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

Energy Systems Division
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by
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work sponsored by the
Office of FreedomCAR and Vehicle Technologies
Automotive Lightweighting Materials
Advanced Materials and Processes

September 25, 2006
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The opinions expressed in this report are those of the primary 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

APC American Plastics Council
API American Petroleum Institute
APME Association of Plastics Manufacturers in Europe
ARA Automotive Recycling Association
BP British Petroleum
BSEF Bromine Science and Environmental Forum
CAR Certified Automotive Recyclers (Program)
CD(s) compact disc(s)
CMP Center for Materials Production
CRADA Cooperative Research and Development Agreement
CTU Conzepte Technik Umwelt AG
CWT Changing World Technologies
DEG diethylene glycol
DM Deutsche Mark
DOE U.S. Department of Energy
DSD Duales System Deutschland
ECUT Energy Conversion and Utilization Technologies
ELV(s) End-of-Life Vehicle(s)
ENPA Environment National Protection Agency
EPA U.S. Environmental Protection Agency
EPIC Environment and Plastics Industry Council
EU European Union
EV(s) electric vehicle(s)

FBP final boiling point
Fs fluorinated
FTC Federal Trade Commission

GC-ECD Gas Chromatography-Electron Capture Detector
GC/MS Gas Chromatography/Mass Spectroscopy
GDL gas diffusion layer
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>HEV(s)</td>
<td>hybrid electric vehicle(s)</td>
</tr>
<tr>
<td>HF</td>
<td>hydrogen fluoride</td>
</tr>
<tr>
<td>IBP</td>
<td>initial boiling point</td>
</tr>
<tr>
<td>IDIS</td>
<td>International Dismantling Information System (software)</td>
</tr>
<tr>
<td>IGEA</td>
<td>German abbreviation of “Syndicate for the Environmentally Compatible Disposal of Nonmetallic Waste from Vehicles”</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>ISRI</td>
<td>Institute of Scrap Recycling Industries</td>
</tr>
<tr>
<td>KDS</td>
<td>Kinetic Energy Separators</td>
</tr>
<tr>
<td>KT</td>
<td>Krupp/Thyssen</td>
</tr>
<tr>
<td>MEA</td>
<td>membrane electrode assembly</td>
</tr>
<tr>
<td>MEK</td>
<td>methyl ethyl ketone</td>
</tr>
<tr>
<td>MFR</td>
<td>melt flow rate</td>
</tr>
<tr>
<td>MSW</td>
<td>municipal solid waste</td>
</tr>
<tr>
<td>NRT</td>
<td>National Recovery Technologies, Inc.</td>
</tr>
<tr>
<td>OEM(s)</td>
<td>original equipment manufacturer(s)</td>
</tr>
<tr>
<td>ORNL</td>
<td>Oak Ridge National Laboratory</td>
</tr>
<tr>
<td>PAHs</td>
<td>polycyclic aromatic hydrocarbons</td>
</tr>
<tr>
<td>PAN</td>
<td>polyacrylonitrile</td>
</tr>
<tr>
<td>PCBs</td>
<td>polychlorinated biphenyls</td>
</tr>
<tr>
<td>PCDD</td>
<td>polychlorinated dibenzo-P-dioxins</td>
</tr>
<tr>
<td>PCR</td>
<td>post-consumer recyclate</td>
</tr>
<tr>
<td>PEM</td>
<td>polymer electrolyte membrane</td>
</tr>
<tr>
<td>PIA</td>
<td>Plastics Institute of America</td>
</tr>
<tr>
<td>PMC</td>
<td>polymer-matrix composite</td>
</tr>
<tr>
<td>PUF</td>
<td>polyurethane foam</td>
</tr>
<tr>
<td>PUR</td>
<td>polyurethane rubber</td>
</tr>
<tr>
<td>PURRC</td>
<td>The Polyurethane Recycle and Recovery Council</td>
</tr>
<tr>
<td>PVC</td>
<td>polyvinyl chloride</td>
</tr>
<tr>
<td>RBRC</td>
<td>Rechargeable Battery Recycling Corporation</td>
</tr>
<tr>
<td>RCRA</td>
<td>Resource Conservation and Recovery Act of 1976</td>
</tr>
<tr>
<td>RPI</td>
<td>Recovery Plastics International</td>
</tr>
<tr>
<td>SARS</td>
<td>Stiftung Auto Recycling Schweiz</td>
</tr>
<tr>
<td>SB</td>
<td>Sthlwerke Bremen</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SG</td>
<td>specific gravity</td>
</tr>
<tr>
<td>S.N.A.M.</td>
<td>Société Nouvelle D’Affinage des Métaux</td>
</tr>
<tr>
<td>SOCs</td>
<td>substances of concern</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>SPORT</td>
<td>Sustainable Polymers to Olefins Recycling Technology</td>
</tr>
<tr>
<td>SVC</td>
<td>Siemens Venture Capital Gmbh</td>
</tr>
<tr>
<td>TCLP</td>
<td>Toxicity Characterization Leaching Procedure</td>
</tr>
<tr>
<td>TCP</td>
<td>Thermal Conversion Process</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Content</td>
</tr>
<tr>
<td>TOX</td>
<td>total organic halogens</td>
</tr>
<tr>
<td>USCAR</td>
<td>United States Council for Automotive Research</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>VAI</td>
<td>Voest-Alpine Industrieanlagenbau GmbH &amp; Co.</td>
</tr>
<tr>
<td>VOCs</td>
<td>volatile organic compounds</td>
</tr>
<tr>
<td>VRP</td>
<td>Vehicle Recycling Partnership</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photon spectroscopy</td>
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**ELEMENTS AND COMPOUNDS**

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<tr>
<th>Acronym</th>
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<tbody>
<tr>
<td>ABS</td>
<td>acrylonitrile butadiene styrene</td>
</tr>
<tr>
<td>CFCs</td>
<td>chlorofluorocarbons</td>
</tr>
<tr>
<td>CO</td>
<td>carbon monoxide</td>
</tr>
<tr>
<td>DecaBDE</td>
<td>Decabromodiphenyl ether</td>
</tr>
<tr>
<td>EMPP</td>
<td>elastomer (rubber) modified polypropylene</td>
</tr>
<tr>
<td>EPDM</td>
<td>ethylene propylene diene-monomer</td>
</tr>
<tr>
<td>HCl</td>
<td>hydrogen chloride</td>
</tr>
<tr>
<td>HDPE</td>
<td>high-density polyethylene</td>
</tr>
<tr>
<td>Hg</td>
<td>mercury</td>
</tr>
<tr>
<td>HIPS</td>
<td>high-impact polystyrene</td>
</tr>
<tr>
<td>KOH</td>
<td>potassium hydroxide</td>
</tr>
<tr>
<td>Li-ion</td>
<td>lithium-ion</td>
</tr>
<tr>
<td>Ni-Cd</td>
<td>nickel-cadmium</td>
</tr>
<tr>
<td>Ni-MH</td>
<td>nickel-metal hydride</td>
</tr>
<tr>
<td>NOx</td>
<td>nitrogen oxides</td>
</tr>
<tr>
<td>PA</td>
<td>polyamide</td>
</tr>
<tr>
<td>PA6</td>
<td>polyamide 6 (also known as nylon 6)</td>
</tr>
<tr>
<td>PA66</td>
<td>polyamide 6/6 (also known as nylon 66)</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
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<td>-------------</td>
</tr>
<tr>
<td>PBDEs</td>
<td>polybrominated diphenyl ethers</td>
</tr>
<tr>
<td>PBT</td>
<td>polybutylene terephthalate</td>
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<tr>
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<td>polybutylene terephthalate</td>
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<tr>
<td>PC</td>
<td>polycarbonate</td>
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<td>PE</td>
<td>polyethylene</td>
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<td>PET</td>
<td>polyethylene terephthalate</td>
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<tr>
<td>PMMA</td>
<td>polymethyl methacrylate</td>
</tr>
<tr>
<td>PP</td>
<td>polypropylene</td>
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<tr>
<td>PPO</td>
<td>polyphenylene oxide</td>
</tr>
<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>Pt</td>
<td>platinum</td>
</tr>
<tr>
<td>Ru</td>
<td>ruthenium</td>
</tr>
<tr>
<td>SAN</td>
<td>styrene acrylonitrile</td>
</tr>
<tr>
<td>SOx</td>
<td>sulfur oxides</td>
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**UNITS OF MEASURE**

