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RECOVERY OF RECYCLABLE MATERIALS FROM SHREDDER RESIDUE

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Abstract

Each year, about 11 million tons of metals (ferrous and nonferrous) are recovered in the U.S. from about 10 million discarded automobiles. The recovered metals account for about 75% of the total weight of the discarded vehicles. The balance of the material or shredder residue, which amounts to about 3 million tons annually, is currently landfilled. The residue contains a diversity of potentially recyclable materials, including polyurethane foams, iron oxides, and certain thermoplastics. This paper discusses a process under development at Argonne National Laboratory to separate and recover the recyclable materials from this waste stream. The process consists essentially of two-stages. First, a physical separation is used to recover the foams and the metal oxides, followed by a chemical process to extract certain thermoplastics. The status of the technology is discussed, and the process economics are reviewed.

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Introduction

In 1991, the automobile shredder industry supplied in excess of 10 million tons of recovered ferrous scrap for use in the iron and steel industry. The single largest source of that raw material is obsolete automobiles, although materials from other sources (such as obsolete refrigerators, washing machines, and other appliances that are commonly referred to as "white goods") also contributed to the supply of recovered metals. Based on available data and vehicle statistics [1-3], we estimated that in 1991 the recycling potential from shredded automobiles was about 10.3 million tons of ferrous scrap, 0.8 million tons of nonferrous metals, 0.8 million tons of plastics/composites, and 2.1 million tons of other materials. Since only metals were recycled, the shredder industry was left with about 3 million tons of residual material that needed to be disposed of. This amount was in addition to a smaller quantity of waste that resulted from recovering metals from shredded white goods. Almost all of this waste was disposed of in landfills. The cost of landfilling, which has increased dramatically over the past few years, combined with more stringent regulations, long-term liability concerns, and shrinking landfill space dictate that viable disposal alternatives be developed to maintain a healthy metals recycling industry. The impact of the landfill constraints and cost will also be exacerbated by the increasing nonmetal content of vehicles, primarily plastics. For example, the consumption of plastics/composites in domestic automobiles increased from 176 pounds in 1978 to 243 pounds in 1992 (Figure 1). This contributed to the decline in the total weight of the average passenger car from 3494 pounds in 1978 to 3136 pounds in 1992. Of the five main categories of construction materials used in vehicles (Figure 2), only plastics/composites showed increased market penetration over the same period. The share of plastics/composites in domestic cars increased from 5.0% in 1978 to 7.7% in 1992 (Figure 3).

By 2000, the average automobile is expected to weigh about 3000 pounds and contain 300 pounds of plastics. The weight ratio of metals to automobile shredder residue (ASR) is estimated to decrease from about 4.1 for model year 1978 to 3.4 for model year 1992 [1]. Therefore, economic handling and disposal of the ASR will become a more pressing issue. In February 1990, Waxman Metals Group estimated the fluff disposal fee to be \$125/per ton for a 1979 passenger car [4, 5]. The net value of a typical 3150 lb hulk was estimated to be \$48.75 based on the following assumptions: 2250 lb of scrapped steel at 6¢/lb, 150 lb of nonferrous metals at 12¢/lb, 750 lb of fluff with disposal fee of 6.25¢/lb, freight of \$10 per car, and processing cost at 15¢/lb [4, 5]. Field and Clark, using the Waxman data, estimated the constant dollar value of average scrapped car for model years 1976 to 1989 assuming fixed operating, transportation, and disposal costs [5]. Using the average automobile material contents, the value of a scrapped car in constant 1990 dollars was estimated to be \$60.57 for model year 1976, \$55.01 for model year 1979, and \$51.51 for model year 1989. Field and Clark [5] stated that this simplistic analysis illustrates that the value of the scrap car is falling as the material content changes.

