

Clean Energy from Waste and Coal

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M. Rashid Khan, EDITOR
Texaco, Inc.

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by the Division of Fuel Chemistry
at the 202nd National Meeting
of the American Chemical Society,
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Foreword

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Before a symposium-based book is put under contract, the proposed table of contents is reviewed for appropriateness to the topic and for comprehensiveness of the collection. Some papers are excluded at this point, and others are added to round out the scope of the volume. In addition, a draft of each paper is peer-reviewed prior to final acceptance or rejection. This anonymous review process is supervised by the organizer(s) of the symposium, who become the editor(s) of the book. The authors then revise their papers according to the recommendations of both the reviewers and the editors, prepare camera-ready copy, and submit the final papers to the editors, who check that all necessary revisions have been made.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

M. Joan Comstock
Series Editor

Preface

THE USE OR DISPOSAL OF OUR ENORMOUS WASTE RESOURCES in an efficient and environmentally acceptable way constitutes one of the major challenges of our time. Currently, nearly half the petroleum consumed in the United States annually is imported. The billions of dollars the U.S. spends for imported oil underlines the magnitude of this country's energy needs and rate of consumption. Both domestic consumption and dependence on imported energy are expected to grow. Therefore, conversion of our wastes into clean energy is a significant—and urgent—technical challenge for our scientists.

More than 160 million tons of garbage are produced in the United States every year, about two-thirds of a ton per person. In our culture of planned obsolescence, even durable goods find their way to the junkyard. It is often more convenient and economical to throw away clocks and cabinets than to repair them, as is generally done in other nations. Use of solid wastes, agricultural residues, and trees through thermal conversion processes have been practiced to a varying extent in many parts of the world. Energy shortages and environmental issues during the past decades, however, have introduced new perspectives in developing energy resources from these waste materials.

We need to develop environmentally acceptable and economical waste-based fuel forms by appropriate pre- and posttreatment. The objective of this book is to identify problems and opportunities in deriving clean energy from waste. The following wastes are considered: municipal solid waste, sludge, biomass, plastics, and tires. The chapters can be divided into two broad categories: (a) fundamental and applied aspects of waste to energy conversion and (b) the characterization, use, and disposal of byproduct ash. In many chapters, co-utilization of coal and waste have been considered. No book of this sort can hope to be comprehensive; we have tried to present an interdisciplinary treatment of some of the major topics to stimulate scientific collaboration.

This book would not have been possible without the dedicated work of the authors, reviewers, and the ACS Books Department staff. The efforts of Rhonda Bitterli, Cheryl Shanks, and Bruce Hawkins of the ACS are greatly appreciated.

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Chapter 1

Clean Energy from Waste

Introduction

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It has been stated that the North Americans are short on energy but long on wastes. On a per capita basis, the United States is the largest consumer of energy but the greatest producer of waste in the world. The US cities dispose of about half a million tons of municipal solid waste (MSW) daily (about 95% of which is land-filled), while importing over 15 million barrels of crude daily. Over 80% of the cities are expected to run out of landfills by the end of this decade. The enormity of the problem has been depicted by the story of a garbage-laden barge from NY crossing international waterways in desperate search of a dump-site.

The US uses about 5% of its MSW to generate electricity, while the other industrial nations have been doing so at a much larger scale for a longer time. For example, Japan uses 26% of its waste in 361 plants. The use by other nations are as follows: Germany 35%; Sweden 51%; Switzerland over 75%. The slow growth in the waste utilization facilities in the US is primarily a result of concern over air pollution generated from these facilities.

In addition to MSW problems, to the treatment plants in the US, the total daily flow of wastewater is expected to increase from a current 28 billion gallons to about 33 billion gallons by the year 2000. Much of the sewage, present in the wastewater, and industrial sludges had been traditionally landfilled or ocean dumped.

Over a decade ago, the US embraced several waste-to-energy facilities, but plant failures and operational difficulties were the norm. Years later, the technology is now more mature but the problem still exists in terms of public perception and governmental support. There are barriers on both scientific and social/institutional aspects. For example, in response to mounting pressures on municipalities to meet increasingly stringent

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environmental regulations by installing expensive control equipment, many simply decided to retire their facilities to "moth-ball" status. When an organization plans a waste-to-energy plant, the community typically responds by expressing the "not-in-my-backyard" syndrome.

There are serious concerns over the potential release of some products of incomplete combustion (products such as benzopyrene, dioxin, and benzofurans) and emission of volatile metals from incinerators. Numerous studies have been initiated by the US DOE, EPA and various industries for identifying ways to mitigate these problems. Energy recovery from waste has received broad technical acceptability as new and advanced technologies demonstrate their capability. For example, in contrast to direct combustion, advanced gasification technologies can be used to produce a clean synthesis gas from waste. The synthesis gas can be combusted in advanced gas turbines to generate electricity without contributing to air pollution. Coal represents 90% of the U.S. proven reserves of fossil fuels. In many cases, both waste and coal are used for energy generation. Co-utilization of waste and coal offers many technical and economic advantages not achieved by processing waste alone. Thus, in several chapters of this book, the use of coal has been considered along with waste.

The objective of this book, contributed by internationally recognized experts, is to present the state-of-the-art data related to waste-to-clean energy processes. The major wastes of interest are: sewage and industrial sludge, municipal solid waste, tires, biomass, plastics and polymeric wastes. The reader will recognize that several other important wastes (refinery waste, black liquor, etc.), may well serve as excellent sources of energy, but are not considered here.

Sewage and Industrial Sludge

Dumping of sludge in the Boston Harbor became a hot debate issue during the 1988 presidential election, although a relatively small portion of sludge produced is ocean dumped (Table I). Major cities in the Eastern US (New York City, Boston, and municipalities located in major counties such as Westchester and Suffex) had been dumping sewage sludge in the ocean. Treatment plants in the US produce about 7 million tons of dry sewage sludge daily. About 20% of the sludge produced is incinerated and about 60% of it is landfilled, while only a small portion of the overall production is ocean dumped. The EPA, however, has imposed a stiff penalty for ocean dumping of sludge. After January, 1992, the penalty for ocean dumping was increased to \$600 per dry ton of sludge in the Eastern US. The alternatives of ocean dumping, namely landfilling or incineration, are meeting strong opposition for environmental reasons.

Table I. Disposal and End Use of Sludge

Method	(dry ton/y) Amount	Percent
Landfilling (dumping)	3,094	40.8
Incineration	1,541	20.3
Land application (usage)	1,424	18.8
Ocean disposal	498	6.6
Distribution/marketing	455	6.0
Other	541	7.7

SOURCE: Adapted from ref. 1.

Before sludge can be burned or gasified autogeneously (without auxiliary fuels) some level of water removal is needed. The major technical steps involved for the use of sewage sludge as a source of energy are the following: dewatering, conditioning, and processing to recover energy by combustion or gasification. For example, processes using the multiple hearth furnace, fluid-bed combustor, or one of the many gasification technologies can be readily used to extract energy from sludge.

Primary sewage sludge is generally thickened by gravity, but the sludge can also be mechanically dewatered to produce a relatively dry cake. Secondary sludge is generated by the biological treatment processes. The typical heat content of the primary sludge is about 7000 Btu/lb, which is greater than that of the secondary sludge which contains a heating value of about 4000 Btu/lb. The solids content of the primary sludge is low, generally lower than 10 percent. The types of water that can be associated with a particle of sewage sludge can be classified as follows: water bound to oxygenated functional groups and/or cations, capillary or micropore bound water, monolayer water, and bulk or free water. Polymeric additives are generally added to agglomerate the sludge particles and thereby water removal is facilitated. About 3 to 8 lbs of polymer is used per ton of dissolved solids. Polymer usage is not only expensive, but added polymers may also adversely affect the slurring and pumping characteristics of the dewatered sludge. The major technology currently in use is incineration. Land usage of sludge, however, may require some conditioning of sludge to lessen the biological activity. Pyrolysis based processes apply relatively high temperatures to produce a liquid fuel from sewage sludge. However, no such process has ever been commercialized. Because of concerns related to environmental issues, incineration has become an unpopular option to dispose of sludge. In particular, the fate of heavy metals present in sludge during incineration is not well known. There are concerns

regarding the release of some heavy metals into the atmosphere. Wet air oxidation processes serve to dewater the sludge but do not address the issue of ultimate disposal of sludge or the metals present in it. During gasification, however, the organics present in sludge are converted to useful synthesis gas (CO & H₂) while the minerals present in the feed are converted into rigid non-leachable slag potentially useful in the materials industry.

The major technical issues associated in processes aimed at extracting energy from sewage and industrial sludges are the following: (a) low-cost dewatering operation; (b) improvement of the rheological and pumpability of concentration sludge (containing >20% solids); (c) nature, type and fate of inorganics present in sludge during advanced processing; (d) improvements in emission and odor control during sludge processing. Some interesting papers on sewage sludge can be found in references 1-5. Details of the issues are beyond the scope of this chapter.

Municipal Solid Waste

Municipal Solid Waste (MSW) is one of the least used by-product resources in the United States (6,7). Until recently the common practice for disposal of MSW was dumping. The dumping sites were usually either the ocean or an open pit (8,9). The disposal of refuse is an increasing concern of municipalities and state governments throughout the United States. In the year 1990, it was estimated that 160-200 million tons of MSW was disposed from the residential, commercial, and institutional sectors and is increasing yearly (9). Each ton of municipal solid waste is equivalent in energy content to more than a barrel of oil (10).

Cities are running out of space for landfills. One of the attractive solutions to landfills is incineration. In the early 1970s, environmental concern began to rise causing citizens to become increasingly cautious of residing near landfill sites. Due to air pollution, the garbage or MSW was no longer burned. At that time there were many landfills, and new landfill sites were available for disposal of garbage. Those landfills are either full or becoming full, and new landfills are expensive and difficult to site.

Americans dispose of 80-90 percent of their MSW into landfills filling them very quickly. The landfills in America have been reduced from 10,000 in 1980 to 6,500 in 1988, to less than 5,000 in 1992 (11,12,13). Not only is the air polluted because of MSW, but the ground water is polluted as well when the garbage decomposes. Changes in the weather and rainfall are major factors contributing to garbage decomposition. It has been estimated that water polluted today will be affected for hundreds of years (14).

In 1989, the Environmental Protection Agency (EPA) proposed regulations for stricter control of new and preexisting landfills. These measures, which went into effect in 1991, will help in solving the problem, but are expensive. It is estimated that it will cost over 800 million dollars per year to implement these methods nationwide. The regulations and controls include monitoring ground water for contamination, allowing for the controlled escape of methane which forms as the garbage decomposes, and permanently sealing landfills after they are filled (15).

Sources of Municipal Solid Waste. Municipal refuse is a heterogeneous mixture of organic and inorganic wastes discarded by homes, schools, hospitals, and a variety of other sources in the community. The major contributors to solid waste are (16):

- a) Domestic: single and multiple dwellings
- b) Commercial: offices and retail stores
- c) Entertainment centers: restaurants, hotels and motels, and service stations
- d) Institutional: schools, hospitals and municipal buildings
- e) Municipal services: demolition and construction, street and alley cleaning, landscaping, catch basin cleaning, parks and beaches, and waste treatment residues

Content of Municipal Solid Waste. Municipal solid waste is an aggregate mixture of waste materials that can be classified as an organic fraction, an inorganic fraction, and moisture. The organic fraction, which makes up to 30% of the waste, is primarily cellulose (wood fibers). It is considered a major source for energy recovery. The inorganic fraction is noncombustible. It can be either recyclable or after combustion constitutes the ash residue. Table II shows the summary of the chemical characterizations of MSW (17).

Another aspect or objective of many of the recovery processes of MSW is to utilize its thermal energy. The heat content of MSW is important. The heat content of the as-received refuse can reach 3,500 to 5,500 Btu/pound (16). A reduction of the moisture or inert contents will increase the heat content. Decreased quantities of plastics will also decrease the heat content of MSW (18).

There are many solutions that have been proposed for the problem of growing landfills and the increase in MSW. These solutions include mass burning, burying, recycling, and use as an energy source using Refuse Derived Fuel (RDF).

The analyses shown in Table II were developed by one of the authors during experimental work on the Denton, Texas landfill during 1980-81 (17). The composition was based on repeated sampling and testing of the Denton landfill.

Table II. Municipal Solid Waste Composition (moisture free) in Denton, Texas - 1981

a. Combustible	
Paper	52%
Plastic	14%
Wood	5%
Garden Waste	4%
Food Waste	3%
Rubber	1%
Leather	1%
b. Non-Combustible	
Glass/Ceramic/ Stone	9%
Ferrous	6%
Aluminum	2%
Industrial/ Commercial	2%
Residual	
Dirt	1%

SOURCE: Reprinted from ref. 17.

Table III presents results of the manufacturing operations of the Eden Prairie Recycling plant in Eden Prairie, Minnesota (Division of Green Isle Environmental Services, Inc.). The data presented are recycling data for the months of June, July and August of 1992 (19).

Conversion or Oxidation of Municipal Solid Waste.

Burning MSW not only reduces the volume of garbage by 80% but may also provide usable energy. MSW can be used in three different ways:

1. Direct combustion, mass burn: the MSW is fed into the furnace through a moving grate where the temperature reaches 2400°F. The problems with the mass burn incinerators are the cost of the incineration facility and the emissions.
2. Conversion of MSW into liquid or gaseous fuel by means of gasification, pyrolysis, biodegradation, or hydrogenation. The liquid or gaseous fuel produced can then be easily cofired with coal or oil.
3. Burning of the combustible portion of MSW, Refuse Derived Fuel (RDF), after separating the incombustible portion.

The incombustible portion of MSW and the ash are discarded in landfills which create a new problem, namely pollution. Ash contains some organic constituents and some trace elements at different levels. Ash is considered hazardous if the levels of toxic constituents are high.

Table III. Eden Prairie Recycling, Inc. (19)					
	1992 Tons			Total	Total
	June	July	August	Tons	%
<u>Recyclables</u>					
Aluminum	16.40	14.11	10.73	41.24	0.15
Metal	0.00	0.00	0.00	0.00	0.00
Plastic	3.21	3.12	5.54	11.87	0.04
Corrugated	170.81	191.47	121.24	483.52	1.71
Ferrous Mtl	114.87	95.51	102.14	312.52	1.11
Scrap Metal	107.18	91.37	79.56	278.11	0.99
TOTALS	412.47	395.58	319.21	1127.26	4.00
<u>Fuel</u>					
RDF	2982.16	3376.23	2563.49	8921.88	31.62
<u>Composted/Incinerated/Other</u>					
	4091.09	3170.64	2286.46	9548.19	33.84
<u>Landfilled</u>					
Heavies	1714.97	3246.49	1992.34	6953.80	24.65
Rejects	496.55	609.67	557.72	1663.94	5.90
TOTALS	2211.52	3856.16	2550.06	8617.74	30.55
TOTAL TONS	9697.24	10798.61	7719.22	28215.07	100.01

Table IV shows that the use of MSW as a source of renewable energy is expected to grow at a rate higher than 8% between 1989 and 2010 (20).

Landfilling MSW. Sanitary landfills were increased in 1976, when the Resource Conservation and Recovery Act (RCRA) gave the EPA the authority to close open landfills and upgrade the quality of sanitary landfills. Sanitary landfills are typically huge depressions lined with clay to minimize leakage of pollutants into the groundwater. Heavy equipment is used to spread the MSW out and compress it every day. After the landfill has been packed to capacity, a layer of dirt and/or plastic is used to cover the day's haul.

Table IV. Renewable Energy
(Quadrillion Btu per Year)

Electricity and Non-Electric	1989	2010	Annual Growth 1989-2010 %
Electricity			
Capability (gigawatts)			
Convent. Hydropower	75.48	78.46	0.2
Geothermal	2.47	10.65	7.2
MSW	1.98	10.81	8.4
Biomass/Other Waste	5.31	8.88	2.5
Solar Thermal	.33	1.78	8.4
Solar Photovoltaic	.00	.01	2.1
Wind	1.93	5.30	4.9
Total	87.51	115.90	1.3
Generation (billion Kilowatthours)			
Convnt. Hydropower	276.90	314.80	.6
Geothermal	15.05	78.52	8.2
MSW	13.31	74.22	8.5
Biomass/Other Waste	29.54	49.55	2.5
Solar Thermal	.69	5.06	10.0
Solar Photovoltaic	.00	.00	2.2
Wind	3.38	12.97	6.6
Total	338.90	535.10	2.2
Consumption/Displacement			
Convent. Hydropower	2.88	3.27	.6
Geothermal	.16	.82	8.2
MSW	.20	1.27	9.2
Biomass/Other Waste	.20	.33	2.5
Solar Thermal	.01	.05	10.0
Solar Photovoltaic	.00	.00	2.3
Wind	.04	.13	6.6
Total	3.48	5.88	2.5
Non-Electric Renewable Energy			
Residential, Commercial & Industrial			
Hydropower	.00	.00	-
Geothermal	.00	.39	-
Biofuels	2.63	4.54	2.6
Solar Thermal	.05	.54	11.6
Solar Photovoltaic	.00	.00	-
Wind	.00	.00	-
Transportation			
Ethanol	.07	.14	3.5
Total	2.75	5.62	3.5
Total Renewable Energy	6.23	11.50	3.0

SOURCE: Reprinted from ref. 20.

Sanitary landfill operators follow strict guidelines. They control and monitor methane gas generation, surface water runoff, and groundwater contamination by the landfill.

Refuse Derived Fuel

Refuse Derived Fuel (RDF), shredded MSW with most glass and metals removed, is an attractive solution since it also addresses another problem affecting the United States: depleting energy reserves. One ton of RDF has the energy equivalent of one barrel of oil (21). RDF has a 7,000 to 8,000 Btu/pound heat content. The powdered RDF, embrittled and pulverized refuse, will even have a higher heat content of over 8,500 Btu/pound (16).

RDF Technology. The starting material of RDF is MSW. The exact composition of MSW varies according to the area, the time of the year it was collected, and the make-up of that particular community. RDF refers to the heterogeneous mixture of the combustible portion of MSW (22).

The concept of RDF has existed since the early 1970s (23). There are seven forms of RDF that have been defined as described in Table V (22). RDF is commonly used in two forms, fluff (RDF-1) and densified RDF (RDF-5; dRDF).

There are several problems with using RDF-1 that make it less attractive, such as: it is hard to handle, it is usually burned in suspension: and often causes problems in ash handling since much of it remains unburned (14). On the other hand, the main benefits of using RDF rather than raw refuse are:

- * RDF when properly processed, can be stored for an extended period of time
- * RDF technology allows for the recovery of saleable material
- * RDF can be combusted in a wide range of existing boilers, fluidized bed combustors, gasifiers, and cement and brick kilns
- * RDF can also be used as a feedstock for anaerobic digesters to produce methane gas
- * RDF can easily be transported from one location to another
- * RDF can be burned on a supplemental basis with other fuel, such as coal or wood

Table V. Types of Refuse Derived Fuel

RDF-1	waste used as fuel in as-discarded form
RDF-2	waste processed to coarse particle size with or without ferrous metal separation
RDF-3	shredded fuel derived from MSW that has been processed to remove metals, glass and other inorganic materials (95 wt% passes 50-mm square mesh)
RDF-4	combustible waste processed into powder form (95 wt% passes 10 mesh)
RDF-5	combustible waste densified (compressed) into a form of pellets, slugs, cubits or briquettes (dRDF)
RDF-6	combustible waste processed into liquid fuel
RDF-7	combustible waste processed into gaseous fuel

SOURCE: Adapted from ref. 22.

- * RDF is more homogeneous, yielding low variability in fuel characteristics, thereby making combustion control easier to implement. It also burns more evenly at a higher sustained temperature.
- * RDF has a lower percentage of unburnable residuals such as metals and glass, and this has a higher heat content per unit weight than does unprocessed solid waste.
- * RDF when burned in a dedicated boiler has a greater thermal efficiency (8-10 percent greater).
- * RDF can have a beneficial effect on air emissions and ash residue, compared to burning MSW.

In order to effectively utilize the combustible portion of MSW, known as RDF, it is necessary to densify the RDF in order to transport it economically and easily. It is then called Densified Refuse Derived Fuel (dRDF). This densification step can increase the density of RDF from 2 to 3 pounds per cubic foot to 40 or more pounds per cubic foot (10). If dRDF is going to be stored for a period of time longer than several days, a binder must also be added. Calcium hydroxide ($\text{Ca}(\text{OH})_2$), which has been proven to be the best binder, is often added to RDF before densification. The binder delays biological and

chemical degradation for years and reduces SO_x , NO_x and other emissions by cofiring with coal (12,23).

Plastics

Plastics, unrecyclable and recyclable, make up 9% of MSW by weight and approximately 19% by volume. In 1987, over 57 million pounds of plastics were sold in the US. Although plastics have been recycled for over a decade, only a little over 1% of the plastics produced are recycled. Even with a large increase in recycling, there is considerable room for research and development to find ways to derive clean energy from plastics.

Governments have taken or are considering taking actions that affect plastic recycling. A significant one involves the banning of certain plastics outright. One target of such laws is polystyrene, the foamed, insulating plastic that is most often used for coffee cups and fast food packaging. Some areas have banned polystyrene packing; others have banned polystyrene foam made with chlorofluorocarbons as a blowing agent. The US Congress has been considering measures that would encourage recycling by placing a tax on the use of virgin materials. If industries could successfully demonstrate the usage of these materials as a feedstock for making useful chemicals or energy, then the urgency to ban making them would be reduced. Once the technical issues of feed collection and preparation were addressed, these wastes could be used as a source of clean energy.

Virtually each type of plastic has unique chemical and physical properties. These qualities effect the recyclability of the plastics and the use of recycled plastics. For example, polyurethane mixed into a batch of polyethylene terephthalate (PET) can greatly reduce the strength of the PET and render it unsuitable for many applications. That means, the recyclers must separate the different types of plastics before doing anything with them. This also shows that there are limits on the recyclability of plastics.

With many plastics being unrecyclable, the processing required for recycling often being limiting, and the fact that plastics have a high energy content (18,000 Btu/lb.), there exists an opportunity for plastic waste as a fuel. The current options for plastics, in addition to recycling, are combustion (incineration) and landfilling, both of which are unpopular. Successful use of plastics as a feedstock for a process such as gasification would help to reduce landfilling and incineration and would provide a clean source of energy.

Other Wastes

There are numerous waste materials which can be considered as potential clean energy sources, in addition to the sludge, MSW and plastics considered above. Tires, for example, are being discarded in the United States at the rate of about one tire per person per year. Tire rubber has an energy content of about 18,000 Btu per pound but has some environmental concerns from a combustion perspective.

Concluding Remarks

Each waste material is a problem requiring extensive study and assessment of sound technology. Nor are these problems mutually exclusive: as (for example) tires and biomass are commonly encountered in MSW. However, each major waste area has the potential of becoming a waste-to-clean energy process. Through the dedication and efforts of recognized experts in this book and elsewhere, technologies will be developed to produce clean energy from wastes.

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Chapter 2

Efficient and Economical Energy Recovery from Waste by Cofiring with Coal

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Cofiring fuels derived from municipal and nonhazardous industrial wastes with coal in industrial and utility boilers is an efficient and cost-effective method of energy recovery from wastes in many cases. Waste fuels such as scrap tires, tire-derived fuel, refuse-derived fuel, paper mill sludge, sewage sludge, sawdust, wood, and industrial waste can be cofired with coal in many stoker, pulverized coal, cyclone, and fluidized bed boilers with only minimal modifications and with minimal impacts on environmental emissions and plant safety. Waste cofiring with coal usually exhibits a higher waste-to-energy conversion efficiency than 100 percent waste firing in dedicated waste-to-energy plants, because coal-fired plants typically operate at higher steam pressures and temperatures and therefore higher steam-cycle and thermal efficiencies than dedicated plants. In addition, waste cofiring generally requires a much lower incremental capital investment than waste firing in a dedicated waste-to-energy facility. Both factors can contribute to a lower breakeven waste disposal cost or tipping fee for waste fuel cofiring with coal than for dedicated plants. This economic advantage should be highest for low-volume, low heating-value fuels, such as municipal solid waste and sewage sludge, and lowest for high-volume, higher quality fuels, such as scrap tires.

In response to the environmental crisis in the U.S. created by the growing volume of municipal and industrial wastes and declining availability of landfill disposal sites, many urban communities are developing integrated waste management plans to both reduce the volume of the wastes sent to landfill and recover valuable raw materials and energy as steam and/or electricity. Most integrated waste management plans involve a combination of recycling, composting, waste-to-energy technology, and landfilling of residues, applied in sequence. Waste-to-energy plants will therefore be the last stop for the large portion of the waste stream that is not recyclable.

The waste fuels burned in waste-to energy plants are derived from a variety of sources, including residential and commercial refuse, sewage sludge, automotive tires, urban demolition wastes, agricultural wastes, wood waste from forestry operations and lumber mills, paper mill sludge, and other industrial wastes. Most waste-to-energy

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facilities use dedicated waste-to-energy technology designed to efficiently recover energy as steam or electricity while controlling environmental emissions. In addition, several existing fuel combustion facilities have been retrofitted to burn waste fuels either alone or in combination with coal or oil, including industrial and utility boilers and cement kilns.

This paper addresses the current and future generation of waste fuels in the U.S., waste fuel properties, alternate waste-to-energy technologies, and energy conversion efficiencies and costs of the alternate technologies. To represent the range of waste fuels available, the discussion focuses on scrap tires, refuse-derived fuel, wood waste, and sewage sludge.

Annual Generation and Properties of Waste Fuels

Of the 185 million tons of municipal wastes and 200 million waste tires generated each year, it is estimated that up to 25 percent could be recycled and reused, leaving about 75 percent for disposal in landfills and waste-to-energy facilities. The remaining 140 million tons of MSW contains the energy equivalent of 58 million tons of bituminous coal and would be sufficient to provide 11 thousand megawatts of generating capacity. The corresponding figures for waste tires are 1.9 million tons of coal and 640 MW of generating capacity. Currently, about 16 percent of the municipal solid waste stream and a small fraction of the waste tires are processed in waste-to-energy facilities, and these fractions are expected to grow significantly by the year 2000, perhaps to 40 percent. At the same time, annual waste generation can be expected to grow at about two percent per year (1).

Typical fuel properties are presented in Table I for tire chips, refuse-derived fuel, wood waste, and sewage sludge (2,3). The rubber tire chips are made by shearing waste tires to one-inch top size and removing as much of the steel belt and bead material as possible by magnetic separation, producing a fuel containing 1.2 percent sulfur, 14.8 percent ash, and 12,500-14,500 Btu/lb. The refuse-derived fuel (RDF) is produced from municipal solid waste by shredding, screening, and magnetic separation and contains 0.2 percent sulfur, 12 percent ash, 24 percent moisture, and 5,900 Btu/lb. The wood waste is a mixture of chipped forest residue, bark, and milling waste, containing 0.02 percent sulfur, 0.7 percent ash, 39 percent moisture, and 5,140 Btu/lb. The municipal sewage sludge has been dewatered to 86.2 percent moisture content in a centrifuge and contains 6.8 percent ash. Due to its high moisture content, the high heating value is only 464 Btu/lb and the low heating value is negative (-484 Btu/lb).

Table I. Coal and Waste Fuel Properties

	<u>WV Coal</u>	<u>Tire Chips</u>	<u>RDF</u>	<u>Wood Chips</u>	<u>Sewage Sludge</u>
% S:	0.85	1.19	0.20	0.02	0.07
% Ash:	16.04	14.76	12.0	0.74	6.8
% Moisture:	6.60	8.55	24.0	39.10	86.2
Btu/lb:	11,680	13,500	5,900	5,139	464

SOURCE: Adapted from ref. 2.

Due to their low sulfur contents, cofiring wood chips or RDF with coal would reduce emissions of sulfur dioxide (SO₂) relative to those for coal firing. However, as discussed below, the high moisture contents of wood chips and RDF lead to degradation of power plant efficiency and performance. Relative to heat content, tire chips and sewage sludge have moderate sulfur contents, and cofiring with coal can either increase or decrease SO₂ emissions, depending on the coal sulfur content.

Waste-to-Energy Technologies

Several methods are available for energy recovery from waste fuels, including construction of dedicated waste-to-energy facilities and conversion of existing coal-fired facilities to burn the waste fuels. Most dedicated waste-to-energy facilities use mass-burn, stoker firing, or fluidized bed combustion technology to burn the waste fuels (4,5). In mass burn plants (Figure 1), waste fuels are typically burned in a refractory lined furnace or on a sloping reciprocating grate without prior size reduction or processing to remove noncombustibles. Stoker-fired and fluidized bed plants typically require at least some size reduction to avoid plugging the fuel handling and injection equipment (4). In Japan, several fluidized bed units are burning industrial and municipal wastes without significant size reduction (4,6).

Many existing facilities, including industrial boilers, cement kilns, and coal-fired power plants, can be converted to burn waste fuels either alone or in combination with other fuels such as coal. Figure 2 is a schematic of a utility boiler converted for RDF cofiring. Currently, RDF is cofired with coal at one cyclone and three pulverized coal power plants (7), cofired with wood at two fluidized bed plants (8,9), and fired alone at three converted utility stoker-fired plants (10). Whole tires are cofired with coal at one wet-bottom pulverized coal plant, and tire-derived fuel has been cofired with coal at four cyclone-fired plants and at three stoker-fired plants (11). In addition, one utility has cofired pulverized wood chips with coal (12).

It should be noted, however, that cofiring alternate fuels is not always technically feasible and that the maximum heat input fraction is often limited by practical or economic considerations. Factors that need to be considered include the boiler type (pulverized coal, cyclone-fired, stoker-fired, or fluidized bed), operating and performance limitations on coal, and required fuel specifications.

Pulverized coal boilers are designed to burn finely-ground coal in suspension. Most must be modified with a bottom dump grate to handle solid fuels such as RDF and tire and wood chips, although, as mentioned earlier, whole tires have been successfully tested in a slagging wet-bottom boiler without a dump grate (11). Cyclone-fired units burn the solid fuels in external cyclone burners, and because they remove most of the ash as a molten slag in the burners, a bottom dump grate is not required. It is unlikely that more than 20 percent of the heat input could be provided by alternate fuels in either case, due to adverse impacts on burner performance and heat release and absorption profiles in the boiler. Stoker-fired and fluidized bed combustion units would be generally more suited to cofiring alternate fuels at higher heat input fractions, subject to the operating and performance limitations discussed below.

Some utility boilers may exhibit operating and performance limitations on the net generating capacity while firing coal (13,14). These include the boiler convection pass flue gas velocity, ID fan capacity, electrostatic precipitator performance, ash handling capacity, and boiler tube slagging and fouling. In this case, cofiring low grade fuels such as RDF, wood chips, or sewage sludge would likely result in a loss of net generating capacity, even at low heat input fractions. This is because cofiring increases flue gas and bottom ash volumes and worsens any existing slagging and fouling problems. These boilers would not be suitable for cofiring alternate fuels.

The degree of fuel processing, which affects fuel particle size and ash, moisture, and heat contents, can also determine the feasibility of cofiring waste fuels. High ash, glass, and metal contents can lead to increased boiler slagging and fouling in pulverized coal boilers and plugging and jamming of moving grates in stoker-fired boilers (13).

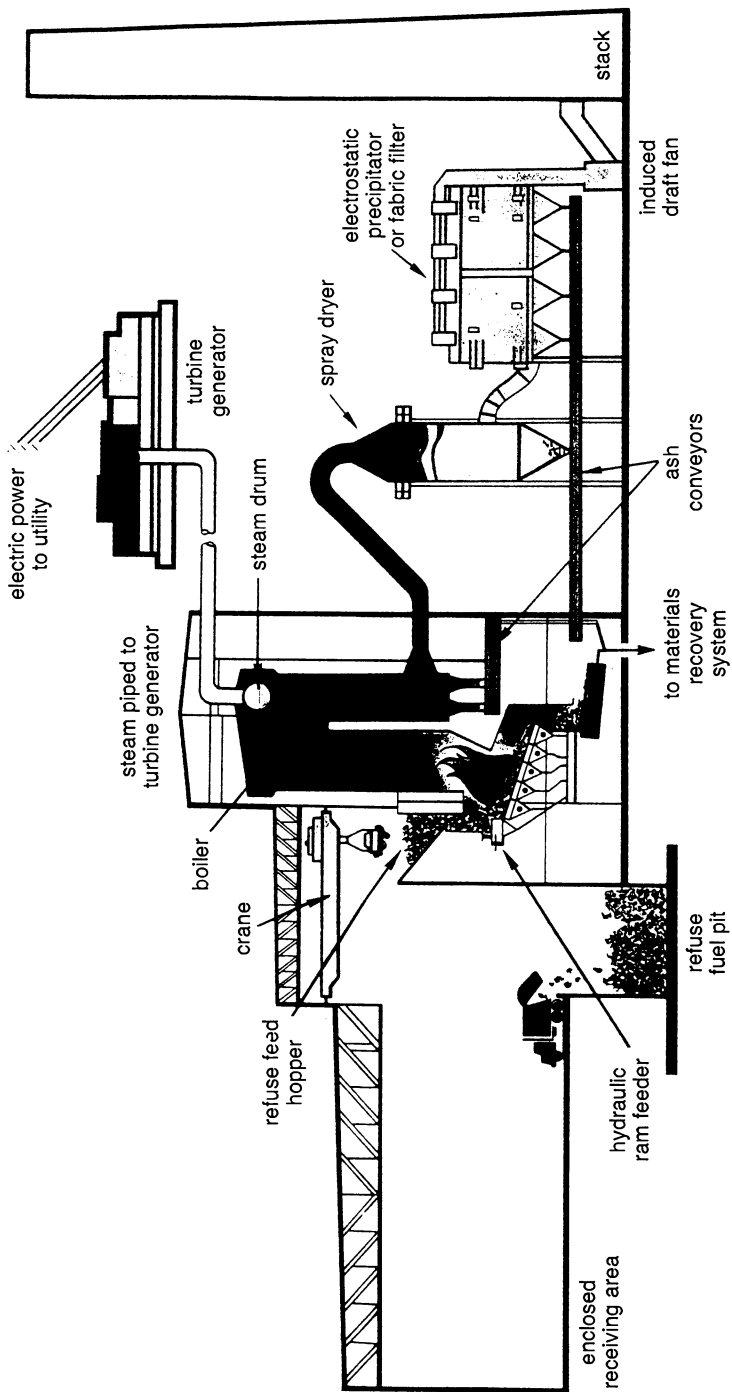


Figure 1. Schematic of Mass Burn Waste-to-Energy Facility
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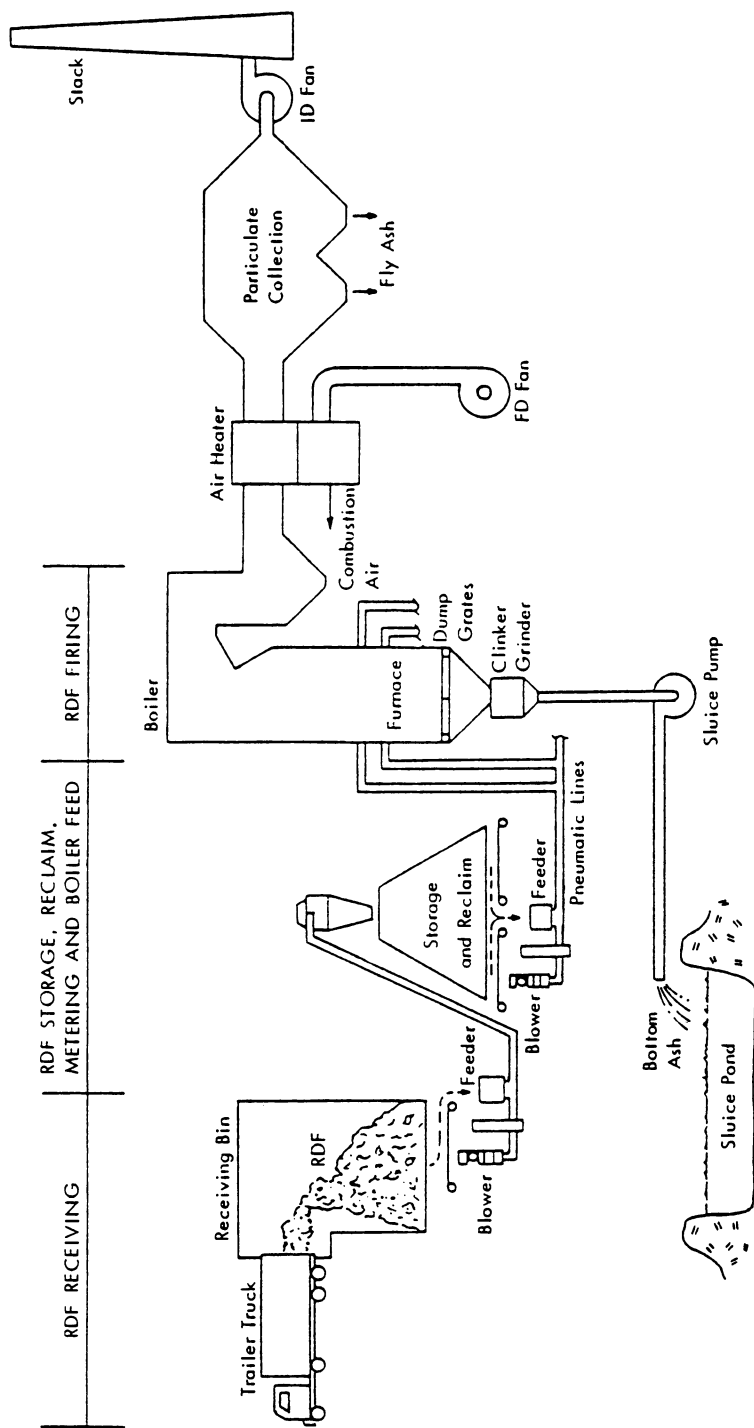


Figure 2. Schematic of Electric Utility RDF Cofiring System
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Large particles can jam and plug fuel feeding and ash removal systems and cause poor combustion efficiency. Increased processing improves fuel quality and uniformity, and reduces the possibility of fuel handling and other problems.

Environmental Emissions and Plant Safety

Environmental emissions in air, water, and solid effluents from waste-to-energy facilities depend on both the chemical analysis of major components as well as the trace metal contents of the waste fuels and the emissions control equipment used by the facility. As shown in Table 1, most of the waste fuels have very low to moderate sulfur contents relative to coal and thus are not significant producers of sulfur dioxide during combustion. However, many of the wastes contain trace metals and can produce hazardous substances during combustion. For example municipal refuse is known to contain variable levels of lead, cadmium, and mercury, and chlorine derived from salt, plastics, and bleached paper can form polychlorinated dibenzo dioxins and furans under certain conditions involving poor fuel/air mixing and insufficient combustion air.

Modern dedicated waste-to-energy and coal-fired power plants are typically designed to effectively control carbon monoxide, acid gas, trace metal, and organic emissions to levels below state and federal requirement emissions limits. Wet or dry scrubbers and fabric filters or electrostatic precipitators are used to control acid gas (SO₂ and HCl) and particulate/trace metal emissions. Nitrogen oxide emissions are typically controlled using low-NO_x burners, combustion modification, or ammonia thermal de-NO_x systems. Carbon monoxide and trace organic emissions are controlled by designing the boiler for "good combustion practice."

Waste fuel cofiring, however, can either decrease, increase, or have little impact on emissions relative to those for 100 percent coal firing. For example, sulfur dioxide emissions typically decrease when cofiring low-sulfur fuels such as RDF and wood, but may increase or decrease when cofiring moderate-sulfur fuels such as tire chips, depending on the coal sulfur content. Nitrogen oxide emissions also decrease for most waste fuels due to low nitrogen contents relative to coal and to the impact of high fuel moisture contents on flame temperature and thermal NO_x formation. Particulate emissions often increase slightly for units with electrostatic precipitators due to increased flue gas volumes and fly ash resistivity for many waste fuels. It is interesting to note that no dioxin and furan emissions have been detected during stack emissions testing of utility boilers cofiring coal and refuse-derived fuel.

The primary safety concern with waste fuel cofiring is fire prevention in waste fuel, receiving, storage, and reclaim areas, particularly with highly combustible wastes such as scrap tires and dried refuse and wood.

Overall Energy Efficiency and Costs

To illustrate the overall energy efficiency and economics of waste energy recovery, simplified examples of waste fuel/coal cofired and dedicated waste-to-energy plants are presented below. These examples have been refined since they were first reported in 1991 (15).

Four waste fuels are considered for each system: tire-derived fuel, RDF, wood, and sewage sludge for the retrofitted coal/waste cofired plants; and whole tires, RDF, wood, and municipal solid waste (MSW) for the dedicated plants. In addition to the coal and waste fuel properties listed in Table I, major assumptions include:

- Waste fuel/coal-cofired plants:
 - 250 MW pulverized coal power plant
 - West Virginia bituminous coal
 - Steam conditions: 2400 psia/1000 deg F superheat/1000 deg F reheat
 - Wet limestone flue gas desulfurization and cold-side electrostatic precipitator
 - Retrofit fuel receiving, storage, and pneumatic transport systems and dump grate installed above ash hopper in furnace
 - 20% heat input from TDF, RDF, and wood waste; 2% heat input from sewage sludge.
- Dedicated waste-to-energy plants:
 - Same annual waste fuel consumption rates as cofired plants
 - Steam conditions: 900 psi/830 deg F.
- Reference date of capital and annual cost estimates: December 1990.
- Busbar energy cost includes fixed and variable O&M, coal, and capital charges (16.5%/yr fixed charge rate).
- Waste fuels available at zero cost.
- Zero credit for recovered byproducts such as aluminum and steel.

For waste fuel cofiring, the analysis is based in part on waste fuel cofiring performance and cost estimates reported previously (13). The boiler efficiencies, heat rates, thermal efficiencies, fuel consumption rates, and busbar energy costs were estimated using a revised version of the RDFCOAL RDF Cofiring Boiler Performance Model (14). RDFCOAL predicts the impact of RDF cofiring on boiler efficiency, net heat rate, unit derating, fuel consumption, flue gas volume and composition, and bottom and flyash production as functions of the fraction of fuel heat input provided by RDF.

For the dedicated wood-fired plant case, the performance and cost data are based on reported estimates (16). For the whole-tire, RDF, and MSW-fired plant cases, the data were estimated using the EPRI Waste-to-Energy Screening Guide and software (5). The WTE Screening Guide presents performance and cost data for alternate waste-to-energy technologies, and the software was used to prepare the estimates for the RDF/stoker fired and MSW mass burn plant cases. The estimates for the whole tire-fired dedicated plants were derived by scaling the MSW mass burn data, based on waste fuel throughput, flue gas volume, and gross MW generating capacity.

Table II and Figures 3 to 6 compare the energy recovery inefficiencies, annual waste fuel consumption rates, and incremental capital and annual costs for the cofired and dedicated waste-to-energy plants.

Boiler and Thermal Efficiencies. Energy conversion efficiency is measured by the fraction of energy in the fuel converted to steam and/or electricity, expressed as boiler efficiency and thermal efficiency, respectively.

Figure 3 compares the predicted overall boiler efficiencies as functions of waste fuel heat input fractions for utility boilers cofiring three waste fuels with coal, including tire-derived fuel, refuse-derived fuel and wood (13). As the waste fuel heat input fraction increases, the boiler efficiencies for RDF and wood cofiring decline significantly from 89 percent at zero percent heat input (100 percent coal firing) to 78 and 75 percent, respectively, at 100 percent heat input. This results primarily from the high moisture contents and higher excess air requirements of the waste fuels, which increase the dry

Table II. Performance and Economic Comparison of Waste Fuel-Cofired and Dedicated Power Plants (December, 1990 Dollars)

250 MW Waste Fuel/Coal-Cofired Power Plant

Assumptions: West Virginia Bituminous Coal @ \$1.60/MBtu, 65% Capacity Factor

	<u>Tire-Derived Fuel</u>	<u>RDF</u>	<u>Wood</u>	<u>Sewage Sludge</u>
Waste Fuel Performance:				
Heat Input	20%	20%	20%	2%
Tons/Day	434	1018	1177	1335
Tons/Year	103,000	241,000	279,000	317,000
Thermal Efficiency	34.2%	30.5%	29.6%	8.5%
Net Btu/kWh	9,997	11,175	11,536	40,140
Incremental Total Capital Requirement:				
\$/Ton/Day Waste	22,000	9500	8200	900
Breakeven Fuel Payment:				
\$/MBtu	\$0.03	-\$0.17	-\$0.13	-\$4.78
\$/Ton Waste	\$0.74	-1.96 (RDF) -1.65 (MSW)	-1.37	-4.44
Breakeven Tipping Fee (\$/Ton Waste):				
Processing Cost	\$20.00	\$40.00 (MSW)	\$10.00	\$0.00
Less Fuel Payment	(0.74)	(-1.65) (MSW)	(-1.37)	(-4.44)
B.E. Tipping Fee	\$19.26	\$41.65 (MSW)	\$11.37	\$4.44
Sensitivity Range (\$2.50 to \$0.50/MBtu Coal)				
	\$-4 to 48	\$34 to 51	\$4 to 20	\$6 to 2

Dedicated Waste Fuel-Fired Power Plant

Assumptions: Electricity Sale @ \$0.05/kWh, 80-85% Capacity Factor

	<u>Whole Tires</u>	<u>RDF</u>	<u>Wood</u>	<u>MSW</u>
Waste Fuel Performance:				
Tons/Day	332	827	900	927
Tons/Year	103,000	241,000	279,000	288,000
Net Capacity (MW)	27.1	25.4	22.5	22.0
Thermal Efficiency	24.8%	21.4%	19.9%	20.2%
Net Btu/kWh	13,800	16,000	17,100	16,900
Total Capital Requirement:				
\$/Ton/Day Waste	\$258,000	\$164,000	\$54,000	\$117,000
\$/kW Net	\$3200	\$5300	\$2150	\$4960
Breakeven Tipping Fee (\$/Ton Waste):				
Processing Cost	\$205.40	\$151.90	\$38.80	\$102.90
Less Electricity Rev.	(97.90)	(36.90)	(30.00)	(28.50)
B.E. Tipping Fee	\$107.50	\$115.00	\$8.80	\$74.40
Sensitivity Range (\$0.10 to \$0.03/kWh)				
	\$9 to 147	\$78 to 130	\$-21 to 21	\$46 to 86

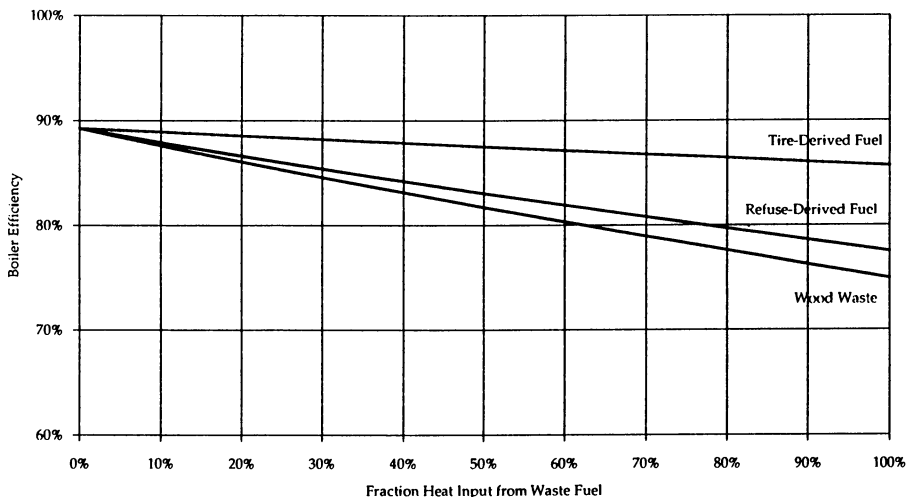


Figure 3. Boiler Efficiency for Waste Fuel/Coal Cofiring

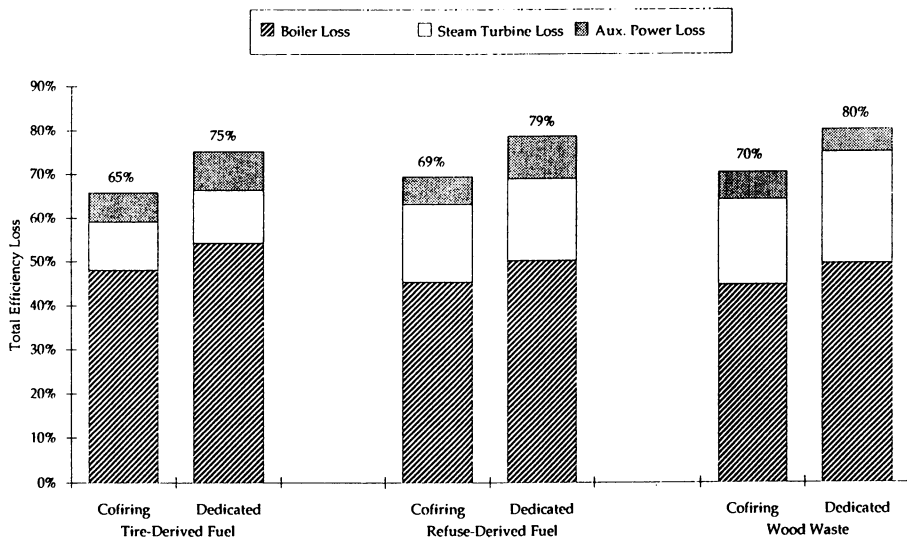


Figure 4. Total Efficiency Loss: Waste Fuel to Electricity

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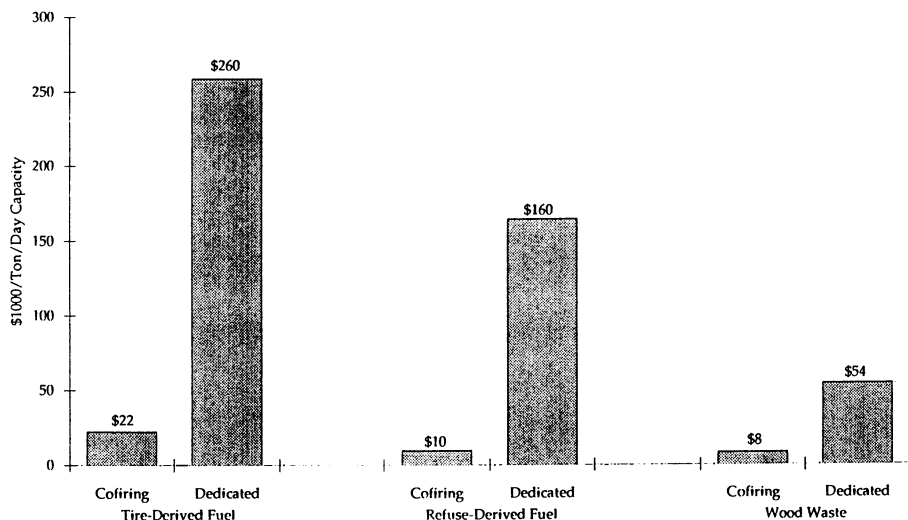


Figure 5. Total Capital Requirement for Waste Fuel Energy Recovery
Incremental Impact of Waste Processing (1990 \$)

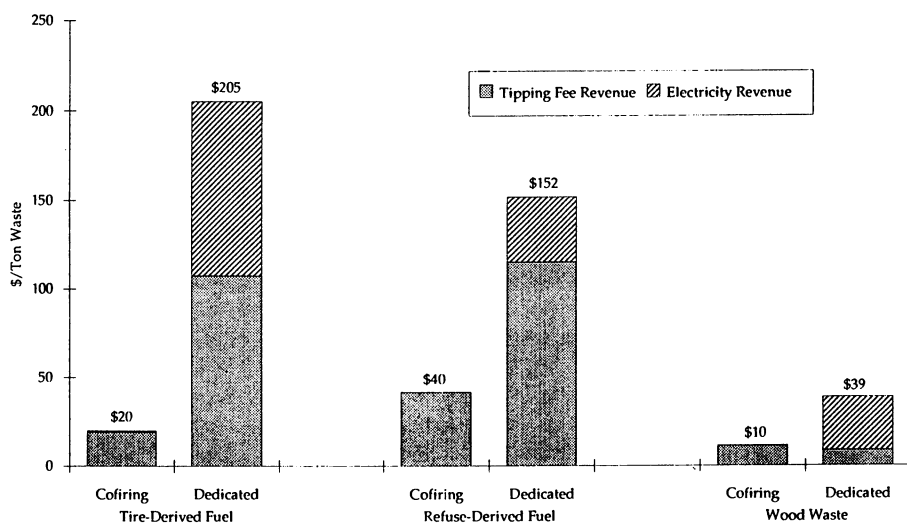


Figure 6. Total Waste Processing Cost
Coal @ \$1.60/MBtu, Electricity @ \$0.05/kWh, 1990 \$

gas and moisture loss components of the boiler efficiency loss. For tire-derived fuel which has low moisture and high heat contents like coal, the boiler efficiency declines slowly to 86 percent at 100 percent heat input from tires. Thus, waste fuel cofiring with coal can be expected to provide higher boiler and steam conversion efficiency than 100 percent waste fuel firing, which in turn contributes to higher overall electricity conversion efficiency in most cases, as discussed further below.

The waste fuel thermal efficiency is a function of boiler efficiency, gross turbine heat rate, and auxiliary power consumption. Modern coal-fired power plants typically operate at higher steam conditions than dedicated waste-to-energy plants (e.g. 2400 psi/1000 F superheated steam with one reheat to 1000 F vs. 900 psi/830 F superheated steam) and have lower auxiliary power requirements (8% vs. 11%). As a result, the waste fuel thermal efficiency can be expected to be higher for the cofired plants than for the dedicated plants, which is confirmed by the data in Table II and Figure 4. For tires, RDF, and wood waste, the waste fuel thermal efficiencies range between 30 and 34 percent for the cofired plants and 20 and 25 percent for the dedicated plants.

Waste Fuel Consumption. Annual waste fuel consumption is proportional to capacity factor and inversely proportional to fuel heat content and thermal efficiency. The 250 MW coal plant operates at 65 percent capacity factor, and the waste fuel consumption ranges between 434 tons/day (103,000 tons/year) for tire-derived fuel and 1177 tons/day (279,000 tons/year) for wood waste, based on 20 percent heat input from the waste fuel. Sewage sludge is cofired at 2 percent of total heat input, and the annual sludge consumption is 1335 tons/day (317,000 tons/year). The dedicated waste-to-energy facilities are sized to consume the same annual quantities of waste fuels, while operating at 80 to 85 percent capacity factor. As shown in Table II, net generating capacities range between 22 and 27 MW, and waste fuel consumption varies between 332 tons/day (103,000 tons/year) for whole tires and 900 tons/day (279,000 tons/year) for waste wood. The MSW-fired mass burn plant consumes 927 tons/day (288,000 tons/year) of unprocessed MSW.

Total Capital Requirement. Total capital requirement includes direct and indirect field erection costs, as well as the costs of engineering and home office services, project and process contingencies, escalation, interest during construction, preproduction and startup, inventory, and land. Table II and Figure 5 illustrate that total capital requirements for waste fuel energy conversion are significantly lower for the waste-fuel/coal cofired plants (\$900 to \$22,000/ton/day) than for the dedicated waste-to-energy plants (\$54,000 to \$258,000/ton/day).

Breakeven Fuel Price. The breakeven fuel price for the waste fuel-cofired plants is the price that results in no change in the cost of power generation relative to the unconverted coal-fired plant. The breakeven fuel price is \$0.74/ton for tire-derived fuel cofiring, and is negative for the other fuels (-1.37 to -4.44 \$/ton), i.e., the utility is paid to take the fuel. This occurs, because the incremental capital and O&M charges exceed the coal savings for RDF and wood cofiring. Sewage sludge cofiring actually increases coal consumption due to its large negative impact on boiler efficiency, and the fuel credit therefore decreases with increasing coal price.

Breakeven Tipping Fee. The breakeven tipping fee represents the charge for waste disposal required to balance total processing costs and total revenues derived from tipping fees and sale of recovered energy and byproducts. As shown in Table II and Figure 6, at \$1.60/MBtu coal purchase price, the breakeven tipping fee for the waste fuel-cofired plants ranges between \$11.40 and \$41.65/ton waste. For the dedicated plants, at \$0.05/kWh electricity sale price, the breakeven tipping fee ranges between \$8.80 and \$115.00/ton waste. Because these breakeven tipping fee estimates are quite

sensitive to the assumed coal and electricity prices, the tipping fee ranges were also estimated for coal prices between \$0.50 and 2.50/MBtu and for electricity prices between \$0.03 and \$0.10/kWh (Table II). Even for the wide ranges of coal and electricity prices, the cofired plants offer generally lower breakeven tipping fees than the dedicated plants. Note that the breakeven tipping fee range in Table II is reversed for sewage sludge cofiring (\$6 to 2/ton) due to the inverse relationship between the fuel credit and coal price described in the previous paragraph.

Discussion

Although the estimated breakeven tipping fees are lowest for waste fuel cofiring in utility boilers, there are several institutional and economic factors that create barriers to implementing such projects. Regulated utilities typically pass on fuel savings to the rate payer as part of the rate making process and thus do not share directly in the economic benefits of waste fuel cofiring. Thus there is little incentive for a utility to participate other than to provide a service to the community and reduce landfill requirements. Economic dispatch of the utility system may also limit the hours when the power plant is available to consume waste to the point that the plant must operate at a higher rate and incur an economic dispatch penalty in order to consume all of the waste. Other important factors include the uncertainties created by potential environmental emissions from the waste fuels, and the separate and sometimes conflicting interests of the utilities, waste haulers, and municipalities. Clearly, a mechanism needs to be developed to share the financial and other risks as well as the economic benefits of waste fuel cofiring among all participants.

Conclusions

- Significant and growing quantities of alternate fuels are available for partial replacement of coal in steam and power generation.
- Cofiring waste fuels with coal in retrofitted coal-fired power plants and other industrial boilers offers the potential for higher energy recovery efficiency and lower breakeven waste tipping fees than dedicated waste-to-energy plants.
- Institutional constraints may limited cofiring of waste fuels in the future, unless the fuel supplier and user develop a mechanism to share the profits as well as the risks.

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Chapter 3

Recovery of Ethanol from Municipal Solid Waste

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Methods for disposal of MSW that reduce the potential for groundwater or air pollution will be essential in the near future. Seventy percent of MSW consists of paper, food waste, yard waste, wood and textiles. These lignocellulosic components may be hydrolyzed to sugars with mineral acids, and the sugars may be subsequently fermented to ethanol or other industrial chemicals. This chapter presents data on the hydrolysis of the lignocellulosic fraction of MSW with concentrated HCl and the fermentation of the sugars to ethanol. Yields, kinetics, and rates are presented and discussed. Design and economic projections for a commercial facility to produce 20 MM gallons of ethanol per year are developed. Novel concepts to enhance the economics are discussed.

The United States generates about 200 million tons of MSW annually, or about 4 pounds per capita per day (1). The average composition of MSW is given in Table I, and varies slightly with the season (2). This material has traditionally been disposed of in landfills. However, recent environmental concerns over ground water pollution, leaching into waterways, and even air pollution, as well as increasing costs, have resulted in this technology becoming unacceptable in most areas. Few new landfills are being approved, and the average remaining life of operating landfills is only about five years.

Alternatives to landfilling include incineration, composting, anaerobic digestion, and recycling. Incineration can result in energy recovery as steam. However, concerns over hazardous components in exhaust gases and high capital and operating costs detract from this alternative. Large areas required for composting and the ultimate use or disposal of compost with high metals content makes this technology uncertain. Very slow reaction rates and large reactors for anaerobic digestion makes this technology uneconomical at present.

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Table I. Municipal Solid Waste Composition
(Weight Percent as Discarded)

<u>Category</u>	<u>Summer</u>	<u>Fall</u>	<u>Winter</u>	<u>Spring</u>	<u>Average</u>
Paper	31.0	38.9	42.2	36.5	37.4
Yard Waste	27.1	6.2	0.4	14.4	13.9
Glass	17.7	22.7	24.1	20.8	20.0
Metal	7.5	9.6	10.2	8.8	9.8
Wood	7.0	9.1	9.7	8.2	8.4
Textiles	2.6	3.4	3.6	3.1	3.1
Leather & Rubber	1.8	2.5	2.7	2.2	2.2
Plastics	1.1	1.4	1.5	1.2	1.2
Miscellaneous	3.1	4.0	4.2	3.7	3.4

Recycling of glass, metals, plastics, and paper reduces the quantity of material to be landfilled by about 60 percent, as seen from Table I. Most states have decided that recycling offers the best solution to the environmental concerns associated with solid waste disposal and many have implemented regulations for curbside segregation of recyclable components. Markets for recycled aluminum and steel are well established, however, markets for recycled paper, glass, and plastics are not well developed. Low prices (negative in some areas for paper) will impede the application of recycling.

Alcohol Production. The United States currently imports about half of its crude oil and must produce another 120 billion gallons of liquid fuels annually to become energy self sufficient. Ethanol can be produced from lignocellulosic matter, like paper, by hydrolysis of the polysaccharides to sugars, which can be fermented into ethanol. This technology would enable the use of the entire carbohydrate fraction of MSW (paper, yard and food waste, wood and textiles), which constitutes 75 percent of the total, into a useful and valuable product. Ethanol can be blended with gasoline and, currently, nearly one billion gallons of ethanol, primarily made from corn, are used as a transportation fuel in this country. The potential market (at 10 percent alcohol) is 10 billion gallons per year. Blending of ethanol with gasoline reduces emissions and increases the octane rating. Some states, like California and Colorado where air quality has degraded seriously in metropolitan areas, are mandating the use of alcohol fuels.

The purpose of this paper is to describe a process for converting the lignocellulosic fraction of MSW into ethanol. The residue is contacted with concentrated mineral acid at room temperature to give theoretical yields of monomeric sugars, which are readily fermented into ethanol. Procedures to give high sugar concentrations are described. Data for fermentation in immobilized cell columns in a few minutes are presented. The economics of this process is then developed and key economic parameters identified.

HYDROLYSIS/ETHANOL PRODUCTION

The hydrolysis of biomass to sugars and fermentation of glucose to ethanol are technologies that have been commercial around the world for many years. The U. S. produced up to 600 million gallons of ethanol per year by fermentation during World War II. Also, the Germans produced fuel ethanol from wood by hydrolysis and fermentation during World War II. Today, Brazil produces most of its liquid fuel from sugar cane.

It has been known for nearly two centuries that cellulose could be converted into sugars by the action of mineral acids (3). The process became commercial early in this century with dilute acid plants built in Georgetown, South Carolina, and Fullerton, Louisiana to produce 2-3 million gallons of ethanol per year from wood (4). These plants operated through the end of World War I when wood sugars could not compete with cheap by-product molasses from cane.

During World War II, the Germans developed a percolation process and built 20 plants for the production of fuel alcohol from wood (5). Similar plants were also built in Switzerland, Sweden, China, Russia, and Korea. In attempts to produce ethanol for butadiene rubber production, the United States built a 4 million gallon per year wood hydrolysis to ethanol facility in Springfield, Oregon in 1944. The Germans also operated plants based upon the Bergius concentrated hydrochloric acid technology at Mannheim and Regensburg during World War II (6). Concentrated sulfuric acid plants were also operated in Italy (Giordani Leone) and Japan (Hokkaido) (7). Most of these facilities were closed after World War II with the development of processes to produce ethanol from petroleum. However, about 40 percolation plants are still operated in Russia today.

Hydrolysis Technology. Biomass materials are comprised of three major components: hemicellulose, cellulose, and lignin. The composition of various biomass materials is shown in Table II. As noted, most of these materials contain 50-70 percent carbohydrate (hemicellulose and cellulose). These polysaccharides can be hydrolyzed to monomeric sugars, which can be converted by microorganisms into fuels or chemicals. The lignin cannot be hydrolyzed, but has a high heating value and can be used as a source of fuel. From Table II, most of the MSW biomass is cellulose.

Table II. The Composition of Selected Biomass Materials

<u>Material</u>	<u>Percent Dry Weight of Material</u>		
	<u>Hemicellulose</u>	<u>Cellulose</u>	<u>Lignin</u>
Tanbark Oak	19.6	44.8	24.8
Corn Stover	28.1	36.5	10.4
Red Clover Hay	20.6	36.7	15.1
Bagasse	20.4	41.3	14.9
Oat Hulls	20.5	33.7	13.5
Newspaper	16.0	61.0	21.0
Processed MSW	25.0	47.0	12.0

The carbohydrate hydrolysis can be carried out by contact with cellulase or xylanase enzymes, or by treatment with mineral acids. Enzymatic hydrolysis has the advantage of operating at mild conditions and producing a high-quality sugar product. However, the enzymatic reactions are quite slow (30 hour retention time), and the biomass must be pretreated with caustic or acid to improve the yields and kinetics. The expense of pretreatment and enzyme production, and the large reactors required make this an uneconomical alternative.

Acid hydrolysis is a much more rapid reaction and various combinations of temperature and acid concentration may be used. Two methods of acid hydrolysis have been studied and developed: a high temperature, dilute acid process (8,9) and a low temperature, concentrated acid process (10,11). For example, complete conversion of the hemicellulose and cellulose in corn stover into monomeric sugars and sugar degradation products requires mineral acid concentrations of 2N at temperatures of 100-200°C (12). However, acid concentrations of 10-14N yield complete conversions at room temperature (30°C).

At high temperatures, xylose degrades to furfural and glucose degrades to 5-hydroxymethyl furfural (HMF), which are both toxic to microorganisms. Yields from dilute acid processes are typically only 50-60 percent of theoretical because of sugar losses by degradation and reverse polymerization at high temperatures. Also, equipment corrosion at high temperatures is a serious problem. Work in our laboratories has focused attention on concentrated acid processes which produce theoretical yields at low temperatures. However, since high acid concentrations are used, acid recovery is an economic necessity (10).

Studies in our laboratories have resulted in both single step and two-step hydrolysis processes, using concentrated mineral acids, which result in nearly 100 percent yields of sugars from hemicellulose and cellulose. The reactions are conducted at room temperature, without significant degradation or reverse polymerization (11-13). An acid recovery process has been developed and tested, yielding an energy efficient method of separating sugar and acid (14). The resulting sugar solution has been successfully fermented to ethanol and other chemicals without pretreatment (15).

Process Description. Figure 1 shows the proposed process for the acid hydrolysis of MSW consisting simply of a mixed reactor where acid and MSW are contacted at a constant temperature. The unconverted solids (lignin and ash) are separated by filtration, washed, and used as fuel. Acid and sugars are separated and the acid returned to the reactor.

If desirable to separate the sugars, the hemicellulose, which degrades at milder conditions, may be first hydrolyzed to produce a mixture of five and six carbon sugars. The solids from this first stage reactor are separated and contacted with acid in a second step to hydrolyze the cellulose. Only six carbon sugars are obtained from cellulose in this second stage. This two step hydrolysis gives two streams; a xylose rich prehydrolyzate and a glucose rich hydrolyzate; and may be used where sugar separation

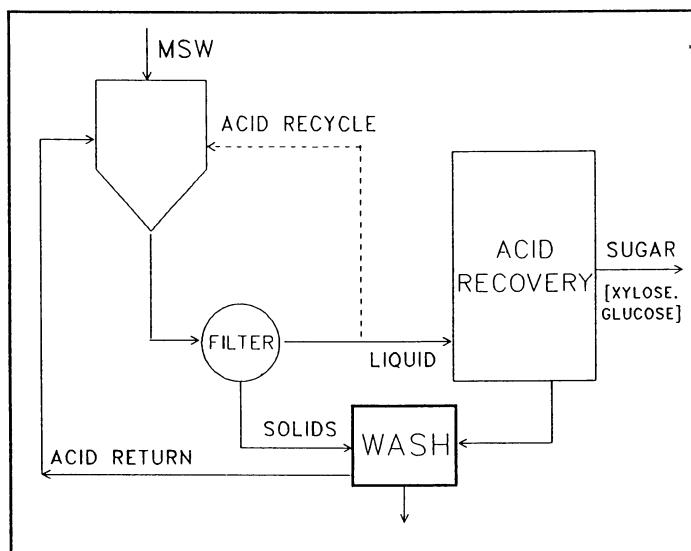


Figure 1. Schematic of Acid Hydrolysis. (Reproduced with permission from *Energy from Biomass and Waste XV*, Institute of Gas Technology, 1991. Copyright 1991 Michael D. Ackerson.)

is desirable. In the usual case, as with MSW, the simpler single step process will be preferred.

Hydrolysis Conditions. The two major factors which control the hydrolysis reactions are temperature and acid concentration. Studies in our laboratories have been made to define the appropriate conditions to maximize reaction rates and yields. Sugar degradation is promoted more at high temperature than at high acid concentration. Also, fast rates of hydrolysis are achieved at acid concentrations exceeding 12N. Therefore, the best conditions are a high acid concentration (80 percent H₂SO₄ or 41 percent HCl) and a mild temperature (-40°C).

The sugar concentrations and yields from a typical hydrolysis of MSW from our laboratories are given in Table III (11). The prehydrolysis step yields 8 percent of the initial MSW as xylose. The combined yield of glucose is 60 percent. These yields represent nearly complete conversion of hemicellulose and cellulose to sugars. However, very dilute (3-7 percent) sugar solutions result from these reactions.

Feedstock Preparation. In order to speed up the hydrolysis reactions, the size of the biomass particles must be reduced to increase the accessibility to the polymeric structure. A high solids concentration is desirable since this concentration controls the sugar concentration and the size of the hydrolysis and fermentation equipment. The size of the particles also affects the fluidity of the solids/acid slurry. It is desirable to maintain fluidity of the slurry to promote mass transfer and to facilitate pumping and mixing. Therefore, the particle size is an important variable in the biomass conversion process.

Table III. MSW Acid Hydrolyzates

	Concentration g/L	Yield g/100q
Prehydrolyzate		
Xylose	9.5	8.0
Glucose	18.5	16.0
Hydrolyzate		
Xylose	0.0	0.0
Glucose	67.8	44.0
Combined		
Xylose		8.0
Glucose		60.0

Table IV gives the maximum solids concentration to maintain fluidity of the slurry, as a function of particle size. A maximum concentration of about 10 percent is possible with particle sizes less than 40 mesh. Grinding to 20 mesh gives a particle size distribution in which 90 percent of the material is less than 40 mesh. Therefore, grinding biomass to pass 20 mesh gives the appropriate size and produces the maximum possible slurry concentration. Also, grinding to smaller sizes does not improve the reaction rate.