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<thead>
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<th>Unit</th>
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<tbody>
<tr>
<td>bbl</td>
<td>barrel(s)</td>
</tr>
<tr>
<td>Btu</td>
<td>British thermal unit</td>
</tr>
<tr>
<td>cc</td>
<td>cubic centimeters (cm³)</td>
</tr>
<tr>
<td>cm</td>
<td>centimeter(s)</td>
</tr>
<tr>
<td>cPs</td>
<td>centipoise</td>
</tr>
<tr>
<td>DTUL</td>
<td>deflection temperature under load</td>
</tr>
<tr>
<td>ft³</td>
<td>cubic feet</td>
</tr>
<tr>
<td>g</td>
<td>gram(s)</td>
</tr>
<tr>
<td>gal</td>
<td>gallon(s)</td>
</tr>
<tr>
<td>GPA</td>
<td>gigaPascal (tow tensile modulus)</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>in.</td>
<td>inch</td>
</tr>
<tr>
<td>kg</td>
<td>kilogram</td>
</tr>
<tr>
<td>kJ</td>
<td>kilo Joule</td>
</tr>
<tr>
<td>ksi</td>
<td>kips per square inch (kips/in.²)</td>
</tr>
<tr>
<td>lb</td>
<td>pound</td>
</tr>
<tr>
<td>m²</td>
<td>square meter(s)</td>
</tr>
<tr>
<td>MHz</td>
<td>mega Hertz</td>
</tr>
<tr>
<td>MJ</td>
<td>mega Joule</td>
</tr>
<tr>
<td>MPa</td>
<td>mega Pascal (tow tensile strength)</td>
</tr>
<tr>
<td>mm</td>
<td>millimeter</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>psi</td>
<td>pounds per square inch (lb/in.²)</td>
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SUMMARY

Each year, more than 50 million vehicles reach the end of their service life throughout the world. More than 95% of these vehicles enter a comprehensive recycling infrastructure that includes auto parts recyclers/dismantlers, remanufacturers, and material recyclers (shredders). Today, about 75% of automotive materials 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 automobiles, 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 (about 25% of the weight of the vehicle) — commonly called shredder residue — is disposed of in landfills.

Over the past 10 to 15 years, a significant amount of research and development has been undertaken to enhance the recycle rate of end-of-life vehicles (ELVs), including enhancing dismantling techniques and improving remanufacturing operations. However, most of the effort has focused on developing technology to recover materials, such as polymers, from shredder residue.

To make future vehicles more energy efficient, more lighter-weight materials — primarily polymers and polymer composites — will be used in manufacturing these vehicles. These materials increase the percentage of shredder residue that must be disposed of, compared with the percentage of metals. 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 at end-of-life.

Argonne National Laboratory (Argonne), in cooperation with the Vehicle Recycling Partnership (VRP) and the American Plastics Council (APC), is working to develop technology for recycling materials from shredder residue. Several other organizations worldwide are also working on developing technology for recycling shredder residue. Without a commercially viable shredder industry, our nation may face greater environmental challenges and a decreased supply of quality scrap and be forced to turn to primary ores for the production of finished metals.

This document presents a review of the state of the art in shredder residue recycling. Available technologies and emerging technologies for the recycling of materials from shredder residue are discussed.
1 INTRODUCTION AND BACKGROUND

Sustainable recycling of automotive materials can have a significant impact on the conservation of materials and domestic energy use. The automobile industry is one of the largest consumers of materials. In 1993, materials use in the domestic U.S. automotive industry approached 33 million tons (Table 1.1). The automotive industry’s consumption of steel accounts for 20% of all domestic steel use. In the case of aluminum, the automotive industry uses about one-third of the total domestic use of aluminum. The primary energy consumed in the production of the 33 million tons of material used in the automotive sector is estimated to be about 1.5 quadrillion Btu, which is 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).

As one of the largest consumers of materials, vehicles also represent one of the largest sources of recycled materials. In 1999, about 12 million obsolete vehicles were retired from service and entered the domestic recycling infrastructure (Table 1.2). In that year, sales of all vehicles in the United States exceeded 17 million vehicles, and the total number of vehicles in use exceeded 200 million.

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. Since 1978, the total weight of a typical passenger car has decreased by almost 300 pounds. In that same period, the amount of regular steel and iron used in a typical car has decreased by almost 700 pounds, the use of high-strength steel has increased by about 200 pounds, the use of

<table>
<thead>
<tr>
<th>Table 1.1 Automotive Industry Materials Use in 1999*</th>
</tr>
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<tbody>
<tr>
<td><strong>Material</strong></td>
</tr>
<tr>
<td>Aluminum</td>
</tr>
<tr>
<td>Copper</td>
</tr>
<tr>
<td>Iron</td>
</tr>
<tr>
<td>Lead</td>
</tr>
<tr>
<td>Plastic</td>
</tr>
<tr>
<td>Rubber</td>
</tr>
<tr>
<td>Steel</td>
</tr>
<tr>
<td>Zinc</td>
</tr>
<tr>
<td>Other Materials</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

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*Includes materials for cars, trucks, buses and replacement parts.  
Source: Ward’s (2000); other materials estimated by author.
aluminum has increased by more than 100 pounds, and the use of plastics has increased by almost 75 pounds (Ward’s 2000). Clearly, the trend has been a substitution of higher-performance, lighter-weight materials to achieve increased fuel efficiency.

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

Obsolete vehicles are typically processed first by automotive dismantlers. In North America, 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.

Remanufacturing is an important component 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, and testing of the remanufactured component to ensure that the performance specifications of the remanufactured part are met.
Once useable and remanufacturable parts have been 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 15,000 dismantling facilities in the United States to one of 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 a car hulk in about one 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 non-ferrous 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. Automotive materials recycling is not subsidized by either taxpayers or car buyers in North America.

Without a commercially viable shredder industry, our nation may face greater environmental challenges and a decreased supply of quality scrap and be forced to turn to primary ores for the production of finished metals (Menken and Voigt 2002).

### 1.1 THE AUTOMOBILE INDUSTRY

The automobile industry has grown very rapidly in the last 100 years (see Table 1.3 and Figure 1.1). The number of vehicles in use is expected to triple in the next 50 years (Levizzari et al. 2002). Of these vehicles, 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 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.

<table>
<thead>
<tr>
<th>Year</th>
<th>Number of Cars</th>
<th>Number of Trucks and Buses</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1900</td>
<td>4,192</td>
<td>0</td>
<td>4,192</td>
</tr>
<tr>
<td>1968</td>
<td>169,994,128</td>
<td>46,614,342</td>
<td>216,608,470</td>
</tr>
<tr>
<td>1985</td>
<td>375,000,000</td>
<td>109,000,000</td>
<td>484,000,000</td>
</tr>
<tr>
<td>1996</td>
<td>485,954,000</td>
<td>185,404,000</td>
<td>671,358,000</td>
</tr>
<tr>
<td>2030</td>
<td></td>
<td></td>
<td>1,200,000,000</td>
</tr>
</tbody>
</table>
As new materials are introduced, as is the case with hybrid and fuel cell vehicles, for example, the composition of shredder residue will change. The increasing content of plastics in vehicles also shows how the composition of materials in vehicles is changing. For example, in 1977, the average automobile weighed approximately 3,666 pounds and contained about 168 pounds of plastics. In 1987, the weight of the average automobile had decreased to about 3,178 pounds, which included approximately 222 pounds of plastics, and in 1992, the average automobile weighed approximately 3,136 pounds and had 243 pounds of plastics. These numbers remained about constant through 1998. ¹ Figure 1.2 shows the weight percent of plastics in cars during the same period. (Figure 1.2 is based on data given in footnote 1).

1.2 THE METALS RECYCLING (SHREDDING) INDUSTRY

Today, we estimate that the 200 or so shredders in the United States shred well over 12 million vehicles annually (in addition to white goods and other source materials) (Daniels et al. 2004). As a result, U.S. shredders supply in excess of 16 million tons of recovered ferrous and non-ferrous scrap for use in the metals industry (12 million cars × 1.5 tons per car × 75% metal content of the car × 95% of the metals are recovered, and what is recovered from cars is about 80% of the total metals recycled by shredders). Over 8 million passenger cars are scrapped each year in Western Europe (Costes and Monteil 2000).

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In the process of recovering the metals from obsolete materials, the U.S. shredder industry is left with over 5 million tons of shredder residue that must be disposed of. Approximately 4.5 million tons of that are from vehicles (12 million vehicles × 1.5 tons per vehicle × 25% of the vehicle’s weight end up as shredder residue). Shredder residue has a density range of about 15–25 lb/ft³ and a moisture content that can be as high as 25% by weight.

1.3 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 et al. 1978; Ellsworth et al. 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 Toleciss 1961; Dean and Sterner 1969; Adams 1972; Luntz 1973; Dean, Sterner, and Valdez 1974; Daellenbach et al. 1974; “Auto Shredder Reduces Junk Cars in Michigan” 1974; 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; Plastics Institute of America [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: landfilling and incineration. Landfilling 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. Because the disposal costs of and environmental concerns over shredder residue are expected to continue to escalate, more economical and environmentally acceptable alternatives are needed.

Because approximately 40–50% of the shredder residue is hydrocarbon-based materials (such as plastics, fibers, wood, paper, tar, oils, and rubber), the amount that needs to be disposed of can be reduced significantly by:

- Separation and recovery of recyclable materials from the shredder residue, such as plastics and rubber.
- Incineration with or without heat recovery. The heating value of shredder residue varies from about 4,000 to 6,000 Btu/lb and averages approximately 5,400 Btu/lb (Hubble, Most, and Wolman 1987).
- Conversion to liquid and gaseous fuels via pyrolysis or gasification of its organic content.