Characterization of ASR

Development of technology for recycling ASR is complicated because ASR is a very heterogeneous waste material; its composition, density, and moisture content change from site to site, and from day to day at the same site, as different types of source materials and different models and years of obsolete automobiles and white goods are shredded [6]. As shown in Table I, ASR contains a large number of intermingled species. Approximately 40-55% of the ASR is combustible material, and its heating value may vary from approximately 4000 to 6000 Btu/lb and average about 5400 Btu/lb [7]. In some cases, polychlorinated biphenyl (PCB) contamination can result from the inadvertent shredding of capacitors contained in old white goods. ASR also contains heavy metals, such as lead, cadmium, and mercury. An approximate composition of ASR (including that generated by the shredding of white goods) is shown in Figure 4.

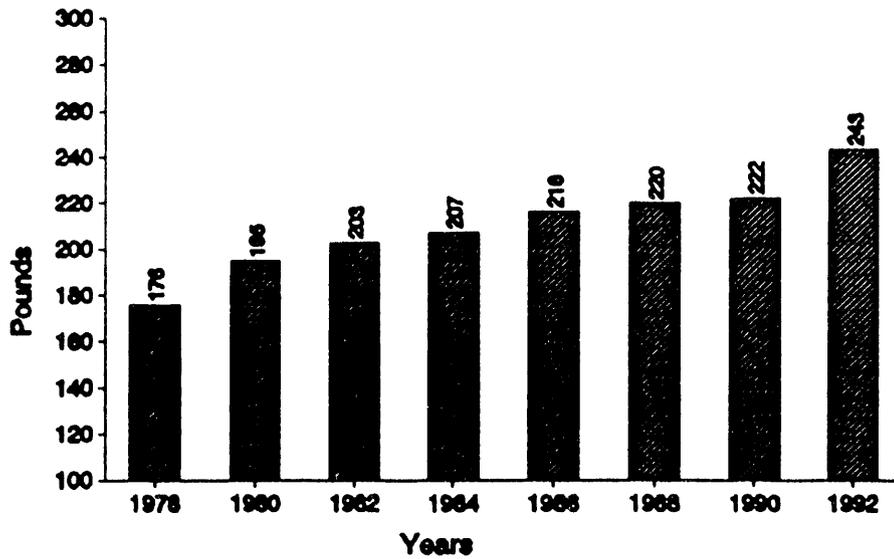


Figure 1 - Average Plastics/Composites Consumption in Domestic Cars
(Source: Ref. 2)

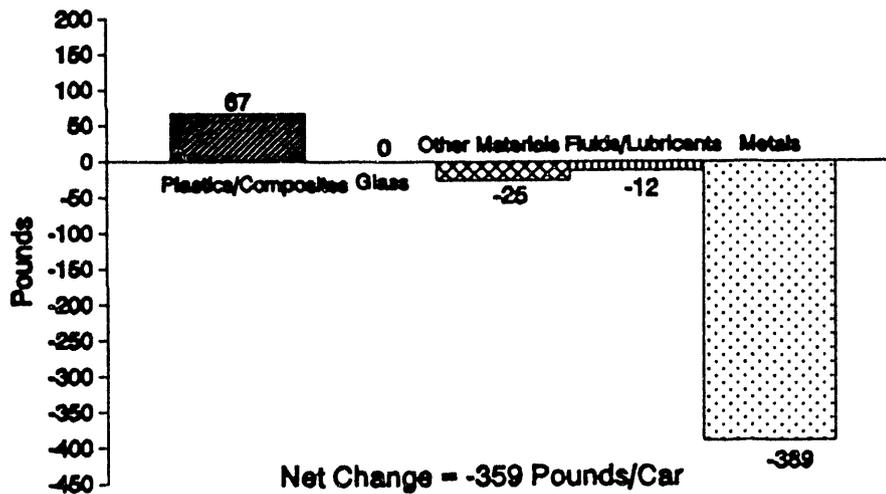


Figure 2 - Changes in Average Material Consumption in Domestic Cars,
1978-1992 (Source: Ref. 2)

