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PROBLEMS ASSOCIATED WITH SOLID WASTES
FROM ENERGY SYSTEMS

by

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CONTENTS

EXECUTIVE SUMMARY	ix
1 INTRODUCTION	1
1.1 Background.	1
1.2 Quantities of Solid Waste Produced.	1
1.3 Study Objectives.	2
2 REVIEW OF ENVIRONMENTAL REGULATIONS.	4
2.1 Clean Air Act Amendments of 1977 (PL 95-95)	4
2.2 Federal Water Pollution Control Act (PL 92-500) As Amended by the Clean Water Act (PL 95-217).	6
2.3 Safe Drinking Water Act (PL 93-523) and Underground Injection Control Act (PL 95-150)	6
2.4 Surface Mining Control and Reclamation Act (PL 95-87)	7
2.5 Toxic Substances Control Act (PL 94-409).	7
2.6 Resource Conservation and Recovery Act (PL 94-580).	9
2.6.1 Resource Conservation and Energy Recovery.	9
2.6.2 Criteria for Defining Hazardous Wastes	10
2.6.3 Testing and Analysis Procedures.	16
2.6.4 Solid Waste Disposal Requirements.	17
2.6.5 Hazardous Waste Disposal Requirements.	25
2.6.6 Future Options	32
3 SOURCES AND NATURE OF ENERGY RELATED SOLID WASTES.	33
3.1 Solid Wastes Associated with Coal Utilization	33
3.1.1 Coal Ash and Char.	35
3.1.2 Inorganic Solids and Sludges	47
3.1.3 Tars and Oil Sludges	56
3.1.4 Biosludges	58
3.1.5 Spent Catalysts.	60
3.1.6 Coal Cleaning Wastes	60
3.2 Solid Wastes Associated with Oil Shale Processing	63
3.2.1 Raw Shale Fires.	63
3.2.2 Retorted Shales.	63
3.2.3 Other Shale Derived Wastes	65
3.2.4 Nonshale Solid Wastes.	67
3.3 Solid Wastes Associated with Other Energy Technologies.	68
3.3.1 Geothermal Technologies.	68
3.3.2 Oil and Gas Extraction	71
3.3.3 Tar Sands.	72
3.3.4 Nuclear Power Generation	74
4 HAZARD CHARACTERISTICS	79
4.1 Coal Utilization.	79
4.1.1 Ash from Coal Combustion	79
4.1.2 Ash and Char from Coal Conversion.	85

CONTENTS (Cont'd)

4.1.3	FBC Spent Solids	97
4.1.4	Sludges from Chemical Treatment of Process Wastewater. . .	99
4.1.5	Tars and Oil Sludges	99
4.1.6	Biosludges	102
4.2	Oil Shale Processing Wastes	104
5	PROBLEMS ASSOCIATED WITH HAZARDOUS WASTE STORAGE AND DISPOSAL.	113
5.1	Disposal Options.	113
5.1.1	Ponding.	113
5.1.2	Landfill	114
5.1.3	Mine Disposal.	115
5.1.4	Ocean Disposal	116
5.1.5	Deep Well Disposal	116
5.1.6	Soil Application	116
5.1.7	Incineration	117
5.1.8	Chemical Treatment	117
5.2	Long-Term Environmental Problems.	118
5.2.1	Deterioration of Landfill Covers	118
5.2.2	Limited Soil Attenuation Capacity.	119
5.2.3	Long-Term Reliability of Impervious Liners	120
6	SOLID WASTE UTILIZATION.	122
6.1	Building Material	122
6.1.1	Ash from Convention Boilers.	122
6.1.2	FGD Sludges.	123
6.1.3	Fluidized Bed Material	123
6.1.4	Other Solid Wastes	124
6.2	Road Construction Material.	124
6.2.1	Ash.	124
6.2.2	FGD Sludge	124
6.2.3	Fluidized Bed Material	125
6.2.4	Other Solid Wastes	125
6.3	Agricultural Use.	125
6.3.1	FGD Wastes	125
6.3.2	Fluidized Bed Material	125
6.4	Environmental Impacts	126
6.5	Extent of Utilization	126
7	CHARACTERIZATION OF SELECTED HAZARDOUS WASTES FROM THE INDUSTRIAL SECTOR	129
7.1	Coke Industry	130
7.1.1	Industrial Profile and Process Description	130
7.1.2	Hazardous Properties of the Wastes	131
7.2	Petroleum Refining Industry	132

CONTENTS (Cont'd)

7.2.1	API Separator Wastes	133
7.2.2	Dissolved Air Flotation Float.	134
7.2.3	Slop Oil Emulsion.	135
7.2.4	Heat Exchanger Bundle Cleaning Wastes.	135
7.2.5	Tank Bottoms	135
7.2.6	Biosludges	136
7.2.7	Spent Catalysts.	137
7.3	Electroplating and Metal Finishing Industries	137
7.3.1	Process Description.	138
7.3.2	Waste Stream Description	138
7.4	Creosote Production Industry.	139
7.4.1	Process Description.	140
7.4.2	Hazardous Components of the Waste.	140
7.5	Wood Preserving Industry.	141
7.5.1	Industry Profile	142
7.5.2	Process Description.	142
7.5.3	Hazardous Waste Constituents	143
7.6	Phenol/Acetone Production Industry.	144
7.6.1	Process Description.	144
7.6.2	Hazardous Properties of the Wastes	145
7.7	Secondary Lead Smelting Industry.	145
7.7.1	Process Description.	146
7.7.2	Hazardous Waste Constituents	147
7.8	Primary Zinc Smelting and Refining Industry	147
7.8.1	Process Description.	147
7.8.2	Hazardous Properties of Waste.	148
REFERENCES.		150

TABLES

1	Summary of Energy Wastes and Relative Hazard Potential.	x
1.1	Estimated Solid Wastes from Energy Related Activities (10 ⁶ Tons).	2
2.1	Summary of Potential Regulatory Actions Affecting the Hazardous Solid Wastes from Energy Industries	5
2.2	Hazardous Constituents Identified in RCRA	13
2.3	Maximum Concentration of Contaminants for Characteristics of EP Toxicity.	16
2.4	Hazardous Waste from Nonspecific Sources.	17

TABLES (Cont'd)

2.5	Hazardous Waste from Specific Sources	18
2.6	Basis for Listing Hazardous Wastes.	19
2.7	Test Methods for Evaluating Solid Wastes.	20
2.8	Analytical Methods for Organic Chemicals.	21
2.9	Analytical Methods for Inorganic Species.	22
2.10	State Readiness to Use the Solid Waste Disposal Criteria.	26
2.11	Interim Status Standards for Hazardous Waste Disposal	28
3.1	Quantities of Solid Waste Generated	34
3.2	A Partial Identification of Trace Elements in Coal Ash.	37
3.3	Major Chemical Constituents of Coal Ash	38
3.4	The Separation of Elements in the Geochemical Classification Scheme.	38
3.5	Chemical Constituents of Bottom Ash and Flyash.	39
3.6	Estimated Saturated n-Hydrocarbon Concentrations in Coal Ash. . . .	41
3.7	Estimated Polycyclic Aromatic Hydrocarbon (PAH) Concentration in Coal Ash	42
3.8	Natural Radionuclides Observed in Coal, Bottom Ash, and Flyash. . .	43
3.9	Contents of the Various Radionuclides in Coal, Bottom Ash, and Flyash.	44
3.10	Representative Analyses of Coals and Chars (Wt. %).	45
3.11	Inorganic Elements in the Mineral Residue from the H-Coal Utilizing Illinois #6 Coal.	46
3.12	Trace Element Concentrations (ppm) in Illinois Coal and in the Unquenched Gasifier Ash Obtained from Lurgi Gasification. . . .	48
3.13	Chemical Composition of Coal Ashes from Gasification/Liquefaction Plants	50
3.14	Chemical Analysis of Lime Process Sludges on a Dry Solid Basis (%)	52
3.15	Chemical Analysis of Flue Gas Desulfurization Sludges	53
3.16	Elemental Composition of Scrubber Sludge Leachate	54
3.17	Major Components of German High-Temperature Conversion Process Coal Tar.	57
3.18	Organics in Product Water from Gasification of Illinois No. 6 Coal.	58
3.19	Trace Elements Reported in Product Gas Quench Waters.	59
3.20	Catalysts Used in Coal Conversion Processes	61
3.21	Trace Element Concentration for Drainage Produced by Illinois Basin Coal Refuse	62

TABLES (Cont'd)

3.22	Typical Analysis of Organic and Mineral Matter in the Raw Shale	64
3.23	Ash Composition of Typical Retorted Oil Shale	64
3.24	Distribution of Trace Metals During Oil Shale Retorting	66
3.25	Inorganic Ions Leachable from Freshly Retorted Shales (kg/T) - Based on Laboratory Tests.	67
3.26	Typical Composition of Shale Oil Coke	68
3.27	Average Concentration in Geothermal Brines and in Water Samples (mg/L).	70
4.1	Composition of Ash Pond Liquors and Sluicing Waters (mg/L).	80
4.2	Equilibrium Concentrations of Trace Elements in Coal Ash Leachate.	82
4.3	Levels of Chromium and Lead in Solid Residues and Leachates from Coal Combustion Compared to Solid Wastes from Selected Industries.	84
4.4	Chemical Composition of Lurgi Ash and Slurry Supernatant Solutions of the Ash from an Illinois No. 6 Coal at Several pH Levels	86
4.5	Elements Exceeding Recommended Water Quality Levels	89
4.6	EPA-EP Leaching Results for Five Gasification/Liquefaction Solid Wastes.	90
4.7	Levels of Chromium and Lead in Solid Residues and Leachates from Coal Conversion Compared to Those of Solid Wastes from Selected Industries	91
4.8	Chemical and Bioassay Test Results for Gasification Ash	92
4.9	Chemical and Bioassay Test Results for Gasification Ash Leachate.	93
4.10	Chemical and Bioassay Test Results for Gasification Cyclone Dust.	94
4.11	Chemical and Bioassay Test Results for Gasification Cyclone Dust Leachate	95
4.12	Acute Toxicities of Lurgi Ash Leachates to Daphnia Magna.	96
4.13	Toxicity of Lurgi Ash Leachates to Raphanus Sativus L	98
4.14	Comparison of Process Wastewaters from Coal Conversion and Coke Making Processes (mg/L).	100
4.15	Bioassay Test Results for Crude Tar Samples and Fractions	101
4.16	Polynuclear Aromatic Hydrocarbon Concentration in Creosote and Coal Tar (g/kg)	102
4.17	Polynuclear Aromatic Hydrocarbons in Coal Tars and Bottom Sediment Sludge from a Wood Preserving Plant (g/kg)	103

TABLES (Cont'd)

4.18	Known or Suspected Carcinogens that may be Present in Waste Streams from Coal Liquefaction.	103
4.19	Studies of the Acute Effects of Shale Oil and Shale Oil Products.	104
4.20	The Number and Types of Abnormality Found in Rabbit Embryos after Oral Doses of Spent Shale	105
4.21	Mutagenicity of Chemicals Identified in Shale Oil Using Salmonella Tester Strains	106
4.22	Levels of Benzo(a)pyrene (BaP) Reported in Oil Shale and Natural and Industrial Materials.	108
4.23	Carcinogenic Potency of Two Raw Shale Oils.	109
4.24	Benzo(a)pyrene Content of Shale Oil Products.	109
4.25	Carcinogenic Potency of Raw and Upgraded Shale Oil.	110
4.26	Carcinogenic Potency of Shale Oils and Shale Oil Products	111
6.1	Electric Utility Ash Utilization Patterns	127
6.2	Sulfur Produced by Individual Energy Technologies and Sulfur Sold in the U.S..	128
7.1	Levels of Chromium (mg/L) in Leachate from Solid Wastes and Coal Ash from Two Petroleum Refineries.	136
7.2	Levels of Chromium and Lead (mg/kg) in the Solid Waste Streams from a Petroleum Refinery and in the Solid Residues of Conventional Coal Combustion.	137
7.3	Levels of Chromium (mg/L) in Leachate for Electroplating Sludges and Coal Ash.	139
7.4	Levels of Lead (mg/L) in Leachate from Coal Ash and Zinc Smelting Processes.	149

EXECUTIVE SUMMARY

Over six billion tons of solid waste are annually produced in the United States. At least 40 million tons of these wastes contain toxic chemicals, many of which are man-made organic compounds that may possess mutagenic, carcinogenic, teratogenic or acutely toxic properties. Unfortunately, certain technological and scientific breakthroughs have had the adverse impact of increasing the presence of these toxic chemicals in our environment by many orders of magnitude. Prior practices for disposing of wastes containing these chemicals demonstrated that little consideration had been given to the possibility of future generations coming into contact with these toxic species.

The most frequently cited examples of inadequate waste management are those of chemical industries; however, the energy development sector may also have problems with toxic waste disposal, if precautions are not taken. Under the Fuel Use Act, passed in November 1978, emphasis is placed on increased use of conventional coal combustion in place of oil and gas. Efforts are also underway to develop and improve technologies that produce liquid and gaseous products from coal and liquids from oil shale. These coal use initiatives run counter to many environmental initiatives and, except for their possible impact on air quality, these energy developments will most affect environmental initiatives on solid waste generation. Present federal initiatives call for approximately two billion tons of coal to be mined by 2000.

The amount of coal cleaning wastes, fly ash, and scrubber sludge to be disposed of from conventional combustion, already estimated at 66 million tons per year, will escalate dramatically to more than 200 million tons per year. Of perhaps greater importance, however, is that 600 million tons of coal per year will be converted to synfuels by 2000. It is estimated that up to 50 million tons of solid waste will be generated from these conversion processes. Although much of the waste streams from these processes will contain ash and scrubber sludge, new types of wastes will also be produced. In particular, the reducing nature of the conversion processes will produce considerable amounts of coal char, tars, and oils. These wastes could contain considerable amounts of organic chemicals that are toxic or carcinogenic. In addition to coal, oil shale development will produce 180 million tons per year of solid wastes by 1995. Continuing problems will also exist in disposing of nuclear fuel cycle wastes and drilling brines and muds from domestic oil and gas production.

In this study, we review waste streams from many energy-related technologies including coal, oil shale, tar sands, geothermal, oil and gas extraction, and nuclear power generation, with an emphasis on waste streams from coal and oil shale technologies. A number of waste streams are listed in Table 1, in which we attempt to rank these streams on the basis of harmful effects on health and the environment. Given the limited data available, these comparisons must be considered somewhat subjective.

Regulatory Uncertainties

Although "hazardous" criteria may be relaxed under the current Resource Conservation and Recovery Act (RCRA) regulations, it appears that the EPA

Table 1 Summary of Energy Wastes and Relative Hazard Potential

Technology and Waste Stream	Characteristic or Chemical of Concern	Potential Hazard Ranking ^a
Conventional Coal Boiler		
Ash	Various trace elements	2
Lime/limestone scrubber sludge	Various trace elements	2
AFBC		
Ash	Various trace elements	2
Spent bed material	pH, total dissolved solids (TDS), sulfates	1
Coal Gasification		
Coal cleaning	pH, trace organics and inorganics	3
Gasifier ash/char	Fused aromatics, trace elements	3
Boiler ash	Various elements	2
Boiler FGD sludge	Various elements	2
Spent catalysts	Nickel (Ni), Cobalt (Co), Arsenic (As), Cadmium (Cd), Polycyclic organic matter	3
Acid gas clean up and pollution control wastes	Phenolics, aromatics, various elements	3
Tar and oil sludges	Heterocyclics, polynuclear aromatics (PNA), other organics	3
Biosludges	Heterocyclics, PNA, other organics	3
Coal Liquefaction	pH, trace organics and inorganics	3
Coal cleaning	pH, trace organics and inorganics	3
Liquefaction waste (chars, ash, filter cake)	Fused aromatics, trace elements	2
Boiler ash	Various elements	3
Spent catalysts	Ni, Co, As, Cd, POM	3
Acid gas clean up and pollution control wastes	Phenolics, aromatics	3
Tar and oil sludges	Heterocyclics, PNA, other organics	3
Biosludges	Heterocyclics, PNA, other organics	3
Oil Shale		
Raw shale dust	Respirable particulates	2
Spent shale	Trace organics, PNA, trace inorganics	3
Shale oil coke	As, Selenium (Se), PNA, other organics	3
API separator sludge	Phenolics, trace elements	3
Nonshale wastes	Heterocyclics, other organics, variety of trace inorganics	3
Geothermal	As, Lead (Pb), Potassium (K), Fluorine (F), TDS	2
Tar Sands	Similar to oil shale	3
Nuclear		
Low-level wastes	Low radioactivity	2
High-level wastes	High radioactivity	3
Oil Exploration		
Drilling muds	Bactericides, metals, organics	2
Drilling brines	TDS	1

^a1:low -- concentrations of chemicals are known to be low, with few additional data necessary.

2:intermediate -- concentrations of chemicals approach criteria and/or additional data may illustrate that toxic levels of the chemicals are high.

3:high -- concentrations of chemicals exceed criteria and/or there is a high potential that additional data will illustrate severe problems associated with toxic constituents.

will have considerable latitude to define hazardous wastes, particularly under the "toxic" category.

The EPA has recently revised the rules and regulations under Subtitle C of the RCRA (Federal Register, May 19, 1980). One area where changes have affected the legal standing of solid wastes is in the definition of hazardous wastes. First, a pH range of 2.5-12.5 was defined as noncorrosive and acceptable, thus reducing the number of waste streams considered hazardous. Practically all waste streams from energy industries are thus removed, with two possible exceptions. Untreated coal refuse drainage can exhibit a pH range of 1.7 to 2.9, whereas untreated, spent residue from fluidized bed combustion can exhibit a pH greater than 12.5. Second, the concentrations for Extraction Procedure (EP) toxicity were increased to one hundred times those of the National Interim Primary Drinking Water Standards (NIPDWS), and, as a result, practically all waste streams for coal and oil shale do not meet hazardous criteria. It should be noted, however, that many coal technology wastes have not been analyzed according to EP toxicity protocols. The net effect of these changes has been to take large volumes of wastes and remove them from hazardous lists in these "interim final" rules. However, extracts from some coal cleaning wastes may contain 100 times the NIPDWS concentrations for chromium.

The EPA did put two new categories in place for defining solid waste: "acute hazard" and "toxic." Since a waste may be deemed "toxic" if any one of over 350 chemicals is present, the Administrator may designate it as hazardous. The regulations provide many nonquantitative qualifiers for "toxic." Thus, it appears that the EPA will have considerable latitude in defining hazardous wastes in this category. Needless to say, many of these 350 chemicals are present in coal and oil shale solid wastes. Spent catalysts, biosludges, acid gas treatment sludge, and tars and oily sludge may have problematic characteristics with regard to the toxic criteria. In addition to the heavy metals that they already contain, spent catalysts contain trace metals and highly polymeric organic materials derived from coal and oil shale. Biosludge, acid gas treatment sludge, tars, and oily sludge tend to concentrate certain trace elements and organics originating from coal and oil shale. Thus, it is in the "toxic" category that many energy wastes may be considered hazardous.

It is possible that many energy wastes will be classified as "hazardous." Energy waste streams, in general, are presently poorly characterized and may be regulated in the future on development of a legally defensible data base. The waste streams most likely to be affected include selected streams from coal liquefaction and gasification and coal cleaning waste streams. This conclusion is based on our review and analysis of the available data presented in the following text.

The Nature and Problems of Coal and Oil Shale Wastes

A typical coal gasification plant is expected to produce up to five million tons per year of coal ash, which can contain considerable amounts of trace inorganics and organics. Leachate from Lurgi ash, containing high concentrations of boron, lead, cadmium, and antimony, has been shown to be

toxic to aquatic life. Few data are available on the organic species in coal gasification waste streams.

Coal liquefaction waste streams have been shown to contain many trace elements. Of greater concern here, however, are data showing that these streams contain a number of known or suspected carcinogens, including ben-zidine, nitrosamine, fluoranthrene, benzo(a)pyrene, -naphthylamine, benzene, and pyrene. Coal tars from both gasification and liquefaction processes are highly aromatic; studies have shown that as much as 50% of coal tar constituents contain three or more benzene rings, whereas 20% are two-ring heterocyclic compounds. Although much research needs to be done, many com-pounds in these organic classes have already been shown or are suspected to be carcinogenic. Naphthalene, fluoranthrene, and phenanthrene, which are found in large amounts in these tars, are toxic.

Oil shale wastes also contain toxic materials. Arsenic and selenium are two trace elements of concern, but the organics produced during the processes are of greater concern. Oil shale wastes contain phenols, hetero-cyclic amines, and polynuclear aromatics, which include known carcinogens (in the benzene extract of shale ash) such as 1,2-benzanthracene, 3-4-benzopyrene, 1,2,7,8-dibenzacridine, 7,12-dimethylbenz(a)anthracene, and 3-methycholan-threne. The latter two are particularly potent carcinogens. Benzo(a)pyrene can occur in concentrations of up to 3 parts per million (ppm).

Ames tests on coal liquefaction wastes have determined that mutagenic agents occur in the basic and neutral tar fractions of high-boiling extracts of SRC-II tars. Tumor incidence was 100% following sufficient applications of heavy distillate to mouse skin. In a similar test, syncrude extracts were identified as carcinogens following application to mouse skin, whereas similar crude oil extracts were found to be noncarcinogenic. Ames tests for tar base fractions from three coal gasification processes showed more severe mutagenic effects on a particular bacteria strain than the crude tar samples themselves.

Epidemiological studies have shown that prolonged exposure to shale oil can produce skin cancer in humans. Extracts from shale wastes have been shown to be mutagenic (Ames test) and carcinogenic (mouse skin). Although data are available on some organic compounds in shale wastes, it should be noted that at least five different technologies, producing different waste streams, may be developed for oil shale retorting.