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 maybe the glass.

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 also occur, resulting in dangerously high temperatures.
1.4 REGULATORY ISSUES

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 (21 October 2000), the directive must 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 (see Figure 1.3). Member States would have to implement the directive, although they have not yet done so (Schliessner 2002; Duncan 2005).

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 Pb, Hg, Cd, and Cr(VI) in vehicles built after January 1, 2003;

- Requiring the removal of catalysts and components containing Cu, Al, or Mg before shredding; and

- Noting that regulations concerning polyvinyl chloride (PVC) in ELVs is still pending.

There are two other 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, NO$_x$, SO$_x$, CO, hydrogen fluoride (HF), Total Organic Content (TOC), polychlorinated dibenzo-P-dioxins (PCDD), heavy metals, and Hg apply to municipal, medical, and hazardous wastes;

- Hazardous waste that contains over 1% halogenated organic materials must comply with 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.

The effect of these directives on the definition and legal and economic future of shredder residue treatment technologies is unknown. 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.

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).

A committee recently 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.

In Japan, a law governing the recycling of ELVs (End-of-Life Vehicle Recycling Law) went into effect on January 1, 2005 (Togawa 2006; also see Honda 2005 Annual Report, “End-of-Life Vehicle Recycling Law, 2005”). The law dictates that all automakers (domestic and foreign) charge car buyers recycling fees and assume responsibility for properly collecting and disposing of refrigerants, air bags, and shredder residue from scrap dealers.
In the United States, no such stringent regulations 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 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.
2 RECYCLING INFRASTRUCTURE AND STRATEGIES

Barriers to recycling in general and to plastics recycling in particular include available amounts, perceptions of quality, and lack of technology to recover quality recyclables economically.

At present, shredders are able to recover about 95% of the ferrous and non-ferrous metals in an automobile. To facilitate the recycling of non-metallic materials from shredder residue, the dismantling industry, shredding industry, and automobile manufacturers must work together. The shredding industry can provide expertise in shredding and separation of shredder residue components, and car manufacturers can design cars for easy dismantling of potentially reusable parts so that the dismantlers can recover more parts for reuse and recycling more efficiently and economically. The car manufacturers can also help by reducing the number of polymer species used in building vehicles and avoid using materials and substances of concern that could make recycling more difficult or more expensive.

Many 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) and greenhouse gas emissions. Water should be checked for contamination from liquid residue streams and by leachate from solid residue (Gesing 2004).

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 was on the second and fourth types. Later, emphasis shifted toward primary and chemical recycling of the organic materials.

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. It could also apply to the separation of individual components from shredder residue at high purity, with the intent of using those components as a blend with virgin material. 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. 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).

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 was that funded by the Energy Conversion and Utilization Technologies (ECUT) branch of the U.S. Department of Energy (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 were 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 listed below:

- Shredder residue contains substances of concern, including heavy metals and PCBs.
- The continuously changing composition of shredder residue demands that the design of the process incorporate ample tolerances to regularly meet product specifications and to prevent obsolescence.

Equipment that has been developed for the recycling of plastics from municipal solid waste 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’s r 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, solvents, 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). 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 produces steam and/or electricity. Shredder residue can be mixed with other wastes (such as municipal solid waste) and incinerated. Tests conducted in the United States and in other countries showed that shredder residue incineration is technically feasible. 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, and shredders) have to 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. They also have to comply with governing regulations.

3.1.1 Dismantling for Direct Resale

Over 80% of the 95% end-of-life vehicles that are recycled start their final journey at one of the more than 15,000 dismantling facilities in the United States, commonly called junkyards (Duranceau and Londell 1999). The other 20%, because of their age or condition, go directly to the shredders. At the dismantling facility, usable parts (such as radios, batteries, bumpers, windshields, whole car seats, door panels, transmissions, and engines) are manually removed for direct resale and reuse. Such parts as starters and alternators may be removed, refurbished, or remanufactured and sold.

U.S. dismantlers have also collected several items that are unusable at present for recycling. These include:

- Car batteries are collected for recycling of their lead, sulfuric acid, and polypropylene content.
- Catalytic converters are recycled for their precious metal catalysts.
- A few dismantlers also experimented with dismantling bumpers for recycling. Among the problems encountered in recycling the bumpers are the paint on the bumpers (Schultz 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 about 10 years ago. Polypropylene and thermoplastic olefinic (TPO) bumpers are also collected for recycling. Collecting, separating, and handling old bumpers is not always economical. American Commodities, Inc., developed a process for removing paint and other contaminants from polymeric regrind particles (Wisner 1999).
- Dismantlers also 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 that would be collected by an average dismantler would be small and, therefore, difficult to market

- Dismantlers also extract refrigerants from the vehicle. These generally end up being reused in some applications after purification.

In general, however, dismantling for the recovery of such materials as polyurethane foam, plastics, and rubber is not cost-effective (Christen 2002; Emblemsvag and Bras 1995; Chen, Navin-Chandra, and Prinz 1993; Coulter et al. 1996), primarily because (1) dismantling is labor-intensive and (2) only a small amount of material can be recovered at each of the more than 15,000 dismantling yards in the United States; therefore, the storage and transportation costs for most such materials are generally prohibitive.

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:

1. The U.S. infrastructure meets the recyclability targets of the EU Directive.

2. 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.
3. Significant improvements in recyclability are likely to come from increased glass or plastics recycling.

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

5. ARA members, in general, are likely to come very close to meeting many of the EU standards.

6. 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 will yield about 25 pounds of plastics available for potential recycling (Mark 2001). The economics of the process will still depend on other costs, including those for storage and transport. If the instrument panel can be built by using a single plastic material (such as polypropylene), then polypropylene will be less expensive to separate and recover.

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 determined.

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 recently 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:

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

2. 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; polyethylene terephthalate [PET] vs. polybutylene terephthalate [PBT]).
3. Specular-reflectance instruments are not adequate for identifying foams and elastomers because of their poor reflectance and inadequate signals.

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

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 Original Equipment Manufacturers (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 Londell 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 48 cents per pound (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, polyurethane 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.

- Type of vehicle did not matter much after the dismantler gains enough experience and can 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 had a lower melt flow rate than the virgin (prime) PP commonly used in automotive applications. Table 3.1 shows the properties of the recovered polypropylene and compares them with the properties of virgin automotive polypropylene.

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.

The study concluded that for ABS:

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

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

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

* PCR is post-consumer recyclate.
** 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)

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

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

- 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 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 housings 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. ABS containing recycled material from ELVs and electronics was used to make auto radiator grilles. No changes in tooling or processing conditions were needed. 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.

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 100% level.

- 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 is 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.
• The properties of PP are listed in Table 3.3, and the properties of ABS are listed in Table 3.4.

• Heavy metals are problem for PVC recycling.

3.1.1.3 Case Study 3 – BMW Dismantling

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 economics of dismantling operations, and

TABLE 3.3 Properties of Polypropylene (reproduced with permission; see Weatherhead 2005)

| Recycled PP Property                  | PRoVE 2 | | | | PRoVE 1 | 25/75 | PRoVE 1 | 25/75; 20% | PRoVE PP | 20% Talc filled | Specification |
|---------------------------------------|---------|---|---|---|---|---|---|---|---|---|---|---|
| MFR (melt flow rate) (g/10 min)      | 10.3    | 7.6 | 11.2 | 10.2-13.8 |
| Filler Content (%)                    | 11.6    | 22.3 | 26.6 | 17.4-23.6 |
| Density (g/cc)                        | 0.98    | 1.1 | 1.12 | 1.03-1.07 |
| Flexural Modulus at RT (MPa)          | 1800    | 2300 | 2320 | >2300 |
| Flexural Modulus at 140°C (MPa)       | 111     | 133 | 103 | >550 |
| Flexural Yield Strength at RT (MPa)   | 36.3    | 35  | 33  | 31.2-42.2 |
| Tensile Strength at yield (MPa)       | 22.7    | 22.4 | 20.2 | 21.7-29.3 |
| Tensile Strength at Max Load (MPa)    | 22.7    | 22.4 | 20.2 | 18.8-25.3 |
| Elongation at Yield (%)               | 4.3     | --  | --  | --  |
| Elongation at Break (%)               | 13      | --  | --  | --  |
| Shear Modulus at RT                   | --      | 726 | 644 | 926-1294 |
| Izod Impact Strength at 23°C (kJ/m²)  | 4.7     | 3.1 | 3.8 | 3.25-4.45 |
| Izod Impact Strength at 10°C (kJ/m²)  | 3.8     | 2.6 | 3.3 | 1.7-2.2 |
| Izod Impact Strength at -40°C (kJ/m²) | 2.6     | 2.2 | 2.3 | 0.85-1.15 |
| Heat Deflection Temperature Bf (°C)   | 94      | 93  | 102 | 100-130 |
| Heat Deflection Temperature Af (°C)   | 60      | 57  | 61  | 46.6-63.3 |
| Restricted Metals (ppm)               |         |     |     |     |
| Sb                                    | 10      | 10.9 | 5.4 | <5  |
| As                                    | <0.5    | 0.1  | 0.8 | <5  |
| Cr                                    | 5       | 49   | 15.2 | <25 |
| Cd                                    | 10      | 1    | 7.9 | <100|
| Pb                                    | 15      | 5    | 76.4 | <100|
| Hg                                    | <0.5    | 0.7 | 4.5 | <1  |
| Total Halogens (ppm), Cl, Br, I, F   | <15     | <15-25 | <15-25 | <50 |
| Windscreen Fogging (1 hr/16/hr)       | 77/87   | 74/81 | 53/77 | >90 |
TABLE 3.4 Properties of ABS (reproduced with permission; see Weatherhead 2005)

