

CHEMICAL AND MECHANICAL RECYCLING OF SHREDDER FLUFF

by

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INTRODUCTION

Each year, the secondary metals industry recovers about 55-60 million tons of prompt and obsolete scrap which is used in the production of finished steel products. The single largest source of this scrap is the obsolete automobile. The shredder industry recovers about 10-12 million ton/yr of ferrous scrap, most of which is from shredded automobiles. However, for each ton of steel recovered, over 500 lb of fluff are produced. Shredder fluff is comprised of the nonmetallic content of the automobile and other shredded materials, such as refrigerators, dryers, and dishwashers, which are commonly called white goods.

The plastics content of shredder fluff is typically about 15-20% by weight and is expected to increase over the next decade due to the significant increase in the use of automotive plastics over the past 10-15 years. At present, shredder fluff is landfilled. The rapidly escalating landfilling cost, along with environmental concerns over the fate of this waste, poses a significant cost and liability to the shredder industry. Research is being carried out to identify and develop recycling technologies that will reduce the volume and the mass of shredder fluff going to landfills and to minimize its cost impact on the recycling of secondary metals.

Previous research has focused on exploiting the plastics content of shredder fluff and other hydrocarbons present in fluff for secondary recycling (e.g., production of wood-products substitutes) and for quaternary recycling (e.g., energy generation). Limited work was also conducted on tertiary recycling (e.g., pyrolysis and gasification). Although the previous research has established the technical feasibility of most, if not all, of the alternatives that were examined, none have proven to be cost-effective.

This paper describes some research at Argonne National Laboratory (ANL) to develop a process to recycle some of the fluff content, primarily the thermoplastics.

CHARACTERISTICS OF SHREDDER FLUFF

Shredder fluff is an extremely nonhomogeneous waste material. Its composition can change from site to site and from day to day at the same site. It contains plastics (thermoplastics, thermosets, polyurethane foam [PUF]), rubber, wood, paper, fabrics, glass, sand, dirt, ferrous and nonferrous metal pieces, tar, and whatever else people leave in their cars when they junk them. Overall, it consists of about 50% combustible material and 50% noncombustible (inert) material. The shredder fluff may be contaminated with brake fluid, gasoline, engine oil, windshield washing fluids, antifreeze (ethylene glycol), freon refrigerants, and in some cases PCBs. (PCB contamination can result from the inadvertent shredding of such white goods as obsolete refrigerators, washing machines,

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and dishwashers with intact capacitors). In addition, shredder fluff may contain heavy metals, such as lead and cadmium. Finally, shredder fluff contains varying amounts of moisture, depending on the type of shredding operation (i.e., wet or dry) and the extent of exposure of the shredder fluff to rain while in inventory. The approximate composition of shredder fluff is

Plastics	15-25%
Paper, wood and tar	15-25%
Inert material	25-75%
Moisture	2-40%

The expected composition of the plastics portion (based on automotive plastics use in model year 1981) of the shredder fluff is:

Polyurethane Foam	23%
RP, BMC, SMC	22%
Polypropylene	11 %
PVC	15%
ABS	7%
Nylons	4%
Acrylic	3%
Phenolic	2%
Other	5%

Such thermoplastics as polypropylene, ABS, and PVC appear to account for a significant share of the anticipated plastics content in shredder fluff. Because thermoplastics are amenable to recycling as plastics, these materials are the focus of the separation technology under investigation by ANL.

Shredder fluff is also nonhomogeneous with regard to density and shape. For example, the flexible PUF, with absorbed moisture and oils, might constitute about 10% of the shredder fluff mass, but could constitute over 50% of its volume. On the other hand, fines (<1/4 in.) might constitute about 25% of the mass, but only about 5% of the volume. The volume ratio of the large to the small PUF pieces could be as high as 250:1. The physical variability of shredder fluff is in itself problematic in terms of attempting to recycle the material.

