being evaluated for use in the automotive industry. The major barriers to their widespread use are their relatively high cost and the uncertainty about whether they can be recycled (Jody et al. 2004). Argonne has developed a thermal treatment process to recover carbon fibers from obsolete PMC materials. This process involves heating scrap to elevated temperatures under different environments. The process was tested by using PMC samples made with different thermoset or thermoplastic polymers and on samples as large as 4 in. by 12 in. or as small as 0.5 in. by 0.5 in. Tests were conducted in a batch oven and in a continuous thermal reactor (Jody, Pomykala, and Daniels 2003a; Jody et al. 2004). Under the appropriate operating conditions, over 90% of the polymeric substrate can be removed in a few minutes. However, removing the remaining portion may require additional treatment and different treatment temperatures and/or oxygen environments, especially for the last 1% or 2%.

Samples were first submitted to Oak Ridge National Laboratory (ORNL) for preliminary evaluation.[34] The results indicated that those recovered carbon fibers had properties that compare favorably with those of virgin carbon fibers produced from polyacrylonitrile (PAN). This finding is significant, although it is not known if the scrap samples that were processed were originally produced from PAN. A picture of the recovered fibers from a 12-in. by 4-in. panel is shown in Figure 11.7.

ORNL[35] and Hexcel Corporation[36] evaluated the recovered fibers further to determine their suitability for reuse. The results are presented below.

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[34] Analysis conducted by Dr. Felix Paulauskas, Oak Ridge National Laboratory.

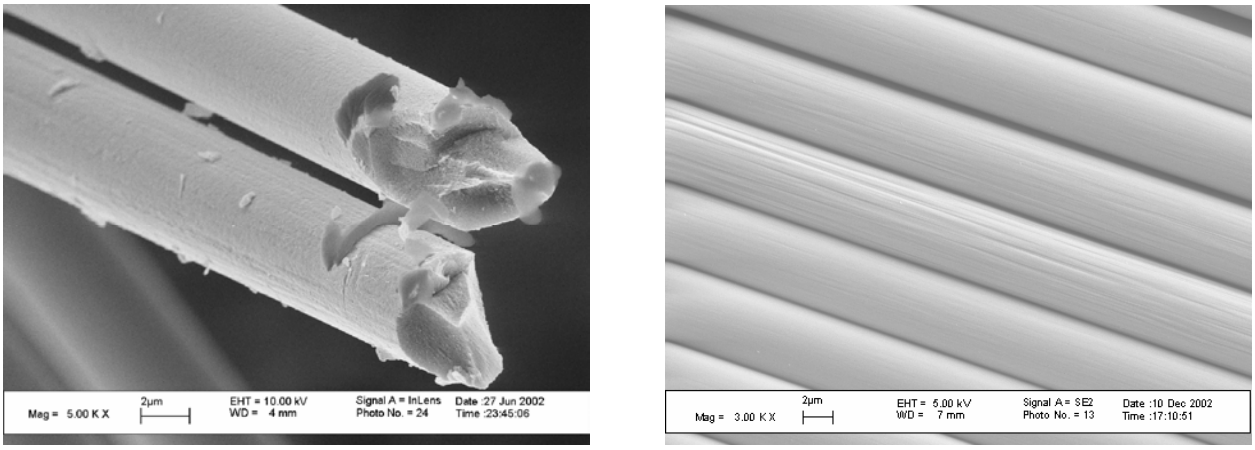
[35] Analysis conducted by Dr. Felix Paulauskas, Oak Ridge National Laboratory.

[36] Analysis conducted by Dr. Mohammad Abdallah, Hexcel Corporation.

Scanning Electron Microscope Analysis. Figure 11.8 shows scanning electron microscope (SEM) pictures of recovered fibers: (a) at 5,000X, of virgin fibers (b) at 3,000X (see footnote 34). The rough edge of the recovered fibers is the result of using scissors to cut the fibers. The recovered fibers were from a PMC panel made with epoxy resin. Small amounts of residual material were still scattered on the surface of the fibers. Other than that, no mechanical damage to the surface is apparent.

FIGURE 11.7 Fibers Recovered from a 12-in. by 4-in. Panel

Surface Chemistry. Researchers at ORNL (see footnote 34) also used X-ray photon spectroscopy (XPS) to determine the concentration (atomic %) of principal elements and functional groups found on unsputtered fiber samples. Table 11.1 and Figure 11.9. summarize the results. The carbon concentration on the surface of the recovered fibers is essentially the same as that for the treated virgin surface. Interestingly, the oxygen concentration of the recovered fibers was higher than that for the treated virgin surface. This finding is important because complete re-treatment of the recovered fibers may not be necessary. Eliminating the need for re-treatment will save about $0.10–0.15/lb of fibers. The nitrogen concentration for the recovered fibers is lower than that for the treated virgin fibers. However, the nitrogen concentration is not critical. The trace amount of silicon observed on one of the recovered fibers may be contamination from the thermal reactor, which was also used for the recovery of glass fibers.