<table>
<thead>
<tr>
<th>Recycled ABS Property</th>
<th>PRoVE 2 100% ELV</th>
<th>PRoVE 1 25/75 (S1-Electronics)</th>
<th>PRoVE 1 25/75 (S2-Auto)</th>
<th>PRoVE ABS Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFR (melt flow rate) (g/10 min) 220°C</td>
<td>24.6</td>
<td>17.8</td>
<td>13.2</td>
<td></td>
</tr>
<tr>
<td>MFR (melt flow rate) (g/10 min) 230°C</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>14.5-19.6</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>1.08</td>
<td>1.05</td>
<td>1.05</td>
<td>0.74-1.21</td>
</tr>
<tr>
<td>Flexural Modulus at RT (MPa)</td>
<td>2130</td>
<td>2400</td>
<td>2410</td>
<td>&gt;1370</td>
</tr>
<tr>
<td>Flexural Modulus at 80°C (MPa)</td>
<td>1360</td>
<td>1560</td>
<td>1680</td>
<td>&gt;1450</td>
</tr>
<tr>
<td>Flexural Yield Strength at RT (MPa)</td>
<td>66.6</td>
<td>68.2</td>
<td>65.1</td>
<td>40.4-54.6</td>
</tr>
<tr>
<td>Tensile Strength at yield (MPa)</td>
<td>39.9</td>
<td>46.2</td>
<td>41.6</td>
<td>27.6-37.4</td>
</tr>
<tr>
<td>Tensile Strength at Max Load (MPa)</td>
<td>39.9</td>
<td>46.2</td>
<td>41.6</td>
<td>29.8-40.3</td>
</tr>
<tr>
<td>Elongation at Yield (%)</td>
<td>2.8</td>
<td>1.9</td>
<td>2.0</td>
<td>--</td>
</tr>
<tr>
<td>Elongation at Break (%)</td>
<td>7.4</td>
<td>13</td>
<td>8.2</td>
<td>10.4-14.4</td>
</tr>
<tr>
<td>Shear Modulus at RT</td>
<td>--</td>
<td>838</td>
<td>773</td>
<td>680-920</td>
</tr>
<tr>
<td>Izod Impact Strength at 23°C (kJ/m²)</td>
<td>6.2</td>
<td>16</td>
<td>9.4</td>
<td>&gt;15</td>
</tr>
<tr>
<td>Izod Impact Strength at 0°C (kJ/m²)</td>
<td>5.6</td>
<td>12</td>
<td>6.6</td>
<td>&gt;7</td>
</tr>
<tr>
<td>Izod Impact Strength at -40°C (kJ/m²)</td>
<td>3.7</td>
<td>7.4</td>
<td>4.4</td>
<td>&gt;4</td>
</tr>
<tr>
<td>Heat Deflection Temperature Bf (°C)</td>
<td>90</td>
<td>93</td>
<td>93</td>
<td>&gt;90</td>
</tr>
<tr>
<td>Heat Deflection Temperature Af (°C)</td>
<td>81</td>
<td>81</td>
<td>82</td>
<td>69.3-93.7</td>
</tr>
<tr>
<td>Vicat (°C)</td>
<td>97</td>
<td>98</td>
<td>105</td>
<td>82-112</td>
</tr>
<tr>
<td>Restricted Metals (ppm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>1</td>
<td>&lt;0.01</td>
<td>15</td>
<td>&lt;5</td>
</tr>
<tr>
<td>As</td>
<td>0.5</td>
<td>&lt;0.01</td>
<td>&lt;0.5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Cr</td>
<td>0.5</td>
<td>1</td>
<td>5</td>
<td>&lt;25</td>
</tr>
<tr>
<td>Cd</td>
<td>1.5</td>
<td>&lt;0.01</td>
<td>1</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Pb</td>
<td>10</td>
<td>4</td>
<td>&lt;0.5</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Hg</td>
<td>0.5</td>
<td>1.1</td>
<td>&lt;0.5</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Total Halogens (ppm), Cl, Br, I, F</td>
<td>&lt;15</td>
<td>&lt;15-25</td>
<td>&lt;15-25</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Windscreen Fogging (1 hr/16/hr)</td>
<td>96/98</td>
<td>91/94</td>
<td>93/92</td>
<td>&gt;90</td>
</tr>
</tbody>
</table>

- 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,
- Jig for safe shattering and collection of window glass,
- 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 Study of Radiator End Caps

The VRP and the 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 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 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 pounds of interior trim parts obtained through selective dismantling has been completed, and streams of ABS and PP have been 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:

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

2. Vehicles with extensive damage have lower recyclability.

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

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

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

6. 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 to 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.

After the dismantler is finished with the vehicle, the “hulk” is sold to a shredder for its metals value.
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. In the United States alone, the scrap metal processors handle over 62 million tons of scrap metal annually. 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 4).

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, cook tops, 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;

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• 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 polyurethane foam insulation. 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 ABS as polystyrene (PS), while the opposite is true for units built in Europe.

The American Plastics Council (2005) estimated that by 2007, refrigerators alone will contain 126 million pounds of polyurethane foam and 203 million pounds of other plastics (primarily ABS and HIPS).

Obsolete white goods (home appliances and related products) are collected by three main routes: (1) people who deliver new appliances and pick up the old ones, (2) municipal waste collectors, and (3) at the landfill. Some of these units are refurbished and sold while others are shredded.

When old units are collected, they are generally examined so that the units that can be refurbished and resold can be selected. Other units that could not 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 substances of concern (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 present in the compressor of refrigeration equipment. 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, such components 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. 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 pounds of shredder residue over a period of about six months. Data for shredder residue 2 represent the averages from processing over 75,000 pounds of shredder residue over a period of about six 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>
<thead>
<tr>
<th>Material</th>
<th>Weight Percent in Shredder Residue 1</th>
<th>Weight Percent in Shredder Residue 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fines (&lt;1/4 in.)</td>
<td>24</td>
<td>60</td>
</tr>
<tr>
<td>Polymer concentrate</td>
<td>36</td>
<td>14</td>
</tr>
<tr>
<td>Oversized lights (polyurethane foam)</td>
<td>05</td>
<td>01</td>
</tr>
<tr>
<td>Oversized heavies (metals, rocks)</td>
<td>08</td>
<td>02</td>
</tr>
<tr>
<td>Lights rejects</td>
<td>06</td>
<td>02</td>
</tr>
<tr>
<td>Ferrous-metal-rich fraction</td>
<td>01</td>
<td>01</td>
</tr>
<tr>
<td>Non-ferrous-metals-rich fraction</td>
<td>04</td>
<td>05</td>
</tr>
<tr>
<td>Loss (moisture, dust, sweeps)</td>
<td>16</td>
<td>15</td>
</tr>
</tbody>
</table>
TABLE 4.2 Composition of Polymer Concentrates Produced from Two Shredder Residues Described in Table 4.1

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

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 it varies over a wide range. For example, the reported hydrogen values are between 2 and 7.
### TABLE 4.3 Elemental Analysis of Organic Fraction of Shredder Residue (weight percent, dry basis)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>55</td>
<td>51</td>
<td>57</td>
<td>18</td>
<td>60</td>
<td>60–90</td>
</tr>
<tr>
<td>H</td>
<td>7</td>
<td>7</td>
<td>8</td>
<td>2</td>
<td>7</td>
<td>4–6</td>
</tr>
<tr>
<td>N</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>&lt;1</td>
<td>2</td>
<td>0.6–3</td>
</tr>
<tr>
<td>O</td>
<td>13</td>
<td>–</td>
<td>21</td>
<td>17</td>
<td>8</td>
<td>–</td>
</tr>
<tr>
<td>Cl</td>
<td>1.82</td>
<td>3.7</td>
<td>0.2</td>
<td>0.05</td>
<td>2.5</td>
<td>5–30</td>
</tr>
</tbody>
</table>

* 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; Lundqvist et al. 2004) and 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 two billion pounds of synthetic polymers (five million tons shredder residue × 2,000 lb/ton × >20% polymers) in the five million tons of shredder residue that are disposed of in landfills. The embodied energy of these polymers is about five trillion Btu (two billion pounds × 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, not just as fillers. These technologies include removal of SOCs to acceptable levels.