SHREDDER FLUFF TREATMENT/DISPOSAL ALTERNATIVES

The potential applicability of all four modes (primary, secondary, tertiary, and quaternary) of recycling is expected because of the plastic and hydrocarbon content of shredder fluff and its inherent fuel and chemical value. A literature search revealed a fair amount of research related to the treatment/disposal/recycling of shredder fluff (Jody et al. 1991). Most of the reported research has focused on exploiting the plastics and the other hydrocarbons in the shredder fluff for secondary recycling (e.g., production of wood-products substitutes) and for quaternary recycling (e.g., energy generation). Limited work was also reported on tertiary recycling (e.g., pyrolysis, gasification, and PUF hydrolysis). The only reference to the potential of primary recycling (i.e., recovery of "pure" plastics) was the early work conducted by the Bureau of Mines to physically separate various plastics from shredder fluff (Dean et al. 1985). It is noteworthy that while many different alternatives for recycling shredder fluff have been reported in the literature, there has been little mention of preprocessing the shredder fluff in an attempt to concentrate the constituents for which the recycling technology is targeted; the exception is the work conducted by Dean et al. (1985) at the Bureau of Mines. We believe that

some form of physical separation to concentrate the target recyclable constituents of shredder fluff and to reduce the chemical variability, the particle size distribution, or both will be essential, regardless of the type of recycling mode employed.

Secondary recycling of fluff, or the production of such secondary products as park benches, lamp posts, road traffic furniture, shingles and other construction materials, etc., suffers from two key limitations, even if it were technically feasible: (1) the market for such products is small and (2) the cost of making such secondary products is not insignificant. This makes it more difficult for such products to compete with their counterparts made from virgin materials (such as wood, sand, and gravel), even when the avoided cost of disposal is considered.

Quaternary recycling is motivated by the fact that shredder fluff has a fuel value equivalent to that of a low-grade, high-ash coal (2,900-9,260 Btu/lb, with an average of 5,400 Btu/lb) (Hubble et al. 1987). Typically, incineration of the material could be expected to reduce the mass of the shredder fluff for disposal by about 50%. However, shredder fluff may also contain high concentrations of chlorine and sulfur, which require either scrubbing of the resultant combustion gases and/or attempting to scrub these compounds by adding such materials as limestone or dolomite to combine with the chlorine and sulfur to keep them in the ash. In either case, the variability of the content of acid-gas precursors in the shredder fluff will necessitate a significant overdesign of the scrubbing capability, which will significantly affect cost. For example, the chlorine content of 12 samples tested by EnerGroup (Hubble et al. 1987) ranged from 0.7% to 16.9%. The cost and complexity of incinerating raw shredder fluff is also exacerbated by the possibility of the presence of PCBs in the shredder fluff.

Although incineration is technically feasible, it is also capital-intensive. For example, an incinerator sized to handle about 12,000 ton/yr of shredder fluff (operating at design capacity for 7,884 h/yr is estimated to cost over \$1 million. A simple pay-back period of three years or less could be achieved only if landfill costs exceeded \$60/ton of shredder fluff. (This assumes a mass reduction of about 50% of the input shredder fluff and ignores incineration operating costs). Off-site incineration of the shredder fluff at a large-scale waste-incineration facility, if available, would eliminate the need for the capital investment, but would not significantly affect the economics of incineration as an option. Anecdotal evidence suggests that off-site incineration of shredder fluff is less of an alternative than indicated by costs alone. Most incinerator operators are paid for mass reduction of the material processed. Even though shredder fluff might have a good heating value in terms of wastes, this does not enter into the equation as significantly as the high-ash content of shredder fluff and the fact that there is a more than adequate supply of low-ash wastes competing for the limited incineration capacity.

An alternative to straight incineration for mass or volume reduction is incineration with heat recovery for the production of steam or electricity. This option is also technically feasible; the only technical uncertainty rests with the combustion process, as in the case of straight incineration. But, again, the issue is one of capital costs and economics. Nonetheless, there is an opportunity for significantly reducing the payback period relative to the investment required, especially in the case of steam, if there is an on-site use for the steam. For example, an incinerator with a design capacity of 12,000 ton/yr of shredder fluff fitted with a heat-recovery steam generator could produce about 14,000 lb/h of steam (at 1,000 Btu/lb, a boiler efficiency of 85%, a fluff heating value of 5,400 Btu/lb, and 7,884 operating hours per year). The estimated capital cost of such a system would be about \$1.6 million. If the steam were valued at about \$5/1000 lb (the fuel-cost component of steam produced in a conventional gas-fired boiler using a

natural gas price of \$4/million Btu), the annual value of the steam would be about \$550,000. If landfill costs were \$60/ton of shredder fluff, the savings in landfill cost via incineration would be \$360,000/yr, which would yield a simple payback of less than two years. However, there are very few shredder facilities that have a use for steam.