Comparison of Coal and Oil Shale Wastes to Other Waste Streams. In this portion of the study we characterized waste streams that are similar to coal and oil shale waste streams (e.g., petroleum refining, iron steel, coke scrubber sludge). Such streams were determined to be toxic as one or more of the following chemicals were present: arsenic, cadmium, chromium, lead, cyanide, phenolics, and fuel aromatics (naphthalene). A comparison of solid waste and leachates from these industries and energy industries indi-cates the following possible areas of energy waste regulation. Coke plant waste streams contain concentrations of phenolics on the order of 1000 ppm, and Lurgi and SRC-I waste streams contain 3500 and 45,000 ppm, respectively. Dissolved air flotation (DAF) wastes from petroleum refining contain chromium

concentrations between 28 and 260 ppm. Chromium values for bottom ash (270 ppm), fly ash (300 ppm), synthane bottom ash (240 ppm), fluidized bed combustion (FBC) spent bed (450 ppm) and Lurgi wastes (590 ppm) are all within or above this range. These values are for solids, not leachates; however, these regulated wastes were considered hazardous in the toxic category rather than the EP toxic category. Thus, no leachate tests may be necessary. Creosote wastes are considered hazardous, in part due to the presence (0.2 ppm) of benzo(a) pyrene (BAP). Coal tar has BAP concentrations of up to 2 ppm. Tars are by-products found particularly in coal liquefaction and gasification wastes.

The comparison described in the preceding paragraph is little more than cursory. However, similarities do exist between regulated "hazardous" wastes and energy wastes. Future studies and legislation will determine if it will be necessary to regulate these energy wastes in a manner similar to that used for "hazardous" wastes.

Comparison to Water Quality Criteria. Water quality criteria that allow for acceptable ambient surface water concentrations have recently been developed, most on the basis of test results, for many consent decree chemicals. Although the acceptable limits for many pollutants are very low (often on the order of g/L), concentrations of these constituents in energy solid wastes and leachates are rather high. Ash from conventional coal combustion and coal conversion and sludges from desulfurization processes can contain up to 50 trace elements, many actually found in significant quantities. Specifically, ash may contain aluminum, antimony, arsenic, barium, beryllium, boron, chlorine, chromium, cobalt, copper, gallium, germanium, iron, lead, nickel, tin, titanium, vanadium, and zinc in concentrations greater than 1000 ppm. These elements are often in forms easily dissolved and mobilized into the environment at potentially harmful levels.

Other trace constituents are also contained in coal fly and bottom ash. Benzo(a)pyrene may occur in concentrations approaching 200 ppm. Other heterocyclic amines and polynuclear aromatics in this residue are probably toxic and mutagenic.

Engineering Concerns of Disposal Site Integrity. Chemical composition data indicate a pollution problem from the leaching of many energy-related solid wastes and a need for careful site selection and monitoring. In some cases, installation of special control measures, such as liners, sealants, underground collection systems, and devices for routing ground and surface flow, may be needed. Although these control measures are potentially applicable to landfill as well as pond disposal sites, their long-term effectiveness is still a matter of concern.

There are some mechanisms by which solid waste containment areas may be breached, thus causing environmental pollution. The effectiveness of landfill cover, for example, could be decreased over the long term as a result of numerous natural phenomena, including erosion, cracking, landslide, and subsidence. Each of these phenomena can either deteriorate the structure of a landfill or produce a change in a site, thereby enhancing the rate at which contaminants reach the environment.

In many cases, landfills or ponds will be lined with either natural or artificial materials designed to provide attenuation of leachate contamination or to completely isolate the waste from the environment. The effectiveness of liner materials can decrease with time, however. For example, for a specific site condition, the leachate attenuation capacities of liner soils have limits beyond which the migration of pollutants to the environment will increase. Because most pollutants may be leached from solid residues over a long period of time, long-term protection of groundwater supplies is a serious environmental concern.

Numerous artificial liners have been proposed, including both flexible films of rubber or various plastics and nonflexible liners such as asphalt, cement, or even stabilized flue-gas desulfurization (FGD) wastes. The possible chemical reaction between the liner and a waste can result in decomposition of liner material, and thus the useful lifetimes of potential liners are a matter of concern. Flexible liners are generally guaranteed for 20-25 years, and nonflexible liners are expected to have a somewhat longer life. However long-term service data for waste containment are not yet available for either type of liner.

Solid Waste Utilization Potentials. Commercial use of solid wastes is clearly an attractive alternative to disposal, as a means of reducing both environmental impacts and costs. Only 20% of coal ash from utilities is now used; a possible increase in the use of ash and possible uses for other wastes, such as FGD sludge and fluidized-bed materials, are being evaluated. The major areas of use are in building materials, road construction, agriculture, and elemental sulfur and sulfuric acid production.

Although many technically sound applications, already developed, could potentially absorb more than the wastes generated annually, that is not likely to occur in the near future because of customer uncertainties about reliability, technical complexity of application, uniformity, and quality of products. Many of these barriers may be overcome with time, after which the extent of utilization will depend on economic considerations. Many industrial firms and research organizations are active in the development of new applications and markets for power plant coal ash.

The outlook for use of wastes other than coal ash is uncertain; for example, little use of FGD waste in the near future is foreseen. Major deterrents to the utilization of lime/limestone scrubber wastes are their variable physical and chemical properties, high transportation costs, dewatering requirements for many applications, and their inability to compete economically with other material.

Many technologies for control of sulfur dioxide and hydrogen sulfide could produce elemental sulfur or sulfuric acid as by-products. The use of recovered sulfur is limited, however, since the potential supply exceeds the total U.S. demand. Development of either new sulfur uses or acceptable methods for environmental sulfur disposal is essential.

Problems of Other Energy-Related Wastes

Spent Geothermal Fluids. Disposal of spent geothermal fluid is a major environmental concern. Such fluids, produced when water and steam in the geothermal zone are tapped, may contain sodium chloride and bicarbonates in much higher concentrations than normally found in groundwater. Other elements such as boron, lithium, manganese, strontium, arsenic, lead, and potassium also exist in geothermal brines and may occur in high concentrations in some areas.

Oil and Gas Drilling Fluids. Oil and gas extraction wastes include drilling fluids and oil production brines. The latter are produced in association with crude oil from underground reservoirs and consist primarily of brackish waters. Drilling fluids, used in cooling and lubricating the drilling bit, transporting drill cuttings, balancing formation pressure, sealing the walls of the bore hole, and performing various other related functions, may contain many toxic substances. The basic drilling fluid predominantly used by the industry is a water-based bentonitic or attapulgite clay suspension with additives to provide specifically desired properties. Many additives to drilling fluids contain materials considered toxic. Of particular concern are the bactericides (e.g., aldehydes, quaternary amines, diamine salts, sodium pentachlorophenate, and other chlorinated phenols) and corrosion inhibitors (e.g., benzoic acids, dihydroxybenzenes, substituted naphthalenes, amines, and imidazolines). Many drilling fluid additives are water soluble; therefore, leachate from drilling fluid disposal could contain dissolved toxic and caustic materials as well as a high salt concentration.

Wastes Associated with Tar Sand Development. The solid wastes from a major tar sand operation include topsoil, over burden, and tailing from tar sand extraction, and coke and oily sludge from bitumen conversion. The pollution of surface and groundwater resources may result from the leaching of salts and toxic materials from these solid wastes. However, there is a lack of quantitative information concerning the hazard characteristics of solid wastes from tar sand processing.

Radioactive Wastes. Radioactive wastes, the inevitable by-products of the generation of electricity by nuclear reactors, are encountered at all stages of the nuclear fuel cycle -- in mining and milling, in fuel fabrication, in reactor operation, in spent fuel assemblies, and in the reprocessing of spent fuel, should the last become a reality. Plutonium and other waste components present special problems since they decay very slowly and remain dangerous for hundreds of thousands of years. It would constitute a major catastrophe or a major health risk if radioactive waste materials were to escape to the environment in large quantities.

Until safe permanent disposal is devised, nuclear wastes remain a very serious health and environmental problem, and many disposal techniques are under investigation. These include deep geological burial; seabed, ice sheet, and extraterrestrial disposal; transmutation; and disposal by rock

melting in deep mine cavities and in deep drill holes. Some of these technologies are suitable for one or several types of radioactive waste. However, because some important decisions concerning nuclear energy, namely, spent fuel reprocessing and use of the breeder reactor, have been deferred indefinitely, work is continuing on methods to dispose of all kinds of wastes. Furthermore, many methods need to be researched and developed as a hedge against one or more of them proving to be technically impossible or environmentally undesirable.

Future DOE Options

As is evident from the preceding overview, although the development of the country's energy resources is a needed national policy, this policy can have considerable impact on public health and the environment. Given uncertainties in existing data and possible regulation, it would be to DOE's benefit to develop its own program for solid wastes in the near term. This appears to be a positive step the Department could take while Congress debates the issues. This program would necessarily stress the development of an organic chemical data base and increased biological testing. DOE would thus be better prepared to develop environmental control programs based on scientific data on toxic wastes rather than waiting for a new legal definition of "toxic" and "hazardous" for a given waste stream.

To develop a program in which DOE would play the leading formative and conceptual role, a number of specific items, listed below, need to be addressed:

- (1) All solid wastes from energy systems must be evaluated and analyzed to determine their true toxic nature. These analyses should be chemical and biological. There are few data, and the sampling and analytical data that do exist apply only to a few waste streams. Emphasis should be placed on those technologies nearest to commercialization.
- (2) Control technologies for waste streams found to contain toxic or mutagenic species must be further developed and demonstrated. This effort should be directed toward the streams' isolation, containment, and ultimate disposal.
- (3) Additional research should be expended on groundwater modeling for toxic species contained in energy wastes. This effort should be specifically directed toward public health and aquatic ecosystem impacts.

These are three major areas for study. To pull these and other research and development efforts together, a center for energy toxic wastes should be established. This would provide a mechanism for the centralized collection, evaluation, and dissemination of solid and toxic waste data. Concurrently, a committee should be set up to develop requirements that would provide a consistent framework for data collection. As part of its activities, this committee would develop and oversee continuing assessment programs to evaluate the toxic nature of energy-related solid wastes on the

basis of collected data and environmental controls developments. These efforts would provide DOE with a strong continuing program for supporting solid waste policy, and research and development.

1 INTRODUCTION

1.1 BACKGROUND

Solid waste from energy technology has become a subject of increasing concern. As the regulations for air and water pollution become more stringent, a larger fraction of residuals ends up as solid waste. Some pollution control technologies such as flue gas desulfurization (FGD) not only shift the residuals from other media to the solid but also multiply the absolute quantity of wastes severalfold. Collection of residuals as solid wastes can concentrate toxic contaminants, which allows better containment and control. On the other hand, such concentration can increase occupational exposure and, if controls are inadequate, can lead to population exposures to higher concentrations of toxic materials.

An additional reason for increased concern with solid wastes from the energy sector is the recent call for increased coal use to reduce U.S. dependence on foreign oil. Moreover, it is likely that oil shale and tar sand resources will be developed. All of these technologies yield more solid wastes.

Finally, increasing public attention to the problems resulting from improper management of hazardous wastes in other industries has raised general awareness of the potential environmental problems associated with solid wastes. This has been reflected in the passage of the Resource Conservation and Recovery Act (RCRA). The RCRA has forced the energy industry to take a much closer look at solid waste disposal practices.

1.2 QUANTITIES OF SOLID WASTE PRODUCED

On the basis of quantitative estimates of solid wastes, we projected a significant increase in energy-related solid wastes (Table 1.1). Ash from electric utility sources was estimated to increase from 58×10^6 tons in 1976 to 134×10^6 tons in 1995; ash from industrial coal combustion will increase from 7.0×10^6 tons in 1976 to 46×10^6 tons by 2000, a sixfold increase. FGD sludge will increase fiftyfold from 0.8×10^6 tons in 1976, to 51×10^6 tons in 2000. These estimates were based on an energy scenario used in a DOE annual report to Congress (1978).¹

The amount of solid waste from oil shale processing is also projected to increase, reaching some 177×10^6 tons by 1995. Generation of these wastes will occur in the few counties in the Rocky Mountain region where oil shale development will occur.

One major concern about problems of solid waste from energy production entails the continued uncertainty over the disposal of high-level radioactive wastes from commercial nuclear reactors. Nuclear generation in 1995 is projected to be six times that in 1976.

Table 1.1 Estimated Solid Wastes from Energy-Related Activities (10⁶ Tons)^a

Waste	1976	1985	1990	1995
Conventional Coal Boiler				
Utility				
Ash	58.0	71.0	105.0	134.0
Lime/Limestone Scrubber Sludge	0.8	5.0	30.0	51.0
Industrial				
Ash	7.0	24.0	33.0	46.0
Coal Gasification				
Coal Cleaning		0.2	0.7	1.8
Gasifier Ash		2.0	7.0	18.0
Boiler Ash		0.2	0.7	1.7
Boiler FGD Sludge		0.04	0.15	0.4
Biosludge		0.08	0.3	0.7
Acid Gas Clean-up		0.003	0.01	0.02
Spent Catalysts		N/A	N/A	N/A
Tar and Oil Sludges		N/A	N/A	N/A
Coal Liquefaction				
Coal Cleaning		2.0	2.0	18.0
Liquefaction Waste		0.9	0.9	8.0
(Chars, Ash, Filter Cake)				
Boiler Ash		0.025	0.025	0.2
Boiler FGD Sludge		0.03	0.03	0.3
Biosludge		0.09	0.09	0.8
Spent Catalysts		N/A	N/A	N/A
Acid Gas Clean Up		N/A	N/A	N/A
Tar and Oil Sludges		N/A	N/A	N/A
Oil Shale				
Raw Shale Dust		0.5	0.9	4.0
Spent Shale		19.5	39.0	173.0
Spent Shale Dust		0.04	0.08	0.35
Arsenic Waste		0.0002	0.0005	0.002
Nuclear				
High Level Waste (10 ⁶ x ft ³)	0.007	0.02	0.03	0.04
Low Level Waste (10 ⁶ x ft ³)	229.0	716.0	1030.0	1380.0

^a1976 figures were estimated on the basis of energy consumption reported in DOE/EIA Monthly Energy Review. Figures for future years were estimated on the basis of Scenario C (medium supply, medium demand, medium cost) given in Ref. 1.

1.3 STUDY OBJECTIVES

Recently, the EPA developed interim rules for the designation and disposal of hazardous wastes.^{2,3} Eighty-five generic (nonspecific) and process (specific) waste streams were identified as hazardous under the RCRA.

For the near term, the EPA has avoided including most energy-related wastes (e.g., coal ash and FGD sludge) on the hazardous waste list. Nevertheless, even though classified as nonhazardous, these wastes will require greater attention under the RCRA. In addition, the exemption was declared temporary while the situation is studied further. The EPA has clearly left open the possibility of classifying selected coal combustion wastes as hazardous if that should be necessary.

The study reported here was undertaken in this period of uncertainty with two objectives. The first objective is to outline the available information on energy-related solid wastes. Data on chemical composition and hazardous biological characteristics are included, supplemented by regulatory reviews and data on legally designated hazardous waste streams. The second objective is to provide disposal and utilization options. Solid waste disposal and recovery requirements specified under the RCRA are emphasized. Information presented herein should be useful for policy, environmental control, and research and development decision making regarding solid and hazardous wastes from energy production.

2 REVIEW OF ENVIRONMENTAL REGULATIONS

The following environmental laws affect both the quantity of solid waste produced and the manner of its management and disposal:

- Resource Conservation and Recovery Act (RCRA)
- Toxic Substances Control Act (TSCA)
- Clean Air Act (CAA)
- Federal Water Pollution Control Act (FWPCA), as amended by the Clean Water Act (CWA)
- Safe Drinking Water Act (SDWA) and Underground Injection Control Act (UICA)
- Surface Mining Control and Reclamation Act (SMCRA)

The Clean Air Act and Clean Water Act are of interest because the controls required by these laws result in greater volumes of solid wastes. The Surface Mining Control and Reclamation Act and the Safe Drinking Water Act only indirectly affect solid waste production and control. Of greater importance are the Toxic Substances Control Act, with its explicit control of toxic chemicals, and the Resource Conservation and Recovery Act, passed specifically to control solid and hazardous wastes. These laws are summarized in Table 2.1.

2.1 CLEAN AIR ACT (CAA) AMENDMENTS OF 1977 (PL 95-95)

Increasingly stringent air pollution control requirements have led to a growing solid waste burden. The 1970 Federal Clean Air Act Amendments established a common framework within which federal, state and local governments could work together to control air pollution. The provisions of this act were expanded by enactment of the Clean Air Act Amendments of 1977. Key elements of these laws include:

- Promulgation by the EPA of national ambient air quality standards (NAAQS) for major pollutants, including NO_x, SO_x, and total suspended particulates (TSP), with states having the option to establish more stringent standards.
- Development of state implementation plans (SIPs) to be submitted to the EPA for approval. In the SIP, each state specifies how the NAAQS (or its own standards, if more stringent) will be achieved (including emission limitations, compliance schedules, and enforcement provisions) within three years of promulgation of the SIP.
- Establishment by the EPA of national emission standards for certain source categories, e.g., new sources.
- Prevention of significant air quality deterioration in areas where the air quality is already better than the NAAQS.

Table 2.1 Summary of Regulatory Actions Affecting Hazardous Solid Wastes from Energy Industries

Regulation	Section(s) (as applicable)	Concern	Type of Control
RCRA (PL 94-580)	3	Hazardous solid wastes from energy must be prevented from entering the environment	Waste reuse; environmentally sound disposal site
	4	Large volumes of simple solid wastes must be properly disposed of	
TSCA (PL 94-469)	4,5,6,8	Chemicals produced in process or waste streams of emerging technologies must be stringently controlled if they might adversely affect worker health and safety, public health, or the environment	Process controls, EPA banning of process in case of harm to human health or the environment, extensive testing and recordkeeping
SMCRA (PL 95-87)	5	Ground and surface water contamination of mine wastes; Reclamation of spoil piles	Reclamation
FWPCA (PL 92-500) and CWA (PL 95-217)	Subtitle III	Priority pollutants from emerging technologies; Wastewater discharges must be stringently controlled	BAT and total recycle; These processes produce additional solid wastes
CAA (PL 95-95)		Stringent control of criteria pollutants and NESHAPS (Sec. 112)	ESP, scrubbers, etc. These will produce additional solid wastes
SDWA (PL 93-523) UICA (PL 95-190)		Wastes from energy process will cause groundwater pollution	RCRA type controls, requirement of permits for any deep well injections

State regulations control emissions of particulates and SO₂ from both old and new industrial and utility boilers. The extent of control varies from state to state. All states require particulate control, the ash becoming solid waste. SO₂ regulations are stringent enough to require scrubbers, thus adding to the solid waste burden.

Federal emission standards for new boilers of capacity over 250 x 10⁶ Btu/hr were promulgated in June 1979. These standards restrict particulate emissions to 0.03 lb/10⁶ Btu heat input. This will require over 99% control, and virtually all the ash will become solid waste. The SO₂ regulations are on a sliding scale and limit emissions to 1.2 lb/10⁶ Btu and 90% removal or 0.6 lb/10⁶ Btu and 70% removal. In all cases, some degree of scrubbing will be required, greatly increasing the quantities of solid waste produced.

2.2 FEDERAL WATER POLLUTION CONTROL ACT (FWPCA) PL 92-500 AS AMENDED BY THE CLEAN WATER ACT (CWA) PL 95-217

These acts are aimed at restoring and maintaining the integrity of the national waters. The Act directs the EPA to develop and enforce standards for waste discharges to navigable water or publicly owned wastewater treatment plants. The recent amendments require Best Available Technology (BAT) for 129 pollutants (consent decree pollutants), many of which are found in energy system waste streams. Control of these streams will create sludge that will require some form of disposal, thus increasing the volume of solid waste.

2.3 SAFE DRINKING WATER ACT (SDWA) PL 93-523 AND UNDERGROUND INJECTION CONTROL ACT (UICA) PL 95-190

The SDWA provides a program for the protection of public drinking water. This program entails the development of national drinking water standards to protect health and provides for the enforcement of such standards.

Section 1424(e) of the Act allows the EPA to designate a sole source aquifer, which, if contaminated, would create a significant public health hazard because it is the sole or principal source of drinking water for an area. Under Section 1442 of SDWA, a study of the nature and extent of the impact on underground sources of drinking water of ponds, pools, lagoons, pits and other surface impoundments will be performed. This assessment will involve an inventory of surface impoundments. The RCRA and SDWA inventories will be coordinated. The SDWA inventory and assessment will be used as a screening device to establish priorities for the RCRA inventory and the application of RCRA regulations so that the worst drinking water problems may be addressed first.

The Underground Injection Control Act was designed as a permitting program to protect the nation's aquifers from degradation. It will require permits for any deep well injection of wastes; these wastes may be liquid but are considered solid wastes under the RCRA because of their containment requirements.

2.4 SURFACE MINING CONTROL AND RECLAMATION ACT (SMCRA) PL 95-87

The overall objective of SMCRA is to protect the environment from the adverse effects of surface coal mining operations. The act provides for reclamation of the mined areas to a condition capable of supporting premining or better uses. Section 508 of the Act requires submission for federal or state approval of a reclamation plan as part of the request for a mining permit. Section 515 of the Act requires that the reclamation effort insure that all debris, acid forming materials, toxic materials, or materials constituting a fire hazard be treated or burned and compacted or otherwise disposed of in a manner designed to prevent contamination of ground and surface waters.