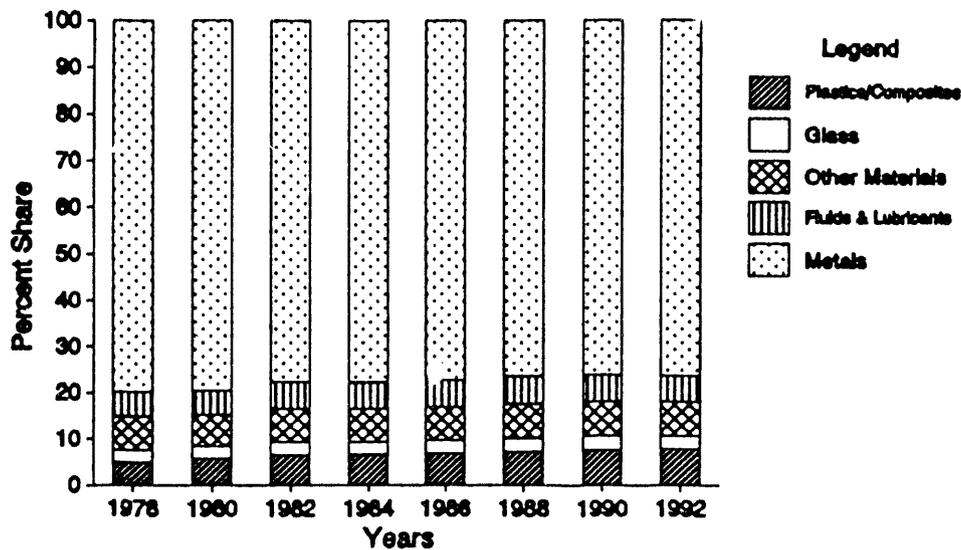


Figure 3 - Average Material Consumption Share in Domestic Cars
(Source: Ref. 2)

TABLE I Composition of ASR

Recyclables	Energy Value	Inerts
Thermoplastics	Paper	Glass
Foams	Brake Fluid	Dirt
Fibers	Engine Oil	Sand
Metal Chunks	Transmission Oil	Gravel
Rust	Grease	Moisture
Wires	Wood Chips	
	Thermosets	
	Rubber	
	Tar	

ASR is also heterogeneous with regard to density and shape. For example, the polyurethane foam (PUF), with absorbed moisture and oils, might constitute about 10% of the ASR mass but could account for over 30% of its volume. On the other hand, fines (<1/4 in.) might constitute about 25% of the mass and only about 5% of the volume. The volume ratios of the large and small PUF pieces could be as high as 250:1.

An expected composition of the plastics portion (based on automotive plastics use in model year 1981) of the ASR is given in Table II [8]. In this paper, we do not address the potential for dismantling some of the plastics prior to shredding. Even though we believe that it can be technically feasible, it is unlikely to be economical, at least, until cars that are designed for dismantling reach the end of their useful life, which might be 15-25 years from now. Hock

et al. [9] estimated that the "cumulative costs associated with recovery, by selective dismantling, through reclamation of the automotive plastic parts...fall between \$0.36-\$1.08 per lb and average \$0.72 per lb" [9].

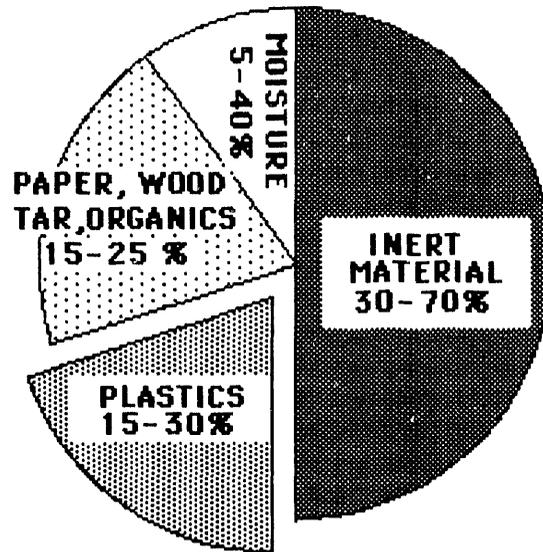


Figure 4 Approximate Composition of ASR

Table II. Composition of Plastics in Model Year 1981 Cars (Source: Ref. 6)