If the heat were recovered for the production of electricity, the amount of electricity that could be produced (again based on 12,000 ton/yr of shredder fluff) would be about 11.5 million kWh/yr (based on a 30% electricity generation efficiency). The estimated cost of the equipment would be about \$2.4 million. If the value of the electricity were \$0.08/kWh, its annual value would be \$920,000, which added to a landfill cost savings of \$360,000/yr would also yield a simple payback of less than two years.

Another option is compaction of the fluff to produce pellets for sale as a supplemental fuel in coal or solid-waste-fueled boilers. The estimated cost of pelletizing, briquetting, or cubing shredder fluff using binders is about \$20/ton. The cost of the binders is estimated at about \$6/ton of shredder fluff. Previous attempts to compact shredder fluff have been unsuccessful, primarily because of the high foam and moisture content of the raw shredder fluff. Chemical binders, which have since been tested at ANL for producing refuse-derived fuel pellets, might also be applicable to shredder fluff. This option is attractive from the standpoint that it is the least capital-intensive alternative (other than a secondary market for raw shredder fluff) available to the shredder. We estimate that to process 12,000 ton/yr of shredder fluff, the materials-handling equipment and pelletizer would cost about \$250,000. The potential value of shredder fluff as a supplemental fuel would have an upper limit equivalent to that of coal -- at most a \$1.50/million Btu or approximately \$16/ton of shredder fluff. This would result in a simple payback of slightly more than a year, assuming the pellets were marketable.

However, the market for shredder fluff as a supplemental fuel might be constrained regardless of its quality or price. For example, a single 1000-MW electricity-generating plant consumes about 10,000 tons of coal per day, with an approximate heat content of 2.40×10^{11} Btu. A median shredder operation produces 12,000 ton/yr of residue (or, on a constant daily basis, about 32 ton/d) with an approximate heat content of 3.45×10^8 Btu. The average amount of residue available from a single shredder would appear to be so trivial, relative to the coal required for a typical power plant, that the utility should be indifferent to using it or even perhaps be a "good neighbor" and dispose of the shredder residue at no cost to the shredder. Most utilities, however, must obtain permits for the fuels that are used in their power plants. The transactions costs of permitting procedures required for an alternate fuel might preclude the utility from using a fuel supply that meets less than a tenth of a percent of the fuel needs of a single plant. On the other hand, pelletized shredder fluff might represent a viable alternative fuel for small-capacity, solid-fuel-fired industrial or utility boilers.

Landfilling is currently the default option for the disposal of shredder fluff. Even though landfill costs have escalated dramatically over the past few years and some shredders are faced with out-of-state transportation costs for available landfill, shredders can currently dispose of shredder fluff in conventional landfills at costs less than \$25/ton; other shredders have to pay over \$80/ton. If shredder fluff were classified as "hazardous," it would need to be treated prior to landfilling, or else landfill costs would increase by at least a factor of ten. A number of commercial processes are available that could "fix" hazardous materials that might be contained in shredder fluff. The cost of these processes varies depending on the materials present and the type of process utilized.

The least expensive options appear to be chemical fixation techniques, which are estimated to cost about \$10 to \$20/ton of shredder fluff.

While landfill is presently an option in many cases, its continued viability is a critical concern. The neverending "cradle to grave" regulatory liability of landfilling compounds that concern.

THE BASIC ANL PROCESS CONCEPT

Argonne National Laboratory has developed and is currently testing a process for the recovery of thermoplastics from shredder fluff. The concept of recovering the plastics for reuse 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. On the basis of the expected plastics content of the shredder fluff, we would expect that more than 60% might be recoverable by dissolution of the plastic in solvents. 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 three-step process was developed: (1) mechanical separation of the fluff, (2) extraction of the thermoplastics, and (3) regeneration of the solvents for reuse.

Physical Separation Unit

Attempts to separate the shredder fluff into three fractions (PUF, a plastics-rich stream, and fines) using small commercially available multideck vibrating-screen units were 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 PUF and could not be shaken loose by the vibration of the screens. A laboratory classification column was built, 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 1). 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 fines that dropped out of the bottom of the column. Therefore, it was operated in a batch mode. An elephant trunk connected to a vacuum system, which 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. At present, we are designing a large-scale continuous process employing the same principle.