(a) **(b)**

FIGURE 11.8 SEM Pictures of Recovered Fibers (a) at 5000X, of Virgin Fibers (b) at 3000X

TABLE 11.1 Surface Chemistry of the Recovered and Virgin Fibers

Sample	C	O	N	Traces
Recovered 1	84 ± 1.4	11 ± 1.3	5 ± 0.5	Na
Recovered 2	80 ± 0.9	15	5 ± 0.2	Na, Si
Untreated virgin	95 ± 0.7	3 ± 0.4	2 ± 0.6	—
Surface-treated virgin	83± 1.1	10	7 ± 0.7	Na

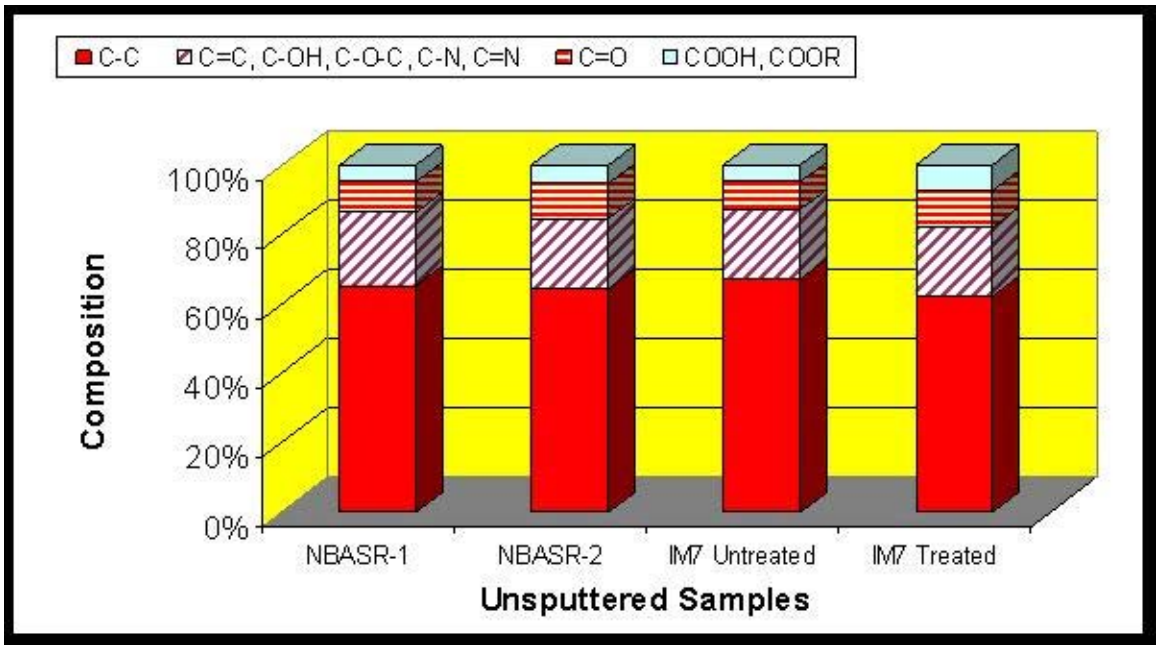


FIGURE 11.9 Relative Concentration of Functional Groups Based on Areas of the Fitting Curves/Peaks of High-Resolution Carbon Spectra (XPS Binding Energy), Unsputtered (beneath the top surface) (NBASR refers to recovered samples, and IM7 is a virgin sample with surface treatment applied but no thermal treatment by the Argonne process.)

Further, the same functional groups are on both the virgin and recycled surface (Figure 11.9). These groups are aliphatic carbon and hydrocarbon (C-C and C-H); hydroxyl, ether, aromatic carbon, and single and double nitrogen bonds (C-OH, C-O-C, C=C, C-N, C=N); and carbonyl (C=O) and carboxyl and ester (COOH, COOR).

Fiber Morphology Density and Diameter. ORNL also evaluated the morphology of the recovered fibers by using wide-angle X-ray diffraction. The morphology of the recovered fibers was nearly identical to that of virgin fibers of the same type. The diameter and density of the recovered fibers also were not affected by the thermal treatment.