Table IV. Maximum Solids Concentration for Fluid Slurry

Mesh Range (Sieve Nos.)	Solids Concentration wt. %
0 - 1	4.6
12 - 20	4.6
20 - 30	8.4
30 - 40	8.2
40 - 45	10.2
45 - 70	10.4
70 - 100	10.6
100 ⁺	10.8

Sugar Decomposition. The fermentability of the sugars is dependent upon the sugar decomposition that occurs during hydrolysis. Xylose decomposes to furfural and hexoses decompose to HMF, which are both toxic to yeast. Tolerance can often be developed, and toxicity is difficult to define. However, the toxic limit of furfural on alcohol yeast is reported to be 0.03 to 0.046 percent (16). HMF is reported to inhibit yeast growth at 0.5 percent, and alcohol production is inhibited at 0.2 percent (17).

The rate of decomposition of xylose to furfural and hexoses to HMF have been studied at varying sugar concentrations. Using the method of initial rates, these reactions were found to be first-order. The ratio of rate constants for decomposition to formation are given in Table V. These ratios are small, and subsequent calculations and experiments show that the rate of HMF appearance is insignificant. However, the rate of furfural appearance could reach toxic limits, especially if acid recycle is utilized.

Table V. Ratio of First Order Rate Constants for Sugar Decomposition to Formation Under Prehydrolysis Conditions

Sugar	Acid Concentration	Rate of Formation/Decomposition
Glucose	2N	0.0053
	3N	0.0090
	4N	0.0074
Xylose	2N	0.0257
	3N	0.0402
	4N	0.0374

Hydrolyzate Fermentation/Ethanol Production

Glucose may be fermented to ethanol efficiently by the yeast *Saccharomyces cerevisiae*, or the bacterium

Zymomonas mobilis (18). Batch fermentation experiments were carried out to compare the production rates of ethanol from hydrolyzates and synthetic glucose. *Saccharomyces cerevisiae* (ATCC 24860) was used in the study. As shown in Figure 2, identical results were found when fermenting synthetic glucose and hydrolyzate. Ethanol yields were also nearly identical. As noted in Table VI, the fermentation proceeded well in the presence of a small amount (0.25 percent) yeast extract, which can be obtained by recycle. Almost total conversion of sugars is obtained in only 16 hours. The concentrations of furfural and HMF in the hydrolyzates were found to be negligible. These low levels of byproducts are believed to be the major reason for this highly efficient fermentation.

Table VI. Hydrolyzate Fermentation to Ethanol
Percent Sugar Utilization

Fermentation Time (hrs)	Hydrolyzate			
	<u>With Vitamins and With Yeast Extract</u>			
	Amino Acids	NH ₃ PO ₃	Amino Acids and NH ₃ (PO ₃)	Yeast Extract
16	15.9	21.9	27.3	97.5
23	19.3	24.9	35.8	97.5

Xylose fermentation is much more difficult, and the xylose might be used as a source of energy for generating steam and power. However, future possibilities for xylose fermentation will improve the economics. Recent work with *Pachysolen tannophilus* shows promise for xylose conversion to ethanol (19) but, at present, this technology is not fully developed. Ethanol may also be produced by converting xylose to xylulose, followed by fermentation with yeast (20).

Continuous Fermentation. The standard technology for fermenting sugars to ethanol is in batch vessels. Batch fermentation is used so that contamination and mutation can be controlled. Sterilization between batches and the use of a fresh inoculum insure efficient fermentation. However, most batch alcohol fermentations are designed for thirty hour (or more) reaction time, which results in very large and expensive reactors.

The reactor size can be reduced substantially by using continuous flow fermenters. When fermenting acid hydrolyzates, the problems with maintaining sterile conditions are substantially reduced, since the substrate has been sterilized by contact with the acid. Therefore, the use of continuous fermentation is a natural application for producing alcohol from MSW hydrolyzates.

A number of continuous fermentation schemes have been studied, including the CSTR (21), cell recycle reactor (22), flash fermentation (23) and immobilized cell reactors (24,25). Immobilized cell reactors (ICR) show potential in substantially

decreasing reactor size and decreasing substrate and product inhibition (25-28). Reaction rates for ethanol production in an immobilized cell reactor are as high as 10 times the values obtained in a stirred tank reactor (24). A wide variety of immobilization techniques have been employed, including cross-linking, entrapment, and covalent bonding (25).

Data are given in Figure 3 for laboratory columns with immobilized *S. cerevisiae*. The glucose profiles are given for initial sugar concentrations from 50-200 g/L. As noted, 90 percent conversion is achieved in one hour or less. Productivities to achieve 99 percent conversion were about 40 g/L-hr, or about an order of magnitude greater than the CSTR and 60 times more than the batch reactor. Furthermore, alcohol inhibition and toxicity to either inhibitors is reduced in the ICR. The volume of the ICR for MSW hydrolyzate fermentation is about 5 percent that of the batch fermenter and substantial capital savings result.

Increasing the Sugar Concentration

Perhaps the single most important factor in the economics of this process is the sugar concentration that results from acid hydrolysis. Dilute concentrations increase both the equipment size and the energy required for purification. Methods to increase the sugar and ethanol concentrations have been developed.

Solids Concentration. The ultimate sugar and alcohol concentrations are direct functions of the initial solids concentration in the hydrolysis. Since fluidity in a stirred reactor is a requirement, a 10 percent mixture has been considered maximum. Therefore, the resultant sugar concentrations have been only 2-7 percent and alcohol concentrations only half as much.

If the limiting factor is considered to be fluidity in the reactor, instead of the feed mixture, the feed concentration could be increased by roughly the reciprocal of one minus the solids conversion in the reactor. Of course, solids and liquid would have to be fed separately, which could also save equipment cost. For biomass, containing 75 percent carbohydrate, the reactor size could be reduced by 75 percent. Attendant reductions would also result in the filtration and washing units.

Equally important are the resultant increases in sugar concentrations. The glucose concentration would be quadrupled to about 280 g/L (28 percent). Energy and equipment costs in the fermentation area would be reduced proportionately. This simple alteration in the process has a profound impact on the economics. It is estimated that the capital cost reduced by 40 percent in the hydrolysis and acid recovery sections and 60 percent in the fermentation and utilities areas. Furthermore, the energy requirements for distillation are reduced by 60 percent.

Acid Recycle. Another method to increase the sugar concentration is to recycle a portion of the filtrate (acid and sugar solution) in the hydrolysis step. The acid would catalyze further polysaccharide hydrolysis to increase the sugar concentration. Of course, recycle of the sugars would also increase the possible degradation to furfural and HMF.

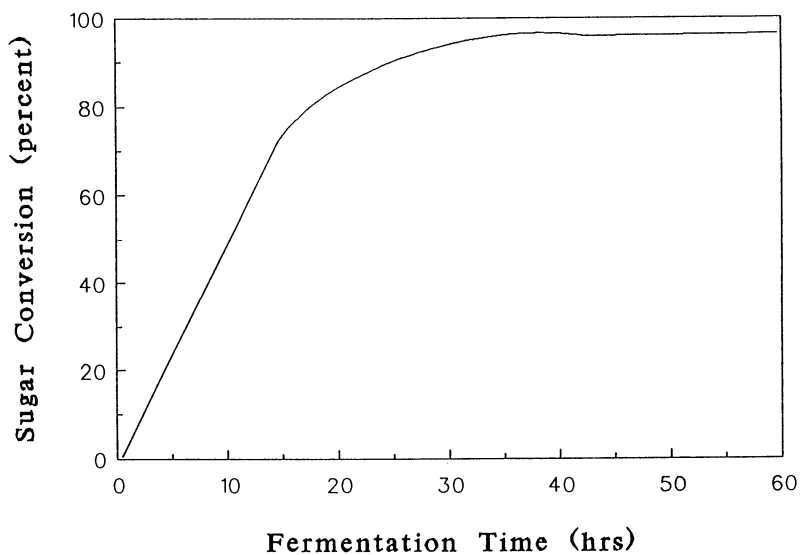


Figure 2. Fermentation of Hydrolyzate and Synthetic Glucose. (Reproduced with permission from *Energy from Biomass and Waste XV*, Institute of Gas Technology, 1991. Copyright 1991 Michael D. Ackerson.)

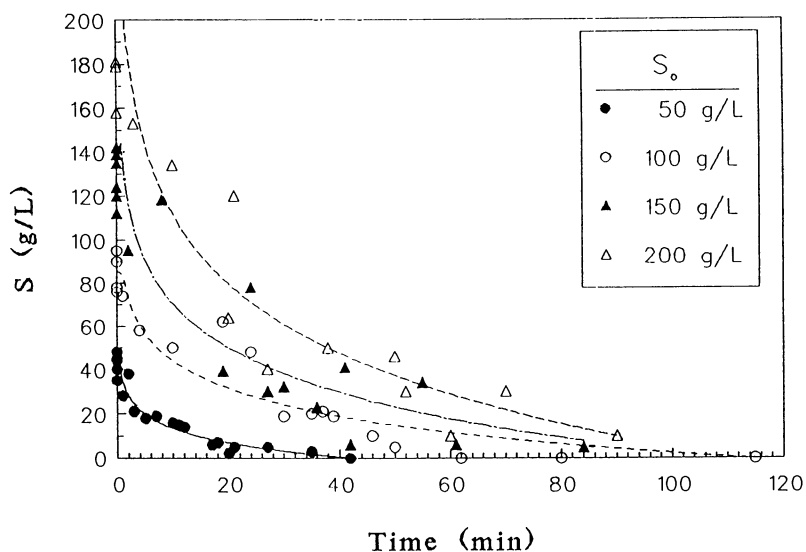


Figure 3. Glucose Profile in the ICR. (Reproduced with permission from *Energy from Biomass and Waste XV*, Institute of Gas Technology, 1991. Copyright 1991 Michael D. Ackerson.)

Experiments have been conducted to determine the enhancement possible with acid recycle. Various amounts of the acid and sugar solution from the filtration were recycled to determine the resulting sugar and by-product concentrations. Acid and solids concentrations and temperatures were kept constant. These experiments have shown that the sugar concentrations can be increased sixfold at total recycle. It should be noted that not all the filtrate can be recycled, since a portion adheres to the solids in filtration. In order to minimize sugar decomposition, a recycle fraction of 50 percent has been used, which results in doubling the sugar composition, without significant furfural or HMF levels.

The effect of acid recycle on the economics is significant. A recycle rate of 50 percent, coupled with high solids concentrations, would result in a xylose concentration of 15 percent and a glucose concentration of over 50 percent could be achieved. Practically, sugar concentrations should not exceed 25 percent, so a smaller recycle fraction is required. It should be noted that these concentrations have been achieved in the laboratory, while maintaining furfural and HMF less than 0.05 percent. These high concentrations reduce the equipment size in the acid recovery section by 50 percent and in the fermentation section by another 60 percent. Energy consumption is also reduced another 60 percent.

Acid Recovery. Acid recovery is essential when using concentrated acid hydrolysis. Processes for recovery of both hydrochloric and sulfuric acids have been developed. A number of possible recovery schemes were examined, including electrodialysis, distillation, etc.

The recovery technology that has been selected is based upon solvent extraction. Solvents have been identified that extract HCl and H₂SO₄ from the aqueous sugar solutions. Near complete acid recovery is possible and solvent losses are minimized. For HCl, the acid is separated from the solvent by distillation, and the solvent recycled. A hexane wash of the sugar solution is used to recover trace quantities of solvent, and hexane is separated by distillation for recycle.

Some solvent is lost in the process; however, the losses are quite small and solvent replacement costs are only \$0.02 per gallon of alcohol. Acid losses are minimized and acid costs are \$0.025 per gallon of alcohol. The total heat requirement for solvent and acid recovery is low and amounts to less than \$0.05 per gallon of alcohol. As shown later, the energy cost may be recovered from the lignin and xylose streams.

ECONOMIC PROJECTIONS

To illustrate the economics of this process, a design has been performed for a facility to convert MSW into 20 million gallons per year of ethanol, utilizing the acid hydrolysis procedures previously described. The capital and operating costs are summarized in Table VII.

MSW would be collected and delivered to the plant site as

needed. Feedstock preparation consists of plastic, metal and glass removal, shredding, grinding and conveying to the reactors. The cost of the removal of glass and metals is not included in the feed processing cost, as reports indicate that resale of these materials will offset the capital and operating costs of separation. The hydrolysis section, as shown in Figure 1, consists of continuous reactors. Acid resistant materials of construction are necessary for this equipment. Ethanol fermentation in the ICR and typical distillation units are included. The total capital cost for this plant is \$35 million, including all utilities, storage and offsite facilities.

The annual operating costs are also shown in Table VII. These costs are also given on the basis of unit production of alcohol. As mentioned previously, no cost is included for MSW. A lignin boiler is used to reduce the energy requirements, and energy costs are only \$0.08 per gallon. Fixed charges are computed as a percentage of the capital investment and total \$5.6 million per year. The present ethanol price of \$1.50 per gallon will generate revenues of \$30 million and yield a pre-tax profit of \$18.5 per year (\$.93/gal) or 53 percent per year.

It should be noted that this process does not include utilization of the pentose stream. Acid recovery is included, but fermentation of the xylose is not provided. Xylose could be fermented to alcohol, acids or other valuable chemicals, which would improve the economics. However, since this technology is not perfected, such products have not been included.

Table VII. Economics of 20 Million Gallon Per Year Ethanol Facility

A. Capital Cost		
	<u>Million \$</u>	
Feedstock Preparation		3.0
Hydrolysis		5.0
Acid Recovery		8.5
Fermentation & Purification		8.0
Utilities/Offsites		6.5
Engineering		<u>4.0</u>
		35.0
B. Operating Cost		
	Million \$/yr	\$/gal
MSW	-	-
Utilities	1.5	0.08
Chemicals	1.9	0.09
Labor	2.5	0.13
Fixed Charges		
Maintenance (4%)	1.4	0.07
Depreciation (10%)	3.5	0.18
Taxes & Insurance (2%)	0.7	0.02
Pre-tax Profit (53%)	<u>18.5</u>	<u>0.93</u>
	\$30.0	\$1.50/gal

Sensitivity analyses show that the economics are particularly sensitive to capital cost and revenue. A 20 percent reduction in capital cost raises the pre-tax return to 70 percent. Similarly, a 20 percent increase in the ethanol price increases the return to 70 percent. A tipping fee of \$20 per ton of MSW would increase the return to 65 percent. Increasing the plant size would have a similar positive affect on the economics.

CONCLUSIONS

Concentrated acid hydrolysis of residues, such as MSW, requires mild temperatures and results in near theoretical yields. The resulting hydrolyzates, containing primarily xylose and glucose, can be fermented to ethanol or other chemicals. The acid can be recovered for reuse by solvent extraction. The sugar concentration can be increased by using high solids reactions with acid recycle. Continuous fermentation of the hydrolyzates can be achieved in an hour or less in an immobilized cell column. The capital cost for a process to produce 20 million gallons of ethanol is estimated to be \$35 million. The pre-tax profit from this facility is sufficient to encourage commercialization.

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Chapter 4

Converting Waste to Ethanol and Electricity via Dilute Sulfuric Acid Hydrolysis

A Review

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In April 1990, TVA began a project to evaluate the processing of municipal solid waste (MSW) to recyclables, ethanol, and electricity. The project includes evaluation of front-end classification processes for recovery of recyclables, hydrolysis and fermentation of the cellulosic fraction of MSW to ethanol, and combustion of the hydrolysis residue for steam and electricity production. Laboratory hydrolysis and fermentation tests have resulted in yields of up to 36 gallons of ethanol per dry ton of the cellulosic fraction of MSW. Yields of up to 29 gallons per dry ton have been attained in pilot plant runs. Analyses of process effluents have been performed to evaluate the environmental acceptability of the overall process. A preliminary economic evaluation has been conducted based on these tests.

Each year about 240 million tons of municipal solid waste (MSW) are generated in the United States. Of this amount, about 160 million tons are generated by consumers in the form of residential and commercial waste. This figure is expected to reach 193 million tons by the year 2000 (1). While MSW generation is increasing, the number of landfills is dropping significantly. According to the Environmental Protection Agency (EPA), more than half of our existing landfills will reach their capacity within the next eight years. Many landfills will be forced to close because of tougher environmental regulations and because of potential ground-water contamination from leaking and leaching.

As a result of these problems, several disposal alternatives have been developed to reduce the amount of MSW requiring landfilling. These alternatives to landfilling include incineration/mass burn (burning the entire waste stream) and refuse-derived fuel (RDF) combustion (burning the waste after recyclables have been removed). About 13% of the United States' waste is treated in this manner (2). Both of these alternatives produce steam and electricity, but are expensive and environmentally questionable. In response to the nation's waste problem, the

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Tennessee Valley Authority (TVA) is developing technology to produce recyclables, electricity, ethanol, and other chemicals from MSW.

The National Fertilizer and Environmental Research Center (NFERC) at TVA has conducted laboratory hydrolysis and fermentation research to convert cellulosic biomass materials to ethanol and other chemicals since 1980. In 1985, a 2-ton-per-day pilot plant was built to convert hardwoods to ethanol and other chemicals. Previous TVA research was designed to maximize sugar yield from both hemicellulose and cellulose in a two-stage process. Because of the costs associated with hemicellulosic sugar conversion and the small quantity of pentose sugars associated with MSW cellulosics, conversion by a one-step hydrolysis of cellulose is being evaluated for producing hexose sugars. In contrast to previous work on hardwood and agricultural residue conversion, there are important environmental questions which must be answered before an economical large-scale wastepaper or MSW-cellulosics conversion facility is possible. Recently, TVA conducted preliminary laboratory and pilot-plant tests with MSW and waste paper to evaluate their potential and also to address environmental concerns related to these feedstocks. Based on the results of these tests, a preliminary technical and economic evaluation was performed.

In April 1990, TVA began research to evaluate conversion of MSW-cellulosics to ethanol and electricity. This paper presents a process description, laboratory and pilot plant results, and safety and environmental concerns. TVA's integrated processing system produces recyclables, ethanol, chemicals, and electric power from MSW. This system is divided into three areas: MSW classification, RDF processing, and energy production. A schematic of the system is shown in Figure 1. The first step involves classification of MSW to remove the recyclables (glass, plastics, aluminum, steel, and other metals, etc.). Cardboard, newsprint, and paper products are left in the waste stream (RDF) as potential feedstocks for chemical production.

The second step involves RDF processing. Dilute sulfuric acid hydrolysis is used to convert the RDF to fermentable sugars for ethanol production. A flow diagram of the hydrolysis and fermentation process is shown in Figure 2. RDF is fed to the hydrolysis reactor where dilute sulfuric acid (2-3%) is added. The mixture is then steam heated to 160-190^o C with retention times ranging from 5 to 30 minutes. Under these conditions, the cellulose and hemicellulose are converted to sugars (glucose and xylose/mannose respectively). During hydrolysis, small quantities of acetic acid and sugar degradation products such as furfural and hydroxymethyl furfural are also formed. The mixture is dewatered, and the remaining solids are used for boiler fuel. The sulfuric acid in the solution is neutralized with lime, and the resulting mixture is filtered to remove the gypsum. The sugar solution is fermented to ethanol. Beer from fermentation is distilled, and the ethanol dehydrated for use as a motor fuel additive(3).

The third step in the process is energy production. This involves combustion of the solid residue remaining after hydrolysis. About 40% of the solids that enter the hydrolysis process are removed as residue. This solid residue contains lignin (about 15-25% of the original feedstock), unreacted cellulose, and ash, and has an energy content of about 8,500 Btu/pound. These solids are fed to a boiler where

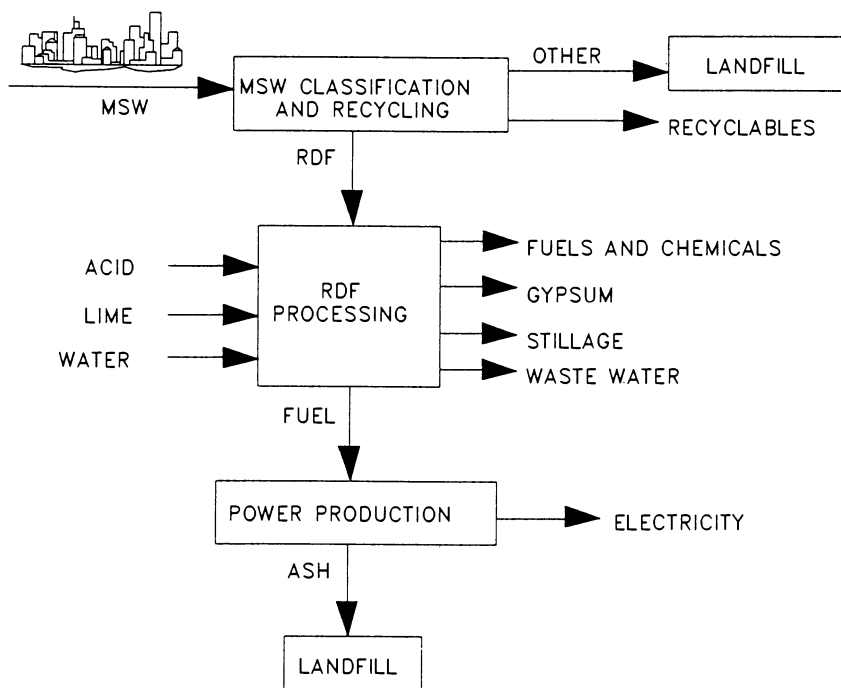


Figure 1. Integrated MSW Processing System.

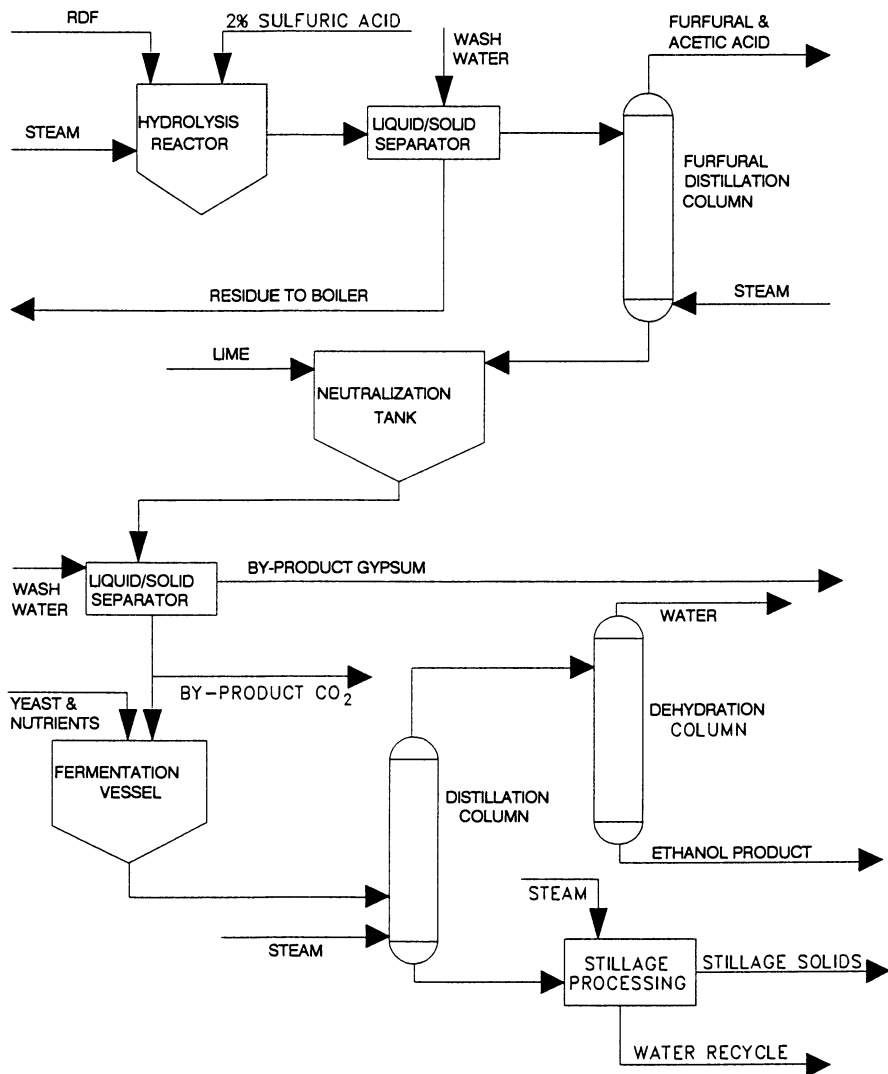


Figure 2. Flow diagram of RDF hydrolysis processing system.

process steam and electricity are produced. More electricity is produced than is needed in the process, and it can be sold as a by-product.

Laboratory And Pilot Plant Results

A series of dilute sulfuric acid hydrolysis tests were conducted using shredded newsprint, cardboard pellets, newsprint pellets, and RDF pellets as feedstocks. The shredded newsprint was newsprint that had the glossy and highly-colored sections removed. The pelletized feedstocks were received from a commercial classification facility in Humboldt, Tennessee. The pellets were approximately 0.5 inches in diameter and of variable lengths of up to three inches.

Laboratory hydrolysis tests were conducted at 130-190° C in an acid-resistant, Monel-lined, 20-liter, rotating digester using either 1% (w/w), 2% (w/w), or 4% (w/w) sulfuric acid in a one-stage dilute sulfuric acid hydrolysis. In preliminary tests, samples of the hydrolysis liquid were collected at 5-to-10 minute intervals for 3 to 4 hours. Additional tests were performed where samples were collected at 1-minute intervals. Tests were performed to evaluate the effect of liquid-to-solid ratio (liquid-to-solid ratios adjusted for moisture content) on sugar production. It has been determined that a 5:1 liquid-to-solid ratio was adequate to maintain free liquid to saturate the feedstock. Several additional tests were performed where the residues were hydrolyzed a second time to evaluate increases in sugar yields from the cellulose remaining from the one-step hydrolysis. Total reducing sugars were measured by the dinitrosalicylic (DNS) method and selected samples were analyzed by HPLC. Residues were analyzed for moisture content, weight loss, Btu content, and compositional changes. Inorganic analyses were conducted by TVA's Chemical Environmental Analysis Section.

Laboratory Results. Previous work by Strickland et al., 1990, (4), Broder et al., 1991, (5), Broder et al., 1991, (6), and Barrier et al., 1991, (7) discussed results of TVA laboratory tests using waste cellulosics as feedstock. Table I summarizes yield information from MSW-cellulosics and newsprint hydrolysis in the laboratory. Table I also shows improvements in sugar yield where the residues were hydrolyzed a second time.

Laboratory hydrolysis tests have produced yields of up to 20 gallons per dry ton of RDF with a single-stage process and 27 gallons per ton with a two-stage process. Newsprint hydrolysis tests have produced yields of up to 24 gallons per dry ton with a single stage process and 44 gallons per dry ton with a two-stage process (5). Additional tests at higher temperatures are shown in Table II.

The tests in Table II were different from previous hydrolysis tests because power to the heating element in the digester was cut off at 160-165° C and the heat inside the digester continued to rise to 200-205° C (maximum temperature for previous tests has been 130-190° C). In previous tests, the objective had been to reach and maintain a specified temperature. The tests reported in Table II were conducted after reaching the maximum temperature for the digester as quickly as possible with hydrolyzate samples being collected along this temperature profile. Due to an increase in pressure (over 20 atmospheric bars), all tests did not reach

Table I. Laboratory sugar yields from MSW-cellulosics and newsprint^a

	Time (min) ^b	Temp (C)	Max Sugar Concentration (%)	Ethanol Yield (gal/t) ^c
ONE-STAGE HYDROLYSIS				
Humboldt-160	15	160	1.94	15.0
Humboldt-170	12	170	2.18	16.6
Humboldt-180	-42	178	2.25	17.4
Humboldt-190	-34	180	2.65	20.5
Newsprint-150	120	150	2.65	20.5
Newsprint-160	15	160	3.01	23.8
Newsprint-170	15	170	2.69	20.8
Newsprint-180	0	180	2.86	22.1
TWO-STAGE HYDROLYSIS				
Humboldt-one	15	160	1.94	15.0
Humboldt-two	25	170	2.32	12.0
TOTAL^d				27.0
Newsprint-one	15	160	3.01	23.8
Newsprint-two	30	170	3.94	20.5
TOTAL				44.3

^a 5:1 liquid-to-solid ratio and 2% sulfuric acid^b Positive numbers indicate hydrolysis time after reaching target temperature; negative numbers indicate time from start of heat-up. (35-45 minutes were required to reach the desired temperature after starting the tests.)^c Assumes 100% sugar recovery, 100% sugar conversion, theoretical ethanol yield, and 100% ethanol recovery.^d Yield from one ton of feedstock.Table II. Results of high temperature hydrolysis tests in the rotating digester^a

Feedstock ^b	Time ^c (min)	Temp (C)	Glucose (lb/t)	Mannose (lb/t)	Ethanol (gal/t)
CB pellets	32	194.2	377	39	32.1
CB pellets	33	197.6	423	30	35.0
CB pellets	34	199.8	449	22	36.4
CB pellets	35	201.8	388	17	31.3
Newsprint	32	189.9	204	57	20.2
Newsprint	34	198.7	331	37	28.4
Newsprint	35	200.4	337	25	28.0
Newsprint	36	202.4	282	16	23.0
NP pellets	31	185.4	270	38	23.8
NP pellets	32	189.3	271	33	23.5
NP pellets	33	190.1	232	15	19.1
NP pellets	34	186.2	230	14	18.9
RDF pellets	34	196.8	191	52	18.8
RDF pellets	35	197.9	202	41	18.8
RDF pellets	36	198.9	214	36	19.3
RDF pellets	39	200.2	227	22	19.2

^a Yields assume 100% sugar recovery, theoretical conversion efficiency and 100% ethanol recovery.^b CB = Cardboard, Newsprint = Shredded Newsprint, NP = Newsprint, and RDF = Refuse Derived Fuel^c Time from start of test

the maximum temperature. Pressures over 20 atmospheric barrs exceed the pressure limits of the vessel.

These tests were performed using 2% (w/w) sulfuric acid concentration, a 5:1 liquid-to-solid ratio, 1,500 g of dry material, peak temperatures ranging from 185-205° C, and a retention time of up to 45 minutes. Retention times were determined from time of initial start until the end of the test. Previous laboratory tests determined the retention time starting when the material reached the desired temperature until the end of the test and did not include the start-up period. Samples were taken every minute starting at 150° C until the end of the test to determine the maximum sugar production.

From the test results shown in Table II, yields of 36, 28, 24, and 19 gallons of ethanol per dry ton were achieved from cardboard pellets, shredded newsprint, newsprint pellets, and RDF pellets, respectively. The yield for cardboard pellets is higher than the other feedstocks. Feedstock analysis has shown potential glucose content to be higher in cardboard than in the other feedstocks. This may be due to the fact that as cardboard is produced, it is processed more than the other feedstocks which removes more hemicellulose and leaves a greater proportion of cellulose. Also, starch is used in the processing of cardboard which could increase the amount of glucose recovered in the hydrolyzate.

Table II also shows the amount of glucose and mannose produced during the high temperature hydrolysis tests which is the amount of total fermentable sugar (TFS). Only glucose and mannose are included in TFS because they are the sugars fermented to ethanol using traditional yeasts. For the cardboard pellets, maximum TFS occurred at 199.8° C and 34 minutes after initial start-up. The intended temperature of 205° C for this test was reached after 37 minutes and maintained through the end of the test. The maximum TFS production for shredded newsprint occurred at 198.7° C and 34 minutes after initial start-up (the highest temperature reached during this test was 205° C at 44 minutes). For the newsprint pellets, maximum TFS production was at 185.4° C and 31 minutes after initial start-up. The intended temperature for this test was 200° C, but due to an increase in pressure in the digester, 197° C was the highest temperature attained. Maximum TFS production for RDF pellets occurred at 198.9° C and 36 minutes after initial start-up. The target temperature for this test was 200° C. This was reached after 37 minutes and maintained until the end of the test. With the exception of the newsprint pellet tests at minimum, the maximum TFS production for the feedstocks occurred from 34-36 minutes after start-up and at approximately 199° C. The maximum TFS production for the newsprint pellets occurred at a shorter retention time and lower temperature.

On comparing the high temperature hydrolysis with previous hydrolysis tests, there are several important differences to be found. For newsprint, previous hydrolysis tests at 160° C produced yields of 24 gal/ton of ethanol, while high temperature hydrolysis tests produced 28 gal/ton. The newsprint pellet high temperature test produced 5 gal/ton more ethanol than any of the other previous hydrolysis tests. For RDF pellets, previous hydrolysis tests at 180° C produced similar yields. The cardboard and newsprint pellets had not previously been hydrolyzed. These results confirm the fact that, generally, the higher the temperature (up to 200° C) the greater the glucose yield, particularly at short retention

times. Both feedstocks produced good yields during the high temperature tests. The RDF pellets from Humboldt are of poor quality, and tests with higher quality RDF are planned. In the demonstration-scale facility, the front-end processing would leave cardboard and newsprint in the feedstock going to hydrolysis (Humboldt does not) which would produce a higher quality feedstock and result in higher RDF-to-ethanol yields. Future tests also may include different acid concentrations and liquid-to-solid ratios (6).

Pilot-Plant Results. Previous work by Watson, et al., 1990, (4), Broder, et al., 1991, (7), and Broder et al., 1991, (5) discussed results of TVA pilot-plant tests using waste cellulose as feedstock. To verify laboratory yields, tests have been conducted on a much larger scale in TVA's 2-ton-per-day pilot plant using RDF pellets, cardboard pellets, and newsprint pellets. These tests were designed to compare the effects of retention time and operating temperature on the yield of fermentable sugars from these feedstocks. Results are shown in Table III. The best yields using the RDF pellet occurred at an operating temperature of 180° C for 15 minutes. These conditions resulted in yields of up to 16 gallons per dry ton of RDF. The cardboard pellets provided yields of up to 29 gallons, and the operating conditions were 160° C for 20 minutes. The newsprint provided a yield of 23 gallons per ton obtained at 160° C and a 10-minute retention time.

The RDF pellets obtained from Humboldt are variable in quality (non-homogeneous). Several of the crates contained significant amounts of unsorted metal, probably aluminum cans. Pieces of metal passed through the feed system without being noticed and caused erratic operation of the discharge valves. This behavior caused greater than normal fluctuations in hydrolyzer temperature and feedstock level in the hydrolyzer. Tests conducted in October and November 1990 with cardboard and newsprint proved they were more homogeneous feedstocks, and the hydrolyzer performed well. After completion of tests with newsprint in February and March 1991, it was found that the screw feed system was working incorrectly, and temperature and retention times were not accurate. This is being corrected, and yields are predicted to be higher in successive runs (5).

Fermentation Tests. Laboratory fermentation tests were conducted with newsprint and two RDF hydrolyzates. Table IV contains concentrations of potential fermentation inhibitors, primarily sugar degradation products, found in the substrates. Table V contains results of fermentation tests with the three hydrolyzates. Three treatments were used for substrate preparation to improve fermentation in the presence of these inhibitors. The three treatments were (1) adjustment of pH to a desirable range for yeast fermentation, (2) over-liming prior to pH adjustment (overliming the hydrolyzate to pH 10 and readjusting with sulfuric acid to 5.5), and (3) over-liming plus addition of 1 g/L sodium sulfite. Nutrients known to enhance fermentation were added to the hydrolyzates (2 g/L urea, 2 g/L yeast extract, 0.3 g/L KCL, and 0.4 g/L reagent phosphoric acid). *Saccharomyces cerevisiae* and *Candida utilis* were grown in 20 g/L glucose plus 6.7 g/L yeast nitrogen base (Difco) for 24 hours at 30° and 100 rpm on a rotary shaker. Yeasts were recovered by centrifugation and suspended in pH 7 phosphate buffer. Test hydrolyzate preparations were given a 5% by volume inoculum of the respective yeast strains.

Table III. Pilot-plant test results

Nominal Reactor Conditions		Ethanol Yield From Glucose	Total Ethanol Yield
Temp(C)	Time(min)	(gal/t)	(gal/t)
Humboldt RDF Pellets-9/90			
180	15	14.00	16.10
160	20	11.20	12.88
Cardboard Pellets-10/90			
161	20	19.28	29.00
161	25	16.44	25.00
174	20	16.59	23.00
Newsprint Pellets-11/90			
160	10	17.76	23.00
159	20	10.16	16.00
169	15	9.90	17.00
Newsprint Pellets-2/91			
179	10	11.24	16.00
180	20	16.92	20.00
Newsprint Pellets-3/91			
170	15	8.10	14.00
180	10	10.89	16.00

Table IV. Sugar degradation products ^a

	Formic Acid	Acetic Acid	Levulinic Acid	HMF ^c	Furfural
Newsprint	2.9	2.1	6.2	1.3	1.5
RDF ^b #1	4.8	1.4	10.6	1.7	1.6
RDF #2	0.9	1.1	1.5	2.2	1.4

^a Sugar degradation products given in g/L in liquid fraction.

^b RDF = Refuse derived fuel

^c HMF = 5-Hydroxymethyl-2-furfural

The initial growth rates of the yeasts demonstrated a lag for about the first 12 hours. Samples were taken for 8 days due to the slow yeast growth and consequently slow ethanol production rate. The newsprint hydrolyzate showed extreme effects from the treatments, with treatment three resulting in the best yields. The yield of ethanol from glucose and mannose in the two RDF hydrolyzates using *Saccharomyces cerevisiae* was unaffected by the treatment applied. The ethanol produced accounted for conversion of all the glucose and mannose present.

Candida utilis was more sensitive to the hydrolyzate source and treatment. Fermentation of RDF #1 showed good results only with treatment 3. Fermentation of RDF #2 showed good results with treatments 2 and 3. This reflects the difference in the composition of the hydrolyzates. RDF #1 contained higher levels of levulinic and formic acids than RDF #2, and these are known inhibitors of fermentation by yeasts.

The rate of fermentation was much less than desired throughout all tests. All hydrolyzates receiving treatment 3 were fermented by *Saccharomyces cerevisiae* in three days.

The sugar concentrations of the hydrolyzates were relatively low. It is desirable to ferment substrates of greater concentration in order to provide a greater product concentration. These tests were also performed using only two yeasts. There may be other species or treatments that will allow a faster rate of ethanol production and still result in the near theoretical yields achieved in these tests.

Safety and Environmental Aspects

Previous work by Barrier, J.W., 1990, (8), Broder et al., 1991, (7), and Barrier, J.W., 1991, (9) discussed results of TVA's dilute sulfuric acid hydrolysis effluent streams. TVA's dilute sulfuric acid hydrolysis process results in three main effluent streams: gypsum, lignin residue, and stillage. Waste streams are considered hazardous if they exhibit any of the Resource Conservation and Recovery Act (RCRA) characteristics which are set forth by the Environmental Protection Agency (EPA). The characteristics are corrosivity, ignitability, reactivity, and leachability. Analyses of these waste streams were conducted by TVA's analytical laboratory. The leachability analyses were done by the EP Toxicity method which has now been replaced by the Toxicity Characteristic Leaching Procedure (TCLP). The TCLP includes 25 additional chemicals (mostly herbicides and pesticides) not previously included.

Gypsum. Analyses required for a solid include the RCRA characteristic tests for corrosivity, leaching, and reactivity. Tables VI and VII show leaching and reactivity characteristics of gypsum. The gypsum was produced from neutralization of RDF hydrolyzate in the laboratory. Corrosivity of a solid is determined by measuring pH, and the pH must be above 2.0 and below 12.5. For gypsum, the measured pH was 4.9-7.6. The analyses shown in Tables VI and VII indicate that gypsum can be safely landfilled since it does not exhibit the RCRA characteristics of a hazardous waste.

Table V. Results of fermentation tests with three hydrolyzates

Substrate ^a	EtOH (g/L)	Best Conc Reached(day)	Sugars Fed (g/L)	Glu+ Man (% of total sugars)	Total Sugars Used(%)
TREATMENT 1					
Newsprint-S	0.3	8	35.5	79	3
Newsprint-C	0.0	8	35.5	79	0
RDF ^b #1-S	11.2	8	25.1	86	86
RDF #1-C	0.2	8	25.1	86	16
RDF #2-S	4.6	8	15.9	66	69
RDF #2-C	0.3	8	15.9	69	3
TREATMENT 2					
Newsprint-S	0.2	8	35.3	79	4
Newsprint-C	0.0	8	35.3	79	0
RDF #1-S	9.6	8	23.5	85	86
RDF #1-C	0.5	8	23.5	86	8
RDF #2-S	5.2	8	15.9	68	69
RDF #2-C	5.3	8	15.9	70	68
TREATMENT 3					
Newsprint-S	13.1	3	35.2	79	75
Newsprint-C	7.8	8	35.2	79	45
RDF #1-S	9.5	3	24.8	85	86
RDF #1-C	10.0	8	24.8	85	86
RDF #2-S	4.6	3	16.1	67	68
RDF #2-C	5.4	2	16.1	70	70

^a The S and C represent *Saccharomyces cerevisiae* and *Candida utilis*, respectively.

^b RDF = Refuse Derived Fuel

Table VI. Leaching characteristics of gypsum and lignin residue using the EP Toxicity analyses

Chemical	Gypsum (ppm)		Residue (ppm)		Maximum Limit (ppm)
	S1	S2	S3	S4	
Arsenic	<0.23	<0.23	<0.23	<0.23	5.0
Barium	0.029	0.016	0.463	0.275	100.0
Cadmium	<0.024	<0.024	<0.024	<0.024	1.0
Chromium	2.35	0.166	<0.016	<0.016	5.0
Lead	<0.061	<0.061	<0.061	<0.061	5.0
Mercury	<0.052	<0.052	<0.052	<0.052	0.2
Selenium	<0.256	<0.256	<0.256	<0.256	1.0
Silver	<0.007	<0.007	<0.007	<0.007	5.0
Endrin	<0.005	<0.005	<0.005	<0.005	0.02
Lindane	<0.001	<0.001	<0.001	<0.001	0.4
Methoxychlor	<0.05	<0.05	<0.05	<0.05	10.0
Toxaphene	<0.25	<0.25	<0.25	<0.25	0.5
2,4-D	<0.40	<0.40	<0.40	<0.40	10.0
2,4,5-TP	<0.40	<0.40	<0.40	<0.40	1.0

Note: S1 and S2 are two samples where S1 has been neutralized to a pH of 5.5 and S2 has been over-limed to a pH of 10.0. S3 and S4 are similar samples except that sample S3 has had inerts removed.

Lignin Residue. The lignin residue produced from hydrolysis of RDF in the laboratory was analyzed. To recover maximum soluble sugars, lignin residue is washed, and the resulting pH was 2.5- 4.0. Results of the leaching and reactivity tests are shown in Tables VI and VII. These results indicate that the lignin residue does not exhibit any of the RCRA characteristics of hazardous wastes, and the residue can therefore be considered a solid waste.

Stillage. Tables VII-IX show analyses of the stillage. Stillage contains from 96-99% water. Hydrolyzate was analyzed as being representative of stillage. Hydrolyzate is easy to produce in large volumes for analytical purposes and becomes stillage after fermentation and removal of ethanol. As a liquid, the hydrolyzate was analyzed for the RCRA characteristics of reactivity, corrosivity, and ignitability. The analyses of the hydrolyzate indicate that it does not exhibit any of the RCRA characteristics of a hazardous waste.

The analyses of TVA's dilute sulfuric acid hydrolysis processing system have shown the production of no hazardous waste streams. However, since the composition of MSW and RDF is variable, the process effluent streams will continue to be analyzed on a regular basis to ensure safety and environmental acceptability (7).

Economics

Previous work by Bulls et al., 1991, (10), Barrier, J.W., 1990, (11), Broder et al., 1991 (7), Barrier, J.W., 1991, (9), Barrier et al., 1991, (12), Barrier, J.W., 1991, (13), discussed results of TVA's technical economic evaluations of its MSW processing system. An estimate of total capital investment for the MSW processing system for a 1,000-ton-a-day processing system is shown in Table X. These capital costs are based on vendor quotes for the major equipment items and include direct and indirect costs such as piping, electrical, engineering and supervision, contingency, etc. A total capital investment of \$104 million has been estimated for the plant design. Operating costs for the plant are shown in Table XI. Raw material costs include sulfuric acid, lime, yeast, nutrients for fermentation, and an ethanol denaturant. Utilities, landfilling, labor, supplies, and fixed charges make up the balance of the operating costs. Fixed charges include depreciation (straight line, 20 years), insurance, taxes, maintenance, and plant overhead. Because of the tipping fee associated with the disposal of MSW, the "cost" for this feedstock is negative and provides a credit to the process.

Revenue from the process is based on the sale of recyclables, chemicals, and electricity. Recyclables include aluminum, ferrous metals, plastics, and glass. Price estimates are based on national averages for these items. As shown in Table XI, total annual revenue from recyclables is estimated to be \$7.8 million. Chemicals produced in the process include ethanol, furfural, acetic acid, and carbon dioxide. Prices for these items were obtained from industry quotes and the Chemical Marketing Reporter. Total revenue from chemicals produced in the process is estimated to be \$8.5 million per year. Annual revenue from excess electricity is estimated to be \$4.7 million, based on \$0.06 per kWh.

Table VII. Reactivity analyses of gypsum, lignin residue, and hydrolyzate for cyanide and sulfide production

Sample	Reactivity(ppm)		Maximum Limits(ppm)	
	CN-	S-	CN-	S-
Gypsum	< 0.05	< < 500	250	500
Lignin Residue	< 0.05	< < 500	250	500
Hydrolyzate	< 0.05	< 500	250	500

Table VIII. Corrosivity analyses of neutralized hydrolyzate for corroding steel (SAE 1020)

Sample	Corrosivity (inch/yr)	Maximum Limit (inch/yr)
Hydrolyzate 1	0.00895	0.250
Hydrolyzate 2	0.01754	0.250

Table IX. Ignitability of neutralized hydrolyzate

Sample	Ignitability Flash Point	Minimum Limit
Hydrolyzate 1	> 60° C	60° C
Hydrolyzate 2	> 60° C	60° C

Table X. Total capital investment for a 1,000-ton-per-day MSW processing facility

ITEM	COST (\$)
Direct Costs	
Purchased Equipment-Delivered	5,784,355
Equipment Installation	7,735,306
Instrumentation/Controls/Electrical/Piping	9,798,054
Buildings and Yard Improvements	7,219,620
Service Facilities	12,118,647
Land	<u>1,547,061</u>
Total Direct Costs	64,203,044
Indirect Costs	
Engineering and Supervision	5,930,402
Construction Expenses	<u>6,446,089</u>
Total Indirect Costs	12,376,491
Contractor's Fee	3,094,123
Contingency	7,735,306
Working Capital	16,759,831
TOTAL CAPITAL INVESTMENT	<u>104,168,794</u>

Table XI. Production costs for TVA's ethanol-from-MSW process for a 1,000-ton-per-day plant (quantities are in tons unless otherwise noted)

ITEM	QUANTITY	\$/UNIT	AMOUNT(\$/yr)
COSTS			
MSW	330,000	-38.37	(12,662,065)
Sulfuric Acid	8,865	70.00	620,537
Lime	6,493	45.00	292,186
Yeast	414	150.00	62,039
Potas.Dihy.Phos.	208	50.00	10,423
Urea	827	115.00	95,127
Sodium Sulfite	414	475.00	196,458
Denaturant-GAL	221,528	0.50	110,764
Utilities			
-Process Water-MG	40	500.0	020,001
-Cooling Water-MG	615	50.00	30,771
Landfilling	87,737	30.00	2,632,113
Labor	---	---	2,640,538
Supplies	---	---	524,454
Fixed Charges			
-Depreciation-20 YR	---	---	4,293,095
-Insurance	---	---	874,090
-Local Taxes	---	---	874,090
-Maintenance	---	---	3,496,359
-Plant Overhead	---	---	1,320,269
Total Costs			5,431,249
REVENUES			
Recyclables			
-Aluminum	4,158	1,000.00	4,158,000
-Glass	30,490	15.00	457,352
-HDPE	8,465	140.00	1,185,030
-PET	4,389	140.00	614,460
-Ferrous Metals	27,786	50.00	1,389,300
Ethanol-GAL	4,652,086	1.25	5,815,107
Carbon Dioxide	14,592	10.00	145,916
Furfural	2,364	800.00	1,891,568
Acetic Acid	1,107	580.00	641,865
Electricity			
-KWH/YR	7.93 x 10 ⁷	0.06	4,757,969
Total Revenues			21,056,568
RATE OF RETURN ON INVESTMENT			15.00%

Based on the costs and revenues associated with the process, and a required return on investment of 15%, the required tipping fee was calculated to be \$38.37/ton of MSW (10).

Conclusions

Hydrolysis conditions will influence sugar production, fermentation efficiency, and effluent composition. Laboratory tests have shown yields of up to 27 gallons of ethanol can be produced per ton of waste-derived feedstock and 36 gallons per ton of cardboard pellet feedstock. Pilot-plant tests have shown yields up to 16 gallons of ethanol per ton of waste-derived feedstock. Further tests at higher acid concentration, lower liquid-to-solid ratios, higher temperatures and shorter retention times may increase sugar yields, produce more concentrated hydrolyzates and reduce the quantity of residue remaining after hydrolysis. Significant quantities of organic residue remain after hydrolysis which are being evaluated as an energy source to run the process.

Municipal solid waste varies in composition, and analyses will be performed on a regular basis on each supply of MSW. A replicated study is planned to evaluate variability and component distribution in the different processing streams. Analyses of processing effluents from the conversion of RDF in TVA's process has resulted in the production of no hazardous materials based on Environmental Protection Agency (EPA) guidelines. Work is in progress to characterize gases, volatile organics, and semivolatile organics from hydrolysis, fermentation, and residue combustion. Many questions related to process scale-up and effluent management remain to be answered.

Preliminary economic analysis shows a tipping fee of \$38.37 a ton is required for MSW conversion using a 15% rate of return on investment. Additional economic evaluations will be conducted as the process is optimized.

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Chapter 5

Fuel Evaluation for a Fluidized-Bed Gasification Process (U-GAS)

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The gasification characteristics of a solid carbonaceous fuel in the U-GAS fluidized-bed gasification process can be predicted by laboratory examination of the fuel, which includes chemical and physical characterization and thermobalance and agglomeration bench-scale characterization and bench-scale tests. Additional design information can be obtained by testing the feedstock in the U-GAS process development unit or the pilot plant.

The Institute of Gas Technology (IGT) has developed an advanced, single-stage, fluidized-bed gasification process, the U-GAS process, to produce a low- to medium-Btu gas from a variety of solid carbonaceous feedstocks, such as coal, peat, wood/biomass, sludge, etc. The development of the process is based on extensive laboratory testing of these feedstocks as well as large-scale tests in a low-pressure (50 psig) pilot plant and a high-pressure (450 psig) process development unit conducted over a period of several years. Up to 98% feedstock utilization with long-term steady-state operation has been achieved. The testing has provided information related to the effect of various gasification parameters, such as pressure, temperature, and steam-to-carbon feed ratio, on gasification characteristics of the feedstocks. The concept of *in-situ* desulfurization by simultaneous feeding of dolomite/limestone has also been established. Reliable techniques have been developed for start-up, shutdown, turndown, and process control. The process represents the fruition of research and development in progress at IGT since 1974. The product gas will be a low-Btu gas that is usable as a fuel when operating with air, and a medium-Btu or synthesis gas when operating with oxygen. The medium-Btu or synthesis gas can be used directly as a fuel, converted to substitute natural gas, or used for the production of chemical products such as ammonia, methanol, hydrogen, and oxo-chemicals. The low- and medium-Btu gas can also be used to produce electricity generated by a combined cycle or by fuel cells.

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On the basis of the operational results with numerous feedstocks, IGT has developed an experimental program for the evaluation of a solid carbonaceous fuel for use in its fluidized-bed gasification technology.

U-GAS Process

The U-GAS process employs an advanced, single-stage, fluidized-bed gasifier (Figure 1). The feedstock, which is dried only to the extent required for handling purposes, is pneumatically injected into the gasifier through a lockhopper system. Within the fluidized bed, the feedstock reacts with steam and air or oxygen at a temperature dictated by the feedstock characteristics; the temperature is controlled to maintain nonslagging conditions of ash. The gases are introduced into the gasifier at different compositions at different points at the bottom of the gasifier. The operating pressure of the process depends on the ultimate use of the product gas and may vary between 50 and 450 psi. Upon introduction, the feedstock is gasified rapidly and produces a gas mixture of hydrogen, carbon monoxide, carbon dioxide, water, and methane, in addition to hydrogen sulfide and other trace impurities. Because reducing conditions are maintained in the bed, nearly all of the sulfur present in the feedstock is converted to hydrogen sulfide.

The fines elutriated from the fluidized bed are separated from the product gas in two stages of external cyclones and are returned to the bed where they are gasified to extinction. The product gas is virtually free of tars and oils due to the relatively high temperature of the fluidized-bed operation, which simplifies the ensuing heat recovery and gas cleanup steps. The process yields a high conversion, especially because of its ability to produce ash agglomerates from some of the feedstocks and selective discharge of these agglomerates from the fluidized bed of char.

Fuel Evaluation

Three steps are recommended to evaluate the suitability of a potential feedstock for the process:

1. Laboratory analyses
2. Bench-scale tests
3. Process development unit (PDU) or pilot plant gasification test.

Laboratory Analyses. Table I lists those fuel properties that are normally determined for assessing a solid fuel for use in the process. Additional analyses are performed as required with unusual feedstocks. For example, run-of-mine coals with a high mineral content may require mineral identification and evaluation of the effect of high mineral content on the ash fusion properties.

The bulk density, heating value, ash content, and elemental composition of the organic portion of the feedstock usually have no direct effect on the behavior

Table I. Laboratory Analyses of the Fuel

•	Proximate Analysis
•	Ultimate Analysis
•	Higher/Lower Heating Value
•	Bulk Density
•	Particle-Size Distribution
•	Grindability
•	Equilibrium Moisture
•	Free Swelling Index
•	Ash Fusion Temperatures (Reducing Atmosphere)
•	Ash Mineral Analysis

of the feedstock in fluidized-bed gasification. However, they do influence the oxygen requirement, the gas yield, and the gas composition. The higher heating value (HHV) is a measure of the energy content of the feedstock. It relates, with other factors, to the amount of oxygen needed to provide the desired gasification temperature levels. If a feedstock has a low HHV, more oxygen is needed to maintain the gasifier temperature at an acceptable operating level. If the HHV is higher, less oxygen will be required to maintain the desired temperature levels.

The ash fusion temperature reflects the ease of agglomeration of the ash in the gasifier. The free swelling index (FSI) indicates the caking tendency of the feedstock; for highly caking feedstocks, a proper distribution of the feed material, as it enters the gasifier, is critical. In the U-GAS process, the Pittsburgh No. 8 bituminous coal with an FSI of 8 has been successfully gasified and agglomerated with overall coal utilization of 96%. The feedstock is generally sized to 1/4-inch X 0 before it is fed to the gasifier. If a finer size is available, the fluidization velocity is reduced accordingly.

To utilize a feedstock today, one needs to know a great deal about it prior to purchase. It is essential to know the sulfur content to comply with airborne emissions standards and the ash content and its constituents to ensure compliance with solid waste regulations. Other standards are still evolving as new environmental and energy legislation is enacted.

The range of various properties of the feedstocks that have been tested in the U-GAS process development unit or pilot plant is given in Table II.

Bench-Scale Tests. Three types of bench-scale tests are conducted to evaluate the fuel. These bench-scale tests establish a range of operating conditions that can be used to plan tests in the process development unit or the pilot plant facility, and to perform material and energy balances for the gasifier and estimate its throughput. These tests are described below.

Thermobalance Tests. The gasification of a solid carbonaceous fuel consists of two major steps: 1) initial rapid pyrolysis of the feedstock to produce char,

gases, and tar and 2) the subsequent gasification of the char produced. (In addition, some combustion reactions take place if gaseous oxygen is present; these reactions

**Table II. Range of Feedstock Properties
Tested in the U-GAS Process**

Moisture,* %	0.2 to 41
Volatile Matter,** %	3 to 69
Ash,** %	6 to 78
Sulfur,** %	0.2 to 4.6
Free Swelling Index	0 to 8
Ash Softening Temperature, °F	1980 to 2490
Higher Heating Value,** Btu/lb	2,330 to 13,630

* As received.

** Dry basis.

are very rapid.) Because the rate of the second step is much slower than that of the first step, the volume of a gasifier (or the carbon conversion in the gasifier) is primarily dependent on the gasification rate of the char. Due to the relatively well-mixed nature of a fluidized-bed gasifier, the char particles undergoing gasification are exposed to gases consisting primarily of CO, CO₂, H₂, H₂O, and N₂.

The thermobalance testing is performed to determine a relative reactivity constant for the feedstock for comparison with the reference coal, Western Kentucky No. 9 bituminous coal, which has been extensively tested in the thermobalance (1) as well as in the U-GAS process. In the thermobalance, a small quantity of the feedstock is continuously weighed while being gasified at a specific temperature, pressure, and gas composition. This measured weight loss data versus time and the thermobalance operating conditions and analyses of feed and residue are used to calculate the specific relative reactivity constant for the feedstock. The kinetic data, in conjunction with the reference coal information, are used to plan tests in the PDU or pilot plant. As an example, Figure 2 shows the gasification rate for maple hardwood char, peat char, and bituminous coal char, as determined by the thermobalance. The carbon conversion data for Western Kentucky No. 9 coal char under different operating conditions, as determined by the thermobalance, are shown in Figure 3.

Ash-Agglomeration Tests. Prior to the large-scale testing, the ash-agglomeration tests are conducted in the laboratory to determine the possibility of agglomerating the feedstock ash in the gasifier. These tests are performed in a 2-inch fluidized-bed reactor capable of operating at temperatures up to 2200°F. Several tests have successfully demonstrated that ash agglomerates can be produced in this bench-scale unit at conditions that can be related to the pilot plant operating conditions. The 2-inch reactor has a unique grid design that allows close

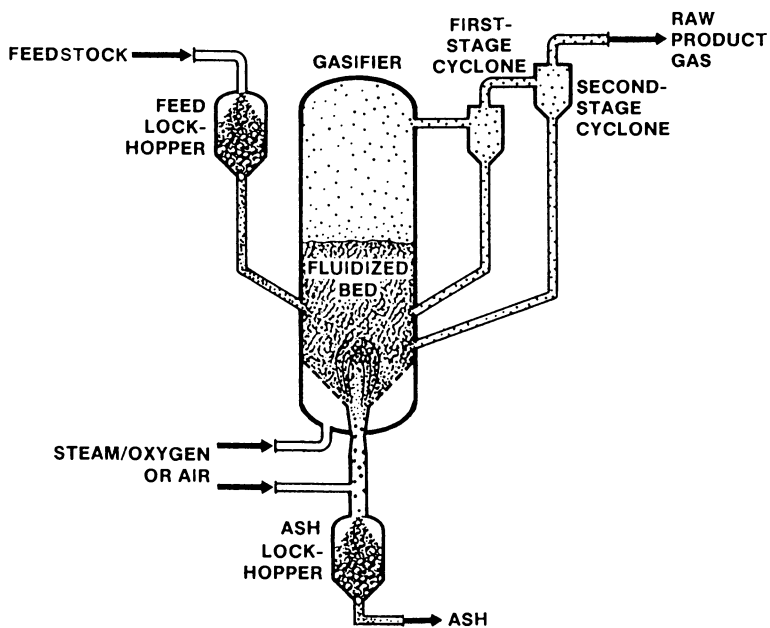


Figure 1. Schematic Diagram of the U-GAS Gasifier

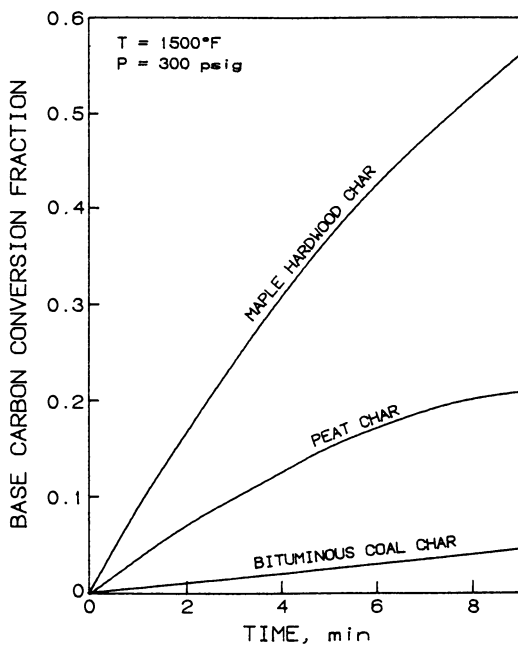


Figure 2. Gasification Rates for Maple Hardwood Char, Peat Char, and Bituminous Coal Char

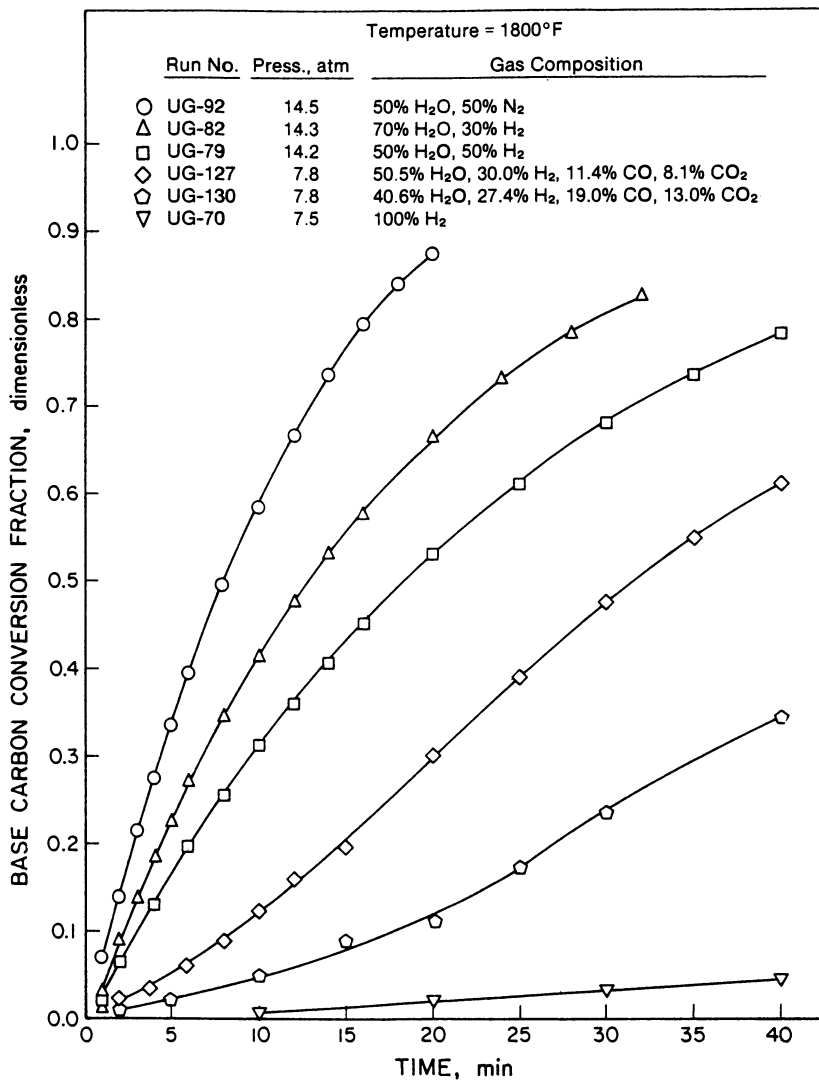


Figure 3. Base Carbon Conversion Fraction Versus Time for Gasification of Western Kentucky No. 9 Coal Char

simulation of the pilot plant fluidized-bed dynamics and mixing characteristics, which are essential for proper ash agglomerate formation, growth, and discharge. The tests are generally conducted at different temperatures, superficial velocities, gas compositions, and operating times to evaluate conditions favoring ash agglomerate formation and growth. The results are quantified using size distribution curves of feed, residue, and fines to show size growth of particles. Visual evaluation of the agglomerates includes separation of the +8 mesh fraction (normally 100% agglomerates) in the residue and, if required, separation of agglomerates by float-sink techniques for each size fraction. The agglomerates thus separated can be easily photographed or examined petrographically. An example of the test results with different coal samples is given in Table III.

Table III. 2-Inch Ash-Agglomeration Tests With Various Feedstocks

Coal Sample	Temp., °F	Char Initial Ash, %	Run Time, h	Fluidizing Velocity, ft/s	Comments
FC-1	1985	31.5	2.0	1.0	Sinter particles plus some agglomerates
FC-1	2100	31.5	1.5	1.5	Agglomerates formed, little or no sinter
FC-2	1990	45.5	1.0	1.5	Small agglomerates present
FC-2	1990	45.5	1.3	1.5	Larger agglomerates found
FC-3	2080	45.4	2.5	1.5	Agglomerates formed
FC-4	1960	15.5	1.0	2.1	No agglomerates found
FC-4	1920	20.9	3.0	1.5	Small agglomerates found
FC-4	2000	15.5	2.5	1.6	Greater number of large agglomerates
KY #9	2000	51.0	1.3	1.5	Many agglomerates produced

Fluidization Test. A fluidization test in a glass column at ambient conditions may also be conducted to determine the minimum and complete fluidization velocities of the material. This information is then translated into the necessary operating velocity in the PDU or pilot plant test. The fluidization test is conducted only if

the feedstock is unusual or if the feedstock size is different than that typically used (1/4 in. X 0) in the process. This test is conducted with the char produced from the feedstock.

Process Development Unit (PDU) or Pilot Plant Gasification Test. IGT has two continuous U-GAS gasification units located in Chicago: 1) An 8-inch/12-inch dual-diameter high-pressure process development unit, which can be operated at up to 450 psig and has a nominal capacity of 10 tons per day (at 450 psig operation), and 2) A 3-foot-diameter low-pressure pilot plant, which can be operated at up to 50 psig and has a nominal capacity of 30 tons per day. A process flow schematic of the U-GAS pilot plant is shown in Figure 4. In addition, a 2-foot/3-foot dual-diameter high-pressure pilot plant has recently been constructed at Tampere, Finland, and testing in this unit has begun. Plans are under way to test various coals, peat, wood and bark waste, and pulp mill sludge in this unit.

A test in the PDU or pilot plant provides the following information:

- It confirms the suitability of the candidate feedstock for the U-GAS process.
- It establishes the base design operating conditions as well as an operating window for the gasifier.
- Design data for fines characteristics, ash agglomeration characteristics, and gas characteristics are obtained.
- Estimates for gas quality, gas yields, and process efficiency are established.
- Necessary environmental data to define the environmental impact are taken.
- Various samples, such as bed material samples, ash discharge samples, fines samples, and wastewater samples, are collected and saved and provided as needed for use during detailed engineering.

The PDU testing is recommended where high-pressure gasifier operation would be required. Each test in the PDU usually consists of 2 days of operation, whereas one 5-day-duration test is usually conducted in the pilot plant with the candidate feedstock. During the test, the gasifier is operated in ash-balanced, steady-state conditions, during which most of the design data are procured. A detailed test plan is generally prepared based on a comparison of the feedstock with a similar feedstock or from information obtained from bench-scale testing. Depending on the feedstock characteristics, the gasifier is operated at a temperature of up to 2000°F and a superficial velocity of up to 5 ft/s.

Numerous solids samples are collected regularly during the test run so that accurate material balances can be prepared. Process sample points include the coal feed, fluidized bed, ash discharge, and cyclone diplegs (for the pilot plant). Samples from the fluidized bed are also collected and analyzed hourly during the test to help the operators determine and maintain steady-state operation.

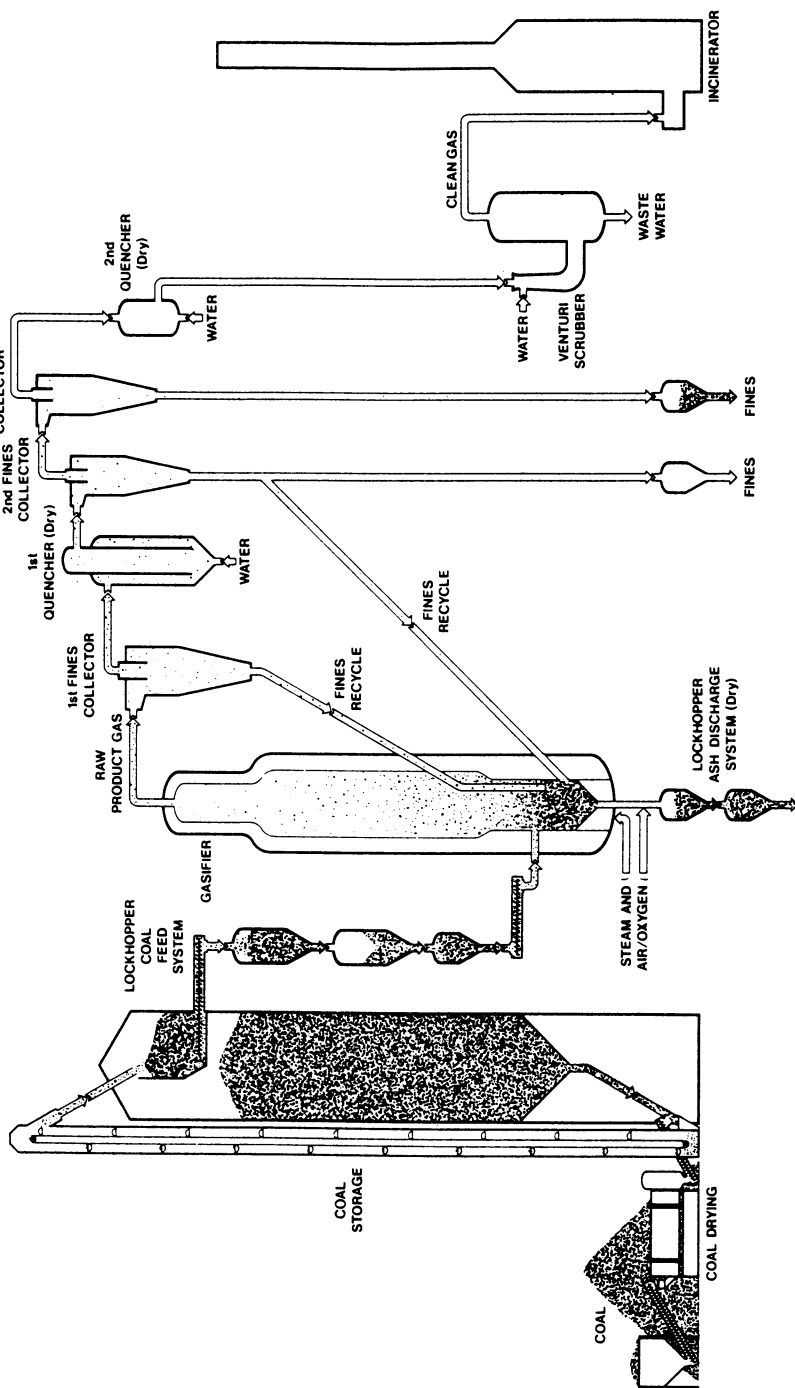


Figure 4. Process Flow Schematic of the U-GAS Pilot Plant

All process solids and gas flow streams are measured and recorded. Temperatures are recorded for all process streams and at several locations within the reactor. Redundancy is provided for the reactor pressure taps used for bed density and height.