Solvent Extraction System

In the first phase of the work, a Soxhlet extraction apparatus was used (Figure 2). It consists of three basic units: (1) the solvent reservoir, (2) the extraction (or sample) chamber, and (3) the condenser. The solvent reservoir was a 2- or 5-L round flask placed in an electrical heating mantle. The shredder-fluff sample chamber is located at the center of the apparatus. The vaporizing solvent, from the solvent reservoir, passes through the annulus between the two chambers. In the process the sample chamber will be maintained at the boiling point of the solvent. After passing through the annulus, the solvent vapor enters the water-cooled condenser where it condenses and falls back in the sample chamber to soak the fluff. As the solvent in the sample chamber reaches a certain level, as determined by an inverted U-tube connecting the sample chamber and the solvent reservoir, the solvent is discharged out of the sample chamber and into the solvent

reservoir. The filling and emptying of the sample chamber continues until the discharged solvent is no longer carrying any appreciable dissolved material. This is determined first, by the color of the discharged solvent and second, by analysis of a sample of the discharged material. A sample is drawn, evaporated, and checked for a solid residue. When no solid residue is detected, the extraction is considered completed. The apparatus is then dismantled, and the shredder-fluff sample is emptied into a preweighed vessel and weighed. The vessel is then connected to a water-cooled condenser and heated to dry the shredder-fluff sample and to recover solvent retained in the shredder fluff. The vessel containing the recovered solvent is then disconnected and reweighed. Drying was conducted at a temperature higher than the boiling point of the solvent. The dried sample is then spread in a clean tray and allowed to dry further overnight in the hood, and its weight is again determined.

Solvent-Regeneration Unit

The solvent reservoir that contains the dissolved plastics is then connected to the solvent-recovery system. The solvent is boiled off and condensed, and the residual solids (plastics) are collected from the reservoir. Because plastics stick to glass after solvent is evaporated, the solvent-recovery system was not run to completion so as to not ruin the glass reactor and jeopardize the mass balance calculations. Rather, after most of the solvent had been evaporated and recovered, the thickened plastic-pregnant solution was poured into a clean tray, weighed, and allowed to dry in the hood overnight.

In the second phase of this program, we built a larger apparatus that can handle up to 100 lb equivalent of original fluff. The new design enables us to extract the thermoplastics, dry the treated fluff, and regenerate the solvents all in the same apparatus. Figure 3 is a schematic diagram of that apparatus. It has a reservoir capable of holding up to 12 L of a solvent; the reservoir is electrically heated in a specially designed heating mantle, which is capable of isolating the solvent from the heating circuits in case of an accident. The distilled solvent vapor rises in the annulus of the double-jacketed column, maintaining the fluff, which is kept in the inner column, at the boiling point of the solvent. The solvent that condenses in the annulus is continuously returned to the solvent reservoir. The solvent vapor that reaches the top of the column is condensed and falls back over the fluff in the inner column. Unlike the Soxhlet unit, no solvent accumulation in the chamber containing the fluff occurs. The liquid solvent percolates through the liquid and returns with the dissolved solids to the reservoir. At the completion of the experiment, the condensed solvent is diverted, by means of a three-way valve, away from the column and into a solvent storage vessel. This constitutes regeneration of the solvent. During the regeneration process, the operator directs the flow of vapors evolving from the fluff into the condenser and then to the storage vessel. This constitutes drying of the fluff.

This apparatus enables the operator to handle large quantities of fluff using small quantities of solvent because the rate at which the solvent is delivered to the fluff depends on the rate of heat supply to the solvent in the reservoir. Further, because fresh solvent is continuously delivered to the fluff, the extraction capacity of the solvent per pass is maximized. This is expected to minimize the required extraction time.

RESULTS

Results of the Phase I part of the research program were presented in a final report (Jody et al. 1992). These results demonstrated that solvent extraction of the thermoplastics from the fluff is technically feasible and is potentially economical. Results obtained so far under Phase II of the program, using a 55-gal-drum sample of

actual fluff from one supplier, are summarized in Figure 4. Because large variations in composition can exist even in fluff generated at one site on a given day, the data reported are specific to that one sample only and should not be generalized. The composition of this fluff sample is significantly different from that of samples we have treated before. We designed our experiments to identify major variables that can impact the design of such facilities. However, at this stage we do not have all the necessary data to do so. The results presented in Figure 4 are discussed below.