2.5 TOXIC SUBSTANCES CONTROL ACT (TSCA) PL 94-469

This legislation provides for regulations concerning removal of hazards from contact with the environment and public health. TSCA has, in many instances, been called a record-keeping act for the industrial sector. This act requires that an industry keep records on worker health and exposure as well as biological testing data. That function, along with the collection of data on as many hazardous species as necessary are two of the primary goals of TSCA. Four key provisions are contained in TSCA to accomplish these goals. Section 4 authorizes the EPA to order companies to test chemical substances or mixtures they manufacture or process. Section 5 requires submission of notice and testing data to the EPA before manufacture of any new chemical substance or of an existing substance for a significant new use. Section 8 authorizes the EPA to require record-keeping and reports and also requires companies to immediately report adverse information. The fourth provision (Section 6) is perhaps the most important since it allows the EPA to regulate the manufacture, processing, distribution, commercial use, labelling and disposal of chemical substances and mixtures, and ban them if necessary, if they present unreasonable risk to human health or the environment. The regulation or banning of a substance is, however, based on unreasonable risk that is so great as to outweigh the benefits of the chemical "using the least burdensome requirements."⁴ The criteria for testing substances that may later be banned as a result of test data are:

1. Any activity involving a chemical substance that presents an unreasonable risk to the environment or health [Sec. 4(a)(1)(A)(i)].
2. There is not enough information to determine potential risk [Sec. 4(a)(1)(A)(ii) and Sec. 4(a)(1)(B)(ii)].
3. A chemical substance will be produced in substantial quantities and "(I) it enters or may be reasonably expected to enter the environment in substantial quantities or (II) there is or may be significant or substantial human exposure." [Sec. 4(a)(1)(B)(i)].⁵

One important TSCA regulation serving as a guideline affecting energy industries relates to the use and disposal of polychlorinated biphenyls

(PCBs). Specifically, "within six months of the effective date of this Act [TSCA] the Administrator shall promulgate rules to:

- prescribe methods for the disposal of polychlorinated biphenyls, and
- require polychlorinated biphenyls to be marked with clear and adequate warnings and instructions with respect to their processing, distribution in commerce, use, or disposal, or any combination of such activities.⁶

As a result of this directive, the EPA published regulations that include specific disposal mechanisms for these activities.⁷ Disposal by incineration (Annex I) is subject to specific combustion criteria such as a two second dwell time at 1200°C for all liquids containing PCB and 3% excess oxygen in the stack gas of incinerators operating at a 99% combustion efficiency. Specific monitoring criteria for incineration were also developed, along with record keeping and reporting procedures. Chemical waste landfills (Annex II) also were required to meet specific technical standards, which included specific requirements for soils, i.e., that they be either clay pans or have high clay and silt content with:

- in-place soil thickness of 4 ft or a compacted soil liner 3 ft thick
- permeability of 1×10^{-7} cm/sec
- soil passing #200 Sieve > 30%
- liquid limits > 30
- plasticity index > 15
- artificial liner thickness > 30 mm

The bottom of the landfill was required to be "substantially above the historical high groundwater table." Flood plains, shorelands, and groundwater recharge areas were to be avoided. If the site was below the level of a 100-year flood, water diversion dikes around the landfill perimeter must be at least two feet above this level. Where the site was above this level, diversion structures capable of diverting all surface water run-off from a 24-hour, 25 year event must be provided. The location of the landfill should be in an area of low to moderate relief to minimize erosion and to prevent landslides.

An extensive set of requirements for monitoring and analysis was required for surface, groundwaters and leachate and includes at a minimum analysis for: (a) PCBs, (b) pH, (c) specific conductance and (d) chlorinated organics. The disposal operations themselves provided for placement to prevent damage to PCB containers and segregation from noncompatible materials. Plans were to be approved by the EPA Regional Administrator. As with incinerators, a system of record keeping and reporting was also developed.

Annex III provided rules for storage of PCB-containing materials prior to disposal. Some important requirements include:

- rain water must not reach containers
- area must be above 100-year flood plain elevation
- any piece of equipment used in storage operations must be decontaminated before removal from site.
- PCB containers must comply with DOT regulations (40 CFR 173.346 as revised 12/31/76)
- records and reports as provided by law

Annexes IV, V, and VI provided rules for decontamination, labelling, and record keeping and monitoring, respectively.⁸ It should be noted that under the TSCA, the EPA later developed rules prohibiting manufacture, processing, distribution and use of PCBs unless provided for under certain stringent conditions.⁹

The thrust of PCB disposal is similar to those being developed for hazardous wastes under the RCRA. Thus, "the Agency has made a tentative decision to merge the TSCA PCB rules into the final RCRA regulations. Unfortunately, it has not been possible to complete this task to date. Both rules are lengthy and complicated and must be carefully coordinated to avoid regulatory loopholes and disruption of the ongoing TSCA PCB program. EPA expects to complete the task of integrating the RCRA regulations and TSCA PCB rules by the fall of 1980."¹⁰

2.6 RESOURCE CONSERVATION AND RECOVERY ACT (RCRA) PL 94-580

The primary objective of the RCRA is to ensure that solid wastes are managed properly. The program areas of particular importance to disposal of energy production waste include:

- hazardous waste management
- solid waste management (land disposal of nonhazardous solid wastes)
- resource conservation and energy recovery

The RCRA includes solids, liquids, semisolids, sludges, and contained gaseous materials as solid wastes. Wastes are included whether they are discarded, used, reused, recycled, reclaimed, stored, or transported.

The impact of the RCRA on the disposal of solid waste depends largely on whether the wastes are designated as hazardous or nonhazardous. In many cases classification will depend on analysis of the individual waste.

2.6.1 Resource Conservation and Energy Recovery

The Act encourages the conservation and recovery of materials and energy from wastes through a number of mechanisms. Subtitles D and F of the Act advocate state and regional solid waste planning that maximizes the utilization of valuable resources and encourages resource conservation. Solid

wastes must be utilized for resource recovery or be disposed of in sanitary landfills or in some other environmentally sound manner. Guidelines have been published to facilitate the identification and development of regional solid waste planning areas. Such regional planning is essential to the development of cost-intensive resource and energy recovery plans.

2.6.2 Criteria for Defining Hazardous Wastes

During the writing of this report, interim final rules were issued by the EPA for Subtitle C hazardous waste control. Specifically, regulations that addressed Sec. 3001 through 3006 were developed.^{11,12} According to EPA cost and impact studies, the annual cost of implementing its program will be \$510 million, or less than 0.2% of the value of sales of the affected industries.¹³

Where possible, the RCRA will be integrated with other acts. No underground injection of hazardous waste will be allowed unless a permit is received according to the Underground Injection Control Act (PL 95-190) as promulgated by the Safe Drinking Act (PL 93-523). Ocean dumping will be regulated under the Marine Protection, Research, and Sanctuaries Act. Clean Water Act (PL 95-217) regulations will take precedence where the jurisdiction of that program allows. Thus, any hazardous waste discharge into water may be regulated under the Best Available Technology (BAT) Toxics program (Sec's. 301, 307, and 311), the pretreatment standards (Section 307), or the National Pollutant Discharge Elimination System (NPDES) permitting system (Sec. 402) of the Clean Water Act. There will be some areas in which RCRA takes precedence. One such example is where municipal sewage sludge would be considered hazardous. This waste would then be controlled under Subtitle C of the RCRA.

Integration with the Clean Air Act (PL 95-95) will occur primarily concerning volatile wastes. No program for these wastes has been developed. Integration with TSCA has already been considered in Section 2.5. At present, the Office of Surface Mining (OSM) of the Department of the Interior controls disposal of mining wastes under the Surface Mining Control and Reclamation Act (PL 95-87). The EPA is negotiating an agreement with the OSM whereby RCRA coverage of mining wastes will be covered under the SMCRA, assuming that the stringency of the controls will be equivalent to those the RCRA would impose.¹⁴

A special category of wastes listed in the December 18, 1978, Federal Register directly affects energy use and specifically coal.¹⁵ In its interim rulemaking, the EPA has removed that category from consideration for a number of reasons. The first reason was mentioned in Section 1.3 concerning future legislative action on coal wastes.² Other reasons entailed the general belief that if these conventional coal combustion wastes are hazardous, the associated risk is low compared to those of other hazardous wastes. Furthermore, the EPA is presently prepared to propose without additional study, specific alternative treatment and disposal technologies.¹⁶

Along with removing the "special" waste category, the EPA believed that it was most appropriate to redefine the categories for hazardous waste in a

more rigorous manner. That is to say, corrosivity and some toxicity requirements were made more stringent. The result of this action is to exclude some wastes from "hazardous" designations. Thus, for corrosivity, the upper pH limit was moved from 12.0 to 12.5 (requiring a more basic or caustic waste for inclusion as hazardous), whereas the lower pH limit was moved from 3.0 to 2.0 (requiring a more acidic waste for inclusion as hazardous than previously defined).¹⁷ One set of the toxicity requirements was modified to allow for less stringent control of wastes. The EPA addressed the problem by developing a test procedure called the Extraction Procedure (EP) designed to identify wastes likely to leach hazardous concentrations of particular toxic constituents into groundwater under conditions of improper management. Under this procedure, species were extracted in a manner designed to simulate leaching in landfills. The extract was then analyzed for parameters identified in the National Interim Primary Drinking Water Standards (NIPDWS).¹⁸ The proposed regulation defined a waste as hazardous if the concentration of any parameter was in excess of ten times the NIPDWS for that parameter.¹⁹ Since there were few empirical data on which to base this dilution factor, the EPA decided to revise this dilution factor to one deemed more appropriate in defining the relative cost/benefit for a hazardous waste listing. Thus, the EPA is adopting a 100-fold dilution factor from NIPDWS on the basis that any waste failing this test (i.e., concentrations are greater than 100 times the NIPDW) has the potential to present a substantial hazard regardless of any attenuation mechanisms.²⁰

The EPA chose two criteria for identifying hazardous waste characteristics. The first was that a characteristic could be described within the statutory definition in terms of some physical, chemical, or other properties. The second criterion was that the properties used to fulfill the first criterion could be measured by standardized and available testing protocols. On this basis, the EPA has removed organic toxicity, carcinogenicity, mutagenicity, teratogenicity, bioaccumulation potential, and phytotoxicity from the list of proposed characteristics listed in the December 18, 1978, Federal Register.²¹ The following categories were retained, however:

- ignitability
- corrosivity (as discussed previously)
- reactivity
- EP toxicity (as redefined and discussed previously)

Two new categories consistent with EPA RCRA goals have been developed:

- (1) Acute Hazardous Waste: classified as such if it contains species that
 - have been found to be fatal to humans in low doses
 - result in oral LD₅₀* (rat) < 50 mg/kg

*LD₅₀ -- lethal dose, 50% -- is that quantity of a substance, administered either orally or by skin contact, necessary to kill 50% of exposed animals within a specified time.

- result in inhalation LC₅₀* (rat) < 2 mg/L
 - result in dermal LD₅₀ (rabbit) < 200 mg/kg
 - are capable of causing or significantly contributing to an increase in serious irreversible or incapacitating reversible illness²²
- (2) Toxic Waste defined as waste containing species listed in Table 2.2,²³ unless deemed nonhazardous by the Administrator following consideration of:
- the nature of toxicity
 - concentration of toxic constituent
 - environmental transport potential
 - environmental persistence
 - rate of degradation to nonharmful species
 - bioaccumulation
 - plausible types of improper management
 - quantities of waste on a local, regional or national basis
 - nature and severity of health and environmental impacts
 - other governmental action
 - other factors as appropriate.²²

The characteristics of ignitability, corrosivity, and reactivity are summarized in Subpart C, Part 261 - Identification and Listing of Hazardous Waste.²² The characteristics that determine Extraction Procedure (EP) toxicity, that is, concentrations of leachate species above which the waste is considered hazardous, are summarized in Table 2.3.²⁴ As mentioned earlier, the maximum concentration of contaminants for extraction toxicity characteristics is now set at 100 times the Safe Drinking Water Standard, rather than 10 times, as originally proposed.

Tables 2.4 and 2.5 contain lists of waste streams which the EPA Administrator has defined as hazardous. The hazard code on the right hand side of each table defines the reason for defining these waste streams as hazardous according to the six characteristics discussed previously:

ignitable	(I)
corrosive	(C)
reactive	(R)
EP toxic	(E)
acute hazardous	(H)
toxic	(T) ³

*LC₅₀ -- lethal concentration, 50% -- is that concentration of a substance, administered by inhalation, necessary to kill 50% of exposed animals within a specified time.

Table 2.2 Hazardous Constituents Identified in the RCRA

Acetaldehyde	Chlorinated benzenes, N.O.S.
(Aceto)phenylmercury	Chlorinated ethane, N.O.S.
Acetonitrile	Chlorinated naphthalene, N.O.S.
3-(alpha-Acetylbenzyl)-4-hydroxycoumarin and salts	Chlorinated phenol, N.O.S.
2-Acetylaminofluorene	Chloroacetaldehyde
Acetyl chloride	Chloroalkyl ethers
1-Acetyl-2-thiourea	p-Chloroaniline
Acrolein	Chlorobenzene
Acrylamide	Chlorobenzilate
Acrylonitrile	1-(p-Chlorobenzoyl)-5-methoxy-2-methylindole-3-acetic acid
Aflatoxins	p-Chloro-m-cresol
Aldrin	1-Chloro-2,3-epoxybutane
Allyl alcohol	2-Chloroethyl vinyl ether
Aluminum phosphide	Chloroform
4-Aminobiphenyl	Chloromethane
6-Amino-1,3a,2,8,8a,8b-hexahydro-6-(hydroxymethyl)-8a-methoxy-5-methylcarbamate azirino(2',3',3,4)pyrrolo(1,2-a)indole-4,7-dione (ester) (Mitomycin C)	Chloromethyl methyl ether
6-(Aminomethyl)-3-isoxazolol	2-Chloronaphthalene
4-Aminopyridine	2-Chlorophenol
Amitrole	1-(o-Chlorophenyl)thiourea
Antimony and compounds, N.O.S. ¹	3-Chloropropionitrile
Aramite	alpha-Chlorotoluene
Arsenic and compounds, N.O.S.	Chlorotoluene, N.O.S.
Arsenic acid	Chromium and compounds, N.O.S.
Arsenic pentoxide	Chrysene
Arsenic trioxide	Citrus red No. 2
Auramine	Copper cyanide
Azaserine	Creosote
Barium and compounds, N.O.S.	Crotonaldehyde
Barium cyanide	Cyanides (soluble salts and complexes), N.O.S.
Benz[c]acridine	Cyanogen
Benz[a]anthracene	Cyanogen bromide
Benzene	Cyanogen chloride
Benzenearsonic acid	Cycasin
Benzenethiol	2-Cyclohexyl-4,6-dinitrophenol
Benzdine	Cyclophosphamide
Benzo[a]anthracene	Daunomycin
Benzo[b]fluoranthene	DDD
Benzo[j]fluoranthene	DDE
Benzo[a]pyrene	DDT
Benzotrichloride	Diallate
Benzyl chloride	Dibenz[a,h]acridine
Beryllium and compounds, N.O.S.	Dibenz[a,j]acridine
Bis(2-chloroethoxy)methane	Dibenz[a,h]anthracene(Dibenzo[a,h]anthracene)
Bis(2-chloroethyl) ether	7H-Dibenzo[c,g]carbazole
N,N-Bis(2-chloroethyl)-2-naphthylamine	Dibenzo[a,e]pyrene
Bis(2-chloroisopropyl) ether	Dibenzo[a,h]pyrene
Bis(chloromethyl) ether	Dibenzo[a,j]pyrene
Bis(2-ethylhexyl) phthalate	1,2-Dibromo-3-chloropropane
Bromoacetone	1,2-Dibromoethane
Bromomethane	Dibromomethane
4-Bromophenyl phenyl ether	Di-n-butyl phthalate
Brucine	Dichlorobenzene, N.O.S.
2-Butanone peroxide	3,3'-Dichlorobenzidine
Butyl benzyl phthalate	1,1-Dichloroethane
2-sec-Butyl-4,6-dinitrophenol (DNBP)	1,2-Dichloroethane
Cadmium and compounds, N.O.S.	trans-1,2-Dichloroethane
Calcium chromate	Dichloroethylene, N.O.S.
Calcium cyanide	1,1-Dichloroethylene
Carbon disulfide	Dichloromethane
Chlorambucil	2,4-Dichlorophenol
Chlordane (alpha and gamma isomers)	2,6-Dichlorophenol
	2,4-Dichlorophenoxyacetic acid (2,4-D)
	Dichloropropane

Table 2.2 (Cont'd)

Dichlorophenylarsine	Hexachloroethane
1,2-Dichloropropane	1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-endo,endo-dimethanonaphthalene
Dichloropropanol, N.O.S.	Hexachlorophene
Dichloropropene, N.O.S.	Hexachloropropene
1,3-Dichloropropene	Hexaethyl tetraphosphate
Dieldrin	Hydrazine
Diepoxybutane	Hydrocyanic acid
Diethylarsine	Hydrogen sulfide
0,0-Diethyl-S-(2-ethylthio)ethyl ester of phosphorothioic acid	Indeno(1,2,3-c,d)pyrene
1,2-Diethylhydrazine	Iodomethane
0,0-Diethyl-S-methylester phosphorodithioic acid	Isocyanic acid, methyl ester
0,0-Diethylphosphoric acid, O-p-nitrophenyl ester	Isosafrole
Diethyl phthalate	Kepone
0,0-Diethyl-O-(2-pyrazinyl)phosphorothioate	Lasiocarpine
Diethylstilbestrol	Lead and compounds, N.O.S.
Dihydrosafrole	Lead acetate
3,4-Dihydroxy-alpha-(methylamino)-methyl benzyl alcohol	Lead phosphate
Di-isopropylfluorophosphate (DFP)	Lead subacetate
Dimethoate	Maleic anhydride
3,3'-Dimethoxybenzidine	Malononitrile
p-Dimethylaminoazobenzene	Melphalan
7,12-Dimethylbenz[a]anthracene	Mercury and compounds, N.O.S.
3,3'-Dimethylbenzidine	Methapyrilene
Dimethylcarbamoyl chloride	Methomyl
1,1-Dimethylhydrazine	2-Methylaziridine
1,2-Dimethylhydrazine	3-Methylcholanthrene
3,3-Dimethyl-1-(methylthio)-2-butanone-O-((methylamino) carbonyl)oxime	4,4'-Methylene-bis-(2-chloroaniline)
Dimethylnitrosamine	Methyl ethyl ketone (MEK)
alpha, alpha-Dimethylphenethylamine	Methyl hydrazine
2,4-Dimethylphenol	2-Methyllectonitrile
Dimethyl phthalate	Methyl methacrylate
Dimethyl sulfate	Methyl methanesulfonate
Dinitrobenzene, N.O.S.	2-Methyl-2-(methylthio)propionaldehyde-O-(methylcarbonyl) oxime
4,6-Dinitro-o-cresol and salts	N-Methyl-N'-nitro-N-nitrosoguanidine
2,4-Dinitrophenol	Methyl parathion
2,4-Dinitrotoluene	Methylthiouracil
2,6-Dinitrotoluene Di-n-octyl phthalate	Mustard gas
1,4-Dioxane	Naphthalene
1,2-Diphenylhydrazine	1,4-Naphthoquinone
Di-n-propylnitrosamine	1-Naphthylamine
Disulfoton	2-Naphthylamine
2,4-Dithiobiuret	1-Naphthyl-2-thiourea
Endosulfen	Nickel and compounds, N.O.S.
Endrin and metabolites	Nickel carbonyl
Epichlorohydrin	Nickel cyanide
Ethyl cyanide	Nicotine and salts
Ethylene diamine	Nitric oxide
Ethylenebisdithiocarbamate (EBDC)	p-Nitroaniline
Ethyleneimine	Nitrobenzene
Ethylene oxide	Nitrogen dioxide
Ethylenethiourea	Nitrogen mustard and hydrochloride salt
Ethyl methanesulfonate	Nitrogen mustard N-oxide and hydrochloride salt
Fluoranthene	Nitrogen peroxide
Fluorine	Nitrogen tetroxide
2-Fluoroacetamide	Nitroglycerine
Fluoroacetic acid, sodium salt	4-Nitrophenol
Formaldehyde	4-Nitroquinoline-1-oxide
Glycidylaldehyde	Nitrosamine, N.O.S.
Halomethane, N.O.S.	N-Nitrosodi-N-butylamine
Heptachlor	N-Nitrosodiethanolamine
Heptachlor epoxide (alpha, beta, and gamma isomers)	N-Nitrosodiethylamine
Hexachlorobenzene	N-Nitrosodimethylamine
Hexachlorobutadiene	N-Nitrosodiphenylamine
Hexachlorocyclohexane (all isomers)	N-Nitrosodi-N-propylamine
Hexachlorocyclopentadiene	N-Nitroso-N-ethylurea
	N-Nitrosomethylethylamine
	N-Nitroso-N-methylurea

Table 2.2 (Cont'd)

N-Nitroso-N-methylurethane	Tetrachloroethene (Tetrachloroethylene)
N-Nitrosomethylvinylamine	Tetrachloromethane
N-Nitrosomorpholine	2,3,4,6-Tetrachlorophenol
N-Nitrosornicotine	Tetraethyldithiopyrophosphate
N-Nitrosopiperidine	Tetraethyl lead
N-Nitrosopyrrolidine	Tetraethylpyrophosphate
N-Nitrososarcoside	Thallium and compounds, N.O.S.
5-Nitro-o-toluidine	Thallic oxide
Octamethylpyrophosphoramidate	Thallium (I) acetate
Oleyl alcohol condensed with 2 moles ethylene oxide	Thallium (I) carbonate
Osmium tetroxide	Thallium (I) chloride
7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid	Thallium (I) nitrate
Parathion	Thallium selenite
Pentachlorobenzene	Thallium (I) sulfate
Pentachloroethane	Thioacetamide
Pentachloronitrobenzene (PCNB)	Thiosemicarbazide
Pentachlorophenol	Thiourea
Phenacetin	Thiuram
Phenol	Toluene
Phenyl dichloroarsine	Toluene diamine
Phenylmercury acetate	o-Toluidine hydrochloride
N-Phenylthiourea	Tolyene diisocyanate
Phosgene	Toxaphene
Phosphine	Tribromomethane
Phosphorothioic acid, O,O-dimethyl ester, O-ester with N,N-dimethyl benzene sulfonamide	1,2,4-Trichlorobenzene
Phthalic acid esters, N.O.S.	1,1,1-Trichloroethane
Phthalic anhydride	1,1,2-Trichloroethane
Polychlorinated biphenyl, N.O.S.	Trichloroethene (Trichloroethylene)
Potassium cyanide	Trichloromethanethiol
Potassium silver cyanide	2,4,5-Trichlorophenol
Pronamide	2,4,6-Trichlorophenol
1,2-Propanediol	2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)
1,3-Propane sultone	2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP) (Silvex)
Propionitrile	Trichloropropane, N.O.S.
Propylthiouracil	1,2,3-Trichloropropane
2-Propyn-1-ol	0,0,0-Triethyl phosphorothioate
Pyridine	Trinitrobenzene
Reserpine	Tris(1-aziridinyl)phosphine sulfide
Saccharin	Tris(2,3-dibromopropyl) phosphate
Sabro	Trypan blue
Selenious acid	Uracil mustard
Selenium and compounds, N.O.S.	Urethane
Selenium sulfide	Vanadic acid, ammonium salt
Selenourea	Vanadium pentoxide (dust)
Silver and compounds, N.O.S.	Vinyl chloride
Silver cyanide	Vinylidene chloride
Sodium cyanide	Zinc cyanide
Streptozotocin	Zinc phosphide
Strontium sulfide	
Strychnine and salts	
1,2,4,5-Tetrachlorobenzene	
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	
Tetrachloroethane, N.O.S.	
1,1,1,2-Tetrachloroethane	
1,1,2,2-Tetrachloroethane	

¹The abbreviation N.O.S. signifies those members of the general class "not otherwise specified" in this listing.