Mechanical Properties of the Fibers. The mechanical properties of the recovered fibers were evaluated by Hexcel Corporation (see footnote 35) and compared with the mechanical

properties of virgin fibers from the same lot (Table 11.2). The recovered fibers retained acceptable mechanical properties.

For most mixtures of PMCs, the process can be energy self-sufficient by using the polymer substrate as an energy source. The fibers retain good properties and characteristics and are suitable for short-fiber applications. The process is technically feasible and potentially economical. To avoid oxidation of the carbon fibers, the treatment reactor must be properly designed to control the rate of air flow into the reactor during treatment. The treatment temperature and residence time should be selected such that:

- Recovered fibers contain the minimum amount of non-fiber residue,
- Fiber loss is kept to a minimum, and
- Energy requirements and VOC emissions are minimized.

Under high air-flow rates, oxidation of the carbon fibers does occur, while at low air-flow rates, the residue on the fibers after the initial treatment will be significant. Therefore, this parameter must be properly controlled.

A preliminary economic analysis of the process was also conducted on the basis of the results of the bench-scale experiments. The results of the analysis suggested that a potential payback of less than 2 years is likely.

TABLE 11.2 Mechanical Properties of Virgin and Recovered Fibers

Sample	Tow Tensile Strength (MPa*)	Tow Tensile Modulus (GPa*)	Strain at Failure (%)
Recycled 1	4.26	295	1.32
Recycled 2	4.63	260	1.66
Virgin**	5.64	295	1.76

* MPa = mega Pascal; GPa = giga Pascal.

** Virgin fibers used in making the composites from which the recycled fibers 1 and 2 were recovered.

11.5 TECHNOLOGIES FOR THE RECYCLING OF HYBRID BATTERIES

Research for the CRADA Team involved two kinds of advanced battery chemistries: NiMH and Li-ion. The technical feasibility of recycling these types of automotive batteries was examined with laboratory-scale experiments to evaluate the utility of materials produced from various recycling processes. The results will be used to project the investment necessary to adopt new recycling technologies in pilot-scale operations.

11.5.1 OnTo Technology, LLC

OnTo Technology has developed new, clean, and cryogenic processes to recycle advanced batteries from consumer electronics (Sloop 2007). The company has received support from the Oregon Department of Energy to build a pilot plant in Bend, Oregon.

OnTo's technology can be used to recycle advanced batteries to recover micro and nanomaterials for reuse in new batteries. This process has recovered cobalt from lithium cobalt dioxide (Li $CoCO_2$) computer pack cells and copper. This technology retains some of the chemical integrity of the metals and resultant compounds. As such, it is more advanced and sustainable than the usual smelting solution, where these valuable materials are burned, and only the crude metal mixtures are recovered.

11.5.2 Kinsbursky Brothers, Inc. (Toxco, Inc.)

TOXCO's lithium battery recycling facility inventories incoming lithium battery waste. The waste is then stored in earth-covered concrete storage bunkers. Residual electrical energy is removed from larger, more reactive batteries. If necessary, the batteries then begin Toxco's patented cryogenic process and are cooled to -325°F. Lithium, although normally explosively reactive at room temperature, is rendered relatively inert at this temperature. The batteries are then safely sheared/shredded, and the materials are separated. Metals from the batteries are collected and sold. The lithium components are separated and converted to lithium carbonate for resale. Hazardous electrolytes are neutralized to form stable compounds, and residual plastic casings and miscellaneous components are recovered for appropriate recycling or scrapping. If the batteries contain cobalt, it also is recovered for reuse. (This process is also known as the Kinsbursky process.)

Toxco's Prismatic Battery Recycling. These non-lithium, non-reactive batteries are made up of flat anode/cathode plates. They are broken open to expose recyclable materials. Lead, nickel, silver, cadmium, plastic, metal, and other materials are separated and sold. The electrolyte is drained and neutralized.

11.5.3 Umicore

The Umicore battery recycling process is sustainable and cost-efficient. It is a proposed real closed loop solution for Li-ion batteries that affords environmentally sound management of end-of-life batteries, as well as high recycling and/or recovery rates.

The Umicore process, which is dedicated to the recycling of rechargeable [(Li-ion) and (NiMH)] batteries and battery packs, transforms end-of-life rechargeable batteries into new batteries. The Umicore battery recycling process relies on the sustainable and cost-efficient technologies developed at Umicore's R&D facility. It is a melting operation where rechargeable batteries, battery packs, and other input materials are injected into a furnace without any pre-processing, thereby minimizing all hazardous risks. This newly developed technology is

preferred because it uses gas to prevent the formation of dioxin and furan. It has well-controlled melting conditions, so a clean slag can be produced and further re-used in construction and/or as an aggregate for concrete. At the cobalt and nickel refining installation, the cobalt- and nickel-containing alloys can be further treated to enable the preparation of pure cobalt and nickel. This is followed by a process for the transformation of cobalt products into the final lithium cobalt dioxide ($LiCoO_2$), which is then used in the production of new Li-ion batteries.