Fluff Drying

This sample contained about 20% moisture, which is about average for the 10 samples we have handled in Phase I of the program. The drying process was conducted in an oven at temperatures in excess of 180°F. Interestingly, when the drying temperature was set at 220°F, some pieces of the fluff started to smolder and smoke. We do not know at this time if some specific material in this sample (e.g., catalyst from a catalytic converter that was inadvertently shredded) caused this effect. We will continue to investigate this phenomenon and establish some guidelines for the drying process. At this time we recommend that extreme care be exercised while drying fluff, including having an operator on-site.

Fluff Separation

The contents of this sample were present in different percentages than we have seen with most samples handled in Phase I. For example, this sample contained less than 2% flexible polyurethane foam. Most other samples contained about 10%. Over 60% of this sample was also separated as fines (<1/2 in.), about double the average of the previous samples. This is at least partially due to the shredding method practiced at the site that supplied us with this sample. The magnetic fines content of the fines fraction is about the same as in other samples.

Recovered Thermoplastics

About 2.75% of the fluff weight (as received) was recovered as thermoplastics. This represents about 17% of the weight of the plastics-rich fraction after its oils content was removed. The 17% is consistent with what was observed with other samples. Because we varied the experimental procedure in this phase of the program from that followed in the previous phase, we were able to increase the concentration of the ABS in the first cut and reduce the concentration of all other plastics. Figure 5 shows the infrared spectra for the ABS-rich material and a commercial-grade ABS. An effort is under way to purify this material further, because ABS is a material that sells for about \$2/lb. If obtained in commercial quality, it could be worth up to \$50/ton of fluff processed.

By isolating the ABS, we are increasing the concentration of PVC in the second cut. This should also increase the value and the marketability of the recovered PVC. We do not have the analysis on the second cut yet. The recovered polypropylene and polyethylene fraction is about the same as what we had before. On the basis of the use of these materials in automobiles, we expect this cut to be predominantly polypropylene.

Recovered Oils

About 1.5% of the fluff (as received) weight was recovered as a mixture of oils. These include brake fluids, engine and transmission oils, grease, and others. Analysis of this free-flowing mixture showed that its specific gravity at 60°F is 0.8956, its density at

the same temperature is 7.437 lb/gal, and its heating value is 17,432 Btu/lb. This corresponds to about 0.5 million Btu/ton of fluff (as received), which is about as much energy as it takes to dry the fluff.

The Residual Material

The residual material from which the thermoplastics have 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 easier to pelletize or cube because it is dry and its foam content has been separated. Samples of that material have been sent for testing at incineration and pyrolysis test facilities. Results are not available at this time.

CONCLUSIONS

It is too early to draw conclusions based on the Phase II work. However, the limited data obtained so far support the conclusions of our Phase I work that this concept is technically feasible and that valuable products can be derived from the fluff. Needless to say, more work is needed before this process can be commercialized.

ACKNOWLEDGEMENT

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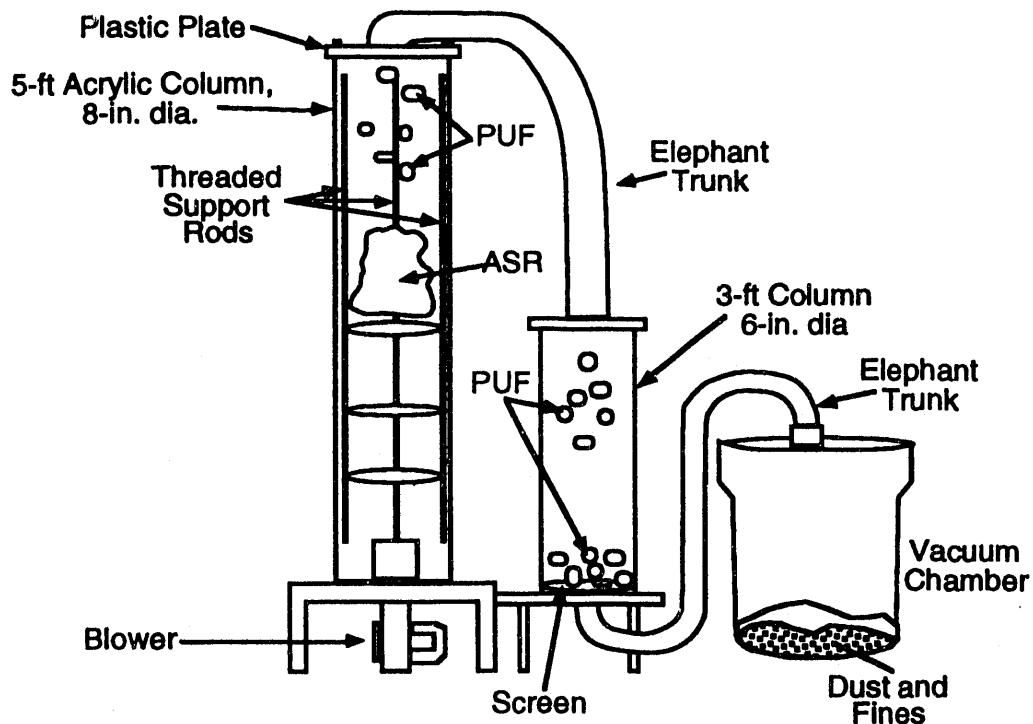