Source: Ref. (22).

Table 2.3 Maximum Concentration of Contaminants for Characteristics of EP Toxicity

EPA Hazardous Waste Number	Contaminant	Maximum Concentration Milligrams Per Liter)
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0
D012	Endrin (1,2,3,4,10,10-hexachloro-1,7 epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo, endo-5,8-dimethano naphthalene	0.02
D013	Lindane (1,2,3,4,5,6-hexachlorocyclohexane, gamma isomer	0.4
D014	Methoxychlor (1,1,1-Trichloro-2,2-bis [p-methoxyphenyl] ethane)	
D015	Toxaphene (C ₁₀ H ₁₀ Cl ₈ , Technical chlorinated camphene, 67-69 percent chlorine)	0.5
D016	2,4-D, (2,4-Dichlorophenoxyacetic acid)	10.0
D017	2,4,5-TP Silvex (2,4,5-Trichlorophenoxypropionic acid)	1.0

Source: Ref. (25)

Table 2.6 lists the chemical species for which each waste stream was deemed hazardous.²⁵ Section 261.33 of Part 261 deals with chemical products, off-specification products, and spill residues.²⁶ These parameters are not as important in terms of energy use and comparative studies as are the characteristics, waste streams, and chemicals discussed previously and listed in Tables 2.2 through 2.6. Although no coal use streams are listed, five petroleum refining streams are listed as containing toxic hazardous wastes.

2.6.3 Testing and Analysis Procedures

An imperative part of RCRA definition and enforcement comes from the proper use of sampling, testing, and analysis procedures and protocols. Many tests are standard and had previously been developed by the EPA or the American Society for Testing and Materials (ASTM), or both. However, given the nature of the unique sampling and analytical problems associated with standardized solid wastes measurements, the EPA developed protocols and publications to document these new methods. These procedures are summarized in Table 2.7. Details of these procedures are given in an EPA report

Table 2.4 Hazardous Waste from Nonspecific Sources

Industry and EPA hazardous waste No.	Hazardous waste	Hazard code
Generic:		
F001	The spent halogenated solvents used in degreasing, tetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, and the chlorinated fluorocarbons; and sludges from the recovery of these solvents in degreasing operations.	(T)
F002	The spent halogenated solvents, tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, o-dichlorobenzene, trichlorofluoromethane and the still bottoms from the recovery of these solvents.	(T)
F003	The spent non-halogenated solvents, xylene, acetone, ethyl acetate, ethyl benzene, ethyl ether, n-butyl alcohol, cyclohexanone, and the still bottoms from the recovery of these solvents.	(T)
F004	The spent non-halogenated solvents, cresols and cresylic acid, nitrobenzene, and the still bottoms from the recovery of these solvents.	(T)
F005	The spent non-halogenated solvents, methanol, toluene, methyl ethyl ketone, methyl isobutyl ketone, carbon disulfide, isobutanol, pyridine and the still bottoms from the recovery of these solvents.	(T, T)
F006	Wastewater treatment sludges from electroplating operations.	(T)
F007	Spent plating bath solutions from electroplating operations.	(R, T)
F008	Plating bath sludges from the bottom of plating baths from electroplating operations.	(R, T)
F009	Spent stripping and cleaning bath solutions from electroplating operations.	(R, T)
F010	Quenching bath sludge from oil baths from metal heat treating operations.	(R, T)
F011	Spent solutions from salt bath pot cleaning from metal heat treating operations.	(R, T)
F012	Quenching wastewater treatment sludges from metal heat treating operations.	(T)
F013	Flotation tailings from selective flotation from mineral metals recovery operations.	(T)
F014	Cyanidation wastewater treatment tailing pond sediment from mineral metals recovery operations.	(R, T)
F015	Spent cyanide bath solutions from mineral metals recovery operations.	(T)
F016	Dewatered air pollution control scrubber sludges from coke ovens and blast furnaces.	(T)

Source: Ref. 3.

Test Methods for Evaluating Solid Waste,²⁹ which was prepared as required by law.^{27,28} The methods are summarized for most of the toxic chemical species in Tables 2.8 and 2.9.²⁹

The biggest difficulty from an analytical standpoint will be to ensure that extraction protocols are rigorously followed. Although the methodology produced reasonable reproducibility, some problems were encountered in this regard,³⁰⁻³² and such problems must be monitored closely. A possible solution would be to certify testing laboratories using procedures similar to those followed for certifying laboratories for drinking water analysis. The laboratories to be certified would differ in many areas, but mechanisms for certification, testing, and recordkeeping could be standardized.

2.6.4 Solid Waste Disposal Requirements

The Section 4004 criteria for Solid Waste Disposal were issued in final form on September 13, 1979. The eight criteria address a broad range of health and environmental effects including floodplains, endangered species, surface water, groundwater, disease, air, application to land used in the production of food chain crops, and safety. These criteria are for determining which solid waste disposal facilities and practices pose a reasonable probability of adverse effects on health or the environment.³³

The criteria apply to the full range of practices for the disposal of solid waste with the following exceptions:

- agricultural wastes, including manures and residues, returned to the soil as fertilizers or soil conditioners
- overburden from mining operations intended for return to the mine site

Table 2.5 Hazardous Waste from Specific Sources

Industry and EPA hazardous waste No.	Hazardous waste	Hazard code
Wood Preservation: K001	Bottom sediment sludge from the treatment of wastewaters from wood preserving processes that use creosote and/or pentachlorophenol	(M)
Inorganic Pigments:		
K002	Wastewater treatment sludge from the production of chrome yellow and orange pigments	(C)
K003	Wastewater treatment sludge from the production of molybdate orange pigments	(C)
K004	Wastewater treatment sludge from the production of zinc yellow pigments	(C)
K005	Wastewater treatment sludge from the production of chrome green pigments	(C)
K006	Wastewater treatment sludge from the production of chrome oxide green pigments (anhydrous and hydrated)	(C)
K007	Wastewater treatment sludge from the production of iron blue pigments	(C)
K008	Oven residue from the production of chrome oxide green pigments	(C)
Organic Chemicals:		
K009	Distillation bottoms from the production of acetaldehyde from ethylene	(C)
K010	Distillation side cuts from the production of acetaldehyde from ethylene	(C)
K011	Bottom stream from the wastewater stripper in the production of acrylonitrile	(R, T)
K012	Still bottoms from the final purification of acrylonitrile in the production of acrylonitrile	(R, T)
K013	Bottom stream from the acetonitrile column in the production of acrylonitrile	(R, T)
K014	Bottoms from the acetonitrile purification column in the production of acrylonitrile	(C)
K015	Still bottoms from the distillation of benzyl chloride	(C)
K016	Heavy ends or distillation residues from the production of carbon tetrachloride	(C)
K017	Heavy ends (still bottoms) from the purification column in the production of epichlorohydrin	(C)
K018	Heavy ends from fractionation in ethyl chloride production	(C)
K019	Heavy ends from the distillation of ethylene dichloride in ethylene dichloride production	(C)
K020	Heavy ends from the distillation of vinyl chloride in vinyl chloride monomer production	(C)
K021	Aqueous spent antimony catalyst waste from fluoromethanes production	(C)
K022	Distillation bottom tars from the production of phenol/acetone from cumene	(C)
K023	Distillation light ends from the production of phthalic anhydride from naphthalene	(C)
K024	Distillation bottoms from the production of phthalic anhydride from naphthalene	(C)
K025	Distillation bottoms from the production of nitrobenzene by the nitration of benzene	(C)
K026	Stripping still tails from the production of methyl ethyl pyridines	(C)
K027	Centrifuge residue from toluene diisocyanate production	(R, T)
K028	Spent catalyst from the hydrochlorinator reactor in the production of 1,1,1-trichloroethane	(C)
K029	Waste from the product stream stripper in the production of 1,1,1-trichloroethane	(C)
K030	Column bottoms or heavy ends from the combined production of trichloroethylene and perchloroethylene	(C)
Pesticides:		
K031	By-products salts generated in the production of MSMA and cacodylic acid	(C)
K032	Wastewater treatment sludge from the production of chlordane	(C)
K033	Wastewater and scrub water from the chlorination of cyclopentadiene in the production of chlordane	(C)
K034	Filter solids from the filtration of hexachlorocyclopentadiene in the production of chlordane	(C)
K035	Wastewater treatment sludges generated in the production of creosote	(C)
K036	Still bottoms from toluene reclamation distillation in the production of disulfoton	(C)
K037	Wastewater treatment sludges from the production of disulfoton	(C)
K038	Wastewater from the washing and stripping of phorate production	(C)
K039	Filter cake from the filtration of diethylphosphorodithionic acid in the production of phorate	(C)
K040	Wastewater treatment sludge from the production of phorate	(C)
K041	Wastewater treatment sludge from the production of toxaphene	(C)
K042	Heavy ends or distillation residues from the distillation of tetrachlorobenzene in the production of 2,4,5-T	(C)
K043	2,6-Dichlorophenol waste from the production of 2,4-D	(C)
Explosives:		
K044	Wastewater treatment sludges from the manufacturing and processing of explosives	(R)
K045	Spent carbon from the treatment of wastewater containing explosives	(R)
K046	Wastewater treatment sludges from the manufacturing, formulation and loading of lead-based initiating compounds	(R)
K047	Pink/red water from TNT operations	(R)
Petroleum Refining:		
K048	Dissolved air flotation (DAF) float from the petroleum refining industry	(C)
K049	Slip oil emulsion solids from the petroleum refining industry	(C)
K050	Heat exchanger bundle cleaning sludge from the petroleum refining industry	(C)
K051	API separator sludge from the petroleum refining industry	(C)
K052	Tank bottoms (lead) from the petroleum refining industry	(C)
Leather Tanning Finishing:		
K053	Chrome (blue) trimmings generated by the following subcategories of the leather tanning and finishing industry: hair pulp/chrome tan/retan/wet finish; hair save/chrome tan/retan/wet finish; retan/wet finish; no beamhouse; through-the-blue; and shearing	(T)
K054	Chrome (blue) shavings generated by the following subcategories of the leather tanning and finishing industry: hair pulp/chrome tan/retan/wet finish; hair save/chrome tan/retan/wet finish; retan/wet finish; no beamhouse; through-the-blue; and shearing	(T)
K055	Buffing dust generated by the following subcategories of the leather tanning and finishing industry: hair pulp/chrome tan/retan/wet finish; hair save/chrome tan/retan/wet finish; retan/wet finish; no beamhouse; and through-the-blue	(T)
K056	Sewer screenings generated by the following subcategories of the leather tanning and finishing industry: hair pulp/chrome tan/retan/wet finish; hair save/chrome tan/retan/wet finish; retan/wet finish; no beamhouse; through-the-blue; and shearing	(T)
K057	Wastewater treatment sludges generated by the following subcategories of the leather tanning and finishing industry: hair pulp/chrome tan/retan/wet finish; hair save/chrome tan/retan/wet finish; retan/wet finish; no beamhouse; through-the-blue and shearing	(T)
K058	Wastewater treatment sludges generated by the following subcategories of the leather tanning and finishing industry: hair pulp/chrome tan/retan/wet finish; hair save/chrome tan/retan/wet finish; and through-the-blue	(R, T)
K059	Wastewater treatment sludges generated by the following subcategory of the leather tanning and finishing industry: hair save/non-chrome tan/retan/wet finish	(R)
Iron and Steel:		
K060	Ammonia still lime sludge from coking operations	(C)
K061	Emission control dust/sludge from the electric furnace production of steel	(C)
K062	Spent pickle liquor from steel finishing operations	(T)
K063	Sludge from lime treatment of spent pickle liquor from steel finishing operations	(C)
Primary Copper: K064	Acid plant blowdown slurry/sludge resulting from the thickening of blowdown slurry from primary copper production	(C)
Primary Lead: K065	Surface impoundment solids contained in and dredged from surface impoundments at primary lead smelting facilities	(C)
Primary Zinc:		
K066	Sludge from treatment of process wastewater and/or acid plant blowdown from primary zinc production	(C)
K067	Electrolytic anode slimes/sludges from primary zinc production	(C)
K068	Cadmium plant leach residue (iron oxide) from primary zinc production	(C)
Secondary Lead: K069	Emission control dust/sludge from secondary lead smelting	(C)

Source: Ref 3.

Table 2.6 Basis for Listing Hazardous Wastes

EPA hazardous waste No.	Hazardous constituents for which listed	EPA hazardous waste No.	Hazardous constituents for which listed
F001.....	tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, chlorinated fluorocarbons, carbon tetrachloride	K020.....	ethylene dichloride, 1,1,1-trichloroethane, 1,1,2-trichloroethane, tetrachloroethanes (1,1,2,2-tetrachloroethane and 1,1,1,2-tetrachloroethane), trichloroethylene, tetrachloroethylene, carbon tetrachloride, chloroform, vinyl chloride, vinylidene chloride
F002.....	tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, o-dichlorobenzene, trichlorofluoromethane	K021.....	antimony, carbon tetrachloride, chloroform
F003.....	N.A.	K022.....	phenol, tars (polycyclic aromatic hydrocarbons)
F004.....	cresols and cresylic acid, nitrobenzene	K023.....	phthalic anhydride, maleic anhydride
F005.....	methanol, toluene, methyl ethyl ketone, methyl isobutyl ketone, carbon disulfide, isobutanol, pyridine	K024.....	phthalic anhydride, polynuclear tar-like materials, naphthoquinone
F006.....	cadmium, chromium, nickel, cyanide (complexed)	K025.....	meta-dinitrobenzene, 2,4-dinitrotoluene
F007.....	cyanide (salts)	K026.....	paraaldehyde, pyridines, 2-picoline
F008.....	cyanide (salts)	K027.....	toluene disocyanate, toluene-2,4-diamine, tars (benzodimidazapone)
F009.....	cyanide (salts)	K028.....	1,1,1-trichloroethane, vinyl chloride
F010.....	cyanide (salts)	K029.....	1,2-dichloroethane, 1,1,1-trichloroethane, vinyl chloride, vinylidene chloride, chloroform
F011.....	cyanide (salts)	K030.....	hexachlorobenzene, hexachlorobutadiene, hexachloroethane, 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, ethylene dichloride
F012.....	cyanide (complexed)	K031.....	arsenic
F013.....	cyanide (complexed)	K032.....	hexachlorocyclopentadiene
F014.....	cyanide (complexed)	K033.....	hexachlorocyclopentadiene
F015.....	cyanide (salts)	K034.....	hexachlorocyclopentadiene
F016.....	cyanide (complexed)	K035.....	cresole, benz(a)anthracene, benz(b)fluoranthene, benzo(a)pyrene
K001.....	benzene, benz(a)anthracene, benzo(a)pyrene, chrysene, 4-nitrophenol, toluene, naphthalene phenol, 2-chlorophenol, 2,4-dimethyl phenol, 2,4,6-trichlorophenol, pentachlorophenol, 4,8-dinitro-o-cresol, tetrachlorophenol	K036.....	toluene, phosphorodithioic and phosphorothioic acid esters
K002.....	chromium, lead	K037.....	toluene, phosphorodithioic and phosphorothioic acid esters
K003.....	chromium, lead	K038.....	phosphate, formaldehyde, phosphorodithioic and phosphorothioic acid esters
K004.....	chromium	K039.....	phosphorodithioic and phosphorothioic acid esters
K005.....	chromium, lead	K040.....	phosphate, formaldehyde, phosphorodithioic and phosphorothioic acid esters
K006.....	chromium	K041.....	toxaphene
K007.....	cyanide (complexed), chromium	K042.....	hexachlorobenzene; ortho-dichlorobenzene
K008.....	chromium	K043.....	2,4-dichlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol
K009.....	chloroform, formaldehyde, methylene chloride, methyl chloride, paraaldehyde, formic acid	K044.....	N.A.
K010.....	chloroform, formaldehyde, methylene chloride, methyl chloride, paraaldehyde, formic acid, chloroacetaldehyde	K045.....	N.A.
K011.....	acrylonitrile, acetonitrile, hydrocyanic acid	K046.....	lead
K012.....	acrylonitrile, acetonitrile, acrolein, acrylamide	K047.....	N.A.
K013.....	hydrocyanic acid, acrylonitrile, acetonitrile	K048.....	chromium, lead
K014.....	acetonitrile, acrylamide	K049.....	chromium, lead
K015.....	benzyl chloride, chlorobenzene, toluene, benzotrithloride	K050.....	chromium
K016.....	hexachlorobenzene, hexachlorobutadiene, carbon tetrachloride, hexachloroethane, perchloroethylene	K051.....	chromium, lead
K017.....	epichlorohydrin, chloroethers [bis(chloromethyl) ether and bis (2-chloroethyl) ethers], trichloropropane, dichloropropanols	K052.....	lead
K018.....	1,2-dichloroethane, trichloroethylene, hexachlorobutadiene, hexachlorobenzene	K053.....	chromium
K019.....	ethylene dichloride, 1,1,1-trichloroethane, 1,1,2-trichloroethane, tetrachloroethanes (1,1,2,2-tetrachloroethane and 1,1,1,2-tetrachloroethane), trichloroethylene, tetrachloroethylene, carbon tetrachloride, chloroform, vinyl chloride, vinylidene chloride	K054.....	chromium
		K055.....	chromium, lead
		K056.....	chromium, lead
		K057.....	chromium, lead
		K058.....	chromium, lead
		K059.....	N.A.
		K060.....	cyanide, naphthalene, phenolic compounds, arsenic
		K061.....	chromium, lead, cadmium
		K062.....	chromium, lead
		K063.....	chromium, lead
		K064.....	lead, cadmium
		K065.....	lead, cadmium
		K066.....	lead, cadmium
		K067.....	lead, cadmium
		K068.....	lead, cadmium
		K069.....	chromium, lead, cadmium

N.A.—Waste is hazardous because it meets either the ignitability, corrosivity or reactivity characteristic.

Source: Ref. 25.

Table 2.7 Test Methods for Evaluating Solid Wastes

Method	Reference Method
Sampling	
Extremely viscous liquid	ASTM ^a D140-70 D346-75 D420-69 D1452-65
Fly Ash	ASTM D2234-76
Containerized liquid wastes	EPA (new methods)
Liquid waste from ponds, lagoons, etc.	EPA (new methods)
Analysis	
Ignitability	ASTM D-93-79 or ASTM D-3278-78
Corrosivity	EPA (new methods)
Reactivity	45 FR 33122 Section 261.23
EP Toxicity	EPA (new methods) or 45 FY 33127 (Appendix II)
Acute hazard	See Sec. 2.2.1
Toxic	See Sec. 2.2.1

^aAmerican Society for Testing and Materials.