11.5.4 INMETCO

INMETCO (North America) provides thermal recovery for Ni-Cd batteries. The EPA has determined that INMETCO's technology is the Best Demonstrated Available Technology (BDAT) for cadmium disposal. INMETCO recycles the large industrial cells used by railroads, electric utilities, the military, and telecommunication companies for back-up power. It also recycles the small Ni-Cd cells used in transceivers, portable power tools and appliances, medical equipment, and emergency lighting systems.

INMETCO installed new cadmium recovery plant in December 1995. The cadmium reclaimed from this operation is proposed to eventually be returned to Ni-Cd battery manufacturers. The nickel and iron become part of the re-melt alloy that is used to make stainless steel. The battery electrolyte is used as a reagent in the facility's wastewater treatment plant. Natural resources are recycled rather than landfilled, thus eliminating any landfill liability for customers. The metal components of Ni-Cd batteries are completely recycled at one, fully permitted site in the United States. This promotes good environmental stewardship of spent Ni-Cd batteries.

In addition to the Ni-Cd, other types of batteries accepted by INMETCO include nickel-iron, Ni-MH, Li-ion, and mercury-free zinc carbon (also known as Carbonaire). INMETCO is the recycling facility for the RBRC. The RBRC's mission is to promote recycling of rechargeable batteries in the United States. INMETCO also provides a pre-paid battery recycling program. This convenient program provides boxes for the shipment of small quantities of Ni-Cd, Ni-MH, alkaline, sealed lead acid, and Li-ion batteries.

12 CONCLUSIONS

Over the past 10 years, activities and innovations related to recovering materials from shredder residue for recycling have been increasing around the world. From a technical perspective, the complexity of the composition of shredder residue and the entanglement of its numerous constituents (as well as the SOCs that it contains) hamper these efforts. The lack of sustainable markets for materials that could be recovered from shredder residue (such as plastics) is an additional hurdle to overcome. Despite these difficulties, several technologies have reached an advanced state of development, and several private companies that focus on recycling materials from shredder residue have been established. The two areas that received the most attention are:

1. Recovery and recycling of polymers and

2. Conversion to fuels and energy.

The consensus among many of the workers in this field is that organic material must be separated from the inorganic material in shredder residue through some degree of bulk mechanical separation before technologies to separate and recover polymers or to convert the shredder residue to fuels can be implemented. A pre-separated fraction of shredder residue has been used in many places as a landfill cover. In the technology area, researchers have tested several separation technologies at a relatively large scale. Mechanical separation technologies have been able to separate the mostly inorganic fines and residual ferrous and nonferrous metals from shredder residue and produce a polymer concentrate. Polymer separation technologies (such as froth flotation) have successfully separated and recovered the polyolefins and engineered plastics (such as ABS) from the polymer concentrate. Dry and wet processes have also succeeded in separating and recovering a mixed-rubber fraction. Gasification, pyrolysis, and depolymerization/hydrolysis processes have proven that diesel-grade and other fuels can be produced from shredder residue. The organic fraction of shredder residue has been showing promising results as a reducing agent (as well as an energy source) when used in blast furnaces.

Despite recent technical advancements, essentially all of the approximately 5 million tons of shredder residue generated every year in the United States is still disposed of in landfills. In Europe and Japan, most shredder residue is disposed of by incineration or in landfills. Recently, proposed regulations (most of which are not implemented) in Europe have increased interest in developing recycling technologies for shredder residue. However, economic drivers will continue to lead the way to successful implementation of the recycling technologies. In the United States, developing reliable and economic technology to deal with the PCBs is another milestone that must be accomplished before technologies can be commercialized.

An efficient and economical solution to recycling shredder residue is likely to be an integrated system of many technologies to produce quality products at the lowest cost. Availability constraints on nonferrous metal quantities for lightweighting materials may be influenced by market usage increase. Upcycling is needed, especially for aluminum, magnesium,

cobalt, nickel, and copper. Replacing substances of concern (e.g., brominated flame retardants) with non-halogenated compounds will required more aluminum, titanium, and antimony usage.

Usage of SOCs is being approached on a substance-by-substance basis, with the focus on trends of sustainability as dictated by EU regulations. These EU regulations are generating global effects, including rates of recycling, overall vehicle recyclability definitions, and disposal (ISO 22628: Road vehicles. Recyclability and recoverability. Calculation method) (ISO 22628, 2002).

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