Figure 1. Laboratory Apparatus for Physical Separation of PUF, Fines, and Plastics-Rich Shredder-Fluff Fractions

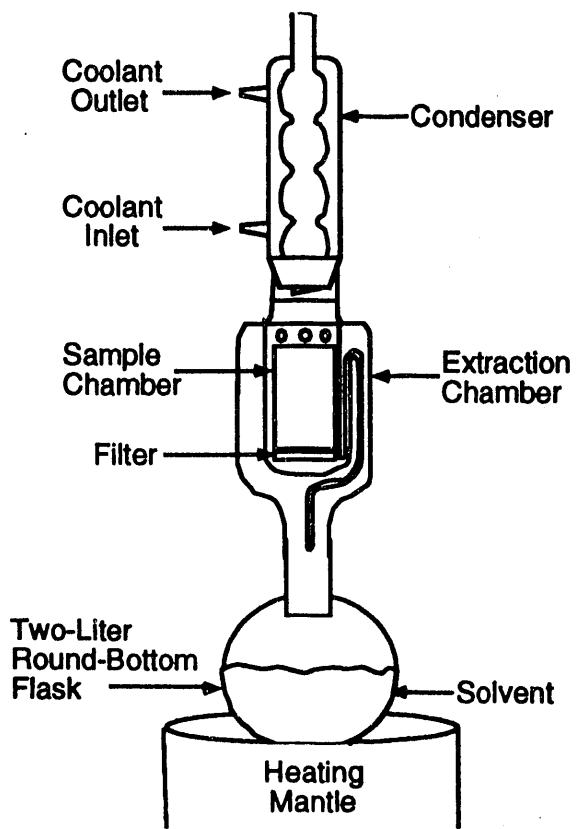


Figure 2. Sohxlet Solvent Extraction Apparatus