A product gas sample stream is drawn continuously from the gasifier freeboard for chromatograph analysis. The chromatograph system provides accurate on-line analysis for CO, CO₂, CH₄, H₂, N₂, H₂O, and H₂S. The chromatograph sequencing is microprocessor-controlled for flexibility in the scope and frequency of the analysis. The product gas samples are also collected in gas bombs for later laboratory analyses.

Special sampling and instrumentation are available for complete chemical characterization (organic compounds as well as trace elements) of the product gas and wastewater streams. Test results of this nature are necessary to satisfy environmental permitting requirements and for proper design of downstream processing equipment. Equipment is also available for determination of product gas dust loading after one, two, or three stages of cyclone separation.

These units use a microprocessor-based data acquisition system to ensure accurate, timely, and reliable collection of all process data of interest. About 85 process data points (temperature, pressure, flow, etc.) for the pilot plant and about 40 data points for the PDU are scanned repeatedly throughout the test. A full scan is completed in approximately 10 seconds and is repeated at 3-minute intervals. The reactor operating status, including various flows, pressures, temperatures, and velocities (grid, venturi, bed, freeboard, cyclone), bed density, bed height, etc., is calculated and displayed on the computer CRT screen. The data are stored on magnetic tape in both raw signal and converted form. The converted data are averaged hourly, and an hourly average report of all data points and the operating status is automatically printed in the control room; in addition, a shift report is printed every 8 hours to allow a shift engineer to review the operation of a previous shift. Particular emphasis is placed on the use of the data acquisition system as an operating tool. Specialized programs have been developed to aid the operators in the approach to and confirmation of steady-state operation. This results in more steady-state operating time, and therefore more useful design data, per test run.

Table IV summarizes various feedstocks tested in the pilot plant and PDU and the results obtained. The details of the PDU system and some test results are given by Goyal *et al.*(2,3). The details of the pilot plant system and some test results are given by Goyal and Rehmata (4,5).

The lowest rank material gasified so far in the U-GAS process is peat; some details are given here. Kemira OY, a chemical company in Finland, was interested in producing synthesis gas from peat for manufacturing ammonia. Two different types of peat were received by IGT from Kemira: Viidansuo and Savaloneva. The two samples represented the extremes in peat quality, with Viidansuo being of poorer quality, very fibrous, and having a van Post index of only 3 to 4. Both peats were obtained by crushing peat sods to 3/8 in. X 0 size. The peats as received contained about 40 weight percent moisture. The two peats were mixed for the gasification test, one batch containing equal parts of each and dried to 35 weight percent moisture and another batch containing two parts Savaloneva to one

part of Viidansuo and dried to 15 weight percent moisture. Despite the different flow properties of these peats, the U-GAS pilot plant lockhopper feed system, after some modifications, was able to feed them at controlled rates for the steady-state duration of the test. The pilot plant was operated for 5-1/2 days from start-up to shutdown. Forty-two tons of the peat were gasified during 50 hours of continuous operation. The test was conducted at three different operating set points at two different temperatures and at a lower steam feed rate. A peat conversion efficiency of 95% to 97% was maintained throughout the three set points. Figure 5 shows a typical balance for the test. After completion of the three set points, the gasifier operating temperature was raised to obtain data on producing a synthesis gas with a lower methane content. The operation of the gasifier throughout the test was stable and easily controlled by adjusting the peat feed rate and oxygen flow to the gasifier. During interruptions in either peat feed or oxygen feed, the gasifier was able to respond in a controlled and logical manner. The recycle of fines entrained from the gasifier was smooth and very effective, as indicated by high peat conversion efficiency (up to 97%). The peat contained a relatively large fraction of discrete particles of quartz stone. The gasifier bottom, because of its simple design, was able to discharge both the stone and peat ash without any problems. The gasifier was operated under stable, ash-balanced conditions despite a wide variation in the operating conditions by discharging the required amounts of ash through the gasifier bottom section. The test showed that synthesis gas can be produced from the two extremes of the peat quality tested. Even the highly fibrous, undercomposed, and reactive Viidansuo peat was gasified without any problem. In addition, the ash properties -- both iron content and fusion temperature -- of the two peats were quite different, indicating that the gasifier can handle peats of a wide range of ash properties. The test also indicated that a minimal amount of peat preparation in the form of drying and crushing is adequate for feed requirements to the U-GAS process. It is not necessary to either pelletize or deep-dry the peat.

Like coal and peat, it is also possible to gasify wood and bark wastes, refuse-derived fuels, sludge, etc. in the U-GAS fluidized-bed gasifier. IGT has extensive experience in the gasification of such materials in its RENUGAS process, which also employs a single-stage fluidized-bed reactor (6-10). The chemistry of converting the waste materials to synthesis gas is quite similar to that of coal and peat gasification. Since there is normally a cost associated with disposal of the wastes, gasification offers an economically attractive application of the technology. Currently, producers of many of the waste materials must pay a premium for their removal. Ultimate disposal of such materials in a gasification facility would prove to be economically attractive.

In September of 1989, IGT entered into a licensing agreement with Tampella Power, Inc. of Tampere, Finland, which will result in the commercial application of the process. Tampella selected the pressurized fluidized-bed technology because of its versatility and applicability to a wide variety of feedstocks, including coal, peat, forestry waste, etc. As a first step toward commercialization, a 10-MW thermal input pressurized (450-psi) pilot plant has been designed and constructed at Tampella's R&D Center in Tampere, Finland, and testing in this unit has begun. In this plant provisions have been made for testing a variety of feedstocks other

Table IV. Summary of U-GAS Pilot Plant and PDU Testing

Feedstock	Hours of Operation	Total Tons Processed	Year	MAF Coal Utilization,* %
A. Pilot Plant				
Coke Breeze and Coal Chars	4700	1100	1974-76	92
Montana Subbituminous "C" Coal	215	170	1976	92
Illinois No. 6 Bituminous Coal	76	40	1977	86
W. Kentucky No. 9 Bituminous Coal	1303	1031	1978-82	98
ROM W. Kentucky No. 9 Bituminous Coal	442	287	1979	87
Pittsburgh No. 8 Bituminous Coal	173	110	1980	96
W. Kentucky Nos. 9 and 11 Mixed Bituminous Coal	58	52	1980	88
Australian Bituminous Coal	62	39	1981	95
Wyoming Subbituminous "A" Coal	77	84	1981	98
Polish Bituminous Coal	74	46	1981	79
French Bituminous Coal	60	48	1983	95
Unwashed Utah Bituminous Coal	120	58	1984	99
Finnish Peat	50	42	1985	97
Total	7410	3107		
B. Process Development Unit (PDU)*				
Pittsburgh No. 8 Bituminous Coal	7	0.5	1985	89
Illinois No. 6 Bituminous Coal	60	4	1986	86
Montana Rosebud Subbituminous Coal	169	31	1985-86	93
North Dakota Lignite	84	14	1985-86	91
Pittsburgh Coal (fed with limestone)	95	9	1987	97
Indiana New Albany Oil Shale	29	6	1987	89
Total	444	64.5		

* The fines escaping the gasifier are not recycled to the gasifier in the PDU. The coal utilization reported includes the char loss in these fines.

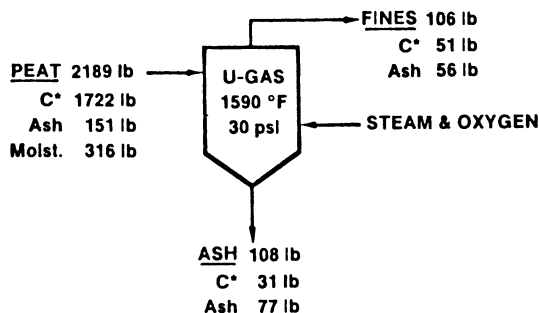


Figure 5. Typical Balance for U-GAS Pilot Plant Test with Finnish Peat. C* represents moisture- and ash-free peat (MAF). Peat conversion = 95.2%.

than coal, including wood and bark waste, peat, and pulpmill sludge. These fuels can be tested separately or as multifuel mixtures. The plant is designed to operate in several gasification modes, including air-blown, enriched air, and oxygen-blown gasification. Provisions have also been made for in-bed desulfurization testing with sorbents such as limestone or dolomite fed directly to the gasifier with the fuel. The pilot plant also provides a versatile testing platform for development and demonstration of various hot-gas cleanup strategies. Included in the plant are high-temperature cyclones for fines removal and recirculation to the gasifier and a high-temperature ceramic filter for complete removal of any remaining fines. A post-bed desulfurization system can also be tested in the plant, allowing testing of the process with both high- and low-sulfur fuels under a wide variety of operating conditions. All fuel gas produced in the plant will be combusted in a waste heat boiler at the end of the gas cleanup train. In addition to providing steam to the process and heat to the city of Tampere via its district heating system, this boiler will allow the combustion and environmental characterization of the fuel gas and combustion products.

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Chapter 6

Treatment of Municipal Solid Waste by the HYDROCARB Process

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The HYDROCARB Process addresses the problem of converting municipal solid waste (MSW) to a clean useable fuel for boilers and heat engines. The process consists of hydrogenation of the biomass to produce methane, followed by decomposition of the methane to carbon and hydrogen and combining the CO and H₂ to produce methanol and recycling the hydrogen-rich process gas. Using natural gas to make up the mass balance, the economics looks attractive for a 3,000 T/D MSW plant, especially when avoidance costs are taken into account. The process is environmentally attractive since processing is performed in a highly reducing atmosphere and at elevated pressure and temperatures where no toxic gases are expected and CO₂ emission is minimized.

It is now generally known that the municipal solid waste problem has become an ever increasing problem in populated areas in the U.S. The increase in the standard of living manifested by a vast array of consumer goods has added to the problem of disposal of industrial and municipal solid waste (MSW). The land-fill disposal sites around metropolitan areas have become less available so that tipping fees are soaring. Municipalities are opting for more waste incineration or mass-burn plants. Legislation is being passed to require separation of waste for recycling and resource recovery. Because separated recyclable material is market demand dependent, the cost of recycling is site specific and time dependent. In fact, there are a number of municipalities that pay carters to remove and transport recyclable material to other locations which instead of becoming a source of income becomes a liability.

MSW roughly consists of 50% paper and plastic and the remainder being glass, metal and kitchen and yard waste. Industrial waste includes paper, wood, metal and used rubber tires etc. The most traditional waste disposal methods are landfilling and incineration. The modern and improved method for the same

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process is now dedicated RDF. In some cases, the energy generated is used to produce steam for electricity generation which can be sold, and therefore constitutes a positive value. The problem here is that the mass-burn plant generates potentially polluting gaseous and solid residue effluents. In the gaseous effluent, dioxin has been one of the most elusive and worrisome pollutants and has caused the shutting down of a number of incinerator plants. There are other gaseous pollutants, including volatile refractory organics, chlorine containing compounds, and particulates from plastic and organic waste. The chemical and biological activity in the remaining solid ash residue from incinerators is also a problem which still requires landfilling or other methods of disposal. There is concern that leachates from incinerated ash will eventually contaminate the aquifers. Municipalities are also passing legislation forbidding the use of materials which do not degrade and tend to remain in long-term storage in the landfill, such as plastics. A number of communities are outlawing disposable plastic products and appear to be returning to paper bags and containers. Much effort is also going into developing biodegradable plastics. Whether this is a sound environmental solution is yet to be determined.

HYDROCARB Waste Process

The HYDROCARB Process offers a viable alternative to mass burn. The process was originally conceived for the purpose of processing our vast resources of coal to produce a clean carbon fuel (1,2). However, the process can operate as well with virtually any carbonaceous raw material and certainly a large fraction of MSW qualifies as a carbonaceous material. The process is new and unique and the products formed can be used primarily as premium clean fuels as well as for the commodity market. The process depends on two basic steps, (1) the hydrogenation of coal to form a methane-rich gas while leaving the ash behind and (2) the thermal decomposition of the methane-rich gas to form carbon black and hydrogen which is recycled. The excess hydrogen and oxygen from the co-products can be a hydrogen-rich co-product which can either be hydrogen, methane, methanol or water. Figure 1 shows a schematic flow with alternative feedstocks, coal, wood or MSW and with co-feedstock additions.

Figure 1 gives a schematic of the process listing various feedstock materials, additives and co-products. The process can be made very efficient because the only raw material used is the carbonaceous material and the energy required to operate the process is relatively small compared to the gasification process. The overall reaction is thermally neutral. The primary product is always carbon black which can be used as a clean burning fuel and can also supply the market for vulcanization of rubber for automotive tires, pigment for inks and paints and for lubricants. The co-product hydrogen-rich gas can primarily be used as a burner fuel and the methanol as an automotive fuel, or as a commodity chemical, or can even be converted to gasoline. The process is fundamentally different than mass-burn in that it operates in a reducing atmosphere rather than in an oxidizing atmosphere and it is run in a closed system under pressure. Temperature conditions are about the same or perhaps even somewhat lower than in mass-burn incinerator plants. Because of the elevated operating pressure and reducing atmosphere, no dioxin can be formed thermodynamically. All the oxygen contain-

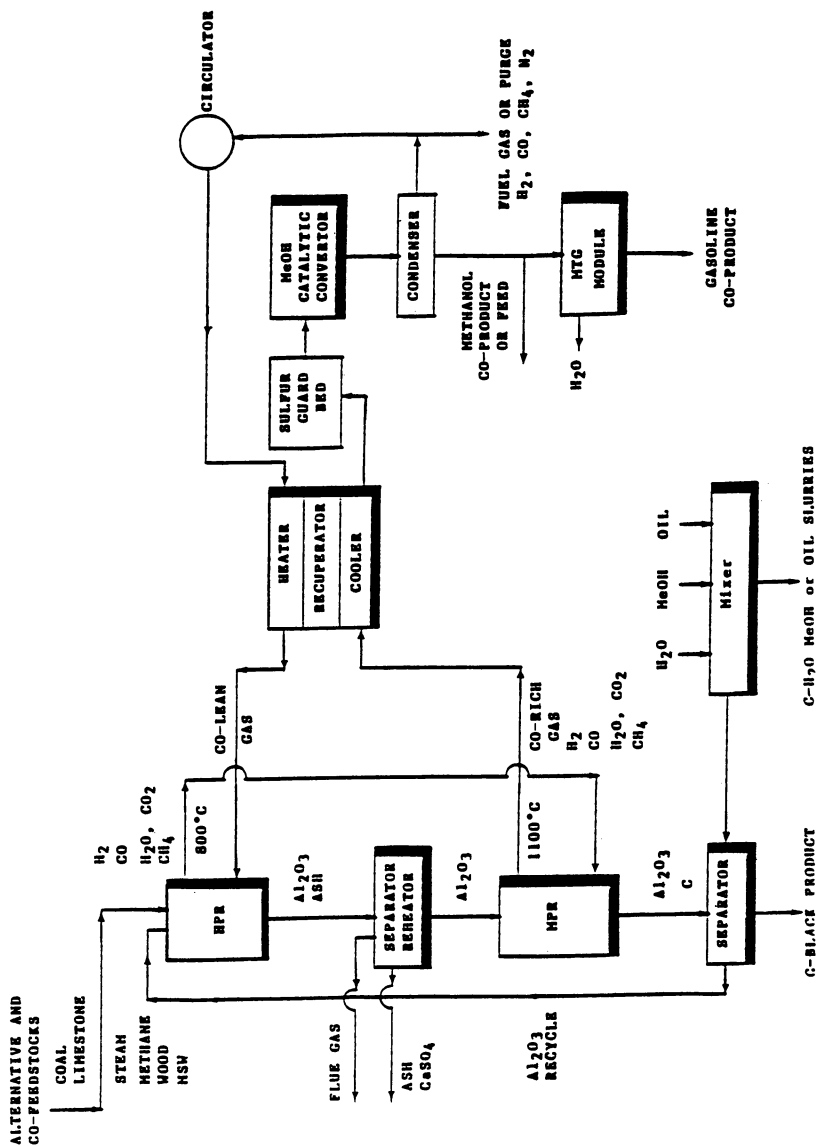
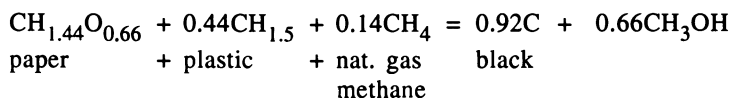


Figure 1. HYDROCARB process—Clean carbon from carbonaceous feedstock with methanol and gasoline co-product. Reproduced with permission from ref. 2.

ing organic material is reduced to carbon and methane and any metals that may be present in the waste are kept in their reduced state as opposed to mass-burn where the metals can become oxidized. The following describes how the process can be effectively used in processing MSW and the economic dynamics of the process.

The process can be used with either separated or non-separated waste. To simplify the example and avoid discussion of front-end costs, we will give examples of the process operating on separated waste. Thus, the main MSW feedstock is paper and plastic and we can include rubber tires for this example. Since paper is essentially produced from wood, the process can be represented by the following chemical stoichiometric formula, limiting the products to carbon and methanol.



Notice that the formula for plastic contains only C and H, like rubber and methane. The oxygen containing material in paper is in the form of hemi-cellulose. The above equation is based on an assumed MSW composition such that the amount of plastic is 25% of the weight of paper. This can be changed for specific sites and the mass balance adjustment can be made by varying the amount of natural gas added. The gas can be purchased from the local gas company in the particular area where the waste is being processed. We now have to set the production capacity of the plant. Mass-burn incinerator plants have been built in the 2,000–3,000 T/D capacities in and around metropolitan areas. Of course, around New York, for example, it might be worthwhile building a 10,000 T/D or more of waste paper and plastic HYDROCARB plant. However, for this and generally more widespread applications, we will fix on a 3,000 T/D MSW processing capacity which would contain 2,400 T/D paper and 600 T/D plastic.

We now calculate that to run this plant, we have to add 226 T/D of natural gas from the natural gas pipeline company's distributing company. This natural gas is equivalent to 10.7 million SCF/D of methane, which must be purchased from the gas company. The separated MSW is thus co-processed with natural gas.

Economics

We now must estimate the capital investment of the plant. We can obtain this estimate by scaling down from a large plant we estimated in detail, operating on 25,000 T/D of coal. Because this is a volumetrically controlled process, we can scale it by the well known 0.6 power factor of capacity. The 25,000 T/D plant making carbon and methanol from coal is estimated to cost $\$800 \times 10^6$. Thus, the 3,000 T/D waste plant will cost:

$$800 \times 10^6 \times \left(\frac{3000}{25000} \right)^{0.6} = \$200 \times 10^6$$

We can now calculate a selling price for the carbon black fuel and methanol co-product. The financial parameters operating on the capital investment are as follows: capitalization 80% debt/20% equity, 20 yr depreciation, 11% interest on debt, 25% return on equity (ROE) and 38% tax on ROE before taxes. This results in a 21.9% annual fixed charge operating on the total capital investment.

We assume a high natural gas cost from the gas company of \$5.00/MSCF which equals a cost of \$0.119/lb CH₄. We then add operation and maintenance cost and the 21.9% fixed charges on the \$200 million capital investment. We can now calculate the price (G) of the MSW value of the waste taken from the municipality, which can range from a negative value, in which case the community pays the processor to take the waste away, to a positive value in which case the processor pays the community to acquire the waste for processing. We shall first calculate a breakeven G price for the waste in \$/Ton in Table I, assuming we obtain \$5.00/MMBtu for the resulting fuel products.

Solving for G = \$41.50/Ton; this is what the processor can afford to pay the town for taking the MSW for processing and while still obtaining a 25% return on equity.

The above is based on a fuel value for a C-methanol composition makeup mixture of 34.3% carbon in 65.7% methanol by weight. The plant produces 700,000 gal/Day of this C-methanol slurry which is equivalent to 11,000 Bbl/D of fuel oil equivalent.

If we assume the processor obtains the waste from the town free, so that G = \$0/Ton, we can then calculate the selling price of \$3.10/MMBtu for both co-products carbon and methanol. This is equivalent to \$18.70/Bbl oil or \$0.44/gal.

Now if the town pays the processor \$25/Ton to cart the waste away (as some towns on Long Island have already done), then the selling price for carbon and methanol can come down to only \$2.00/MMBtu which is equivalent to

Table I. HYDROCARB Waste Processing Plant^a

<i>Production Cost</i>	<i>\$/Day</i>
Waste Cost	= 3,000 T/D × \$G/Ton
Nat. Gas = 0.119 × 226 × 2,000	= 53,000
Op. & Maint. = $\frac{3,000}{25,000} \times 120,000$	= 20,000
Fixed Charges = $\frac{0.219 \times \$200 \times 10^6}{328}$	= $\frac{133,000}{206,000 + 3,000 G}$

Thus,

$$206,000 + 3,000 G = 0.9 \times (3,000 + 226 \text{ T/D}) \times \frac{22.9 \text{ MMBtu}}{\text{Ton}} \times \frac{\$5.00}{\text{MMTU}}$$

^aPlant factor 90%, efficiency 90%, capacity 3,000 T/D, production capacity of fuel – 11,000 Bbl/D fuel oil equivalent.

SOURCE: Reproduced with permission from ref. 2

\$12.00/Bbl fuel oil equivalent or \$0.28/gal while maintaining a reasonable return on the investment equity.

At \$2.50/MMBtu which is highly competitive with oil at \$15.00/Bbl, the town would only have to pay \$13.50/Ton to a processor to take it away.

The conclusion is that even at a waste capacity of 3,000 T/D and an investment of $\$200 \times 10^6$, the processor can sell the carbon and methanol as a clean burner fuel for domestic and industrial boilers, as well as for diesel and turbine engines at an economically attractive price. Additional return can be obtained by the processor selling the methanol and carbon at a higher price to the chemical commodity market so that the cost of waste disposal would even bring a profit to the town by selling the waste to the processor at a higher price.

The above preliminary assessment indicates that the HYDROCARB Process for the disposal of MSW is highly attractive and should be taken up for development on a fast track schedule. Because this process utilizes natural gas for co-processing waste in a reducing atmosphere, not only is the process environmentally acceptable but is potentially economically attractive and thus it should be worthwhile to develop this process in conjunction with a municipality that is generating the waste.

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Chapter 7

Biomass-Fueled Gas Turbines

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Biomass fueled gas turbines offer a low cost means of generating power in areas where fossil fuels are scarce and too costly to import. This chapter presents results of a ten year research and development effort to advance biomass fueled gas turbines to commercial status. Aside from trees the most promising sources of biomass are sugar cane and sweet sorghum. Fuel alcohol can be produced from the sweet juices and grain for food is produced by the sweet sorghum. As the gas turbine start-up and shut-down effort is much less involved than the start-up/shut-down of a steam turbine power plant, the biomass fueled gas turbine is the preferred system for meeting the peak electrical power demands of any system. As CO₂ is extracted from the atmosphere during biomass growth, and ultimate replacement through the gas turbine combustion process is in exact balance, the entire process results in no net increase in CO₂ in the atmosphere.

Use of biomass to produce power in the five to thirty megawatt range is attractive because of higher hauling costs associated with power plants with higher outputs. The higher hauling costs result primarily from the low density of biomass. The ability to fuel gas turbine power generating systems is economically advantageous due to the quick start up and shut down capability. This capability allows restriction of operation to periods of peak usage for which higher prices are paid for power. Steam power generation systems by comparison cost substantially more per installed kw output, and they cannot be economically started up and shut down on a daily basis. Research and development of biomass fueled gas turbine systems over a ten year period has culminated in successful operation of an aircraft derivative gas turbine manufactured by the Allison Division of the General Motors corporation. With the cooperation of the Tennessee Valley Authority the power generating system was successfully integrated into their distribution grid for full demonstration of the system as a small power producer using sawdust as the fuel. The Allison gas tur-

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bine served well in the research and development phase, but it is economically marginal as a power producer in biomass fueled applications. As a result, a larger gas turbine produced by the General Electric Company is the current selection for commercial use. A system using that engine is being prepared for installation at Huddleston, Virginia, where a contract for sale of the output power to the Virginia Power Company has been negotiated. The R&D system which is located at Red Boiling Springs, Tennessee will be upgraded for operation with the General Electric engine. Sugar cane bagasse, an alternative fuel to sawdust which has been tested in the R&D facility, promises to be a major source of fuel in the future. Sweet sorghum bagasse can serve equally well.

Sweet sorghum and sugar cane juices are readily converted to alcohol by yeast fermentation. Sweet sorghum can be grown throughout the United States as well as the tropic and temperate zones of the earth. These plants have the highest conversions of solar energy into biomass of any of the species in the plant kingdom, substantially greater than trees. With the use of bagasse as a fuel for gas turbines in the generation of power, it is possible for the income from power sales to reduce the cost of ethyl alcohol well below that for gasoline. The sorghum grain can be used for fermentation or food. The high volume, high temperature exhaust gases from the turbine can be used to concentrate the juice, make alcohol, dry the bagasse or generate steam for injection into the turbine. There is adequate heat to concentrate the juice and dry the bagasse for year-round use during the harvest period.

Growth of sugar cane and sorghum on the 66.4 million acres of land taken out of production in the U.S. between 1981 and 1988 can supply enough energy to generate 34 percent of the nonnuclear power that was generated in 1986, enough to supply increased power demands into the next century. At the current rates paid by Virginia Electric Power Company for power generated with renewable fuels, 25.4 billion gallons of alcohol can be produced from the profits earned on power sales, enough to supply gasohol to the entire nation.

The system, which can be located at any point where there is a power distribution line and a sorghum or sugar cane source, can provide jobs in the area and an alternative crop for farmers while saving billions of dollars on set-aside payments. At \$20/barrel, approximately \$8 billion could be saved on the trade imbalance by the reduction of oil imports by use of the set aside acres.

Background Information

Research on wood burning gas turbines was started by Aerospace Research Corporation in 1978. It culminated in the operation of an Allison T-56 gas turbine power generating system at a facility located in Red Boiling Springs, Tennessee. Over two million dollars in U.S. Department of Energy funds and a matching amount in private funds were spent in carrying out the program. In addition, gas turbine engines were furnished by the Air Force and Naval Air Systems Command. Results of the research and development effort are provided in Reference 1. A schematic diagram of the system is provided in Figure 1 and a view of the R&D facility in Figure 2. The gas turbine, electric generator, and electrical switch gear configuration are the same as that for the thousands of aircraft derivative gas turbine

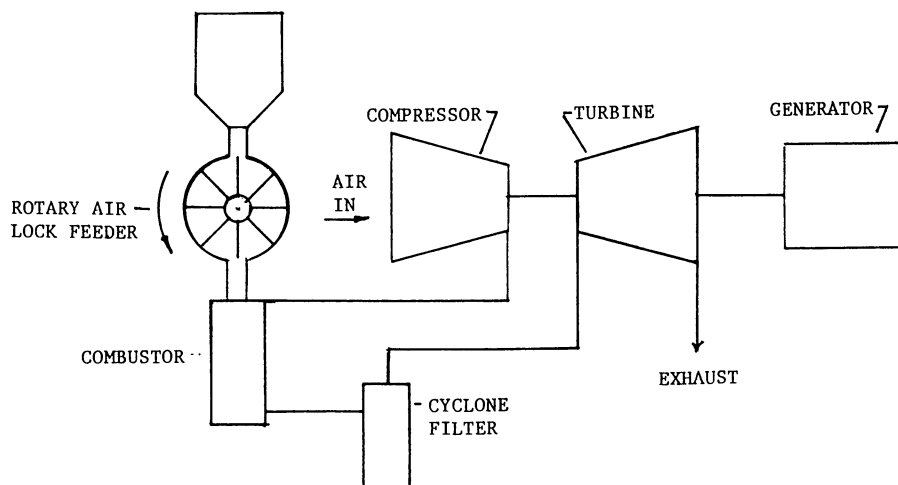


Figure 1. Schematic Diagram of Biomass Fueled Gas Turbine Power Generating System

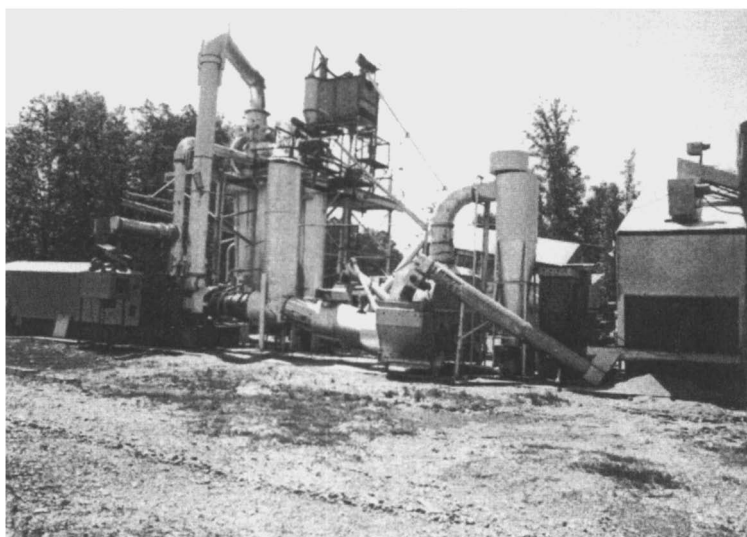


Figure 2. View of Facility at Red Boiling Springs, Tennessee

generator sets now in use throughout the world. The difference is in the fuel system. The normal arrangement for the combustion chambers of commercial gas turbines derived from those used on aircraft is the same as that used on the aircraft, namely a configuration sandwiched in between the compressor and turbine. Because of the slower burning rate for biomass solids, the greater difficulty in feeding the fuel into the combustion chamber, and the need for cleaning the ash from the combustion products, a different arrangement is necessary. To meet that requirement, the space between the compressor and turbine must be adequate to provide room for ducting to take air off the compressor for movement to an offset combustion system and room for return ducting to the turbine. Both the Allison T-56 gas turbine used in the R&D system and the General Electric LM1500 gas turbine meet that requirement. Meeting that requirement allowed rotating components in both gas turbines to remain unchanged, thus providing the same mechanical reliability for the biomass fuels as for liquid fuels without prohibitively expensive modifications.

At the outset of the R&D program reports on work involved with solids fueled gas turbine systems (2-5) were thoroughly reviewed. It was determined from research work with coal performed by the British at Leatherhead, England (2) that single large cyclones operating alone or in series would be best for ash cleaning. The combustion chamber design was based upon information provided by the Australians in Reference 3. An indication of problems that might be encountered with biomass were provided by the report from Combustion Power Company, Inc. of California (4). From experience gained by Yellot et al (5) in coal fired gas turbine research in the United States on solids feeding it was learned that attempts to use lock hoppers to feed solids into a combustor resulted in erratic operation of the gas turbine. As a result, rotary air lock feeders, which were used in all of the systems reported in References 3, 4, and 5, were selected as the feeders in the R&D program.

Operational difficulties which resulted in learning curves peculiar to the system such as wood processing, conveying, drying, combustion ash removal, engine starting, synchronization with the TVA power distribution grid, and development of emergency procedures are covered in Reference 1. Feeding a pulverized solid into a high pressure chamber and dealing with turbine blade fouling presented the greatest challenge. An anticipated problem that was most feared at the outset, eroding of the turbine blades, never materialized. In over 1500 hours of operation, no erosion has been detected. The measures taken to resolve the two problems and the approach taken with the General Electric LM1500 gas turbine in meeting the problems are presented.

Modern aircraft engines which require very high power to weight ratios are designed for high turbine inlet temperatures and high compressor discharge pressures. As turbine blade cooling techniques, advanced materials and more sophisticated design methods have become available the pressure ratios and allowable turbine inlet temperatures have increased to high levels. As a result, the modern aircraft derivative gas turbines are less suitable for operation with biomass than the earlier models. The current need for low turbine inlet temperature and low combustor pressure with biomass makes earlier models more compatible. The LM1500 gas turbine fits well into the biomass picture.

The Rotary Air Lock Feeder

The rotary air lock feeder is also referred to as a rotary valve. A schematic view of a rotary feeder is shown in Figure 1. Referring to Figure 1, the tips and sides of the vanes are fitted with seals that compartmentalize particles fed into a low pressure sector for movement around to a zone of high pressure and thence into the combustor. A major effort was directed toward development of long lasting sealing methods and materials. Sawdust is an extremely abrasive material that requires special techniques that were developed in the program. To meet the 130 psig requirement of the R&D installation two air lock feeders operating in series proved adequate. To provide conservative design margins, it is planned to use two feeders in series for the 90 psig pressure requirements of the Huddleston installation as well as in succeeding installations up to 6000 kw.

Turbine Blade Fouling

The primary problem with coal fired turbines was erosion of the turbine blades. A secondary problem was fouling of the blades. In work performed by the Coal Utilisation Research Laboratory at Leatherhead, England (2) it was determined that single cyclones in series adequately cleaned the ash from the combustion gases to prevent erosion. Therefore, it was decided to use only single cyclones in the wood burning program. As a result, there has been no erosion of the turbine blades in the more than 1500 hours of operation with the gas turbines used in the R&D program. In the R&D program performed by the Australians (3) on brown coal it was found necessary to limit the turbine inlet temperature to 1200°F to avoid deposition of ash on the turbine blades. In the R&D performed at Leatherhead, England with stationary blades there was no significant deposition at 1450°F after 1000 hours of operation with black coal. In tests with pine sawdust in early operation at Roanoke with a small Garrett turbine no significant deposition occurred at 1450°F in 200 hours of operation. In tests with the Allison T-56 at Red Boiling Springs it was found necessary to periodically clean the turbine blades with milled walnut hulls when firing with a mixture of oak and poplar sawdust at 1450°F turbine inlet temperature. Above 1450°F the particles adhered to the blades and could be removed only by scraping. The 1248°F turbine inlet temperature needed to produce 4000 kw with the LM1500 gas turbine in the Huddleston installation is well below any problem zone for disposition with sawdust.

Discussion of LM1500 Gas Turbine Performance And Factors Favoring Its Selection

When the advancement was made from the Garrett 375 kw gas turbine to a larger engine, the Allison T-56-9 gas turbine selection was made on the basis of its perceived easy adaptability to the system and the availability of used engines from the U.S. Air Force. As the R&D program advanced, it became clear that the turbine inlet temperature would have to be restricted to 1450°F to avoid excessive turbine blade fouling. The turbine inlet temperature of the T-56-9 is 1700°F at its normal rated overall electrical output of 2332 kw. With a

1450°F turbine inlet temperature the output drops to 1500 kw, a value too low for economical operation.

A search for a more suitable gas turbine from standpoints of availability, adaptability to wood fueling, and electrical output led to selection of the General Electric J-79 gas generator and companion power turbine. The combined gas generator and power turbine was given the designation LM1500 by General Electric. For aircraft propulsion the hot gases leave the engine at high velocity, propelling the aircraft forward. For use in power production the hot gases are ducted to a power turbine. A favorable feature of a two shaft arrangement, such as this one, is that the gas generator can operate efficiently at part load by adjusting its speed downward while the power turbine operates at the required constant speed for power generation. The compressor efficiency is high over a broad range. This is made possible by adjustment of variable stators in the first six stages of the compressor. By adjustment of the stators to match the compressor speed and air flow, rotating stall is avoided and good compressor efficiency is maintained. Rotating stall is a phenomenon associated with flow separation on the compressor blades as the angle of attack on the blades increases with changes in rotative speed and air flow. Compressor efficiency over the speed range results in economical operation over a wide range of power production. Detailed information on turbine inlet temperature, compressor discharge pressure, and wood feed rate as a function of power output was derived from General Electric specification MID-S-1500-2.

Turbine Inlet Temperature. Figure 3 shows a straight line relationship between turbine inlet temperature and generator output. This characteristic provides a significant amount of latitude in operation with untried species of plants or sources of fuels such as clean waste. For example, it can be safely predicted that in the worst case the turbine inlet temperature of 1200°F required for a 3400 kw output will not result in excessive or difficult to clean accumulations on the turbine blade. Minimum performance guarantees would be warranted in such cases. With most wood species a 7000 kw output probably can be tolerated.

Compressor Discharge Pressure. Figure 4 shows a straight line relationship between compressor discharge pressure and generator output. The primary concern with pressure is the feeding of solid fuel into the combustion chamber. The demonstrated maximum sustained pressure in the R&D system is 130 pounds per square inch. Thus, the ability to sustain feeding of sawdust from 3000 kw to approximately 7500 kw is assured. The pressure required to produce the 4000 kw projected for the production facility now being prepared for installation at Huddleston, Virginia is only 90 psig.

Wood Feed Rate. The wood feed rate in Figure 5 is based upon a heat value of 8,200 Btu/lb. for sawdust. The heat value ranges from 8100 Btu per pound for oak to 8,600 Btu per pound for yellow pine. Green sawdust as delivered from the mill averages approximately 45 percent water content. Trailers 40 ft. long normally deliver on the order of 25 tons of green sawdust per load. For the 4000 kw output projected for the Huddleston facility five trailer loads per day will be required. Shelter for approximately fifty truck loads will be needed to assure continued operation in the winter months.

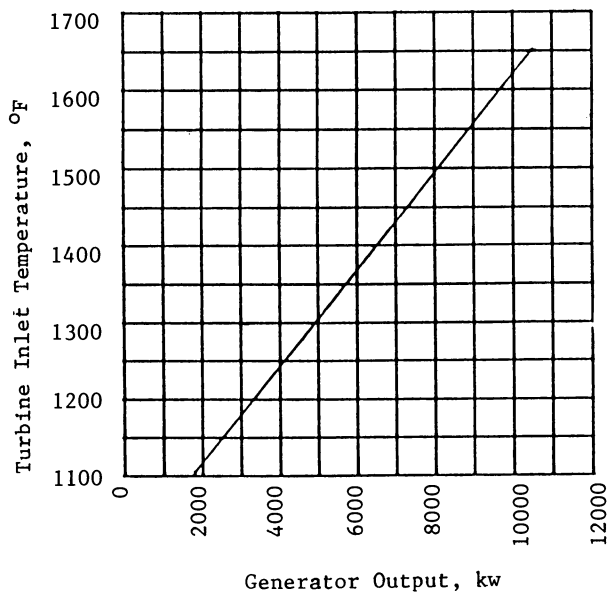


Figure 3. Plot of Turbine Inlet Temperature Versus Generator Output With G.E. LM1500 GAS TURBINE at 1000 ft. Altitude and Compressor Inlet Air at 70°F

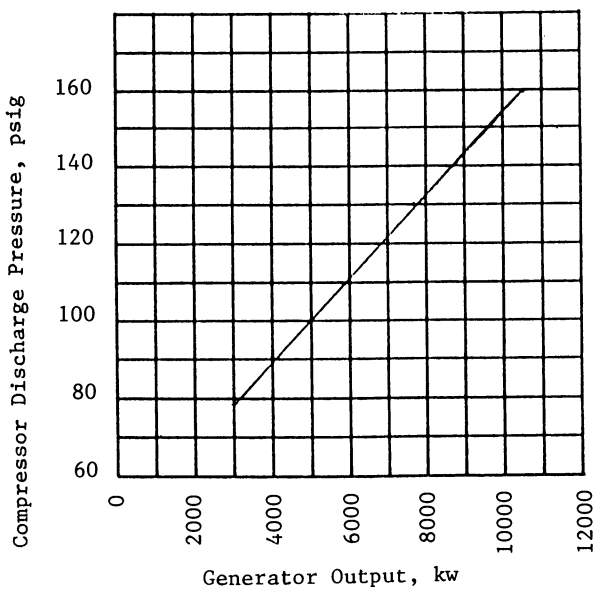


Figure 4. Plot of Compressor Discharge Pressure Versus Generator Output With the G.E. LM1500 GAS TURBINE at 1000 ft. Altitude and Compressor Inlet Air at 70°F

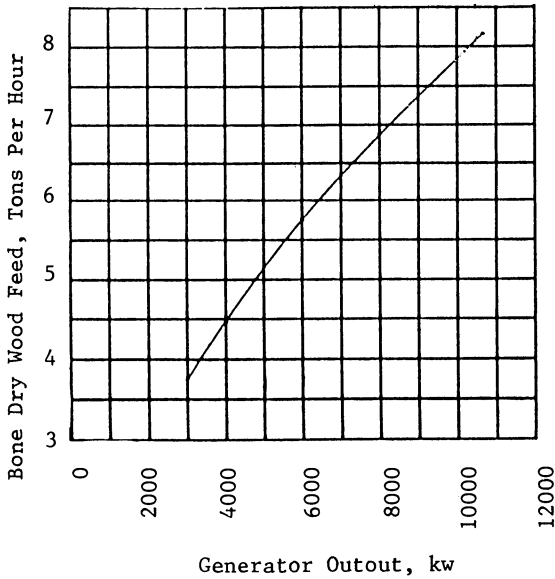


Figure 5. Plot of Wood Feed Versus Generator Output With G.E. LM1500 GAS TURBINE at 1000 ft. Altitude and Compressor Inlet Air at 70°F

Engine Durability

A question frequently arises as to the life of an aircraft derivative gas turbine in stationary power applications. The answer is that the lower power output and lower turbine inlet temperature that are projected for this application make for very favorable longevity for the LM1500 gas turbine. A twelve year life or greater before overhaul is predictable. The gas generator in the stationary application is never exposed to the extreme power requirements and high turbine inlet temperatures that exist during airplane take off. The primary requirement for long engine life in stationary applications is adequate filtration of the air entering the compressor. While longer term operation may prove otherwise, no erosion or corrosion of the turbine has been detected due to ash or dirt escaping the cyclone filter or from chemicals in the combustion products.

Sugar Cane and Sweet Sorghum Fuels

Sweet sorghum which is highly drought resistant can supply two to three times as much fiber energy per acre as trees in some areas in addition to the sugar produced for alcohol and grain for food. The yield from sugar cane, in the areas where it can be grown, is even higher than for sweet sorghum. A further advantage is that there is no stigma attached to its use as a fuel, as there is with trees. This renewable fuel will result in a zero net increase in carbon dioxide. Based on the published research results (6) for sweet sorghum, the 66.4 million acres taken out of production between 1981 and 1988 can supply the energy to generate 34 percent of the nonnuclear power generated in 1986 in the U.S. The annual payment for setting land aside is estimated to be over \$5 billion. Much more additional acreage can be easily devoted to sorghum as an alternative crop. Besides providing fuel for electric power the grain and sugar can produce in excess of 25.4 billion gallons of ethanol which equals fifteen percent of the energy supplied from imported oil. Intensive cultivation of sugar cane and sorghum in states bordering the Gulf of Mexico can result in tripling these outputs. Research results from Reference 6 are shown in Table 1.

Table 1. Maximum Sweet Sorghum Yields at 8 Sites in 1978 & 1979

Location	Maximum Yields, 1978-1979				Wray Cultivar Yields 1979	
	Biomass		Total Sugars		Biomass	Total Sugars
	Metric Tons Per Hectare					
	1978	1979	1978	1979		
Baton Rouge, LA	28.8	31.7	8.5	11.19	16.2	8.8
Belle Glade, FL	40.5(a)	12.0	13.2(a)	5.5	34.8(b)	13.2(b)
Columbus, OH	22.2	18.5	6.5	3.1	17.5	3.1
Fargo, ND(c)	--	12.5	--	2.9	12.5	2.7
Lincoln, NE(c)	--	19.3	--	6.3	16.0	6.3
Manhattan, KS(c)	--	24.7	--	4.0	19.2	3.9
Meridian, MS	22.4	28.8	7.7	8.6	28.8	8.6
Weslaco, TX	30.5	30.0	9.0	6.5	18.0	5.7

(a) This value is the sum of two crops of sweet sorghum produced during the 1978 growing season.

(b) This value is from 1978 results since Wray was not grown in Florida during 1979. Wray was double-cropped in Florida in 1978.

(c) This site was not included in sweet sorghum experiments in 1978.

It is indicated by the results shown for Belle Glade, Florida that in many regions of the earth two crops per year can be grown. The versatility of the biomass fueled gas turbine system in connection with disposal of waste and in cogeneration is currently under-going evaluation.

Cogeneration Applications

The temperature of the exhaust gases from the biomass fueled LMI500 gas turbine ranges from 620°F to 685°F depending upon the turbine inlet temperature that can be tolerated by the biomass material in use. In the case of the General Electric LMI500 gas turbine the exhaust gas flow ranges from 125 to 135 lbs. per second. At 620°F and 125 lbs. per second, and cooling to 125°F the exhaust gases would yield approximately 55 million Btu per hour, the equivalent of approximately 460 gallons of gasoline per hour. The heat thus generated can be used in drying lumber, heating buildings, chemical processing as with ethanol production, or injection of steam into the turbine for increased efficiency and power. Ethanol can be produced directly from fermentation of the sweet juice pressed from sugar cane or sorghum or from conversion of cellulosic feed stock to alcohol through hydrolysis and fermentation as discussed in References 7 and 8. For example, bagasse from either sugar cane or sweet sorghum can be burned directly in the gas turbine or processed for production of ethanol. In the latter case approximately 26 percent of the bagasse winds up as high heat content residue that can be burned in the gas turbine.

Alcohol Production From Sweet Juice. Approximately 15 percent of the exhaust gases will be needed to dry the bagasse for feeding into the combustion process. The remainder is available for drying the bagasse for storage and alcohol production. In some geographical areas it may be necessary to use bagasse to supplement the residue from the hydrolysis process to provide the needed fuel for the gas turbine.

Systems Producing Ethanol From Biomass. Biomass from municipal waste, logging residue or biomass plantations can be converted to ethanol by way of the processes addressed in References 7 and 8. According to Reference 8 lignocellulosic materials can be fractionated into cellulose, hemicellulose, lignin and extractives by a number of different technologies including solvent extraction and various degrees of steam-aqueous treatment. The authors of Reference 8 point out the environmental advantage of steam-aqueous treatments for which the water solvent is widely available at low cost with no environmental impact. Fractionation is followed by enzymatic treatment of the carbohydrates toward production of ethyl alcohol and burning of the noncellulosic components to produce power and heat. There has been no economic assessment of a system involving direct conversion to ethanol with subsequent burning of the residue in gas turbines.

Steam Injection for Increased Power and Efficiency. Steam injection for increased power was reported by Australian investigators (3) as early as 1958. Steam injection was shown to increase power by 64 percent and efficiency by 25 percent for the case that was cited. Similar results for power output were achieved with water injection in tests with the Allison T-56 gas turbine at Red Boiling Springs, Tennessee. It was determined that water from the available sources at Red Boiling Springs would have to be deionized for a long term operation. A major consideration in use of either water or steam injection is the availability of water, as the water or steam that is injected is lost to the atmosphere. For example, to increase the output of the LM1500 gas turbine from 6 to 9 mw will require on the order of 90 gallons of water per minute. Whether to use water or steam will depend upon the cost of fuel. Steam does not require an increase in the amount of fuel as heat from the exhaust gases produces the steam. Direct water injection requires additional fuel.

Summary

The General Electric LM1500 gas turbine has been chosen for use in the wood burning power production system because of its highly compatible performance characteristics, the ease with which it can be mechanically adapted to the system, and its ready availability. Salient points are as follows:

1. The 4000 kw power output projected for the production system being readied for installation at Huddleston, Virginia can be achieved with a 1250°F turbine inlet temperature and compressor discharge pressure at 90 psig. Both are well below the 1450°F turbine inlet temperature and 130 psig compressor discharge pressure found acceptable in the R&D program.
2. Power outputs up to 7500 kw can be achieved with oak sawdust while remaining below the 1450°F turbine inlet temperature and 130 psig compressor discharge pressure found acceptable in the R&D program.
3. There is adequate distance between the compressor and turbine to adapt the engine to the external burner required for wood and other biomass fuels.
4. J-79 gas generators are readily available on the overhaul and used market. New power turbines are available from manufacturers. In addition, a limited number of serviceable complete LM1500 sets are available for immediate use.
5. Because of the high heat content of the exhaust gases, the biomass fueled gas turbine can serve in a wide range of cogeneration systems involving use of cellulosic materials.
6. Both Red Boiling Springs and Huddleston facilities are ideally located for demonstration of combined electrical power and fuel alcohol production from sweet sorghum.

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Chapter 8

Transition Metals as Catalysts for Pyrolysis and Gasification of Biomass

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The addition of Fe or of Cu ions to lignocellulosics such as wood or newsprint specifically catalyzes the pyrolytic formation of levoglucosan (LG) (up to 32% based on cellulose). The yield of charcoal is also increased (*e.g.* to 50% at 330 °C). The ions may be added by ion exchange *via* the hemicelluloses, or by sorption of acetate salts from aqueous solution. The sulfate salts catalyze formation of levoglucosenone (LGO) in addition to LG. These effects probably involve complexing of the transition metal cations with lignin. The copper-doped charcoals obtained at ca. 350 °C have been shown to contain elemental Cu, which can act as catalyst for clean gasification, either in nitrogen (to yield predominantly CO, CO₂ and hydrocarbons) or in an oxidizing gas.

When air is used to gasify the catalyzed charcoals a so-called "jump phenomenon" is often observed in the dependence of apparent gasification rate on gasification temperature. This effect may involve an increase of two orders of magnitude in rate for an increase of 5-10° in temperature when the rates are measured by TG. We have now shown that the "jump phenomenon" is partly, but not entirely due to an increase in sample temperature above reactor temperature during gasification. This increase is probably associated with exothermic oxygen chemisorption on the char and occurs on admission of air and on exposure of new reactive sites during gasification. Procedures have been designed to minimize errors from such effects on measurement of gasification rates by TG.

In the late 1980's the combustion of wood, agricultural crop residues and municipal solid waste to supply residential heat, process heat and steam, and

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electricity comprised about 4% of the total annual U.S. energy requirement (1). Although this contribution by simple combustion of biomass is significant, the potential of more technologically advanced thermochemical processes (*viz.* pyrolysis, liquefaction and gasification) promises an even greater contribution to future energy requirements. Consequently, thermochemical conversion of biomass to energy and useful chemicals continues to be a topic of active research.

The predominant approaches to thermochemical conversion of biomass involve either pyrolysis to oils (with or without hydrogenation) or alternatively direct gasification to combustible gases. These two approaches involve "overlapping" chemistry. The production of pyrolysis oils also generates chars, which are potential substrates for subsequent gasification. Direct gasification of biomass produces gases that may include both primary pyrolysis products and secondary reaction products. For example water, a pyrolysis product, may further react with the char to produce water gas. The major disadvantage of direct gasification is the inevitable co-production of tars, phenolics and acids. Although washing the gases removes these co-products (and produces gases for clean combustion), the composition of the washed gases is complex and they have only limited use for synthesis purposes.

We have adopted the approach that in some circumstances the optimum route to utilization of biomass may be to pyrolyze at moderate temperatures and then separately to gasify the resulting char, *e.g.*, with CO_2 to CO or with H_2O to $\text{CO} + \text{H}_2$. Hence, we envision a two stage process for the conversion of lignocellulosic waste (such as sawdust or newsprint) into useful chemicals and simple gases. In the first stage, pyrolysis at relative low temperatures produces a charcoal, a condensible organic liquid (pyrolysis tar) and a noncondensable low Btu fuel gas. Obviously, the process would benefit by the formation of useful chemicals in the pyrolysis tar in relatively high yields. In the second stage, the charcoal which contains a major portion of the energy content of the feedstock is either pyrolyzed at high temperatures, or gasified to produce simple gases. Since the gasification is free from tar forming reactions the product gases are cleaner and have greater value for synthesis (*e.g.* of methanol). The energy balance and product gas composition would be dependent on the composition of the reactant gas (2,3).

It is well known that pyrolysis of pure cellulose under vacuum produces a pyrolysis tar containing 1,6-anhydroglucose (levoglucosan; LG), in a relatively high yield (up to 66%) (4). The production of LG from vacuum pyrolysis of wood has also been reported (*e.g.* 5,6), but the pyrolysis of wood normally gives very low yields of LG relative to the cellulose content of the wood. However, we have recently reported higher yields of LG from wood pyrolysis after prior removal of the indigenous metal ions bound to the hemicellulose in the wood by washing with very dilute acid (6,7). In fact, numerous publications from this laboratory have described the catalytic influence of both indigenous and added metals and metal ions on pyrolysis and gasification of biomass (6-19). These effects have been studied by the addition of salts to wood (*e.g.* 10) and also by exchanging the indigenous metal ions in wood for other ions (*e.g.* 11). In the

latter case the metal ions are held as counterions to the uronic acid constituents of the cell wall and can be controlled by ion-exchange procedures (7).

We have recently (17) studied the effect of individual metal ions (ion exchanged into wood) on gaseous products from pyrolysis of wood using coupled TG/FTIR. These studies showed that K but not Ca, acts as a catalyst in pyrolysis reactions resulting in formation of CO₂, CO, and formic acid (especially from polysaccharides), acetic acid (from hemicellulose), and methanol (from lignin). This type of study has now been extended to include a wider range of metal ions, and to embrace newsprint as well as wood with the aim of optimizing anhydrosugar yields in pyrolysis tars. Since the major motivation in this work lies in the thermochemical utilization of lignocellulosic waste, we have especially included metal ions which are known to increase char yield and to act as catalysts in char gasification.

The thermochemical conversion of biomass chars to synthesis gas and the catalytic effect of both indigenous and added metals in gasification of such chars have received relatively little attention compared to the similar studies on coal. Also, several studies have been made of the catalytic effects of copper and its salts in accelerating the oxidation of graphite (20-23). By comparison, to the best of our knowledge, there have been no prior reports on copper catalysis of biomass char gasification.

In two separate studies (15,16) of the influence in gasification of indigenous cations of biomass, we have been able to show that the rate of gasification in CO₂ of a range of biomass materials correlates well with the total metal ion content of the biomass, provided that biomass materials with high silica are omitted from the correlation. In such studies the chemical and physical heterogeneity of biomass presents problems in obtaining a uniform representative sample. Furthermore, most biomass materials are poor thermal conductors and hence during the course of thermal conversion of a biomass sample (a complex interaction of heat and mass transfer processes *via* a porous surface) even small particles may exhibit temperature gradients. For these reasons it is appropriate to model biomass gasifications on more uniform and definable carbon sources (*e.g.* CF11 cellulose and carboxymethyl cellulose). Even municipal solid waste, a highly variable material, contains on average *ca.* 50% cellulosic materials (43% paper, 10% yard waste, 10% glass, 7% metals, 15% food and 5% plastic) (24). The use of these model carbon sources also allows particularly exact control of the distribution and concentration of metal species in the substrate. Thus we have utilized carboxymethylcellulose (CMC) for incorporation of ion exchanged cations and cellulose fibers (CF-11) for incorporation of salts by sorption from aqueous solution.

Here we are specifically concerned with air gasification of the chars doped with metal ions that result from pyrolyses designed to optimize production of LG and LGO (*i.e.* Fe and Cu-doped chars). In the case of coal (Spanish lignite char), copper is reported to be the most effective catalyst of the carbon-air reaction of the first transition series of elements (25,26). The same authors report (for air gasification of Cu-doped lignite char) a dramatic jump

from a region of low reactivity and high apparent activation energy to a region of high reactivity and low apparent activation energy for a 5 °C temperature increase (27). In fact, we have also observed this jump phenomenon for copper catalysis (19) and for iron catalysis (28) in the air gasification of cellulosic chars. For this study we utilized the model carbon sources described above. These Cu-doped cellulosic fibers were then pyrolyzed to chars for gasification studies. We were able to report "jump temperatures" (T_j , defined by Moreno-Castilla *et al.* (27) as the lowest temperature of the high reactivity region) for ion-exchanged Cu CMC and sorbed Cu salt CF-11 samples. Part of this chapter reports our continued study of the jump phenomenon.

Experimental

The ion-exchanged wood (milled cottonwood sapwood, *Populus trichocarpa*) and carboxymethylcellulose and salt-sorbed samples were prepared as described earlier (17,18). Newsprint samples were prepared from the Wall Street Journal, macerated with deionized water (or salt solutions for salt-sorbed newsprint) in a Waring blender, filtered and air-dried to a mat ca. 2 mm thick. The mats were cut into cubic pellets (ca. 2 mm³) before pyrolysis. Metal ion contents were measured by inductively coupled argon plasma spectrometry (see Tables I to IV).

Pyrolyses were carried out at 2 Torr under flowing nitrogen as described previously (29) with tars condensed at room temperature and "distillate" condensed at -50 °C. LG contents of tars were determined by GLC of tri-*O*-methylsilyl ethers (29) and the compounds in the second condensate (other than water) were determined by ¹H NMR (30). The yield of (LGO) in the second distillate was determined by relating the integrated signal for the C-1 hydrogen (5.31 ppm, s, 1H) (31) to the internal standard (2-methyl-2-propanol; 1.21 ppm, s, 9H).

The thermogravimetry system used to measure gasification rates has been described (19). The samples were first pyrolyzed at a heat treatment temperature (HTT) for 15 min in nitrogen *in situ* (80 mL min⁻¹), and subsequently gasified (gasification temperature = GT) in air (80 mL min⁻¹, 22% O₂). The TG balance was purged with helium (20 mL min⁻¹). The temperature program and weight loss curve of a typical gasification experiment are shown in Figure 1.

The apparatus for measuring differences in sample and furnace temperatures is described elsewhere (32). Essentially, a thermocouple was placed in the furnace near to the sample (similar to TG temperature measurement) and a second thermocouple embedded in the sample. The temperature program and gas flow control was similar to a typical gasification, and during the course of the experiment the two thermocouple readings were compared.

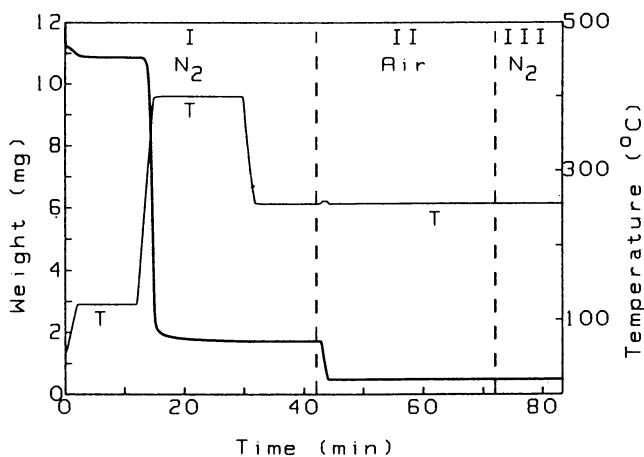


Figure 1. CuCMC-1 Gasification in air; HTT 400°C, GT 255°C. Reproduced with permission from reference 19. Copyright 1990 Butterworth-Heinemann Limited.

RESULTS AND DISCUSSION

Pyrolysis of Ion-exchanged Wood. The yields of char, tar, and distillate from the pyrolysis of ion-exchanged wood are shown in Table I. The alkali metal and calcium wood samples showed increased char formation, low tar and high distillate yield compared to acid-washed wood. All other ion-exchanged wood samples showed char and tar yields similar to acid-washed wood, with the transition metals especially favoring tar formation. The analysis of the tar for LG shown in Table I indicates that the tars from Li, K and Ca wood samples were not only obtained in reduced yield, but also contained a lower proportion of LG than tar from acid-washed wood. All other metal ions produced yields of LG above 10.5% compared with 5.4% from acid-washed wood. In other words, wood samples ion-exchanged with transition metals gave higher yields of a cleaner tar.

Table I. Vacuum pyrolysis of ion-exchanged wood

Sample	Metal ion ^a	Char ^a	Tar ^a	Distillate ^a	LG ^a
Acid-Washed Wood	---- ^b	19	43	16	5.4
Li	----	19	25	44	0.7
Mg	0.08	16	45	29	10.5
K	0.20	22	21	40	0.4
Ca	0.14	20	32	27	4.1
Mn[II]	0.19	15	44	29	10.6
Fe[II]	0.37	15	50	30	15.8
Co[II]	0.20	15	49	29	12.4
Ni[II]	----	14	56	25	13.0
Cu[II]	0.19	17	54	26	13.5
Zn	0.26	16	45	31	11.4
CF-11 cellulose	----	13	67	14	41.5
CuAc ₂ /CF-11 ^c	----	24	51	14	31.0

^a% weight based on dry ash free wood. Pyrolysis at 350°C/30 min.

^bNot determined.

^cCupric acetate sorbed on CF-11 (not ion-exchanged).

The best yield of LG observed was 15.8% from the iron(II)-exchanged wood sample. Assuming that LG is derived only from cellulose and that the latter represents 50% of the wood (33), then the conversion of cellulose to LG was 31.6%. This yield may be compared with 41.5% obtained from pure cellulose (CF-11 cellulose).

The mechanism whereby the yield of LG is increased by the presence of these metal ions is not known. However, since cupric acetate sorbed in pure cellulose does not catalyze the formation of LG, we tentatively conclude that

catalysis of LG formation in wood may involve some interaction with lignin. The low yield of LG from original wood (0.4%) is probably associated with two inhibiting factors, *viz.* indigenous metal ions (especially K and Ca) and lignin. When the metal ions are removed by acid washing, the LG yield increases to 5.4% (*i.e.* 10.8% based on cellulose), but the lignin effect presumably holds the LG yield well below that from cellulose (41.5%). The presence of some metal ions, especially the transition metals, may decrease the interference by lignin in the conversion of cellulose to LG.

Pyrolysis of Wood Sorbed with Salts. Since the improved yields of LG from wood pyrolysis induced by the presence of added metal ions are of considerable interest (in connection with thermochemical utilization of biomass), this study was extended to determine whether it is necessary to remove the indigenous cations in the wood, and whether the "beneficial" metal ion can be added more simply and economically as salts by sorption rather than by ion-exchange. This study concentrated on cuprous and ferrous salts because these ions were most effective in increasing LG and charcoal yields when ion-exchanged, and also because the chars from such pyrolyses are likely to contain elemental Cu or active Fe species which are known to be catalysts of gasification reactions (19).

The products of pyrolysis of wood sorbed with cupric acetate, ferrous acetate and ferrous sulfate are shown in Table II.

Table II. Vacuum pyrolysis of wood sorbed with salt solution

Sample ^a	Metal ion ^a	Char ^a	Tar ^a	Distillate ^a	LG ^a
Original wood		19	25	24	0.4
Acid-Washed (AW)		15	43	16	5.4
AW/CuAc ₂	0.45	29	38	---	11.2
AW/CuAc ₂	0.74	30	40	---	11.2
AW/CuAc ₂	1.10	20	42	---	12.5
CuAc ₂	0.43	15	43	21	5.9
AW/FeAc ₂	3.34	22	24	26	7.5
FeAc ₂	3.18	28	19	28	5.2
AW/FeSO ₄ ^c	1.43	38	18	25	6.1

^a% weight based on dry ash free wood. Pyrolysis at 350°C/30 min.

^bNot determined.

^cPyrolysis at 300°C/60 min.

The addition of cupric ion by sorption of the acetate salt in acid-washed wood (to 0.45% Cu) is effective in increasing LG yield to 11.2%; higher concentrations of copper did not significantly improve the LG yield. When the indigenous ions (predominantly K and Ca) are not removed by acid washing before addition of the cupric acetate, the improvement in LG yield is much less marked. The indigenous cations negate some of the catalytic influence of the

Cu. The results with sorbed ferrous acetate were similar, although the LG yield with the salt sorbed in the acid-washed wood (7.5%) was considerably less than for the corresponding ion-exchanged wood (15.8%).

The pyrolysis of wood sorbed with ferrous sulfate was studied as an example of an anion likely to remain in the pyrolyzing solid and to generate acid conditions (acetate ions are lost from the solid at the pyrolysis temperature). Acid-washed wood containing ferrous sulfate yielded 6.1% LG and an additional 3.0% levoglucosone (1,6-anhydro-3,4-dideoxy- β -D-glycero-hex-3-enopyranos-2-ulose, LGO), which was found in the distillate. LGO is a known product of acid-catalyzed cellulose pyrolysis (34) and its formation was observed only in the presence of the sulfate anion. The yields of LGO from wood, shown in Table II (and not yet optimized) are greater than those commonly reported from pure cellulose or paper. This is particularly opportune in view of current interest in use of LGO as a versatile synthon.

Application to Newsprint. Newsprint comprises about one-third of the solid municipal waste in developed countries, it is likely soon to be excluded from landfill disposal and there is a limit to the proportion which can be recycled into paper. Thermochemical processes have the potential to account for the utilization of large amounts of waste newsprint. Our sample contained 24% lignin as determined by the method of Iiyama and Wallis (35). It was therefore expected, on the basis of the above experiments with wood, to be similarly amenable to the "beneficial" effects of ferrous sulfate in terms of increased LG and LGO yields.

Table III shows the influence of sorbed ferrous sulfate on products of pyrolysis in nitrogen at 400°C for 30 min. In the absence of added ferrous sulfate, pyrolysis of newsprint yielded 3.2% LG, but no LGO. Sorption of ferrous sulfate (to 2.08% FeSO₄) before pyrolysis increased the yield of LG to 16.6%, and also yielded 4.2% LGO. Char yield also increased from 15% for newsprint to 20% for FeSO₄ sorbed newsprint. Thus we have a procedure to generate chemical feedstocks (LG and LGO) from pyrolysis of newsprint, while simultaneously forming in increased yield a char which already contains an efficient gasification catalyst.

Table III. Vacuum pyrolysis products from newsprint (NP)^a

Sample	Char	Tar	Distillate	LG	LGO
Original NP	15	44	32	3.3	ND
NP + 2.08% FeSO ₄	20	43	37	16.6	4.2

^a% weight based on dry ash free wood. Pyrolysis at 400°C/30 min.
ND Not detected.

Gasification of Cu and Fe Ion-exchanged CMC Chars. We have previously reported the effect of HTT and mode of addition of metal ions on the T_j of Cu-doped chars (19). Jump temperatures were determined in a series of gasification experiments where GT was successively lowered 5°C until the low reactivity region was reached. The T_j for Fe-doped CMC char (HTT 400°C , [Fe] 2.47% d.a.f.), determined by the same method, was 295°C . Figures 2 and 3 show rate-time plots for the gasification in air of Cu- and Fe-doped cellulose chars (HTT 400°C) at and below the jump temperature ($T_j = 255^\circ\text{C}$ for Cu and 295°C for Fe). Copper appears to be a superior catalyst over iron; the T_j of Cu is lower and the rate maximum ($R_g(\text{max})$) is higher. In the case of Cu-doped chars, the initial rate of gasification increases *ca.* 160-fold for a 5°C temperature increase at T_j .

In a series of experiments to determine the effect of Cu concentration on T_j we gasified Cu-doped CMC chars in a temperature program (HTT 400°C , GT $200^\circ\text{C} + 5^\circ/\text{min}$). Table IV shows the effect of Cu concentration on the apparent T_j . Increasing Cu concentration in the range shown in Table IV effected a decrease in the apparent T_j but did not change $R_g(\text{max})$. We expected to measure T_j as the temperature at which the rate suddenly increased, and that the T_j of our CuCMC-1 sample would be as previously determined (*i.e.* 255°C). However, the T_j of CuCMC-1 determined by this method was significantly different. We conclude that this jump in reactivity is also affected by the thermal history of the char.

Table IV. The effect of copper concentration on the apparent jump temperature^a

Sample ^b	Cu in char (% d.a.f.)	T_j ($^\circ\text{C}$)	$R_g(\text{max})$ (min^{-1})
CuCMC-1	2.82	312	1.6
CuCMC-2	1.54	320	1.8
CuCMC-3	0.67	340	1.8

^aFor HTT 400°C , GT $200^\circ\text{C} + 5^\circ/\text{min}$.

^bCarboxymethylcellulose, ion exchanged with various loadings of Cu^{2+} .

Effect of Oxygen Chemisorption on Sample Temperature in the Furnace. It seemed likely, based on the observation of small spikes in the TG thermocouple reading on the introduction of air into the furnace (see Figure 1), that the TG apparatus may not be recording the true temperature of the sample during rapid gasification. In fact, when a *ca.* 20 mg CuCMC-1 char (HTT 400°C) was gasified (GT 260°C) with a thermocouple in contact with the char, the temperature of the char ran ahead of the furnace temperature soon after air was admitted (see Figure 4).

We also observed (32) that for calcium-doped chars prepared at relatively low temperatures (*e.g.* HTT 400°C), the initial rate of gasification in

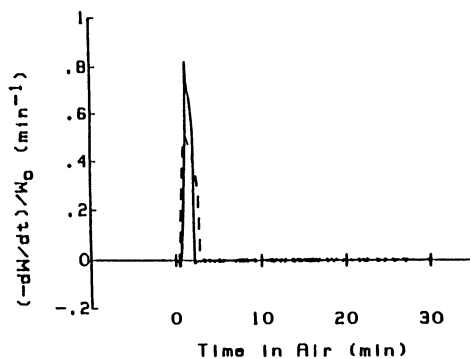


Figure 2. DTG curves for Fe and CuCMC at T_j . — CuCMC-1 GT 255; - - FeCMC GT 300.

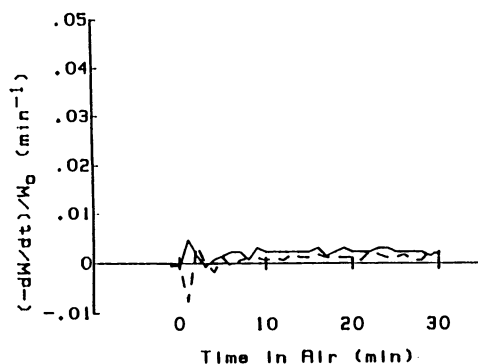


Figure 3. DTG curves for Fe and CuCMC below T_j . — CuCMC-1 GT 250; - - FeCMC GT 250.