- domestic sewage or treated domestic sewage (criteria do apply to disposal of sludge resulting from the treatment of domestic sewage)
- solid or dissolved materials in irrigation return flows
- source, special nuclear or by-product materials
- industrial discharges subject to permits under Section 402 of the Clean Water Act as amended
- hazardous waste disposal facilities subject to regulation under Subtitle C of RCRA
- underground well injection facilities subject to regulations for the Underground Injection Control Program.³⁴

The criteria are flexible and provide the opportunity for state and local solid waste management agencies to take into account site-by-site variations and make assessments on local conditions. The EPA tried to set specific performance standards that defined unacceptable environmental effects so as to provide a concise and measurable means of determining compliance. However, in some situations it was not possible to devise a meaningful performance standard for an environmental effect, given the lack of experience with regulation of solid waste.³³

The criteria are the same for existing facilities and new facilities, although it was suggested that there be less stringent criteria for existing

Table 2.8 Analytical Methods for Organic Chemicals

Compound	Sample handling class/fraction	Non-GC methods	Measurement techniques			Compound	Sample handling class/fraction	Non-GC methods	Measurement techniques		
			GC/MS	Conventional GC	Detector				GC/MS	Conventional GC	Detector
Acetonitrile	Volatile		8.24	8.03	NSD	Nitrobenzene	Extractable/BN		8.25	8.09	FID
Acrolein	Volatile		8.24	8.03	NSD	4-Nitrophenol	Extractable/A		8.24	8.04	ECD, FID
Acrylamide	Volatile		8.24	8.01	FID	Paraldehyde (trimer of acetaldehyde)	Volatile		8.24	8.01	FID
Acrylonitrile	Volatile		8.24	8.03	NSD	Pentachlorophenol	Extractable/A		8.25	8.04	ECD
Benzene	Volatile		8.24	8.02	PID	Phenol	Extractable/A		8.25	8.04	ECD, FID
Benz(a)anthracene	Extractable/BN	8.10 (HPLC)	8.25	8.10	FID	Phorale	Extractable/BN			8.22	FPD
Benzof(a)pyrene	Extractable/BN	8.10 (HPLC)	8.25	8.10	FID	Phosphorothioic acid esters	Extractable/BN			8.06	ECD, FID
Benzotrithione	Extractable/BN		8.25	8.12	ECD					8.09	ECD, FID
Benzyl chloride	Volatile or Extractable/BN		8.24	8.01	HSD					8.22	FPD
			8.25	8.12	ECD	Phthalic anhydride	Extractable/BN		8.25	8.06	ECD, FID
Benz(b)fluoranthene	Extractable/BN	8.10 (HPLC)	8.25	8.10	FID	2-Picoline	Extractable/BN		8.25	8.06	ECD, FID
Bis(2-chloroethoxy)methane	Volatile		8.24	8.01	HSD					8.06	ECD, FID
Bis(2-chloroethyl)ether	Volatile		8.24	8.01	HSD	Pyridine	Extractable/BN		8.25	8.06	ECD, FID
Bis(2-chloroisopropyl)ether	Volatile		8.24	8.01	HSD					8.09	ECD, FID
Carbon disulfide	Volatile		8.24	8.01	HSD	Tetrachlorobenzene(s)	Extractable/BN		8.25	8.12	ECD
Carbon tetrachloride	Volatile		8.24	8.01	HSD	Tetrachloroethane(s)	Volatile		8.24	8.01	HSD
Chlordane	Extractable/BN		8.25	8.06	HSD	Tetrachloroethene	Volatile		8.24	8.01	HSD
Chlorinated dibenzodioxins	Extractable/BN		8.25	8.06	ECD	Tetrachlorophenol	Extractable/A		8.24	8.04	ECD
Chlorinated biphenyls	Extractable/BN		8.25	8.06	HSD	Toluene	Volatile		8.24	8.02	PID
Chloroacetaldehyde	Volatile		8.24	8.01	HSD	Toluenediamine	Extractable/BN		8.25		
Chlorobenzene	Volatile		8.24	8.01	HSD	Toluene diisocyanate(s)	Extractable/nonaqueous		8.25	8.06	FID
				8.02	PID	Toxaphene	Extractable/P		8.25	8.06	HSD
Chloroform	Volatile		8.24	8.01	HSD	Trichloroethane	Volatile		8.24	8.01	HSD
Chloromethane	Volatile		8.24	8.01	HSD	Trichloroethene(s)	Volatile		8.24	8.01	HSD
2-Chlorophenol	Extractable/BN		8.25	8.04	FID, ECD	Trichlorofluoromethane	Volatile		8.24	8.01	HSD
Chrysene	Extractable/BN	8.10 (HPLC)	8.25	8.10	FID	Trichlorophenol(s)	Extractable/A		8.25	8.04	HSD
Cresote	Extractable/BN		8.25	8.10	ECD	2,4,5-TP (Silvex)	Extractable/A		8.25	8.40	HSD
Cresol(s)	Extractable/A		8.25	8.04	FID, ECD	Trichloropropane	Volatile		8.24	8.01	HSD
Cresylic acid(s)	Extractable/A		8.25	8.04	FID, ECD	Vinyl chloride	Volatile		8.24	8.01	HSD
Dichlorobenzene(s)	Extractable/BN		8.25	8.01	HSD	Vinylidene chloride	Volatile		8.24	8.01	HSD
				8.02	PID	Xylene	Volatile		8.24	8.02	PID
Dichloroethane(s)	Volatile		8.24	8.01	HSD						
Dichloromethane	Volatile		8.24	8.01	HSD						
Dichlorophenoxy-acetic acid	Extractable/A		8.25	8.40	HSD						
Dichloropropanol	Extractable/BN		8.25	8.12	ECD						
2,4-Dimethylphenol	Extractable/A		8.25	8.04	FID, ECD						
Dinitrobenzene	Extractable/BN		8.25	8.09	FID, ECD						
4,6-Dinitro-o cresol	Extractable/A		8.25	8.04	FID, ECD						
2,4-Dinitrotoluene	Extractable/BN		8.25	8.09	FID, ECD						
Endrin	Extractable/P		8.25	8.06	HSD						
Ethyl ether	Volatile		8.24	8.01	FID						
				8.02	FID						
Formaldehyde	Volatile		8.24	8.01	FID						
Formic acid	Extractable/BN		8.25	8.06	FID						
Heptachlor	Extractable/P		8.25	8.06	HSD						
Hexachlorobenzene	Extractable/BN		8.25	8.12	ECD						
Hexachlorobutadiene	Extractable/BN		8.25	8.12	ECD						
Hexachloroethane	Extractable/BN		8.25	8.12	ECD						
Hexachlorocyclopentadiene	Extractable/BN		8.25	8.12	ECD						
Lindane	Extractable/P		8.25	8.06	HSD						
Maleic anhydride	Extractable/BN		8.25	8.06	ECD, FID						
Methanol	Volatile		8.24	8.01	FID						
Methomyl	Extractable/BN	8.32 (HPLC)									
Methyl ethyl ketone	Volatile		8.25	8.01	FID						
				8.02	FID						
Methyl isobutyl ketone	Volatile		8.25	8.01	FID						
				8.02	FID						
Naphthalene	Extractable/BN		8.25	8.10	FID						
Naphthoquinone	Extractable/BN		8.25	8.06	ECD, FID						

* Analyze for phenanthrene and carbazole; if these are present in a ratio between 1.4:1 and 5:1, cresote should be considered present.

ECD = Electron capture detector; FID = Flame ionization detector; FPD = Flame photometric detector; HSD = Halide specific detector; HPLC = High pressure liquid chromatography; NSD = Nitrogen-specific detector; PID = Photoionization detector.

Source: Ref. 29.

Table 2.9 Analytical Methods for Inorganic Species

Species	Sample Handling Class	Measurement Technique	Method Number
Antimony	Digestion	Atomic Absorbption-Furnace/Flame	8.50
Arsenic	Gaseous Hydride	Atomic Absorbption-Flame	8.51
Barium	Digestion	Atomic Absorbption-Furnace/Flame	8.52
Cadmium	Digestion	Atomic Absorbption-Furnace/Flame	8.53
Chromium	Digestion	Atomic Absorbption-Furnace/Flame	8.54
Cyanides	Hydrolysis	Atomic Absorbption-Spectroscopy	8.55
Lead	Digestion	Atomic Absorbption-Furnace/Flame	8.56
Mercury	Cold Vapor	Atomic Absorbption	8.57
Nickel	Digestion	Atomic Absorbption-Furnace/Flame	8.58
Selenium	Gaseous Hydride		
	Digestion	Atomic Absorbption-Furnace/Flame	8.59
Silver	Digestion	Atomic Absorbption-Furnace/Flame	8.60

Source: Ref. 29.

facilities. However, with regard to implementation of the criteria, the Act does recognize the need to continue controlled use of existing facilities, while alternatives that comply with the criteria are being developed. A state may issue compliance schedules that allow use of the facility while it is being upgraded or while alternative options are developed.³⁵

In addition, the criteria apply to both small and large facilities, both urban and rural. The EPA felt that exclusion of small facilities would foster the development of additional small facilities in order to escape the cost of compliance.³⁶ The standards established in the criteria constitute minimum requirements. The criteria do not preempt other state and federal requirements.³³

The states have the responsibility of evaluating existing disposal facilities to determine whether they comply with the Section 4004 criteria. Those facilities that do not satisfy the criteria are "open dumps", and the EPA will publish a list of open dumps in the Federal Register. The inventory of "open dumps" will serve two major functions. First, it will inform Congress and the public about the extent of the problem. Second, it will provide an agenda for action by identifying problem facilities routinely used for disposal which should be addressed in state solid waste management plans in accordance with Section 4003 of the Act.³⁷ Specific criteria developed in Section 4004 from disposal of solid wastes are discussed below.

Floodplains

The three components of this criterion are that facilities or practices in flood plains shall not: (1) restrict the flow of the base flood (a flood with a 1% or greater chance of occurring in any one year); (2) reduce temporary water storage of the floodplain; and (3) result in a washout of solid

waste that would pose a hazard to human life, wildlife, or land or water resources.³³

It is generally desirable to locate disposal facilities outside of floodplains because wastes may be carried from the site, affecting downstream water quality and structures. In addition, filling the floodplain may restrict the flow of water causing greater flooding upstream, reduce the effectiveness of the flood-flow retaining capacity, and cause more rapid flooding downstream. The floodplain criterion prevents these adverse impacts; however, it does not prohibit location of a facility in a floodplain.

Endangered Species

The endangered species criterion states that facilities or practices shall not cause or contribute to the "taking" of any endangered or threatened species of plants, fish, or wildlife or destroy or modify the critical habitat of these species.³⁸

The "taking" definition is very broadly stated and encompasses a variety of adverse effects. Taking is defined as harassing, harming, pursuing, hunting, wounding, killing, trapping, capturing or collecting or attempting to engage in such conduct. The proposed criteria used a "jeopardize" standard; however, it was decided that it was inappropriate for a definition that would be applied to a vast number of site specific conditions and that the "taking" definition was more in keeping with EPA's general intent to establish concise, measurable performance standards wherever possible.³⁹

Surface Water

The surface water criterion requires compliance with the Clean Water Act (CWA) as amended. It requires that a facility or practice shall not (1) cause a discharge of pollutants in violation of the National Pollutant Discharge Elimination System (NPDES) under Section 402 of the CWA, (2) cause a discharge of dredged or fill materials that is in violation of Section 404 of the CWA, and (3) cause nonpoint pollution of waters that violates the legal requirements of implementing the water quality management plan developed under Section 208 of the CWA.³⁸

In the final regulation, EPA has sought to coordinate the surface water standards with programs developed under the CWA. However, concerns have been raised over the ability of NPDES permitting agencies to process applications and issue permits for point source discharges of pollutants from solid waste disposal facilities because not many permits have been issued for such discharges.⁴⁰ In addition, very few approved state 208 plans exist.

Groundwater

The groundwater criterion states that a facility or practice shall not contaminate underground drinking water beyond the solid waste boundary or any boundary established by an approved state solid waste management agency.⁴¹

Contamination occurs when leachate from the disposal activity causes the concentrations of certain pollutants in groundwater to either (1) exceed the maximum contaminant level (based on the primary drinking water standards specified for that pollutant), or (2) increase at all where the background concentration of the pollutant already exceeds the applicable contaminant level. An underground drinking water source is an aquifer currently supplying drinking water for human consumption or an aquifer in which the concentration of total dissolved solids is less than 10,000 mg/L.⁴⁰

In establishing the criterion, the EPA recognized that groundwater quality is important for other uses and that differing standards may be appropriate for these other purposes; however, at this time human health effects from direct consumption have the highest priority. In addition, the EPA has developed standards for drinking water but has not established standards for other uses.⁴⁰

Disease

The criterion states that the facility must control the vectors of disease through the periodic application of cover material or other techniques that are appropriate to public health. The criterion also closely defines the conditions under which sewage sludge or septic tank pumpings may be applied to the land surface.⁴²

Air

The air criterion has two components. First, there shall be no opening burning of residential, commercial, institutional, or industrial solid waste. This provision does not apply to infrequent burning of agricultural wastes, silvicultural waste, land clearing debris, and debris from emergency cleanup operations. Second, air emissions caused by a solid waste disposal facility shall not violate requirements developed for SIP's under the Clean Air Act.⁴² No variance on open burning was allowed because it does not lessen the need for disease vector control or leachate control for maintaining groundwater quality. In addition, variance procedures would be difficult to administer because of the dynamic nature of the many variables involved (e.g., wind speed, and vertical dispersion efficiency of the burn).⁴³

Safety

The regulation requires that the concentration of explosive gases do not exceed 25% of the lower explosive limit for the gases in the facility structure and the lower explosive limit for gases at the property boundary. The criterion also contains provisions dealing with fires, bird hazards to air craft, and access.⁴² Although this standard could potentially be applicable to several explosive gases, it is presently only applied to methane.⁴³

The issues that might affect implementation of Section 4004 for disposal of solid wastes are discussed below.

Criteria Flexibility

The criteria were designed to be flexible so that state and local solid waste management agencies can take site-specific conditions into account; however, this flexibility may present a problem. There is concern that too much room exists for individual interpretation and that inspection and evaluation of disposal facilities and subsequent listing on EPA's open dump list may be a very subjective undertaking despite the efforts to make the criteria as objective as possible.⁴⁴

Flexibility is a key issue, especially when one takes into account that most states have little experience in solid waste management and few if any, precedents have been set. Under such conditions, it is difficult for industry to determine how the state plans to act. The EPA has developed a manual (see Ref. 45) to instruct states on how to conduct the inventory, and they will hold training sessions for state personnel; however, it will be up to the individual states to interpret the criteria, conduct the open dump inventory, and determine the process for compliance.

Institutional Barriers

Once of the most critical problems in solid waste management today is the lack of acceptable disposal facilities due, in part, to public opposition to their siting. EPA recognizes this fact and hopes that implementation of the criteria will increase the credibility of disposal operations, thereby aiding in reducing public opposition to acceptable and needed facilities.³³ However, others feel that citizen reaction against facilities will actually intensify because the EPA is calling attention to the bad practices of the past and present by publishing the open dump inventory. Although public opposition may eventually change, it is unlikely that it will do so in the immediate future. Implementation of the RCRA criteria and development of effective solid waste management programs will take years and it is unlikely that public opinion will change before that time.

State Preparedness

An important issue revolves around the question of whether or not the states are prepared to use the criteria to evaluate solid waste disposal facilities. Indications are that most states are not ready. Solid waste management programs in many states are in their infancy. Implementation of the criteria will place a variety of new responsibilities on the states including development and implementation of new laws and regulations, development of assessment procedures, and establishment of monitoring wells. Some criteria will be more easily met than others, but it appears that a majority of the states are not prepared to use a majority of the criteria. Table 2.10 provides a summary of the degree of readiness of the states.

2.6.5 Hazardous Waste Disposal Requirements

The regulations for hazardous waste disposal under Section 3004 of the Act set interim operating and technical standards for the treatment, storage,

Table 2.10 State Readiness to Use the Solid Waste Disposal Criteria

Criteria	Territories and States Not Complying	Comments
Open burning of refuse	22	
Open burning of diseased plants	14	About half the jurisdiction require regulations upgraded
Gas emission	27	Monitoring requirements will affect almost every jurisdiction
Fire control	7	No difficulties complying
Bird hazard to aircraft	33	Urban Northwest will experience problems
Access	0	No difficulties complying
Surface water	53	Totally new sets of regulations and procedures in all jurisdictions
Groundwater	48	Substantial changes in monitoring procedures
Endangered species	50	Total revision of existing laws and regulations
Disease vectors	1	No difficulties complying
Floodplains	21	Some procedural changes in all jurisdictions

Source: Ref. 44.

and disposal of hazardous wastes. However, the EPA is aware that it may take several years, in some cases, to adequately develop the data necessary to resolve the more complex technical issues raised by the regulations in a way that will allow promulgation of national, acceptable, detailed standards.⁴⁶

The interim regulations will go into effect in November 1980. By this time all existing facilities must have applied to the EPA for a permit and upgraded their facilities to meet the interim standards. As soon as a facility applies for a permit it obtains interim status, however, EPA recognizes that processing permits could take years for some facilities.

Theoretically, a facility could obtain a permit from a state solid waste management agency; however, it is not anticipated that any states will have approved hazardous waste management programs in the near future. The interim status standards are minimum requirements that the EPA feels are broadly applicable to large numbers of facilities and vast amounts of hazardous wastes. The standards address manifests, recordkeeping, reporting, waste

analysis, training, contingency plans, groundwater monitoring, and closure (see Table 2.11 for a complete listing). These standards have a significant degree of flexibility.⁴⁶

These interim status standards, however, are only the bare outline of what will occur in Phases II and III. EPA expects to publish the Phase II regulations in the fall of 1980. They will be a set of technical regulations based on the agency's best engineering judgement of technical requirements that a facility must meet. The regulations will allow permits to be processed in a manner that takes into account both site-specific factors and the nature of the waste being handled. The Phase III regulations will be more definitive counterparts of the Phase II regulations and are expected to make the permitting process even more straightforward. The Phase III standards may also include standards for specific industries and wastes that require special management standards. No date has been set for the issuance of these regulations.⁴⁷

The EPA used three major criteria to decide which standards should apply during the interim status. First, the standards had to be met in a straightforward manner without need for substantial interpretation by the EPA. The intent of the EPA was to minimize individual contact during the interim status period so it can concentrate on other aspects of this program. Second, it had to be possible for compliance to be achieved within the six-month period between the date the regulations were promulgated and the date they became effective. The EPA thought it unreasonable to require costly construction that might be disallowed or required to be modified during the final permitting process.⁴⁶ Although, the EPA used these criteria as guidelines to develop the interim regulations, they also included requirements that are exceptions to these guidelines when such requirements were judged to be of unusual importance. The two main exceptions to these criteria are the postclosure and groundwater regulations, which will be discussed in more detail below.

Hazardous Waste Disposal - Interim Status Standards

Table 2.11 provides a list of all items subject to regulation under the Interim Status Standards for Owners and Operators of Hazardous Waste Treatment Storage and Disposal Facilities. The closure and groundwater monitoring standards are considerably more specific and strict than the other interim standards. However, the EPA felt that the benefits obtained from early implementation substantially outweighed the disadvantages. The closure standard requires that facilities closed during interim status will be required to meet full closure and postclosure care requirements, including the requirement to have the plans for those activities approved by the EPA. Although facilities will have an additional 12 months to comply, all hazardous waste landfills, surface impoundments, and land treatment facilities must have groundwater monitoring systems unless a hydrogeological study demonstrates that such a system is unnecessary. The delayed schedule for compliance was allowed so that there would be sufficient time to install the systems.⁴⁸

Table 2.11 Interim Status Standards for Hazardous Waste Disposal

Subpart	Section
B - General Facility Standards	265.10 Applicability
	265.11 Identification number
	265.12 Required notices
	265.13 General waste analysis
	265.14 Security
	265.15 General inspection requirements
	265.16 Personnel training
	265.17 General requirements for ignitable, reactive, or incompatible wastes
C - Preparedness and Prevention	265.30 Applicability
	265.31 Maintenance and operation of facility
	265.32 Required equipment
	265.33 Testing and maintenance of equipment
	265.34 Access to communications or alarm system
	265.35 Required aisle space
	265.36 [Reserved]
D - Contingency Plan and Emergency Procedures	265.37 Arrangements with local authorities
	265.50 Applicability
	265.51 Purpose and implementation of contingency plan
	265.52 Content of contingency plan
	265.53 Copies of contingency plan
	265.54 Amendment of contingency plan
	265.55 Emergency coordinator
	265.56 Emergency procedures

Table 2.11 (Cont'd)

Subpart		Section
E - Manifest System, Recordkeeping, and Reporting	265.70	Applicability
	265.71	Use of manifest system
	265.72	Manifest discrepancies
	265.73	Operating record
	265.74	Availability, retention, and disposition of records
	265.75	Annual report
	265.76	Unmanifested waste report
	265.77	Additional reports
	265.78-265.89	[Reserved]
F - Groundwater Monitoring	265.90	Applicability
	265.91	Groundwater monitoring system
	265.92	Sampling and analysis
	265.93	Preparation, evaluation, and response
	265.94	Recordkeeping and reporting
	265.95-265.109	[Reserved]
G - Closure and Postclosure	265.110	Applicability
	265.111	Closure performance standard
	265.112	Closure plan; amendment of plan
	265.113	Time allowed for closure
	265.114	Disposal or decontamination of equipment
	265.115	Certification of closure
	265.116	[Reserved]
	265.117	Post-closure care and use of property; period of care
	265.118	Post-closure plan; amendment of plan
	265.119	Notice to local land authority
	265.120	Notice in deed to property
	265.121-265.139	[Reserved]

Table 2.11 (Cont'd)

Subpart	Section
H - Financial Requirements	265.140 Applicability
	265.141 [Reserved]
	265.142 Cost estimate for facility closure
	265.143 [Reserved]
	265.144 Cost estimate for post-closure monitoring and maintenance
	265.145-265.169 [Reserved]
I - Use and Management of Containers	265.170 Applicability
	265.171 Condition of containers
	265.172 Compatibility of waste with container
	265.173 Management of containers
	265.174 Inspections
	265.175 [Reserved]
	265.176 Special requirements for ignitable or reactive waste
	265.177 Special requirements for incompatible wastes
	265.178-265.189 [Reserved]
J - Tanks	265.190 Applicability
	265.191 [Reserved]
	265.192 General operating requirements
	265.193 Waste analysis and trial tests
	265.194 Inspections
	265.195-265.196 [Reserved]
	265.197 Closure
	265.198 Special requirements for ignitable or reactive waste
	265.199 Special requirements for incompatible wastes
	265.200-265.219 [Reserved]

Table 2.11 (Cont'd)

Subpart	Section
K - Surface Impoundments	265.220 Applicability
	265.221 [Reserved]
	265.222 General operating requirements
	265.223 Containment system
	265.224 [Reserved]
	265.225 Waste analysis and trial tests
	265.226 Inspections
	265.227 [Reserved]
	265.228 Closure and post-closure
	265.229 Special requirements for ignitable or reactive waste
	265.230 Special requirements for incompatible wastes
	265.231-265.249 [Reserved]
L - Waste Piles	265.250 Applicability
	265.251 Protection from wind
	265.252 Waste analysis
	265.253 Containment
	265.254-265.255 [Reserved]
	265.256 Special requirements for ignitable or reactive waste.
	265.257 Special requirements for incompatible wastes
	265.258-265.269 [Reserved]
M - Land Treatment	265.270 Applicability
	265.271 [Reserved]
	265.272 General operating requirements
	265.273 Waste analysis
	265.274-265.274 [Reserved]
	265.276 Food chain crops
	265.277 [Reserved]
	265.278 Unsaturated zone (zone of aeration) monitoring

Issues

Many of the same issues that are associated with solid waste disposal apply to hazardous waste disposal. The issue of public opposition to siting is even more intense for hazardous waste disposal facilities. The data from a recent study indicate that successful siting in most regions of the country is dubious at best, and grim at worst, using present siting approaches.⁴⁹ Both state and EPA preparedness is going to be a factor in both the development and implementation of hazardous waste regulations. It is clear that hazardous waste disposal practices are not going to change overnight. It will be several years before both the states and the EPA develop the technical expertise and effective management plans to deal with the disposal problem.