- Lack of markets for recycled materials at their fare market value.
- Insufficient quantities that can be generated 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 substances of concern (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 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 (Raschhofer 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 the rubber from the polymer concentrate;
3. Separation of wood and rubber from the plastics;
Several Polymers Appear in Every Specific Gravity Range

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 National Laboratory 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 ARGONNE’S MECHANICAL SEPARATION SYSTEM

Argonne National Laboratory 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 two 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 non-ferrous metals (larger than 6 mm).
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 polyurethane foam. 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 polyurethane foam, 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 fits 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 non-ferrous 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 non-ferrous 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 remove fines and air classified to remove residual polyurethane foam pieces, dust, and other lights.

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

5.2 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 polyurethane foam and contains some fabrics, fibers, and some plastics that are generally larger than what fits 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 polyurethane foam 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 was 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 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 non-ferrous 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 was DM 6.5 million, including DM 5 million for equipment and DM 1.5 million for building and utilities.

5.7 OTHER MECHANICAL EQUIPMENT FOR SEPARATING SOLID MIXTURES

Mechanical systems, such as gravity separators, electrostatic separators, vibrating screens and rapid identification and sorting systems (color, infrared, x-ray, 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.

5.7.1 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**. Automobile shredding is an integral part of Chaparral’s operations. In 1990, Chaparral installed an eddy current system to recover non-ferrous 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.)

### 5.7.2 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 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

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5 This case study was featured in “By-Product Synergy Primer” (1997), produced by the Business Council for Sustainable Development - Gulf of Mexico.
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, will increase the dielectric constant. Plastics generally have high surface resistance (>10¹⁵ 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.

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 PlasSep Ltd., Canada⁶. MBA concluded that:

1. The device did not separate rubber from plastics.

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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 PlasSep 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\(^7\) has reportedly commercialized a highly efficient electrostatic separator (Daiku et al. 2001). Key features are that (1) the device can separate high-purity plastics from mixed plastics (for example, applying this separator to a separation of PE and PP mixture, both plastics are separated with more than 99% purity) and (2) the device is claimed to be novel because in the separator, the charged plastics are supplied to an electrostatic field while touching a drum electrode.

6 COMBUSTION OF SHREDDER RESIDUE FOR ENERGY RECOVERY

Incineration could be a cost-effective technique to dispose of shredder residue because its fuel value is nearly half that of coal — in fact, shredder residue will burn without the need for supplemental fuel. Shredder residue is also low in sulfur. Several studies addressed this topic, and scrap processors built a number of full-scale shredder residue incinerators (Hubble, Most, and Wolman 1987; Dean et al. 1985; Bilbrey et al. 1979; Ellsworth et al. 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. Incineration is not widely accepted because of a combination of economic, environmental, and logistic problems, including the following:

- Disposing of shredder residue in landfills is still less expensive than incineration in most U.S. locations;
- Environmental concerns persist because shredder residue contains substances of concern, including chlorinated materials (PCBs and PVC) and heavy metals; and
- Shredder residue has high ash content (~50%) and 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, will make the flue gas corrosive, which will increase the materials and maintenance costs of the incinerator. Chlorine is also suspected of increasing the risk of producing dioxins and benzofurans during combustion (Hubble et al. 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 will also be required to attain such temperatures, which, of course, increases operating costs. Moreover, location, installation, and operation of incineration facilities can be challenged, which further complicates the permitting process.

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.

A study sponsored by the U.S. Department of Energy (DOE) evaluated the potential of harvesting some of the energy released in 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%.

4. The study demonstrated that the flue gas can be scrubbed to comply with governing environmental regulations by using state-of-the-art equipment.

5. 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 postprocessed 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.

6. 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.

7. On-site electricity generation was also evaluated. In general, the amount of electricity that could be produced from the shredder residue available at most

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8 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.
shredders exceeds the on-site electricity requirements of the shredder, and this excess electricity can be sold back to the utility.\textsuperscript{9}

A later study conducted by the U.S. Environmental Protection Agency (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.”\textsuperscript{10} 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.”

In the 1990s, Switzerland experimented with co-incineration of shredder residue with municipal solid waste (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 and 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\textsubscript{x}, and SO\textsubscript{x} were high. For example, CO concentrations in the flue gas as high as 1.6 vol. \% were observed, even when the O\textsubscript{2} concentration was 15 vol. \%. This indicates that complete combustion was not achieved. In the presence of such high concentrations of O\textsubscript{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.

\textsuperscript{9} 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).

\textsuperscript{10} 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 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 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 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 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 can be obtained dry (<7% moisture), the cost of processing it will 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 will be required to replace a ton of coke in the blast furnace. Therefore, from an economics point of view, it looks like a good potential application, if it can replace some of the coke. This application will 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.

![Capital Cost Distribution, %](image)

**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 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):\(^1\)

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>Moles/lb ASR</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>30</td>
<td>0.025</td>
</tr>
<tr>
<td>O</td>
<td>14</td>
<td>0.0086</td>
</tr>
<tr>
<td>H</td>
<td>4</td>
<td>0.039</td>
</tr>
</tbody>
</table>

- 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 to 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 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 (Stahlwerke 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

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\(^1\) Note: The carbon and hydrogen in one pound of shredder residue contains approximately the reduction capacity of 0.32 pounds of coke. Using the ratio of organic material to actual shredder residue leads to one pound 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.
organics fraction from shredder residue. The objectives were to gain more insight into the 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: \( \text{ASR/Coke (replacement ratio)} = (\text{coal/coke replacement ratio}) \times (\text{ASR energy content/coal energy content}) \). 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):

- It was suggested that the material be dried after granulation.
- 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 what is estimated.

On the basis of discussion 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 per ton of organic product), and the operating cost became $34.25 per 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 and $17 per 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 because it will 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, which is the thermal decomposition of organic material in an oxygen-deficient environment, 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 (cadmium, nickel, and zinc), the solid product could not be disposed of in landfills.
In 1996, Day, Cooney, and Shen 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 CH₄, H₂, CO, CO₂, 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% CO₂ and CO, 5% H₂O, 3.5% HCL, 2.5% NH₃, and 0.4% SO₂ 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.¹²

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).

¹² See http://www.vdq023.org/ssc/annx_039.htm
Some of the advanced pyrolysis processes that processed 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 municipal solid waste (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 Class 2 landfill in Rhine-Westphalia. Slag pH, phenol content, and residual antimony exceeded limits for disposal in a Class 1 landfill. The process requires a tipping fee of 150 Euro per ton. The technology has reportedly been licensed to Mitsui & Co., Ltd. (Tokyo, Japan), which is marketing the technology.

**The Batrec Process.** 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 and 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.

**The Takuma Process.** Another process, known as the Takuma process, is being used in Japan. A plant that has 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.

Another process developed in Europe is the CiTRON oxyreducer process (Brüggler 2002). A large-scale plant is in operation and 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.

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14 “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
oxides and hydroxides to their elemental state. The low-boiling metals (zinc, lead, cadmium, and 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 (FeO₂, Al₂O₃, CaO, and SiO₂) are discharged from the oxyreducing reactor. The chlorine in the waste is converted to sodium and potassium chlorides (NaCl and KCl) (Brüggler 2002).

7.2 GASIFICATION

Gasification is a thermo-chemical process that can convert the organic content of a material (such as shredder residue) into a gaseous mixture of primarily CO, H₂, CO₂, 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, H₂, and light hydrocarbons and
- Reduced metals (e.g., iron, copper, 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 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/ft³. This
product would be considered a low-Btu industrial fuel gas and would have to be used on-site because it is not economical to transport it 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-h 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 (Sekundarohstoff-Verwertungs-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.

Seven reactors, each with a throughput of 11–12 tonnes per hour, were in operation in 2003, and over one million tons of different types of waste have been gasified. The mixed-waste material is processed into high-purity methanol. 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 is necessary for it to be economical. The SVC Commercial gasification facility currently processes 450,000 tons per year of solid waste and 50,000 tons per year of contaminated oil and oil-water emulsions in a Lurgi moving-bed gasifier. The feed to the plant contained 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).

**Plasma Process.** Another form of gasification that has been used experimentally on shredder residue is plasma gasification (Leal-Quirios 2004). This process takes place at very high temperatures (~5,000°C) and atmospheric pressure. In the process, the organic material is converted to a gas consisting primarily of CO and H2. The inorganic residue is melted into a slag that, when cooled, solidifies into a potentially useful construction material. The slag passed the Toxicity Characterization Leaching Procedure (TCLP) test, and the concentration of dioxins in
the gas phase was about 100 times lower than what is common for conventional incineration plants.

**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 employed extensive gas cleanup. Quench and cooling of the combustion gases follows for removal of particulates and acid gases. It also produced 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. Inorganics 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 per ton is estimated by the process developers for a plant processing 50,000 t/yr of shredder residue and producing steam from the heat. The gate fee would increase to 100 Euro per ton for an equivalent-capacity plant converting the steam to electricity. At 10,000 t/yr, the gate fees would exceed 175 Euro per ton.