<u>Material</u>	<u>Weight %</u>
Polyurethane Foam	22.6%
Reinforced polyesters	21.9%
Bulk molding compound	
Sheet molding compound	
Polypropylene	19.2%
Polyvinyl chloride	15.5%
Acrylonitrile butadiene styrene	7.3%
Nylons	3.7%
Acrylic	2.5%
Phenolic	2.1%
Other	5.2%

Recycling

Because ASR has a high hydrocarbon and plastics content, it can conceptually be recycled by all four recycling modes: primary, secondary, tertiary, and quaternary. The greatest emphasis on ASR recycling has been on secondary and quaternary recycling relying primarily on the plastics content of the ASR. The applicability of these recycle procedures to ASR is discussed elsewhere [10]. Argonne National Laboratory (ANL) has developed and is presently testing a process for the recycling of most of the ASR constituents, including the thermoplastics [11-17]. This process is described below.

The ANL Process

The concept of recovering the plastics for reuse as plastics is intuitively appealing because (1) the plastics content of shredder fluff is expected to increase, (2) plastics use in automobiles is a growing market, and (3) the plastics recycling industry, although in its infancy, is growing and, we believe, will continue to grow. Based on the expected plastics content of the shredder fluff,

we would expect that more than 60% of the total thermoplastics content of shredder fluff might be recoverable by dissolution of the plastic in solvents. Conceptually, because of differences in the solubilities of certain plastics and their differences in susceptibility to specific solvents, the intent of the ANL process is to selectively extract specific plastics or groups of compatible plastics from shredder fluff using solvents. A four-step process was developed. The four steps are (1) drying, (2) mechanical separation, (3) extraction of the thermoplastics, and (4) regeneration of the solvents for reuse. We identified polyurethane foam (PUF), polypropylene (PP), polyvinyl chloride (PVC), and acrylonitrile butadiene styrene (ABS) as potential candidates for recovery from ASR for recycling.

Drying

The drying process is by indirect heating (i.e., steam coil) only. Flame or sparks could potentially set the material on fire. Temperatures in excess of about 105°C (220°F) should be avoided in the presence of air. Localized smoldering was observed on occasions, but could not be reproduced, when the material was dried in a regular oven at higher temperatures. Not enough data exist at this time to conclude that drying at lower temperatures is completely safe. Therefore, careful monitoring and control of the dryer is necessary to avoid smoldering fires. Drying at lower temperatures will also minimize the evaporation of organic species along with the moisture, and thus could avoid a potential environmental problem which may require scrubbing or waste water treatment. Further, because of the potentially high (up to 40 wt%) water content of some ASR material, the drying process can be an energy-intensive and time-consuming process. The problem with low-temperature drying is that it is time-consuming, could result in poor drying of the inner material unless the material is agitated or remixed frequently during the drying process.

Physical Separation

Mechanical separation of the polyurethane foam and the fines (< 0.62 cm or 0.25 in. in size) from ASR is necessary for many reasons, including to recover the foam as a potential product. Separation concentrates the plastics in the remaining fraction, which results in smaller and less expensive equipment being required for the solvent extraction operation. There will be smaller solvent losses because less nonplastic material which can absorb solvent (foam) or be wetted by it (dirt) will be present. The presence of the fine nonplastic particles could contaminate the extracted plastics unless excessive and costly filtration of the fine particles from the solution is performed. Attempts to separate the shredder fluff using small commercially available multi-deck vibrating screens was not successful. The wires in the shredder fluff caused plugging of the openings in the upper deck screen in a short period of time. Small pieces of plastics and nonplastic materials were trapped in the fuzz and in the PUF and could not be shaken loose by the vibration of the screens.