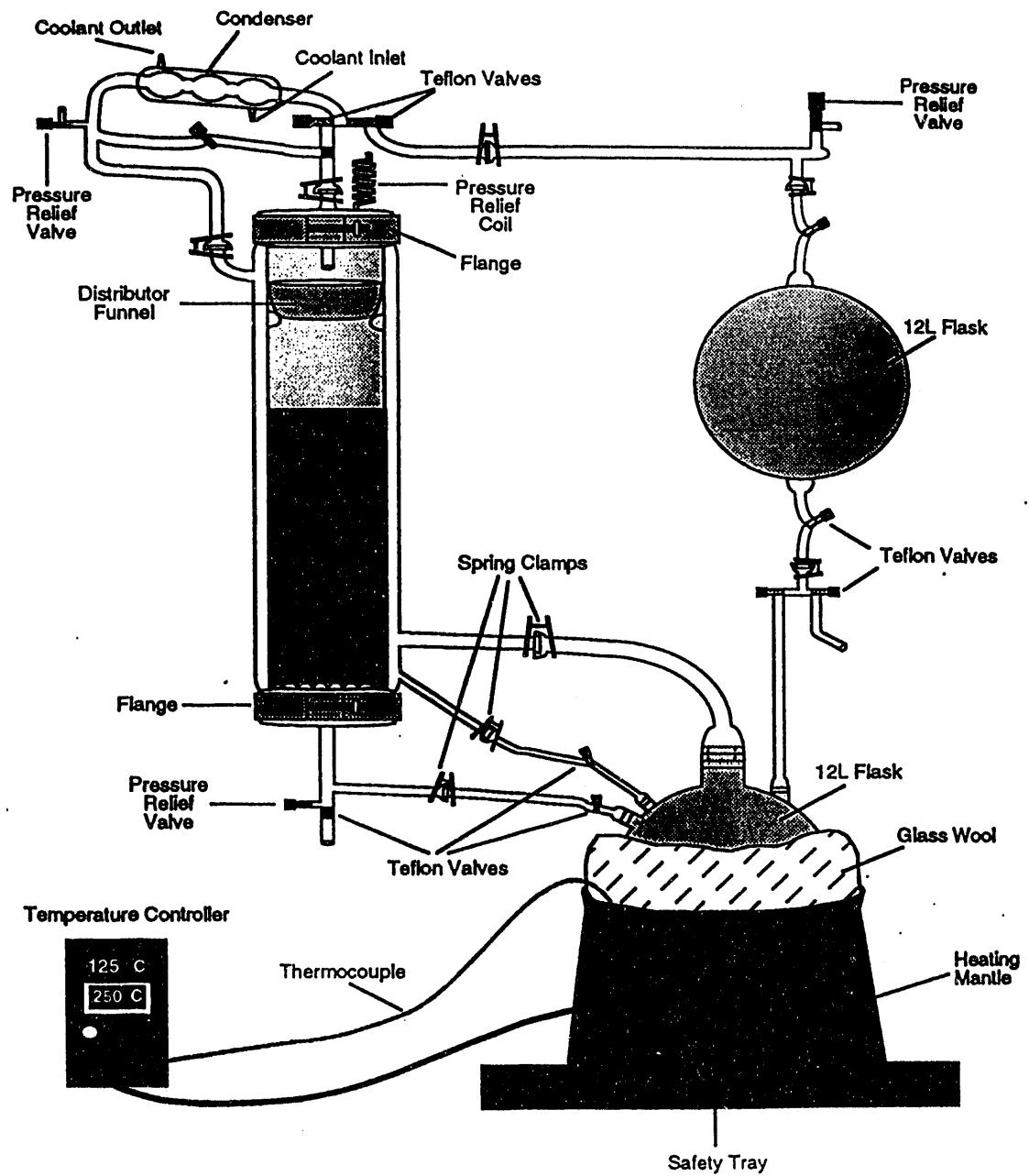


Figure 3: Schematic Diagram of Phase II Test Apparatus

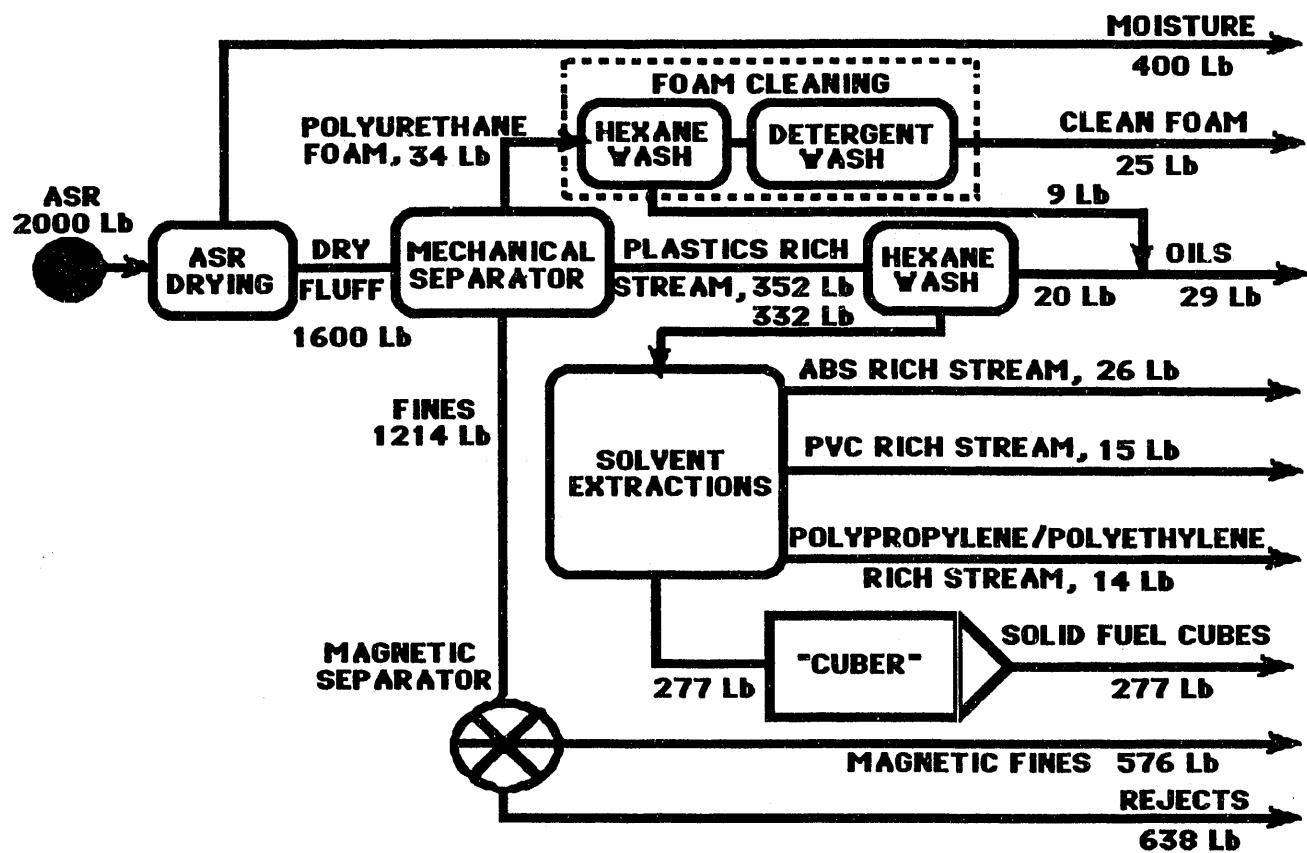


Figure 4. Material Balance for an Actual Fluff Sample Treated in the Scaled-Up Test Facility (Phase II)