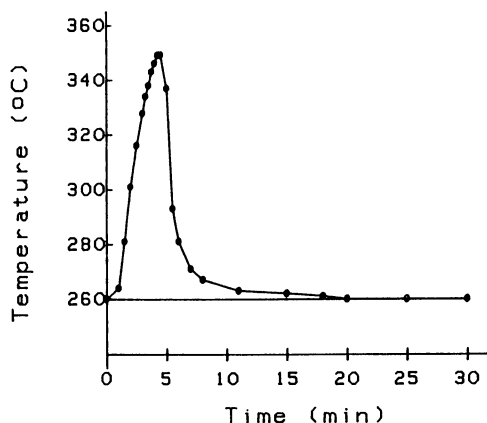


Figure 4. CuCMC-1 gasification in air (HTT, 400°C). —○— sample temperature; — furnace temperature.

air ($R_g(\max)$ from TG) is extremely high for a short time. This effect was due to "run away" temperature increase associated with exothermic oxygen chemisorption. In this case the effect could be avoided by pre-sorption of oxygen below the gasification temperature. However, unlike calcium-doped chars, in the copper-catalyzed gasification the initial high $R_g(\max)$ peak at GT 260 °C could not be eliminated by pre-sorption of oxygen at 200 °C (see Figure 5). We conclude that exothermic oxygen chemisorption contributes to, but does not fully account for the jump phenomenon in copper catalysis of gasification.

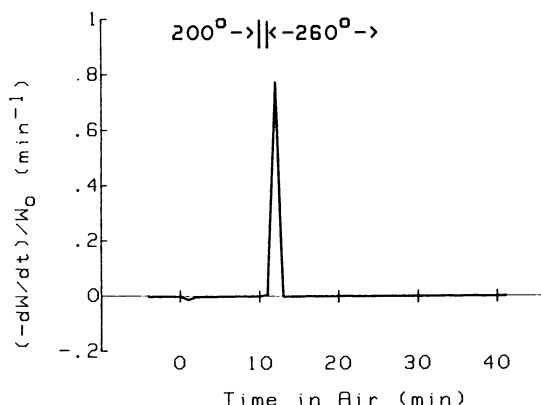


Figure 5. CuCMC-1 Gasification with pre-sorption at 200 °C.

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Chapter 9

Cofiring Tire-Derived Fuel and Coal for Energy Recovery

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This chapter summarizes testing conducted on utility and industrial boilers on the cofiring of tire-derived fuel (TDF) and coal. The disposal of waste tires is a growing problem of national magnitude. Industry is responding to assist government by using waste tires as a fuel supplement with coal. Not all boilers are equally suited to this task. There are risks to the plant that must be evaluated before commercial use of tire-derived fuel can become a regular feed stock to utility and industrial boilers. A summary of test results reported by industry indicate that cofiring of TDF may be a practical solution to the waste tire disposal problem.

National interest concerning removing tires from the waste stream have focused on two fronts: Tires pose a serious health threat if left in open piles; two, burial of tires is a waste of valuable landfill space. It has been estimated that there is a waste tire generated for each person in the nation, each year. It has been estimated that there are over two-billion waste tires stockpiled nationally (1). As vehicle owners replace their old tires, only about twenty five percent are recycled (2). This leaves about seventy five percent of the used tires as new waste. Industry is becoming more aware of the need to assist with this disposal problem. Industrial and utility boilers may be used as a means of disposing of large quantities of tire waste. This is not as simple as it may sound. Not all boilers are suited to firing tires. This paper describes the different types of boilers that have been used for cofiring tires with coal and summarizes data reported from these tests.

Commercial Aspects

The use of tire-derived fuel (TDF) on a wide scale is hampered by the lack of commercial shredding facilities capable of producing the material at a competitive

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price. This is typical of the waste recycling industry in general. The chicken-and-egg problem has been a deterrent to a variety of recycling efforts. To break this cycle in Illinois, the Department of Energy and Natural Resources (ENR) has sought to assist industry by supporting their test programs with the partial payment for costs associated with the tests (3). Both Monsanto and Illinois Power (IP) were requested by the State of Illinois Department of Energy and Natural Resources (ENR) to assist with the disposal of tires in the state. To facilitate this effort, a test program was initiated to determine the viability of cofiring chopped tires, TDF, with coal on a large cyclone fired boiler at IP (4,5) and a stoker boiler at Monsanto (6). This program has demonstrated that IP has the capability of disposing of up to six million tires a year mixed at two percent by weight with the coal at its Baldwin Station, and that Monsanto can dispose of about one and one-half million tires, at a 20 percent by weight blend rate, at its Krummrich Plant in Sauget, Illinois.

The used tire industry has been hesitant to invest in quality tire shredding equipment on a wide scale, until a fuel market is well established. Mr. Trygve Bakkum, of Waste Management of North America, reported that the cost for a single tire shredding machine with a throughput of about 10 tons per hour is a half-million dollars (7). This industry is still developing, and striving to improve the durability of the hardware available. He estimated that tipping fees of 70 to 80 dollars per ton are needed for TDF to be widely available. Fuel cost may limit income on sales to 15 to 25 dollars per ton. Since current disposal costs are about 50 to 60 dollars per ton nationally, there is little margin for commercialization, until other methods of disposal become unavailable or until alternate disposal costs increase sufficiently to cover the cost of making TDF.

The state of Wisconsin has recognized this problem, and provides an incentive or subsidy of \$20/ton to facilities that burn or use waste tires (8). A variety of other states are examining similar programs.

Information Sources

Companies interested in learning more about tire burning can find assistance in their quest for information. As state pollution control agencies struggle with identifying means of coping with the tire disposal problems, they are collecting considerable information. Other sources of information include:

- Scrap Tire Management Council
1400 K Street, N.W., Washington DC, 20005, (202) 408-7781
- Electric Power Research Institute
Generation & Storage Division, Manager of Technical Assessment
P.O. Box 10412, Palo Alto, California, 94303, (415) 855-2445

Both of these organizations have sponsored conferences dealing with the issues of waste tire disposal. They maintain information programs for technology transfer.

Boiler Types

There are a variety of boiler types that are used for generating steam. These are the pulverized coal, the cyclone, the stoker, and the fluidized bed boilers (9). Tires

have been burned in cement kilns as well. Table I lists some of the facilities known to have tested combustion of TDF with coal (2).

The most predominant type of coal-fired boiler is the pulverized coal boiler. This type of boiler requires that fuel be ground to a very fine powder, typically seventy percent less than 200 mesh. The cost to pulverize tires to this size would be prohibitive as a fuel. For this reason, they are generally not considered as a candidate for use. There are two types of pulverized coal fired boilers "dry" bottom and "wet" bottom. Dry bottom boilers are generally not suited to cofiring waste tires with coal. This is because of the steeply sloped bottom used to discharge bottom ash from the boiler, does not lend itself to supporting large particles of burning materials. Also, there is no grate or other device to hold tires in the furnace while the tire chips burn.

There is a select number of pulverized boilers that have a "wet" bottom. A wet bottom means that the fire in the boiler is sufficiently hot to melt the coal ash, which runs as a liquid slag, and collects at the somewhat flat bottom of the boiler. The molten slag is drained out the bottom of the boiler into a tank of water, where the slag is quenched. Ohio Edison has tested burning whole tires in their Toronto Station, which is a 42 MW boiler of this type (10). In order to feed whole tires into the boiler, Ohio Edison developed a lockhopper system to admit the tires to the boiler. Tires are allowed to roll into the boiler about every 10 seconds, through the lockhopper. They have successfully fed up to 20 percent of the fuel to the boiler as tires.

Stoker boilers are typically found in industrial facilities and small urban utility settings. These boilers are fed chunk coal of about an inch in size. The fuel is fed onto a grate, a set of steel bars that support the fuel while it burns. Air for combustion flows up through the grate, providing cooling to the bars. There are a variety of designs used for supporting and feeding the fuel. An example of a stoker boiler is shown in Figure 1 (9). These boilers are well suited to feeding chunky material such as tire-derived fuel (TDF), because the material is about the same size as the coal fuel. About a dozen industrial locations across the country have used or tested TDF cofiring with coal (2). These include the Monsanto Krummrich Plant (6) in Sauget, Illinois and the New York State Electric & Gas (NYSEG) Jennison Station in Bainbridge, New York (11).

Another style of boiler is the cyclone fired boiler. Illinois Power conducted tests on Units 1 and 2 at their Baldwin Station which are 560 MW, B&W cyclone-fired boilers (4,5). Other utilities that have burned TDF in cyclone boilers include Wisconsin Power & Light at their Rock River Station in Beloit, Wisconsin, (12) Otter Tail Power at their Big Stone Plant in Big Stone City, South Dakota, (13) and Northern Indiana Public Service at their Michigan City Station. The Baldwin boiler has 14 cyclones, seven each on the front and rear walls. Operation of a cyclone boiler is different from either a pulverized coal boiler or a stoker boiler. A cyclone boiler burns coal that is crushed to a size of less than $\frac{1}{4}$ of an inch. The coal is fed to the cyclone burners, Figure 2 (9). Air enters the cyclones tangentially creating a cyclonic action. The coal burns at high temperatures, typically 3000°F. The hot gas exits the cyclone into a large furnace. At these temperatures, the ash melts into a liquid slag that flows to the bottom of the furnace, where it is quenched in a pool

Table I. Facilities That Have Tested Cofiring of Waste Tires

COMPANY NAME	City	State
Stoker Boilers		
Champion International	Bucksport	Maine
Champion International	Sartell	Minnesota
Crown Zellerbach	Port Angeles	Washington
Fort Howard Paper	Green Bay	Wisconsin
Great Southern Paper	Ceder Springs	Georgia
Inland - Rome Paper	Rome	Georgia
NYSEG	Binghamton	New York
Port Townsend Paper	Port Townsend	Washington
Rome Kraft Pulp & Paper	Rome	Georgia
Smurfit Newsprint	Newburg	Oregon
Sonoco Products	Hartsville	So. Carolina
Traverse City Light & Power	Traverse City	Michigan
United Power Associates	Elk River	Minnesota
Willamette Industries	Albany	Oregon
Pulverized Boilers		
Ohio Edison	Toronto	Ohio
Cyclone Boilers		
Illinois Power	Baldwin	Illinois
Northern Indiana Pub. Serv.	Michigan City	Indiana
Otter Tail Power Co.	Big Stone	So. Dakota
Wisconsin Power & Light	Beloit	Wisconsin
Fluidized Bed Boilers		
ADM	Decatur	Illinois
Manitowoc Public Utilities	Manitowoc	Wisconsin

(Adapted from ref. 2: Malcom Pirnie, Inc. and other communications.)

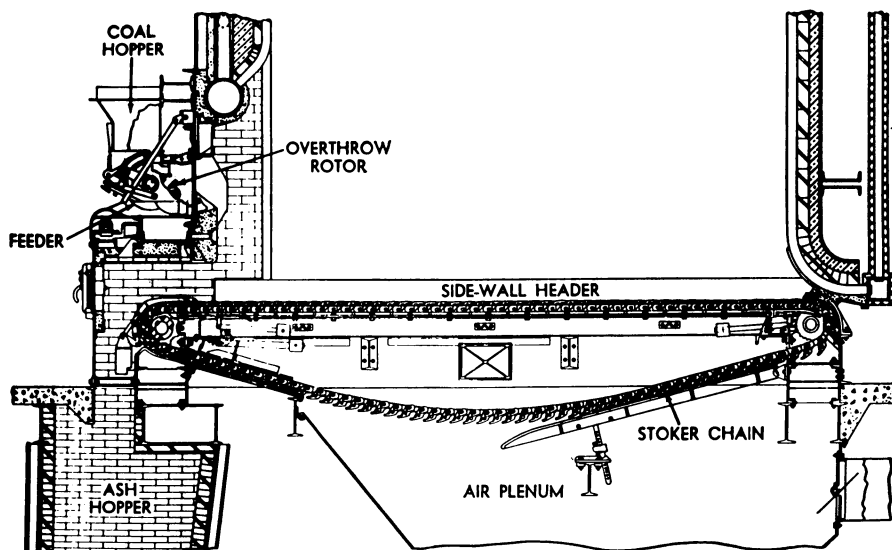
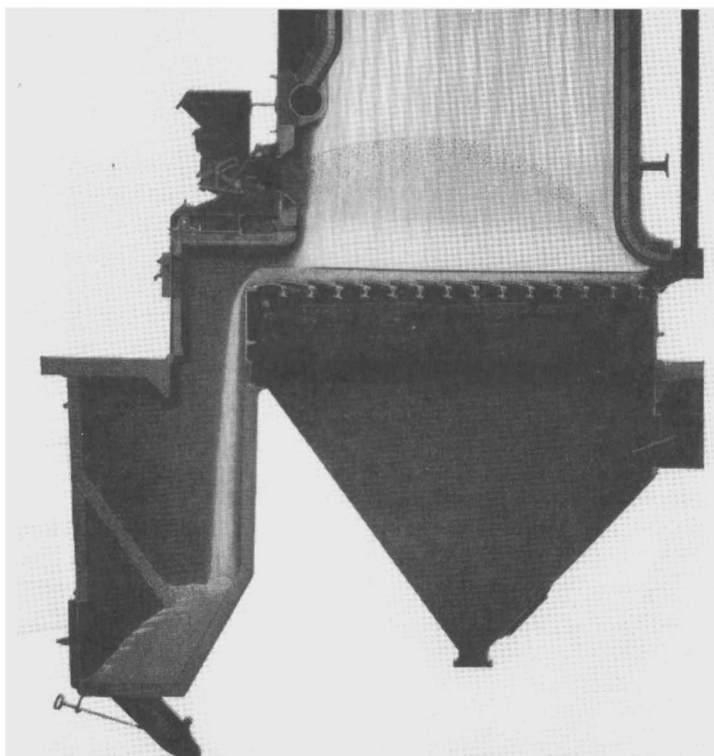


Figure 1. Typical coal feed and ash removal for a reciprocating grate (above) and a traveling grate (lower) stoker boiler. Reproduced with permission from Ref. 9, pp. 16-11 & 12, copyright 1963, B&W.

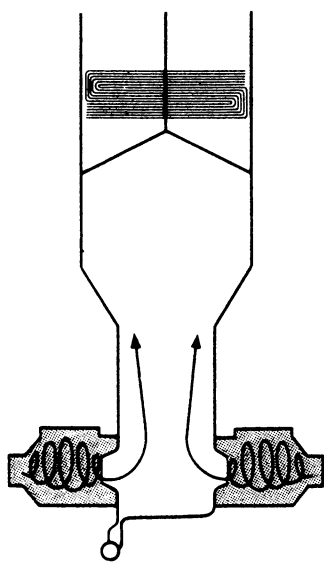
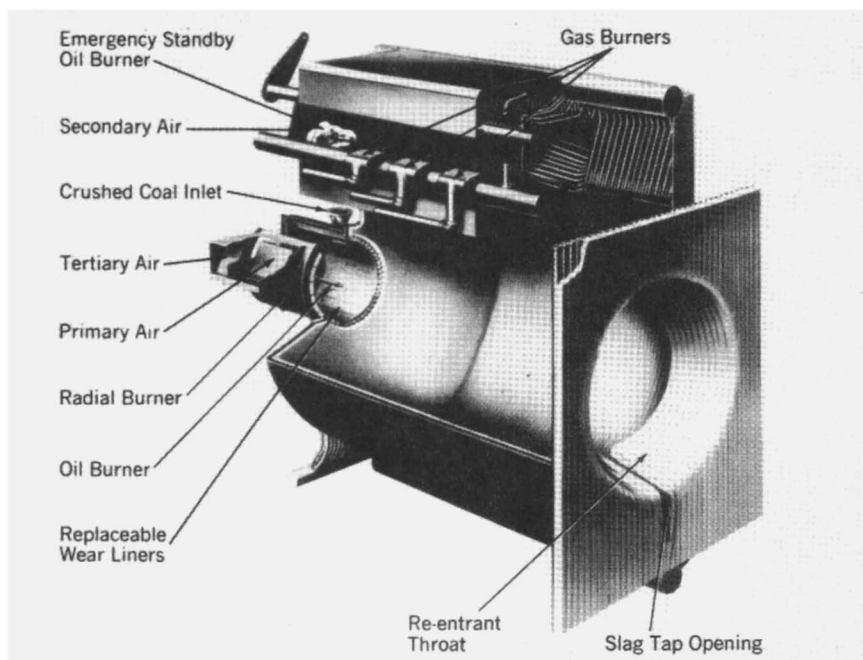


Figure 2. Arrangement of opposed firing cyclones (lower) and design of a cyclone burner (above). Reproduced with permission from Ref. 9, pp. 10-1 & 2, copyright 1972, B&W.

of water. Quenching shatters the slag and the resulting glass-like beads are a saleable product. The slag is sluiced to a pond, where it is collected by the reclaim company.

Fluidized bed boilers are becoming more commonplace over the past five years. These require fuel delivered at a size somewhat like a cyclone boiler. Several fluidized bed boilers have tested combustion of TDF with coal (14). There is limited data available from these facilities, and this paper does not explore the details of their use.

Cement kilns burn coal as a source of heat and ash in the making of cement from limestone. Several cement kilns have tested the use of TDF (2) as a supplement or replacement of the coal as a fuel source. One advantage of tires is that the iron in the tires is a needed ingredient in the cement mix. This paper does not explore the details of the cement industry use.

Technical Concerns

The concerns of a boiler operator about to test any new fuel are increased when the fuel is a waste product, with properties that are not well known. In the case of TDF these include:

- Can tire material be burned in the boiler?
- Can TDF be delivered to the boiler reliably?
- Does TDF combustion pose hazards to the equipment?
- Will TDF affect the environmental operation of the plant?

TDF Combustion. The size of the coal fed to any boiler must be uniform and of the proper size for the style of boiler to ensure good combustion. If TDF is fed in larger pieces, there is concern that complete combustion may not occur. The sulfur content of TDF is lower than high-sulfur coal, but not low enough to meet the 1.2 lbs/MBtu compliance level required by the Clean Air Act. Other differences between TDF and coal are that the tires are high in zinc, and it is not clear whether the zinc will be collected in with the fly ash or will remain volatile. If collected, will the zinc leach out of the ash? A particular concern in a cyclone, is whether unburned material may be carried over into the dust collection equipment. Another concern is whether the TDF non-combustibles, primarily steel belting, will melt in the slag. If TDF adversely effects slag flow or consistency it can interfere with the boiler operation or byproduct sales of the slag (15).

In testing conducted by Illinois Power (IP), there was no evidence of increased carbon carryover due to TDF combustion. IP tested at TDF levels of 2 percent (5). Wisconsin Power and Light (WP&L) has conducted tests with TDF levels up to 10 percent (12). The steel belting did not appear to create any problems. However, a small amount of unburned TDF was evident in the slag from both utilities' tests. This is a concern to IP because all of the slag is sold for grit blasting and other uses. IP plans additional testing to evaluate this aspect of the operation more thoroughly (5). The TDF tested had much of the metal removed at the vendor by means of a magnetic separator. This removed most of the bead wire. There was no evidence of problems associated with the remaining tread wire.

When burning TDF in a stoker, little difficulty has been reported due to changes in the boiler operation. NYSEG noted the appearance of droplets of metal adhering to the grate (11). These have the appearance of weld splatter. However, this has not been a deterrent to the operation of the unit, as the material came off with little effort. NYSEG conducted tests with TDF feed rates as high as 50 percent. Monsanto did not report any problems with their operation (6).

Ohio Edison has not encountered any serious problems with their operation, using whole tires (10). They have voiced some concern about the buildup of iron in the slag from the bead metal in the tires. They plan to monitor this aspect of the process closely.

Material Handling. It is important that the delivery of TDF to the boiler not interfere with the delivery of coal. The coal handling system at each boiler plant is different and unique. This requires that individual review be conducted to evaluate the best means for delivering TDF for a specific plant. However there are many common aspects to coal handling systems. Figure 3 is a diagram of a typical coal feed system for a cyclone boiler (9). By and large, most facilities will prefer that the TDF be mixed with the coal near the front end of the coal handling process. Many have installed temporary conveyors to place the TDF onto the main belt feeding the station. If the TDF has poorly sized or prepared material it can greatly interfere with the coal handling equipment. Common problems include long thin ribbons of TDF becoming tangled in equipment; exposed pieces of wire locking together to form large balls that jam equipment; and loose cording collecting together to form "fur balls" that interfere with coal flow (12).

IP determined that for test purposes, no plant modifications should be made. Thus, the TDF was mixed with the coal prior to the coal crushers. This means that the TDF must be capable of passing through the hammer mills, without either gumming them up or interfering with the crushing of coal or its sizing.

To facilitate coal feeding a one-yard front end loader was rented. It was used to feed coal into a hopper in the reclaim yard. TDF was fed at approximately twenty tons per hour while total material flow was fed at about 1000 tons per hour, yielding the desired mixture of two percent TDF and coal.

During testing it was determined that 2-inch TDF material could not be handled either by the crushers or the coal conveying system. This material caused over-load of the crusher motor and also plugged the coal feed chutes in the tripper (the conveyor that discharges coal to the individual storage silos above the boiler). One-inch TDF material was handled with little difficulty in the plant, although it did increase the motor amps in the crushers. If long term operation were conducted, IP would install a method to feed TDF that could bypass the crushers. Other users of TDF have been able to feed two-inch material, but most agree that it is preferable to receive one-inch TDF.

Environmental Aspects. A major area of concern is the environmental impact of TDF cofiring. Testing was conducted to determine if stack emissions were adversely effected by the TDF. These tests are also required for permit applications. For the tests conducted at IP, Table II presents the analyses of the raw fuels and the

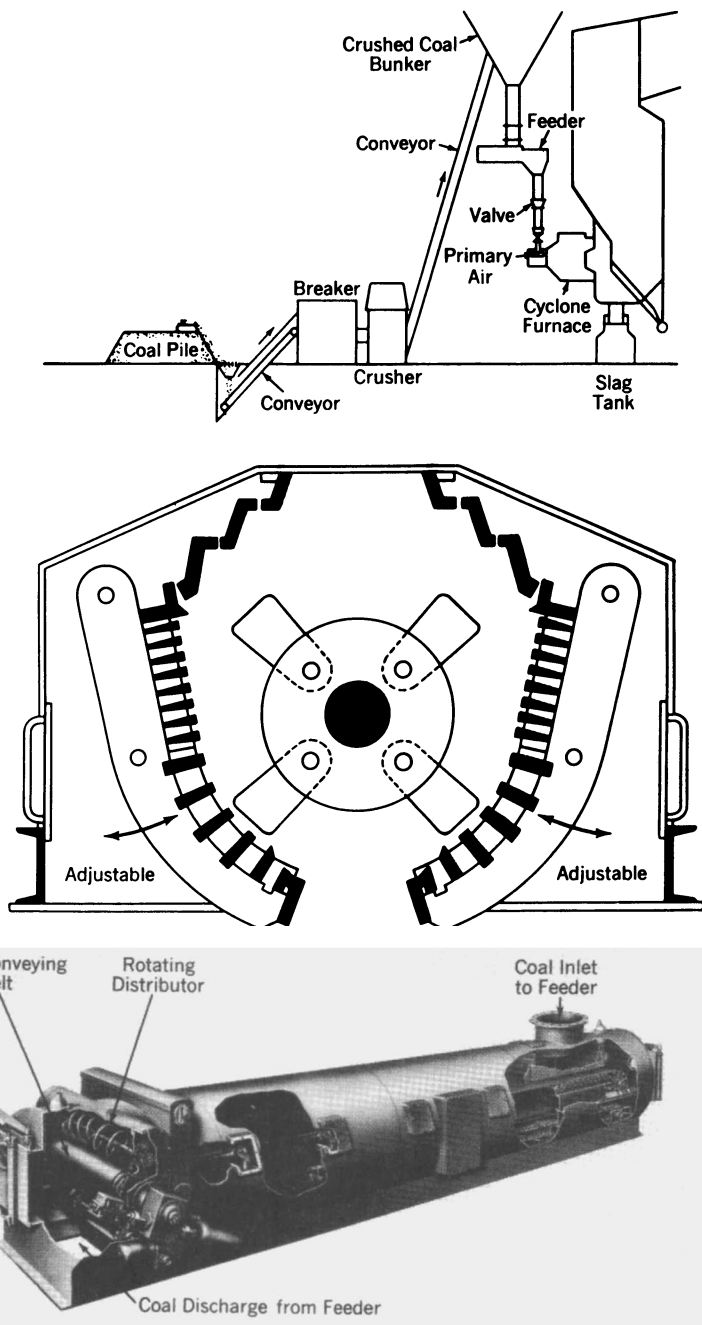


Figure 3. A typical coal feeding system (top), a hammer-mill coal crusher (center), and belt-type coal weighing feeder (bottom). Reproduced with permission from Ref 9, pp. 15-9; copyright 1963, pp. 10-2 & 4, copyright 1972, B&W.

Table II. Fuel Analysis of TDF and Coal

Fuel Analysis	Coal	TDF-A	TDF-B	TDF-C	Calc.2%
Moisture, %	12.8	1.14	0.51	.66	12.6
Ash, %	10.4	5.62	6.38	16.8	10.3
Volatile, %	34.4	68.4	62.6	68.3	35.0
Fixed Carbon, %	42.4	24.8	30.5	14.2	42.1
Btu/lb	11000	15969	15837	14129	11098
Carbon, %	61.1	80.9	80.1	69.9	61.5
Hydrogen, %	4.11	7.30	6.99	6.75	4.17
Sulfur, %	2.84	1.51	1.34	1.39	2.81
Ash Analysis, wt.%					
Silicon dioxide	60.3	23.6	18.3	4.13	59.5
Aluminum oxide	21.74	8.18	7.52	1.12	21.5
Titanium dioxide	0.70	5.60	9.20	0.28	0.86
Iron oxide	2.83	10.6	35.5	80.1	3.40
Calcium oxide	4.49	4.00	3.22	1.80	4.47
Magnesium oxide	1.47	1.28	0.70	0.38	1.46
Potassium oxide	1.02	0.92	0.52	0.20	1.01
Sodium oxide	1.25	0.92	0.70	0.16	1.24
Undetermined	2.14	2.00	1.24	0.21	2.12
Zinc oxide		33.6	17.8	8.96	0.41
Zn (ppm)	188				
Trace Metals					
As	<8	14	8	26	<8
Ba	3400	170	90	45	3334
Cd	7	28	18	<4	7
Cr	28	97	120	150	30
Pb	<20	140	180	40	<20
Hg	<0.02	0.02	0.03	0.02	<0.02
Se	<8	<8	<8	<8	<8
Ag	<4	<4	<4	<4	<4

(Adapted from ref. 5.)

Table III. Range of Data, ESP Emission Test - TDF & Coal

	LOW	HIGH
COAL ONLY		
Inlet Dust Conc. lbs/hr	16,800	17,700
Outlet Dust Conc. lbs/hr	670	710
Outlet Dust Loading, lbs/MBtu	0.13	0.14
ESP Efficiency, %	95.6	96.2
COAL & TDF		
Inlet Dust Conc. lbs/hr	16,400	19,400
Outlet Dust Conc. lbs/hr	840	1,030
Outlet Dust Loading, lbs/MBtu	0.163	0.197
ESP Efficiency, %	93.8	95.7

(Adapted from ref. 5.)

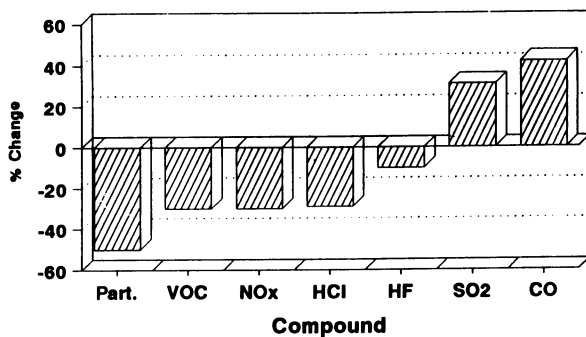


Figure 4. A comparison of stack emissions between the baseline conditions of coal only and when burning a 20% blend of TDF. Reproduced from Ref. 6.

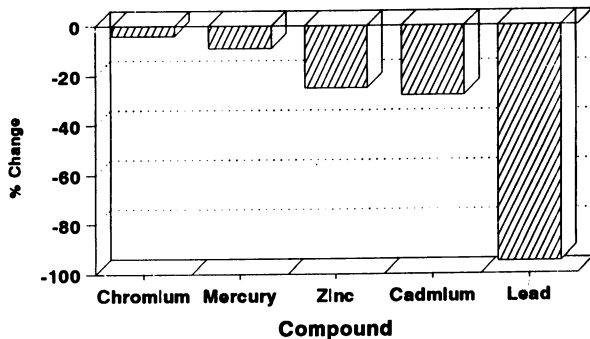


Figure 5. A comparison of metals stack emissions between the baseline conditions and when burning a 20% blend of TDF. Reproduced from Ref. 6.

calculated values for the mixed fuels. TDF analyses A and B are from two different suppliers of one-inch debedded material. TDF C is an analysis of two-inch TDF that includes the bead material. Note that the removal of the bead material increases the heating value of the fuel corresponding to the reduction in the ash material. As stated above, testing was discontinued with TDF C because of handling problems. No discernable difference in opacity was noted as a result of TDF cofiring. Normal opacity readings of 15 to 20 percent were recorded. Control board readings were collected to perform boiler efficiency calculations. Heat rates of about 9600 Btu/KWh were maintained during the performance period. Particulate emission tests were conducted on March 20 (baseline) and on March 21, 1991, by a consultant. The range of data from these tests is listed in Table III. The differences between the results for the two days are within the accuracy of the instrumentation and the variation in the coal quality for the period of operation. Examination of ESP power settings showed little variation as a result of TDF cofiring compared to normal operation with coal (5).

Testing conducted by Monsanto on their stoker boiler revealed that cofiring TDF with coal resulted in substantial reductions of emissions (6). This is shown in Figures 4 and 5. Similar results have been reported by WP&L and Ohio Edison (12,10). NYSEG experienced some reduction in particulates with TDF at both 25 and 50 percent blends with coal (11).

Unburned Material. One aspect of the test program was identified as a cause for further investigation by IP. Several dozen pieces of substantially unburned TDF were found in the boiler slag. Due to the nature of slag discharge, it is very difficult to determine a quantitative amount of this material. Since IP sells all of the slag from Baldwin Units 1 and 2 to a local company, the presence of the TDF remains an area of concern. Additional testing will be required to evaluate the possible cause. The results of these future tests will determine the requirements for plant modifications, if any needed to begin commercial TDF cofiring (5).

WP&L has had similar experiences and has screened their slag before selling it as aggregate.

Conclusions

With the assistance of state agencies, utilities and industrial boiler operators will continue to test cofiring TDF with coal. As plant operators learn to cope with this new fuel, the chicken-and-egg supply problem will end. As financing for facilities becomes more readily available, more operations that can produce TDF at competitive fuel prices will be realized. This will allow our country's industry to help solve a national waste disposal problem.

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Chapter 10

Converting Waste Polymers to Energy Products

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A project was performed to determine the feasibility of converting waste polymers into diesel fuel. The primary waste polymer source of interest was disposable diapers, consisting of a mixture of cellulosic and synthetic polymer material in the presence of biological wastes. The overall project consisted of five phases: (1) reaction equilibrium calculations, (2) batch pyrolysis study, (3) continuous pyrolysis study, (4) continuous liquefaction study, and (5) integrated system demonstration. The integrated system consists of a circulating solid fluidized bed pyrolysis system to produce a synthesis gas for a fluidized bed catalytic liquefaction reactor. The objective for the pyrolysis system is to optimize the composition of hydrogen, carbon monoxide and ethylene in the synthesis gas for conversion to diesel fuel in the catalytic liquefaction reactor. The liquefaction reactor produces a product very similar to commercial No. 2 diesel fuel. In this chapter, results for the first two phases will be presented.

Approximately 18% by volume of municipal solid waste consists of waste plastics (1). The 15.8 billion disposable diapers used annually comprise about 2% of the total waste stream. Due to increasing landfill costs and environmental and regulatory pressure, a flurry of activity has emerged to seek alternatives to landfill disposal of these materials. Proctor & Gamble, for example, has announced an "accelerated composting" program for their disposable diaper products (2). Separation steps are implemented to segregate the non-compostable parts from the cellulosic parts. The intent is to convert the cellulosic parts into "soil enhancer" (compost). Presumably, the plastics part still goes to the landfill. The questions would be the market for the "soil enhancer" and the probable necessity to still landfill the plastics. An alternative approach would be to convert the bulk diaper (all components) into marketable products with minimal landfill requirements. This approach has been

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developed at Arizona State University (ASU) utilizing over 100 different feedstocks, generally falling into the categories of industrial wastes, municipal wastes, hazardous wastes and various agricultural and forest residues. An indirect liquefaction approach is used, i.e., gasification of the feed material to a gas followed by liquefaction of the gas to a No. 2 diesel grade transportation fuel. The sequence is illustrated in Figure 1. The objective in the gasification step is to maximize the production of hydrogen, carbon monoxide and ethylene while the objective in the second step is to maximize the production of diesel fuel from these three reactants. A high octane product can be produced via conventional catalytic reforming of the diesel material. The potential products are thus liquid hydrocarbon fuels, medium quality gas (ca. 500 BTU/SCF) and/or electricity (via heat recovery or combustion of the fuels). Alternative operating conditions and catalysts for the second stage reactor could produce other products (e.g., alcohols, methane etc.).

Prior work on this process has been described elsewhere (see, for example, references 3-6). This paper will present the application for disposable diapers. A five phase approach was used (reaction equilibrium calculations, batch pyrolysis study, continuous pyrolysis study, continuous liquefaction study, integrated system demonstration) with performance limited to an 11 month period. Results for the first two phases will be presented here. The intent was to minimize the project risks and costs for scale-up to a commercial configuration. Using the composition of a particular disposable diaper product ("Huggies") as an example, the maximum yields of diesel fuel (wet and dry basis) are illustrated in Figure 2. Realistic actual liquid product yields are expected to be in the 50-100 gals/ton range (dry basis).

Equilibrium Calculations

Composition analysis for three commercial disposable diaper products is shown in Table I. Since the compositions are similar, Huggies will be used for example calculations. Assuming a gas product slate of hydrogen, carbon monoxide, ethylene, ethane, acetylene, methane and carbon dioxide, the equilibrium product composition was calculated as a function of temperature by minimizing the Gibb's free energy of formation subject to atom balance constraints. The samples under study are composed of carbon, hydrogen and oxygen as major components. The atomic ratio of Huggies for both wet and dry cases is shown in Table II. The computer code utilized to calculate the equilibrium composition used the Gibb's free energy of formation for each expected product to calculate a set of primary reactions with the associated equilibrium constants and the equilibrium mole fraction of each compound in the system. The program used the technique of Myers (7) to estimate an initial composition. A modified Newton-Raphson technique was used in solving the problem. All calculations were performed using an IBM personal computer Model XT with 8087 math co-processor. The thermodynamic data of the expected products is given in Table III (8,9).

The calculated synthesis gas compositions at equilibrium as a function of temperature for both wet and dry samples are shown in Figures 3-6. As shown, all components decrease with temperature except hydrogen and carbon monoxide. Although the dry samples gave a higher hydrogen/ carbon monoxide mole ratio, the wet sample results are of more interest since the real processing feedstock is in a wet condition. The desired hydrogen/carbon monoxide ratio of ca. 1.2 (based on prior work) is achieved at ca. 1100 K

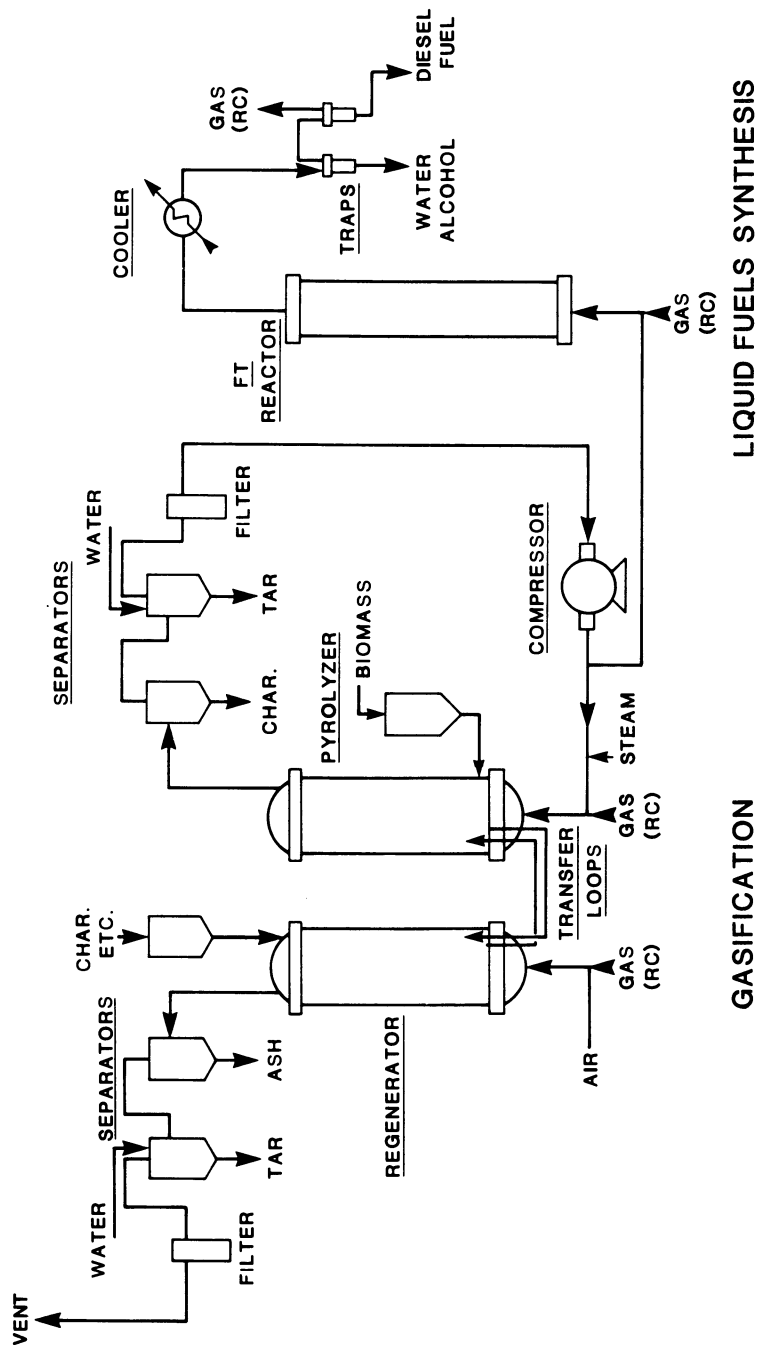
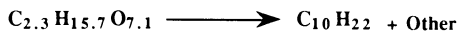
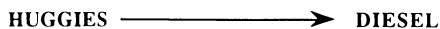


Figure 1. Conversion System Schematic.



Composition (wt %)			
	Huggies (wet)	Huggies (dry)	Diesel
C	17.54	53.4	84.51
H	9.9	7.6	15.49
O	71.92	37.19	0
N	0.0	0.0	0
Na	0.5	1.70	0

$\frac{\text{maximum yield}}{\text{(carbon balance)}} = 67 \frac{\text{gals diesel}}{\text{ton Huggies (wet)}}$

$189 \frac{\text{gals diesel}}{\text{ton Huggies (dry)}}$

Figure 2. Diaper Chemistry and Maximum Product Yields.

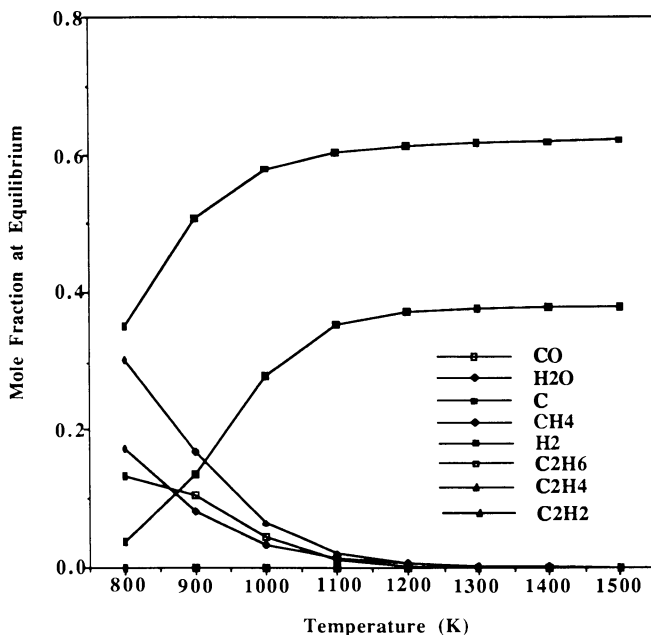


Figure 3. Equilibrium Gas Compositions of Huggies (dry) as a Function of Temperature.

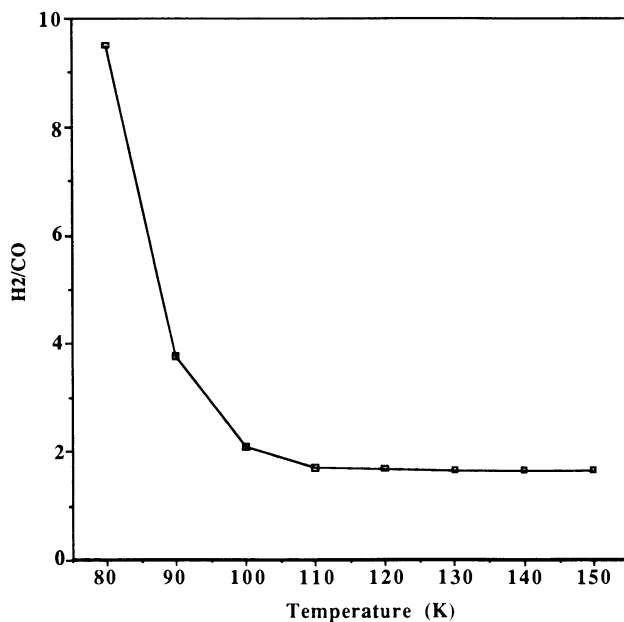


Figure 4. Equilibrium Hydrogen to Carbon Monoxide Mole Ratio of Huggies (dry) as a Function of Temperature.

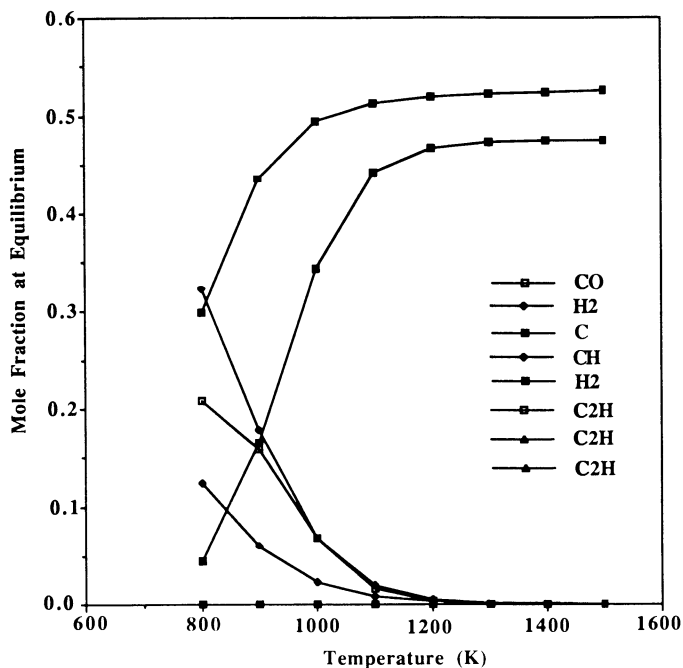


Figure 5. Equilibrium Gas Compositions of Huggies (wet) as a Function of Temperature.

Table I. Elemental Analysis of the Waste Polymer Samples

<i>Compound</i>	<i>Element</i>	<i>(gmole)</i>		
		<i>Sample 1 Huggies</i>	<i>Sample 2 Luvs</i>	<i>Sample 3 Pampers</i>
Cellulose	carbon	1.3	1.3207	1.4417
	oxygen	1.09	1.1073	1.2088
	hydrogen	2.17	2.2045	2.4065
Polypropylene	carbon	0.521	0.2402	0.1865
	hydrogen	1.04	0.4794	0.3723
SAM	carbon	0.153	0.2142	0.2039
	hydrogen	0.167	0.2338	0.2226
	oxygen	0.102	0.1428	0.136
	sodium	0.038	0.0532	0.0507
Polyethylene	carbon	0.2	0.3288	0.304
	hydrogen	0.4	0.6576	0.608
Styrenes	carbon	0.108	0.1635	0.3742
	hydrogen	0.143	0.2165	0.4955
Polyurethane	carbon	0.0126	0	0
	hydrogen	0.0168	0	0
	oxygen	0.0056	0	0
	nitrogen	0.0014	0	0
Urine	carbon	10.72	10.72	10.72
	oxygen	5.36	5.36	5.36
Feces	carbon	1	1	1
	oxygen	0.5	0.5	0.5
Total	carbon	2.2946	2.2674	2.5104
	hydrogen	15.6568	15.5118	15.825
	oxygen	7.0576	7.1101	7.2048
	nitrogen	0.0014	0	0
	sodium	0.038	0.0532	0.0507

<i>Unaccounted for grams</i>			
Urine	3.6	3.6	3.6
Feces	3	3	3
Rubber	0.33	0.075	0.075

Source: Kimberly-Clark Corporation.

Table II. Atomic Ratio of Samples in Task 2

<i>Element</i>	<i>Huggies</i>	
	<i>Dry</i>	<i>Wet</i>
Carbon	1	1
Oxygen	0.5219	3.0757
Hydrogen	1.7157	6.8233

(1550 F) for the wet sample. No ethylene is predicted at equilibrium, as expected in the presence of hydrogen.

Batch Pyrolysis Study

These experiments were performed in a Chemical Data Systems Model 122 Pyroprobe coupled to a Carle Gas Chromatograph Model AGC111H. The Pyroprobe consists of a temperature programmed ampule containing a sample of the desired feedstock with product gas being swept to the gas chromatograph via helium carrier gas. For hydrogen determination, a hydrogen transfer tube was used at a temperature at about 600 C in a nitrogen stream. A SpectraPhysics Model 4270 integrator was used for the quantitative gas analysis. An IBM 9000 computer was connected to the integrator via an RS-232 interface. The computer was operated in a terminal mode using IBM 3101 terminal emulation software. The computer was mainly used to upload or download files to the disc drive. An additional CIT-101 terminal was also used for convenient communication between the operator and the integrator. The overall experimental system is schematically represented in Figure 7.

The feedstocks are a mixture of synthetic and natural polymers. Approximately 3 grams of each dry and clean sample was prepared by using the information from Table I but without the biologically hazardous material. The composition of the sample in the 3 grams mixture is shown below.

Sample 1: Huggies

Bag #1: Polyethylene, Polypropylene, and others	0.6999 g
Bag #2: Fluff cellulose and SAM	2.1131 g
Bag #3: Tissue cellulose	0.1870 g

All of these components were received from Kimberly-Clark Corporation. Polymers and tissue cellulose were delivered in approximately 1 cm. size. After the size reduction process to 60 mesh had been accomplished by a means of Thomas-Wiley Intermediate Mill Model 3383, each component was weighed and well mixed in a PICA Blender Mill Model 2601 and cut again using the intermediate mill. The experimental procedure was as follows:

- 1) Use a quartz capillary tube, ca. 0.2 cm. diameter and 2.5 cm. long as a sample holder. Plug a small piece of quartz wool at one end of the tube. Load and weigh ca. 0.0008 g of a sample in the capillary tube, then plug the other end of the tube with a small piece of quartz wool. The sketch of a sample cell is shown in Figure 8.
- 2) Place the tube in the coil probe smoothly until the end of the thermocouple is imbedded in the ampule as shown in Figure 8.

Table III. Gibb's Free Energy of Formation (kcal/K) at Temperature (K)

Species	800	900	1000	1100	1200	1300	1400	1500
C	0	0	0	0	0	0	0	0
CH ₂ O	-22.749	-21.898	-21.024	-20.134	-19.228	-18.314	-17.391	-16.461
CH ₄	-0.533	2.029	4.625	7.247	9.887	12.535	15.195	17.859
CO	-43.612	-45.744	-47.859	-49.962	-52.049	-54.126	-56.189	-58.241
CO ₂	-94.556	-94.596	-94.628	-94.658	-94.681	-94.701	-94.716	-94.728
C ₂ H ₂	43.137	41.821	40.522	39.234	37.96	36.69	35.432	34.177
C ₂ H ₄	24.628	26.514	28.431	30.373	32.334	34.302	38.266	40.246
C ₂ H ₆	16.010	21.11	26.26	31.4	36.61	41.8	47.02	52.2
C ₃ O ₂	-33.224	-34.653	-36.075	-37.495	-38.906	-40.315	-41.714	-43.11
HCO	-12.307	-13.378	-14.428	-15.462	-16.479	-17.484	-18.475	-19.456
H ₂	0	0	0	0	0	0	0	0
H ₂ O	-48.646	-47.352	-46.04	-44.712	-43.371	-42.022	-40.663	-39.297
H ₂ O ₂	-12.181	-9.519	-6.85	-4.173	-1.495	1.186	3.87	6.554
O ₂	0	0	0	0	0	0	0	0

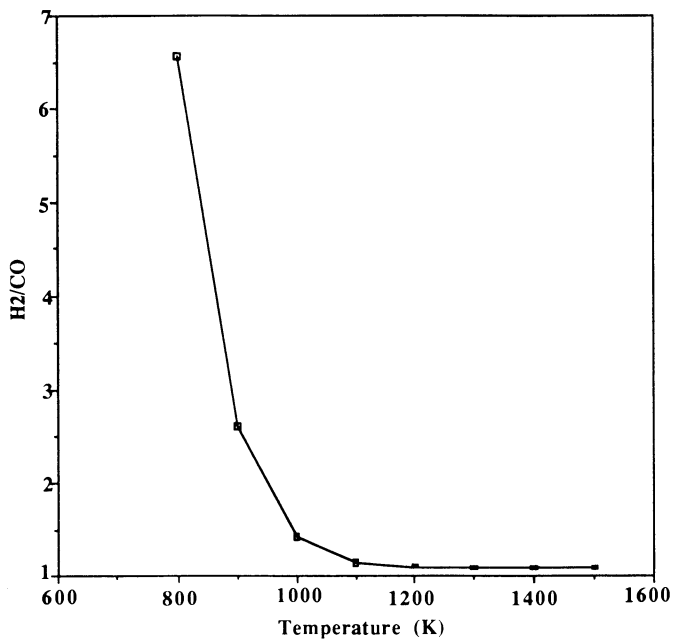


Figure 6. Equilibrium Hydrogen to Carbon Monoxide Mole Ratio of Huggies (wet) as a Function of Temperature.

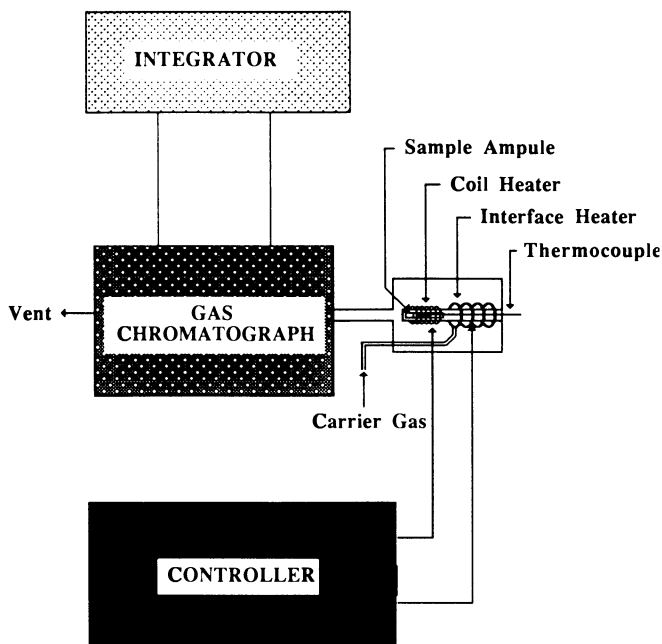


Figure 7. Experimental Apparatus for Small Scale Batch Reactor.

- 3) Place the probe in the interface, maintained at ambient temperature. Set time (20 seconds) and desired final temperature on the controller.
- 4) Wait at least 15 minutes to allow the system to equilibrate by means of helium passing through cell.
- 5) Start the integrator and the temperature recorder. The gas chromatograph is started automatically by the integrator.
- 6) When the gas chromatograph goes to the injection mode, push the pyroprobe start button.
- 7) Record the highest temperature (reaction temperature) from the temperature recorder.
- 8) After this step, all data gathering, gas composition calculations, and experimental termination are automatic.
- 9) After the completed gas chromatograph cycle, removed the probe and cap the interface.
- 10) Remove the capillary tube from the probe.

Safety precautions and procedures for this apparatus consisted of the following:

- 1) Wear a dust mask when preparing samples.
- 2) Study the Material Data Safety Sheets for each chemical before it is used or produced.
- 3) Keep all drinks and flammable liquids away from the pyroprobe/gas chromatograph area.
- 4) Turn on the carbon monoxide emergency detector to sense any gas that may be in the area.
- 5) Review the equipment manuals and Laboratory Safety Manual for further information.

A full factorial designed experiment was performed for the factors temperature and water composition. The experimental design is given in Figure 9 with the results shown in Table IV using Huggies as the example feedstock. The base condition for temperature was set by results from the reaction equilibrium calculations. The three responses of interest are: (1) hydrogen + ethylene + carbon monoxide, (2) hydrogen/carbon monoxide, and (3) ethylene. The superior level for all three responses is at the high level for each factor (experiment E). The factor ranking (via analysis of variance calculations) for each response and experimental error (as calculated by base point replication range divided by factorial experiment range) is shown in Table V. The error could be caused by several factors such as heterogeneity of sample and the platinum coil condition. All response results are considered to be favorable for further investigation in a continuous system (phases 3, 4 and 5 of the project).

A complete mass balance was not possible for this phase due to the small sample size (0.0008 grams). Thus the distribution of polymer to gas, char and tar, was not reported for this batch reactor phase.

Summary and Conclusions

The production of liquid hydrocarbon fuels from biologically contaminated disposable diapers is a technically viable concept. Favorable synthesis gas compositions can be produced. High quality liquid hydrocarbon fuel products are expected to be produced from the synthesis gas. Additional research

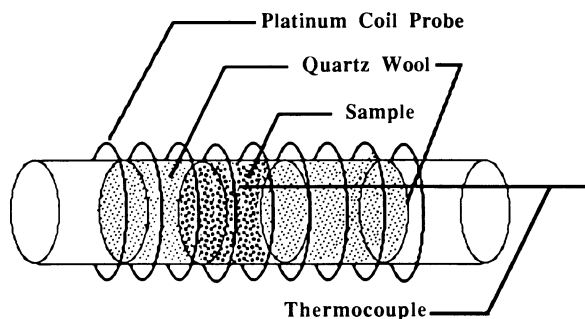
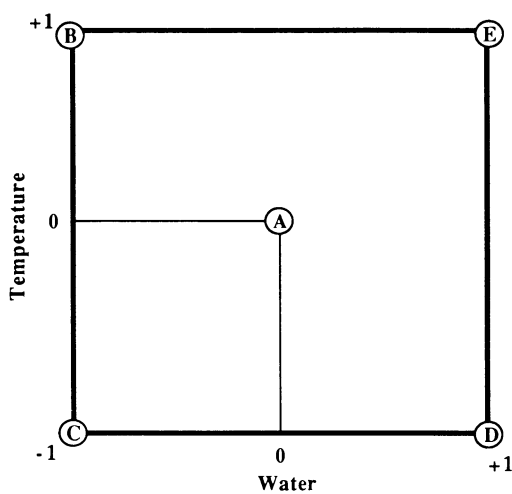


Figure 8. Sample Cell and the Coil Probe.



	<i>Level</i>		
<i>Factor</i>	<i>-1</i>	<i>0</i>	<i>+1</i>
Temperature (K)	1019	1102	1185
(°F)	1375	1525	1675
Water (wt%)	0	64.3	78.3
(μ l/0.1 mg.)	0	0.18	0.36
Pressure:	1 atm		
Residence Time:	20 seconds		

Figure 9. Experimental Design for Huggies.

Table IV. Gas Compositions from Huggies (Factors: Temperature and Water Addition)

<i>Experiment</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>A</i>	<i>D</i>	<i>E</i>
◇ Operating Condition						
Coil Temperature (K)	1373	1467	1277	1373	1277	1467
(°F)	2012	2181	1839	2012	1839	2181
Reaction Temperature (K)	1093	1176	1020	1108	1006	1172
(°F)	1508	1658	1376	1535	1352	1651
Water Added (wt %)	64.3	0	0	64.3	78.3	78.3
(μ l/0.1 mg of sample)	0.18	0	0	0.18	0.36	0.36
◇ Gas Composition (Mole %)						
H ₂	26	29	14.5	28	22	32
CO ₂	19	19	36	16	20	12
C ₂ H ₄	7	5	5	7	6	7
C ₂ H ₆	2	1	2	2	3	1
C ₂ H ₂	0	0.2	0	0	0	2
CH ₄	13	11	10.8	14	14	14
CO	33	34	30.7	33	35	32
H ₂ /CO Ratio	0.80	0.83	0.47	0.85	0.65	0.98

Table V. Analysis of Variance Calculation Results

<i>Response</i>	<i>Factor Rank</i>	<i>% Error</i>
H ₂ + CO + C ₂ H ₄	Temperature, Water	9.6
H ₂ /CO	Temperature, Water	9.8
C ₂ H ₄	Water, Temperature	0

and development work is required to establish reliable mass and energy balances for the continuous system before scale-up is considered. To accomplish this objective, a reliable solids feeder system needs to be designed and tested. This is not considered to be a major obstacle.

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Chapter 11

Gasification—Pyrolysis of Waste Plastics for the Production of Fuel-Grade Gas

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New technologies in gasification, pyrolysis, and environmental control are allowing the use of waste materials for feedstocks in environmentally acceptable ways for the production of electricity or process heat. Ebonite and automotive shredder residue were tested in a TGA using potassium- and calcium-based catalysts, and ebonite was tested in a 1- to 4-lb/hr continuous fluid-bed reactor (CFBR). Analysis of the data determined that fuel-grade gases could be produced in short residence time periods. Gas compositions of over 50 percent hydrogen were recorded with conversions of over 90 percent. Data include carbon conversion, gas production, wastewater treatment, heavy metals analysis, and chlorine content.

Many areas of the United States are experiencing waste disposal problems stemming from a shortage of landfill space, a public concern for the environmental impacts, and the appearance of landfilling. Incineration, another popular waste disposal method, is facing more stringent emissions regulations, has a poor environmental record, and has no additional benefits aside from the disposal of the waste. Although landfilling is still the cheapest method of disposal, the cost is rising due to the implementation of environmentally acceptable landfilling techniques. Thus cost-competitive alternative methods of recycling and conversion of waste to other products such as fuel are becoming more feasible. Table I lists some alternative processes which have been proposed and studied over the past several years.

New gasification and pollution control technologies are making it possible for waste materials to be used as environmentally acceptable sources of energy, providing both disposal and energy production. Two possible waste materials which can be used as feedstocks for energy production: automotive shredder

Table I. Summary of Proposed Processes

Company/Process	Description
Argonne National Labs	Separation and recycling of plastic components of ASR. Uses solvent extraction to separate out plastics.
Voest-Alpine	High-temperature gasification (3000°F).
Cookson/deTOX	Ash treatment. Ash is subjected to submerged arc melting, producing vitrified product.
Puremet	Ash treatment. Removes nonferrous metals from ASR using a cuprous ammonium sulfate solution.
Energy Products of Idaho	Fluidized-bed combustion.
RETECH, Inc./Plasma Centrifugal Reactor	Stabilization of waste materials by vitrifying the solid components in a plasma furnace.
EnerGroup, Inc.	Rotary kiln combustion.

residue (ASR) and ebonite, are being investigated at the Energy and Environmental Research Center (EERC) at the University of North Dakota (UND). This investigation includes some of the special concerns that arise from the use of waste materials in gasification, such as the fate of heavy metals, and the general suitability of these waste materials as gasification feedstocks.

Automotive Shredder Residue (ASR)

Production of Automotive Shredder Residue. Every year eight to ten million cars and trucks are disposed of by shredding at one of the 200 auto shredders located in the United States. ASR is a waste product generated in the dismantling of automobiles by the following procedure, illustrated in Figure 1. An automobile is stripped of its gas tank, battery, tires, and radiator. It is beneficial to have these items removed for safety and environmental concerns, but this is not always accomplished. After removal of some or all of these items, the automobile is shredded to provide a material less than four inches in size and composed of approximately 50 percent organic and 50 percent inorganic fractions. Magnetic separation is then used to sort out ferrous scrap. Twelve to 14 million tons of scrap per year are supplied to the steel industry for electric arc furnace feedstock from the dismantling of automobiles. Air cyclone separators isolate a low density "fluff" from the nonferrous fraction (aluminum, copper, etc.). This fluff (shredder residue) is composed of a variety of plastics, fabrics, foams, glass, rubber, and an assortment of contaminants (1).

The bulk density of the fluff is approximately 20 lb/ft³. A typical composition of fluff is shown in Table II.

In the U.S., approximately 2.5 to 3 million tons per year of shredder residue are generated in this process (1). This is equivalent to filling 500-700 football fields ten feet deep with ASR each year. This figure is expected to rise, since cars are increasingly manufactured with more and more plastics. One study estimates that the fraction of ASR will double between 1987 and 1997, based on the relative amounts of plastics in 1977 and 1987 model cars and the fact that the average age of a car being shredded is 10 years. The cost of landfilling all of this material is now between \$12 to \$100 per ton, depending on location (shipping not included) (1).

Along with autos, "white goods," or old appliances such as refrigerators and washing machines, are disposed of in combination with the automobiles in the shredders. White goods are the main contributor of polychlorinated biphenyls (PCBs) in ASR. Shredder residue also contains a wide variety of heavy metals and halogens, making it a good candidate test feed material for gasification, as it will present many of the common problems to be considered when using waste as a gasification feedstock.

Several additional difficulties need to be addressed when dealing with ASR. The most troublesome are the heavy metals (especially cadmium) content and the previously mentioned PCBs. Heavy metals, in addition to cadmium, that need to be addressed include lead, arsenic, barium, chromium, selenium, and mercury. Table III is a typical analysis from a shredder facility (analysis prepared by Analytical Industrial Research Laboratory, Chattanooga, TN, Lab No. 90356-303, 1990). Lead in ASR comes from items such as car batteries, wheel weights, exhaust systems, body repair filler, and highway contaminants. Lead in ash resulting from processing automotive shredder residue occurs mainly in the form of lead chloride, which indicates a high leachability (2). Shredder residue is not yet considered a hazardous waste by the United States Environmental Protection Agency, but could conceivably be classified as such in the future. Fluff has been classified hazardous in the state of California because of its cadmium content (1). Any process selected to treat shredder residue will have either to eliminate heavy metals before processing, for instance with leaching, or be able to deal with these substances in the ash and/or wastewater. Another problem associated with fluff as a feedstock is the feed variability. ASR provides a wide range of feedstock composition, as shown in Table IV. A process that can gasify this feedstock should be able to handle most plastic feedstocks.

An additional consideration when choosing automotive shredder residue as a test material in the study of waste material gasification is the urgency associated with the problem. In three to four years, the rising cost of landfilling will make shredder operations unprofitable. In order to offset the cost of ash stabilization and disposal, the volume of fluff needs to be reduced. Additional revenues can be generated by the production of electricity or fuel. Due to the fact that fluff has a relatively medium heating value, 5400 Btu/lb, any process for volume reduction which takes advantage of this energy-producing potential seems a logical course of action.

Table II. Typical Auto Fluff Composition

	Dirt, Stone, and Glass Fines Removed (%)	After Screening and Trommeling (%)
Fiber	42.0	47.8
Fabric	3.1	3.6
Paper	6.4	7.3
Glass	3.5	0.5
Wood	2.2	2.5
Metals	8.1	0.5
Foam	2.2	2.5
Plastics	19.3	22.0
Tar	5.8	6.6
Wiring	2.1	0.5
Elastomers	5.3	6.2
	HHV = 5400 Btu/lb	HHV = 6163 Btu/lb
Bulk Density: Approx. 20 lb/ft ³		

SOURCE: Reproduced from ref. 2.

Table III. Automotive Shredder Residue

pH	6.4		
PCBs	19 ppm		
Odor	Oil		
Color	Black and Brown		
Phenolics	8.25 ppm		
Cyanides	< 0.031 ppm		
Sulfides	2.7 ppm		
Flash Point	> 140°F		
Physical State	Solid		
% Free Liquids	None		
Specific Gravity	0.0432		
EP Toxicity Metals			
Arsenic	< 0.002 ppm	Lead	0.81 ppm
Barium	< 0.1 ppm	Mercury	< 0.0002 ppm
Cadmium	0.92 ppm	Selenium	< 0.002 ppm
Chromium	< 0.05 ppm	Silver	< 0.01 ppm

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Table IV. Shredder Fluff Proximate/Fuel Analysis

	High	Low	Average
H ₂ O, wt%	34	2	10
Ash, wt%	72	25	44
Volatiles, wt%	66	24	44
Fixed carbon, wt%	12	0	3
Sulfur	0.5	0.2	0.4
Chlorine	16.9	0.7	3.4
HHV, Btu/lb	9,260	2,900	5,400
maf HHV, Btu/lb	12,830	9,930	11,600

SOURCE: Adapted from ref. 2.

Shredder operators currently raise operational revenue by selling scrap metal to the steel industry for use in electric arc furnaces. It is highly desirable to recycle scrap metal from a steel manufacturer's point of view. When an arc furnace is charged with scrap, instead of iron ore, a 74 percent energy savings is realized (2). Shredders, then, not only dispose of a tremendous number of unwanted cars and trucks, but provide the steel industry with a valuable feedstock. Shredder residue is a problem that must be dealt with soon if the shredder industry is to continue to be a viable member of the recycling community.

Automotive Shredder Residue Gasification/Pyrolysis Results

TGA Procedure. Tests with ASR were conducted in the thermogravimetric analysis (TGA) instrument to determine test matrix conditions for further experiments to be run in the 1- to 4-lb/hr CFBR (continuous fluid-bed reactor). Two tests were conducted to determine reactivity with steam and one catalyst at temperatures of 800° and 900°C.

The TGA graphs in Figures 2 and 3 start at time = 0 (Point A). This point marks the beginning of the heatup period. Weight loss during the heatup period (as measured by a decreasing weight percent value) is due to moisture loss and devolatilization. Devolatilization, determined by prior proximate analyses, is completed before the introduction of steam (Point B). When reaction temperature is reached, steam is added, and the temperature is held at a constant value. When 50 percent of the fixed carbon is converted (Point C), heat is turned off and the steam flow terminated. The point at which 50 percent of the fixed carbon is converted is also determined by examination of proximate analysis data. As stated, each reactivity test was terminated when about half of the fixed carbon of each devolatilized sample had been converted to gas: this point is at about 22 weight percent (1 percent fixed carbon and 21

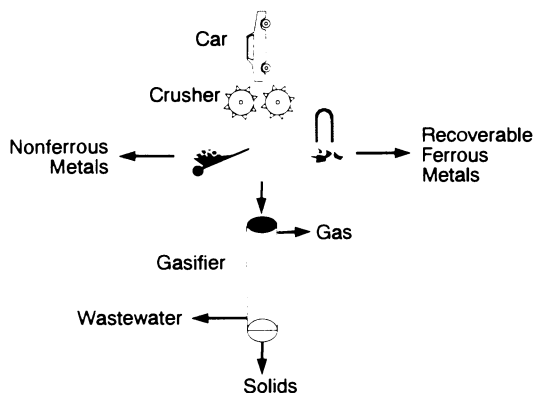


Figure 1. Automotive Shredder Residue Flowchart

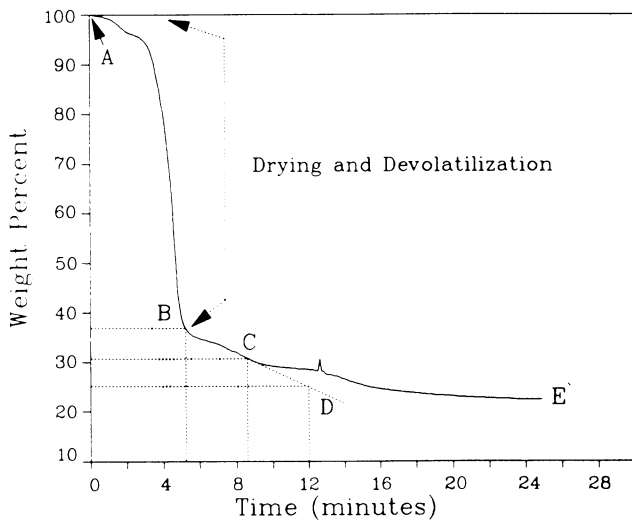


Figure 2. Automotive Shredder Residue at 900°C - No Catalyst

percent ash) of the original sample in the case with catalyst and about 28 weight percent (2 percent fixed carbon and 26 percent ash) of the original sample in the case with no catalyst. Theoretical 100% carbon conversion is shown at Point D. After the termination of heat and steam, the conversion line still continued until the instrument was turned off (Point E), since some residual steam was still present. All tests were performed under flowing argon gas.

To determine the point at which half of the fixed carbon had been converted, TGA proximate analyses were carried out on each sample prior to the reactivity tests. These analyses, summarized in Table V, showed that volatiles are removed from the reactant mixtures, and the remaining material consists of about 2 percent fixed carbon and 21 percent ash for ASR with catalyst and about 4 percent fixed carbon and 26 percent ash for ASR without catalyst. The increased ash content in the uncatalyzed sample was due to variation in the amount of metals within the original sample. Size of the ASR was $\frac{1}{8}$ inch in all tests.

TGA ASR Results. In the case of ASR without catalyst at 900°C, time for complete conversion was approximately seven minutes (Figure 2). Conversion is calculated by subtracting the 100% conversion point (Point D) from the point where conversion began (Point B). A similar curve is also shown for ASR with K_2CO_3 as a catalyst (Figure 3). Time for conversion for ASR with catalyst at 800°C was also seven minutes.

Reactivities at both of these conditions are shown in Table VI. Reactivity changes were slight and only appeared to affect the gasification of the char, which amounts to only a small portion of the entire feed samples, so that no significant variation appeared in the two TGA tests. Gas analyses from the two runs are shown in Table VII.

During continuous fluid-bed tests, devolatilization and gasification would occur simultaneously and would be dominated by devolatilization. Since a bed material will be necessary to prevent entrainment and for sulfur capture, the ASR should have sufficient residence time to devolatilize completely and gasify. Since devolatilization was the primary reaction, gasification may not be justifiable because of the small amount of fixed carbon remaining.