A laboratory classification column was built and fitted with several screens and equipped with a variable output air blower in the bottom that can be cycled on and off to provide agitation of the shredder fluff as it is being separated (Figure 5). This resolved the plugging problem to a large extent. It also pushed the light PUF to the top of the top screen and liberated some of the entrained dust and fines content of the PUF. No material was leaving the column during the agitation and separation process except for some heavy fines that dropped out of the bottom of the column. Therefore, it was operated in a batch mode. An elephant trunk that is connected to a vacuum system that may be activated when the blower is in the off mode was attached to the top of the column. This resulted in the separation of the foam from the top of the top screen. Some features of this system are being incorporated at present into a large-scale system to separate the foam and the fines as part of a demonstration project to separate and recover the foam.

The collected foam constituted about 10 wt% of the ASR. A process to clean the foam using organic solvents and water/detergent solutions was developed, and it was laboratory-tested. About 30-40 wt% of the dirty foam was separated as "oils", or automotive fluids and moisture. A pilot plant for full-scale demonstration of the foam separation and cleaning processes is under construction and could become operational in early 1994. Preliminary economic analysis indicated that the foam separation and cleaning process could pay for itself in about one year.

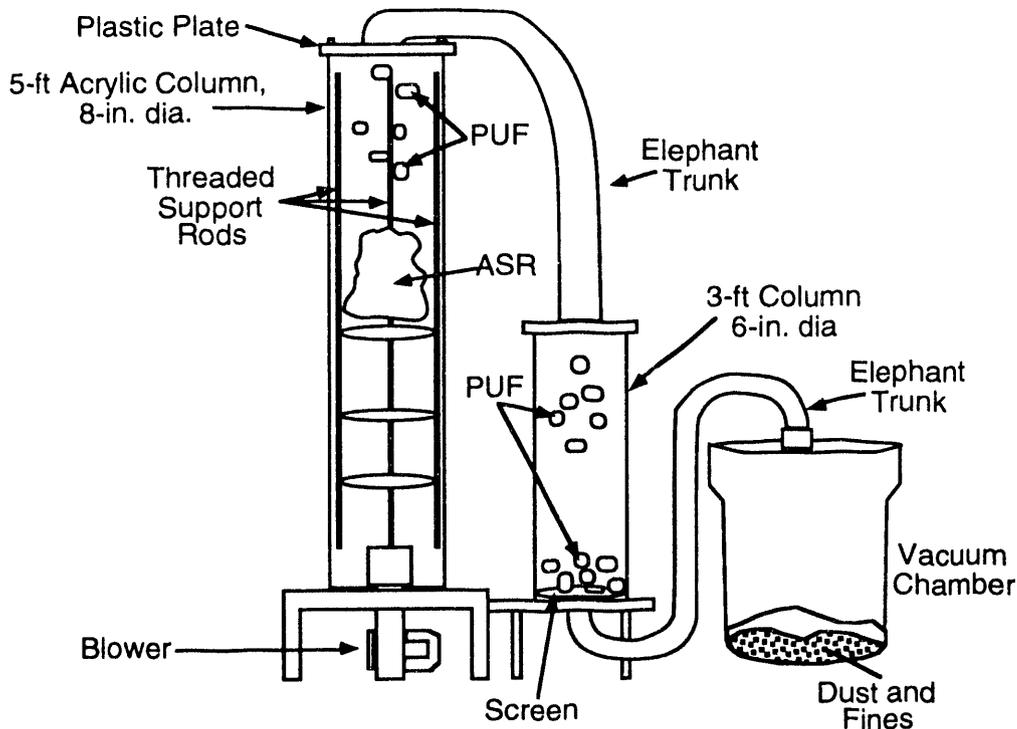


Figure 5-Laboratory Apparatus for Physical Separation of PUF, Fines, and Plastics-Rich Shredder Fuff Fractions