**Montello Process (Italy) Process.** This process is an integrated gasification/scrap iron preheat process. Limited testing of the process was conducted (two months in 1993; two 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 one ton of shredder residue to four 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.

**The RESHMENT® Process.** This process — developed¹⁵ by Conzepte Technik Umwelt AG (CTU), VAI (Sauert et al. 2001), and Babcock Borsig Power¹⁶ 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.\textsuperscript{17}

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\textsuperscript{®} technology for Europe’s first plant to thermally treat shredder residue\textsuperscript{18} (“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 per year, including 55,000 tons per year of shredder residue, and Plant Start-up is scheduled for 2007 (Sauert 2005).\textsuperscript{19}

\textit{Dry Distillation/Gasification.} This process, known as Dry Distillation/ Gasification, was developed in Japan (Horii and Iida 2001; Kusakam 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\textsubscript{2}. The residence time is between 30 and 60 min. The wafers are also doped with 1.2% of Ca(OH)\textsubscript{2} for capturing the chlorine that is 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 (6,665 Btu/lb). The gas contained about 30% combustible gases, primarily CH\textsubscript{4} (93.6%) and C\textsubscript{2}H\textsubscript{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.

\textit{The 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.\textsuperscript{20}) The process was proven in a large-scale demonstration facility and commercialized by the THERMOSELECT company.

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 municipal solid waste 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 h 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 s. The gaseous products leave at

\textsuperscript{17} Swiss Auto Recycling Foundation— Annual Report 2001.


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 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, and no refractory wear beyond what is observed when processing municipal solid waste was apparent.

The inorganic components of the waste will be 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, sulphur, 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 (CWT) 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 and 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:

- The tests demonstrated the ability of the Thermal Conversion Process (TCP) to convert shredder residue into oil and solid product streams (CWT 2004).
- The PCBs in the shredder residue dissolve in the hot oil and are eventually destroyed during hydrolysis. As a result, their concentration was reduced from 35–65 ppm to less than the detection limit of 2 ppm.

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

* American Petroleum Institute
• 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.

• 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 three years would be approximately $4,600,000. The results are summarized in Table 7.2.

<table>
<thead>
<tr>
<th>TABLE 7.2 Results of the Economic Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total cost of plant</td>
</tr>
<tr>
<td>Start-up costs and working capital</td>
</tr>
<tr>
<td>Financing</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Total investment</td>
</tr>
<tr>
<td>Tipping fee</td>
</tr>
<tr>
<td>Number of employees</td>
</tr>
<tr>
<td>Repairs and maintenance</td>
</tr>
<tr>
<td>License fee</td>
</tr>
<tr>
<td>Conversions:</td>
</tr>
<tr>
<td>Oil</td>
</tr>
<tr>
<td>Solids/metals</td>
</tr>
<tr>
<td>End product sale prices:</td>
</tr>
<tr>
<td>Oil</td>
</tr>
<tr>
<td>Metal</td>
</tr>
</tbody>
</table>
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 pounds 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 (“Plastics Recycling” 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 VOCs into the air that otherwise will be emitted during the making of an equivalent amount of virgin PUF.

The Argonne process consist 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 min, while in the conventional rotary drum dryer, drying time was over three 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 eight-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
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/ft³ Argonne foam) was equivalent to that of the conventional fiberpad (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

<table>
<thead>
<tr>
<th>Type of Expenditure or Earning</th>
<th>Expenditure or Earning ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual Revenues @ $0.30/lb foam</td>
<td>600,000</td>
</tr>
<tr>
<td>Credit for Avoided Disposal @ $20.00/ton</td>
<td>20,000</td>
</tr>
<tr>
<td><strong>Total Annual Revenues</strong></td>
<td><strong>620,000</strong></td>
</tr>
<tr>
<td>Operating Costs:</td>
<td></td>
</tr>
<tr>
<td>Labor, 2 operators at $18/h</td>
<td>86,400</td>
</tr>
<tr>
<td>Electricity, 150 kWh/h @ $0.10/kWh</td>
<td>36,000</td>
</tr>
<tr>
<td>Natural Gas, 1 million Btu/h @ $4.00/million Btu</td>
<td>9,600</td>
</tr>
<tr>
<td>Chemicals, 0.01 lb/lb foam @ $0.85/lb</td>
<td>17,000</td>
</tr>
<tr>
<td>Disposal Costs for Wet Dirt @ $20.00/ton</td>
<td>8,000</td>
</tr>
<tr>
<td>Disposal Costs for Oils @ $100.00/barrel</td>
<td>63,500</td>
</tr>
<tr>
<td>Maintenance, @ 3.5% of Capital</td>
<td>22,750</td>
</tr>
<tr>
<td><strong>Total Annual Operating Costs</strong></td>
<td><strong>243,250</strong></td>
</tr>
<tr>
<td>Annual Earnings before Interest, Taxes, Depreciation, and Amortization</td>
<td>376,750</td>
</tr>
</tbody>
</table>
FIGURE 8.4  Noise Reduction of Automotive Carpet Underlayment (lb/ft$^3$)

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 polyurethane foam 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 polyurethane foam product from shredder residue, and production capability of the equipment met design throughput expectations. Although this equipment was successfully operated, 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 have to 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 2003; Jody 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 that 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-fillednylons from the sinkers of step 1.

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


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

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

* pounds per square inch

- Screen changes were required approximately every five minutes, and 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 (RPI) 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) polyurethane foam cleaning for foam recovery. Salyp built a pilot plant, which operated for about a year.

Salyp acquired a license to the polyurethane foam recovery technology developed at Argonne National Laboratory 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 polyurethane foam, 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-SICON RECYCLING PROCESS

Construction of the first large-scale Volkswagen-SiCon plant for recycling shredder residue was initiated in 2005 in Austria.21 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 2005).22 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% non-ferrous. 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.

8.7 THE GALLOO PROCESS FOR RECOVERING 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 non-ferrous 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, non-ferrous metals, and stone and rock; this fraction is processed in a heavy-media separation plant to recover the non-ferrous 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, INC., 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 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 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,” and 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.

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

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

* ksi = kips per square inch
N/A - not analyzed or not determined

### 8.9 THE TOYOTA PROCESS

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 end-of-life vehicles per month. In 2000, the plant demonstrated an overall vehicle recycling rate of 90%. 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 polyurethane foam and fabrics.** The foam and fabric are sorted and recycled into soundproofing material.
- **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.
- **Recycling of automotive glass as raw material for the ceramics industry.** The glass is ground fine and then used for making tiles with “remarkable density and strength, and also used as materials for landscaping pavement.”

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• “Melt-bricking technology,” in which the shredder residue is heated to melt the organics. Heating reduced its volume by about 80%. Lead leaching also reduced its concentration by 75–80%, enabling Toyota to meet the new regulations for controlled landfill sites.

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 about 1,600°C or more to form slag.

8.10 CENTRIFUGATION PROCESSES

Jan H. Schut, in a Plastics Technology article24, reported that Delphi and Result Technology AG 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 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 (see also Section 1.6.3.3).

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

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8.10.2 The Result Technology AG Process

Result Technology AG developed a process for de-laminating multilayered plastics and metals (see footnote 24). 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, “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:

- 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. These can be separated into 99%-pure ABS and 97%-pure PVC, the user reports. With secondary mechanical separation, both streams reportedly can get to 100% purity. Operating cost is about 5¢/lb.”

- In Sweden, a plant recovers metals from the shredder residue.

- Tests were 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 99%-pure PET product.

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

Polyamid 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 to produce 20 million and 26 million pounds 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 RAPID IDENTIFICATION AND SEPARATION AUTOMATED PROCESSES

8.11.1 Infrared Separators

IR separators for mixed plastics containing black plastics that contain significant amounts (>5%) of carbon black are still in the research and development stage. This technology is widespread 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 and no 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;
- Demonstrated 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. The company was acquired by CP Manufacturing in 2003.
- TiTech, which has a representative in Naperville, Illinois.
8.11.2 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 polyurethane foam from the polymer concentrate and
- White plastics from non-white plastics.

The disadvantages of color sorters are that 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) and
- Are still expensive for the tasks they accomplish, when applied to plastic chips.

8.11.3 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.

8.11.4 UV-Fluorescence for the Separation of Nylon-PC Mixtures

This separation method has been successfully applied mostly to the separation of mixtures containing nypons and PC because these two materials fluoresce differently when exposed to an ultraviolet (UV) source.
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 specification 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 being practiced at a commercial scale in Europe (see footnotes 24 and 25). The first is the Solvay Chemicals Co. “Vinyloop” batch process25, and the second is the Delphi process, which was developed by Delphi Automotive Systems, in cooperation with the University of Wuppertal in Germany.

9.1.1 Rensselaer Polytechnic Institute Process

Lynch and Nauman (1989) and Nauman and Lynch (1993, 1994) at 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 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 Argonne Process

Argonne National Laboratory 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 et al. 1990). The approach involved 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 dissolves 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 volatile organic compounds (VOCs).