Ebonite

Production of Ebonite. Ebonite is a hard rubber material used primarily in car battery casings. Like automotive shredder residue, ebonite contains a variety of heavy metals and halogens, making it a suitable test material for waste gasification tests. Ebonite is a more homogeneous feedstock than ASR and thus will have fewer processing difficulties. Specifically, since ebonite is similar in density to coal, for which the EERC system was designed, it proved easier to feed to the reactor and fluidized quite well. Proximate and ultimate analyses for the ebonite are shown in Table VIII.

Table V. Automotive Shredder Residue - Proximate Analysis

	As Rec'd	mf	With K_2CO_3	
			As Rec'd	mf
Moisture, wt%	3.92	-----	2.85	-----
Volatiles, wt%	67.47	70.22	74.64	76.83
Fixed carbon, wt%	3.93	4.09	2.18	2.24
Ash, wt%	24.71	25.72	20.35	20.95

Table VI. ASR Carbon-Steam Reactivities

Run Temperature, °C	Temp. of Steam Addition, °C	Reactivity Constant, k
900	900	11.80
800	800	15.70

Table VII. TGA Gas Analyses

	With K_2CO_3 Catalyst at 800°C	900°C
	H_2 , volume %	53
CO_2 , volume %	47	47
CO, volume %	0	22
Total	100	98
Btu/scf	172	169

Table VIII. Proximate Analyses of Ebonite/Catalyst Mixtures

	Ebonite	Ebonite/ 10% $CaCO_3$	Ebonite/ 10% K_2CO_3
Moisture, wt%	2.00	1.70	2.76
Volatile Matter, wt%	37.10	36.53	36.97
Fixed Carbon, wt%	46.43	39.77	37.64
Ash, wt%	14.46	22.00	22.66

Thermogravimetric Analysis Test Results. TGA tests were also conducted on ebonite to determine test matrix conditions for further experiments to be run in the 1- to 4-lb/hr CFBR unit. Ebonite reactivity with steam and two catalysts was investigated at temperatures of 800° and 900°C (Figures 4 and 5). These tests were conducted in a manner similar to those described for automotive shredder residue, with the exception that, in all ebonite TGA tests, the reactant mixtures contained -60-mesh ebonite. A -60-mesh ebonite was used due to the difficulty in obtaining samples of reproducible size distribution from the bulk sample, which was used in CFBR tests. The +60-mesh-size fraction had the same TGA proximate analysis as the -60-mesh fraction, implying the difference (if any) in the reactivities of these two fractions would likely not be chemical, but due to a difference in surface area.

As in the automotive shredder residue TGA tests, to determine the point at which half of the fixed carbon had been converted, proximate analyses were carried out on each sample prior to the reactivity tests. These analyses (Table VIII) showed that volatiles are removed from the reactant mixtures, and the remaining material consists of about 63 percent fixed carbon and 37 percent ash for ebonite with catalyst and about 76 percent fixed carbon and 23 percent ash for ebonite without catalyst (Table VIII). The y-axis on the ASR TGA tests are slightly different than for the ebonite tests. The y-axis on the ASR tests are from zero to 100 weight percent. The ebonite tests were scaled differently and are from 0 to 180 weight percent. During the ebonite tests, when devolatilization and drying were essentially complete, the y-axis was reset to 100 percent. The y-axis on the ASR tests were done in this manner for ease of comparison to another set of test data.

In all of the ebonite tests, the reactant mixtures were heated to the desired reaction temperature and held at temperature until approximately half of the fixed carbon in the sample had been converted to gas, at which point the reaction was terminated by cutting off the steam and heat supply. As stated, each reactivity test was terminated when about half of each devolatilized sample had been converted to gas: 31.5 weight percent of the sample in the case with catalyst, and 38.1 weight percent of the sample in the case with no catalyst. After the termination of heat and steam, the conversion line still continued until the instrument was turned off, since some residual steam was still present, but it was not linear.

The catalysts investigated were Paris limestone (calcium carbonate) and potassium carbonate. All catalyst tests were performed using mixtures of ebonite and 10 weight percent-added catalyst. The ebonite/limestone test was performed at 900°C, and ebonite/potassium carbonate tests were performed at 800° and 900°C. The TGA data indicated that Paris limestone had a minor effect on the reactivity of the ebonite at 900°C (Figure 4, Line E), compared with the reactivity of ebonite without catalyst at the same temperature (Figure 4, Line D). Potassium carbonate, however, significantly affected reactivity. Conversion at 800° (Figure 5, Line D) and at 900°C (Figure 5, Line E) with a potassium carbonate catalyst occurred quite rapidly. The residence time required for complete conversion with this catalyst at 800°C is 5.5 minutes

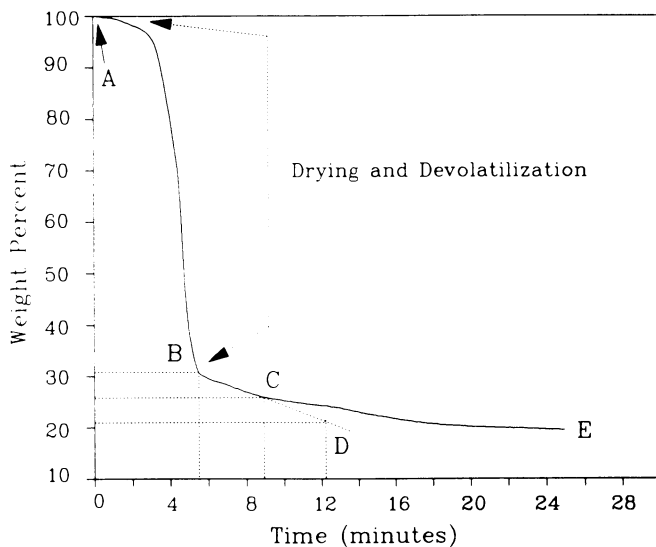


Figure 3. Automotive Shredder Residue at 800°C - With K_2CO_3

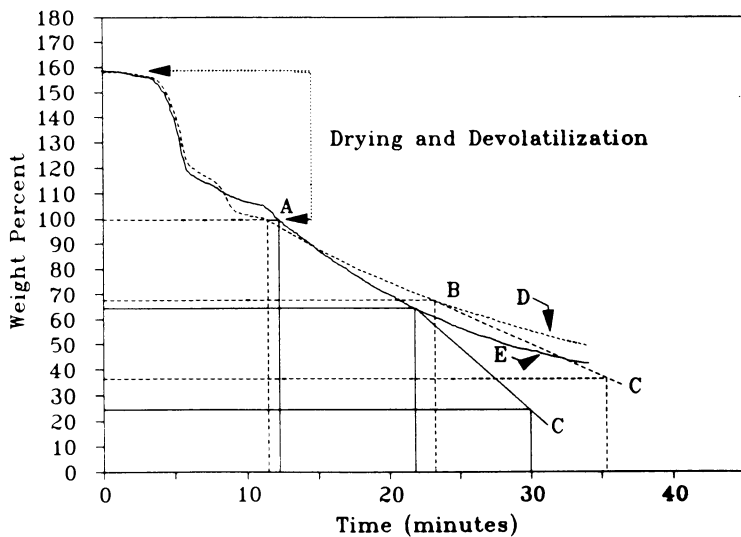


Figure 4. Ebonite at 900°C - With and Without Catalyst

and at 900°C is 2 minutes, whereas conversion time at 900°C without a catalyst is 18 minutes. Residence times for 50 percent and 100 percent conversion were found graphically. The point for 100 percent conversion was found by extrapolating the linear portion of the conversion line. The reaction appears to be zeroth order with respect to carbon. As conversion approaches 100 percent, the reaction is no longer strictly zeroth order because unreactable material (ash) limits access to carbon, but the order goes up only to approximately 0.2, introducing a very small error into the calculated time for total conversion.

Ebonite Continuous Fluid-Bed Reactor Gasification Tests. Bench-scale testing was performed on ebonite in a 1- to 4-lb/hr continuous fluid-bed reactor (CFBR) system, shown in Figure 6. Preheated gas and steam are introduced into the bottom of a 3-inch-diameter reactor. The lower section of the reactor, which is attached to the coal feed system, is made of 3-inch pipe and is 33 inches in length. The freeboard section is made of 4-inch pipe and is 18.75 inches in length. Solids remain in the bed until, through weight loss from gasification, they reach the top of the 3-inch section and fall out through the top bed drain leg, where they are collected in an accumulation vessel. Unreacted fines and some ash particles are entrained and separated from the gas stream by a 3-inch cyclone. Liquids are condensed in one of two parallel, indirect-cooled condensation trains. Gas is then metered and sampled by an on-line mass spectrometer.

Carbon conversion for the ebonite was found to be approximately 90 percent at 900°C, with most of the unreacted ebonite found in the condensation train, indicating that fines blew out of the bed before having sufficient residence time for complete conversion. A narrower particle size for the feed, a lower fluidization velocity, or a larger diameter freeboard section would most likely raise this conversion by reducing fines entrainment. Alternatively, a reactor/cyclone recycle system that is designed for this particular feedstock would also produce higher conversions. Comparing the amount of material in the bed with the feed rate indicates that the residence time for the test was less than one hour. The residence time is extremely dependent on temperature and heatup rate. Ebonite agglomerates at temperatures below approximately 800°C. If the reactor is not above 850°C and at a high heatup rate, the ebonite will agglomerate, greatly reducing the reaction rate and the overall conversion.

Gas produced from gasification and from water-gas shift reactions is between 220 to 280 lbs per 100 lbs of moisture- and ash-free ebonite feed material. The average composition of the product gas is shown in Table IX. Gas produced has a Btu content of approximately 260 Btu/scf. This number does not include nitrogen used in fluidization. Btu content will be lower when inert gas is included, but since the amount of inert gas is process-specific, Btu content of gas produced only is given.

Water conversion was found to be 1.5-2.0 mole water/mole fixed carbon based on material balance data. Trace element analysis showed considerable loss of lead from the ebonite, going from 660 ppm in the feed to 257 ppm in

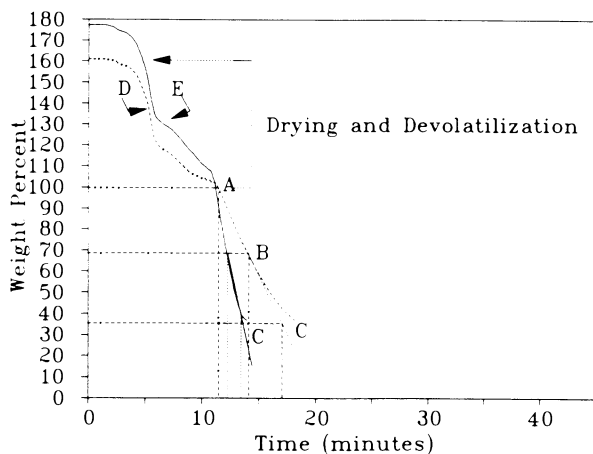


Figure 5. Ebonite - With K_2CO_3 - 800° and $900^\circ C$

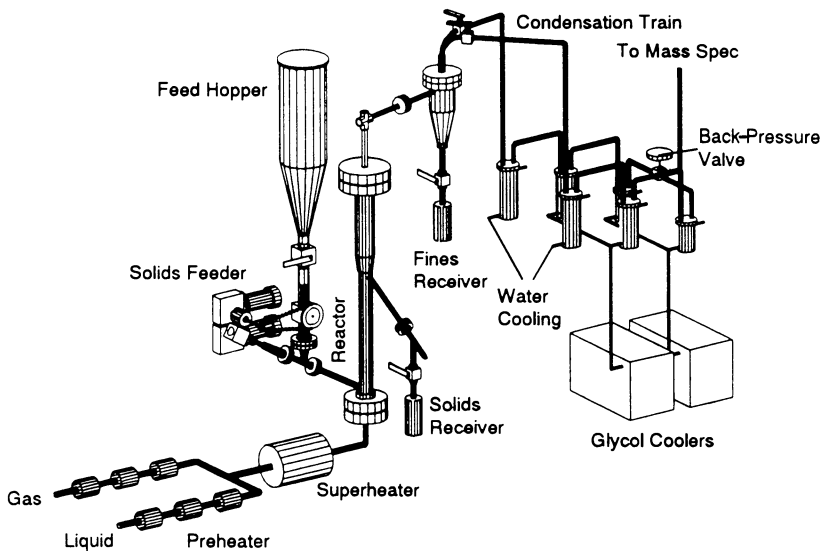


Figure 6. 1- to 4-lb/hr Continuous Fluid-Bed Reactor

Table IX. Ebonite Gas Analysis^a

H ₂	50.1 vol%
CO ₂	28.8 vol%
H ₂ S	0.9 vol%
CH ₄	4.5 vol%
CO	15.0 vol%

^a Without nitrogen fluidizing gas.

the product char. Antimony also decreased considerably, starting off at 696 ppm and ending up at 129 ppm. Chlorine content decreased from 160 ppm to 149 ppm.

Environmental Impacts of Gasifying Waste Material

Gasification of waste materials offers not only the benefit of energy production, but also decreases waste volume that needs to be landfilled. For ebonite, density of the feed material is approximately 0.73 g/mL. Density of the reacted material (top bed drain) is approximately 0.56 g/mL. On an as-received basis, 12.8 m³ out of 100 m³ fed will be left over for landfill (assuming the 90 percent conversion). If 100 percent conversion is achieved, 14.5 grams per 100 grams of feed will be left over to landfill, resulting in a volume decrease of 87 percent. ASR density is approximately 0.32 g/cm³. After reaction, this density is estimated to be about 1.6 g/cm³, resulting in a volume reduction of about 80 percent.

Wastewater from the process may contain some heavy metals, including lead and antimony. Acid leaching the ebonite prior to gasification may be desirable to eliminate as much of the heavy metals as possible in downstream operations. Additionally, leachability studies will need to be conducted on the unconverted material. Gas cleanup problems will include the need to eliminate sulfur- and chlorine-containing compounds such as H₂S and HCl from the gas stream, as well as trace metals that may vaporize and recondense as particulates. The ebonite feed material is fairly high in sulfur, having an as-received sulfur content of 3.9 percent. The opportunity for greater halide removal in reduced forms may be one of the most important overriding factors for using a gasifier instead of a combustor. For example, HCl is over 50 times more soluble in H₂O than Cl₂ (3).

Summary

The future of waste disposal appears to be moving away from landfilling and incineration and toward recycling and using waste materials as a source of energy. New technologies in pollution control and in energy generation techniques, such as gasification, make energy production from waste materials

an environmentally acceptable alternative. Tests on ebonite, a hard rubber waste material, and ASR, a waste product of automotive shredders, indicate that a high Btu gas can be produced in short residence times. Considerable work remains to be done to optimize operating conditions and to determine how to deal best with heavy metals, chlorine, and sulfur compounds.

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Chapter 12

Estimating the Heating Value of Sewage Sludge

A New Correlation

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On a dry-basis, the heating value of sewage sludge is greater than that of oil shale or tar sand. The volatile matter content of dry sludge can be higher than that of the high volatile bituminous coal. Available correlations in the literature, developed for coals, were applied for predicting the experimentally determined heating values. In addition, the sludge compositional data (C, H, S, and ash) were used to develop a new correlation specifically for raw sewage sludge. Compared to the models tested, the new correlation developed in this study for sewage sludge provided a better fit between the measured and predicted values. Sewage sludge is composed of organic and inorganic materials. The organic portion of the sludge is predominantly composed of C, H, N, and S.

A variety of organic and inorganic materials can be found in a waste-water treatment plant (1). Treatment plants receive tremendous quantities of waste-water containing dissolved and suspended solids from numerous sources including domestic, industrial and urban-offs as well as from storm drainage.

The solid residue or sludge, the principal product of primary and secondary treatments, has been traditionally ocean dumped, incinerated or landfilled. However, current federal regulations restrict such traditional practices. The option to dispose of such materials by landfilling also suffers from psychological (e.g., "not-in-my-backyard" syndrome) and genuine environmental concerns (e.g., contamination of ground water or agricultural products and leaching). A recent survey of compositional characteristics of domestic sludges indicate that most sludges can be

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classified as "hazardous," and consequently not suitable for disposal by landfilling (2). The incineration technology can suffer from emission and public perception problems. Keeping the limitations of these alternatives in mind, conversion of sewage sludge to clean fuels by, for example, gasification (which readily converts essentially all the organic constituents) to synthesis gas (CO and H₂) for power generation or as chemical feedstock, provides an excellent avenue to utilize this renewable resource (3).

The processing and the utilization of sewage sludge requires a better understanding of its physical and chemical properties. In particular, the ability to estimate its calorific value would indeed be of great importance keeping in mind that the measured heating values of sludge are generally not readily available and the reported data can suffer from a relatively large experimental variation (partly due to possible biological/chemical degradation of samples during various treatments). Correlations are important for justification and modeling of the conversion processes now being developed.

The correlations between the coal composition and heating value were reported as early as 1940. Over 20 different equations are reported in the literature which enable one to calculate the heating value of coal based on the ultimate/proximate analyses (4-9). However, essentially nothing could be found in the literature that could be readily applied to specifically estimate the heating value of dewatered sludge.

To assess the utility of existing correlations (developed for coal), the most widely used equations were tested for dry sewage sludge. Mott and Spooner (1940) claimed that their equation will yield heating values agreeing within 200 btu for the whole range of fuels, from peat to anthracite (4). We, however, were much less successful with this equation for dewatered sewage sludge.

Mason and Ghandi (1980) developed a correlation based on coal samples from the Pennsylvania State University coal data base (6). A comparison of the experimental results and the predicted values (based on Mason and Ghandi's equation) was made. Compared to the equation by Mott and Spooner, this equation (termed Data Base [DB] Equation) did a better job in estimating the heating value of sludge. Various equations reported for coal in the literature were attempted for dewatered sewage sludge. However, like Mott and Spooner's equation, these equations (10, 11) appeared to be inappropriate for dewatered sewage sludge.

Experimental

Dewatered sewage sludge samples (originating in various treatment plants of the country) were dried in a lab vacuum oven under N₂. The dry samples were characterized by monitoring the following: ultimate analysis (C, H, S, N), ash content and high heating value. A selected set of

samples were characterized in multiple laboratories which included the following: Huffmann Laboratories, Inc. (Golden, CO), Institute of Gas Technology (IGT, Chicago, IL), and Texaco Research & Development (Beacon, NY) to ensure that analyses in various laboratories provide comparable results. In general, the data obtained from various labs were within the variation allowed by the conventional ASTM guidelines for each analyses. All analyses for a given sample were completed relatively rapidly to minimize degradation of samples due to bacterial growth.

The data (30 observations in total) were analyzed by using the Statistical Analytical System (SAS) package developed by SAS Institute (12). The regression program available in this package was applied to develop an empirical model.

The Heating Value of Sewage Sludge Compared to the Various Fossil Fuels. The mean heating value (gross) of sludge (based on 30 observations) compared to various fossil fuels is shown in Figure 1. The heating value of oil shale (Green River formation of Mahogeny zone; Colorado; 33 gal/ton, described by Khan, and Khan and others [13, 14]) was 3200 Btu/lb. The heating value of eastern Kentucky shale can be significantly lower than the western shale considered in this study. The heating value of the Asphalt Ridge basin tar sand was less than 2000 Btu/lb (13, 14). By contrast, the heating value of an average sewage sludge is considerably higher (6400 btu/lb). The heating value of an industrial biosludge observed in this study to be greater than 9000 btu/lb. However, no industrial sludges were included in the data base aimed at developing the new correlation.

Compared to essentially all fossil fuels (excluding petroleum based fuels), sewage sludge has a higher H/C (atomic) ratio (Figure 2). The mean H/C ratio of sewage sludge was 1.65 (based on 30 observations), considerably higher than that of the bituminous coals (Pitt#8) with H/C ratio of 0.89 or a sub-bituminous coal (H/C of 0.96 for Wyodak coal). The H/C of the sewage sludge is comparable to tar sand bitumen (with H/C of 1.5).

In addition to the elements described above, significant amounts of chlorine and various volatile metals can be present in sewage sludge. For example, the chlorine content of one sludge was as high as 0.6% (dry basis). Other volatile inorganics identified in the this sludge included the following: Beryllium (less than 0.02 ppm), Vanadium (less than 1 ppm), and Manganese (900 ppm). However, this study did not consider the role of chlorine or vaporizable metals on the heating value of sludge.

Variations in the Sewage Sludge Composition. The mean, standard deviation, minimum and maximum values for the compositional analyses are presented in Figures 3 and 4. The variations in the C, H, N and S content in different samples are shown in Figure 3. The sulfur content for various sludges ranged between 0.18 and 3.61 percent with a mean

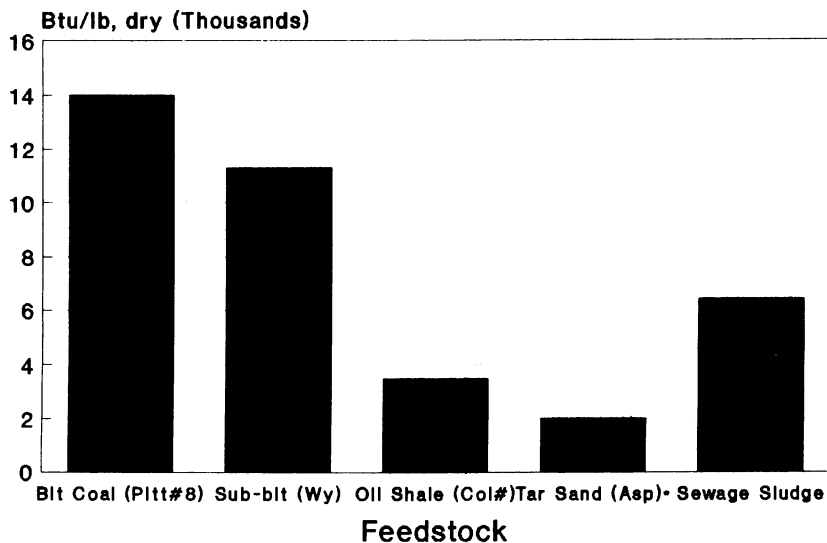


Figure 1. Comparison of Heating Values of Various Feedstocks (Dry-basis)

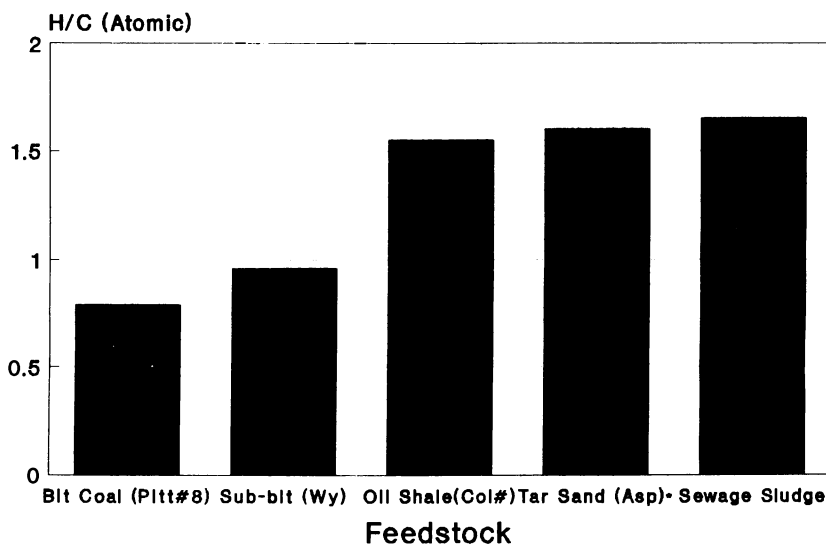


Figure 2. Comparison of H/C of (Atomic) of Various Feedstocks (Dry-basis)

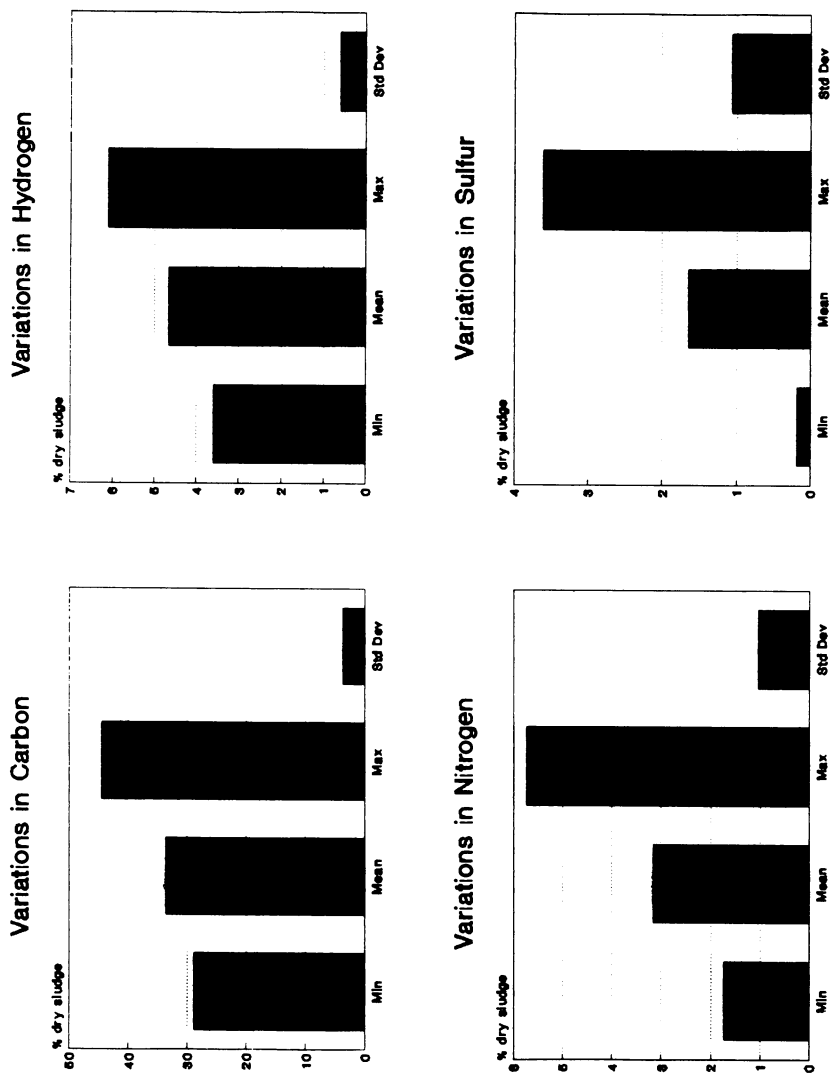
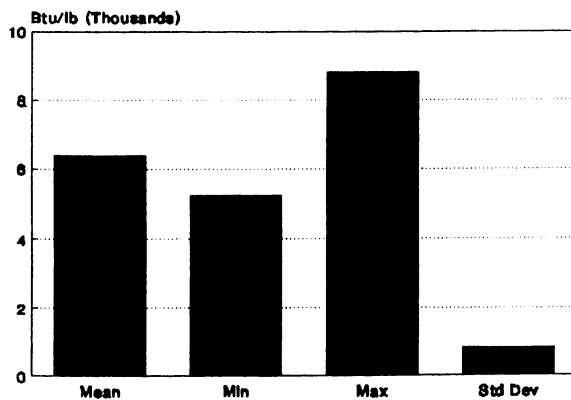


Figure 3. Variations in C, H, N, and S in the Data Set Used

Variations in Sludge Heating Value



Variations in Ash Content

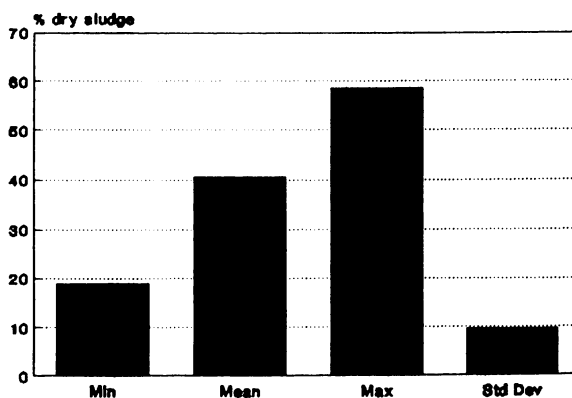


Figure 4. Variations in the Heating Value and Ash Content in the Data Set Used

value of 1.71 (with a standard deviation of 1.05 about the mean). The oxygen content of sludge ranges between 3.5 and 27.8% with a mean of 16.5 (and a standard deviation of 6.3%).

The volatile matter content for a given sludge ranged between 45 and 62% (dry basis). These values are significantly higher than the volatile matter content of a high volatile bituminous coal (with a volatile matter content of 35%, dry basis). The H/C ratio (atomic) for the data set used ranges between 1.44 and 1.86 with a mean of 1.65 with a standard deviation of 0.106.

Figure 4 shows that the mean heating value of the sludge was 6409 with a standard deviation of 816 (based on 30 observations). The measured values for the sludge ranged between 5261 and 8811 Btu/lb. The heating value and the compositional characteristics of sludge are dependent on the nature of sludge as well as on the degree of digestion (or pretreatment) a sludge has undergone. The minimum ash content for the sludge was 18.9% while the maximum value for the sludge was 58.68% (the mean was 40.5%). The higher ash content generally reflects that the sludge has either been digested or heat-treated to convert a large portion of the organic constituents.

The sludge composition is dependent on the nature of pretreatment a given sludge has experienced. For example, the sludge conditioned by a wet oxidation process (intermediate pressure, 300-400 psi; oxidizing atmosphere; temperature of 250-375 F) has a significantly different composition and a lower heating value (Figure 5) compared to the untreated sludge (lower C, H but a higher oxygen content compared to the untreated materials; all data on dry basis).

The compositional differences between various sludges can be significant. For example the differences in the compositional characteristics between the Los Angeles (CA) and Passaic (NJ) are shown in Figure 6. It is interesting to note that the pyritic sulfur is the dominant sulfur type for several sludges (Figure 7). The presence of this large concentration of pyrite is not typical of domestic sludges but suggests the formation of pyritic sulfur from organic sulfur by bacterial action. Such conversion of organic to inorganic sulfur has been reported in the coal literature.

Evaluation of the New Correlation. The variations (between the measured and predicted values) for the three models evaluated in this study are summarized in Figure 8 (discussed in details in the following section). Figure 9 compares the measured and predicted heating values based on the Data Base Model. The disagreement between the predicted and measured values in Figure 9 is much larger than those shown in Figure 10 (based on the new correlation developed in this study).

Figure 10 compares the measured and predicted heating values calculated based on the correlation developed in this study. The following equation describes this model:

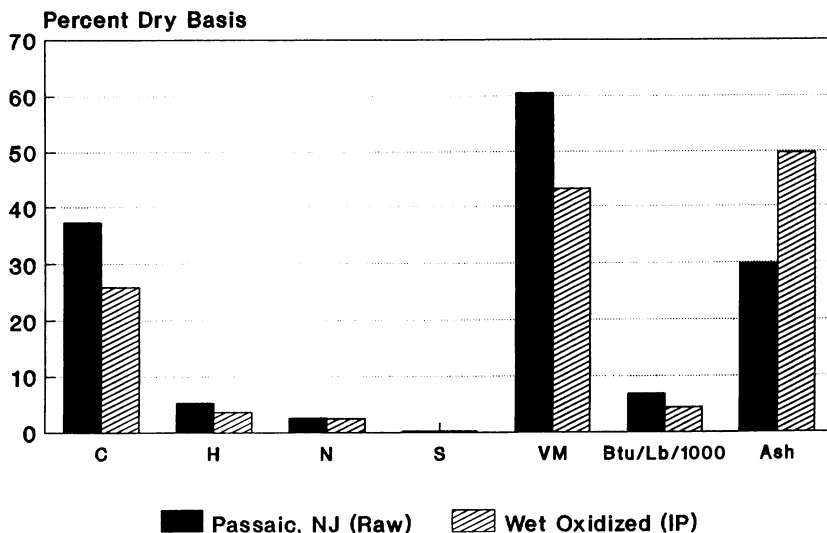


Figure 5. Effect of Wet Oxidation on Sewage Sludge Composition (Passaic Sewage Sludge); Raw and Wet Oxidized (@ Intermediate Pressure)

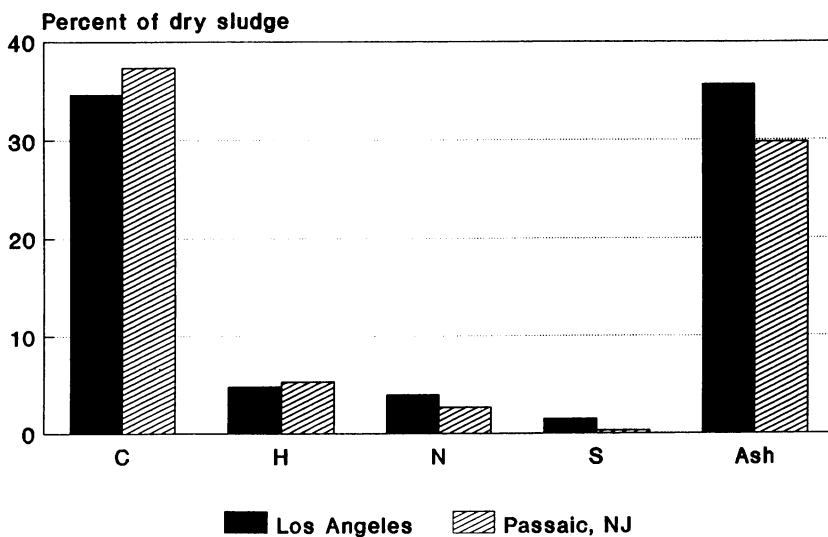


Figure 6. Comparison of LA versus Passaic Sludge Composition

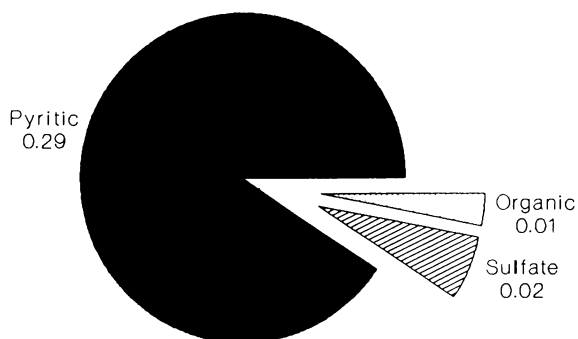


Figure 7. Types of Sulfur Present in the Passaic Sludge (Total Sulfur Content 0.32%)

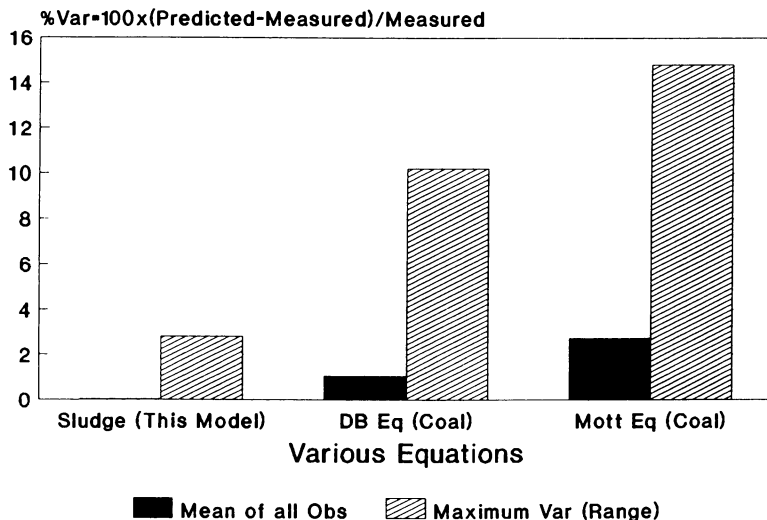


Figure 8. Composition of Various Models Tested for the Data Set

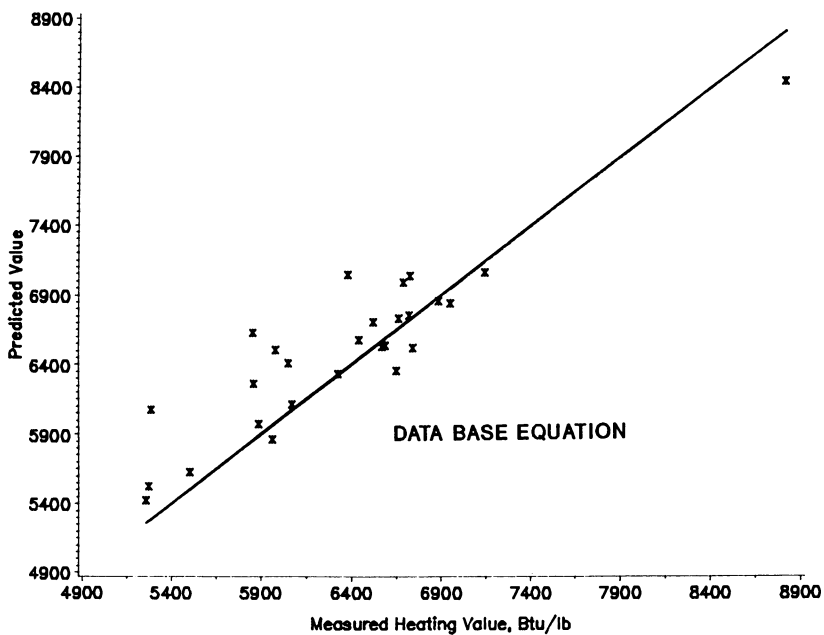


Figure 9. Predicted and Measured Heating Values for Sewage Sludge (Based on the Data Base Equation, i.e., Literature Model)

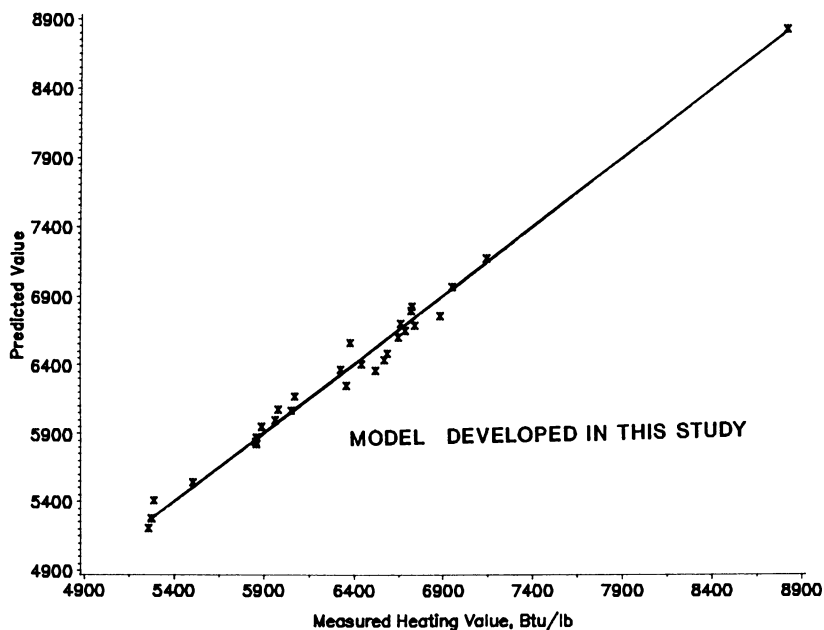


Figure 10. Predicted and Measured Heating Value for Sludge Based on the New Sludge Model

$$Q \text{ (Btu/lb)} = 241.89 \cdot C + 264.26 \cdot H + 236.2 \cdot S + 20.99 \cdot \text{Ash} - 4174.68$$

R^2 for the model is 0.99. The parameter measures the proportion of total variations explained by the regression. It is calculated by dividing the sum of squares due to regression by the total sum of squares. R^2 is related to correlation coefficient, r , by the following in simple linear regression: $r = \text{square root of } R^2$. In addition, r , has the same sign as the slope of the computed regression.

The F value for the model was 650.6. The F ratio is the ratio produced by dividing the mean square for the model by the mean square of error. It tests how well the model as a whole (after adjusting for the mean) accounts for the behavior of the independent variable.

The P value for the model was 0.0001. P defines the "observed level of significance." In statistical terms, the level of significance, alpha, of a test is defined as the probability of rejecting the null hypothesis (i.e., no linear relationship between the dependent and independent variables), given the null hypothesis is true. The P-value gives us the largest value of alpha that would lead to the acceptance of the null hypothesis. In other words, from statistical standpoint, the correlation developed in this study for estimating the heating value of sludge is highly significant.

Comparison of Various Correlations. Attempts were made to estimate the heating value of sludge using correlations widely reported in the literature applicable for coal (and oil shale). In particular, the equation by Mott & Spooner and the Data Base equations were compared with the newly developed correlation.

The percent variation between the measured and the predicted values were calculated for each model by the following equation:

$$\% \text{ Variation} = 100 \times (\text{Predicted-Measured})/\text{Measured}$$

The variations (between the measured and predicted values) for the three models are summarized in Figure 8. The model developed in this study provides a mean variation of 0.019% between the predicted and the measured values. The maximum variation between the measured and predicted values was never greater than 2.83%, based on the new model. In contrast, the Data Base Equation provides a maximum variation of 10.2% while the equation by Mott & Spooner yielded a maximum difference of 14.8% between the measured and predicted values.

Summary & Conclusions

The following conclusions are derived based on this study:

- o The heating value of dry municipal sewage sludge is considerably higher than tar sand or oil shale but lower than that of bituminous coal. The atomic H/C ratio of sewage sludge, however, is higher than that of bituminous coal, but comparable to the H/C ratio of oil shale. Some industrial biosludges can have heating value comparable to that of a low rank coal.
- o The volatile matter content of sludge is higher than that of coal, oil shale or tar sand.
- o The compositional characteristics (C, H, N, S and ash) of sludge can vary widely among sewage sludge of different origin. Wet oxidation of sewage sludge significantly reduces its heating value as well as its C and H content.
- o The conventional equations developed for coal are not readily applicable for sewage sludge. The equation developed in this study serve reasonably well for estimating the heating value of sludge of various origin based on its analysis (C, H, S, and ash).

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Chapter 13

Preparing Pumpable Mixtures of Sewage Sludge and Coal for Gasification

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The flow behavior of coal water slurries is significantly degraded when untreated sludge is mixed with coal at a sufficient concentration. Various methods of treating sludge were evaluated in an effort to make coal slurries containing more than 25 per cent sludge solids more fluid so that they could be pumped through pipes and nozzles into a pressurized gasifier. Drying sludge in commercial dryers at temperatures ranging from 180 deg F to 400 deg F significantly improved its slurring characteristics with coal. The fluidity characteristics could also be improved by removing water under vacuum, filtering with high intensity filter presses and subjecting the sludge to shearing stresses. Slurry viscosity measurements were made at 70 to 212 deg F in novel viscometers.

Over 26 billion gallons of waste water are treated by more than 15,000 publicly owned treatment works in the United States serving over 70% of the population (1). This treatment results in the production of 7 million metric tons per year of sewage sludge. Over 40% of this is applied to the land while about 14% is incinerated and another 5% is dumped into the ocean (2). (See Figure 1) The recent ban on ocean dumping--with penalties for continued dumping reaching \$600 per dry ton in 1992--along with a decreasing number of landfills and other environmental concerns, have created a need for environmentally sound sewage disposal alternatives.

The Texaco Coal Gasification Process, (TCGP) which has operated satisfactorily in large scale facilities for several years, appears to offer attractive features as

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such an alternative. Figure 2 shows a slurry of coal being converted into electricity by means of gasification and combined cycle electricity generation. In this process coal is combusted in a deficiency of oxygen to produce synthesis gas--a mixture of carbon monoxide and hydrogen. This mixture can be used for several purposes including use as a fuel for a combined cycle power process. In this process, high temperature synthesis gas is heat exchanged with water to produce steam, which is converted into power in steam turbines, and, after cleanup, the cooled synthesis gas is burned in gas turbines to produce additional power.

Coal/water slurries containing about 60% coal are a usual feed for the TCGP. On the other hand, concentrated sludge slurries in the form of sludge filter or centrifuge cakes containing 70 to 80% water are a common product of water treatment plants. Sludge in this form is a low quality fuel with an insufficient Btu content to be gasified alone in the process. It must therefore be mixed with an auxiliary higher quality fuel such as coal, oil or gas, as shown in Figure 3, to form a satisfactory feed for the process. This study examines only the use of coal as the auxiliary fuel.

In addition to having a satisfactory heat content, slurry mixtures which are suitable feeds for the process must be pumpable at high solids concentrations and contain sufficient sludge to justify the incremental cost of handling it. This paper describes the results of our efforts to characterize the fluidity properties of sludge/coal slurries and to identify a treatment process that would enable sludge concentrations to be increased to practical levels in pumpable slurries with coal.

The hydraulic transport of particulate solids has recently been reviewed (3). Campbell and Crescuolo have examined the rheological characteristics of dilute sludge slurries (4), and Beshore and Giampa have reported on the rheological properties of concentrated coal slurries containing minor amounts of sludge (5). No detailed studies of the rheological characteristics of coal slurries containing high concentrations of raw or thermally treated sludge have been reported. A fuel comprised of raw (non-dewatered) sludge and coal has also been claimed to be pumpable and useful as a boiler fuel (6).

Experimental

The viscometer used for this work was developed in Texaco Research and Development facilities and calibrated with oils of known viscosity. Usually, apparent viscosity vs solids concentration curves were obtained from which the total solids that could be included in a slurry at a given viscosity were determined. About 80 grams of slurry was required for each measurement. Slurries were prepared by mixing the desired amounts of sludge, coal and water to a measurable consistency in the measuring cup and noting the torque at a stirrer speed of 600 rpm. Measurements were

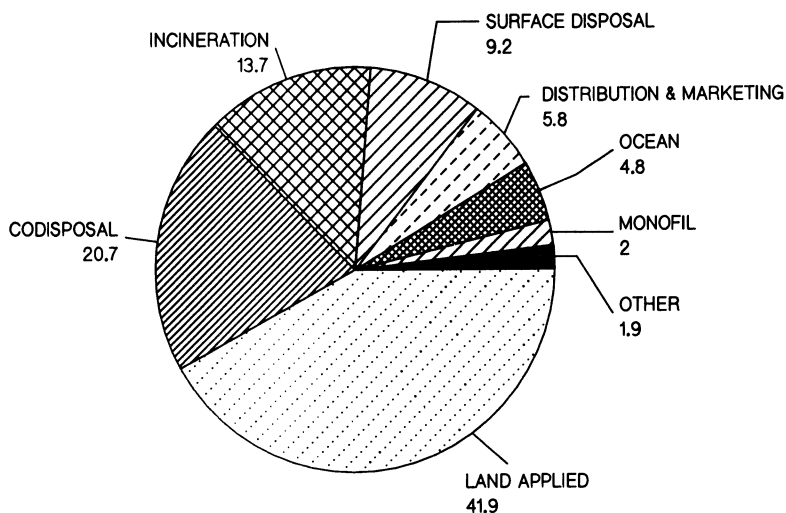


Figure 1. Methods of disposing of sewage sludge in the United States-1990.

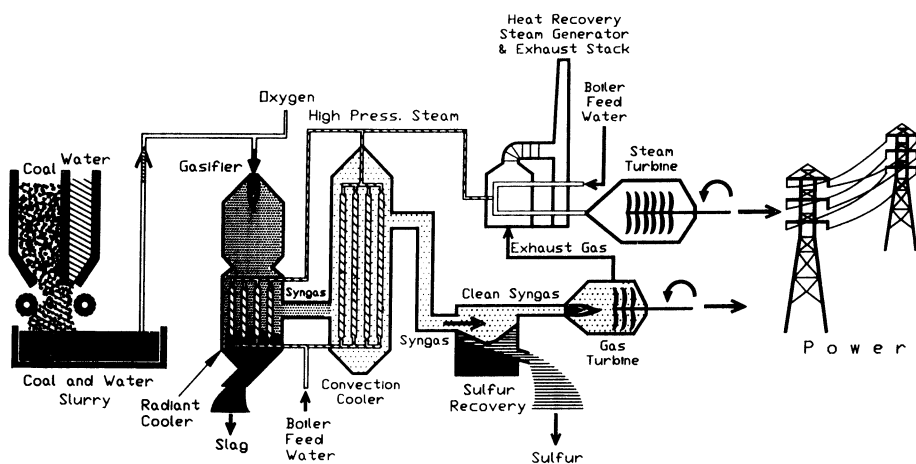


Figure 2. Texaco Gasification Process-combined cycle mode of operation.

then repeated as incremental amounts of water were subsequently added. Torques were related to viscosities by measurements on oils of known viscosity. Typical data are included in Figure 4. Replicate measurements indicated that the standard deviation of measurements using this technique was 0.92 for a sludge sample which contained 13.0% solids at 1000 cp. Most of the error in this measurement originates from sampling the raw sludge because its accuracy is dependent on the accuracy of the % solids determination in the original sample. The standard deviations calculated for solids content measurements in raw sludge samples were between 0.7 and 0.94 for samples containing 23% solids.

A Haake viscometer, RV-100, was also used for rheological measurements.

To establish the patterns of sludge behavior, dewatering of sludge was achieved by an advanced dewatering technique, high intensity press (HIP). The pressing action of the HIP was simulated on a laboratory scale by means of a device designed and constructed by Andritz Corporation, manufacturer of the commercial HIP apparatus. Dewatered cake was distributed on a 4"x4" piece of filter fabric which was supported by a specially designed perforated square metal tray. This was surrounded by a square metal box. A similar piece of fabric was placed over the sample followed by a square upper tray. Pneumatic piston pressure was then applied to the upper tray forcing out the entrapped water. The applied pressure was changed with various retention times to simulate the actual HIP zone pressures. Upon completion of the pressure cycles, the pneumatic lever was pushed up and the pressure box quickly removed. The solid content was determined by actual measurement and the throughput calculated by empirical equations developed by Andritz.

Sludge Characteristics

The digested sludge used for most of the measurements made in this study was obtained from water treatment plants in Los Angeles County, Los Angeles City and San Bernadino County in California. The as-received centrifuge cakes were amorphous, fibrous materials containing 20 to 30% total solids. Polymeric flocculating agents were employed in their preparation at the water treatment plants. These materials were not pumpable but could be made so by diluting to a slurry containing about 15% solids. Their composition is compared with coal and peat in Table I. Digested sludge solids generally contain: 30-60% volatile solids, 5-20% grease and fats, 5-20% protein, 10-20% silica and 8-15% cellulose (7).

As-Received Sludge/Coal Slurries

One of the main purposes of this work was to determine the maximum amount of sludge that could be incorporated into a pumpable slurry with coal. Economics dictated that commercially viable sludge containing feeds should include

Table I
Typical Analysis of Sewage Sludge and Other Solid Fuels

Fuel	Moisture %	Ash	C	H	N	O By Diff	S	BTu/lb (Dry)
Sewage Sludge	80	36	31	4.8	3.9	22.1	1.7	6400
Peat	83.7	3.4	47.1	5.4	1.4	42.6	0.1	
Lignite, TX	29.3	21.5	55.7	4.5	1.0	15.8	1.4	9788
Subbituminous C, Wyoming	28	7.8	68.1	4.9	1.1	17.2	0.6	11840
Bituminous Pittsburgh 8	0.8	8.6	76.5	5.1	1.4	5.8	2.5	13765

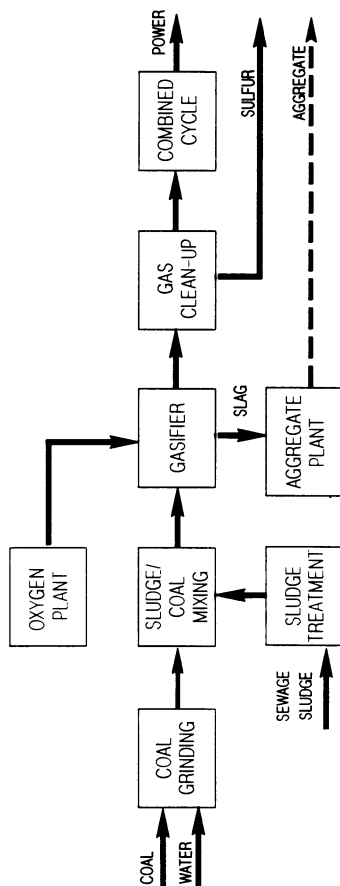


Figure 3. Flow diagram of a conceptual sewage sludge gasification process.

at least 25% sludge solids and have a total solids content of above 50%. Experience with coal slurries indicates that slurries having apparent viscosities of about 1000 cp are pumpable. Results of viscosity measurements on a number of sludge/coal slurries containing varying amounts of Los Angeles sludge in Utah-Sufco bituminous coal are presented in Figure 4. These results, which are typical of many, showed that the amount of total solids which can be incorporated into a pumpable slurry decreases with increasing sludge content. It is also apparent that in the 1000 to 2000 cp range, small increases in total solids content of slurries effect large increases in viscosity. Presenting these data in another way as in Figure 5 shows that plots of sludge content vs total solids content are linear at constant viscosity. None of these mixtures was considered a satisfactory fuel because either their sludge or total solids content was too low at the 1000cP pumpable viscosity for economic operation.

The rheological properties of sludge vary considerably with its treatment history as well as the nature and amount of industrial components in it. As can be seen in Figure 6, the sludge from City A has poor fluidity properties. This is attributable to its containing over 10% short paper fibers from nearby paper recycling plants. City D's sludge appeared to be quite fibrous also making it quite viscous relative to sludges from several cities compared in this figure. Among the factors influencing viscosities are the degree of digestion, the relative amounts of sludge from primary and secondary treatment and the solids content of the filter or centrifuge cakes produced from water treatment plants (Figure 7). Lime treatment, because it removes water from the slurry, also seriously degrades the fluidity of sludge.

Thermal Treatment

Previous work indicated that that thermal treatment of sludge would improve its slurrying characteristics. Innumerable studies (7,8) and a recent review (9) indicate that heat treatment of sludge coagulates the solids and breaks down the colloids and cells. Protein material is also denatured and microorganisms are killed. These changes combine to irreversibly reduce the water affinity of the sludge solids. Heat treated sludge is readily dewatered on filters to solids concentrations of 30 to 50%, while unheated sludge is usually dewatered to about 20 to 30% and only with the aid of polymeric or inorganic conditioning agents.

To examine the effects of thermal treatment on the slurrying characteristics of sludge solids, we obtained samples of sludge that had been thermally treated on a commercial scale in different types of dryers and thermal treatment units throughout the country. Dilute sludge slurries containing 5 to 25% solids are usually fed to

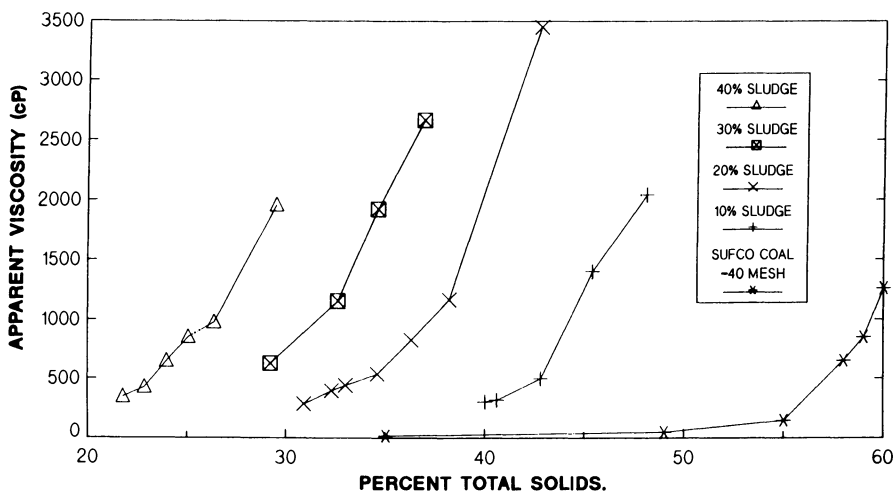


Figure 4. Viscosity concentration curves for mixtures of Los Angeles sludge and Utah Sufco coal.

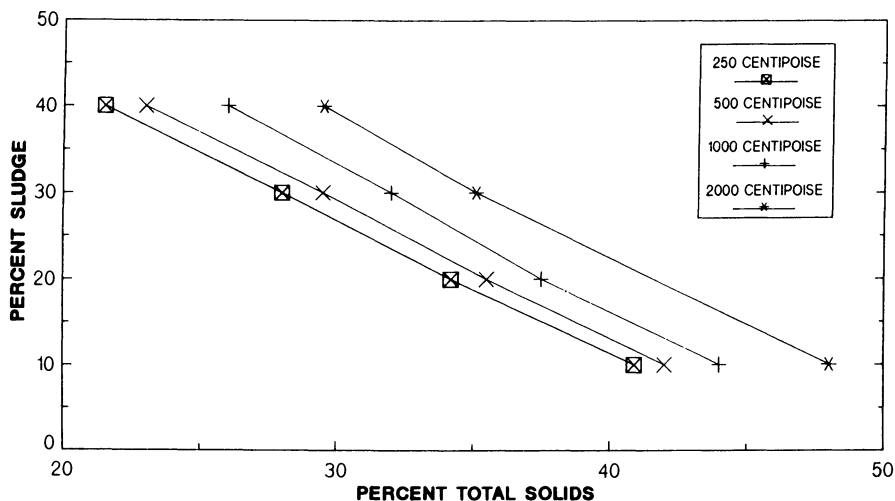


Figure 5. Plots of total solids content vs percentage sludge solids in slurries at selected constant viscosities.

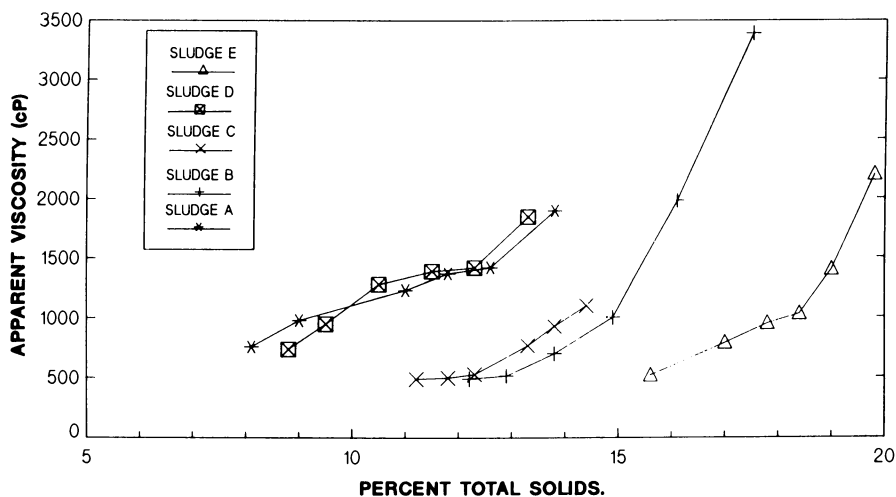


Figure 6. Rheological characteristics of sludge from different water treatment plants.

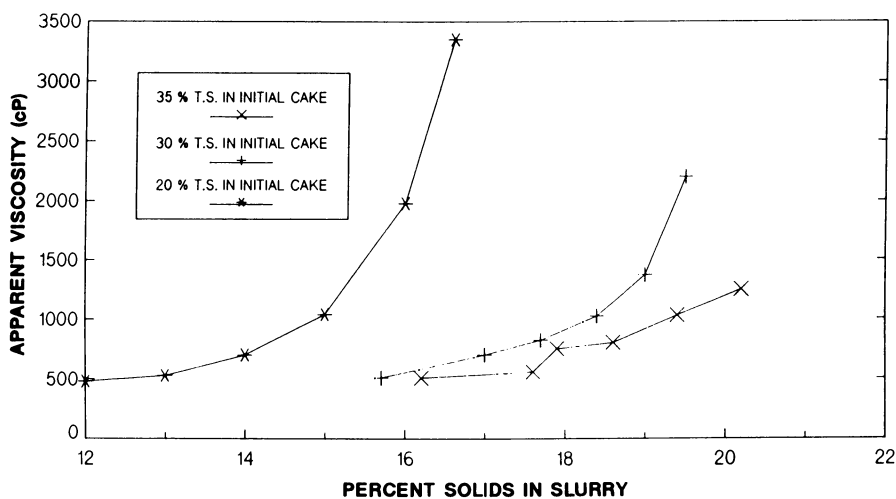


Figure 7. Effects of initial solids content of sludge cake on the apparent viscosities of slurries formed upon dilution.

these dryers. Thermal treatment over the wide temperature range encompassed by these processes did in general improve slurring properties (See Table II).

The products of various treatment processes are physically and compositionally different from raw sludge (Table III). Ash, carbon and oxygen contents vary with treating conditions. Some of the products are dry homogeneous powders somewhat coal-like in appearance while others are quite fibrous containing about 60% moisture. The moist products could not be ground into a powder satisfactorily for slurry testing without drying them first. After drying, they slurried very well.

Results of viscosity tests on slurries prepared from these materials are summarized in Table II. The slurring characteristics of the as-received sludges and of mixtures containing 30% sludge and 70% coal (dry basis) were routinely measured. Clearly, all of these materials demonstrated slurring characteristics far superior to those of untreated sludge. Compare the results in Figure 4 with those in Table II, for example. Some treated sludges were coal-like in slurry behavior hardly affecting the fluidity of the coal at low concentrations, while the other materials degraded the fluidity of the slurries to varying extents. For example, about 60% solids can be included in a 1000 cp pumpable slurry of coal alone. But the solids contents of mixtures containing 30% sludge and 70% coal having viscosities of 1000 cp ranged from 45 to 58.5%. This behavior is not unexpected since these materials have not only been heated at different temperatures but also under different conditions. In one process, sludge is heated while suspended in oil allowing oil soluble compounds to be extracted from it, while in others, organic components in sludge are oxidized or simply volatilized.

Thermally dried sludge could also be slurried in oil but the viscosity of the slurring oil determined to some extent the amount of slurry solids that could be included in a pumpable mixture.

Overall, the rheological characteristics of raw and treated sludge were found to be very consistent. Plotting the total solids in a 1000 cp slurry of as-received or treated sludge against the maximum total solids of the same material that could be incorporated into a 1000 cp 30% sludge/70% coal slurry afforded the linear relationship shown in Figure 8.

Effect of Shear

The rheology of a thermally treated sludge as a function of shear rate is shown in Figure 9. These results, which were obtained with a Haake RV-100 viscometer, show that the viscosity of dried sludge is dependent upon shear rate and temperature--with the viscosity decreasing, for example, from about 900 cp to a little over 400 cp as the temperature is increased from 30 to 90 degC. Basically, dried sludge particles are very friable with no real structure--and break quite readily under shearing stress.

Table II
Slurrying Characteristics of Commercially Available
Thermally Treated Sludges

Process	Max Temp, F	% Ash	Slurry Composition Sludge & Coal %	Total Solids at 1000 CP
A	250	50.9	30 100	51.0 36
B	1200	32.29	30 100	58.5 48.2
C	365	33.8	30 100	45 30
D	358	44.0	30 100	62 53

Table III
Analyses of Dried Sludge from Various Processes

	Los Angeles as Received	Process A	Process B	Process C	Process D
% Moisture	80.20	3.03	7.93	2.79	9.20
% Ash	36.30	50.90	32.29	31.38	44.00
% C	31.30	30.47	34.70	33.80	28.90
% H	4.83	4.48	4.99	5.32	3.80
% N	3.92	3.95	5.51	2.57	3.20
% S	1.65	1.60	0.71	0.63	1.10
% O (By Diff)	22.00	8.60	21.80	26.30	19.00
BTU Value Lb/Dry	6140	5856	6797	6304	4886

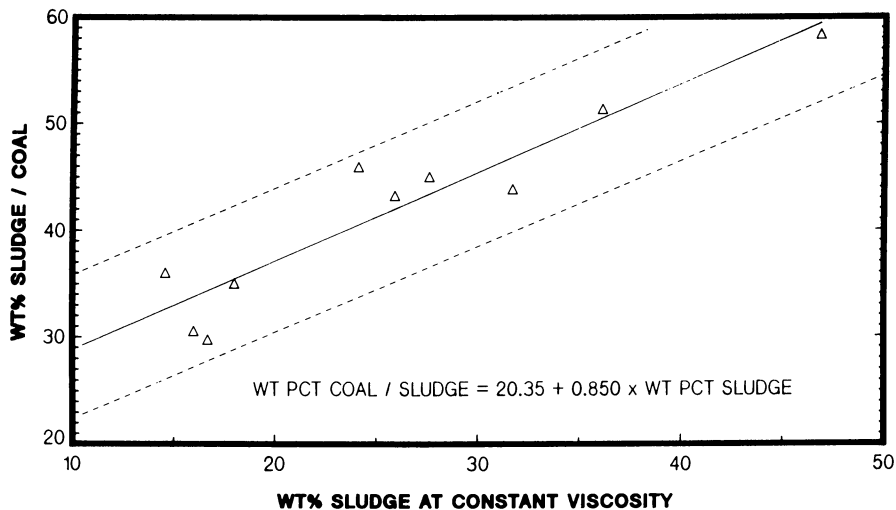


Figure 8. Plots of solids contents of 1000cp slurries of raw and treated sludge vs solids contents of 1000cp slurries of 30/70 sludge/coal slurries.

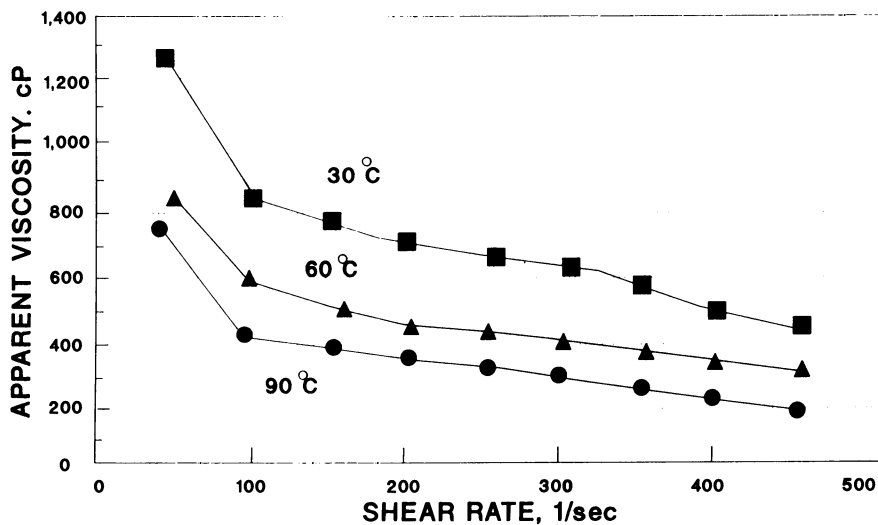


Figure 9. Apparent viscosity vs shear rate plots for a 38wt% solids slurry of dried sludge in water.

Their breakdown is probably non-reversible although no attempts were made to prove it.

Raw sludge is also quite unstable to shearing stress. Hatfield (10) many years ago and others more recently (4) reported that shearing reduces the viscosity of sludge. Results reported here using sludge containing high concentrations of solids are consistent with the previous reports. As would be expected, more of this sheared product could be incorporated into a pumpable slurry than the "as-received" sludge.

A picture of what may be occurring when sludge is sheared is shown in Figure 10. The sludge being sheared consists of coagulated and flocculated colloidal sludge particles. The particles are coagulated with the aid of positively charged polymers, usually polyamides, which neutralize the negatively charged colloidal particles. The observed viscosity reduction is no doubt attributable to at least two factors: the first of these is the simple shearing of the cellulosic and polyamide flocculating polymers in the sludge. The second is a consequence of the shearing stresses on the flocculated colloidal particles. The drag forces and unfolding of the flocculated particles probably release trapped water and make it available as a carrier fluid with a consequent decrease in viscosity.

High Intensity Press Treatment

To further establish the effects of water removal on the patterns of sludge behavior, dewatering of sludge was achieved by an advanced dewatering technique: high intensity pressing (HIP). A schematic of how a HIP operates is depicted in Figure 11. Quite simply, filter cake from a conventional belt filter, which contains 15 to 25% solids, is fed to a high intensity press where it is subjected to increased mechanical pressure to remove water. HIP applied a pressure of 125 psi compared to only 25 psi for a conventional belt filter press. As described in the experimental section, we simulated the HIP treatment in the laboratory.

This treatment improved the rheological properties of sludge--increasing the amount of solids that can be included in a 1000cp pumpable slurry from about 12 to 16% (Figure 12). Worth noting is that high intensity pressing is a way of applying a high shear to sludge.

Vacuum Drying

Results of the shearing and thermal treatment experiments indicated that the most important aspect of improving the slurryability of sludge was to free the water trapped in the sludge. In the shearing case, the trapped water becomes available as part of the carrier fluid while thermal treatment simply volatilizes the water--apparently somewhat irreversibly. This suggested that removing water

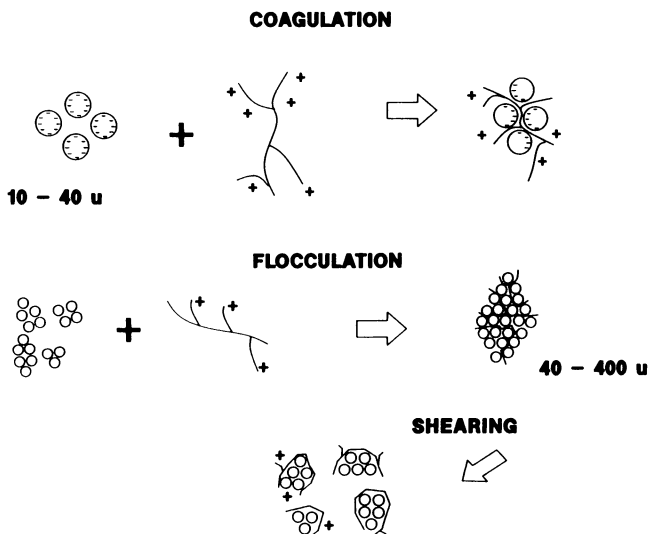


Figure 10. Conceptual diagram showing the formation of flocculated sludge particles from colloidal sludge particles using cationic polymers and their breakup by shearing stress. Adapted from reference 11.

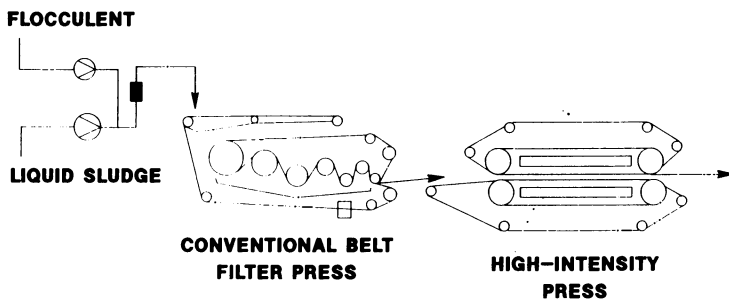


Figure 11. High intensity press flow scheme.