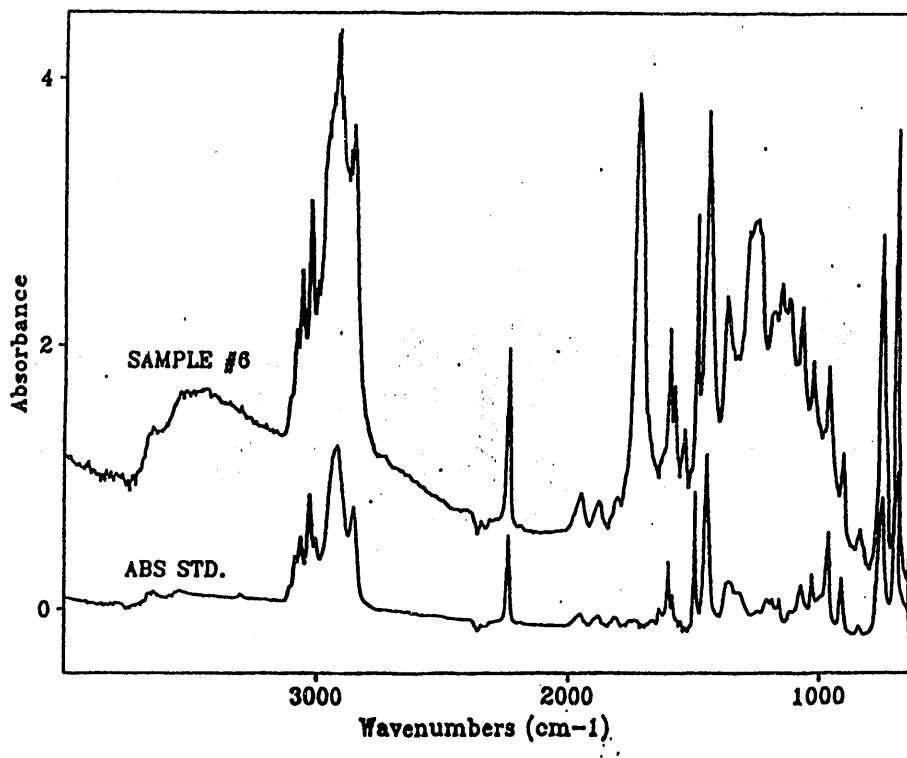


Figure 5. Infrared Spectra for the Recovered ABS-Rich Sample and a Commercial-Grade Material.

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