2.6.6 Future Options

Disposal requirements for both solid wastes and hazardous wastes will continually be refined as more information becomes available. As states begin to develop their own solid waste management programs, many of them will add more stringent standards than those required by the "open dump" inventory criteria. Hazardous waste regulations are truly in their infancy, and the EPA is already planning on issuing more detailed and technical standards.

The development of new approaches to hazardous waste siting will be critical to the success of the RCRA. It is estimated that between 1980 and 1985 about 100 new hazardous waste facilities will be needed,⁵⁰ and public opposition is considered to be the most critical problem in the siting of these facilities. National publicity concerning abandoned sites has made citizens increasingly aware of hazardous waste problems. Even if opposition is not successful, opponents may increasingly turn to the courts to delay siting.⁴⁹

Unless circumstances change, it will be up to the states, not the EPA, to play the lead role in siting. Thus, it will be up to the states to develop and implement innovative approaches to siting. However, the EPA plans to provide assistance and is considering grants for projects that develop different approaches to siting. The first such grant is for the New England Regional Commission, which will develop siting criteria for the New England states, explore compensation and incentive approaches, and develop a region-wide implementation strategy.⁵⁰

3 SOURCES AND NATURE OF ENERGY-RELATED SOLID WASTES

Solid wastes from energy-related activities can vary in form from liquids and wet sludges to dry particles, depending on the technology and process. This section presents characteristics of the wastes from conventional coal combustion, atmospheric fluidized bed combustion, coal gasification, coal liquefaction, oil shale mining and retorting, and other energy activities including geothermal, tar sands, nuclear, and gas and oil exploration.

This characterization of solid waste is of a general nature since there is a great deal of variation in the quantity and composition of wastes even within the same technology. For example, the character of the coal will determine both the quantities and composition of coal ash. The amount of ash produced will depend on the ash content of the coal which can vary from 5 to 25%. The quantities of trace elements in coals can also vary widely.

The quantity of waste produced is dependent in large part on air pollution regulations. The amount of spent solid from fluidized bed combustion (FBC) or sludge from flue gas desulfurization (FGD) will depend on both the sulfur content of the coal and the amount of SO_2 that needs to be removed to comply with regulations. The nature of the waste depends on the particular technology employed. Some gasifiers produce a dry ash whereas others produce a molten slag.

We compared the quantities of solid waste produced by the various technologies at a heat input of 10^{12} Btu. In order to take into consideration the different efficiencies of the processes, we also considered the waste produced from the production of 10^{12} Btu of energy. Both sets of values are listed in Table 3.1. However, care must be taken when comparing such technologies since the forms of energy produced are different, e.g., electricity from FBC and gas from coal gasification.

3.1 SOLID WASTES ASSOCIATED WITH COAL UTILIZATION

Utilization of coal as an energy source results in large amounts of solid waste in six major categories: (1) Chars and ashes from combustion and conversion (gasification and liquefaction), (2) inorganic solids and sludges from FBC, air and water pollution control, and acid gas removal, (3) tars and oil sludges, (4) biosludges, (5) spent catalysts, and (6) coal cleaning wastes. Some, if not all, of these wastes may pose environmental hazards if not managed carefully. This section reviews the sources and characteristics of these wastes. Their hazard potentials are discussed in Sec. 4.

The wastes listed above are produced regularly from energy generation activities. There are other wastes that are typically part of a processing step and not commonly handled. These process streams may be under high pressure or temperature and pose a serious danger to occupational safety. If wastes from these streams must be removed from the system because of process malfunction or mishap, e.g., valve, pump, or line failure, the handling and deposition of these wastes in an environmentally sound manner may become a significant problem. Characterization of transient material from process failure is outside the scope of the present study. It would require a more

Table 3.1 Quantities of Solid Waste Generated

Technology and Waste Stream	Solid Waste Generation	
	tons/10 ¹² Btu heat input (dry weight)	tons/10 ¹² Btu produced (dry weight)
Conventional Coal Boiler		
Ash	5,000	16,000
Limestone/limestone scrubber sludge	5,200	16,000
AFBC		
Ash	5,000	13,000
Spent bed material	12,500	33,800
Coal Gasification		
Coal cleaning	1,330	2,300
Gasifier ash	13,000	22,480
Boiler ash	1,160	2,000
Boiler FGD sludge	280	480
Spent catalysts	NA ^a	NA
Acid gas cleanup sludge	17	30
Tar and oil sludges	NA	NA
Biosludges	500	850
Coal Liquefaction		
Coal cleaning	17,055	27,070
Liquefaction waste (chars, ash, filter cake)	7,000	11,100
Boiler ash	225	360
Spent catalysts	NA	NA
Acid gas cleanup sludge	NA	NA
Boiler FGD sludge	260	420
Tar and oil sludges	NA	NA
Biosludges	730	1,160
Oil Shale		
Raw shale dust	--	4,600
Spent shale	--	180,000
Spent shale dust	--	360
Arsenic waste	--	0.5
Spend catalysts	--	2.0
Nuclear Energy		
High-level waste (ft ³)	5	16
Low-level waste (ft ³)	165,000	500,000

^aNA = not available.

exhaustive literature search, a more detailed analysis of the available data, and direct sampling and testing of process streams. It should be noted that the issues relating to the hazard potential of these wastes are significant and should be addressed when data are available.

3.1.1 Coal Ash and Char

Ashes and chars are the primary solid residue produced in coal utilization processes. The characteristics of solid residues produced from combustion and conversion (gasification and liquefaction) could be somewhat different and are discussed separately below.

3.1.1.1 Ash From Coal Combustion

Coal combustion produces several types of ash ranging in diameter from $< 1\mu$ to 4 cm and consisting of the inorganic mineral constituents present in coal, as well as the incompletely burned organic matter.

Fly ash is that fraction of noncombustible coal residue that is too small to settle out in the combustion chamber and becomes suspended in the high velocity flue gas. The fly ash fraction generally consists of fine spherical particles ranging in diameter from 0.5 to 100 μ . As much as 5% by weight or 20% by volume of fly ash consists of cenospheres, which are silicate glass spheres filled with nitrogen and carbon dioxide. These very lightweight particles tend to float on ash pond surfaces.

The bottom ash fraction of the coal combustion residue is composed primarily of coarser, heavier particles with porous surfaces. If the bottom ash melts to slag at burner operating temperatures, the residue resolidifies as angular, black particles with a glassy appearance.

The type of particulate collector employed determines the particle size distribution and total surface area of the collected fly ash. An electrostatic precipitator collects a much higher percentage of the very small particles (smaller than 1.5 μ) than does a mechanical collector. The collected fly ash, however, is much less sensitive to changes in efficiency of collection than is the fly ash released to the atmosphere. The difference is most dramatic in the total mass. A change from 98% removal of total mass to 99% removal results in slightly more than a 1% increase in the mass of fly ash collected but a 50% decrease in the mass emitted to the atmosphere.

Mather⁵¹ analyzed size-differentiated fractions of fly ash and concluded that lithophile materials (aluminosilicates) and alkalis (Na and K) were generally more concentrated in the finer fractions and thus in ash collected by an electrostatic precipitator. Magnetite-hematite materials (iron-bearing) were more concentrated in the coarser fractions of ash collected from the mechanical collector than they were in ash collected from the electrostatic precipitator. Carbon particles also increased in abundance as the particle size increased. Natusch⁵² demonstrated that the toxic trace elements arsenic, antimony, cadmium, lead, selenium and thallium were most concentrated in the smallest respirable particles emitted from coal burning plants. These elements are probably volatilized during combustion and

preferentially adsorb or condense on small particles with the greatest surface area. As collection efficiency is increased, larger fractions of these particles with high concentrations of toxic elements will be collected as solid waste. Since the total additional mass is small, however, this will not lead to great changes in the overall concentration of these toxic elements in the solid waste.

The major constituents of coal ash, including silicon, aluminum, iron, and calcium, make up 95-99% of the total composition. Minor constituents, such as magnesium, titanium, sodium, potassium, sulfur, and phosphorus, generally make up 0.5-3.5%. Coal ash can also contain trace concentrations of from 20 to 50 elements, including antimony, arsenic, barium, beryllium, boron, copper, fluorine, lead, manganese, mercury, molybdenum, nickel, selenium, tellurium, thallium, tin, uranium, vanadium, and zinc. A partial identification of trace elements in coal ash is given in Table 3.2.⁵³

Trace Elements - Coal ash is composed almost entirely of oxides. The composition varies over a wide range and there is no typical ash analysis. Table 3.3 gives the range of variation of the principal constituents of coal ash.⁵⁴

Available data indicate that partitioning and concentration of trace metals occur during combustion and that certain elements can concentrate in selected size ranges of particulates.^{55,56} Enrichment and volatilization behavior of trace elements in coal combustion is determined by the geochemical properties of the elements, the nature of the combustion process, and the reactions occurring in the emission control devices. Geochemically, the trace elements in coal are separated into four general classes: (I) lithophile; (II) chalcophile; (III) volatile elements; and (IV) unclassified elements.⁵⁷ Trace elements in each class are listed in Table 3.4.

Trace elements in Class I are lithophiles and are associated with aluminosilicate minerals in coal. As such they are high boiling compounds and do not decompose on combustion. Elements in this class are not enriched during combustion.

Class II elements are generally present in coal as sulfides. These sulfides may be fairly volatile or, upon combustion may decompose, leaving the trace elements in the vapor phase. The volatile sulfides or elements can then condense on the extensive surface area presented by particulates, thus leading to a surface enrichment. This enrichment is usually most prevalent in the fine particle fraction.

Class III elements boil below the furnace and flue gas temperatures and can exit from the stack as vapors.

The elements in Class IV are judged to exhibit behavior intermediate between the first two groups. Chromium and nickel tend to show chalcophile (or volatile) characteristics.

Many recent studies have attempted to quantify the chemical constituents of coal ash. Table 3.5 is a composite of these studies, showing the maximum and minimum value found for 64 elements present in bottom ash and

Table 3.2 A Partial Identification of Trace Elements in Coal Ash

Aluminum (Al)	Gallium (Ga)	Samarium (Sm)
Antimony (Sb)	Germanium (Ge)	Scandium (Sc)
Arsenic (As)	Hafnium (Hf)	Selenium (Se)
Barium (Ba)	Holmium (Ho)	Silicon (Si)
Beryllium (Be)	Indium (In)	Silver (Ag)
Bismuth (Bi)	Iodine (I)	Sodium (Na)
Boron (B)	Iron (Fe)	Strontium (Sr)
Bromine (Br)	Lanthanum (La)	Tantalum (Ta)
Cadmium (Cd)	Lead (Pb)	Tellurium (Te)
Calcium (Ca)	Lithium (Li)	Terbium (Tb)
Cerium (Ce)	Lutetium (Lu)	Thallium (Tl)
Cesium (Cs)	Magnesium (Mg)	Thorium (Th)
Chlorine (Cl)	Manganese (Mn)	Tin (Sn)
Chromium (Cr)	Mercury (Hg)	Titanium (Ti)
Cobalt (Co)	Molybdenum (Mo)	Tungsten (W)
Copper (Cu)	Neodymium (Nd)	Uranium (U)
Dysprosium (Dy)	Nickel (Ni)	Vanadium (V)
Erbium (Er)	Niobium (Nb)	Ytterbium (Yb)
Europium (Eu)	Potassium (K)	Yttrium (Y)
Fluorine (F)	Praseodymium (Pr)	Zinc (Zn)
Gadolinium (Gd)	Rubidium (Rb)	Zirconium (Zr)

Source: Ref. 53.

flyash. The studies were made on different sizes and types of systems with respect to megawatt output, furnace type, collector configuration, and, of course, type of coal burned.⁵⁴ The data illustrate a tremendous variability in the concentrations of many elements present in coal ashes.

Trace Organics - Researchers at Oak Ridge National Laboratory have reported trace quantities of hydrocarbon compounds in coal ash.⁵⁹ Individual hydrocarbon compounds exhibited concentration ranges from 66-816 ppb, with a total detected concentration of about 9 ppm. The C28-C30 hydrocarbons were in greatest concentration, with C29 the highest. Table 3.6 summarizes the estimated hydrocarbon concentration in the ash sampled. The same ash was analyzed by ORNL for the presence of polycyclic aromatic hydrocarbons (PAH). Concentrations were low, ranging generally from about 10 to 20 ppb for

Table 3.3 Major Chemical Constituents
of Coal Ash

Constituents	Range (%)
Silica (SiO_2)	6.0 - 68
Alumina (Al_2O_3)	4.0 - 44
Ferric Oxide (Fe_2O_3)	1.0 - 44
Calcium Oxide (CaO)	0.2 - 52
Magnesium Oxide (MgO)	0.1 - 14
Titanium Dioxide (TiO_2)	0.4 - 4.17
Potassium Oxide (K_2O)	0.1 - 4.0
Sodium Oxide (Na_2O)	0.09 - 28
Sulfur Trioxide (SO_3)	0.1 - 32
Carbon (C) and Volatiles	0.1 - 20

Source: Ref. 54.

Table 3.4. The Separation of Elements in the
Geochemical Classification Scheme

Class I	Class II	Class III	Class IV
Al Mn	As	Hg	Cr
Ba Rb	Cd	Cl	Cs
Ce Sc	Cu	Br	Na
Co Si	Ga	F	Ni
Eu Sm	Pb		U
Fe Sr	Sb		V
Hf Ta			
K Th			
La Ti			
Mg			

Source: Ref. 58

Table 3.5 Chemical Constituents of Bottom Ash and Flyash

Element	Flyash (ppm)		Bottom Ash/Slag (ppm)	
	Minimum	Maximum	Minimum	Maximum
Aluminum (Al)	11,500.0	144,000.0	88,000.00	135,000.0
Antimony (Sb) ^a	0.8	1,000.0	0.14	12.0
Arsenic (As) ^a	2.3	1,700.0	0.98	40.0
Barium (Ba)	96.0	13,900.0	500.00	4,000.0
Beryllium (Be) ^a	1.0	1,000.0	3.00	10.6
Bismuth	<10.0	30.0	--	--
Boron (B)	10.0	3,000.0	70.00	300.0
Bromine (Br)	0.3	670.0	2.00	11.0
Cadmium (Cd) ^a	0.1	250.0	<0.50	<250.0
Calcium (Ca)	5,400.0	177,100.0	8,400.00	50,600.0
Cerium (Ce)	28.0	320.0	84.00	310.0
Cesium (Cs)	1.4	17.0	7.70	--
Chlorine (Cl)	13.0	25,000.0	<1,100.00	1,800.0
Chromium (Cr) ^a	11.0	7,400.0	15.00	270.0
Cobalt (Co)	6.0	1,500.0	3.60	380.0
Copper (Cu) ^a	30.0	3,020.0	2.80	720.0
Dysprosium (Dy)	4.2	31.0	37.00	--
Europium (Eu)	1.0	16.7	1.11	15.0
Fluorine (F)	0.4	624.0	10.60	100.0
Gallium (Ga)	10.0	10,000.0	5.00	64.0
Germanium (Ge)	<10.0	11,000.0	--	--
Gold (Au)	0.004	0.5	0.10	--
Hafnium (Hf)	1.4	11.0	4.60	8.5
Indium (In)	0.1	2.4	1.00	--
Iodine (I)	0.1	200.0	9.50	--
Iron (Fe)	7,800.0	289,000.0	27,000.00	203,000.0
Lanthanum (La)	17.0	270.0	155.00	75.0
Lead (Pb) ^a	3.1	1,600.0	<5.00	35.0
Lithium (Li)	77.0	120.0	60.00	78.0
Lutetium (Lu)	0.41	4.3	2.50	--
Magnesium (Mg)	4,900.0	60,800.0	4,500.00	32,500.0
Manganese (Mn)	31.0	4,400.0	100.00	720.0
Mercury (Hg) ^a	0.01	22.0	0.01	<4.0

Table 3.5 (Cont'd)

Element	Flyash (ppm)		Bottom Ash/Slag (ppm)	
	Minimum	Maximum	Minimum	Maximum
Molybdenum (Mo)	6.5	500.0	3.00	45.0
Nickel (Ni) ^a	1.8	8,000.0	10.00	700.0
Niobium (Nb)	16.0	<20.0	12.00	<20.0
Palladium (Pd)	0.2	—	—	—
Phosphorus (P)	600.0	2,500.0	300.00	1,600.0
Platinum (Pt)	0.7	—	—	—
Potassium (K)	1,534.0	34,700.0	7,300.00	15,800.0
Rhodium (Rh)	0.02	—	—	—
Rubidium (Rb)	25.0	300.0	48.00	300.0
Samarium (Sm)	3.7	43.0	8.20	46.0
Scandium (Sc)	2.0	400.0	10.00	85.0
Selenium (Se) ^a	1.2	<500.0	0.08	7.7
Silicon (Si)	196,000.0	271,000.0	180,000.00	273,000.0
Silver (Ag) ^a	1.0	50.0	25.00	—
Sodium (Na)	1,180.0	20,300.0	1,800.00	13,100.0
Sulfur (S)	0.11	0.25	0.06	0.09
Strontium (Sr)	40.0	9,600.0	170.00	1,800.0
Tantalum (Ta)	0.5	2.6	0.95	1.03
Tellurium (Te)	0.11	10.0	<0.02	—
Thallium (Tl)	1.1	100.0	0.25	0.30
Thorium (Th)	1.8	68.0	12.00	15.0
Tin (Sn)	<3.0	4,250.0	—	—
Titanium (Ti)	400.0	15,900.0	3,300.00	7,210.0
Tungsten (W)	2.9	42.0	38.00	—
Uranium (U)	0.8	30.1	6.78	14.9
Vanadium (V)	20.0	1,180.0	44.00	670.0
Ytterbium (Yb)	1.7	23.0	18.00	0.0
Yttrium (Y)	21.0	800.0	30.00	44.0
Zinc (Zn) ^a	14.0	13,000.0	24.00	950.0
Zirconium (Zr)	100.0	5,000.0	220.00	—

^aOn the EPA list of 65 priority pollutants.

Source: Ref. 54.

Table 3.6 Estimated Saturated n-Hydrocarbon Concentrations in Coal Ash

Component	Concentration, ppb
C ₁₅	T ^a
C ₁₆	192
C ₁₇	608
C ₁₈	740
C ₁₉	383
C ₂₀	308
C ₂₁	528
C ₂₂	548
C ₂₃	480
C ₂₄	308
C ₂₅	319
C ₂₆	366
C ₂₇	516
C ₂₈	664
C ₂₉	816
C ₃₀	660
C ₃₁	596
C ₃₂	344
C ₃₃	199
C ₃₄	66
Total	8.6 ppm

^aT = Trace.

Source: Ref. 59.

individual species. The total PAH concentration was estimated to be at maximum about 0.2 ppm. Table 3.7 gives the PAH concentrations found in the ash sampled.

Concentrations of monomethyl and dimethyl sulfate in fly ash collected in the flue-line of a power plant burning low-sulfur coal were found to be as high as 830 ppm. Dimethyl sulfate has been shown to have mutagenic and carcinogenic properties.*

*Lee, M.L., et al., *Dimethyl and Monomethyl Sulfate: Presence in Coal Fly Ash and Airborne Particulate Matter*, Science, 207:186-188 (1980).

Table 3.7 Estimated Polycyclic Aromatic Hydrocarbon (PAH) Concentration in Coal Ash

PAH	Concentration ppb
Naphthalene	8.3
2-Methylnaphthalene	5.0
1-Methylnaphthal	5.2
Biphenyl	10.3
1,6- and/or 1,3-Dimethylnaphthalene	T ^a
2,6-Dimethylnaphthalene	T ^a
1,5- and/or 2,3-Dimethylnaphthalene	T ^a
9,10-Dihydroanthracene	12.6
Phenanthrene	17.6
2-Methylanthracene	9.1
1-Methylphenanthrene	<24.8 ^b
Fluoranthene	<13.4 ^b
Pyrene	<19.0 ^b
1,2-Benzofluorene	36.8
2,3-Benzofluorene	11.8
1-Methylpyrene	T
Picene	T
Total	<0.2 ppm ^b

^aT = Trace

^b< = Interference allows estimate only of maximum possible concentration.