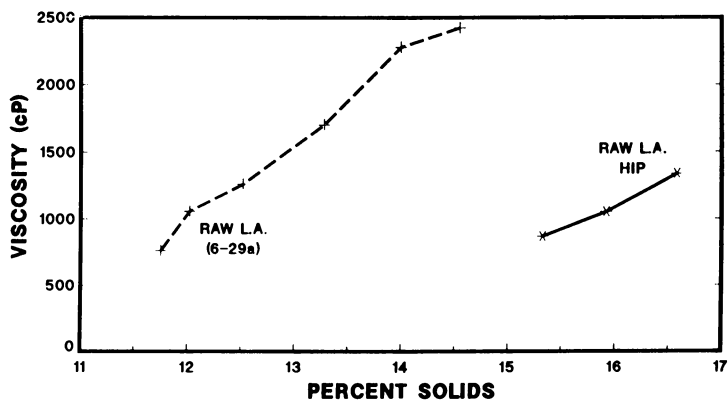


Figure 12. Effect of HIP treatment on the rheological properties of Los Angeles sludge.

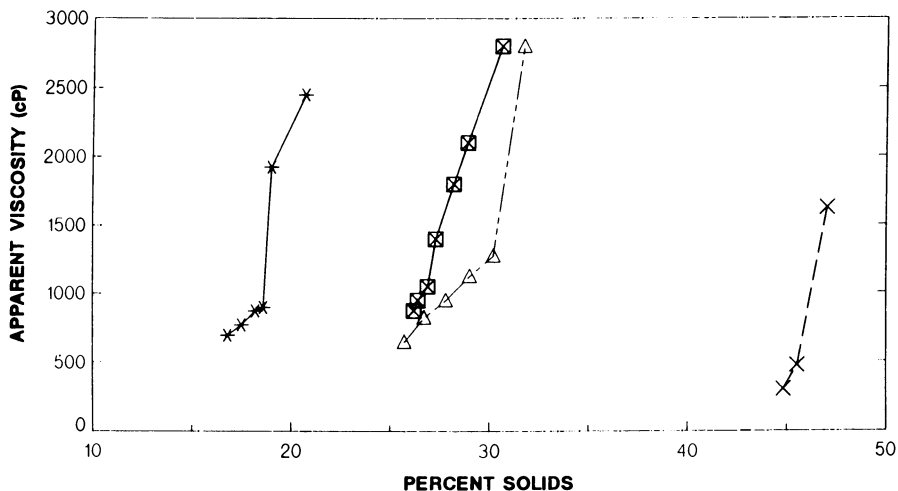


Figure 13. Comparison of the rheological characteristics of sludge which has been dewatered by different methods. * Raw sludge, 23.8% solids. X Raw sludge dried to 98.4% solids. □ Dewatered to 43% solids by vacuum drying. △ Dewatered to 45.3% solids by high intensity pressing.

by simple air or vacuum drying might improve the slurring characteristics of sludge. And indeed this was found to be true as can be seen in the results presented in Figure 13. Also included in this figure are the results of another experiment in which the same amount of water was removed by vacuum drying and by high intensity pressing. These techniques both afforded products having similar rheological properties

Summary

In an effort to explore various means for treating sewage sludge in order to improve its slurring characteristics with coal, it has been found that virtually all means of removing water trapped in the raw sludge centrifuge filter cake including thermal treatment, shearing, vacuum drying and simple air drying will improve the slurring characteristics.

Acknowledgments

We would like to express our appreciation to Ronald J. McKeon and Christine A. Albert for their contributions to the work which made this paper possible.

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Chapter 14

Metal Emissions Control Technologies for Waste Incineration

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Control of metals emissions from municipal, hospital, and hazardous waste incinerators has recently been mandated in regulations proposed by the U.S. Environmental Protection Agency. An understanding of regulatory requirements and control technologies is needed to select the most cost-effective system for site-specific applications. This chapter presents a review of the current U.S. regulations covering incinerator emissions and describes technologies used for their control. Typical emission levels and control efficiencies achievable are presented.

A major issue facing industrialized nations is the environmentally sound disposal of municipal solid wastes, hospital wastes, and industrial hazardous wastes. The amounts of these wastes generated have grown annually over the past several decades (1), and improper disposal has resulted in numerous environmental problems. Incineration in properly designed combustion systems has been demonstrated as a method of achieving a very high degree of destruction and control of these wastes. Incineration is often combined with heat recovery systems to simultaneously recover energy in the form of steam or electricity. A wide variety of incinerator types, boilers, and industrial furnaces are used for destroying these wastes.

Incineration of municipal and hazardous waste has the potential for increasing air pollution due to emissions of constituents contained in these waste streams and products of their combustion. These wastes are likely to contain sulfur and chlorine compounds, as well as numerous toxic metals (e.g., arsenic, beryllium, cadmium, chromium, lead, mercury, and silver). Highly chlorinated hydrocarbons and polynuclear aromatic compounds such as dioxins and furans may also be present. During combustion, sulfur and chlorine compounds are converted to the acid gases SO_2 and HCl ; toxic metals are converted to their oxide or chloride forms. The high combustion

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temperatures employed in modern incinerators will cause many of the metal compounds present to volatilize and be carried out of the incinerator in the hot flue gas stream. These compounds can then condense out as fine particulate matter or in some instances leave the system while still in vapor form. High combustion temperatures and residence times are used, as they have been shown to effectively destroy complex organic compounds which may be in the waste stream.

The increase in waste incineration has been accompanied by increased public concern over air pollution and an increase in local, state, and federal regulations. The USEPA recently revised federal regulations to further limit incinerator emissions. This increased regulatory climate has resulted in an increase in the complexity and efficiency of air pollution controls employed for emissions control.

This paper presents a review of the current U.S. regulations covering incinerator emissions and describes technologies used for their control. Typical emission levels and control efficiencies achievable for various metals are presented.

Air Pollution Regulations

Air pollution regulations governing incinerator flue gas emissions vary widely in the compounds controlled, emission levels allowed, removal efficiencies required, averaging times used, and testing requirements. On the national level, municipal waste incinerators are regulated under Clean Air Act (CAA) provisions, whereas hazardous waste incinerators are regulated under the Resource Conservation and Recovery Act (RCRA). In addition to national regulations, local or state permitting agencies may require more stringent emissions controls or control of additional pollutants as part of a facility's operating permit. The EPA has recently been active in setting standards for municipal waste incinerators, hazardous waste incinerators and boilers, and industrial furnaces which burn hazardous wastes. The EPA is currently in the process of setting regulations for hospital waste incinerators.

Municipal Waste Incinerators. The EPA promulgated "New Source Performance Standards and Emissions Guidelines for Existing Facilities" for Municipal Waste Combustors (MWCs) in February 1991 (2). These standards are summarized in Table I.

In setting these standards, EPA recognized differences in facility size, type of incineration (mass burn fired versus refuse derived fuel fired), and new sources versus existing sources. The facility capacity refers to the total burn rate for all refuse combustors at a single site. EPA selected total particulate matter emission limits as a way of controlling trace toxic metal emissions. EPA will add emission limits for mercury, cadmium, and lead in the coming year based on applying Maximum Achievable Control Technology (MACT). EPA has until late 1992 to establish comparable emission standards for smaller combustors, those less than or equal to 250 tons per day per train.

Opacity limits are set at 10 percent and must be continuously monitored. Opacity is used as an indication of particulate matter emissions.

Table I. USEPA Municipal Waste Combustion Emission Standards^o

	New Source Performance Standards		Emission Guidelines For Existing Facilities	
	Unit	Unit	Facility	Facility
Capacity (tons/day)	>250	>250 ≤ 1100	>1100	>1100
Particulate Matter (gr/dscf)	0.015	0.030	0.015	0.015
Opacity (%)	10	10	10	10
Organic Emissions (ng/dscm) Total Chlorinated PCDD Plus PCDF*				
-Mass burn units	30	125	60	60
-RDF fired units	30	250	60	60
Acid Gas Control % Reduction or Emissions (ppm)				
HCl	95 (25)	50 (25)	90 (25)	90 (25)
SO ₂	80 (30)	50 (30)	70 (30)	70 (30)
NO _x	(180)	None	None	None
Carbon Monoxide (ppm)	50-150**	50-250**	50-250**	50-250**

- ^o All emissions limits are referenced to dry gas conditions at 20°C and 7% oxygen.
- * PCDD - Polychlorinated Dibenzodioxins; PCDF - Polychlorinated Dibenzofurans.
- ** Range of values reflect differing types of MWC's.

Cumulative emission limits have been established for polychlorinated dibenzodioxins (PCDD) plus polychlorinated dibenzofurans (PCDF). These compounds were selected as surrogates for organic emissions because of their potentially adverse health effects. In addition, EPA has established carbon monoxide (CO) emission limits as a measure of "good combustion practices"

to limit the formation of PCDD, PCDF, and their key precursors. CO emission limits vary from 50 to 150 ppm (7% O₂ dry gas conditions) depending on the type of combustion.

Acid gas emissions limits (HCl and SO₂) are based on either a percent reduction or a maximum stack emission level, whichever is least stringent. Nitrogen oxide (NO_x) emissions levels are proposed only for large new sources.

Hazardous Waste Incinerators. In April 1990, the EPA published a proposed rule and requests for comments in the Federal Register for Standards for Owners and Operators of Hazardous Waste Incinerators and Burning of Hazardous Wastes in Boilers and Industrial Furnaces (3). The final rules for "Burning Hazardous Waste in Boilers and Industrial Furnaces" were published in the Federal Register in February 1991 (4). Key provisions of these regulations are presented in Table II.

Table II. USEPA Proposed Hazardous Waste Incineration Standards

Destruction and Removal Efficiency (DRE)		99.9999% Dioxin-Listed Wastes	
		99.99% All Other Wastes	
Particulate Matter		0.08 gr/dscf @ 7% O ₂	
Carbon Monoxide (Tier I)		100 ppmv (d) @ 7% O ₂	
Hydrocarbons (Tier II)		20 ppmv (d) @ 7% O ₂	
Continuous Emissions Monitoring		CO, O ₂ , HC	
<u>Tier III Reference Air Concentrations</u> (annual limits, μ g/m ³)			
Hydrogen Chloride	0.7	Free Chlorine	0.4
<u>Carcinogenic Metals</u>		<u>Non-Carcinogenic Metals</u>	
Arsenic	2.3×10^{-3}	Antimony	0.3
Beryllium	4.1×10^{-3}	Barium	50
Cadmium	5.5×10^{-3}	Lead	0.09
Chromium	8.3×10^{-4}	Mercury	0.3
		Silver	3
		Thallium	0.3

EPA proposed extending current emissions limits covering Destruction and Removal Efficiencies for organic constituents and for particulate matter. EPA

also proposed establishing risk-based emission limits for individual toxic metals, hydrogen chloride, and organic compounds. EPA added limits for chlorine when they published their final rule for boilers and industrial furnaces (BIFs) (4). Reference Air Concentrations (RACs) were proposed for maximum modeled annual average ground concentrations of these pollutants. RACs for the carcinogenic metals were set at levels which would result in an increased cancer risk for a Maximum Exposed Individual of less than 1 in 100,000. RACs for the non-carcinogenic metals and chlorine were set at 25 percent of the Reference Dose (RfD) with the exception of lead, which was set at ten percent of the National Ambient Air quality level. The RAC for HCl is based directly on inhalation studies. RfD's are estimates of a maximum daily exposure (via injection) for the human population that is not likely to cause deleterious effects.

In setting these standards, EPA established a three tiered approach for demonstrating compliance. The tiers are arranged from the easiest to demonstrate and most conservative to the more complex to demonstrate and less conservative. Compliance with any tier is considered to prove compliance with these regulations.

- Tier I EPA established conservative maximum feed rates (lb/hr) for each constituent as a function of effective stack height, terrain and land use. In setting these limits, EPA assumed no partitioning in the incinerator, no removal in an air pollution control system, and reasonable worst case dispersion. Demonstration of compliance is through monitoring of feed composition. Two examples of Tier I screening limits are 2.4×10^{-4} to 4.1×10^{-3} for arsenic and 9.4×10^{-3} to 1.6 pounds per hour for lead, depending on stack height, terrain, and land use.
- Tier II EPA established conservative emission rate limits for each constituent as a function of effective stack height, terrain, land use and assumed reasonable worst case dispersion. Demonstration of compliance is through periodic stack emission testing and continuous emission monitoring of carbon monoxide, hydrocarbons and oxygen. Two examples of Tier II screening limits are 3.1×10^{-5} to 5.3×10^{-3} grams per second for arsenic and 1.2×10^{-3} to 2.0×10^{-1} grams per second for lead.
- Tier III EPA established RACs which must be met for each component. Demonstration of compliance is through periodic emissions testing and site specific dispersion modeling to demonstrate actual (measured) emissions do not exceed RACs. For the carcinogenic metals, the ratios of each metal's measured value to its RACs are added to give a cumulative value which must be below 1.0 (risk of 1 in 100,000). Tier III RACs for all metals are shown in Table II.

The standards will be implemented through limits on specific incinerator and air pollution control system operating parameters. In addition, emissions

testing of all dioxin/furan tetra-octa congeners, calculation of toxic equivalents, dispersion modeling, and health risk assessments will be required for incinerators equipped with dry particulate control devices (electrostatic precipitators or fabric filters) operating at an inlet temperature between 450° and 750°F, or if hydrocarbon emission levels exceed 20 ppmv (d) (4).

EPA also established a requirement for continuous emissions monitoring of stack carbon monoxide (CO), oxygen (O₂), and total hydrocarbons (HC). Compliance with Products of Incomplete Combustion (PICs) limitations will be demonstrated through monitoring data that meet specified rolling hourly averages for CO and HC. If these emissions levels are not achieved, then the incinerator operator must demonstrate PIC compliance through dioxin/furan emissions measurements, toxic equivalent calculations, and health-risk assessments.

Air Pollution Controls

The major fraction of toxic metals found in incinerator flue gases exists as fine particulate matter, although a significant fraction of some metals can exist in the vapor phase at typical incinerator exit flue gas conditions. The fraction of toxic metals present in the vapor phase is a function of the specific metal and its chemical form, the combustion conditions, and the flue gas temperature.

Control of the particulate fraction is achieved by utilizing traditional particulate control devices. Control of the vapor phase fraction is achieved through cooling of the flue gas and collection of the fine particulate thus formed. Table III lists the types of controls typically employed to control toxic metals.

Table III. Toxic Metal Controls

<u>Fraction</u>	<u>Control Device</u>
Particulate	Electrostatic Precipitators Fabric Filters Wet Scrubbers
Vapor Phase	Spray Dryer Absorbers Wet Scrubbers Condensing Wet Scrubbers

Particulate Metals Fraction Control. Traditionally, particulate matter control from incinerator flue gases was achieved utilizing either a wet venturi scrubber or an electrostatic precipitator (ESP). As emissions regulations have become more stringent and control of the fine particulate fraction has become more important, there has been a shift to using fabric filters and combinations of ESP with wet scrubbers.

Electrostatic Precipitators. Electrostatic precipitators collect particulate matter along with toxic metals and trace organics condensed on it by introducing a strong electrical field in the flue gas, which imparts a charge to the particles present. These charged particles are then collected on large plates which have an opposite charge applied to them. The collected particulate is periodically removed by rapping the collection plates. The agglomerated particles fall into a hopper, where they are removed. Key design parameters for ESP's include: particulate composition, density, and resistivity; flue gas temperature and moisture content; inlet particulate loading and collection efficiency; specific collection area (SCA = square feet of collecting surface per 1,000 cubic feet of flue gas); number of fields; flue gas velocity; collector plate spacing; rapping frequency and intensity; and transformer rectifier power levels.

Properly sized ESP's applied to waste incinerators can reduce particulate matter emissions to the range of 0.01 - 0.015 gr/dscf and achieve collection efficiencies of greater than 95 percent of fine particulate. These ESP's would typically have 3 to 5 collecting fields, specific collecting areas of 400 to 550, flue gas velocities of 3 to 3.5 feet per second, and transformer rectifiers capable of supplying secondary power levels of 35-55 KV at 30-50 milliamps per 100 square feet of collecting area. ESP sizing for hazardous waste incinerator application presents a challenge because of the wide range of materials which may be incinerated.

Fabric Filters. Pulse-jet-type fabric filters are typically used for particulate, toxic metal, and trace organics emissions control for waste incinerators. Fabric filters are always installed downstream of a quenching device because of temperature concerns and to minimize the chance of burning embers reaching the fabric. Fabric filters achieve particulate emission levels between 0.01 and 0.015 gr/dscf and fine particulate control greater than 99 percent.

Fabric filters offer some significant advantages over ESP's for waste incinerator applications. Fabric filters are relatively insensitive to ash properties, flue gas conditions, or operating loads. Fabric filters are more efficient chemical reactors when they are applied as a component of a spray dryer absorption system. They appear to achieve higher control efficiencies for toxic metal and trace organic compounds.

Fabric filters also have some limitations when compared to ESPs. They have a narrower range of operating temperatures. Under some operating conditions, the fabric is subject to blinding, with an associated high-pressure drop and shortened bag life. Fabric filters are more prone to corrosion problems due to their inherent design and operation. Selection of either an ESP or fabric filter should be based on an overall evaluation of site-specific conditions and requirements.

Wet Scrubbers. Wet scrubbers are generally used for particulate control in waste incineration applications that do not require very low emissions of total and fine (< 10 micron) particulate, or where the inlet loading is not too high. Wet scrubbers used for particulate control include: venturi scrubbers, wet

ionizing scrubbers, and condensation scrubbers. Venturi scrubbers are used as a primary particulate control device for flue gas with high particulate loadings. Ionizing wet scrubbers and condensation scrubbers are normally used as a part of a total control system where inlet particulate loadings are low. Figure 1 shows a schematic of a common venturi scrubber design used for particulate and acid gas control.

Flue gas enters the venturi, where it is contacted with water sprays and is accelerated to a high velocity (100-150 feet per second) through the venturi. The primary mechanism for particulate removal is impaction with water droplets, although some condensation also takes place. From the venturi, the flue gas stream enters a second stage, where liquid de-entrainment takes place. The second chamber may contain sprays or packing where an alkaline reagent is introduced to remove acid gases present. The flue gas may then pass to another scrubber type for additional particulate and toxic metal control.

Vapor Phase Metals Control. Vapor phase toxic metals are removed from the flue gas stream through condensation and collection of the particulate formed. This is typically accomplished in a two-step process. The most commonly employed systems are spray dryer absorption systems. Also employed are two-stage processes utilizing an ESP followed by a wet scrubber designed for fine particulate removal.

Spray Dryer Absorption Systems. Spray dryer absorption (SDA) has been widely applied for waste incinerator emissions control and has demonstrated high collection efficiencies for most toxic metals present in the flue gas. SDA has been specified as best available control technology (BACT) in a number of municipal waste incinerator air permits.

Figure 2 shows a simplified process flow diagram of the SDA process. The SDA system is comprised of a reagent preparation system, a spray dryer absorber, and a dust collector. Incinerator flue gas enters the spray dryer, where it is contacted by a cloud of finely atomized droplets of reagent (typically hydrated lime slurry). The flue gas temperature decreases and the humidity increases as the reagent slurry simultaneously reacts with acid gases and evaporates to dryness. In some systems a portion of the dried product is removed from the bottom of the spray dryer, while in others it is carried over to the dust collector. Collected reaction products are sometimes recycled to the feed system to reduce reagent consumption.

Several different spray dryer designs have been employed for incinerator SDA applications. These include: single rotary, multiple rotary, and multiple dual fluid nozzle atomization; downflow, upflow, and upflow with a cyclone pre-collector; and single and multiple gas inlets. Flue gas retention times range from 10 to 18 seconds, and flue gas temperatures leaving the spray dryers range from 230° to 400°F (5).

Toxic metals removal in the dust collector is enhanced by cooling of the incoming flue gas (from 2,000° to 450°F) as it passes through the spray dryer. Subsequent to the cooling, some vaporized metals condense to form fine particulates, which grow through impaction and agglomeration with the very

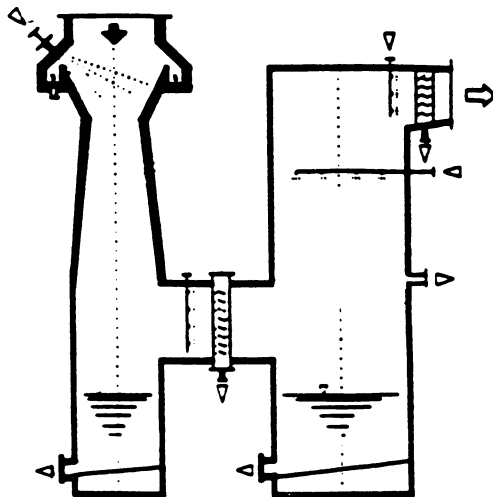


Figure 1. Venturi with Spray Scrubber

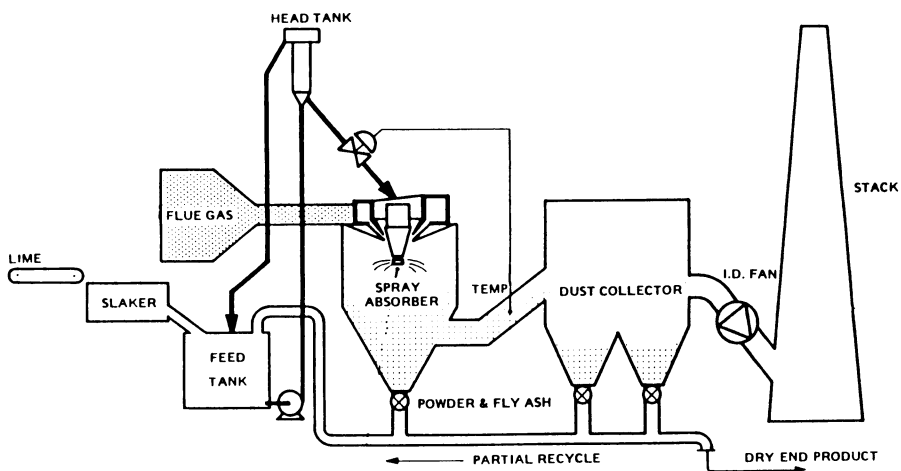


Figure 2. Spray Dryer Absorption Process

high number of lime droplets produced by the atomization devices. These agglomerated particles are then easily removed (6).

Generally, the lower the spray dryer outlet temperature, the more efficient is the acid gas absorption and vaporized toxic metals removal. The minimum reliable operating outlet temperature depends on the spray dryer and dust collector design and on the composition of the dry fly ash reaction product. The spray dryer outlet temperature must be maintained high enough to ensure complete reagent evaporation and the production of a free-flowing product. Low outlet temperature operation requires efficient reagent atomization, good gas dispersion and mixing, adequate residence time for drying, and dust collector design that minimizes heat loss and air in-leakage.

The dust collector downstream from the spray dryer may be an electrostatic precipitator, a reverse-air baghouse, or a pulse-jet type baghouse. The selection of dust collector type is dependent on site specific factors such as particulate emission limits, overall acid gas removal requirements, and project economics. Each of the dust collection devices offers process advantages and disadvantages that need to be evaluated on a site specific basis. When strict acid gas control is required, (95+ % HCl, 85+ % SO₂), baghouses are generally utilized, as they are better chemical reactors than electrostatic precipitators. Toxic metals control efficiencies achievable with a SDA system are quite high (99+ %) except for the relatively volatile mercury. Mercury emissions, however, can be controlled at greater than 90 percent efficiency levels through the use of additives such as sodium sulfide or activated carbon (1,7).

Wet Scrubbers. Wet scrubbers control vapor phase emissions through gas cooling and collection of the resulting condensed fine toxic metal particulate. The most commonly used wet scrubbers for this type of service are the ionizing or electrostatically enhanced wet scrubbers and the condensing wet scrubber.

Electrostatically-enhanced scrubbers capture the condensed fine particulate by imparting a charge to the incoming particulate and then collecting these charged particles on neutral packing material or on negatively-charged collecting electrodes. Prior to entering the charged section of the scrubbers, the flue gas typically passes through a presaturation stage, where it is cooled to its adiabatic saturation temperature (140° - 180°F). The cooling causes a significant fraction of vapor phase metals to condense out either as fine particulate on the surfaces of existing particulate matter or on the surfaces of water droplets. These scrubbers also remove acid gases by reaction with an alkali that is added to the scrubber water. Typically, caustic or soda ash is used as the alkali.

Condensing wet scrubbers sub-cool the incoming flue gas to below its adiabatic saturation temperature. This causes a larger fraction of the vapor phase metals to condense and in addition causes water vapor to condense forming a large number of droplets to aid in the collection of the fine toxic metal particulate. Figure 3 shows major components of a condensing wet scrubber.

In this system flue gas enters a quench section where it is first cooled to its saturation temperature. The gas is then ducted to a condenser/absorber where it is contacted by a cooled reagent stream and further cooled to about 80° - 90°F. The flue gas (now containing condensed toxic metal particulate and water droplets) is passed to a collision scrubber, where the fine droplets impinge on a flat surface. Here the fine particulate and water droplets interact and agglomerate, resulting in particulate capture. The flue gas then passes through an entrainment separator for droplet removal and is discharged through the stack.

The reagent streams from the various scrubbing stages are combined and pumped to a cooling tower (or refrigeration system) for cooling prior to being recycled to the scrubbing system. Condensing wet scrubbers have achieved very high removal efficiencies for acid gases, toxic metal, and fine particulate matter.

Metals Emissions

Metals emissions can be effectively controlled from municipal, hospital, and hazardous waste incinerators. The types of controls typically employed vary with the type of incinerator and local regulatory requirements. Table IV presents data on typical emissions levels for municipal waste incinerators.

Table IV. Typical Refuse Incinerator Uncontrolled and Controlled Emissions

Pollutant	Uncontrolled Emissions	Controlled Emissions	Percent Reduction
Particulate Matter, gr/dscf	0.5-4.0	0.002-0.015	99.5+
Acid Gases ppm _{dv}			
HCl	400-100	10-50	90-99+
SO ₂	150-600	5-50	65-90+
HF	10-0	1-2	90-95+
NO _x	120-300	60-180	30-65*
Toxic Metals mg/nm ³			
Arsenic	<0.1-1	<0.01-0.1	90-99+
Cadmium	1-5	<0.01-0.5	90-99+
Lead	20-100	<0.1-1	90-99+
Mercury	<0.1-1	<0.1-0.7	10-90+
Total PCDD/PCDF ng/nm ³	20-500	<1-10	80-99

* Reference conditions - Dry Gas 20°C and 12% carbon dioxide.

SOURCE: Adapted from refs. 1 and 4.

The controlled emissions levels are typical of modern large municipal waste incinerators equipped with spray dryer adsorption pollution control systems.

Table V presents controlled emissions estimates for the major toxic metals found in hazardous waste incinerator flue gas.

Table V. Hazardous Waste Incinerator Emissions Estimates

	EPA* Conservative Estimated Efficiencies	Typical Actual Control Efficiencies	Typical Range of Emissions Rates
Particulate matter	99+ %	99.9+ %	0.005-0.02 gr/dscf
Arsenic	95	99.9+	1-5 $\mu\text{g}/\text{m}^3$
Beryllium	99	99.9	<0.01-0.1
Cadmium	95	99.7	0.1-5
Chromium	99	99.5	2-10
Antimony	95	99.5	20-50
Barium	99	99.9	10-25
Lead	95	99.8	10-100
Mercury	85-90	40-95+	10-200
Silver	99	99.9+	1-10
Thallium	95	99+	10-100

* Based on spray dryer fabric filter system or 4-field electrostatic precipitator followed by a wet scrubber.

SOURCE: Adapted from rdfs. 5-9.

The control efficiencies and emissions rates presented are based on the application of a spray dryer absorption system equipped with a fabric filter dust collector or a four-field electrostatic precipitator followed by a wet scrubber designed for fine particulate removal. All of the toxic metals can be controlled at greater than 99 percent efficiency except for mercury. High-efficiency mercury removal (95 percent) requires the use of an adsorption enhancer in the spray dryer absorption system or a condensing wet scrubber following a dust collector.

Conclusions

The increased use of incineration for control and destruction of municipal and hazardous wastes has led to increasingly stringent air pollution control

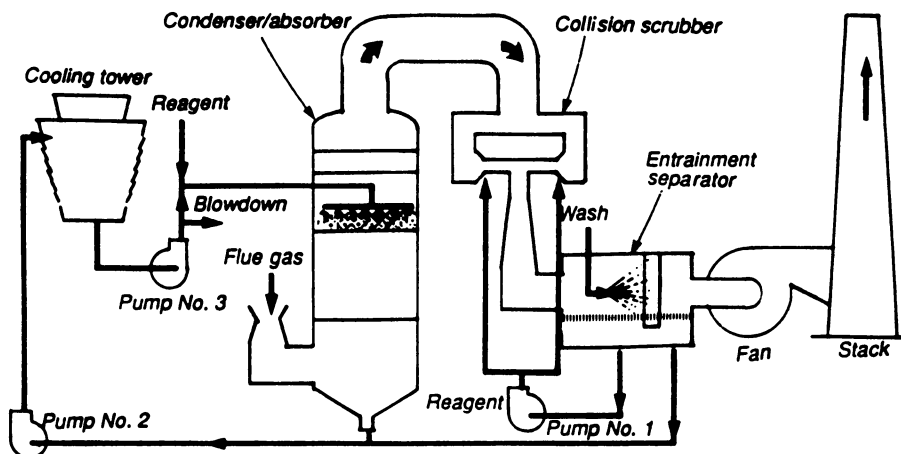


Figure 3. Condensing Flue-Gas Cleaning System

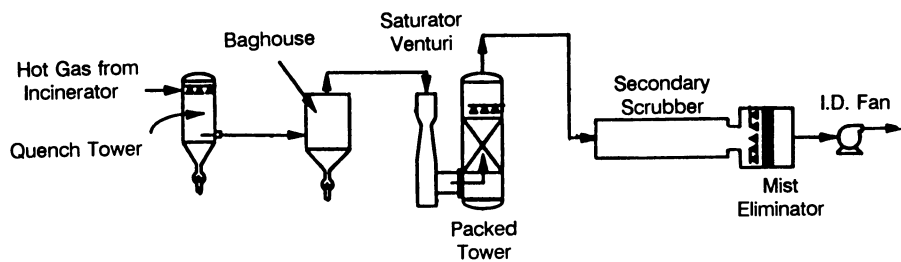


Figure 4. Combined Systems Approach - Emissions Control Scheme

regulations. EPA has recently promulgated New Source Performance Standards for municipal waste combustors which require health risk based emissions limits for specific metals to be established within the next year. EPA has also proposed hazardous waste incinerator emissions limits which include health risk based emissions limits for ten toxic metals. EPA is currently preparing new standards for hospital waste incinerators.

Spray dryer absorption is considered to represent BACT for many municipal waste incinerator applications and is capable of achieving high collection efficiencies for the metals of concern. Spray dryer absorption is also used for control of emissions from hazardous waste incinerators. Dust collectors with downstream wet scrubbers are also commonly used to control metals emissions from hazardous waste incinerators. Both systems have demonstrated the ability to achieve high collection efficiencies for the ten toxic metals proposed for regulation. Emissions rates of medium to large incinerators equipped with properly designed air pollution control systems can comply with current regulations.

Emissions levels of toxic metals from incinerators equipped with modern air pollution control systems are orders of magnitude lower than for 1980 levels. Current regulations are based on health risk assessments and set emissions limits that are highly protective of human health and the environment. Continued public concern regarding incinerator emissions, however, may result in additional and more complex control systems being required in the future. Figure 4 shows a combined systems approach to control incinerator emissions.

The quench tower and fabric filter would result in capture of the major fraction of toxic metals and greater than 99 percent removal of particulate matter. The venturi and packed tower scrubber stages would achieve additional toxic metal removal and act as acid gas control devices. The secondary scrubber would be a fine particulate control device and remove additional toxic metals. The subsequent mist eliminator might be followed by an activated carbon absorber for removal of any residual vapor-phase metals and toxic organic compound present in the flue gas.

Cleanup levels of greater than 99 percent for all major pollutants can be achieved by employing multiple control devices but at significant additional cost and loss of overall system reliability without significant increases in protection of human health or the environment. Industry, the public, and regulators must balance all factors in setting reasonable future emissions limits.

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Chapter 15

Metal Behavior During Medical Waste Incineration

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Toxic metals such as lead, cadmium, and mercury are contained in medical waste. Consequently, the incineration of medical waste may result in the emissions of trace metals into the environment, if incinerators are not properly designed and operated. EPA's Risk Reduction Engineering Laboratory initiated a study in 1988 to document what is known about medical waste treatment, particularly in the area of medical waste incineration. This paper is to summarize the findings from this study regarding the behavior of metals in incineration processes. Highlights of these findings are as follows: (1) Lead and cadmium are the two most-often-found metals in medical waste; (2) Metals can partition into different phases (gas, liquid or solid) but cannot be destroyed during incineration; (3) There are several potential pathways that metals follow to reach the environment. They exit incinerators with siftings, bottom ash, fly ash, scrubber waste, and flue gas; (4) Data on the capture efficiency of metals by air pollution control equipment used at medical waste incinerators is very limited; and (5) Wet scrubbers generally capture cadmium moderately well but normally perform poorly in removing chromium and lead. Fabric filter systems efficiently capture all metals.

Medical waste contains toxic metals such as lead, cadmium, and mercury. These metals will only change forms (chemical and physical states) but will not be destroyed during incineration. They can be emitted from incinerators on small particles capable of penetrating deep into human lungs. Thus, the emission of trace amounts of heavy metals from medical waste incinerators is one of the major concerns to those who are involved in medical waste management. A clear understanding of metals behavior in medical waste incinerators is critically needed.

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EPA's Risk Reduction Engineering Laboratory initiated a study in 1988 to document what is known about medical waste treatment, particularly in the area of medical waste incineration. Potential toxic metal emissions from medical waste incineration was one of main subjects studied. This paper is to summarize the findings of that study.

Metal Sources

University of California at Davis researchers conducted a study to identify the sources of toxic metals in medical wastes (1). The research effort focused on lead and cadmium because they were the two most-often-found metals in medical waste. They concluded that plastics in the waste contributed most to the presence of these two metals. Cadmium is a component in common dyes and thermo- and photo-stabilizers used in plastics. Lead was found in many materials including plastics, paper, inks, and electrical cable insulation. However, the primary source of lead appeared to be plastics. Like cadmium, lead is used to make dyes and stabilizers which protect plastics from thermal and photo-degradation. It is ironic to note that the dyes made from lead and cadmium are used to color plastic bags. Thus, part of the lead and cadmium emissions could be due simply to the "red bags" that infectious waste is placed in.

Under the authority of the hazardous waste program required by the Resource Conservation and Recovery Act, EPA has identified ten (10) metals of most concern from 40 CFR 261 Appendix VIII. Four of the ten metals are classified as carcinogenic and the other six metals are considered to be toxic. The EPA's Carcinogen Assessment Group has estimated the carcinogenic potency for humans exposed to low levels of carcinogens. An assigned "Unit Risk" indicates the relative health threat of the metals. Unit Risk (UR) is the incremental risk of developing cancer to an individual exposed for a lifetime to ambient air containing one microgram of the compound per cubic meter of air. Inhalation is the only exposure pathway considered in determining UR.

Data on toxicity are used to define concentrations for the six toxic metals below which they are not considered dangerous. Ambient concentrations should not exceed this concentration. The EPA has defined the maximum toxic concentration, or Reference Air Concentration (RAC), for each metal. If ground level concentrations of any of these metals exceeds its RAC, adverse health effects are likely. The Unit Risk of the four carcinogenic metals and the RAC of the six toxic metals are listed in Tables I and II.

Table I. Unit Risk (UR) Values for Four Carcinogenic Metals

Metals species	Unit risk
Arsenic (As)	0.0043
Beryllium (Be)	0.0025
Cadmium (Cd)	0.0017
Chromium (Cr ⁺⁶)	0.012

UR: incremental lifetime cancer risk from exposure to 1 µg/cubic meter

Table II. Reference Air Concentrations (RACs) for Six Toxic Metals

Metals species	RAC ($\mu\text{g}/\text{m}^3$)
Antimony (Sb)	0.025
Barium (Ba)	50.00
Lead (Pb)	0.09
Mercury (Hg)	1.70
Silver (Ag)	5.00
Thallium (Tl)	500.00

Emission Pathways

A majority of metal emissions is in the form of solid particulate matter and a minority is in vapor form. It was generally concluded that particulate emissions from the incineration of medical wastes are determined by three major factors:

- (1) Suspension of noncombustible inorganic materials;
- (2) Incomplete combustion of combustible materials (these materials can be organic or inorganic matter); and
- (3) Condensation of vaporous materials (these materials are mostly inorganic matter).

The ash content of the waste feed materials is a measure of the noncombustible portion of the waste feed and represents those materials which do not burn under any condition in an incinerator. Emissions of noncombustible materials result from the suspension or entrainment of ash by the combustion air added to the primary chamber of an incinerator. The more air added, the more likely that noncombustibles become entrained. Particulate emissions from incomplete combustion of combustible materials result from improper combustion control of the incinerator. Condensation of vaporous materials results from noncombustible substances that volatilize at primary combustion chamber temperatures with subsequent cooling in the flue gas. These materials usually condense on the surface of other fine particles.

The transformation of mineral matter during combustion of metals-containing waste is shown in Figure 1. The Figure is self-explanatory. There are several potential pathways to the environment that metals may follow. Most metals remain in the bottom ash. A small fraction of the ash (on a weight basis) is entrained by the combustion gases and carried out of the primary chamber as fly ash. Volatile metals may vaporize in the primary combustion chamber and leave the bottom ash. These metals recondense to form very small particles as the combustion gases cool. Some of the entrained ash and condensed metals are captured

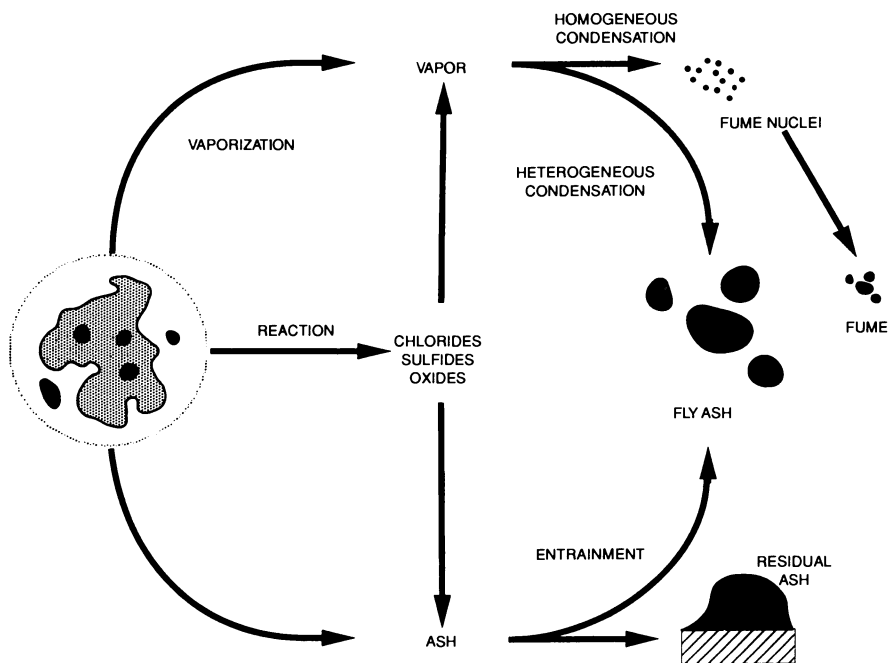


Figure 1. Metal transformation during incineration. Reproduced from ref. 2.

in the air pollution control equipment (APCE). The rest enters the atmosphere. Four key variables affecting the vaporization of metals are (2):

- Chlorine concentration in the waste;
- Temperature profiles in the incinerator;
- Metal species concentration in the waste; and
- Local oxygen concentration.

Current Control Practice

Typically, two strategies are used to minimize metals emissions: (1) The primary chamber is operated at conditions which do not promote vaporization or entrainment of metals; and (2) Any metals which do escape can be captured in the APCE, if present. The parameters usually used to control the escape of metals from the primary chamber are the primary chamber temperature and gas velocity. The key APCE parameters used are specific to the device which is utilized.

- (1) Combustion control: Most operating medical waste incinerators are simple single-chamber units with an afterburner located in the stack. The ability of batch incinerators to control metals emissions is limited because only the temperature in the stack is usually monitored.

Most new incinerators are starved-air units. The primary chamber is designed to operate at low temperatures and low gas flow rates. This minimizes the amount of materials entrained or vaporized.

To ensure that metal emissions are minimized, operators must maintain the primary chamber at the temperatures and gas flow rates for which it was designed. Usually the only parameter that system operators can directly control is feed rate. High feed rates can lead to high temperatures and high gas velocities. Thus, many operators carefully control the feed rate. The feed rate is reduced when primary temperatures increase.

- (2) APCE control: When metals reach the APCE, they are present in one of three forms. Non-volatile metals are on large entrained particles. Metals which have vaporized and recondensed are usually present on fly ash particles with diameters less than 1 micron. Extremely volatile metals are present as vapors. Table III summarizes the ability of common APCE to control these different metal forms. The Table is based on data and worst case predictions. Wet scrubbers are often used to minimize the temperature of the

flue gases. Use of low temperatures ensure that all metal vapors have condensed. As indicated in Table III, vapors are much more difficult to capture than particles (2).

TABLE III. Typical APCE Control Efficiencies

APCE	Control Efficiency (%)		
	Particulate	Fume	Vapor
Venturi scrubber 20" pressure drop	90	85	60
Venturi scrubber 60" pressure drop	98	97	90
Fabric filter	95	90	50
Spray drier/fabric filter	99	95	90

Emission Data

Figure 2 compares the concentration of arsenic (chosen merely for illustrative purposes) in flue gases before any APCE, and in emitted gases for a variety of incinerators. As shown, a wide variety of flue gas cleaning equipment is used. The Figure indicates the effectiveness of the various types of APCE. Arsenic is predicted to be relatively volatile, compared to other metals. Significant amounts of arsenic are therefore expected to vaporize in an incinerator. Figures 3 and 4 present similar data for the two most common metals found in medical waste, lead and cadmium (2).

Conclusion

Some metals and metal species found in medical waste are volatile and will vaporize at the conditions found in medical waste incinerators. The vapors are carried away from the waste by the exhaust gas and they recondense as the gas cools. The vapors condense both homogeneously to form new particles and heterogeneously on the surfaces of existing fly ash particles. To control metal emissions, metals which are of a highly volatile nature are of main concern in terms of installing the proper APCE. Because there are many APCE sizes and types, it is very important to fully understand metal emissions characteristics, combustion control and operating possibilities, and expected APCE performance so that metal emissions can be minimized from medical waste incinerators.

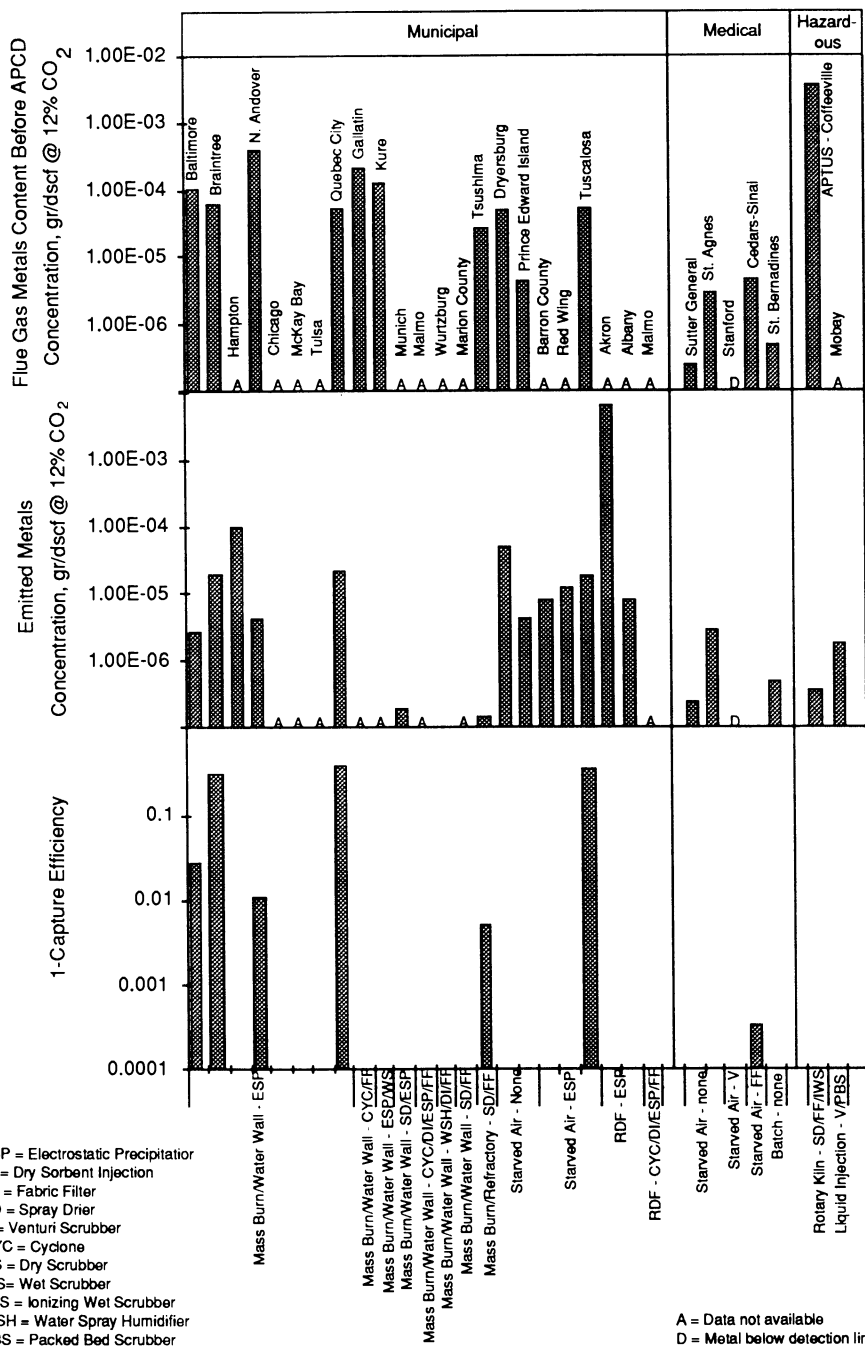


Figure 2. Arsenic emissions. Reproduced from ref. 2.

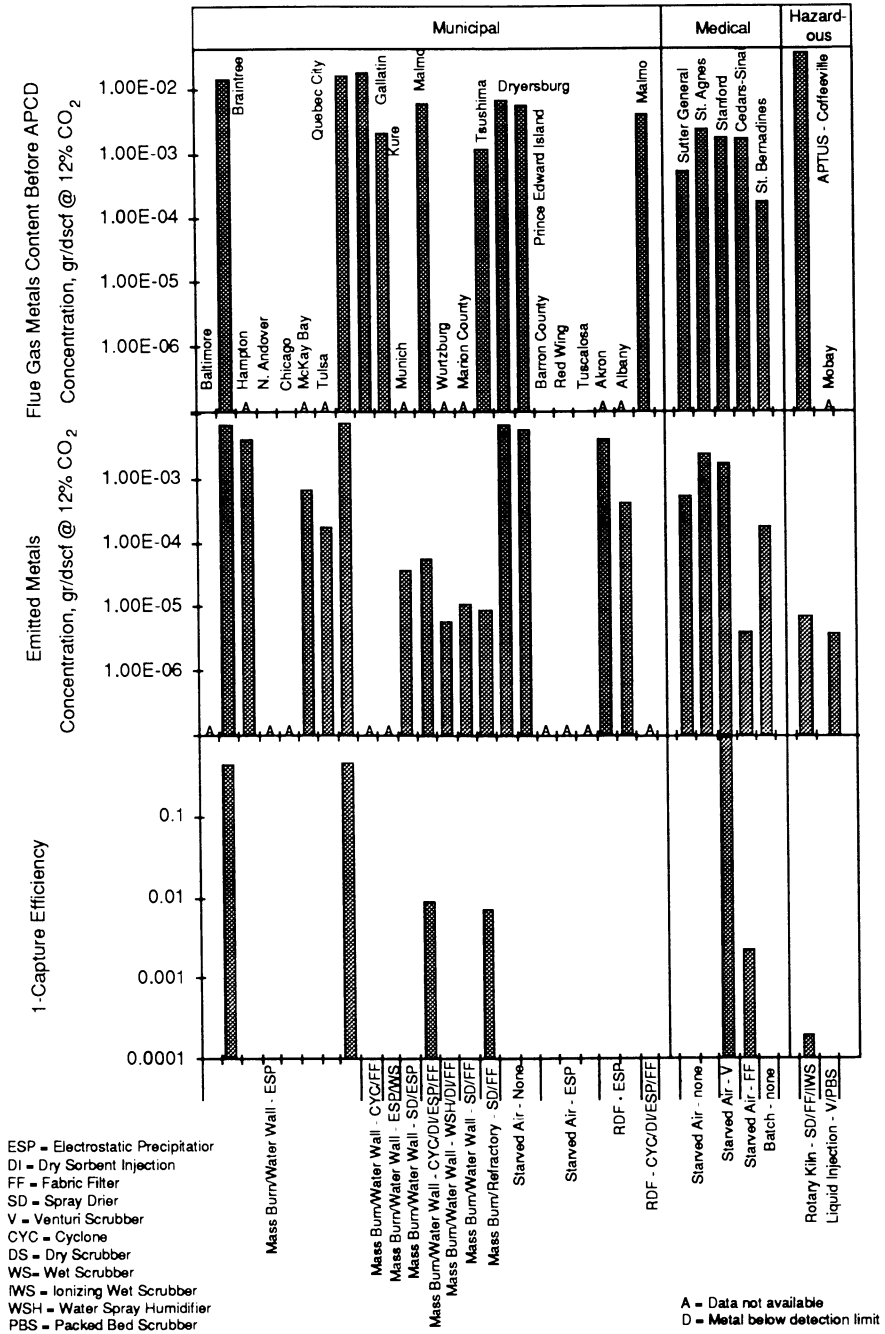


Figure 3. Lead emissions. Reproduced from ref. 2.

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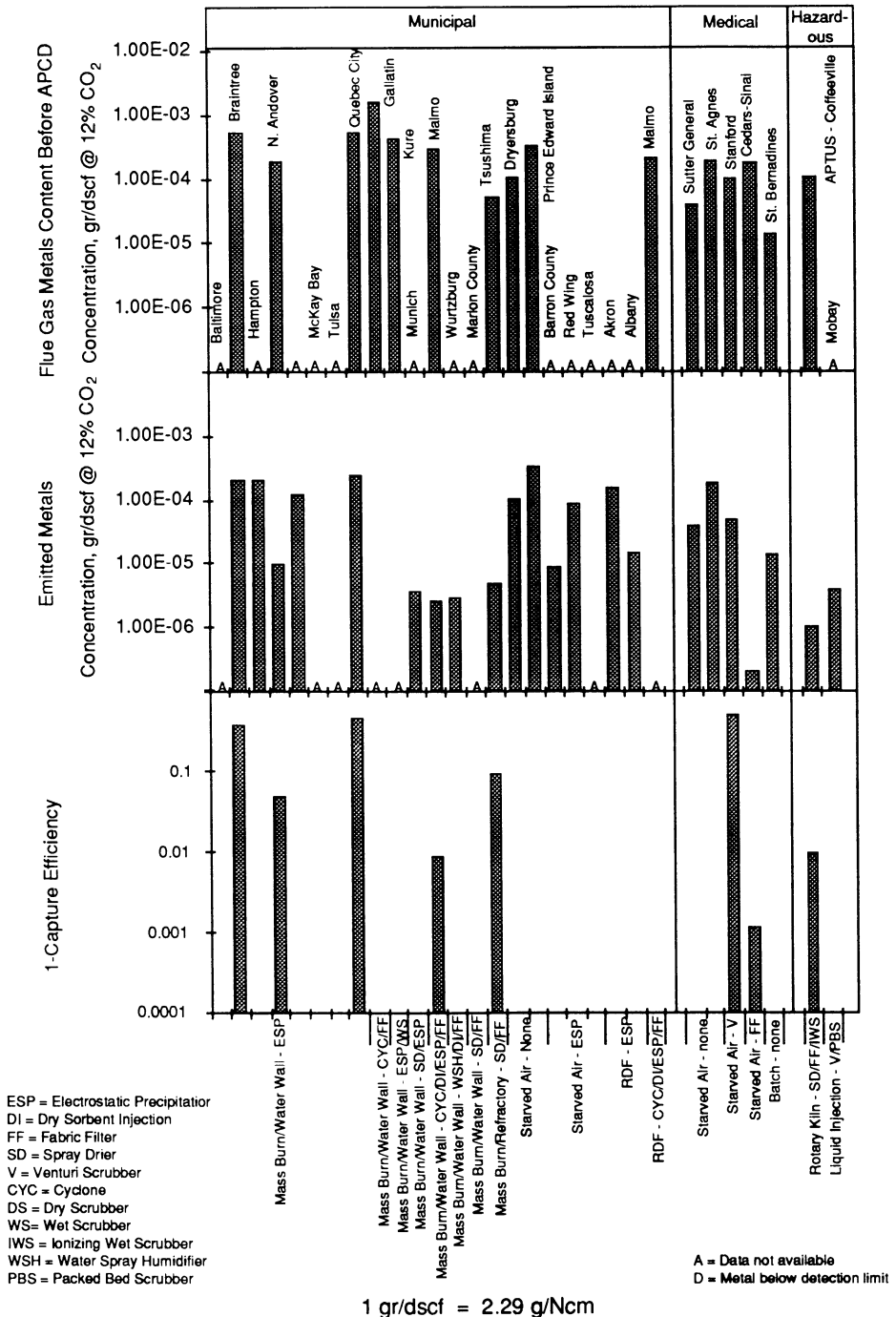


Figure 4. Cadmium emissions. Reproduced from ref. 2.

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Chapter 16

Trace Metal Analysis of Fly Ash from Combustion of Densified Refuse-Derived Fuel and Coal

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Analysis of the trace metals in fly ash produced from the combustion of quicklime binder enhanced densified refuse derived fuel (bDRDF) with coal is discussed.

In 1987 a full-scale cofiring of bDRDF and high sulfur coal was conducted at Argonne National Laboratories. About 567 tons of bDRDF pellets were cofired with coal at 0 to 50 percent bDRDF by Btu content and 0, 4, and 8 percent binder.

Analysis has continued on the samples acquired at Argonne. The fly ash was dissolved in a mixture of aqua-regia and hydrofluoric acid in a Parr bomb using a microwave dissolution method. The solution was then analyzed by Inductively Coupled Plasma (ICP) for As, Ba, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, V, and Zn. Results indicated that some trace elements decreased in fly ash with the increase in dRDF percentage while others increased.

The disposal of refuse is an increasing concern of municipalities and state governments throughout the U.S. Ten years ago there were approximately 10,000 sanitary landfills in the country. Currently there are less than 5,000. By the year 2000, many existing landfills will become filled to capacity, and new landfills will be more costly to site (1-3). The NIMBY syndrome, or Not IN My Back Yard, dominates peoples minds when it comes to siting new landfills. The development of an attractive disposal method is critical to overcome these problems.

There are three ways to dispose of Municipal Solid

Waste (MSW). It can be landfilled, dumped at sea or burned. Incineration is the major potential solution to the landfill problem (4-6). The conventional way to conduct incineration of MSW is called mass burn, in which the entire incoming garbage stream is run through a high temperature kiln. There are several potential problems with mass burn. Since all of the materials that are in the garbage stream are incinerated, there are high levels of metals in the ash. Because of the nature of the materials, there are also high levels of residual ash which can be up to 25 percent by weight and up to 10 percent by volume of the incoming MSW (5). Also, there are concerns about air emissions if the kiln temperatures are not kept at proper levels.

An increasingly attractive option is to separate the metals, aluminum, high density plastic, corrugated cardboard and glass from the incoming MSW so that they can be recycled. Then any remaining non-combustible materials are separated from the combustible materials that remain. These remaining combustible materials (approximately 50% of the MSW by weight) consists largely of paper. This can be ground and turned into an alternative energy source called Refuse Derived Fuel (RDF) which can then be cofired with coal. There is obviously a need to densify the material so that it can be transported to end users. Also, in order to reduce any chemical and biological degradation that might occur during storage, a binder material might need to be incorporated into the densified material.

Approximately 150 potential binders were tested at the University of North Texas (UNT), to be used as binding agents with RDF. This initial study took into account the cost and environmental acceptability of these materials to determine the best candidates to be used in pelleting trials. A commercial test of pelletizing RDF was conducted at Jacksonville, Florida, Naval Air Station in the summer of 1985 with the binder candidates that were identified earlier. Durability tests along with analysis of the effectiveness of the binder to impede degradation were conducted. The results of the test proved that quicklime ($\text{Ca}(\text{OH})_2$) is the best binder.

The material was then ready for full scale plant demonstration. This cofiring of RDF with coal was conducted at Argonne National Laboratories (ANL) in the summer of 1987 and involved the combustion of over five hundred tons of the binder enhanced dRDF with a high sulfur coal over a six week period. Over 1500 emission samples were collected from the combustion test and included flue gas emissions, fly ash, bottom ash, and feed stock samples.

There are two types of ash that result due the combustion of any material. Fly ash consists of fine

particulate matter that escapes in the flue gas. It is collected by electrostatic precipitators or baghouses, although approximately 1-2 percent of fly ash does escape to the atmosphere (3) even with the pollution control devices on-line. There is also bottom ash which is a courser material that drops through the grates in the furnace.

Fly ash is the major by-product of burning MSW (7,8). There are about 35,000 tons of fly ash produced for each million ton of waste incinerated (9,10). Fly ash consists of 70-95% inorganic matter and 5-30% organics (3). There are many constructive ways to use fly ash, including as an additive to improve the performance of Portland cement and as a soil stabilizer (11).

Since fly ash is the major by-product of incineration and incineration is the main attractive solution to landfills the physical and chemical characteristics of fly ash is important in determining its method of disposal or use (12). Trace metals are important because of their relationship to regulatory criteria under the Resource Conservation and Recovery Act (RCRA) regarding toxicity (13). Trace metals play a major role in whether a fly ash is hazardous and is disposed of or if it can be used in a productive way.

The most toxic elements of concern in ash are arsenic, barium, beryllium, cadmium, chromium, copper, mercury, nickel, lead, antimony, selenium, thallium, vanadium and zinc. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), was selected over other methods for determining these toxic elements because of the trace nature of the elements involved, the need for quantitation and the ability to determine all of the elements in the samples sequentially.

A microwave oven dissolution method was used to dissolve the ash in a mixture of aqua-regia and hydrofluoric acid using a Parr bomb. The solution was then analyzed by ICP.

Methodology

Fuel Preparation. The binder enhanced dRDF pellets for the 1987 ANL study were supplied by two facilities, one a 40 ton per day plant located at Thief River Falls, Minnesota (Future Fuel Inc.) and the other a 470 ton per day plant at Eden Prairie, Minnesota (Reuter Inc.). The dRDF was made with 0, 4, and 8 percent $\text{Ca}(\text{OH})_2$ binder.

Before each test run, dRDF pellets and coal were blended together using a front-end loader until the material appeared approximately homogenous. Due to differences in bulk densities and energy values of the materials, to produce a blend close to 10 percent dRDF by Btu content it takes a mixture of three volumes of a high-

sulfur Kentucky coal and one volume of dRDF . The blend was moved by front-end loader to the coal pit and transported by conveyor to coal bunker prior to use in the ANL stoker fired boiler. Nine tons per hour of the fuel mixture on average were burned.

Sampling Plan. A total of 567 tons of dRDF pellets were cofired with 2,041 tons of sulfur-rich coal in 12 separate test runs. The runs were classified according to the different Btu contents of dRDF in the fuel and different binder content of dRDF (Table I). Runs 1 and 12 used coal alone in order to establish base line data. To avoid cross-contamination between the different runs, coal only runs were also performed between the other runs to cleanout the dRDF from the coal pit and to reduce any memory effects that might occur in the boiler due to the inclusion of the calcium binder from previous runs.

Sample Collection. Over 1,500 samples of flue gas emissions, fly ash, bottom ash, and feedstock were collected during the 12 runs. A total of 190 bottom ash samples were collected from under the grate and through the traveling grate in the boiler. A total of 176 fly ash samples were collected from the multi-cyclone and from the economizer. Random ash samples were taken every eight hours. The samples were collected either by one of the UNT research teams or one of the ANL operators at the required times. Aluminum containers were used to collect the ash samples. After the samples cooled they were transferred into ziplock bags which were then labeled with the date, run number, and the time the sample was collected. The ash samples were then packed and transported to UNT where they were arranged according to the run number, date, and time of collection.

Equipment

Parr Bombs. Parr Teflon acid bombs were obtained from Parr Instrument Company. The bomb is made of a microwave transparent polymer. A compression relief disc is built into the closure to release excessive pressure if the bomb reaches an internal pressure of over 1500 psi. In most cases all parts of the bomb were reusable except for the O-ring.

Microwave Oven. Microwave digestion is becoming increasingly accepted as a fast and reliable alternative to the traditional hot plate method for the digestion of samples before elemental analysis. A Kenmore commercial microwave oven was used to facilitate this work. The oven has a variable timing cycle from 1 second to 100 minutes

Table I. Coal/dRDF Test Run Schedule

Run #	Date	Composition	%Binder
1	1-5 June	Coal	xxxxxx
2	5-8 June	Coal, 10% dRDF	0
3	8-12 June	Coal, 10% dRDF	4
4	12-15 June	Coal, 10% dRDF	8
1	15-18 June	Coal	xxxxxx
5	18-23 June	Coal, 20% dRDF	0
7	23 June	Coal, 20% dRDF	4
6	23-26 June	Coal, 30% dRDF	8
7	26-28 June	Coal, 20% dRDF	4
8	28 June-1 July	Coal, 20% dRDF	8
12	1-4 July	Coal	xxxxxx
11	4-5 July	Coal, 50% dRDF	4
12	5-6 July	Coal	xxxxxx
9*	6-7 July	Coal, 30% dRDF	0
10*	7-8 July	Coal, 30% dRDF	4
12	8 July	Coal	xxxxxx

* reduced plastic content dRDF pellets

and a variable heating cycle based on its' power settings from 70 watts through 700 watts at full power.

Inductively Coupled Plasma Atomic Emission Spectrometry ICP-AES. A Perkin-Elmer ICP-5500 Atomic Emission Spectrometer with a 27.12-MHz RF generator was used in this analysis.

The performance characteristics of ICP, namely its versatility, wide applicability, and ease of use are almost unparalleled among other methods of elemental analyses (14). ICP is theoretically capable of determining any element in the sample matrix except argon, which is used to form the plasma (15).

The application of ICP to simultaneous determination of major, minor, and trace level elements in various matrices has been well documented (16-19). ICP offers several advantages as an alternative approach for the analysis of geochemical and environmental samples (20-24). ICP permits the determination of a large number of elements with high sensitivity and precision and with relative freedom from chemical interferences (25-27).

Sample Analysis

After the samples were returned to the laboratory, they were arranged according to the dates and times they were collected. To determine the trace metal content of each sample, about 10 grams of the ash was ground to pass a 75 mesh sieve. A 400 mg sample was placed in a teflon container and treated with 1 mL of hydrofluoric acid and 3 mL of aqua regia. The teflon container was then placed in the Parr bomb and the bomb was tightly capped. The bomb was placed in the microwave oven and heated for 4 minutes and left for several hours to cool. After cooling, the teflon container was uncapped and 2 mL of saturated boric acid was quickly added. The container was then recapped, returned to the microwave oven and reheated for 1 minute, then cooled again (28-30).

At this stage some uncombusted carbon remained, so the solution was filtered to remove the residue. The residue was washed with deionized water and the filtrate was diluted to 50 mL in a polyethylene volumetric flask.

The solution was finally analyzed by ICP using a blank and a standard solutions containing the same amounts of acids. Standards with varied concentrations of As, Ba, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, V, and Zn were used for the analysis.

Results and Discussion

The chemical composition of the coal and dRDF ash depends on many factors. The geological and geographic factors

related to the coal deposits have a major effect on the initial composition of the fuelstock. Also, the combustion temperatures, residence time in the combustion zone and air flow rate in the boiler along with the efficiency of air pollution control devices have an effect on the elements present in the fly ash.

The fly ash samples which were investigated in this study by ICP were the from the economizer which comes after the multicyclone in the pollution control system. The results from this study are summarized in Table II. Fourteen metals were analyzed in this study. They were arsenic, barium, beryllium, cadmium, chromium, copper, mercury, nickel, lead, antimony, selenium, thallium, vanadium, and zinc. The metals arsenic, cadmium, mercury, lead, antimony, selenium and thallium are not included in these results because their concentrations were too low to be detected by ICP. Table III summarizes the ICP detection limits under the conditions of this study of all of the elements examined.

Effect of dRDF content on trace metals. The processing of MSW to RDF removes much of the unwanted trace metals since many of the metal containing pieces of waste are separated before incineration to be recycled. The metal content of the coal and RDF blend ash is expected to be affected by the different percentages of RDF. Elements such as barium, cadmium, chromium, copper, mercury, lead and zinc are known to be enriched in RDF related to coal. However, the levels of cadmium, mercury and lead observed were below detection limits for all of the coal and bDRDF mixes examined in this study.

Table II and Figures 1-7 show the amount of each metal in the fly ash. Each figure illustrates the variance of the level of the given metal based upon the percent replacement by Btu content of RDF for coal and upon the percent binder used in conjunction with the bDRDF.

The graphs show an increase in copper and zinc concentration with an increase in bDRDF concentration. Since these elements are generally higher in RDF, this was expected. The elements barium and chromium varied greatly but showed a general increase with an increase in bDRDF concentration at different binder percentages. These increases are also due to these elements being more enriched in RDF ash than in coal ash.

The elements vanadium, beryllium and nickel generally were decreased in concentration with an increase in bDRDF percentage. Those elements are believed to be at approximately the same concentration or slightly lower in RDF than coal.

Obviously the amount of all of these metals will deviate as their concentrations vary in the incoming waste

Table II. Summary of Toxic Metals Concentration in Economizer Fly Ash (ug/g)

Run#	Ba	Be	Cr	Cu	Ni	V	Zn	Btu% dRDF	Binder %
1.	158.2	25.3	105.2	152.7	130.0	223.4	324.8	0	-
2.	240.1	27.7	111.3	199.5	135.3	234.1	338.5	10	0
3.	202.2	19.6	100.3	151.8	122.2	177.9	293.7	10	4
4.	144.4	14.7	94.9	143.7	100.8	160.7	390.8	10	8
5.	227.7	20.2	143.8	243.4	137.4	231.0	404.6	20	0
6.	155.7	11.3	108.3	208.5	149.0	187.1	478.2	20	4
7.	182.8	13.3	127.6	243.6	121.3	193.4	466.7	20	8
8.	160.1	11.4	114.4	360.6	92.7	181.3	443.6	30	0
9.	158.3	10.5	115.9	207.9	75.6	149.6	455.9	30	4
10.	190.2	10.5	112.2	227.6	130.5	161.3	470.8	30	8
11.	228.5	14.9	126.1	353.5	97.7	179.8	372.1	50	4
12.	177.4	16.6	93.5	217.1	97.8	171.6	240.3	0	-

Table III. Detection Limits of ICP (ug/g)

Detection Limits of ICP (ug/g)	
As	62.50
Ba	12.50
Be	6.25
Cd	6.25
Cr	6.25
Cu	6.25
Hg	125.00
Ni	12.50
Pb	125.00
Sb	125.00
Se	62.50
Tl	125.00
Zn	6.25

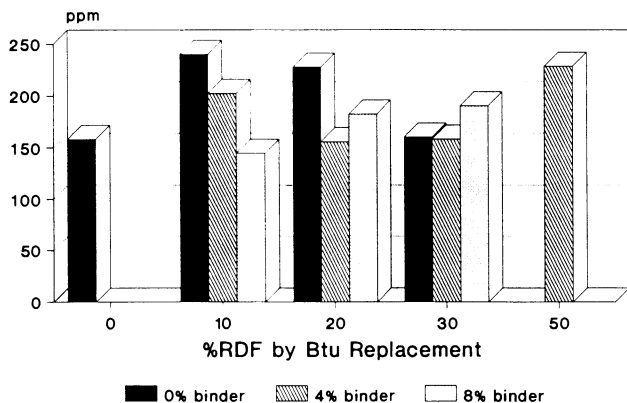


Figure 1. Barium concentrations in the fly ash.

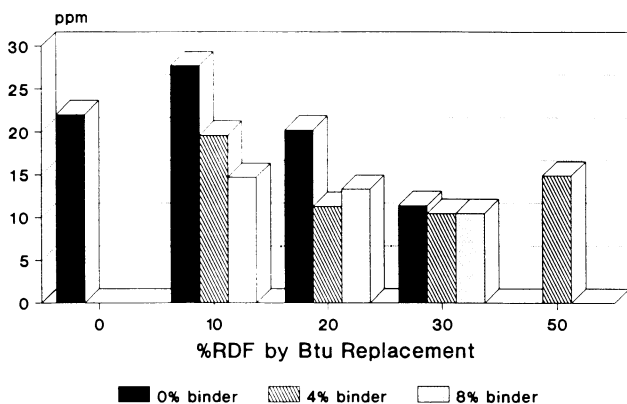


Figure 2. Beryllium concentrations in the fly ash.

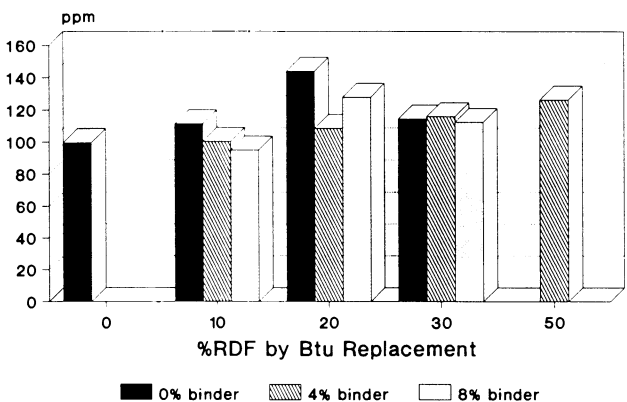


Figure 3. Chromium concentrations in the fly ash.