Although the process was technically feasible in that it produced ABS, PVC, and PP/PE at high purity (>98%), process economics were not favorable because the auxiliary system costs associated with the safety and environmental control equipment required when solvents are used were prohibitive relative to the quantity of specific thermoplastics that could be recovered per

pound of shredder residue processed (Jody, Daniels, and Teotia 1996; Jody, Daniels, and Pomykala 1996; Jody, Daniels, and Brockmeier 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 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, and the first commercial-scale plant was built in Italy in 2001 at a cost of $7.2 million and has a design capacity to recover 22 million pounds of PVC annually. The estimated cost of PVC recovery was 13¢/lb. Another 20-million-lb/yr plant was built in Italy in 2002, and 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.

9.1.4 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 Corporation26, 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 end-of-life vehicles in Europe.

See: “Delphi Recycling Efforts in Europe Benefit the Environment, 400 Metric Tons of PVC Recycled Annually.”
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 polyurethane foam (Braslaw and Gerlock 1984; Mahoney et al. 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 cost. 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) and Sendijarevic and Sendijarevic (2005) have been developing a process for the hydrolysis of polyurethane foams that does not require different foam materials to be presorted.

9.2.1 The Ford Motor Co. Process for Producing Very High Quality Polyols

Mahoney, Weiner, and Farris (1974) of Ford Motor Co. 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 because 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 flow becomes negative. More recent developments in the hydrolysis of shredder residue polymers are discussed below.

9.2.2 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 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 to 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

---

**FIGURE 9.1 Glycolysis Conceptual Process Flow Sheet**

---

**FIGURE 9.2 Glycolysis Process Concept**
TABLE 9.1 Glycolysis Reaction Input Materials and Product Yield

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

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.

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 substances of concern 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). 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. KOH was preferred over NaOH as a catalyst. By using optimized reaction conditions with diethylene glycol (DEG) and 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.

Initial 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 per pound, and the polyol (10% propoxylated) can be produced at $0.33 per pound. The market value of the virgin propoxylated polyol is estimated at $0.80 per pound.

9.2.3 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.27

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.28 The process consists of five basic sections: feed preparation, fluidized bed depolymerizer, hydrochloric acid removal section, a quench bath, and products separators.


Another process was 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 was first melted and filtered to separate the glass fibers. The PA was then depolymerized to produce the monomer, caprolactam. The recovered caprolactam was subsequently used to make PA6, the physical properties of which were not significantly different from those of the virgin original PA.

9.4 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.

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.”
10 SUBSTANCES OF CONCERN IN SHREDDER RESIDUE

Substances of concern 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.

The presence of SOCs in current vehicles and/or in other durable goods that are presently recycled with end-of-life vehicles 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 original equipment manufacturers (OEMs), chemical suppliers, and two professional organizations are working together on the development of a common data base of substances of concern. The data base 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 PBCs and heavy metals from both dirty plastics and polyurethane foams. 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 need to 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, will also require a similar or even higher stringent removal for selected metals and PCBs (Mark and Picotl 2001).

Specific substances of concern are discussed in Sections 10.1–10.3.

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 the PCBs is still not completely understood but historically 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 (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 (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>
<thead>
<tr>
<th>Output Stream</th>
<th>Input Material to Shredder</th>
<th>Mean PCBs Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh fluff</td>
<td>Auto</td>
<td>32</td>
</tr>
<tr>
<td>Fresh fluff</td>
<td>Mixed</td>
<td>180</td>
</tr>
<tr>
<td>Fresh fluff</td>
<td>White Goods</td>
<td>80</td>
</tr>
<tr>
<td>Stored fluff</td>
<td>–</td>
<td>68</td>
</tr>
<tr>
<td>Spillover from conveyors</td>
<td>–</td>
<td>28</td>
</tr>
<tr>
<td>Ferrous</td>
<td>–</td>
<td>0.2</td>
</tr>
<tr>
<td>Nonferrous</td>
<td>–</td>
<td>1.0</td>
</tr>
<tr>
<td>Soil under fluff</td>
<td>–</td>
<td>44</td>
</tr>
</tbody>
</table>
10.1.1 Troy Polymers, Inc., Studies

Troy Polymers conducted studies for VRP, Argonne, and APC to develop technology to identify and/or cost-effectively remove PCBs and other substances of concern 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 Removal of PCBs

Bench-scale screening of 11 surfactants and three organic solvents for the removal of PCBs and other contaminants from polymers derived from shredder residue was conducted (Sendijarevic 2004). Multiple samples of mixed plastics and foam that was recovered from shredder residue were used in the study. The surfactant TRITON RW 50 was found to be the most efficient surfactant among the ones tried. 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>
<thead>
<tr>
<th>Designation</th>
<th>PCBs before Washing (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plastics</td>
<td>2.8 ± 1.4</td>
</tr>
<tr>
<td>Foam</td>
<td>27.2</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Surfactant or solvent used</th>
<th>PCBs in plastics after washing (ppm)</th>
<th>PCBs in foam after washing (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triton DF-12</td>
<td>&lt;1</td>
<td>2.4</td>
</tr>
<tr>
<td>Triton RW-100</td>
<td>&lt;1</td>
<td>2.7</td>
</tr>
<tr>
<td>Tergitol TMN-6</td>
<td>&lt;1</td>
<td>4.1</td>
</tr>
<tr>
<td>Bio-Terge Pas-8S</td>
<td>3.2</td>
<td>6.0</td>
</tr>
<tr>
<td>Triton RW-50</td>
<td>&lt;0.08</td>
<td>2.0</td>
</tr>
<tr>
<td>Triton RW-75</td>
<td>—</td>
<td>4.7</td>
</tr>
<tr>
<td>No surfactant used</td>
<td>—</td>
<td>6.2</td>
</tr>
</tbody>
</table>

10.1.1.2 Testing of Commercially Available Cleaning Equipment Using Aqueous Solutions

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

1. Conventional methods that include 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 and 0.5 in. In each of these large tests, the washed material was “visually” clean in terms of dirt and oils. However, PCBs analyses were highly variable and indicated that in some cases, the PCBs concentration had increased. As a result, it was determined that the PCBs 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 will be recovered from shredder residue — efficiently and economically.

10.1.2 Evaluation of the Variability of PCB Sampling and Analytical Procedures

Troy Polymers 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 analysis 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,
• PCBs extraction procedure,
• Analytical procedures, and/or
• Interference from other compounds.

To investigate the possible interference of phthalates in the PCBs 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

<table>
<thead>
<tr>
<th>Weight-Percent of Phthalates Added</th>
<th>PCBs Concentration (ppm) by GC/ECD</th>
<th>PCBs Concentrations (ppm) by GC/MS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.6+/-0.3</td>
<td>7.9+/-1.0</td>
</tr>
<tr>
<td>0.5</td>
<td>4.7+/-0.3</td>
<td>7.4+/-0.2</td>
</tr>
<tr>
<td>1.0</td>
<td>5.1+/-0.6</td>
<td>7.0+/-0.4</td>
</tr>
<tr>
<td>2.5</td>
<td>4.8+/-0.3</td>
<td>7.4+/-0.3</td>
</tr>
</tbody>
</table>

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 made of chips that were about 0.2 in., and the other was granulated to about 0.04 to 0.08 in.). Typically in PCBs analyses, extractions are done on a few grams of material, even though the dirt, oil, and the 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 PCBs analytical procedures. Extracts from nine sonications of 300-g samples were also analyzed for PCBs by the three laboratories. The analysis leads 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 for the un-granulated, it was 10 ppm. Obviously, the granulated samples have 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 un-granulated samples.
10.1.3 Evaluation and Testing of Solvent-Based Washing Systems

Troy Polymers 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. Environmental Technology Unlimited 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.
- itec Environmental Group reduced PCB levels in the plastics from 11 ppm to 2.8 ppm via solvent washing; no CO₂ treatment, which normally follows the basic process, was used.
- Cool Clean Technologies technology used CO₂ only. Washing failed to remove the PCBs.

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 of the samples that were cleaned.