Source: Ref. 59.

Polycyclic aromatic hydrocarbons are among the most common chemical carcinogens. Considering coal's polycyclic aromatic nature, it is not surprising that many coal products are potentially carcinogenic. Even in the late 1700s it was recognized that some coal products were carcinogenic, as evidenced by the high incidence of scrotal cancer in chimney sweeps working in areas where bituminous coal was used as fuel.

Radionuclides - The presence of radionuclides in coal ash was studied by Coles, et al.⁵⁷ Natural radionuclides identified in coal bottom ash and fly ash are listed in Table 3.8. The results of their analysis of specific concentrations of the various radionuclides in ash are given in Table 3.9. All of the radionuclides studied do become enriched in ash relative to the

Table 3.8 Natural Radionuclides Observed in Coal, Bottom Ash, and Flyash

Natural Decay Chain Origin	Source After Fractionation	Gamma-Producing Nuclide	Gamma Energy (keV)
^{232}Th	^{228}Ra	^{228}Ac	338
^{232}Th	^{228}Ra	^{228}Ac	911
^{232}Th	^{228}Th	^{212}Pb	238
^{232}Th	^{228}Th	^{208}Tl	583
^{238}U	^{234}Th	^{234}Th	63
^{238}U	^{226}Ra	^{226}Ra	185
^{238}U	^{226}Ra	^{214}Pb	295
^{238}U	^{226}Ra	^{214}Pb	352
^{238}U	^{214}Bi	^{214}Bi	609
^{238}U	^{214}Bi	^{214}Bi	1120
^{238}U	^{214}Bi	^{214}Bi	1764
^{238}U	^{210}Pb	^{210}Pb	46
^{235}U	^{235}U	^{235}U	185

Source: Ref. 57.

input coal and in general tend to concentrate on the finer particles. The control of radionuclide emissions to the atmosphere may become a major EPA initiative under NESHAPS requirements.

3.1.1.2 Ash and Char From Coal Conversion

Three types of coal ash can be produced in gasification and liquefaction operations: (1) dry (including fly ash); (2) melted (slag); or (3) softened (self-agglomerating). Some conversion processes, such as Synthane gasification, and H-Coal liquefaction, also produce char.

Nearly all of the inorganic constituents present in the feed coal are contained in the ashes and chars. Reported values for the residual carbon in ash and char range from a few percent to over 50%. The carbonaceous material in chars and ashes is primarily elemental carbon with small amounts of highly polymeric aromatic and heterocyclic organics.

Char Characteristics^{60,61}

If carbon removal during the conversion process is incomplete, char will be produced. Char is the solid residue after removal of moisture and volatile matter from coal. Depending on the nature of the process, coal

Table 3.9 Contents of the Various Radionuclides in Coal, Bottom Ash, and Fly Ash^a

	ppm			pCi/g ^b						
	U	Th	K	40K	228Th	228Ra	210Pb	226Ra	238U	235U
Plant A ^c										
Coal	0.71	1.6	860	0.73	0.17	0.17	0.26	0.21	0.24	0.012
ESP fly ash	5.6	15	9400	8.1	1.7	1.7	1.4	2.3	1.9	0.093
Bottom ash	4.6	14	7900	6.8	1.5	1.5	0.58	1.9	1.5	0.072
Plant B ^d										
Coal	2.6	5.0	1660	1.4	0.56	0.55	0.68	0.64	0.85	0.037
ESP fly ash	11	22	7400	6.3	2.4	2.4	2.2	2.9	3.5	0.14
Bottom ash	8.4	19	7200	6.2	2.2	2.1	0.84	2.5	2.8	0.11
Scrubber ash	11	22	7200	6.2	2.5	2.5	2.8	3.0	3.6	0.14
Plant B ^d Post-ESP (stack)										
Fly ash (mmd) ^e										
17 μ m	16	25	8200	7.0	2.8	2.7	4.3	3.3	5.4	0.17
6 μ m	20	31	8600	7.3	3.3	3.5	10	4.6	6.8	0.28
3.8 μ m	30	36	8600	7.4	3.3	4.0	14	5.3	10	0.39
2.5 μ m	36	38	8100	7.0	3.3	4.2	17	5.9	12	0.50

^a10-20% propagated 1 error from the mean.

^bPicocuries per gram.

^cSamples from Plant A; input coal contains 11.3% H₂O, 9.2% ash, and 0.52% sulfur.

^dSamples from Plant B; input coal contains 6.8% H₂O, 23.2% ash, and 0.46% sulfur.

^emmd = mass median diameter determined by centrifugal sedimentation.

Source: Ref. 57.

conversion can produce net char amounts ranging between 10 and 55% of coal feed weight.⁵³ A single gasification plant can produce as much as four to five million tons of char per year. In general, there is a considerable reduction in total sulfur, volatile matter, hydrogen, and oxygen in char, compared to the original coal. Table 3.10 shows the analyses of the coal feeds and resulting chars for the synthane gasification process.⁵³ Table 3.11 shows the analysis of the inorganic content of the char from the H-Coal liquefaction process using Illinois #6 coal.⁶²

After extraction, char can be used in a variety of ways. Provided that there is sufficiently high carbon content, char can be used for conversion chamber feedstock, utility combustion fuel as a hydrocarbon source, or as an absorbent in pollution control devices. Ash produced from utilization of char may have characteristics similar to that from combustion or conversion of coal.

Ash Characteristics^{60,61}

The composition of ash from conversion processes is a function of the coal characteristics, severity of treatment, and location within a reactor

Table 3.10 Representative Analyses of Coals and Chars (Wt. %)

Component	Illinois Number 6	Western Kentucky	Wyoming Subbituminous	North Dakota Lignite	Pittsburgh Steam
Coals					
Moisture	8.3	4.3	18.1	20.6	2.5
Volatile matter	37.5	34.6	31.9	32.9	30.9
Fixed carbon	43.0	44.5	32.0	38.2	51.5
Ash	11.2	16.6	18.0	8.3	15.1
Hydrogen	5.3	4.7	5.4	5.7	4.7
Oxide	15.9	10.9	30.3	32.6	9.3
Carbon	63.0	62.7	45.2	51.5	68.4
Nitrogen	1.1	1.2	0.6	0.7	1.2
Sulfur	3.5	3.9	0.5	1.2	1.3
Chars					
Moisture	0.8	1.2	0.5	1.2	1.4
Volatile matter	4.0	4.8	5.1	10.0	1.6
Fixed carbon	69.9	63.3	38.1	50.2	69.3
Ash	25.3	30.7	56.3	38.6	27.7
Hydrogen	1.0	1.0	1.0	0.9	1.0
Oxygen	1.3	1.1	1.2	0.0	1.7
Carbon	70.4	64.5	40.6	58.9	68.9
Nitrogen	0.6	0.7	0.4	0.2	0.5
Sulfur	1.4	2.0	0.5	2.0	0.2

Source: Ref. 53.

Table 3.11 Inorganic Elements in the
Mineral Residue from the
H-Coal Process Utilizing
Illinois Number 6 Coal

Element	Concentration in Coal Residue (ppm)
Aluminum (Al)	17,253
Antimony (Sb)	1.2
Arsenic (As)	1.5
Barium (Ba)	40
Beryllium (Be)	1.8
Boron (B)	300
Bromine (Br)	6.7
Cadmium (Cd)	0.4
Calcium (Ca)	7,862
Cerium (Ce)	16
Cesium (Cs)	1.7
Chlorine (Cl)	1,000
Chromium (Cr)	27.5
Cobalt (Co)	4.45
Copper (Cu)	14
Europium (Eu)	0.69
Fluorine (F)	100
Gallium (Ga)	4.6
Germanium (Ge)	4.9
Gold (Au)	-
Hafnium (Hf)	0.86
Iron (Fe)	23,662
Lanthanum (La)	9.8
Lead (Pb)	32
Lithium (Li)	-
Lutecium (Lu)	0.024
Magnesium (Mg)	884
Manganese (Mn)	77
Mercury (Hg)	-
Molybdenum (Mo)	6.4
Nickel (Ni)	21
Phosphorus (P)	44
Potassium (K)	2,490
Rubidium (Rb)	16
Samarium (Sm)	2.3
Scandium (Sc)	4.1
Selenium (Se)	-
Silicon (Si)	39,641
Silver (Ag)	0.16

Table 3.11 (Cont'd)

Element	Concentration in Coal Residue (ppm)
Sodium (Na)	619
Strontium (Sr)	30
Sulfur (S)	18,000
Tantalum (Ta)	0.17
Tellurium (Te)	0.1
Thallium (Tl)	1.7
Thorium (Th)	3.5
Tin (Sn)	0.6
Titanium (Ti)	1,019
Tungsten (W)	4.4
Uranium (U)	5.7
Vandium (V)	33
Ytterbium (Yb)	1.0
Yttrium (Y)	-
Zinc (Zn)	71
Zirconium (Zr)	41

Source: Ref. 62.

bed. Similar to coal combustion ash, major components of conversion ash include such substances as SiO_2 , Fe_2O_3 , and Al_2O_3 ; lesser components will include CaO , MgO , and SO_3 . In addition, many trace elements will be included and enriched in comparison to their abundance in coal. However, it is possible that the composition of conversion ash may vary substantially from that of ash generated in conventional power plants because portions of the ash may be produced by different pathways (e.g., at lower temperature in some conversion processes).

A few studies have generated the data on the composition of coal and the ash from coal conversion. Trace element concentrations of coal and the ash generated by various conversion processes are given in Tables 3.12 and 3.13.^{53,63}

3.1.2 Inorganic Solids and Sludges

The major sources of inorganic solids and sludges from coal utilization facilities include: (1) sludges and solids from SO_2 emission control processes; (2) spent residues from FBC boilers; (3) bottom sludges from acid gas treatment processes; and (4) sludges from chemical treatment of wastewater and water supplies. Sources and characterization of these wastes are presented below.

Table 3.12 Trace Element Concentrations (ppm) in Illinois Coal and in the Unquenched Gasifier Ash Obtained from Lurgi Gasification

Element	Illinois Number 5 Coal				Ash			
	Peabody ^a	Argonne ^b			Peabody ^a	Argonne ^b		
Ag	0.3				3.0			
As	1.6	1.9	+	1.003 (B)	0.3			
B	307				673			
Ba						490	+	250 (B)
Be	2.2	2.0	+	0.1	22	19.8	+	1.0
Br		6.6	+	1.0 (A)				
Cd	<0.3				<0.3			
Ce						41	+	4 (AA)
Co	3.7	3.8	+	0.6 (A)		38	+	4 (AA)
Cr	15	15	+	2 (A)	551	592	+	59 (AA)
Cs						11	+	2 (A)
Cu	10				273			
Dy								
Eu								
F	59	55	+	11		4.6	+	0.9
Fe (x10 ⁴)		1.3	+	0.1 (AA)		15	+	2 (AA)
Hg	0.20	0.17	+	0.02	0.01	0.016	+	0.002
K (x10 ³)		1.3	+	0.1 (AA)		14	+	1 (AA)
La		3.6	+	0.5 (A)		42	+	4 (AA)
Li	5.5				54			
Mn	21	23	+	2 (AA)	338	305	+	30 (AA)
Mo	7				8			
Na (x10 ²)		2.8	+	0.3 (AA)		29	+	3 (AA)
Ni	32				462			
Pb	30	28.1	+	2.8	219	200	+	10
Sb	0.3	0.1	+	0.02 (A)	0.3	19	+	2 (AA)
Sc		1.6	+	0.2 (AA)				
Se		9	+	5 (B)				
Sm								
Ta						1.3	+	0.7 (B)
Tb					181			(C)
V	21				181			
Yb						11	+	2 (B)
Zn (x10 ²)	1.82	2.4	+	1.2 (B)	15.8	16	+	2 (A)

Table 3.12 (Cont'd)

Element	Illinois Number 6 Coal					Ash				
	Peabody ^a	Argonne ^b				Peabody ^a	Argonne ^b			
Ag	0.3					3.8				
As	1.0	2.1	+	1.0	(B)	0.1				
B	132					622				
Ba										
Be	1.8	1.55	+	0.08		14	13.4	+	0.7	
Br		4.1	+	0.7	(A)					
Cd	<0.3					<0.3				
Ce							38	+	4	(AA)
Co	4.3	3.2	+	0.5	(A)	40	34	+	3	(AA)
Cr	22	18.3	+	2.7	(A)	705	806	+	81	(AA)
Cs										
Cu	12					239				
Dy							8.5	+	1.3	(A)
Eu		0.2	+	0.1	(B)					
F	79	79	+	16			5.2	+	1.0	
Fe (x10 ⁴)		1.2	+	0.1	(AA)		13	+	1	(AA)
Hg	1.00 ^c	1.18	+	0.12		0.04	0.007	+	0.001	
K (x10 ³)		1.5	+	0.1	(AA)		16	+	2	(AA)
La		3.9	+	0.4	(AA)		40	+	20	(B)
Li	9.2					74				
Mn	20	18.6	+	1.9	(AA)	243	156	+	16	(AA)
Mo	7					6				
Na (x10 ²)		3.0	+	0.3	(AA)		27	+	3	(AA)
Ni	14					456				
Pb	12	8.0	+	0.8		96	46.0	+	2.3	
Sb	0.1				(C)	0.2				
Sc		2.1	+	0.2	(AA)		24	+	2	(AA)
Se					(C)					
Sm		0.005	+	0.003	(B)					
Ta										
Tb							3.1	+	1.6	(B)
V	29					301				
Yb		1.4	+	0.7	(B)		11	+	2	(A)
Zn (x10 ²)	0.43				(C)	4.69				(C)

^aThe precision of the Peabody results is estimated to be +10% in all cases.

^bThe accuracy of the Argonne results for mercury is estimated to be 10%; the precision of the Argonne results for beryllium is +5%; for lead +5 to 10%; for fluorine +20%. The confidence ratings shown for the Argonne results obtained by neutron activation analysis correspond to the following accuracy levels: AA--10%; A--+15%; B--+50%; and C--identification only.

^cNot representative of seam; contamination suspected.

Source: Ref. 53.

Table 3.13 Chemical Composition of Coal Ashes From Gasification/Liquefaction Plants

Element	Waste 1	Waste 2	Waste 3	Waste 4
wt. %				
Al	8.8	10.1	8.8	6.7
Ca	18.5	2.9	2.2	2.4
Fe	3.8	13.4	17.2	13.3
K	0.6	1.5	1.4	1.4
Mg	4.9	0.8	0.5	0.5
Na	0.3	1.8	0.2	0.3
Ti	0.5	0.6	0.6	0.4
Si	17.9	22.5	20.1	16.4
S	0.4	0.3	3.8	4.0
C	1.0	1.8	1.7	20.2
µg/g				
Ag	1.0	0.3	0.3	0.5
B	287.3	1302.2	590.7	386.4
Ba	654.5	454.0	531.0	1013.0
Be	10.3	18.1	12.6	6.3
Cd	1.0	0.8	1.6	5.0
Ce	146.5	85.2	25.9	49.6
Co	7.2	137.3	33.7	16.3
Cr	78.1	386.1	642.0	145.4
Cu	29.8	61.9	93.5	58.7
Ga	65.9	103.6	106.0	98.6
La	152.1	92.5	89.2	61.4
Li	86.3	80.7	63.7	41.4
Mn	3987.2	425.4	293.2	249.4
Mo	4.0	18.8	72.6	43.5
Nb	17.2	11.9	1.7	1.3
Ni	73.0	254.0	150.0	148.0
P	466.7	275.5	436.3	544.8
Sc	30.2	24.4	19.3	12.4
Sr	519.8	503.3	182.1	139.1
Th	28.8	16.2	15.8	12.2
V	154.3	237.2	449.5	416.8
Y	54.8	53.6	41.1	23.8
Zn	8.3	65.7	96.1	413.2
Zr	191.7	196.6	170.2	97.4

Source: Ref. 63.

3.1.2.1 SO₂ Emission Control Wastes

Most of the sulfur in coal is converted to sulfur dioxide in combustion and to hydrogen sulfide in conversion. In combustion processes, removal of SO₂ from flue gas is necessary to meet the Clean Air Act requirements. Removal of sulfur compounds from raw coal-conversion gas prior to gas processing is necessary to prevent fouling of catalysts.

In coal conversion processes, sulfur recovery units are used to convert stripped sulfur compounds to either dilute sulfuric acid or elemental sulfur. The vast majority of sulfur recovery units are designed to utilize Claus technology and to recover sulfur in its elemental form. Tail gas treatment units are usually included as part of the Claus technology units to reduce sulfur emissions. Unrecovered sulfur in Claus plant tail gas includes mainly hydrogen sulfide, elemental sulfur, sulfur dioxide, and lesser amounts of other sulfur compounds. Sulfur dioxide removal technologies developed for industries such as power plants and sulfuric acid plants may be directly applicable to Claus emissions from coal facilities.

The removal of sulfur dioxide by means of scrubbers is accomplished by two general processes -- throwaway and regnerable. The first scrubber type refers to those flue gas desulfurization scrubbers that produce a solid waste stream that is not at present marketable and requires disposal. Regenerable scrubber systems are those which, because of their specific chemical reactions, produce a marketable product of sulfur and, in some cases, regenerate the solvent for reuse. Some common examples of regenerable processes are the Wellman-Lord Sulfite, Westvaco Activated Carbons, AI Aqueous Carbonate, and IFP Catalytic, all of which produce a usable sulfur by-product, such as elemental sulfur, sulfuric acid, or gypsum.

Some sulfur by-products, such as elemental sulfur and gypsum, are likely to contain impurities originating from coal. The nature and extent of contamination are, however, largely unknown, and tests to determine the quality of sulfur by-products from the standpoint of their environmental effects are required.

The wet throwaway processes are at present the major systems used by the utilities for several reasons including lower capital costs in comparison to regenerable processes, availability and ease of use of sorbent, and relative simplicity. They have the major disadvantage of producing large amounts of waste. No dry systems are at present operating commercially. However, four companies have developed spray dryer-based systems, and these are expected to be operating by 1980 and 1981.⁶⁴ The dry systems do not at present achieve as high a degree of SO₂ removal as do the wet systems. However, the NSPS for utility boilers will require some degree of scrubbing, and dry systems could be used in conjunction with low sulfur coal. They may also be used by industry if SO₂ scrubbing is required under the NSPS being developed by the EPA.

The major wet scrubbing systems employ a slurry of either lime or limestone to remove the SO₂ and produce a waste consisting of calcium sulfate, calcium sulfite and unreacted limestone. Factors influencing the composition of sludge from a specific application include composition of the coal, the alkali added, the scrubber process operation, oxidation, and alkali utilization efficiency. Chemical analyses of lime process sludges from various power plant sources are shown in Tables 3.14 and 3.15. They reveal that a great many elements can be included in FGD sludge and that the sludge component concentrations can be highly variable.⁵³ Concentrations of trace elements in leachate from ponded scrubber sludges are the focus of the greatest concern about impacts from flue gas desulfurization processes. As can be seen in Table 3.16, which contains results of leachate monitoring, the

Table 3.14 Chemical Analysis of Lime Process Sludges on a Dry Solid Basis (%)

Component	Sample ^a					
	A	B	C	D	E	F
CaO	18.1	43.2	40.7	43.4	25.6	43.8
MgO	2.4	0.2	b	0.0001	1.2	b
Total sulfur	7.2	18.9	18.1	20.0	10.9	22.9
SO ₂	12.1	33.0	32.9	29.2	10.8	45.8
SO ₃	2.9	5.9	4.8	13.6	13.6	c
CO ₂	3.2	6.7	2.3	7.1	2.2	1.0
Free carbon	b	b	b	2.8	0.14	c
SiO ₂	31.6	4.9	3.76	0.58	21.3	0.18
Al ₂ O ₃	18.3	3.4	1.71	12.1	11.3	0.39
Fe ₂ O ₃	4.3	0.6	0.86	0.39	5.6	0.29
Na ₂ O	b	b	b	0.35	0.76	0.09
K ₂ O	b	b	b	0.03	0.98	0.01
Free base as CaO	0.3	1.3	7.9	0.06	0.06	c

^aA-power station prior to fly ash collections; B-power station after ash collection; C-Chemico using carbide lime; D-power plant using proprietary scrubbing; E-wet limestone pilot plant scrubber; F-molybdenum sulfide pilot plant scrubbing effluent.

^bNot determined.

^cNot detected.

Source: Ref. 53.

concentration of arsenic, barium, boron, cadmium, chromium, lead, mercury, and selenium in leachate equals or exceeds public water supply standards.

In addition to trace elements, the chemical oxygen demand (COD), total dissolved solids (TDS), and the higher levels of sulfate, chloride, calcium, and magnesium are additional sources of potential pollution.

The quality of wet scrubber wastes can be improved by oxidation to gypsum or by chemical stabilization. These treatments are discussed in Sec. 5.

The major dry systems are either a spray drier or dry injection. In the spray drier, the flue gas is contacted with a calcium-based slurry or sodium solution such that the gas is evaporated to apparent dryness. The dry injection system involves the introduction of a dry sorbent, the most promising being nahcolite (sodium bicarbonate), into the flue gas. The

Table 3.15 Chemical Analysis of Flue Gas Desulfurization Sludges

Component	Sludge	Elutriate/Leachate
Total organic carbon (elutriate only)		X
Total solids	X	
Dissolved solids		X
Suspended solids (leachate only)		X
pH		X
Hardness (elutriate only)		X
Conductivity		X
Arsenic	X	X
Beryllium	X	X
Cadmium	X	X
Calcium	X	X
Chromium	X	X
Copper	X	X
Lead	X	X
Magnesium	X	X
Manganese	X	X
Mercury	X	X
Nickel	X	X
Selenium	X	X
Zinc	X	X
Chloride		X
Cyanide	X	X
Fluoride (calcium fluoride sludge only)		
Nitrate	X	X
Nitrite	X	X
Sulfate	X	X
Sulfite	X	X

Source: Ref. 53.

resulting waste, consisting of a dry mixture of sodium or calcium sulfite and sulfate, is collected by a baghouse. A major difference between the dry and wet systems is that in the majority of wet systems, the ash is collected by a precipitator prior to the scrubber, whereas in the dry systems the ash and scrubbing waste are collected together.