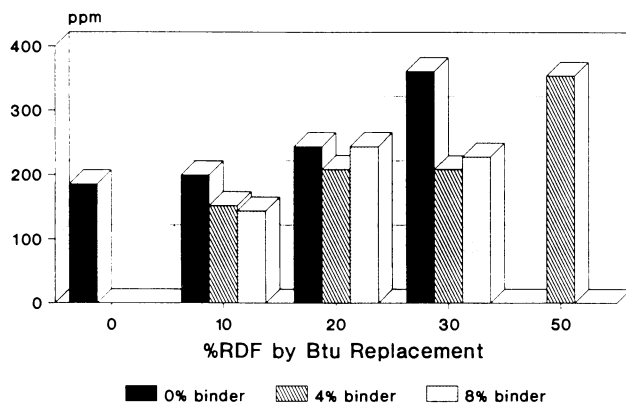


Figure 4. Copper concentrations in the fly ash.

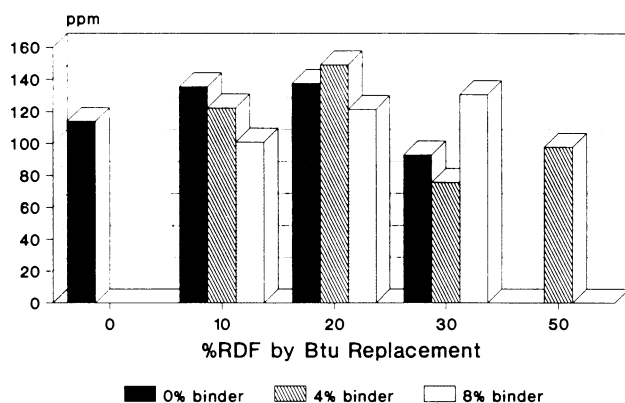


Figure 5. Nickel concentrations in the fly ash.

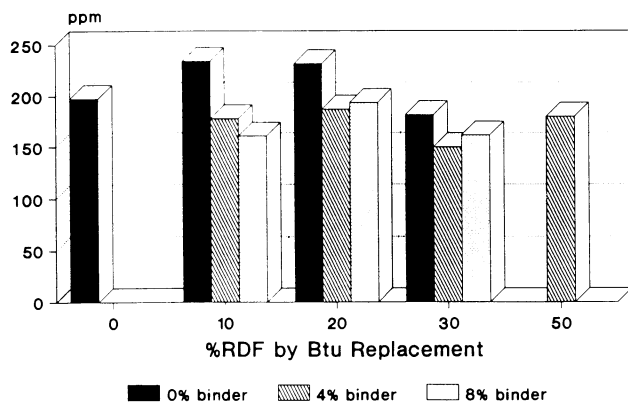


Figure 6. Vanadium concentrations in the fly ash.

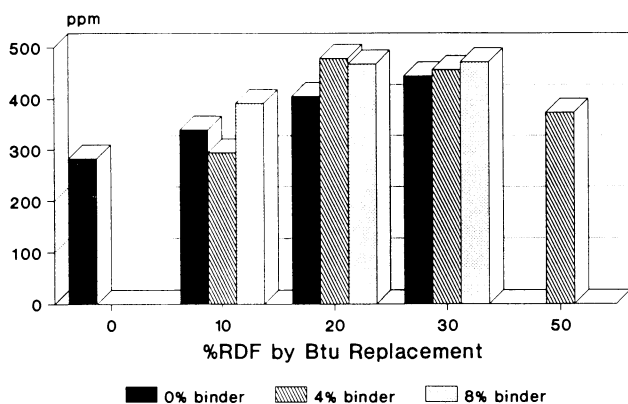


Figure 7. Zinc concentrations in the fly ash.

stream. Care has to be taken in the processing of the MSW to remove all of the possible contaminants. However, the production of RDF is very dependent upon what individuals throw away as garbage.

The most promising aspect of this study is that the metal emissions vary little from that of coal burned alone. Only copper showed a large increase in its presence in the fly ash. As recycling gains popularity in this country, the amount of copper in the countries waste streams should decrease and in turn help decrease the amount of copper in the fly ash of the combustion of refuse derived fuel. However, it should be reiterated that nothing in this study indicates that the ash from the combustion of refuse derived fuel must be landfilled as a hazardous waste and not used in productive activities.

Conclusion

The binder-enhanced dRDF is a promising technique for the future to be used as fuel or as a substitute for coal. It is an economical way of disposal of MSW in the sense that it reduces the heavy cost of landfilling, and this technique generates extra income if sold as fuel. According to the results presented here it shows promise in reducing emissions, especially the trace heavy metals emissions, which also makes it safer to use the fly ash on a large scale, including for many construction projects.

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Chapter 17

Aluminosilicates as Potential Sorbents for Controlling Metal Emissions

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Various aluminosilicate type material were evaluated as potential sorbents for removal of toxic metal compounds such as lead and cadmium chloride and alkali metal compounds such as sodium and potassium chloride. The overall sorption process is not just physical adsorption, but rather a complex combination of adsorption and chemical reaction. The sorbents show high capacities and fast kinetics for metal vapor removal. The sorption mechanism and nature of the final products formed have important implications in the way each sorbent may be used. The overall rate of metal capture can be increased by facilitating intraphase and interphase transport of metal vapors by pore structure optimization and by using different catalyst and reactor geometries.

Emissions of metal compounds during combustion and incineration is becoming an increasingly important problem. Coal contains various compounds of alkali and heavy metals in different forms and concentration. These compounds are released to the gas phase during combustion and gasification of coal. Trace metal compounds could also be present in municipal and industrial wastes. Incineration of these wastes results in emission of toxic metal compounds, causing various environmental problems. Alkali vapors generated during the processing of coal or waste are considered to be the major cause of fouling and slagging on equipment surfaces. Emissions of heavy metal compounds of lead, mercury, cadmium and arsenic etc. could lead to severe environmental problems due to the toxic nature of these compounds. For efficient processing of coal and wastes, the concentration of these metal compounds has to be reduced to levels that are acceptable for both efficient operations and a non-polluting environment.

Removal of metal compounds from the feed stock prior to its high temperature processing is found to be relatively inefficient and expensive. Controlling the release of metal vapors during high temperature processing is very difficult. A promising technique for the removal of metal vapors after they have vaporized

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is through the use of solid sorbents to capture the metal compounds by a combination of reaction and adsorption .

The sorbent can be used in two ways:

- a. It could be injected as a powder (similar to lime injection) for in-situ removal of metal compounds.
- b. The metal containing flue gas could be passed through a fixed or fluidized bed of sorbent. The sorbent could be used in the form of pellets, beads, or monoliths (for high dust applications).

Previous studies by us and other investigators indicate that solid sorbents can be very effective in removing alkali and lead vapors from hot flue gases (1-4). In the present work, a number of potential sorbents were screened and compared for their effectiveness in removing cadmium compounds from hot flue gases. Details of the sorption mechanism were investigated for the selected sorbents.

Cadmium compounds are considered to be among the most toxic trace elements emitted into the environment during fuels combustion and waste incineration. Cadmium and cadmium compounds are primarily used in the fabrication of corrosion resistant metals. Cadmium is also used as a stabilizer in poly-vinyl chlorides, as electrodes in batteries and other electrochemical cells, and for numerous applications in the semiconductor industry (5). Due to this wide range of applications, cadmium is present in many municipal and industrial wastes. Cadmium is also present in coal in trace quantities (6). Consequently, emission of cadmium compounds is a problem in many waste incinerators and coal combustors. The chemical form and concentration of these compounds depend on a number of factors including feed composition and operating conditions (7).

The increased use and disposal of cadmium compounds, combined with their persistence in the environment and relatively rapid uptake and accumulation in the living organisms contribute to their serious environmental hazards. The present technology is inadequate to meet the expected cadmium emission standards. Therefore, new and effective methods need to be developed and investigated for controlling the emission of cadmium and other toxic metals in combustors and incinerators.

Experimental

Materials. In the first part of this study, several model compounds and naturally available materials were evaluated as potential sorbents for removal of gaseous cadmium compounds from hot flue gases. The model compounds included silica (MCB grade 12 silica gel) and alpha alumina (Du Pont Baymal colloidal alumina, technical grade). The naturally available materials included kaolinite (52% SiO₂, 45% Al₂O₃, 2.2% TiO₂, 0.8% Fe₂O₃), bauxite (11% SiO₂, 84% Al₂O₃, 5% Fe₂O₃), emathlite (73% SiO₂, 14% Al₂O₃, 5% CaO, 2.6% MgO, 3.4% Fe₂O₃, 1.2% K₂O) and lime (97% CaO). Cadmium chloride was used as the cadmium source. For the screening experiments, the sorbents were used in the form of particles, 60 -

80 mesh in size. For the kinetic and mechanistic study the sorbents were used in the form of thin flakes (disks). The flake geometry is easy to model and characterize using analytical techniques. All the sorbents were calcined at 900°C for two hours and stored under vacuum until used. All the experiments were conducted in a simulated flue gas atmosphere containing 15% CO₂, 3% O₂, 80% N₂ and 2% H₂O.

Equipment and Procedures. The equipment and procedures used for the screening and mechanistic study are described below.

Screening Experiments. The main components of the experimental system were a Cahn recording microbalance, a quartz reactor, a movable furnace and analyzers for determining the composition of the gaseous products. This system has been previously used for screening of sorbents for removal of lead compounds. Therefore, only the salient features of the system are described here. Details can be found in a previous publication (1). The cadmium source was suspended by a platinum wire from the microbalance, which monitored the weight change during the experiments. A fixed bed of the sorbent particles was made by placing 100 mg of the sorbent particles on a 100 mesh stainless-steel screen in a quartz insert. All experiments in this study were performed with the source at 560°C and the sorbent at 800°C. This method ensured that the concentration of cadmium vapors around the sorbent was much below saturation, thereby preventing any physical condensation on the outer surface of the sorbent.

Heating of the cadmium source resulted in vaporization of CdCl₂ which was carried by the flue gas through the sorbent fixed bed. The percentage of cadmium adsorbed was determined from the amount of cadmium delivered (microbalance measurement) and the cadmium content of the sorbent at the end of the experiment. The cadmium content of the sorbent was determined by dissolving the samples in a H₂O/HF/HNO₃ (2/1/1 proportion by volume) mixture and subsequently analyzing the solution by atomic absorption spectroscopy. Separate water leaching experiments were performed to determine the water soluble fraction of adsorbed cadmium. The leaching of cadmium was conducted at 40°C in an ultrasonic bath for two hours. The cadmium content of the solution was subsequently determined by atomic absorption spectroscopy.

Study of Sorption Details. A microbalance reactor system was used for studying the sorption details. The sorbent flakes were suspended by a platinum wire from the microbalance. The weight of the sorbent was continuously monitored during the experiments by the microbalance. The cadmium source was placed in the horizontal arm of the reactor. The simulated flue gas from the gas preparation section was split in two parts. One part entered the reactor from the inlet below the balance and the remaining gas entered through the horizontal arm in which the cadmium source was placed. The cadmium source was heated by a heating tape and a furnace heated the sorbent flakes. All experiments were conducted with the source temperature of 560°C and the sorbent temperature of 800°C. When steady flow rates and cadmium concentrations were achieved, the sorbent was exposed to the cadmium containing flue gas. The sorbent weight

was continuously recorded as it captured the cadmium vapors. The microbalance was continuously purged with ultra high purity nitrogen gas.

Results and Discussion

Screening Experiments. The results obtained from the screening experiments are given in Figure 1. Multiple experiments were conducted for most of the sorbents and good reproducibility was obtained. Since all experimental parameters except the sorbent type were kept constant, the amount of cadmium adsorbed is a good indication of the sorbent effectiveness (rate) for cadmium removal from hot flue gases. The most obvious feature of these results is the difference in the ability of the sorbents to capture cadmium from the flue gas passing through them. Alumina and bauxite had the highest cadmium capturing efficiencies. A large fraction of the cadmium captured by these two sorbent was water insoluble. Silica and kaolinite were not effective for removal of cadmium. Since cadmium chloride has a high water solubility, the formation of water insoluble compounds on sorption by alumina and bauxite leads to the conclusion that chemical reaction is the dominant mechanism of cadmium capture by these sorbents. Lime, a sorbent used for removal of sulfur compounds, did not have a high cadmium capturing efficiency. Since most of the cadmium captured by lime was water soluble, physical condensation is the dominant mechanism of cadmium capture for lime. From the screening experiments, it seems that compounds containing aluminum oxide have a high cadmium capturing efficiency. Bauxite was therefore further studied to determine the mechanism of cadmium capture. Since previous studies have indicated that kaolinite is a good sorbent for removal of lead and alkali compounds, it was also included in the mechanistic study.

Details of the Sorption Process. In the first part of this study, the cadmium sorption capacity of kaolinite and bauxite was investigated at 800°C. In these experiments the sorbent flakes were exposed to cadmium vapors until no further mass change was observed. The profiles for sorption for both kaolinite and bauxite are shown in Figure 2. The rate of sorption decreases with time and a final limit is achieved beyond which no further cadmium sorption takes place. The observed initial rate for cadmium capture by kaolinite was much slower than that for bauxite. This is consistent with the results from the screening experiments, where kaolinite captured much less cadmium compared to bauxite. Also, the final saturation limit for kaolinite (18%) was found to be lower than that for bauxite (30%) (Figure 2). When the concentration of cadmium in the flue gas was reduced to zero, no desorption from either sorbent was observed indicating that reversible physical adsorption was not the dominant sorption mechanism.

X-ray diffraction (XRD) analysis was used to identify the final products formed by sorption of cadmium chloride on kaolinite and bauxite. Analysis of kaolinite flakes exposed to cadmium vapors indicated the formation of a cadmium aluminum silicate compound, $\text{CdAl}_2\text{Si}_2\text{O}_8$, which is water insoluble.

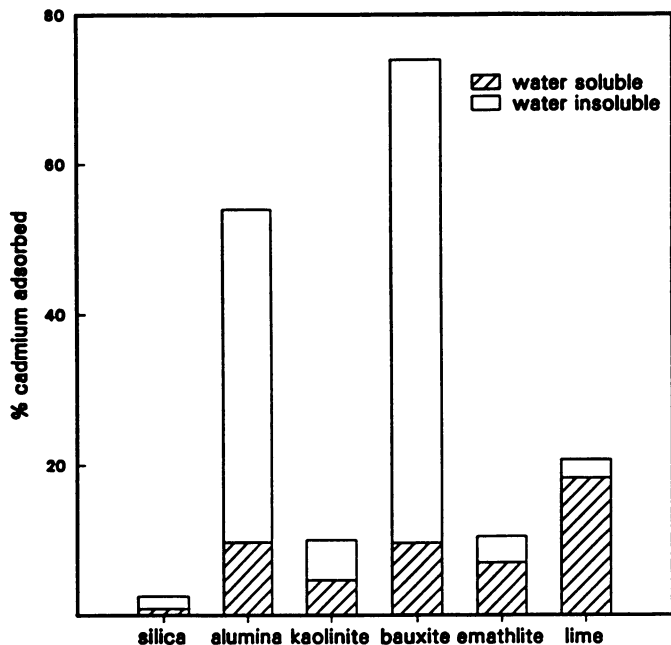


Figure 1. Cadmium removal efficiencies of various sorbents. Mass of sorbent used = 100 mg, $T=800^{\circ}\text{C}$. Amount of cadmium vaporized in each experiment = 6.5 mg.

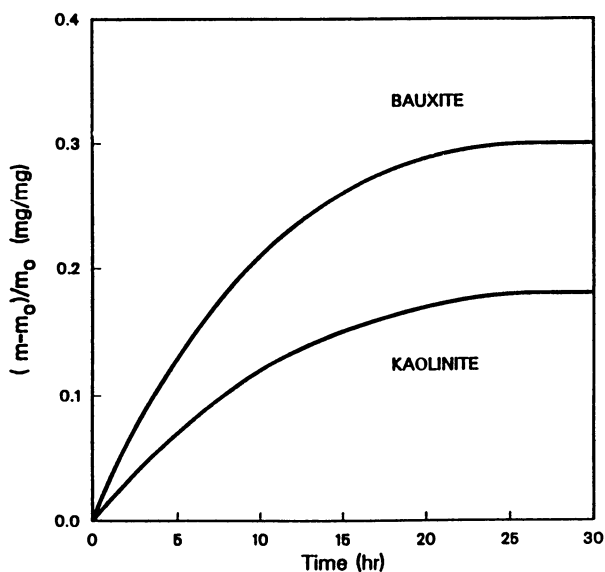
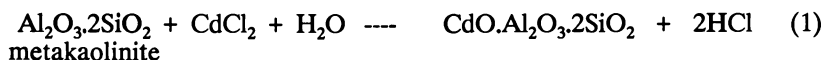


Figure 2. Temporal profiles of cadmium sorption on kaolinite and bauxite. $T=800^{\circ}\text{C}$. Flow rate = 200 cc/min. Mass of flake = 15.1 mg (bauxite); 20.4 mg (kaolinite). Flake thickness = 0.71 mm (bauxite); 1.1 mm (kaolinite).

Based on XRD results, the following reaction scheme is proposed for capture of cadmium :



where metakaolinite is the dehydration product of kaolinite. Holland et al. (8) also observed the formation of this compound when a solid mixture of cadmium carbonate and kaolinite was heated to 800°C for twenty hours. Based on the stoichiometry of the overall reaction, 1 kg of kaolinite can capture 0.51 kg of cadmium, forming a product which is water insoluble and therefore safely disposable. The maximum weight gain postulated from this reaction (58% by weight) is much higher than that obtained experimentally in the microbalance reactor setup (18 wt%).

To further understand the reasons for low sorbent utilization, a kaolinite flake which had captured cadmium to its maximum capacity was mounted in epoxy and analyzed by SEM and EDX analysis. A cadmium map of the flake shows that cadmium is concentrated on the kaolinite edge (Figure 3). An EDX line scan on the flake surface indicated that the concentration of cadmium varied from 49 wt% at the edge to 2 wt% at the center. The concentration of cadmium at the edge (49%) is close to the value calculated from the postulated reaction mechanism assuming complete conversion (51%). This indicates that the surface of kaolinite was completely converted by reaction to form a cadmium aluminosilicate. Silicon and aluminum maps on the kaolinite surface indicate complete uniformity of distribution of these elements on the kaolinite surface. Since this flake had captured cadmium to its maximum capacity (microbalance data, Figure 2), the non-uniform distribution of cadmium indicates incomplete sorbent utilization. Since the volume of the cadmium aluminosilicate phase is higher than that of the aluminum silicate phase, the formation of cadmium aluminum silicate at the outer surface probably blocks the sorbent pores, resulting in incomplete sorbent utilization.

XRD analysis of bauxite particles exposed to cadmium vapors indicated the formation of two crystalline compounds: a cadmium aluminum silicate and a cadmium aluminate. Since the cadmium aluminate has a higher water solubility compared to that of the aluminosilicate, bauxite has a larger fraction of water soluble cadmium in the screening experiments. The amount of SiO₂ present in bauxite is not enough to combine with all Al₂O₃ to form an aluminosilicate compound. Based on the stoichiometry of Reaction 1 and the amount of SiO₂ present, 1 kg of bauxite can capture 0.10 kg of cadmium to form a cadmium aluminosilicate. Based on the remaining alumina, 1 kg of bauxite can capture 0.94 kg of cadmium oxide forming a cadmium aluminate according to the following reaction mechanism:



If all the alumina and silica reacted with kaolinite to form cadmium aluminum

silicate and cadmium aluminate (Reactions 1 and 2), the maximum weight gain possible is 1.06 kg per kg of bauxite. This is higher than the value obtained in the microbalance experiments conducted to completion (0.30 kg/kg bauxite).

To further understand the sorption mechanism, a bauxite flake exposed to cadmium vapors to the point of "no further weight change" was mounted in epoxy and analyzed by SEM and EDX analysis. The cadmium map on the bauxite surface indicated a non-uniform cadmium distribution (Figure 4). Comparison of the cadmium map with the aluminum and silicon maps on the flake surface indicated that regions high in both alumina and silica have high concentrations of cadmium. As confirmed by the XRD analysis, the cadmium present in the alumina phase reacts to form a cadmium aluminate. Regions rich in both alumina and silica combine with cadmium to form a cadmium aluminum silicate. EDX analysis of regions high in both aluminum and silicon indicated that the cadmium concentration was 26 wt%. EDX analysis of regions high in alumina indicated that the cadmium concentration in this phase (11 wt%) was much lower than that postulated by Reaction 2. This indicates that the alumina phase does not completely react with cadmium to form a cadmium aluminate. This could be due to the alumina phase having low porosity thereby preventing complete sorbent utilization. Also, formation of a higher volume product on the outer surface could inhibit further capture of cadmium.

From the mechanistic study it is clear that the sorption process under present experimental conditions is influenced by diffusional resistances. In practical systems, the rate of sorption can be increased by optimization of the sorbent pore structure to facilitate intraphase transport of cadmium vapors into the sorbent. The interphase mass transport limitations can also be reduced to increase the overall sorption rate. For in-situ applications, the efficiency of the sorbent can be increased by decreasing the particle size.

Removal of Other Metal Compounds

Results from previous studies (1,2) indicate that these sorbents can also be used to remove alkali and lead compounds from simulated flue gases. For removal of sodium chloride vapors, kaolinite, bauxite and emathlite were found suitable. However, kaolinite and bauxite were found more suitable than emathlite at temperatures higher than 1000°C since the final reaction products of NaCl adsorption on bauxite and kaolinite (nephelite and carnegiete) have melting points higher than 1500°C. The adsorption of alkali chloride on kaolinite and emathlite is irreversible with the release of chlorine back to the gas phase as HCl vapor. The adsorption on bauxite is partially reversible and part of the chlorine is retained.

Lime was not found to be a good sorbent for lead capture. Although bauxite and kaolinite captured approximately the same amount of lead chloride, kaolinite has a higher ultimate capacity for lead capture and a smaller water soluble fraction of captured lead. The mechanism of sorption for both alkali and lead vapors was found to be a combination of adsorption and chemical reaction.

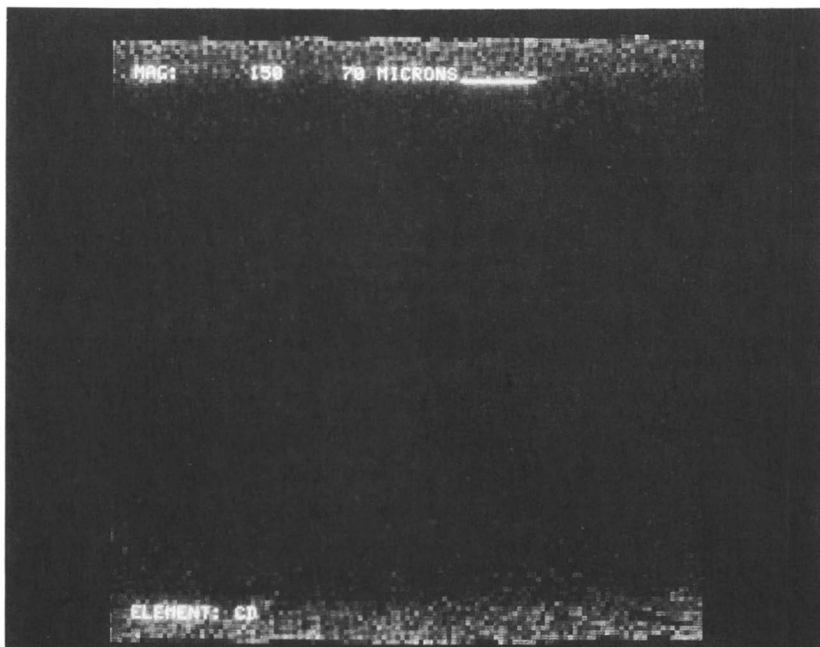


Figure 3. Cadmium concentration map on kaolinite flake surface.

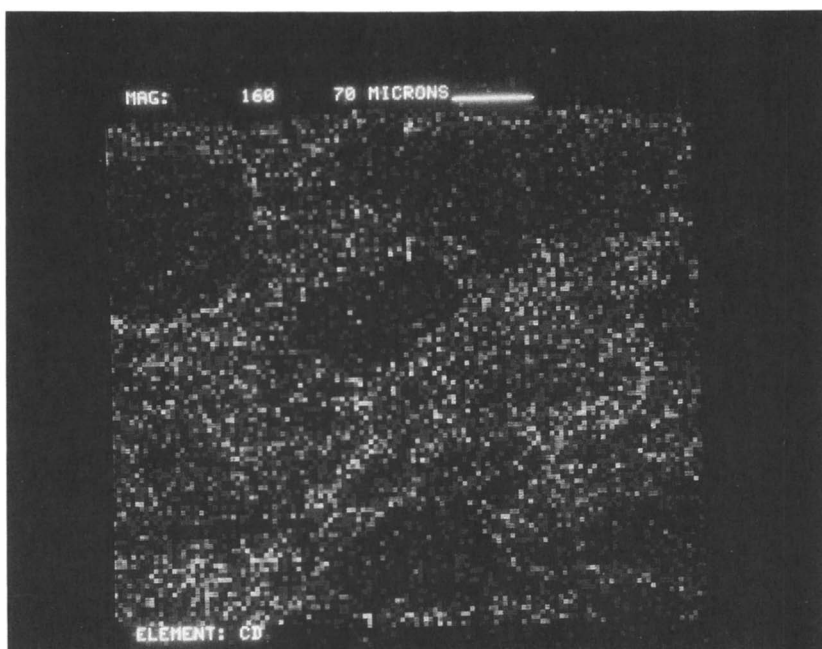


Figure 4. Cadmium concentration map on bauxite flake surface.

Conclusions

1. Aluminosilicate type material are effective sorbents for removal of metal compounds in combustors and incinerators.
2. The sorption mechanism and the nature of final products formed have important implications in the way each sorbent may be used.
3. The overall sorption process is a complex combination of adsorption, condensation, diffusion and chemical reactions.

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Chapter 18

Analysis of Organic Emissions from Combustion of Quicklime Binder-Enhanced Densified Refuse-Derived Fuel-Coal Mixtures

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Emission testing for PCBs and PCDDs has been performed on the combustion gases produced by cofiring a quicklime binder enhanced densified refuse derived fuel/coal mixture. Analysis found that the PCBs were reduced in the presence of the Ca(OH)₂ binder and PCDD concentrations were below detection limits. Samples were obtained from the 567 ton, full scale, cofiring of bDRDF at various concentrations with high sulfur coal at Argonne National Laboratory, 1987. An EPA Modified Method 5 sampling train was used to iso-kinetically obtain samples prior to and after pollution control equipment. After sample clean up, analysis was completed using low and high resolution GC/MS. In an attempt to correlate PCB and PCDD reductions with binder concentrations, calcium and chloride analysis were performed on feedstock, fly ash and bottom ash samples.

Two of the nations current major concerns are municipal solid waste and energy. The combustion of refuse derived fuel (RDF) is increasingly being recognized as an attractive alternative to both problems.

On average 5 pounds of municipal solid waste (MSW) per day is being produced by each U.S. citizen. This waste cumulates to over 200 million tons per year, the majority of which is disposed of in landfills (1). Up until the formation of the Environmental Protection Agency (EPA) in 1970, most of the landfills were simple open dumping grounds with little control measures in place. In the mid 1970's under authority of the Resource Conservation Recovery Act, the EPA began shutting down open dumping and promoting sanitary landfills (2). Sanitary landfills are typically huge depressions lined with clay to minimize

possible leaching into the area groundwater. These landfills have guidelines detailing packing, covering, and monitoring procedures (3). Industry has recently begun to pay attention to this overwhelming problem and new products for containment and monitoring are constantly being developed. However, a slow start has postponed industrial solutions to the distant future, while at the same time, an increasingly concerned public is demanding immediate solutions. Between 1982 and 1987 approximately 3000 landfills were shut down without replacement (4). The Office of Technology Assessment (OTA) predicts that 80% of idle landfills will be closed within twenty years (5).

The "Not in my Backyard Syndrome" (NIMBY), has significantly contributed to the decrease in development of many new landfill sites. A classic example of public opposition is the 1988 Marbro barge incident. The barge carried 3000 tons of garbage 6000 miles down the eastern U.S. coastline looking for a landfill willing to accept its cargo (6).

This new found public consciousness has forced landfill sites to be placed farther from population centers. The result has been higher transportation costs. The northeastern states, which have traditionally exported garbage, are finding it increasingly difficult and costly to find anyone willing to accept the waste. Even states with the potential to locate many new sites are being cautious in response to public opinion. Texas, with its open space, awarded 250 permits per year in the mid 1970s, but was down to less than 50 per year by 1988 (7). Stricter regulations proposed by the EPA in 1991 are expected to eventually lead to a drastic cost increase of approximately 800 million dollars per year (8). These facts, coupled with the potential for large liability costs, have forced the MSW industry to look for other prospective solutions.

An obvious alternative to landfilling MSW is incineration. Mass burn incineration, where refuse is fed into a furnace with moving grates at temperatures of 2400°F, was a popular solution in the 1970s. Increased air pollution, as well as ground water contamination due to leaching of ash residue, has currently placed mass burning in a state of disfavor. Mass burn incineration also tends to be prohibitively expensive (up to \$400 million per facility) (7,9).

Pollution produced by the combustion of MSW is certainly a justifiable concern. However, if a means for controlling emissions to reasonable levels is found, then another combustion product could be put to good use - ENERGY.

The energy potential of the 200 million tons of MSW produced annually in the U.S. equals approximately 326 million barrels of oil (9). This renewable resource can only be tapped if an environmentally acceptable alternative

to mass incineration is found. A promising alternative is that of resource recovery followed by incineration. This process involves removing valuable recyclables such as cardboard, plastics, glass, metals, and compost materials, all from a central receiving station. The chief by-product of this process, consisting primarily of paper, is known as refuse derived fuel (RDF).

RDF has a energy value of about 7500 Btu/lb, similar to a high grade of lignite coal. It can be cofired with coal using cement kilns or other coal burning facilities. The two most common forms are RDF-3 or "fluff" and RDF-5 or "densified".

Fluff RDF typically varies in particle size from a few inches for spread stoker boilers, down to 0.75 inches for suspension fired boilers. It is either burned in dedicated boilers or cofired with coal. There are a number of problems with fluff RDF.

1. It tends to compress under its own weight limiting storage time.
2. Its bulk density (2-3 lb/cubic foot) makes it difficult to transport.
3. If wet it can decay rapidly.
4. It can be difficult to deliver to a furnace in a controlled manner.

Many of these difficulties can be overcome by extruding fluff RDF to create 2-3 inch long by 1/4 inch in diameter pellets of densified RDF (dRDF). Densified RDF has a bulk density on the average of 35 lbs/cubic foot. Transportation, storage, degradation, and processing problems are all reduced by densification.

Typically dRDF processing begins on the plant tipping floor. Large items are removed from the waste and the remainder is loaded onto conveyor belts. The material first passes through a rotary drum sieve to remove the fines (mostly organic material) for composting. The material is then hand picked from the conveyor belt for recyclables. Hammermills or grinders reduce the material in size. Next, ferrous metals are removed magnetically. Air classifiers are used to separate the fine, predominantly paper material from small pieces of glass, rock, etc. which must be landfilled. The fraction of material requiring landfilling in an efficient plant will only amount to about 10-15% of the total original volume. The paper and plastic RDF is now dried to the proper moisture level for densification. Binders are occasionally added prior to densification to increase physical durability and combustion performance.

In 1985 the University of North Texas (UNT), under contract with Argonne National Laboratory, investigated over 150 materials as possible binders for dRDF. A binder was sought that would improve pellet integrity for transportation and storage purposes. A sample of the

materials used exemplifies the diversity of materials investigated:

glues	carbon black
natural starches	urea resins
urea formaldehyde	epoxy resins
sulfite waste liquors	weed additive
beeswax	gelatins
fly ashes	asphalt
animal adhesive	roof tar sludges
limestone	paint sludges
cement kiln dust	cotton burrs
slags	portland cement

Initially, agents were selected based on expected availability, cost, environmental acceptance, and potential binding ability. Because of cost, it was felt that the binder used with RDF should show cementitious bonding as opposed to bonding necessitating a high temperature operation. Generally, cementitious bonding involves inorganic adhesive bonds holding together an aggregate, such as a RDF particle. The adhesion results primarily from hydrogen bonding. This type of cementing provides pellets that possess limited physical strength but are durable for transportation and long term storage. They are also resistant to water attack and biodegradation. Advantages of cementitious bonding include the facts that the cements can be poured or gunned directly into place. They cause little or no dimensional changes during binding, and they are relatively inexpensive.

The densification technique will remove the pores between the RDF particles (accompanied by shrinkage of the components), as a result of grain fusion and strong interactions between adjacent particles. Before densification of RDF can occur, the following criteria must be met. A mechanism for material transport must be present and a source of energy to activate and sustain this material must exist.

The two primary mechanisms for heat transfer are diffusion and viscous flow. Heat is the primary source of energy, in conjunction with energy gradients due to particle-particle contact and surface tension.

The difference in free energy or chemical potential between the free surfaces of RDF particles, is crucial to the densification process. Diffusion properties, temperature, and particle size are also important.

The 150 binding agents were first screened based on cost and environmental effects. Cost was weighted at 60%, environmental effects at 40%. Environmental acceptability, was further broken into the 3 categories of: toxicity 10%, odor 10%, and emissions 20%. The list was reduced to 70 potential binders in this manner. These binding

agents were analyzed in a laboratory study broken into 11 characteristics:

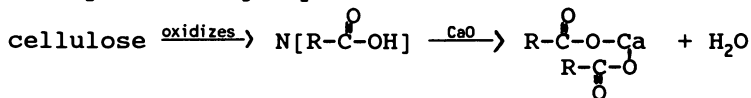
binder Btu content	binder dispersibility
binder ability to wet	binder ash content
pellet water sorbability	pellet caking
pellet ignition temperature	pellet moisture content
pellet durability	pellet aerobic stability
pellet weatherability (110/32°F)	

The tests were grouped into two classes, the first four characteristics being binder properties and the last seven characteristics being classified as pellet properties. The binder properties were weighted at 7% per characteristic, and the pellet properties were weighted as 4% per characteristic. Laboratory test results produce the 13 top binders for further processing. The highest ranked binders were:

calcium oxide (CaO)	bituminous fly ash
calcium hydroxide (Ca(OH) ₂)	lignite fly ash
dolomite	western coal fines
Ca(OH) ₂ /dolomite	Iowa coal fines
cement kiln dust	Ca(OH) ₂ /lignite fly ash
portland cement	calcium lignosulfonate
CaO/dolomite/Portland Cement	

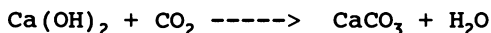
Some observations that can be made on the most effective binders are (a) the binder must have large surface areas, (b) the binders are basic. The basic binders (those using Ca(OH)₂) are believed to be effective due to:

(1) the calcium binding agent breaks the RDF substrate down producing a by-product with acidic groups such as a carboxylic acid group



(2) the calcium from the basic binder reacts in a complex or chelate formation mode with the acidic groups of RDF

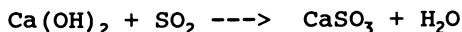
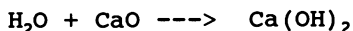
(3) the calcium hydroxide produced by the basic groups reacting with moisture in the RDF, or present initially in the binder, gradually carbonates



These final binding agents were tested in a pilot plant operation performed at the Jacksonville Naval Air

Station, Jacksonville, Florida in the summer of 1985. The test involved over 7000 tons of RDF, and pilot plant experiments. Mixing processes and testing procedures were previously published (10,11). Bulk density was used as an estimate of pellet durability during on-site testing. Ca(OH)_2 was found to increase bulk density over a variety of pellet moisture contents and allowed pressing of pellets at moisture levels normally too high for processing.

UNT suspected the binder's basic nature might help reduce the emission of acid gases. Sulfur dioxide is reduced by burning dRDF simply because of dRDF's lower sulfur content (0.1-0.2%) as compared to western coal's (2.5-3.5%). Additional reductions can be realized through the well known reaction of sulfur oxide, a lewis acid, with the base function of the calcium oxide's surface in ionic form. Hydrolysis of the oxide is known to increase the reaction kinetics. The reaction rate is believed to be determined by the concentration of hydroxide sites. The following equations depict this process. (12).



In the combustion center the binder should be predominantly in the oxide form. After transport to cooler areas within the system the previous listed equations become applicable. The result is a reduction of SO_x emissions. Furthermore, lower combustion temperatures obtained when cofiring dRDF tend to favor the gas solid reaction of SO_2 with CaO . Lower combustion temperatures are also known to lead to decreases in nitrogen oxide emissions.

Hydrochloric gas emissions will tend to increase due to increased chlorine concentrations from plastics. The increase in HCl can be expected to be minimal compared to reduction in SO_x/NO_x emissions. It was further proposed that the binder might physically reduce the production of polychlorinated biphenyls and dioxins by adsorbing halogens prior to their formation or by absorbing the species directly as typically demonstrated in spray dryer absorber systems. (10,11)

These hypotheses were tested at a pilot plant operation at Argonne National Laboratory in 1987. The six week program combusted over five hundred tons of binder enhanced dRDF (bdRDF) blended with Kentucky coal at heat contents of 10, 20, 30 and 50 percent. The Ca(OH)_2 binder content ranged from 0 to 8 percent by weight of dRDF. Emission samples were taken both before and after pollution control equipment (multicyclone and spray dryer absorber). All samples were taken to UNT for analysis.

A discussion of the significant reductions in sulfur and nitrogen oxides has been previously published (13).

The following discussion reports results for analysis of polychlorinated biphenyls, polyaromatics, polychlorinated dioxins, and polychlorinated furans.

Experimental

Isokinetic samples were taken for the analysis of polychlorinated biphenyls (PCB's), polyaromatics (PAH's), polychlorinated dioxins (PCDD's) and polychlorinated furans (PCDF's). The following sampling sites were investigated.

Site 1 combustion zone (2000°F); sample site (1200°F)

Site 2 prior to pollution control equipment (300°F)

Site 3 after pollution control equipment (170°F)

Sample collection was completed using an EPA modified Method 5 sampling train, and a XAD-2 resin for trapping the majority of organics. Various samples were spiked with isotopically labeled standards prior to soxhlet extraction for 24 hours with benzene. The percent recovery of these standards provided a means to determine extraction efficiency and detection limits. Possible interferants were removed by sample elution through a minimum of two acid and base modified silica gel columns followed by an alumina column. Standard mixtures of native and isotopically labeled analytes were prepared for calculation of relative response factors and calibration of the gas chromatography mass spectrometer (GC/MS). The GC/MS analysis was performed with a Hewlett-Packard Model 5992B. (14)

Results and Discussion

The EPA's sixteen most hazardous PAH's (Table V) and all congener groups of PCB's were tested. The results are reported as total PCB and PAH concentrations found at a particular site because it is felt that the overall production of PCB's/PAH's is the parameter of primary concern. No specific compound was produced at inordinately high levels. The results of site 2 and site 3 sampling areas are found in Tables I and II. Figures 1 and 2 clearly depict a reduction in PAH and PCB emission as the binder concentration is increased. Data are not available on all compositions due to the mixing and sampling methods used. Tables III and IV show the calcium and chloride contents of fly ash from the multicyclone for a series of specific compositions. The calcium is used as an indicator of the binder present in the boiler system during a particular sampling period. The increase in calcium occurring between the first coal "blank" run and the second blank occurring 3 weeks later, suggest a build-up of residual binder throughout the boiler configuration. It is noteworthy that the increase in water soluble chloride

Table I
Polyaromatic Hydrocarbons (PAH's);
Polychlorinated Biphenyls (PCB's) at Site 2

Run#/Sample#	Site	mg PAH's cubic meter of gas sampled	mg PCB's cubic meter of gas sampled
Coal	2	1.7×10^{-2}	6.2×10^{-3}
Coal/10%RDF/0%B	2	1.0×10^{-3}	1.3×10^{-2}
Coal/10%RDF/0%B *	2	7.6×10^{-2}	2.7×10^{-1}
Coal/10%RDF/4%B	2	1.6×10^{-2}	1.4×10^{-2}
Coal/10%RDF/8%B	2	4.0×10^{-3}	7.6×10^{-3}
Coal/10%RDF/8%B	2	8.1×10^{-3}	7.7×10^{-3}
Coal/20%RDF/0%B	2	3.5×10^{-2}	9.7×10^{-3}
Coal/20%RDF/0%B	2	4.6×10^{-2}	7.7×10^{-3}
Coal/20%RDF/4%B	2	2.2×10^{-1}	2.0×10^{-3}
Coal/20%RDF/4%B	2	3.5×10^{-1}	2.9×10^{-1}
Coal/20%RDF/8%B	2	2.4×10^{-1}	1.3×10^{-2}
Coal/20%RDF/8%B	2	3.0×10^{-1}	3.4×10^{-3}
Coal	1	3.4×10^{-1}	5.4×10^{-3}
Coal	2	1.3×10^{-1}	3.9×10^{-4}

* This sample was lighter in color than all the rest

B = Binder

Table II
Polyaromatic Hydrocarbons (PAH's);
Polychlorinated Biphenyls (PCB's) at Site 3

<u>Run#/Sample#</u>	<u>Site</u>	<u>mg PAH's cubic meter of gas sampled</u>	<u>mg PCB's cubic meter of gas sampled</u>
Coal	3	4.6×10^{-3}	5.3×10^{-4}
Coal/10%RDF/0%B	3	6.3×10^{-3}	1.2×10^{-3}
Coal/10%RDF/0%B	3	1.5×10^{-2}	*
Coal/10%RDF/0%B	3	8.1×10^{-3}	1.6×10^{-3}
Coal/10%RDF/4%B	3	7.3×10^{-3}	9.1×10^{-3n}
Coal/10%RDF/8%B	3	7.3×10^{-3}	1.1×10^{-4}
Coal/10%RDF/8%B	3	3.1×10^{-3}	3.1×10^{-3}
Coal/20%RDF/0%B	3	3.6×10^{-4}	2.8×10^{-4}
Coal/20%RDF/0%B	3	4.0×10^{-3}	1.2×10^{-3}
Coal/20%RDF/4%B	2	7.9×10^{-2}	4.2×10^{-2}
Coal/20%RDF/4%B	3	4.9×10^{-2}	6.5×10^{-3}
Coal/20%RDF/8%B	3	1.0×10^{-3}	2.4×10^{-3}
Coal/20%RDF/8%B	3	8.1×10^{-3}	8.5×10^{-4}
Coal	3	7.0×10^{-2}	4.0×10^{-3}
Coal	3	1.4×10^{-3}	4.3×10^{-4}

* Interference made it impossible to determine the quantity of PCB's in this run

B = Binder

Table III
Calcium Levels in Fly Ash

<u>Fuel</u>	<u>ppm of Calcium</u>
First coal blank	3,000
Coal - 10% dRDF (0% binder)	6,700
Coal - 10% dRDF (4% binder)	10,600
Coal - 10% dRDF (8% binder)	15,000
Second coal blank	4,200

Table IV
Soluable Chloride Levels in Fly Ash

<u>Fuel</u>	<u>ppm of Chloride</u>
First coal blank	100
Coal - 10% dRDF (0% binder)	190
Coal - 10% dRDF (4% binder)	280
Coal - 10% dRDF (8% binder)	320
Second coal blank	280

Table V
EPA Priority PAH's

Naphthalene	Benzo-a-anthracene
Acenaphthylene	Chrysene
Acenaphthene	Benzo-b-fluoranthene
Fluorene	Benzo-k-fluoranthene
Phenanthrene	Benzo-a-pyrene
Anthracene	Dibenzo-a,h-anthracene
Fluoranthene	Benzo-g,h,i-perylene
Pyrene	Idendo-1,2,3,-g,d-pyrene

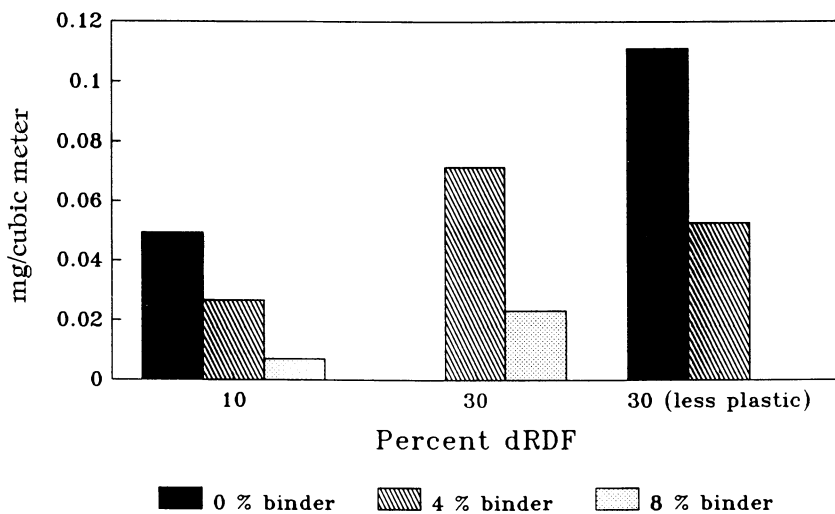


Figure 1. PAH Concentrations Detected

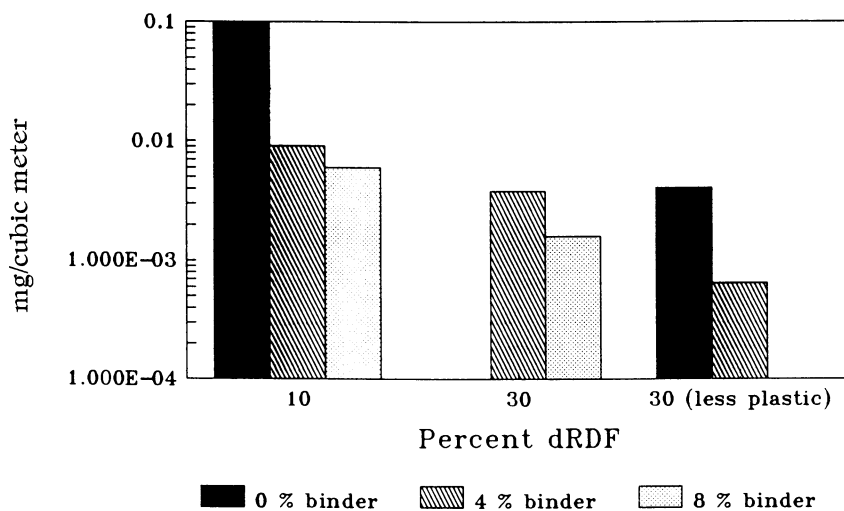


Figure 2. PCB Concentrations Detected

in the fly ash for the 10% RDF samples is on the same order as the reduction of PCB's seen in Figure 2. This is presumably due to the lime's ability to bind the chloride in the combustion area. The much higher chloride content of the second coal blank ash relative to the first blank can be explained by assuming a longer contact time for chloride adsorption on the residual binder as the binder became saturated throughout the boiler system. (15)

The dioxin and furan analysis initially concentrated on the tetra chlorinated species present after the pollution control equipment at sample site 3. Priority was given to detecting the 2,3,7,8 congeners because of their higher toxicity. Sample site 3 was chosen because of the importance of determining what concentrations of the analyte, if any, were reaching the environment. Table VI shows that no dioxins or furans were found at the listed detection limits.

In order to discover if the analyte was simply depositing on fly ash, samples of composited fly ash were also analyzed for adsorbed PCDD's and PCDF's. The five fly ash samples chosen to represent the full spectrum of test burn compositions are listed in Table VII. Analysis results represented by Tables VIII through XII again demonstrate no detectable trace of dioxins or furans. Additional analyses were subsequently performed for penta, hexa, hepta, and octa congeners at sample site 3. In all cases, no dioxins or furans were detected.

These somewhat surprising negative results led to a search for a means to improve detection limits. Lower detection limits were thought to be obtainable through the use of a high resolution mass spectrometer (HRMS). Triangle Laboratories at Research Triangle Park, NC, was contracted for use of their equipment and expertise in this area. Eight representative samples were chosen for HRMS analysis. Three of the previously analyzed samples from site 3 were chosen as verification on the accuracy of UNT's results. The remaining samples were of various burn compositions from site 2 prior to pollution control equipment. These samples were selected because UNT's results suggested that no PCDD's or PCDF's were present after pollution control.

Triangle Laboratories generally improved results only on the order of one magnitude, and confirmed UNT's findings with negative results for dioxins and furans at site 3. Only one of the site 2 samples had any detectable analyte. Emissions of 0.41 ng/m^3 total HxCDD and 0.66 ng/m^3 total OCDD were found for the sample from a 20% dRDF/0% binder/ coal burn mixture. It should be noted that the toxicity equivalent factor (TEF) for HxCDD is 0.0004 leading to a emission rate of 0.16 pg/m^3 while the TEF for OCDD is 0. Emission rates for both are certainly much lower than any current standards. Results of the same sample at site 3 found no trace of dioxin or furan.

Table VI
Tetra-Chlorinated Dioxins and Tetra-Chlorinated
Furans at Site 3

<u>Run#/Sample#</u>	<u>Site</u>	<u>Tetra- Chlorinated Dioxin Level</u>	<u>Tetra- Chlorinated Furan Level</u>	<u>Detection Limit ng/m³</u>
Coal	3	BDL	BDL	0.72
Coal/10%RDF/0%B	3	BDL	BDL	1.99
Coal/10%RDF/0%B	3	BDL	BDL	4.07
Coal/10%RDF/0%B	3	BDL	BDL	5.24
Coal/10%RDF/4%B	3	BDL	BDL	4.80
Coal/10%RDF/8%B	3	BDL	BDL	4.27
Coal/10%RDF/8%B	3	BDL	BDL	4.27
Coal/20%RDF/0%B	3	BDL	BDL	0.49
Coal/20%RDF/0%B	3	BDL	BDL	0.47
Coal/20%RDF/4%B	3	BDL	BDL	4.16
Coal/20%RDF/4%B	3	BDL	BDL	4.10
Coal/20%RDF/8%B	3	BDL	BDL	4.78
Coal/20%RDF/8%B	3	BDL	BDL	4.78
Coal	3	BDL	BDL	3.85
Coal	3	BDL	BDL	4.85

ng/m³ = nanograms per cubic meter

BDL = Below Detection Limits

B = Binder

Table VII
Analyzed Fly Ashes Compositions

Date	Composite Sample #	Composition
June 21-22, 1987	1	20% Btu Content Reuter RDF and 70% Btu Content Coal - 0% Binder
July 7, 1987	2	30% Btu Content Reuter RDF and 70% Btu Content Coal - 0% Binder (no plastic)
June 15-16, 1987	3	Coal Only
June 23-24, 1987	4	30% Btu Content Reuter RDF and 70% Btu Content Coal - 8% Binder
July 4-5, 1987	5	50% Btu Content Reuter RDF and 50% Btu Content Coal - 4% Binder

Table VIII
GC/MS Analysis of Ash Sample 5 for Polychlorinated Dioxins and Furans

Mass	Analytes	Amount Found (ng/g sample)	Detection Limit (ng/g sample)
304/306	TCDF	BDL	0.9966
320/322	TCDD	BDL	0.9966
340/342	PeCDF	BDL	2.4916
356/358	PeCDD	BDL	2.4916
374/376	HxCDF	BDL	2.4916
390/392	HxCDD	BDL	2.4916
408/410	HpCDF	BDL	2.4916
424/426	HpCDD	BDL	2.4916
442/444	OCDF	BDL	4.9832
458/460	OCDD	BDL	2.4916

% Extraction Efficiency = 57.9

BDL = Below Detection Limit

Table IX

GC/MS Analysis of Ash Sample 4 for Polychlorinated Dioxins and Furans

Mass	Analytes	Amount Found (ng/g sample)	Detection Limit (ng/g sample)
304/306	TCDF	BDL	1.0001
320/322	TCDD	BDL	1.0001
340/342	PeCDF	BDL	2.5002
356/358	PeCDD	BDL	2.5002
374/376	HxCDF	BDL	2.5002
390/392	HxCDD	BDL	2.5002
408/410	HpCDF	BDL	2.5002
424/426	HpCDD	BDL	2.5002
442/444	OCDF	BDL	5.0005
458/460	OCDD	BDL	2.5002

% Extraction Efficiency = 9.2

BDL = Below Detection Limit

Table X

GC/MS Analysis of Ash Sample 3 for Polychlorinated Dioxins and Furans

Mass	Analytes	Amount Found (ng/g sample)	Detection Limit (ng/g sample)
304/306	TCDF	BDL	1.0022
320/322	TCDD	BDL	1.0022
340/342	PeCDF	BDL	2.5055
356/358	PeCDD	BDL	2.5055
374/376	HxCDF	BDL	2.5055
390/392	HxCDD	BDL	2.5055
408/410	HpCDF	BDL	2.5055
424/426	HpCDD	BDL	2.5055
442/444	OCDF	BDL	5.0111
458/460	OCDD	BDL	2.5055

% Extraction Efficiency = 53.1

BDL = Below Detection Limit

Table XI

**GC/MS Analysis of Ash Sample 2 for Polychlorinated
Dioxins and Furans**

<u>Mass</u>	<u>Analytes</u>	<u>Amount Found (ng/g sample)</u>	<u>Detection Limit (ng/g sample)</u>
304/306	TCDF	BDL	0.9965
320/322	TCDD	BDL	0.9965
340/342	PeCDF	BDL	2.4913
356/358	PeCDD	BDL	2.4913
374/376	HxCDF	BDL	2.4913
390/392	HxCDD	BDL	2.4913
408/410	HpCDF	BDL	2.4913
424/426	HpCDD	BDL	2.4913
442/444	OCDF	BDL	4.9825
458/460	OCDD	BDL	2.4913

% Extraction Efficiency = 81.2

BDL = Below Detection Limit

Table XII

**GC/MS Analysis of Ash Sample 1 for Polychlorinated
Dioxins and Furans**

<u>Mass</u>	<u>Analytes</u>	<u>Amount Found (ng/g sample)</u>	<u>Detection Limit (ng/g sample)</u>
304/306	TCDF	BDL	0.9992
320/322	TCDD	BDL	0.9992
340/342	PeCDF	BDL	2.4980
356/358	PeCDD	BDL	2.4980
374/376	HxCDF	BDL	2.4980
390/392	HxCDD	BDL	2.4980
408/410	HpCDF	BDL	2.4980
424/426	HpCDD	BDL	2.4980
442/444	OCDF	BDL	4.9825
458/460	OCDD	BDL	2.4980

% Extraction Efficiency = 133.6

BDL - Below Detection Limit

Thus the pollution control equipment is apparently efficient in removing the analyte at these low concentrations. (16)

There is a natural disinclination to report results such as found in Table VI and Tables VIII through XII. No concrete values for dioxin and furan concentration produced during the combustion of the RDF are presented. Instead, one finds detection limits for which PCDD and PCDF levels were found to be below.

When attempting to investigate the environmental impact of a developing industry, it is important to contribute all technically responsible information for the development of a reliable database. This becomes particularly imperative when dealing with sensitive topics, such as the production of dioxins and furans during the combustion of refuse derived fuel.

The presented data provides baseline values as a means for predicting potential pollution levels for future industrial demonstrations and for the development of adequate detection techniques.

Conclusion

Results of the pilot plant program indicates that the binder enhanced densified refuse derived fuel can be cofired with coal, at the levels tested, without producing detectable amounts of dioxins or furans. PCB's and PAH's are apparently reduced as a function of the quicklime binder content.

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Chapter 19

Ash Utilization and Disposal

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There are many changes taking place in the utilization and disposal of ash and related materials and each day it seems that there are more restrictions on the disposal of ash. In one project, mass burn ash has been screened to remove the plus one inch pieces and then combined with the fly ash and portland cement to produce a pellet that is very slow-leaching with all of the heavy metals "fixed".

In the northeastern United States, the ash from circulating fluidized bed combustors needs to be pelletized so it can be transported back to the mine for easy disposal. The ash can also be blended with digested municipal sewage sludge to form a soil additive which contains lime and nutrients.

The new clean air standards are making it necessary for utilities to install sulfur dioxide scrubbers which produce gypsum. This gypsum filter cake can be pelletized so that the pellet produced can be utilized in the final grind of portland cement or can be disposed of in a very slow-leaching pile.

We have taken the lead in producing these agglomeration techniques and many more processes which we will describe and show the detailed process flow diagram for each of these methods.

The utilization and disposal of fly ash in a legal and environmentally safe manner is becoming a major engineering challenge because of rapidly changing government laws and regulations. In addition, the ongoing search for lower cost power and alternative fuels and combustion methods is continually changing the fly ash. Government regulations limit the amount of sulfur released during combustion of coal. To limit sulfur emissions from a pulverized coal combustor we are now adding a dry sulfur dioxide scrubber in which a lime $[\text{Ca}(\text{OH})_2]$ solution is sprayed into the exhaust gas stream where

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some of the lime reacts with the sulfur dioxide to form calcium sulfate (CaSO_4) or calcium sulfide (CaSO_3) which is a solid and can be removed from the gas stream with the fly ash. Another new type fly ash is that from a circulating fluidized bed combustor where the sulfur is reacted with calcined limestone in the bed to form calcium sulfate (CaSO_4) or calcium sulfide (CaSO_3) which again is removed with the fly ash.

There are many changes taking place in ash management based on the fact that pellets can be produced which are very slow-leaching. Pellets can be moved with conventional bulk material handling equipment without producing a dusty environment. The pellets can be disposed of in almost any type of state permitted site and do not need to be placed in a lined landfill. In addition, slight modifications to the pelletizing process can produce usable products such as lightweight aggregate or aggregate to be utilized in asphalt.

We see that each situation or plant needs to be treated as a separate problem and a process developed to solve that particular problem. We had been trying to pelletize fly ash for twenty years with only limited success until we discovered that the real requirement to allow us to produce consistent pellets was to first condition the fly ash in an intense mixer so that each particle becomes coated with water. The two key pieces of equipment required to pelletize fly ash are the Ferro-Tech-Turbulator (Figure 1) and the Ferro-Tech Disc Pelletizer (Figure 2). The Ferro-Tech-Turbulator is a proprietary, intense, highly efficient, agitative agglomeration device covered by Patent No. 4,881,887. The unit has high efficiency because it operates by fluidizing the material and atomizing the injected liquid which may be water or a liquid binder. Each whirling dust particle is uniformly coated with a very thin layer of the liquid binder. Ideally, the liquid binder coating is one molecule thick, however, this thickness is not practical so the layer is a few molecules in thickness. This coating of the individual particles with a liquid is called "conditioning". These coated dust particles, moving at a high velocity in suspension, collide and impact with great force with the other coated, spinning particles within the turbulent wake created behind the pins, forming a very uniformly sized and dense particulate or microgranule which is held or pulled together by the surface tension of the liquid layer. The thick, resilient polymer liner in the Turbulator combined with critical close pin tip tolerance causes the pins to fully sweep or wipe the liner, eliminating product build-up on the inner casing of the Turbulator body. Because of the intensity of the Turbulator, it can efficiently pre-blend, de-dust, blend, "condition", densify, hydrate and micropelletize all types of fine powders, dust, fume and hard-to-wet particles. The fly ash particles are uniformly coated with water in the Turbulator before they are discharged to be pelletized in the disc pelletizer. The conditioning step in the Ferro-Tech-Turbulator compensates for the variation in composition, particle size and surface area which is a characteristic of fly ash from coal combustion due to changes in combustor operations and variation in fuel.

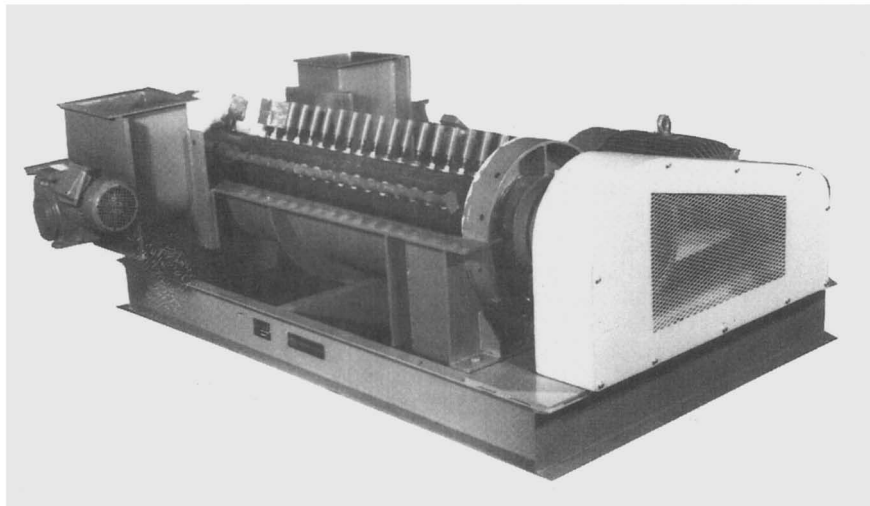


Figure 1. Ferro-Tech-Turbulator



Figure 2. Ferro-Tech Disc Pelletizer

Circulating Fluidized Bed Combustor Ash Agglomeration

Most of the new cogeneration plants are utilizing a circulating fluidized bed combustor principle which burns coal having reasonable levels of sulfur (up to 3%). The ash from these combustors consists of two fractions, bed drain or bottom ash and fly ash. The bed drain ash is approximately 25 to 30% of the total ash. The best ash systems keep the two ash fractions separated so they can be blended uniformly for agglomeration. The fly ash can be agglomerated alone, but the bed drain ash must be blended with at least 50% fly ash before quality pellets can be produced.

The basic process flow diagram for producing a 1/4" x 1/2" pellet is shown in Figure 3. This system includes two (2) surge bins with feeders feeding the ash into a Ferro-Tech-Turbulator where approximately 2/3 of the 18 to 20% (wet basis) of the water required for pelletizing is added. This ash should be near ambient temperature, however, it may be as high as 200°F when discharged from the feeder. The conditioned ash from the Turbulator discharges directly into the disc pelletizer where pellets are formed. This disc pelletizer is designed for this specific agglomeration application. The pellets or green balls from the disc pelletizer have a modest amount of strength so that they can withstand the treatment of the material handling system to the pellet curing area. The curing of these pellets is very similar to the curing of concrete or any cementitious blend. In this case the curing can take place in a ground pile where temperatures can be up to 150°F. Heat is gained as the hydration reaction of the curing takes place. Normally the pellets have gained enough strength to be handled in 24 to 48 hours. Strength enough to be handled is a crush strength of 10 to 15 pounds for a 1/2 inch diameter pellet. Figure 4 shows the effect of curing temperature on the strength of the pellets. The 150°F can easily be reached when the pellets cure in a pile or bin. After extended curing (30 to 60 days), a typical 1/2 inch diameter pellet may require a force of 200 to 300 pounds to crush it. These pellets can easily be utilized as road bed material or as aggregate in concrete.

High Sulfur Coal. When a high sulfur coal (above 3%) is burned in a circulating fluidized bed combustor, this fly ash acts very differently. When water is added to the fly ash in a Ferro-Tech-Turbulator, the ash very quickly (5 to 10 minutes) gains temperature. A typical temperature curve is shown in Figure 5 where the temperature rose to 290° F in seven minutes. This heating is a result of the hydration of the lime (CaO) by the water to form hydrated lime [Ca(OH)₂]. Since this fly ash can contain 30 to 40% lime (CaO), we can see that there is much heat generated. If enough water has been added to produce pellets, that is, 18 to 20% (wet basis) of water, the pellets will quickly begin to hydrate, heat up and expand and will completely disintegrate becoming an even finer dust than it was in the beginning.

The process shown in flow diagram Figure 6 is necessary if a pellet is to be produced which will hold together and gain strength. This process is covered by Patent No. 5,008,055. The fly ash and bed drain ash are added at a uniform rate into Turbulator No. 1 where 8 to 10% water (wet basis) is added. The discharge from Turbulator No.

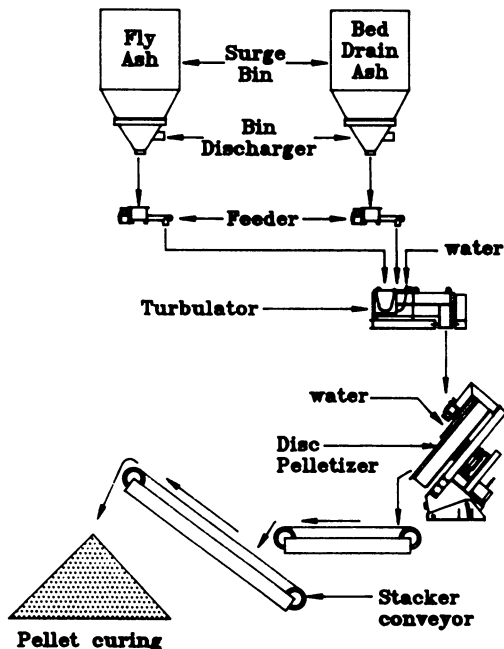


Figure 3. CFB Ash Pelletizing System

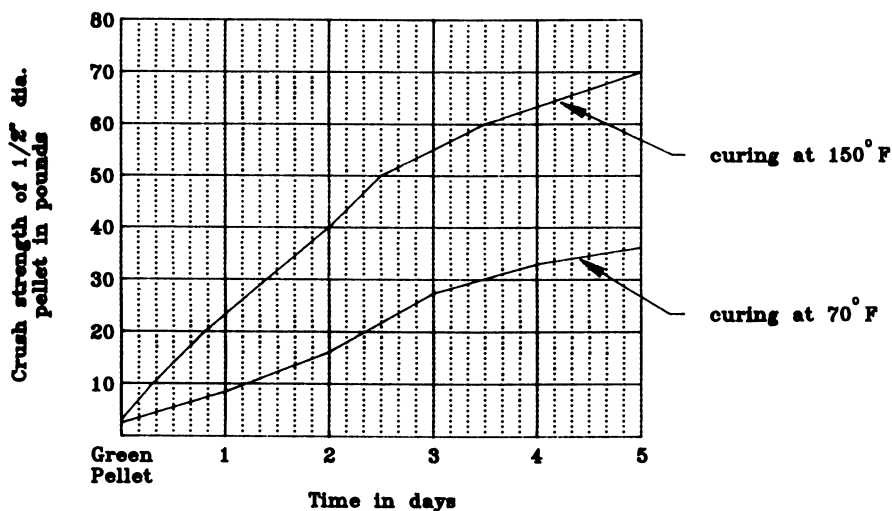


Figure 4. CFB Ash Pellets

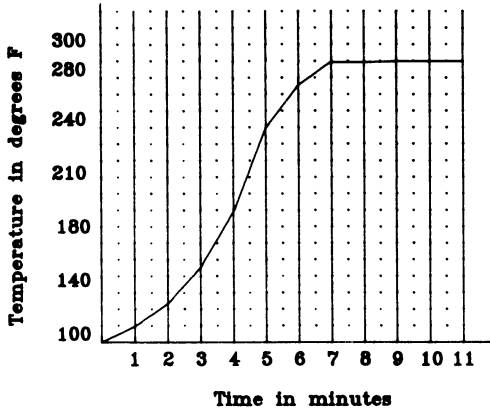


Figure 5. Hydration Temperature Curve

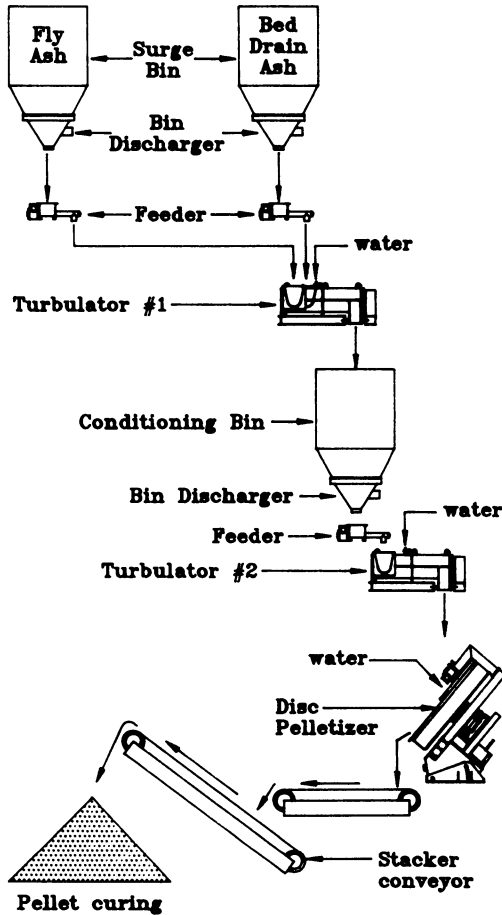


Figure 6. CFB Ash Pelletizing System for High Sulfur Coal

1 drops directly into a conditioning bin where the temperature, due to the hydration reaction, is as much as 300°F. The material is retained in the conditioning bin until all of the free water is chemically reacted and a hydrate is formed. The conditioning bin is carefully designed to be a mass flow bin so that the ash moves uniformly toward the discharge. The partially hydrated ash is discharged from the bottom of the conditioning bin through a screw feeder into Turbulator No. 2 where 10 to 12% (wet basis) of water is added to the ash. The uniformly wet ash is discharged from Turbulator No. 2 directly into a disc pelletizer where 8 to 10% (wet basis) of additional water is added and pellets are formed. As before, the pellets are placed in a curing area for 24 to 48 hours or until they gain satisfactory strength.

Fly Ash Lightweight Aggregate

One of the better uses for Class F and Class C fly ash from pulverized coal power plants is to produce lightweight aggregate. This aggregate can be utilized to produce lightweight concrete block and other masonry forms. The basic process flow diagram for the process is shown in Figure 7. The aggregate seems to have many advantages over other lightweight aggregates including its spherical shape. The aggregate produced by this process bonds to the mortar with both a mechanical bond and a chemical bond instead of just a mechanical bond as is true of other non-reactive aggregates.