The fines, which constituted about 30 wt% of the ASR (values as low as 20% and as high as 55% were observed for different samples), were separated further using a magnet into two different fractions: a magnetic fraction and a nonmagnetic fraction. The magnetic fraction was about 40% of the total fines. The heating value of a sample of the magnetic and a sample of the nonmagnetic fines were determined and found to be 3844 Btu/lb and 2355 Btu/lb, respectively. This is an indication that some of the brittle plastics, mainly thermosets, and wood chips were also broken down into smaller pieces and were screened with the fines. Because of the significant changes that one can encounter in the composition of the fines from shredder to shredder, the heating values reported here should be interpreted carefully and may not be the typical values.

In terms of mass, organics represented about 20-30 wt% of the total fines and about 10-20 wt% of the magnetic fines. Elemental analysis of the inorganics was also performed after the samples were combusted to burn off the organics. The results of the analysis are shown in Table III.

We are pursuing using the fines as raw materials (source of iron oxide, and silica) for the cement-making process. Further conditioning of the fines may be necessary to produce a consistent product for such an application.

Solvent Extraction of the Plastics

Evaluation of the plastics-rich-stream, which remained after the separation of the foam and the fines, identified ABS, PVC, PP, and polyethylene (PE) as potential candidates for recovery and recycling. ABS was targeted because of the high market value of the virgin resin and because of its good solubility characteristics in several mild organic solvents at low and moderate temperatures. FVC was selected because its chlorine content could be an obstacle if the stream is to be processed for its energy or chemical value (incineration, pyrolysis). In addition, reasonably clean PVC can also be used for making numerous products with flexible specifications. PVC, however, is susceptible to degradation upon thermal cycling. Among the first signs of

degradation is the appearance of a blackish color. PP was targeted for recovery because it is present in large quantities and its use by the automotive industry is on the rise. Further, because it is soluble only at high temperatures, it can be recovered with little contamination, except for the PE which dissolves under very similar conditions.

Table III Inorganic Composition Of The ASR Fines

<u>Element</u>	<u>Weight % In Total fines</u>	<u>Weight % In Magnetic Fraction</u>
Iron	43.2	64.0
Zinc	1.08	0.54
Copper	0.82	0.24
Lead	0.10	0.06
Chromium	0.03	0.07
Calcium		0.71
Barium		0.21
Aluminum		0.27
Nickel		0.13
Manganese		0.31
Magnesium		0.12

To minimize the contamination of the recovered plastics, the first step in the extraction process was to use a mild solvent such as hexane to extract the automotive fluids without dissolving the targeted plastics. The "oils" recovered in the process, including those recovered from the polyurethane foam, constituted about 5-10 wt% of the ASR and had heating values between 16,000 and 18,000 Btu/lb. However the hexane also extracts the PCBs that may be present in the ASR. Therefore, the recovered oil may require disposal as a hazardous waste instead of being considered as an energy source. Table IV shows the results of the analysis conducted on one composite sample prepared from oils derived from ASR obtained from several shredders.

After the "oils" are extracted, the extraction of the plastics at ambient pressure was tested in two methods. In the first method, selective solvents were used to extract individual plastics in series. In the second method, a solvent was used to dissolve all of the plastics of interest at atmospheric pressure and elevated temperatures, and then the mixed plastics were separated using different solvents. Table V shows some of the solvents for the plastics of interest. Each of these methods has advantages and disadvantages. For example, in the first method, the ABS and the PVC can be recovered without being exposed to the high temperature required for the recovery of PP and PE. However, the extraction steps all take place in large reactors, because all of the plastics-rich stream will be used in the extraction process. In the second method, only one extraction has to be done in a large vessel. The separation of the mixed plastics can be conducted in smaller reactors. In addition this method enables more efficient cascading of the heat between the stages to minimize the energy requirement of the process. However, all of the plastics will be exposed to the high temperature, and will experience a higher number of thermal cycles. Therefore, potential degradability of some of the products is higher. Products generated by both methods are under evaluation at present.