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 10.4). The Troy Polymers, Inc. (Sendijarevic 2004), study determined the concentration of 10 metals in the shredder residue plastics and foam, before washing (Table 10.5). The results show that the concentration of lead is the highest. Washing was
# TABLE 10.4 Heavy Metals in Shredder Residue (EPA 1991)

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Mean Concentration (ppm*)</th>
<th>95% Confidence Interval (ppm*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Lead</td>
<td>2,800</td>
<td>1,800–4,100</td>
</tr>
<tr>
<td>Total Cadmium</td>
<td>47</td>
<td>31–65</td>
</tr>
</tbody>
</table>

* ppm = parts per million

# TABLE 10.5 Concentration of Heavy Metals in Plastics and Foam from Shredder Residue before Washing (Troy Polymers, Inc., study)

<table>
<thead>
<tr>
<th>Heavy Metal</th>
<th>Dirty Foam (ppm*)</th>
<th>Dirty Plastics (ppm*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>&lt;0.2</td>
<td>&lt;0.36</td>
</tr>
<tr>
<td>Barium</td>
<td>38.9</td>
<td>28</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1.34</td>
<td>0.89</td>
</tr>
<tr>
<td>Chromium</td>
<td>5.54</td>
<td>4.8</td>
</tr>
<tr>
<td>Copper</td>
<td>37.9</td>
<td>17</td>
</tr>
<tr>
<td>Lead</td>
<td>200</td>
<td>61</td>
</tr>
<tr>
<td>Selenium</td>
<td>&lt;0.2</td>
<td>1.3</td>
</tr>
<tr>
<td>Silver</td>
<td>&lt;0.05</td>
<td>&lt;0.26</td>
</tr>
<tr>
<td>Zinc</td>
<td>618</td>
<td>380</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.15</td>
<td>0.05</td>
</tr>
</tbody>
</table>

* ppm = parts per million

effective in reducing the concentration of all heavy metals (Table 10.6), except for mercury, which was initially low. The concentration of chromium on plastics did not appear to have changed upon washing, although it was reduced to below-detectable levels in the foam.

## 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.
The brominated group, or polybrominated diphenyl ethers (PBDEs), appears to have gained an increased share of the market in the last decade. PBDEs are used in plastics, foams, circuit boards, rubber, carpets, textiles, and other products. 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 found rising levels of PBDEs in breast tissue and in sport fish and bird eggs from San Francisco Bay (Kay 2003; Madsen, Lee, and Olle 2003). They are also suspected of interfering in 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 pounds of PBDEs were used in North America alone, which is about half the world market (Madsen, Lee, and Olle 2003). In early 2003, the European Union 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 that studies show that it does not present any significant risk to humans or the environment.
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. 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 that they can incorporate recyclability into the process of designing polymer electrolyte membrane (PEM) fuel

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 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 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 will be sold in 2008.30 Rising oil prices will most likely accelerate the production and sales of such vehicles. 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). HEVs are powered by a

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30 Dr. Ken Heitner, Advanced Battery Readiness ad hoc working group meeting, Feb. 28–Mar 1, 2001, Hyatt Arlington Hotel, Washington, D.C.
combination of an internal combustion engine and a battery. Therefore, HEVs can get higher 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.\(^{31}\)

Since the 1980s, several battery chemistries were studied for EV and HEV applications, including sodium beta, nickel-cadmium (Ni-Cd), nickel metal hydride, lead-acid, lithium-ion, lithium polymer, lithium-ion with polymer electrolyte, and lithium nickel manganese batteries. Today, nickel metal hydride and lithium batteries are the leading candidates. The batteries used or considered for use in such vehicles include lithium ion, lithium polymer, magnesium-lithium, nickel metal hydride, sodium nickel chloride, lead acid, and nickel zinc batteries.\(^{32}\) 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 iron 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 of Construction of the Leading Batteries and Their Values

#### 11.2.1.1 Nickel-Metal Hydride (Ni-MH) Cells for EVs

Figure 11.1 shows the approximate weight % of materials that make up the nickel-metal hydride 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 (for example, 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, when present, do exist. Metal hydride electrodes, which represent about 23% of the weight and cost of the materials, are not recycled as value-added.

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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)
products at present. For example, in the Inmetco process, they go to low-value use as road aggregate. These contain rare earth metals — zirconium and titanium — that are expensive, and 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” because most of the cost is in making it from its materials of construction.

11.2.1.2 Lithium-Ion (Li-Ion) EV Battery

Figure 11.3 shows the approximate weight % 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 have to 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. It may be used for other applications.

![Wt % of Different Materials in Li-ion EV Batteries](image)

**FIGURE 11.3 Materials of Construction of the Li-Ion Battery for EVs** (Gaines 2000; Gaines, Elcock, and Singh 2002)
11.2.1.3 Li-Ion HEV 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).
Materials Distribution in Li-ion HEV Batteries

- Cathode, 23%
- Electrolyte, 14%
- Separator, 5%
- Aluminum, 28%
- Copper, 13%
- Anode, 4%
- Other, 14%

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

Cost of Different Materials in Li-ion HEV Batteries, %

- Cathode, 35%
- Electrolyte, 22%
- Separator, 25%
- Can & Vent, 6%
- Graphite, 4%
- Copper, 5%
- Aluminum, 3%

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

**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 Ni and Fe for use in stainless steel, and
4. Send the metal hydride elements to slag (low value; use as road aggregate).

Inmetco also recycles nickel cadmium, alkaline, sealed lead acid, and lithium 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, in Dothan, Alabama, recycles lithium 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 h, 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 who 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 nickel-metal hydride 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 ALUMINUM AND MAGNESIUM FROM FUTURE VEHICLES

To build lighter-weight vehicles, automakers will likely replace some steel with 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 has to be recycled. However, there are some obstacles that need to be overcome to maximize the value of the recovered light metals. One of the obstacles is the need for cost-effective technology 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; and (iv) finally achieve a >80% recycling goal, since the market for mixed scrap is limited to the automotive market.”
11.4 ARGONNE THERMAL TREATMENT PROCESS FOR RECYCLING 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 National Laboratory 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 2003; Jody et al. 2004). Under the appropriate operating conditions, over 90% of the polymeric substrate will be removed in a few minutes. However, removing the remaining portion may require additional treatment and different treatment temperatures and/or oxygen environments, especially the last 1% or 2%.

Samples were first submitted to Oak Ridge National Laboratory for preliminary evaluation. 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.

Oak Ridge National Laboratory (ORNL) and Hexcel Corporation evaluated the recovered fibers further to determine their suitability for reuse. The results are presented below.

Scanning Electron Microscope (SEM) Analysis. Figure 11.8 shows SEM pictures of recovered fibers: (a) at 5,000X and of virgin fibers (b) at 3,000X (see footnote 34). The rough edge of the recovered fibers is a 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.

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33 Analysis conducted by Dr. Felix Paulauskas, Oak Ridge National Laboratory.
34 Analysis conducted by Dr. Felix Paulauskas, Oak Ridge National Laboratory.
35 Analysis conducted by Dr. Mohammad Abdallah, Hexcel Corporation.
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 Si observed on one of the recovered fibers may be contamination from the thermal reactor, which was also used for the recovery of glass fibers.

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).

### Table 11.1 Surface Chemistry of the Recovered and Virgin Fibers

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>Traces</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recovered 1</td>
<td>84 ± 1.4</td>
<td>11 ± 1.3</td>
<td>5 ± 0.5</td>
<td>Na</td>
</tr>
<tr>
<td>Recovered 2</td>
<td>80 ± 0.9</td>
<td>15</td>
<td>5 ± 0.2</td>
<td>Na, Si</td>
</tr>
<tr>
<td>Untreated virgin</td>
<td>95 ± 0.7</td>
<td>3 ± 0.4</td>
<td>2 ± 0.6</td>
<td>—</td>
</tr>
<tr>
<td>Surface-treated virgin</td>
<td>83± 1.1</td>
<td>10</td>
<td>7 ± 0.7</td>
<td>Na</td>
</tr>
</tbody>
</table>
FIGURE 11.9 Relative Concentration of Functional Groups Based on Areas of the Fitting Curves/Peaks of High-Resolution Carbon Spectra (XPS Binding Energy), Sputtered (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.

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 were also 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tow Tensile Strength (MPa*)</th>
<th>Tow Tensile Modulus (GPa*)</th>
<th>Strain at Failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recycled 1</td>
<td>4.26</td>
<td>295</td>
<td>1.32</td>
</tr>
<tr>
<td>Recycled 2</td>
<td>4.63</td>
<td>260</td>
<td>1.66</td>
</tr>
<tr>
<td>Virgin**</td>
<td>5.64</td>
<td>295</td>
<td>1.76</td>
</tr>
</tbody>
</table>

* Mpa = mega Pascal, Gpa = giga Pascal
** Virgin fibers used in making the composites from which the recycled fibers 1 and 2 were recovered.
For most mixtures of PMCs, the process can be energy self-sufficient by using the polymer substrate as an energy source. The fibers have retained 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 needs to be properly designed to control the rate of air flow into the reactor during treatment, and the treatment temperature and residence time should be selected such that:

- The 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 take place, while at low air-flow rates, the residue on the fibers after the initial treatment will be significant. Therefore, this parameter has to be controlled properly.

A preliminary economic analysis of the process was also conducted on the basis of the results of the bench-scale experiments, and the results of the analysis suggested that a potential payback of less than two years is likely.
12 CONCLUSIONS

Over the last 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 substances of concern 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 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 non-ferrous 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 proved 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.

In spite of recent technical advancements, essentially all of the about 5 million tons of shredder residue generated every year in the United States is still disposed of in landfills. In Europe and Japan, most of 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 has to 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.
13 REFERENCES


ARIC: Appliance Recycling Information Center


CWT: Changing World Technologies, Inc.


EPA: U.S. Environmental Protection Agency


PIA: Plastics Institute of America


SAE: Society of Automotive Engineers