The bulk density of the aggregate is approximately 45 to 50 lbs./cu.ft. The typical sieve analysis (ASTM C136) of the aggregate required to produce concrete for the manufacture of concrete blocks is:

<u>Sieve Size</u>	<u>Product Percent Passing</u>	<u>Specification Percent Passing</u>
1/2"	100	100
3/8"	99	90 - 100
4 mesh	83	65 - 90
8 mesh	49	35 - 65
16 mesh	31	---
50 mesh	19	10 - 25
100 mesh	15	5 - 15

Synthetic Gypsum & Fly Ash Pelletizing

One of the major problems at pulverized coal power plants burning high sulfur coal which have a wet sulfur dioxide lime scrubber is how to dispose of the synthetic gypsum slurry. One very simple solution is to produce a pellet by blending dry fly ash with the gypsum filter cake or even with the gypsum slurry. Figure 8 shows the basic process flow diagram for the required system. In this system, the filter cake is metered into the Ferro-Tech-Turbulator at a constant rate. The feed rate of the fly ash is controlled by a moisture control system on the disc pelletizer, Patent No. 5,033,953. This system adjusts the feed rate to maintain a constant surface moisture of 18 to 20% (wet basis) on the pellets which are about to discharge

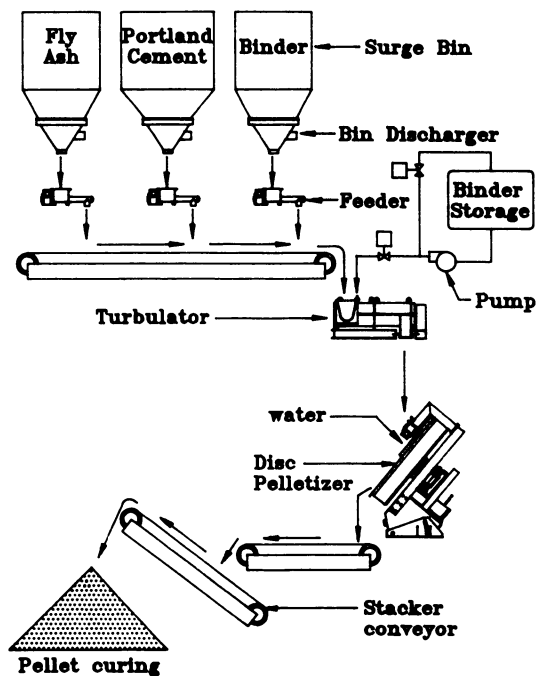


Figure 7. Fly Ash Lightweight Aggregate Pelletizing System

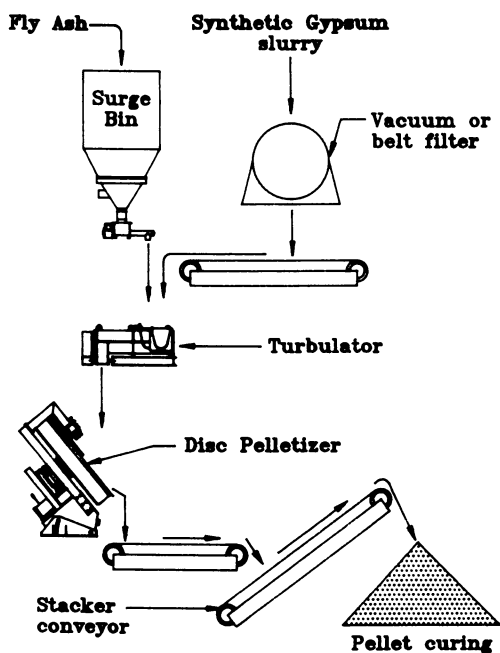


Figure 8. Synthetic Gypsum & Fly Ash Pelletizing System

from the disc pelletizer. The moisture control system utilizes an infrared emitter and sensor to optically determine the surface moisture of the pellets. The pellets from the disc pelletizer are placed in a curing pile where they gain strength before being placed in a landfill. Figure 9 shows a typical curing curve for these pellets.

Mass Burn Ash Agglomeration

The processing of mass burn ash is in a state of change since there is obviously a need to produce a product that has all of the heavy metals "fixed" so they do not leach from a landfill. The requirement is to process both the bottom ash and the fly ash. Processing the bottom ash alone is very difficult because of the extreme variation in the size of the pieces and in the high moisture [20 to 25% (wet basis)] of the material. A finger screen can be utilized to separate the plus one inch particles from the minus one inch pieces even though the moisture may be as high.

As shown in Figure 10, the plus one inch material in the bottom ash is removed and the minus one inch bottom ash is blended with the available fly ash (normally 50% of bottom ash) along with portland cement. The portland cement is normally 15 to 20% (wet basis) of the bottom ash. The three of these materials are all fed directly into a disc pelletizer which is equipped with a reroll ring. Moisture is added to the disc pelletizer through spray nozzles until pellets are produced. It normally requires a total of 16 to 20% (wet basis) moisture to produce pellets.

The completed pellets are discharged from the disc pelletizer pan into the reroll ring where 1 to 3% (wet basis) portland cement is added to coat the pellets. The coating of the pellets with portland cement serves two purposes. The first purpose is to seal the surface of the pellets which will assist in minimizing any leaching, the second purpose is to keep the pellets from sticking together as they cure in the tote bin.

After approximately seven days of curing, the heavy metals in the ash are fixed to the point that they will pass the T.C.L.P. leaching test. The pellets will have strength enough to be easily handled and should not crush under normal handling.

Orimulsion Fly Ash Agglomeration

With the world searching for lower cost fuels we now have an interest in the combustion of Venezuelan heavy bitumen. Due to its extremely high viscosity at ambient temperature, the raw bitumen is unsuitable for conventional transport to utility stations for subsequent combustion. As a result, a bitumen-in-water emulsion (hereinafter called Orimulsion) has been developed to ease handling of the bitumen by reducing its viscosity to a range similar to heavy fuel oils.

The fly ash from combustion of Orimulsion is very unusual with 98% (by weight) of the particles being less than 10 microns in size. This leads to an aerated bulk density of 5 lbs./cu.ft. and a deaerated bulk density of 10 to 12 lbs./cu.ft. The fly ash contains 10 to 15% vanadium which makes it valuable as a concentrate for vanadium production.

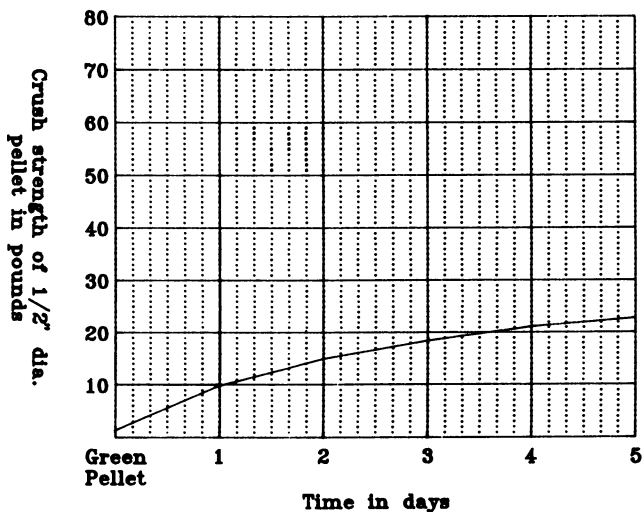


Figure 9. Synthetic Gypsum & Fly Ash Pellets

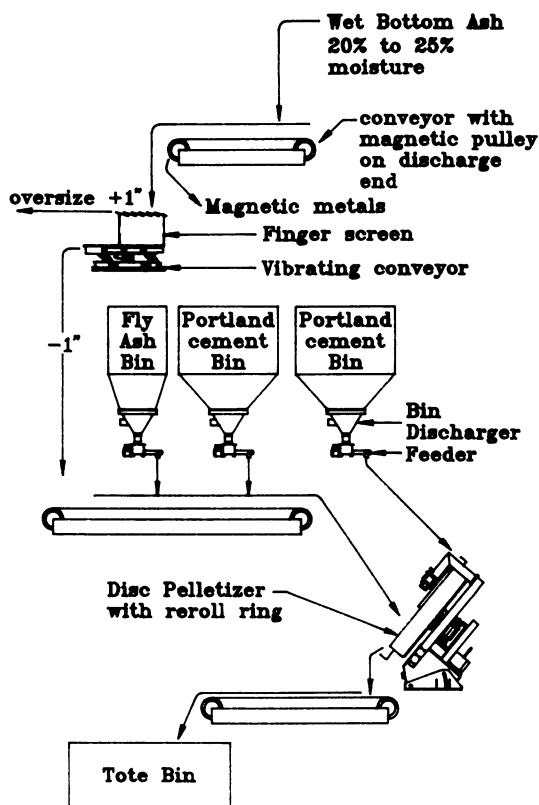


Figure 10. Mass Burn Ash Agglomeration

The fly ash is very fine, reactive and very difficult to wet; therefore, the wetting of the fly ash with water is very critical. It has been found that the only effective method of wetting this fly ash is the Ferro-Tech-Turbulator. Once the fly ash is wet, a hydration reaction takes place. The reacting material quickly heats and all of the water is either chemically bound or is evaporated. The partially hydrated fly ash is again introduced into a Ferro-Tech-Turbulator where more water is added. The wet fly ash is discharged onto a disc pelletizer where pellets are formed. This process is covered by Patent No. 5,008,055. The bulk density of the pellets will be increased to 60 to 70 lbs./cu.ft. from the initial 5 to 10 lbs./cu.ft. The pellets will cure in a few minutes and become hard enough for normal material handling; that is, a 1/2 inch diameter pellet will require 40 to 50 pounds force to crush it.

Conclusions

Essentially any fly ash can be agglomerated into non-dusting and very slow-leaching agglomerates. The requirements for the agglomerates keep changing and become more restrictive as the regulators try to make the environment safer. Our goal is to assist the customer in developing the best process to fulfill the regulators present and future demands. Many of the processes appear to be simple, but there has been much experience involved in the development. We feel that the simplest process is the best process if it meets all of the customer's goals. We know that each situation is unique and a process must be adapted to the special ash from a specific plant. It is advisable to cooperate with a someone who has the most experience so you can have confidence in their recommendations.

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Chapter 20

Utilization of Coal Gasification Slag Overview

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Coal gasification generates solid waste materials in relatively large quantities, and their disposal can represent a significant expense. For example, a 100-MW power plant based on IGCC technology using 1000 tons of 10% ash coal per day may generate over 110 tons/day of solid waste or slag, consisting of vitrified mineral matter and unburned carbon. As coal gasification technologies, considered clean and efficient methods of utilizing coal, find increasing applications for power generation or chemical feedstock production, it becomes imperative that slag utilization methods be developed, tested, and commercialized in order to address the costly problems associated with its disposal as solid waste. This chapter presents an overview of the experimental work that has been conducted to characterize samples of slag from various gasifiers and to identify and test a number of commercial applications for their utilization, and discusses various issues with regard to slag utilization. In the course of examining various utilization applications for a number of coal gasification slags that parallel those developed for fly ash, a better understanding of slag as a construction material has been achieved. The applications tested include the use of slag as an aggregate for road construction, cement concrete and asphalt concrete, and production of lightweight aggregate from slag.

In the past decade, fly ash, bottom ash, and boiler slag have increasingly been utilized in construction and other applications. A number of scientific studies have been conducted to develop utilization manuals applicable for general use. Examples include: *Fly Ash as a Construction Material for Highways: A Manual*, in 1976,(1) and *Fly Ash Structural Fill Handbook* in 1979.(2) In addition, recent applications for fly ash were summarized at the Eighth International Ash Utilization Symposium in 1987.(3)

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A comprehensive survey of coal combustion by-products was undertaken by the Electric Power Research Institute (EPRI) in 1983 in the preparation of the *Coal Combustion By-Products Utilization Manual*.⁽⁴⁾ Volume 2 of this manual comprises an annotated bibliography.⁽⁵⁾ As indicated in the manual, in 1984, 66.4 million tons of boiler ash (comprising fly ash, bottom ash, and boiler slag) was generated nationwide, of which 12.4 million tons (or 18.7%) was utilized in a variety of applications including blasting grit, fill material, roofing granules, roadway construction, de-icing grit, and cement additives. By comparison, in Europe and Japan, combustion solid wastes are utilized to a greater extent; this is attributed to the demand for construction aggregate and fill materials, the shortage of space for waste disposal, and environmental and economic factors.

The search for utilization applications for coal gasification slag parallels that of fly ash, which has been tested successfully for a variety of applications including aggregate stabilization in airport, highway, and dam construction, engineered backfill, soil amendment, cement additive, and lightweight aggregate production. A number of similar applications for gasification slag have been studied by Praxis Engineers, Inc. under a series of contracts funded primarily by the Electric Power Research Institute (EPRI) with additional support from Texaco, Inc. and Southern California Edison.

Development of Slag Utilization Technology

Using fly ash utilization as a model, Praxis started work in 1986 to develop the utilization of gasification slag. The steps involved in this approach can be summarized as follows:

- Measurement of physical and chemical properties expected to affect the utilization of slag,
- Screening of conventional industrial and construction materials and products for potential slag utilization applications,
- Comparison of the properties of gasification slag with the specifications established for other materials to identify possible slag substitution,
- Testing of promising applications at the bench scale,
- Enhancement of the properties deemed significant from the utilization viewpoint by simple, low-cost preparation techniques, and
- Selection of successful applications for further testing at the pilot or demonstration level.

Initial testing was undertaken using slag samples from the Cool Water Demonstration Plant (CWDP). The Cool Water Demonstration Program was based on a Texaco gasification process and used a number of major U.S. coals, including a western bituminous coal and an Illinois Basin coal. Details of the program are provided in a 1985 EPRI report.(6)

Sixteen potential applications for the utilization of gasification slag were initially identified based on a comparison of the preliminary characteristics of a CWDP slag generated from a western bituminous coal feed with those of ash by-products. The most promising of these applications included use of slag as a soil conditioner, abrasive grit, roofing granules, ingredient in cement and concrete manufacture, road construction aggregate, and lightweight aggregate. The results of this work were summarized in a paper(7) and presented in an EPRI report.(8)

Once successful utilization concepts had been identified for this slag, samples of another slag generated at CWDP from a different coal feedstock and three other slags generated from different gasifiers were also evaluated. The three additional gasifier technologies were the Shell Coal Gasification Process, the British Gas Corporation/Lurgi slagging gasifier, and the Dow Chemical entrained-flow gasification process, using single-stage operation.

In a parallel study, use of slag as a feed material for the production of synthetic lightweight aggregate was investigated. The findings of this study were presented in an EPRI report.(9) In a follow-on project, the production of lightweight aggregate from slag was successfully advanced to the pilot scale.

Coal Gasification Slag Properties

Among the early work on the identification of coal gasification slag properties is a 1983 chemical characterization study comparing coal gasification slag samples obtained from pilot projects with coal combustion solid wastes, conducted by Oak Ridge National Laboratory.(10) It was determined that, though there are some differences between various slags, in general gasification slag was nearly as inert chemically as slag from cyclone furnaces.

In characterization testing conducted by Praxis Engineers in 1987-88, focusing on slag utilization, the physical and chemical properties of five coal gasification slags were found to be related to the composition of the coal feedstock, the method of recovering the molten ash from the gasifier, and the proportion of devolatilized carbon particles (char) discharged with the slag ("Characterization of Coal Gasification Slags," EPRI Contract No. RP2708-3. Final report in publication). The rapid water-quench method of cooling the molten slag inhibits recrystallization, and results in the formation of a granular, amorphous material. Some of the differences in the properties of the slag samples that were characterized may be attributed to the specific design and operating conditions prevailing in the gasifiers. For instance, the British Gas/Lurgi gasifier produced a slag with a distinct iron-rich phase in addition to the silicate phase, and the Texaco gasifier generated slag containing a higher proportion of discrete char particles.

In general, slag is nominally in the 5-mm x 0.3-mm size range, which is equivalent to the classification for fine aggregates used in cement concrete and asphalt concrete. The apparent specific gravity of slag ranges between 2.64 and 2.81, and its dry compacted unit weight is between 70.1 and 104.9 lb/ft³. The water absorption capacity of slag varies from 2 to 16% and increases with its char content. The leachability of the slags is generally very low. Both EP toxicity and ASTM extraction tests reported nonhazardous levels of the eight metals regulated under these tests. These findings confirm the work done on slag by the developers of several gasifier technologies such as Texaco, Shell, and Dow.

The elemental composition of the slag samples with respect to both major and trace elements is similar to that of the gasifier feed coal ash, as shown in Table I. The major constituents of most coal ashes are silica, alumina, calcium, and iron. Slag fluxing agents, when used to control molten ash viscosity inside the gasifier, can result in an enrichment of calcium in the slag.

The Cool Water slag was classified as nonhazardous under the RCRA regulations. EP toxicity and ASTM extraction tests were run on a number of slags to evaluate their leachability. The slags appear to be nonleachable with respect to RCRA-listed metals. Tests for eight RCRA heavy metal anions were run, with only sulfate anions being detected at significant concentrations (25 to 200 mg/l).

Table I. Comparative Composition of Typical Blast-Furnace Slag, Cool Water Feed (Utah) Coal Ash, and Cool Water Slag

<i>Mineral</i>	<i>Blast Furnace Slag</i>	<i>Cool Water (Utah) Coal Ash</i>	<i>Cool Water Slag</i>
SiO ₂	32-42	48.0	40-55
Al ₂ O ₃	7-16	11.5	10-15
CaO	32-45	25.0	10-15
MgO	5-15	4.0	2-5
Fe ₂ O ₃	0.1-1.5	7.0	5-10
MnO	0.2-1.0	NA	NA
S	1.0-2.0	NA	<1

Evaluation of Potential Utilization Concepts

Selection of applications to utilize gasification slag must take into account the fact that it is in competition with conventionally used materials whose acceptability has been established over long periods. In this effort, the emphasis was placed on evaluating the functional requirements of various applications (such as compressive strength in the case of cement concrete) in order that existing specifications--written for natural materials--do not rule out slag utilization. Ultimately, if slag is found to satisfy the functional requirements of an application, suitable standards can be established for its use in particular

cases. A precedent for this procedure is the creation of a standard such as ASTM C 989-87a which was adopted for utilization of ground blast-furnace slag as cement.

Selection of the specific utilization concepts was guided by the following criteria:

- Similarity between the properties of slag and those of the material it replaces, and
- Achievement of comparable final products meeting the necessary functional requirements.

Based on these criteria, a number of utilization concepts were identified. These include:

Agriculture:	Soil conditioner, lime substitute, low analysis fertilizer, carrier for insecticides
Industrial material:	Abrasive grit, catalyst and adsorbent, roofing granules, industrial filler, mineral (slag) wool production, filter media
Cement and concrete:	Concrete aggregate, mortar/grouting material, pozzolanic admixture, raw material for portland cement production, masonry unit production
Road construction and maintenance:	De-icing grit, fine aggregate for bituminous pavement, base aggregate, subbase aggregate, seal-coat aggregate
Synthetic aggregate:	Lightweight construction aggregate, landscaping material, sand substitute
Landfill and soil stabilization:	Soil conditioner to improve stability, structural fill, embankment material
Resource recovery:	Source of carbon, magnetite, iron, aluminum, and other metals

Of these, a number of high-volume applications were tested at the laboratory scale and found to be suitable. For example, the potential for using slag as a fine aggregate for base, subbase, and backfill applications is suggested by the slag size gradation. Shear strength, permeability, and compaction test data also indicate that slag would perform well as an aggregate fill material.

While these applications would consume large quantities of slag they provide few economic incentives to the construction industry to replace cheap and abundant conventional materials with slag at this stage. However, as concern about the environment increases and recycling of waste products becomes a priority, this situation could change rapidly.

Use of Slag in Road Construction

Slag produced by the Cool Water Demonstration Plant was studied in road construction applications by testing various asphalt mix designs incorporating slag. By itself, the slag was not found to be suitable for surface pavement applications due to the lack of coarse particles and the tendency to degrade when abraded. However, its use as a subbase and base material in road construction is quite feasible as it meets the resistance value requirements for the California Department of Transportation standards for Class 1, Class 2, and Class 3 subbases, and Class 2 aggregate base. In order to offset the high proportion of fines in the slag, it may need to be mixed with coarser conventional materials prior to use as a specification base material and as an asphalt concrete aggregate.

Asphalt concrete hot mixes containing varying concentrations (6-10%) of asphalt and 30-50% slag by weight as the fine aggregate were tested for their strength (S-values) in a laboratory. A mix in which 30% slag was used with 6% asphalt yielded an S-value of 50, which is much higher than the minimum value of 30-37 required for various grades of asphalt concrete. This mix, which had good workability, compares favorably with the control test mix containing 5% asphalt, which has an S-value of 58.

Use of Slag in Cement and Concrete Applications

The composition of the CWDP slag and its natural pozzolanic properties are similar to the raw material used to make portland cement clinker. In this application, the slag carbon (char) content may be beneficial and may provide some of the fuel needed to make the clinker. The slag could also be added to cement clinker and ground with it.

The char content of some of the slags is far higher than the 1% limit placed on aggregate. This makes it necessary to recover the unconverted carbon from the slag, both in order to meet the standard for aggregate and to improve the process economics. Char removal was accomplished by means of simple specific gravity devices. The recovered char is a usable by-product.

Several batches of concrete were prepared using slag to replace varying quantities of the sand in the mix. Specimens in which 50% and 75% of the sand was replaced by slag had compression strengths of 2790 and 2480 psi respectively, over a 28-day curing period. This compared well with the control sample containing no slag, which had a compression strength of 3410 psi. These results indicate that slag could be used to replace a large proportion of the fine aggregate in making nonstructural concrete.

Tests to replace some of the fine aggregate used to make concrete with slag were performed by substituting 50% of the sand by slag. The test specimens achieved satisfactory results, with compressive strengths ranging from 3000 to 3500 psi, compared with a control strength of 3900 psi at the same cement content. These results satisfy typical compressive strength requirements of 2000 psi for concrete pads for sidewalks, driveways, and similar applications. Based on these tests, a large batch of concrete was prepared using 50% slag to replace the fine aggregate in the cement concrete mix and used to cast a concrete pad at the Cool Water Demonstration Plant site. In subsequent monitoring, its performance was found to be comparable to that of standard cement concrete.

A similar study was conducted by Shell Development Company to test the utilization of slag for replacing part of the fine aggregate in cement concrete.⁽¹¹⁾ In a mix in which nearly all of the fine aggregate was replaced by slag, a 28-day compressive strength of 3000 psi was obtained. Slag was subsequently routinely used on site in the preparation of cement concrete mixes.

In a series of tests conducted by Praxis Engineers, slag ground to a fine powder was used as a cement replacement ("Characterization of Coal Gasification Slags," EPRI Contract No. RP2708-3. Final report in publication). Cement additive requirements have been established for blended cements in ASTM C 595, which covers five classes of blended hydraulic cements made from conventional materials for both general and specific applications. Following initial exploratory tests, it was concluded that it was necessary to process the slag samples to remove potentially deleterious substances. The lighter char fraction was removed from one of the slags by density separation, and an iron phase was recovered from another slag by magnetic separation. The percentages of cement replaced by slag in these tests were 15% and 25% respectively. The use of processed slags resulted in a more successful replacement of cement by slag. All of the 15% slag-cement blend samples exceeded the 3-, 7-, and 28-day strength requirements of 1800, 2800, and 3500 psi respectively, and one of the four slags tested exceeded these requirements at the 25% replacement level. The other three 25% replacement level slag samples achieved the required 28-day strength but did not satisfy the 3- and 7-day requirements. The average 28-day strength for the 15% blend was 5600 psi, and that of the 25% blend was 4900 psi.

The success of the prepared slag-cement blends in achieving long-term compressive strength suggested that ground slag would also qualify as a pozzolanic mineral admixture. A pozzolan is a finely ground siliceous material which can react with calcium ions, in the presence of water and at room temperature, to form strength-producing calcium silicate minerals in a manner similar to cement reactions. A 35% replacement of cement by slag was evaluated in accordance with the procedures outlined in ASTM C 311. The success of a pozzolanic test is measured by the Pozzolanic Index, which indicates the ratio of the sample's compressive strength to that of an ordinary portland cement control sample. All of the concrete samples thus produced exceeded the

Pozzolanic Index requirement of 75%, with index values ranging between 90 and 118%.

Slag Lightweight Aggregate

Lightweight aggregates (LWA) have unit weights that are approximately 40-60% those of standard aggregates. Annual consumption of LWA in the United States for various applications is approximately 15 million tons. Major applications of LWA are in the production of lightweight structural concrete used in highrise buildings and lightweight precast products such as roofing tiles, masonry blocks, utility vaults, cement concrete pipes, etc. Conventional LWAs are produced by pyroprocessing of naturally occurring expandable shales or clays at temperatures ranging between 1880 and 2200°F, after pulverizing, working into a paste, and extruding them to produce pellets of the desired size. The strength requirements for lightweight concretes made from LWA are given in Table II.

Slag-based lightweight aggregates (SLA) were produced by Praxis Engineers (see ref. 9) by duplicating the processing methods used for commercial LWA manufacture. These steps included grinding the slag, mixing it with a clay binder and water, and extruding it to form long strands that were cut to the desired sizes. These wet green pellets were then dried and fired in a laboratory muffle furnace at 1800°F for 4 minutes. A unit weight of 45 lb/ft³ was measured for the SLA, which is below the minimum coarse LWA specification of 55 lb/ft³. Concrete made from the SLA had a 28-day compressive strength of 3100 psi and a unit weight of 105 psi, which exceeds the ASTM requirements shown in Table II.

Table II. Lightweight Aggregate Unit Weight, Minimum Compressive Strength, and Tensile Strength (28-Day Requirements for Structural Concrete, ASTM C 330)

<i>100% LWA Mix</i>		<i>Sand/LWA Mix</i>	
<i>Unit Weight lb/ft³</i>	<i>Compressive Strength, psi</i>	<i>Unit Weight lb/ft³</i>	<i>Compressive Strength, psi</i>
115	--	115	4000
110	4000	110	3000
105	3000	105	2500
100	2500	100	--

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Further tests have confirmed that the density of the SLA can be controlled as a function of the firing temperature, as shown in Figure 1. This indicates that SLA products can be produced to meet specific density

requirements such as those for cement concrete LWA, lightweight concrete masonry units, or ultra-lightweight material used in insulating concrete.

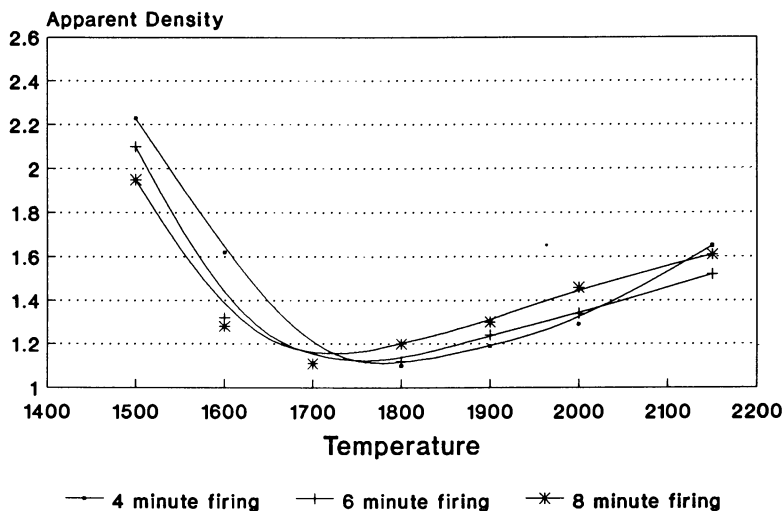


Figure 1. Time/Temperature/Density Relationship for Expansion of Slag Pellets

Tests on discrete 2-mm particles of each slag showed that they also expand to form a lightweight material when fired at 1600-1900°F. Further tests on all particles larger than 0.3 mm, without pelletization, confirmed this phenomenon. The materials resulting from these tests had unit weight values of 15-25 lb/ft³. The concrete produced from one of the expanded slag samples had a unit weight of 33 lb/ft³, which qualifies it to be classified as an insulating concrete. However, it had a compressive strength of only 125 psi, which is somewhat lower than the strength of commercially available insulating concretes at 200-250 psi. It is expected that the strength can be considerably increased with minor adjustments to aggregate gradation and the cement proportions used to formulate these test samples.

The experimental work on slag utilization has been developed to the continuous pilot scale for the production of SLA from slag. The results from this test program have been very encouraging and have confirmed the bench-scale test results. During the tests, engineering information on energy requirements, scale-up information, and off-gas analysis was obtained, and the mechanism of slag expansion was investigated. The energy requirements for SLA production are considerably lower than those for conventional LWA production due to the lower kiln temperatures required for the expansion of slag. Samples of SLA with different unit weights produced during the pilot tests

are undergoing extensive testing ("Production and Testing of a Large Batch of Slag Lightweight Aggregate," Final Report for EPRI Project No. RP1459-26, in publication.)

In 1989, Ube Ammonia Industry Company, Ltd. of Japan reported having expanded the slag produced from their Texaco-type gasification process.⁽¹²⁾ A flash furnace was used to expand a selected portion of prepared slag to make a lightweight product equivalent to perlite for the local market.

Conclusions

Gasification slag has been determined to be an environmentally nonhazardous material, whose unique properties may be attributed to the composition of the mineral matter in the coal feedstock and the method of quench-cooling applied in the gasifier. Bench-scale test data have shown that there are a number of promising applications for the utilization of gasification slags. In particular, the utilization of slag in applications such as road, cement concrete, and construction aggregates, cement additives, and lightweight aggregates has been demonstrated. Production of slag-based lightweight aggregates (or SLA) is feasible and should be established as a priority. The high unit price of lightweight aggregates will permit SLA to be transported for greater distances while remaining economically competitive, thus rendering slag utilization less sensitive to the location of the gasifier.

Future of Slag Utilization

Currently, in most utilization scenarios, gasification slag would be used as a replacement for materials that have a relatively low unit cost, such as cement concrete and road aggregates. Unless potential commercial users of slag are provided with extensive characterization and utilization data, the economic incentives alone are unlikely to be sufficient to cause them to incorporate slag into their mix designs and production scenarios. The initial resistance to the use of new materials that may be encountered in the construction materials manufacturing industry can be addressed in two ways. First, the slag producer can supply complete engineering data on slag utilization to the prospective end user, who would then be responsible for any slag processing steps that might be required for a particular application. An alternative, more comprehensive approach would be for the slag producer to deliver physically prepared slag to the end user in a form that meets the user's specifications; these specifications could vary depending on the market demand in the vicinity of the gasifier. If recent legislation in California can be used to gain an insight into coming regulatory trends, at least 50% of the slag produced in the state will be required to be utilized in the coming decade, thereby creating additional incentives for producers and prospective end users to work together to realize its utilization potential.

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Chapter 21

High-Strength Portland Cement Concrete Containing Municipal Solid Waste Incinerator Ash

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The commercial use of solid wastes from energy-producing units, such as coal-fired boilers and oil shale combustors, has been practiced for several decades in the United States and in Europe. Recently, work by numerous organizations has begun on a variety of methods to render hazardous solid residues non-hazardous and to create beneficial uses for ash from municipal solid waste incinerators. One method for both purposes is the replacement of a portion of the fine aggregate in Portland cement concrete. The strength of the concrete drops significantly as the portion replaced increases, even with normal additives. This chapter presents the greatly improved strengths obtained with ash, which has been exposed to a new additive. These results show that up to 35% of the concrete can be made up of ash, while still obtaining compressive strengths of over 5000 psi (34.5 MPa). Micrographs of the original ash, ash and additive, concrete with ash but without additive, and concrete with ash and additive indicate the role of the additive. TCLP extractions of this novel new concrete and evaluations of its engineering properties have yet to be conducted. The economics, commercialization and extension of the development to other situations are discussed.

Power generation facilities and the construction industry many years ago recognized a remarkable opportunity for an exchange of great mutual profitability. With considerable development work, they transformed fly ash from coal-fired power plants, a waste requiring ever more expensive landfill for disposal, into a useful substance for inclusion in materials for building highways and other structures. The operators of municipal solid waste (MSW) incinerators are investigating a parallel opportunity for the beneficial use of the ash from their facilities. This chapter begins with a brief survey of the extent of coal ash

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utilization and what was required to institutionalize it. Next, the article will survey the current state of development of beneficial use of MSW ash and the effort that is yet required for its institutionalization. The article will conclude with a report on the status of one program for developing the beneficial use of MSW ash in precast concrete.

Commercial Use of Solid Wastes from Coal-Fired Boilers

Coal ash is formed by an extensive, complex processing of the mineral matter in coal, through a sequence of high temperatures and both reducing and oxidizing environments. As the composition of the mineral matter and the nature of the processing conditions vary, so will the characteristics of the resulting ash. However, the principal constituents of mineral matter are always silica and alumina, which are two of the principal ingredients of manufactured Portland cement (the third ingredient of which is lime). The third principal constituent of coal mineral matter is usually iron sulfide (bituminous coals) or limestone (subbituminous coals and lignites), although recently certain sulfur removal technologies provide lime (or limestone) as a cofired ingredient, particularly with bituminous coal.

A comparison between the processing of mineral matter in pulverized coal (PC) boilers and the manufacturing of Portland cement in rotary kilns is instructive. In a PC boiler the processed mineral matter experiences temperatures up to 1900°K, which are well above the melting point of the ash (usually between 1300 and 1500°K). The resulting fly ash is composed largely of very small particles of alumina-silica glass, in the form of mixtures of glasses and crystalline mullite ($3Al_2O_3 \cdot 2SiO_2$), quartz (SiO_2) and metal silicates (*1*). In a cement kiln, producing a glassy Portland cement clinker, a mixture of typically 60 percent lime, 25 percent silica, 5 percent alumina and 10 percent iron oxide and gypsum are exposed to temperatures between 1700 and 1900°K. The cooled clinker is ground to a fine powder and marketed as cement.

It is not surprising, then, to find that fly ash from a PC boiler is a pozzolan, having good cementitious characteristics when mixed with lime and water (*1*). It is also not surprising, considering the large amounts of electricity produced by PC boilers in this country, to find that electric utilities and concrete manufacturers years ago began to develop methods for directly using fly ash from PC boilers as an admixture with Portland cement in concrete production. This development has been very successful. In 1986, for example, of 49 million short tons of fly ash produced in the United States, 9 million short tons (or 18%) were in beneficial use, half of this in concrete (*2*). This represents a major business activity, which has seen the establishment of its own "niche" trade organization, the American Coal Ash Association.

It may be noted in passing at this point that ash from the combustion of oil shale is also an excellent pozzolanic admixture for Portland cement. While this material has not yet been commercialized in the United States (in the absence of the commercial use of oil shale itself as an energy source), it has found acceptance

in other countries, notably in China and certain of the republics of the former USSR (3).

The first use of coal fly ash with Portland cement was to repair a tunnel spillway at the Hoover Dam in 1942. The first relevant specifications for fly ash in concrete were promulgated by the American Society for Testing and Materials (ASTM) over twenty years later in the mid-1960's. The current version of these standards is the very comprehensive ASTM C 618. The amount of fly ash, having properties within the range allowed by ASTM C 618, in typical concrete applications, for example, will vary from 15 to 25 percent by weight with amounts up to 70 percent for massive walls and girders (2).

As noted above, however, less than 10 percent of the fly ash produced by PC boilers in the United States is used in concrete. The reason for this limited utilization is that only one-quarter of the fly ash produced in this country meets the ASTM C 618 standard. Thus, to be used beneficially the remaining three-quarters of the fly ash, as well as all of the bottom ash and boiler slag produced -- a total of nearly 60 million short tons per year, must find its way into products with less restrictive standards. About 10 million short tons per year have done so, going into such uses as concrete products (as aggregate), structural fills, road base, asphalt fillers, snow and ice control, blasting grit and roofing granules, grouting and mine back-filling (2).

The electric power industry continues to seek ways in which to expand the beneficial use of coal ash. In 1984 the Electric Power Research Institute (EPRI) established an Ash in Cement/Concrete Products research project (RP 2422). Its purpose is to better define coal ash characteristics as they relate to ultimate material properties of the wide range of products, mentioned in the previous paragraph. The project continues at this writing. Ultimately, EPRI will make recommendations for broadening the standards for these products, which will allow expanded utilization of coal ash and further reduce the need of the U.S. electric utility sector for landfills (4).

EPRI has also established an Advanced SO₂ Control Management research project (RP 2708) to define the characteristics of a new solid residual from coal-fired power plants -- by-products of SO₂ removal technologies, including:

- Atmospheric Fluidized Bed Combustion
- Calcium Spray Drying
- Limestone Furnace Injection
- Sodium Sorbent Duct Injection
- Calcium Sorbent Duct Injection

These materials all contain significant amounts of gypsum and other sulfates, along with the coal ash as previously generated. A variety of markets and products are being explored for these by-product materials, similar to the markets, listed above, which are already enjoyed by coal ash itself. Work on this project continues at this writing also. Preliminary research suggests that proper by-product conditioning and overall product mix design modification may result in acceptable product performance in "concrete-type" applications (5).

Beneficial Use of MSW Incinerator Ash

As landfill space becomes more limited, the operators of MSW incinerators are beginning to follow the same path toward possible beneficial use of ash from their plants, that electric power plant operators created for themselves over the past few decades. Ash from MSW combustors can have less than 10% of the original volume entering the facility. It should be noted, however, that for the public, which bears the ultimate ownership for MSW incinerators, there are two other approaches to reducing the amount of waste needing landfilling. Recycling, of course, is one of these, while waste minimization is the other. But no matter how much these other two approaches are implemented, there will always remain a residual whose volume can be effectively reduced in a waste-to-energy process, such as an MSW incinerator, and that waste-to-energy process will ultimately yield an ash.

Because of the very low quality of incinerator ash, it would appear rather inconceivable to use it as an admixture in Portland cement. The most commonly considered beneficial use for it, therefore, is as an aggregate in either bituminous or Portland cement concrete. This method has the further advantage, just as does the use as aggregate of bottom ash and boiler slag from coal-fired plants, of displacing sand and gravel, which must be mined from sometimes environmentally sensitive locations. Another short-term advantage of this method is its ability to bind the toxic metals, entering with the MSW (6), into the concreted mass. Controversy over the long-term implication of the presence of these metals in the concrete has arisen, however. The Environmental Defense Fund has expressed vigorous concern for the long-term release of these metals as the concrete eventually degrades or is reduced to rubble (7).

Utilizing MSW incinerator ash in Portland cement concrete has been investigated by several organizations. At a number of locations, bottom ash (slag) from high-temperature MSW combustors is utilized as coarse aggregate in regular concrete (8,9). Utilization of low-strength concretes containing either fly ash or mixed fly and bottom ash (combined ash) are moving toward commercial use in three directions.

One of these directions is to make block secondary products, such as artificial reef blocks, construction blocks, and shore protection devices (10,11). Artificial reef blocks, prepared at the State University of New York, Stony Brook, consist of 85% combined ash and 15% Portland (Type II) cement, and have compressive strengths of about 1000 psi (6.9 MPa) (10). By comparison, standard precast Portland cement concrete contains 40% coarse aggregate, 40% fine aggregate and 20% Portland cement and has a compressive strength of over 3500 psi (24.2 MPa).

Construction blocks, prepared at SUNY Stony Brook, consist of 35-60% combined ash, 25-50% sand, 15% Portland (Type IP) cement, and sufficient Acme-Hardesty superplasticizer to allow the mix to flow easily (10). Compressive strengths vary from 1600 psi (11.0 MPa) to 2600 psi (17.9 MPa). A boathouse, built recently at SUNY Stony Brook from 14,000 such construction blocks, is being evaluated for structural and environmental acceptability (10,12). Finally, shore

protection devices require the use of a patented admixture, Chloranan (manufactured by Hazcon, Inc., of Brookshire, Texas) at a ratio of cement to admixture of 10:1. Using cement percentages between 17 and 33, compressive strengths up to 4200 psi (29.0 MPa) are reported (10).

An extension of the work at SUNY Stony Brook on the manufacturing of construction blocks containing incinerator ash is being conducted at SUNY Buffalo (11). There, concrete masonry units (CMU's or construction blocks) have been prepared using a modified ASTM C 109 standard. A wide range of ASTM standards have been used to characterize the ash which is used in the CMU's. In manufacturing the CMU's a variety of techniques, known to improve the durability, strength and sulfate resistance of Portland cement concrete, have been used to improve the commercial properties of the ash-containing mixes. Compressive strengths in excess of 1500 psi (10.3 MPa), satisfactory for commercial CMU's, have been obtained from mixes utilizing Portland (Type V) cement.

A second approach to MSW ash utilization is the accretion of combined ash with Portland cement (8-14%) into coarse aggregate for use in roadbeds and concrete (12,13). This level of concretization provides aggregate with strengths of about 1200 psi (8.3 MPa), similar to the material described in Reference 10.

Finally, a third approach is the stabilization of combined ash with Portland cement (6-10%) to create landfill covers (12,14). In all of these approaches, the ability of Portland cement concrete to reduce the leachability of trace metals from the concreted mass to meet TCLP standards has been a key element of their development.

The U.S. Environmental Protection Agency's Risk Reduction Engineering Laboratory (Municipal Waste Technology Section) is currently completing an evaluation of the effectiveness of five different solidification/stabilization processes for treating MSW residues (12,15). These processes include Portland cement only, Portland cement with polymeric additives, Portland cement with soluble silicates, waste pozzolans, and phosphate addition treatments. A major portion of the work is being conducted at the Waterways Experiment Station of the U.S. Army Corps of Engineers in Vicksburg, Mississippi. There, physical properties and durability testing include unconfined compressive strength (UCS), UCS after immersion, and wet/dry and freeze/thaw testing. Leaching characterization include TCLP, serial distilled water extraction, availability tests and monolith leaching tests (16). Results of this work are expected to be published in late 1991 (12).

A major area which these projects do not appear to address is the precast concrete market. For entrance into this arena, compressive strengths between 3500 psi (24.2 MPa) and 5500 psi (38.0 MPa) must be achieved. In addition, extensive physical testing must be applied and minimum standards met. These tests include tensile strength, freeze-thaw, deicing, and abrasion. As the preceding brief review shows, obtaining the compressive strengths required by precasters has proven impossible with significant amounts of combined ash, even with standard additives. Only those concretes made with the addition of large amounts of Chloranan enter this range.

The School of Engineering at the University of Pittsburgh has recently discovered an inexpensive method which permits high-strength concrete to be produced, containing large amounts of combined ash from a MSW combustor. The method, which has just been disclosed to the University as the first step in the patent process, will now be described as thoroughly as possible within the limits imposed by that process.

Portland Cement Concrete Manufacture

In October 1988 the University of Pittsburgh began to study the utilization of MSW combustor ash in Portland cement concrete. Four 750-lb (340-kg) samples of ash have been obtained during the past two years from the MSW combustor at Poughkeepsie, New York, operated for the Dutchess County Resource Recovery Agency by Dutchess Resource Energy, a subsidiary of the Resource Energy Systems Division of Westinghouse Electric Corporation. The primary combustor in this facility is an O'Conner water-wall rotary kiln. The bottom ash drops into a water-filled pit, from which it is reclaimed past a grizzly to take out large particles, and a magnet for iron removal. The hot gases from the primary combustor pass through a secondary combustor, a boiler, and a dry scrubber. The fly ash and spent limestone (injected in the scrubber for acid gas removal) are added to the bottom ash just before the combined ash is loaded into trailers for hauling to a land disposal site.

The first two samples of ash were composited from 5-pound (2.3-kg) sub-samples of combined ash, collected six times daily for 25 days. Ash Sample #1, combined ash collected from mid-July to early September 1989, contained 8-21% moisture, 15.1% calcium oxide, 2.21% sulfur trioxide and 7.2% iron oxide and exhibited a 7.26% loss of ignition. Ash Sample #2 was bottom ash collected during January 1990. Ash Samples #3 and #4 were bottom ash collected in essentially one quick draw on May 24-25, 1990, and March 1-2, 1991, respectively. Ash Sample #3 contained 11.9% calcium oxide, 2.58% sulfur trioxide and 9.8% iron oxide and exhibited a 8.04% loss of ignition.

Six batches of concrete were made with Ash Sample #1 and fifteen batches with Ash Sample #2. The basic recipe was 17% coarse aggregate, 40% ash and 43% Portland cement. An air entrainment additive, a water reduction additive and a silica fume additive were all tried individually with certain of these batches. The slump of each batch was held as close as possible to 1.75 inches (4.45 cm) by varying the water content. Concrete batches were produced in a small commercial mixer in the Concrete Laboratory of the Civil Engineering Department, following standard procedures. A number of cylinders (3 inches (7.6 cm) in diameter and 6 inches (15.2 cm) long) were formed from each batch. Cylinders were stored in an environmentally controlled room. Compressive strengths were measured on a Baldwin hydraulic compression tester, also located in the Concrete Laboratory of the Civil Engineering Department. Sets of four cylinders were cracked, and the load at breaking were averaged to obtain reported values of compressive strength.

Compressive strengths were generally in the range of 1000 psi (6.9 MPa) to 2300 psi (15.9 MPa). The ash in the first six batches of concrete were subjected to the Standard Extraction Procedure Method (the EP TOX procedure). The extractions were performed in the Environmental Laboratory of the Civil Engineering Department and leachates were sent to a commercial laboratory for analysis. Neither the ashes nor the concretes exceeded the EP TOX limits for any constituent. However, the ash and one of the six concrete batches (which happened to contain a lower amount of Portland cement and a higher amount of coarse aggregate than according to the usual recipe, and which also contained some sand) exceeded the NYCRR limits for cadmium and lead. The presence of fly ash in Ash Sample #1 appeared to cause a number of "popouts". A white crystalline material, identified as a physical assemblage of aluminum chloride and calcium oxide crystals, was found at the focal point of all the popouts examined.

As Ash Sample #2 was running out, it was decided to attempt to modify the chemical and/or physical makeup of the surface of the ash particles to increase the strength of the bond between the ash and the cement. Two different commonly available chemicals were tried as additives in the last two batches of concrete made from Ash Sample #2. One of these novel additives did, in fact, yield compressive strengths of nearly 4000 psi (36.0 MPa). Therefore, a set of batches with varying amounts of this effective, inexpensive, novel additive were prepared with ash from Ash Sample #3. The results are shown in the Table I. The amount of additive is given as a percentage of the weight of cement present in each batch. A second batch of concrete, Batch Number 44, was made with the last portion of Ash Sample #3, using the same recipe as Batch Number 32.

Table I. Variation of Compressive Strengths with Additive

Batch Number	Additive (%)	90-Day Compressive Strength, Psi (MPa)
29	3.47	0 (0)*
30	1.73	4940 (34.1)
32	0.87	6200 (42.8)
36	0.65	3750 (25.9)
37	0.43	3210 (22.1)
34	0.17	2260 (15.6)
42	0.07	1560 (10.8)**

* All cylinders of this batch broke apart by 90 days.

** 14-day compressive strength.

Samples of ash and concrete were examined in the Scanning Electron Microscope (SEM) in the secondary electron imaging mode. The phases present

were also compared using X-ray microanalysis in the SEM. Figures 1 and 2 are examples of micrographs for Batches Number 42 and 44, respectively, in the secondary electron imaging mode. It appears from an examination of these micrographs that, even with a 12-fold increase in additive from Batch Number 42 to Batch Number 44, the same basic cement structure is present in both concretes.

Figures 3 and 4 are SEM micrographs of ash. Figure 3 is for Ash Sample #4 as received. Figure 4 is for Ash Sample #3, which has been mixed with an aqueous solution of the chemical additive, using the same amounts of ash and additive as was used in preparing Batch Number 32. It may be observed from an examination of these micrographs that the surface of the as-received ash is heavily contaminated with fine particles, which are not present on the treated ash.

It is hypothesized from the observations reported above that the elimination of the fine particles in the concrete formulations with the chemical additive renders the surface of the ash particles (serving as fine aggregate) more amenable to strong bonding with the hydrated Portland cement, yielding high-strength concrete as a product.

A preliminary cost analysis of one ton (908 kg) of concrete (dry basis), composed of

- 420 pounds (191 kg) coarse aggregate
- 750 pounds (340 kg) of ash
- 830 pounds (377 kg) of Portland cement
- chemical additive at the level of Batch Number 32

shows that purchase of the materials for its manufacture would require \$23.50. The cost of materials for a 2:2:1 precast concrete is \$10.00. The ash-containing concrete with the formulation of Batch Number 32 would be \$13.50 more expensive than the standard concrete. Since the former contains 750 pounds (340 kg) of ash, the ash would have to be forced into this beneficial use with a tipping fee of \$36.00 per ton (\$79.30 per Mg), which is less than one-third of the current tipping fee at landfills.

Future Work

One final technical step in developing concrete with the same recipe as Batch Number 32 needs to be taken. Durability tests (tension strength, expansion, freeze/thaw, deicing and abrasion) and a TCLP extraction need to be carried out. When these results are available, precasters in the vicinity of the MSW combustor, operated by the Dutchess County Resource Recovery Agency, can make an informed technical decision on the use of the ash from this combustor in their products. Regulatory permission for this use of the MSW combustor ash would then have to be sought from the State of New York.

Several other aspects of the beneficial use of MSW combustor ash in Portland cement concrete should be examined. First, the current 0.5:0.9:1 recipe may not be the optimal one for commercial use. A range of formulations should be explored. Second, additives similar to the one used in these first experiments could be tried, especially if durability and TCLP tests uncover any problems. Third, ash from other types of combustors could be tested for the applicability of

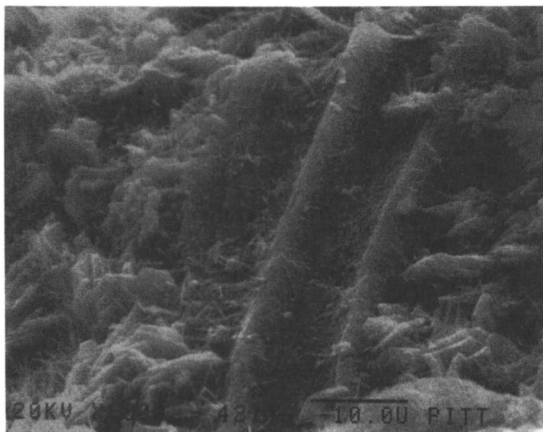


Figure 1. SEM micrograph of the fractured surface of Batch Number 42, made with 0.07% additive; the bar is 10 micrometers.

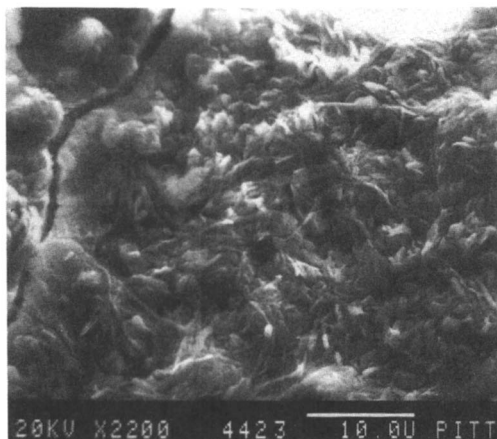


Figure 2. SEM micrograph of fracture surface of Batch Number 44, made with 0.87% additive; the bar is 10 micrometers.

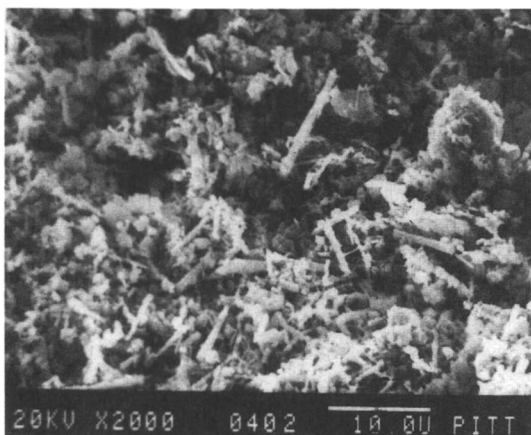


Figure 3. SEM micrograph of Ash Sample #4 as received; the bar is 10 micrometers.

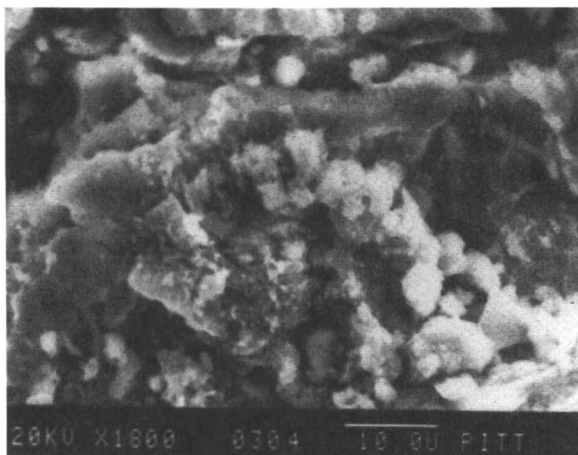


Figure 4. SEM micrograph of Ash Sample #3, mixed with additive; the bar is 10 micrometers.

the new additive. These combustors would include other MSW combustors with different methods for ash removal from the unit. They could also include industrial and hazardous waste combustors.

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Chapter 22

Assessing the Feasibility of Developing and Transferring New Energy Technology to the Marketplace

A Methodology

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Any new process intended to produce clean energy from waste should be characterized for its ultimate feasibility of becoming commercially successful. A four-phase strategy to analyze the process and plan for scale-up is presented. First, the new technology is assessed in terms of its market potential based on laboratory, bench scale or pilot data. A comparison with competing commercial technology is performed to compare the technology with its competition by estimations of factors such as life cycle cost, public acceptance, and adaptability to changing conditions and fuels. Second, the current status is reviewed with respect to theory, laboratory or pilot scale results, and available cost data. Third, the path to commercialization is outlined. The stages of scale-up and data required to prove the concept and remove risks of commercialization are identified. Finally, the financing needs for the various stages of scale-up and for a commercial unit are determined.

Development of any new technology has traditionally been a controversial subject due to high expectations shared by proponents and results which many times fall short of these expectations. Solid and liquid waste management has seen both success and failure in the implementation of new technology. For example, promises to commercially produce liquid or gaseous fuels and/or chemicals from municipal solid waste (MSW) or refuse derived fuel (RDF) have so far been unfulfilled after several attempts at demonstrating various technologies. These failures encourage us to examine new and undeveloped technology in a more sophisticated and step-wise manner than has been previously done. By learning from past failures and taking a methodical and proactive approach to scaling-up suitable technology, we can better direct development so that realistic expectations can be made and met. The approach discussed here will increase chances for successful development of new waste management technologies.

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The following phases outline the approach to be presented:

- I. Determine if a technology at its current state of development, either conceptual, bench, or pilot scale, can be potentially competitive with commercial technologies today.
- II. Establish the current status of the technology and determine what needs to be better understood before progressing.
- III. Establish the path which would most logically be taken to result in commercializing the technology.
- IV. Identify the requirements of different financing options necessary to commercialize the technology.

These phases follow a progression in which the results of each builds on the results from the preceding phases. This review can be started at any time in the development process and should be updated to account for new data on the technology, the competition, or the market as they become available.

Review and analysis of new technology can be biased according to the perspective of the reviewer. The investigators, developers, and sponsors all have vested interests in the technology which may prevent a balanced view of the technology, its development, or its commercialization. Investors and lenders typically look for independent reviews of the technology prior to committing large amounts of capital. This can best be accomplished by persons without conflicts of interest and with an adequate background reviewing development of the technology.

Review of the Concept

In this initial stage of analysis, the technology is looked at objectively to assess its niche in current markets. The first step is to identify the market or markets where the technology would most likely be competing and to broadly establish a range of competitive pricing for the service provided or product produced. It is important to consider all areas where the technology could potentially compete, including those outside the primary field of interest. High value chemicals, resins, and plastics, for instance, may be more economically feasible to produce than fuels from certain feedstocks.

Questions to resolve before proceeding are those which would be important to an investor. These generally will establish if the market is potentially strong and lasting. In the area of solid waste management, the following questions can be used as guidelines to ascertain the market's potential. Similar questions can be developed for any particular field.

Is the market for the products expanding? A market analysis should be made to determine the value of the primary products at the location of the initial commercial facility and subsequent facilities. While the products may have

a high value to the end user, transportation and broker costs should be accounted.

- Is the market monopolistic or controlled by a few companies? Some commodity markets may be hard to break into due to certain restrictions. Long-term supply contracts may be in place with the end users. The end user may be unwilling to bear the risk of a new supplier who is unknown in terms of quality and interruptions in service. Significant discounts on product price may need to be made to obtain contracts which will lead to a track record of quality and supply.
- What are the minimum or maximum requirements for waste needed to be processed? There will be physical constraints on the process in terms of maximum throughput. Economic and/or physical constraints will dictate the minimum throughput possible. The local waste "market" and need for waste disposal must be examined to see if the technology makes sense for a given location.
- Is the waste composition changing due to recycling, composting, changes in consumption, etc.? The waste composition changes by locality, season, consumers spending habits, product packaging, and programs or technology put into place to manage waste. Source separation and recycling, yardwaste composting, automated mixed waste separation with recycling, waste reduction, and reuse can make significant changes to the remaining waste's composition. The trends for waste composition changing should be determined to the excess possible.
- Do long-term contracts for feedstocks already exist which would interfere with this technology? The feedstock (waste) must be available before a commercial facility can be introduced. While a market for products may be strong in a certain location, the ability to secure long-term waste system contracts may be poor.
- What are the standards for the product(s) produced? Product quality and consistency must be met to insure long-term markets. Product specifications should be identified and the process evaluated as to its ability to meet these specifications. Examples of products are steam, electricity, fuel, and chemicals and recovered and/or processed materials.
- Can environmental permits be obtained? Environmental issues can become a barrier to the commercialization of a technology in a specific locale. Non-attainment areas will require additional analysis of options. State and local regulations may also increase the cost of compliance.
- What is the public perception of the technology? Public perception will vary from place to place. This is an intangible property which can prevent a technology from being developed.

- What are the characteristics of markets for byproducts of the process? The byproducts of a process can make or break the economic feasibility of the technology. A byproduct here is something which is produced in a relatively low quantity, or something which has relatively little value, or no value at the location where it is produced. For instance a process which produces a high value chemical, may also make a gas with a reasonable BTU value. But in some cases, as with waste, the byproducts could be a concentrated mix of hazardous materials which could cost more to dispose of than the original MSW. Hazardous byproducts will also increase public resistance, as in the case of incineration ash from MSW waste to energy plants.

The next step in reviewing a new technology is to compare the technology with those commercial technologies currently in the identified market(s). This comparison can be as brief or extensive as is desired, depending on if we are considering a revolutionary change or just an evolutionary advance in the market. At a minimum, cost and environmental comparison should be made between the new technology and what is available in the market. The cost should be assessed on a life-cycle basis, accounting for capital, operation and maintenance, disposal of residue costs, and revenues from tipping fees, the primary product and any byproducts. The general environmental assessment could include a number of considerations including impacts on air, water, workers, flora and fauna.

There are many other considerations in performing this initial assessment. The feedstock must be compatible with the technology, and the product(s) compatible with the existing markets. Flexibility can be quite advantageous in the waste management industry, as the quantities and composition of waste is rarely fixed. While some technologies might only be competitive for a certain type and quantity of waste, others could take many types of waste, in a range of quantities. Effects on other related technologies should be assessed, as today municipalities and other organizations are interested in integrated solid waste management. Generally no one technology can solve the waste problems for a given location. Thus, technologies which can work effectively together may be more desirable than those which prevent other technologies and strategies from being employed successfully.

In order to compare the new technology with existing ones, it must be emphasized that the new technology should be judged on a realistic basis. A conservative estimate for costs, revenues and efficiency of the new process should be used for comparison purposes. Often a new technology assessment underestimates commercialization costs and greatly over-estimates potential revenues from products.

Establishing Current Status of the Technology

The second phase of this review is to establish the current status of the new technology, providing a baseline or framework from which further development can be compared. The initial limited economic feasibility developed in Phase I, can be updated with new information gained in this phase. Technical and economic gaps

in knowledge should be identified in this phase and either resolved now or targeted for later development work and/or analysis.

Existing Data Review

This stage of review is many times performed by the researchers in order to propose further expenditures or justify previous funding. Therefore, some data may already exist for this analysis.

The first part of establishing the current status is to verify that the process proposed is physically possible and practically attainable. This will require checking previous assumptions, reviewing theory and obtaining correct parameter values for thermodynamic, kinetic and mass and heat transfer. Mass and energy balances should be done to check process feasibility. A second law analysis could be performed on the process to identify inefficiencies. This second analysis can identify the appropriateness of the technology with respect to energy conversion. It can also help to point to process steps which could be improved to yield more efficient conversion rates.

Once the theory has been reviewed, operational data from the lab, bench, and/or pilot facility should be assessed to determine the deviation from theory. This will allow a better estimate of expected yields as the process is scaled-up further. It will also serve to highlight areas where the process can be improved or is not performing as well as expected. In some cases, it will point to the fact that the data is inaccurate or insufficient for reasonable analysis and that additional and more accurate data must be obtained before further progress can be made. It is important in this review that sufficient data be available to determine the precision of the data. This review should determine if enough replicates have been run to achieve the desired confidence in the results. QA/QC protocol used to perform experiments and acquire data should be reviewed and verification of its use may be established. This may be a weakness in many developing technologies, as sufficient independent testing to produce adequate statistical data can be costly.

There should be an adequate review of the instrumentation and data acquisition system to determine any measurement biases which exist. For example, biases occur in high temperature measurements, and when measurements are made close to the detection limit of the instrumentation. There may be a need to perform an uncertainty analysis. This allows for a couple of benefits. First, we can see how all the measurement errors are propagated into the errors of calculated quantities such as conversion efficiency. Secondly, the analysis can show which measurement errors are the most critical to measure accurately. For example, a flow measurement can be 100 times as important as a temperature measurement in closing a mass balance.

Once a thorough review of the available data has been accomplished, we need to update our original economic model. Existing cost data should be reviewed to better establish costs of the technology at its present state of development. These costs should be segregated as much as possible into standard technologies and developmental technologies to identify which areas need more accurate estimates

as development proceeds. If possible, costs for each piece of equipment or unit operation should be tabulated.

Many costs will not be available based on pilot plant data, such as upstream and downstream equipment which may not be implemented at this stage of development. But this equipment can be estimated if standard technology is used. Equipment in this category may include material waste recovery systems, gas cleaning, liquid cleaning, heat recovery equipment, and emissions, effluent and residue treatment systems.

Costs for operation and maintenance (O&M) are difficult to determine as pilot scale or smaller equipment will rarely run for long continuous periods of time. Some costs may be determined such as on energy requirements, energy losses, and other requirements of the process such as gases, water, or other utilities. Costs associated with running the process for long periods of time will generally not be available. But preliminary estimates can be made, and ranges input to the economic model to establish a current economic status.

Technical and Economic Questions

The review of the current status will raise various questions on both a technical and cost basis. Technical questions which are easily resolved with current equipment should be addressed as soon as possible prior to going on to this Phase.

It is generally far less expensive to acquire data at the initial stages of development than later on, and this data can provide many benefits. The additional data taken may indicate unusual phenomena occurring which need to be understood for successful scale-up. Extra information may point to flaws in the technology such as larger heats of reaction than calculated, poor kinetic rates, or poor catalytic activity. Such results might be indicated using extra thermocouples, calorimetry, pressure transducer, etc. These may be economical to measure at this stage of development, but not once the technology is scaled up. Instruments used for pilot plant scale equipment can be less durable due to less demanding use and shorter operations requirements than in a commercial plant. Pilot plant work allows the fixing of varying operational parameters widely without the risk of interfacing with revenues or ruining costly equipment.

Development is a time to understand the processes as well as possible in order to be able ultimately to optimize and control it. This can be even more important with a variable feedstock like waste, since we need to be able to predict performance of a technology for changes in the waste stream. Modeling of the process is an important tool to use to take our understanding of the process and mathematically describe it. The model can eventually be used as a tool for scaling up the process. Discrepancies between actual operating data and theoretical projections may indicate poorly understood phenomena, inaccurate data, or invalid assumptions in the theory. These technical data gaps may need to be filled before further progress should be attempted. Otherwise, scale up may bring with it some unforeseen problems.

Technical questions which may be unanswerable include environmental impacts, reliability of equipment over time, labor necessary to run and maintain

operations full time, and degradation of the process over time due to unknown phenomena. These questions will need to be revisited in later phases of development, and should be noted to trigger later activity.

Economic questions which may not yet be answered should be identified at this point and noted for later resolution. These may include questions of costs for upgrading the products and byproducts for sale, prices for the products and byproducts, and disposal costs for residues and effluents. Some of these questions are best left for later stages in development, when more representative products and residues will be produced. By initially establishing costs of upgrading or treating products or residues, it may be revealed that further consideration needs to be given to different methods of treatment. This may need to be worked on before, or concurrent to scaling-up.

Establishing a Path to Commercialization

Now that the current status of the emerging technology has been established and we have updated the economic model with new information, which still projects a competitive technology, we can establish how to proceed. This third phase of development can consume fairly large amounts of capital, so a critical assessment should be conducted to establish a deliberate agenda so that an investor may be convinced to fund this phase.

The initial task of this phase is a risk assessment to identify any technical flaws in the concept, and establish a plan to address and overcome any obstacles. As an example, the process data from bench scale operations has confirmed the kinetic viability of the process but has left unanswered certain mechanical questions. For instance, we know the reactor works but we have assumed in our model a feeder that can use unprocessed feedstock. The problem identified is, how do we introduce the solid feedstock in a uniform, continuous manner without excessive preprocessing. This risk assessment, which should include all components, is intended to identify components of the process that either require further development prior to proceeding to the first scale-up or to find an acceptable alternative.

For solid waste, feeding and residue removal have been historical non-trivial unit operations. There are still problems observed in feeding and ash removal in state-of-the-art incinerators which operate at pressures slightly below atmosphere to prevent refugee emissions. With reactors demanding air tight seals for control of certain processes, solids feeding and removal takes on a more important role and is naturally more complex.

The final piece of the risk assessment is to critically look at the question of scale-up. One may ask the question, how far can we proceed, in this initial step from bench scale? But the right question is, what is the maximum scale-up possible from the final development unit to the commercial demonstration? Answering this question is a key to determining the total path to commercialization. We can then decide on how many scale-up steps to take and when critical components should be scaled-up. These steps may include any or all of the following: an integrated

pilot plant, a semi-works to prove out critical components or a complete demonstration system.

After planning the global technical approach, and the required component development has been identified, we need to feed any revisions to our overall cost model to reconfirm feasibility. The next stage is to determine the additional technical data, whether mechanical or process, that is required.

Typical questions which help identify such data include:

- Does each component work as intended? The importance of each component to a commercial facility's success cannot be over-emphasized. The failure or chronic problems associated with a single component can mean an inability to meet availability guarantees, which will have a direct financial consequence.
- Does the system as a whole work together in a safe manner? Safety is a key element of commercial operation. Without the ability to 1) build passive and active safety protection and 2) maintain a strong safety record, the process will never garner interest of financial institutions due to the risk and liability associated with it.
- Does proper selection of materials take into consideration "corrosive and erosive" elements in the process? Solid waste, even when put through separation equipment such as trommels, magnets, and air classifiers, contains metal and glass. These can cause wear on surfaces with which it contacts, and at higher temperatures will lead to fouling and corrosion of surfaces. Proper design of equipment in handling these effects is essential for long-term and cost effective operation.

In addition, the duration of acquiring the answers to these questions should be established. Typical goals of this first scale-up may be 5,000 hours of total test time with perhaps 1,000 hours of continuous operation under design conditions. The purpose of this scale-up is to work through the operational and process problems, confirm yields and product quality, and obtain an indication of reliability. The "other" objective is to be able to again refine the economic model with the data obtained from this first scale-up for both capital and operations costs. We will need this information, since we are approaching the time that additional capital will be needed for the next scale-up or for a continuously operational demonstration facility.

Once we have established technically what type of data and scaled-up system the technology requires, we need to establish a cost of this phase of the work and raise additional capital. At this stage, it is important to consider if any revenue can be derived from the operation of the development unit to offset the operational costs. This may not be realistic, but an investor typically likes to see some "pay as you go" operation while development is progressing.

After the development unit has completed the technical data acquisition, it is again time to refine our feasibility model with new cost data, operational data and

reliability data. The level of success of the development unit will at times determine the type of financing that the process developer can consider. The final section discusses the various options.

The First Commercial Unit - How Can It Be Financed

As we complete the previous phase, the additional data collected from the scaled-up operation is again fed back into the economic model to reconfirm feasibility. A positive result will now enable the project to proceed to raise the capital necessary to build a full scale facility which, by definition, when successful will be the first commercial unit.

Financing can be obtained from a variety of sources, ranging from total equity, where the investor assumes all the risk, to non-recourse project financing where the risk of failure is divided between the lender and the equity participant. Technologies concerned with the disposal or processing of solid waste are currently eligible to obtain tax exempt bonding authority. The lower cost of capital by using tax exempt bonds is a commonly used method to enhance the overall economics of a project.

As we proceed to raising the required funds to build the first commercial project, it is important to understand the risk posture of the various sources of capital that are available to build the first commercial plant. Two general types of capital are available, loans and equity. Lenders, either banks, insurance companies or the public bond market, have one basic concept in common. Their upside potential, in any project, is a return of capital with interest at the agreed upon rate. While the downside risk, if the project totally fails, is a total loss of capital. Equity participants, although they have the same potential loss as a lender, have a much larger upside potential if the project is successful. Due to this basic difference between risk and reward, a lender typically assumes a much more conservative view of a project that is going to be a stand alone business entity.

As a direct consequence of this risk/reward posture of various sources of capital, the cost of this capital, to a technology developer, differs. Although equity capital does not carry a defined interest rate, suppliers of this type of capital desire a substantially higher return on that capital than does a lender.

Funding a new technology using non-recourse project financing, typically requires either some level of equity participation or a guarantee to pay back the debt, or some combination of the two. The level of equity participation or debt guarantee depends on the characteristics of the project and the projected economics as determined by an Independent Engineering Review. This Independent Engineering Review is critical to both lenders and equity participants, since it is intended to confirm both the technical and economic viability of the technology.

From a lender's point of view, the typical characteristics of a strong project include some or all of the following:

- o A turnkey construction contract including a fixed price, fixed completion date, detailed performance test and penalties for non-performance.

- o An operations and maintenance contract with a fixed price and incentives for positive performance and penalties for poor performance.
- o Independent projections based on the technology and contract structure which show adequate cash flow to cover all expenses and debt service. These projections should be done for both the expected operational scenarios and in cases where potential problems may arise that are either technical or economical in nature.

In the ideal world of a supplier of capital only second of a kind facilities would be financed, thereby minimizing any technology risk. Today we are seeing more first of a kind facilities looking for funding. The more detailed the process of technology development, producing data that can be evaluated in a positive light by an independent engineer, should allow the financing of a first commercial facility with a maximum of debt capital.

Raising the capital for a new technology can be as challenging as completing the technical development. However, this job is easier when the proper groundwork has been laid by following the methodology presented here.

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