Solvent Regeneration

After a thermoplastic(s) is dissolved in a solvent, the plastic(s) is (are) recovered by one of several different methods, depending on the characteristics of the solution. These methods include cooling, using an anti-solvent, and evaporation of the solvent. When anti-solvents are used, the binary liquid mixture remaining after the plastics are recovered is distilled to recover both the solvent and the anti-solvent. In all cases, the solvent is reused. We have regenerated the same solvent over 10 times without any measurable degradation in its performance.

TABLE IV Approximate Analysis Of A Composite Sample Of Oils Recovered From ASR Obtained From Several Shredders

<u>Component</u>	<u>Weight %</u>
Silicon	0.082
Iron	0.059
Calcium	0.039
Copper	0.030
Aluminum	0.028
Titanium	0.026
Zinc	0.025
Lead	0.024
<u>Magnesium</u>	<u>0.021</u>

TABLE V Solubility Of Some Plastics In Organic Solvents

<u>Thermoplastic</u>	<u>Solvents</u>
ABS, PVC	Chlorinated hydrocarbons, ketones, tetrahydro-ABS/PVC alloys furan and aromatics
Polyethylene and Polypropylene	Hot aromatic and chloroaromatic hydrocarbons,
Polystyrene	Aromatic and chlorinated hydrocarbons
Polyvinyl chloride	Esters, ketones, chlorinated hydrocarbons
Nylons	Phenols
Acrylics	Aromatic and chlorinated hydrocarbons, ketones and esters

Residual Material

The residual material from which the thermoplastics had been recovered is a dry mixture that could be used as a solid fuel. It is low in ash and chlorine, and it should be easy to pelletize or cube because it is dry and its foam content has been separated. Samples of that material have been sent for testing in incineration and pyrolysis test facilities. Results are not available at this time.

Economic Analysis of the ANL Process

Our preliminary cost analysis indicates that the total capital cost for a centrally located ASR recycling plant with a design capacity of 90,000 tons per year is about \$7 million. Operating costs are estimated at about 20¢/lb of recovered material. This would yield a payback of about three years based on values of recovered materials as follows: 25¢/lb of PUF, 40¢/lb of ABS, 15¢/lb of PVC, and 5¢/lb of PP and PE. This study assumed that the plant will charge no tipping fees for accepting the ASR and will pay no fees for disposal of the nonmagnetic fines. It was, however, assumed that the recovered oil will be disposed of as a hazardous waste. No revenues were assumed for the material left after the extraction process is completed, even though it has a heating value of about 3000-5000 Btu/lb and is virtually dry, PCB-free, and has very little chlorine left in it.

Conclusions

In the last three decades, several treatment and disposal methods for ASR have been investigated. Landfilling of ASR is still the most common practice. However, increasing transportation, tipping, and metal fixation (in some states) costs, and concern over long-term liabilities associated with landfilling of waste in general, are reducing the economic attractiveness of this approach. This has resulted in increased interest in ASR recycling, and in particular, in recycling the polymers content because of the potential marketability of these polymers. Problems associated with recycling ASR include its heterogeneity and the variability in its composition (i.e., plastics contents, nonplastics combustibles, and inert compounds). All four types of recycle have been investigated for the recovery of recycled materials from the ASR. Using the ASR as is for making even low-grade products does not appear technically feasible or economical, nor is it recommended because of the potential presence in the ASR of contaminants such as lead, cadmium, mercury, PCBs, and sharp objects. Therefore, preprocessing of the ASR to concentrate and clean the potentially useful components appears necessary. Argonne National Laboratory has been developing a process to selectively recover the potentially recyclable materials from this waste stream. The process is essentially a two-stage process in which physical separation is used for the recovery of the foams and the oxides, followed by a chemical process for extraction of certain thermoplastics. The second stage in the process involves the separation of thermoplastics from ASR using organic solvents. Our preliminary cost estimate for the overall process indicates a potential payback of about three years.

Acknowledgment

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