Very little information is available on the characteristics of dry scrubbing wastes. The lime spray dryer systems are expected to have similar impacts to wet lime/limestones systems. However, being dry, the waste should be easier to handle and dispose. There is, however, concern about the sodium-based systems because sodium compounds are 100 times more soluble than calcium compounds.⁶⁵

3.1.2.2 FBC Spent Residues

Fluidized bed combustion (FBC) technology involves the combustion of crushed coal in a bed of inert ash and limestone or dolomite, which has been

Table 3.16 Elemental Composition of Scrubber Sludge Leachate

Element	Public Water Supply Standard	Leachate Composition (mg/L)		Drinking Water Standard Exceeded
		Max.	Min.	
As	0.05	0.130 0.300	0.0010 0.0080	yes
Ba	1.00	2.000	0.0020	yes
B	1.00	40.000	0.2200	yes
Cd	0.01	0.047	0.0005	yes
Cr	0.05	0.011 0.250	0.0010	yes
Cu	1.00	0.560	0.0020	no
Pb	0.010	0.040	0.0030	yes
Hg	0.002	0.070 0.003	0.0004	yes
Ni	--	0.050	0.0150	no
Se	0.01	0.540	0.0005	yes
V	--	0.200	0.1000	--
Zn	5.00	4.200	0.0100	no

Source: Ref. 54.

fluidized by the injection of combustion air through the bottom of the bed. The limestone or dolomite in the bed reacts with the sulfur dioxide released by the combustion of the coal and forms a solid sulfate material that can be disposed of as a stable dry solid along with the ash. Instead of disposal sulfated lime residues can be regenerated for reuse in the combustor by contacting it with an appropriate reducing agent under appropriate conditions (e.g., hydrogen and carbon monoxide gases at about 2000°F in a fluidized bed).

There are two major waste streams, both dry, from a FBC plant, the spent bed material and the elutriated fines captured by particulate collection equipment. Potentially, very large amounts of solid waste will be produced if regeneration is not used. At a Ca/S mole ratio of 2:1, the FBC process generates about 0.35 to 0.40 pound of waste per pound of coal burned. This is more than a conventional system and should amount to about 700,000 tons per year at a typical 500 MW plant.⁶⁶

Using limestone as the sorbent the spent bed material is expected to be composed primarily of calcium sulfate and calcium oxide in the approximate ratio of 2:3, with small amounts of calcium carbonate and magnesium oxide.⁶⁷ If dolomite is used, the major components are calcium sulfate and magnesium

oxide in the approximate proportion of 3:1.⁶⁸ It is expected that virtually all the coal ash will be elutriated along with approximately 40% of the spent bed material. About 12% of the carbon is unburnt in the main bed and is elutriated. There will then be a carbon burn up cell that will combust an additional 90% of the remaining carbon. This leaves about 1% of the original carbon in the solid waste. The elutriated material will be collected in a cyclone followed by a baghouse. It is expected that the collected particulate matter will be added to the bed material for disposal.

FBC spent sorbent does not contain CaSO_3 , which, in the form of its hemihydrate, tends to occlude water and impart thioxotropic properties to the slurry (sludge) discharged by the FGD systems. Thus, even if exposed to rainwater or runoff water, FBC spent sorbent is not expected to form a sludge. However, the greater solubility of CaSO_4 , compared to CaSO_3 (2000-3000 vs. 40 ppm), poses a somewhat greater threat of groundwater pollution by leaching. Also, if the calcium oxide is "active," a water runoff of very high pH would result. This possibility has been verified by leaching tests.^{70,71} However, it is also possible that calcium oxide could be rendered "inactive" if it is surrounded by an insoluble calcium sulfate shell. There is some evidence that such a shell may form, at least under certain operating conditions.⁶⁷

The retention of trace elements by the ash will be higher than their retention in the ash of a conventional boiler. Therefore a larger total quantity of trace elements will be present in the waste material. The total concentration, however, might not differ greatly due to the larger amounts of material.⁶⁷

Preliminary tests on the spent bed material and collected elutriated matter from the DOE's Morgantown Energy Research Center⁷² suggest that the following leachate characteristics do not appear to present problems. Total organic carbon and sulfide leachate concentrations are below detection limits. Leachate concentrations of trace metals, for which some type of drinking water standard, regulation, or criterion exists, through the EPA, the Public Health Service, or the World Health Organization (Ag, As, Ba, Be, Cd, Cr, Co, Fe, Hg, Mn, Ni, Pb, Se, Sn, and Zn), are below the water drinking standards. However, these conclusions are tentative.

3.1.2.3 Acid Gas Treatment Sludges

In coal gasification and liquefaction technologies, removal of H_2S and trace sulfur species from raw product gas from the conversion reactor is necessary to prevent catalyst poisoning in the subsequent methanation step. Removal of CO_2 is also necessary to obtain a product gas with heating value equivalent to that of natural gas. H_2S and CO_2 may be removed either simultaneously or separately, depending on the specific acid gas removal process chosen and its design.

Acid gas removal processes utilize at least one of three possible techniques: (1) absorption into a solvent, (2) chemical conversion into another compound, and (3) adsorption on solids. Depending on the characteristics of the acid gas and the acid gas treatment process employed, a sorbent blowdown containing a high concentration of solids (including some organics) may be produced. The treatment of this stream may generate a sludge requiring disposal. Such a sludge would most likely contain coal-derived particulate

matter, sorbent, and sorbent degradation products.⁷³ Characteristic data of acid gas treatment sludges are not available.

3.1.2.4 Sludges From Chemical Treatment of Water and Wastewater

In coal-fired combustion or conversion facilities, large quantities of water are used in treatment of coal, as feed for boilers or conversion reactors, and for cooling or quenching. Water treatment chemicals are used to demineralize and clarify most water supplies.

On the other hand, there are wastewater streams from coal combustion or conversion facilities, such as: (1) coal washing effluents, (2) sluice water from slags and ashes, (3) gas liquor (coal conversion), and (4) condensates from steam units. These wastewater streams require treatment before being discharged or reused.

Some wastewater streams are highly contaminated. For example, the gas liquor of coal conversion contains various components of the product gas (carbon monoxide, carbon dioxide, hydrogen, hydrogen cyanide, and methane) in addition to pollutants such as sulfur and nitrogen compounds, ash, phenols, emulsified tar and oils, and soluble salts. Soluble salts may accumulate in aqueous streams in concentrations as high as 300 ppm.⁵³

Water supply and wastewater treatment may involve the use of chemicals such as lime, iron, and aluminum salts for chemical precipitation (e.g., of heavy metals) or for coagulation of particles from process wastewaters. The sludge produced from such chemical treatments may contain precipitated inorganics (e.g., ferric and aluminum hydrolysis products, other metal hydroxides, and calcium carbonate) and inorganic particulate matter removed from the wastewater.

3.1.3 Tars and Oil Sludges

Tars and oils are produced in several coal conversion processes. Some of these such as BIGAS, CO₂-Acceptor, and Synthane ("deep-bed" coal injection mode of operation), produce little or no tar and oil. Other processes including (gasification)-Hygas, Lurgi, Slugging Gasifier, and COGAS, and (liquefaction)-H-Coal, SRC, and Donor Solvent, produce varied quantities of tar and oil.

Initially, tars and oils may be contained in process water, the treatment of which by gravity separation and/or flotation and by emulsion breaking results in the production of tar and oil sludges. These sludges can contain considerable amounts of water depending on the nature of the raw wastewater and emulsions and the system design. Oil content ranging from 7% to as much as 98% has been reported in sludges from the API separators in petroleum refineries. The organic fraction of the sludge is expected to have characteristics similar to the bulk tars and oils in the process. Furthermore, tar and oil sludge is likely to contain high levels of coal-derived organic and inorganic particulate matter.⁵³ Table 3.17 lists the major components of coal tar produced in the German high-temperature conversion process. The highest reported concentrations are for naphthalene, phenanthrene, and fluoranthene.⁷³

Table 3.17 Major Components of German High-Temperature
Conversion Process Coal Tar

Component	Boiling point (°C)	Melting point (°C)	Average Weight (%)
Naphthalene	217.9	80.3	10.0
Phenanthrene	338.4	100.0	5.0
Fluoranthene	383.5	111.0	3.3
Pyrene	393.5	150.0	2.1
Acenaphthylene	270.0	93.0	2.0
Fluorene	297.9	115.0	2.0
Chrysene	441.0	256.0	2.0
Anthracene	340.0	218.0	1.8
Carbazole	354.8	244.4	1.5
2-Methylnaphthalene	241.1	34.6	1.5
Diphenylenoxide	285.1	85.0	1.0
Indene	182.4	-1.5	1.0
Acridine	343.9	111.0	0.6
1-Methylnaphthalene	244.7	-30.5	0.5
Phenol	181.8	40.9	0.4
Cresol	202.2	12.2	0.4
Benzene	80.1	5.5	0.4
Diphenyl	255.0	69.2	0.4
Acenaphthene	227.5	95.0	0.3
2-Phenylnaphthalene	359.8	101.0	0.3
Toluene	110.6	-95.0	0.3
Chinoline	237.1	-14.2	0.3
Diphenylenesulfide	331.4	97	0.3
Thionaphthene	219.9	31.3	0.3
m-Xylene	139.1	-47.9	0.2
o-Cresol	191.1	31.0	0.2
p-Cresol	201.9	34.7	0.2
Isochinoline	243.3	26.5	0.2
Chinaldine	247.6	-1.0	0.2
Phenanthridine	349.5	107.0	0.2
7,8-Benzochinoline	340.2	52.0	0.2
2,3-Benzodiphenylenoxide	394.5	208.0	0.2
Indole	254.7	52.5	0.2
3,5-Dimethylphenol	221.7	63.3	0.1
2,4-Dimethylphenol	210.9	24.5	0.1
Pyridine	115.3	-41.8	0.02
a-Picoline	129.4	-66.7	0.02
b-Picoline	144.1	-18.3	0.01
y-Picoline	145.4	3.7	0.01
2,6-Intidine	144.0	-6.1	0.01
3,4-Intidine	158.4	-64.0	0.01

Source: Ref. 73.

3.1.4 Biosludges

In gasification and liquefaction processes, the raw gas scrubber water for gas quenching can be highly contaminated. For example, the gas quench water from gasification processes such as Lurgi, Synthane, and Hygas contain high levels of organics (e.g., up to 6600 mg/L of phenols and up to 10,000 mg/L of total organic carbon). These quench waters also contain varying concentrations of trace organics such as carbazoles, benzofurans and benzo(a)-pyrenes, which can be hazardous. Table 3.18 presents the identification and levels of organics in product water from a coal gasification process. In addition to trace organics, the quench waters can also contain significant levels of certain trace elements originally present in the coal. Table 3.19 presents the trace elements concentrations in Synthane and HYGAS quench waters

Table 3.18 Organics in Product Water from Gasification of Illinois No. 6 Coal^a

Compound	Quantity (ppm)
Phenol	3400
Cresols	2840
C ₂ -Phenols	1090
C ₃ -Phenols	110
Dihydrics	250
Benzofuranols	70
Indanols; acetophenones	150
Hydroxybenzaldehyde; benzoic acids	60
Naphthols	160
Indenols	90
Benzofurans	NA ^b
Dibenzofurans	NA
Biphenols	40
Benzothiophenols	110
Pyridines	NA
Quinolines	NA
Indoles	NA

^aLow-voltage mass spectrometry data.

^bNA: Not available.

Source: Ref. 53.

Table 3.19 Trace Elements Reported in Product Gas Quench Waters

Element	Trace Element Concentration (mg/L)		% of Element Originally Present in Coal
	Synthane PDU ^a	Hygas Pilot Plant	
Hg	0.027	-	32
As	0.001	-	90
Zn	0.13	37-63	-
Mn	0.2	40-206	36
Cr	0.043	<24	-
F	39	-	42
B	43	251-12000	3.5
Be	-	<2	1.6
Cd	-	<20	35
Pb	-	<60	3.2
V	-	<200	0.06
Sb	-	-	36

^aProcess Development Unit.

Source: Ref. 73.

and the percentages of the trace elements found in the aqueous condensate from the Lurgi facility at SASOL, South Africa, and originally present in the coal.⁷³

When biological processes are employed for the treatment of quench water and other aqueous wastes, the degradation of organics and the physical entrapment of settling suspended particles produce a biosludge. Sludges produced in the activated sludge and trickling filtration processes are settled in the clarifiers, which follow the aeration tank or the trickling filter. In these processes a portion of the settled sludge is recycled to the aeration tank or the trickling filter, while the excess sludge is wasted and requires disposal. Sludges removed from final clarifiers typically contain 2 to 5% solids, which generally contain 50 to 70% volatile matter. When lagoons and stabilization basins are used for biological treatment, the biological sludge that is produced, and the settleable matter in the raw wastewater, settle to the bottom; the degradable material in the settled sludge undergoes aerobic and/or anaerobic decomposition. Depending on the nature and quantity of the solids in the raw wastewater and the lagoon design, periodic cleaning of the lagoons to remove the settled sludge may be necessary. Certain elements (e.g., heavy metals) and refractory organics that may be present in

the raw wastewater at relatively low concentrations may concentrate in the biosludges. Trace organics and metals may present an environmental problem for disposal of biosludge from coal conversion.

3.1.5 Spent Catalysts

Many types of catalysts are used in coal gasification and liquefaction technologies (see Table 3.20). These catalysts are used to enhance chemical reactions (coal conversion, shift, methanation) and process stream purification. While some organics are used as catalysts, the majority of catalysts are metal-containing solid particles. For example, the shift catalysts are generally cobalt molybdate-based, and the methanation catalysts are nickel-based materials supported on an inert substance such as alumina or silica.

Due to contamination, catalyst activity decreases with increased operating time. Catalysts are frequently poisoned (deactivated) by free carbon, sulfur, and chlorine. The characteristics of the feedstock and catalyst, as well as the operating conditions, are factors that determine the rate of catalyst deactivation. The conceptual design for commercial SNG facilities in the U.S. assumes a catalyst life of six months to two years.⁵³

Spent catalysts can either be regenerated by returning to the manufacturer, or disposed of along with other solid wastes such as coal ash. Because of the proprietary nature of the catalysts, very little information relative to their environmental effects is available. However, it is possible that disposal of spent catalysts may cause environmental problems. For example, it has been indicated that the spent catalysts from both shift conversion and methanation operations contain coal-derived trace elements (e.g., arsenic, cadmium), elemental carbon, and highly polymeric organic materials, in addition to cobalt and/or nickel originally existing in the catalysts.⁷³

3.1.6 Coal Cleaning Wastes

About half of the total coal mined in the U.S. is prepared or cleaned before use to remove some of the noncombustible materials. Coal cleaning is usually done at the minehead, although some may be done at utilization sites. Coal cleaning wastes consist of rocks and mineral matter such as clays, quartz, pyrites, marcasite, as well as small amounts of residual coal and unidentified matter. The rejected material represents, on the average, about 20% by weight of the raw coal.

Most of the coal in the U.S. is cleaned by physical methods.⁷⁴ The mineral wastes produced by such methods amount to 100 million tons per year. Coal cleaning is receiving increased attention as a means of reducing the coal sulfur content, and the annual production rate of coal cleaning waste is expected to double within a decade.⁷⁵

It has been known for several years that the acidic drainage from coal refuse disposal sites is often highly contaminated with various species such as iron, manganese, and sulfate ions. More recently Los Alamos Scientific Laboratory has investigated the structure, weathering, and leaching behavior

Table 3.20 Catalysts Used in Coal Conversion Processes

Catalysts	Use
Activated carbon	Purification
Iron oxide	Purification
Methanol	Purification
Propylene carbonate	Purification
Sodium carbonate	Purification
Potassium carbonate	Purification
Amines	
Monethanolamine	Purification
Diethanolamine	Purification
Diglycolamine	Purification
Zinc oxide	Purification
Cobalt-molybdenum	Shift conversion, liquefaction (hydrotreating), purification
Limestone-dolomite	Sulfur recovery
Molten salt	
Nickel	Methanation or liquefaction
Vanadium	
Dolomite	Purification
Bauxite	Sulfur recovery
Iron	Shift conversion or liquefaction
Isopropyl ether	Phenol recovery
n-methyl-2-pyrrolidine	Purification
Dimethyl ether polyethylene glycol	Purification
K ₃ AsO ₃	Liquefaction
Tungsten	Liquefaction
Zinc chloride	Liquefaction
Sodium sulfite	Purification
Co-Mo/SiO ₂ -Al ₂ O ₃	Liquefaction
Sulfoxide	Sulfur recovery
Chelated iron salt	Sulfur recovery
Nickel-tungsten	Liquefaction (hydrotreating)
Ruthenium	Methanation

Source: Ref. 53.

of trace elements in selected samples of coal cleaning wastes.^{76,77} The study revealed the great potential of these wastes for releasing harmful quantities of trace elements.

Oxidative degradation of the pyrite and marcasite present in the coal cleaning wastes produces leachates with pH values below 2, which would put many untreated coal cleaning wastes on the corrosive waste list, even under the recently relaxed RCRA criteria. The highly acidic leachates can easily dissolve a variety of trace elements present in the wastes, including fluorine, aluminum, manganese, iron, cobalt, nickel, copper, zinc, arsenic, and lead. Some of these elements (e.g., copper, zinc, and cadmium) have been found in concentrations significantly exceeding public water supply criteria (see Table 3.21). On the basis of a priority system using the MEG (Multimedia Environmental Goals) system, six elements (iron, aluminum, manganese, calcium, nickel, and zinc) were identified as present at levels of possible environmental concern, particularly for the wastes resulting from high sulfur coal. The severity of contamination caused by the low sulfur waste would be less pronounced than that caused by the high sulfur wastes.

Table 3.21 Trace Element Concentration for
Drainage Produced by Illinois
Basin Coal Refuse

Element	Leachates Concentration (mg/L)	EPA Public Water Supply Criteria (mg/L)
Na	21 - 700	-
Mg	61 - 369	-
Al	8.1 - 910	-
K	21 - 28	-
Ca	130 - 532	-
Mn	5.6 - 44	-
Fe	610 - 12,000	-
Co	3.7 - 28	-
Ni	5.6 - 43	-
Cu	0.3 - 8	-
Zn	2.2 - 55	5.0
Cd	0.02 - 0.24	0.01
pH	1.7 - 2.9	5.9

Source: Ref. 77.

3.2 SOLID WASTES ASSOCIATED WITH OIL SHALE PROCESSING

The solid wastes resulting from oil shale processing include fines from crushing and conveying of the raw shale and the processed shale remaining after retorting. Together these constitute most of the process solids requiring disposal. Other solids to be discarded depend primarily upon the extent of upgrading of the crude shale oil that is carried out in conjunction with the retorting operations, and may include shale oil coke if experience shows that such material is not usable or marketable. Certain nonshale wastes such as spent catalysts may also be generated during the processing of shale oil. The nature and sources of solid wastes from oil shale processing are given below.⁷⁸ The toxicity potential of these wastes is discussed in Sec. 4.2.

3.2.1 Raw Shale Fines

The primary sources of raw shale fines are the crushing operations conducted on the just-mined shale and dust from raw shale transport within the mine-plant complex. The composition of the fines is essentially that of the mined, raw shale and its organic matter. A typical chemical analysis of the organic matter and associated mineral matter in the raw shale is given in Table 3.22.

3.2.2 Retorted Shales

Pyrolysis of oil shale results in the conversion of most of the original organic material in raw shale to gaseous and liquid hydrocarbons. Retorted shales containing solid organic residues can be disposed of directly as a solid waste, or can be further processed for recovery of heat value of the residue.⁷⁹

Burned Shale (e.g. Paraho Direct Mode (Gas Combustion Retort)): After retorting at approximately 900°F, the remaining processed shale is soft and friable. It usually has an organic "carbon" content of 2 to 3%, depending on the retorting process. Direct Mode Paraho retorting produces a retorted shale that has been partially "burned" after pyrolysis of oil shale kerogen. Residual organic carbon amounts to about 2% by weight, and typically 30% of the contained carbonate minerals have been calcined.⁸⁰ Particle size is greater than 1.2 cm (0.5 inch). It is possible, in principle, to oxidize this carbonaceous material, to create a source of process energy, and to discard a completely carbon-free shale residue, or ash. Typical shale ash has a composition similar to Portland cement and has certain cement-like physical properties. A typical composition of such ash is shown in Table 3.23 for several retorted shale residues.

Carbonaceous Retorted Shale (TOSCO II, Union B, Paraho Indirect Mode): Several retorting processes do not completely utilize as a source of energy the carbonaceous residue remaining on the shale after pyrolysis. Therefore, the retorted shale still contains about 5% organic matter. In addition, the maximum temperature during retorting is commonly less than that at which the dolomite and calcite in the shale rock decomposes, or at which calcium silicates form. Typical chemical composition of the ashes from TOSCO II and Union B processes is given in Table 3.23.

Table 3.22 Typical Analysis of Organic and Mineral Matter in the Raw Shale

Organic Matter	wt. %	Mineral Matter	wt. %
Carbon	80.5	Dolomite	32
Hydrogen	10.3	Calcite	16
Nitrogen	2.4	Quartz	15
Sulfur	1.0	Illite	19
Oxygen	5.8	Albite	10
		Microcline	6
		Pyrite	1
		Anacite	1

Source: Ref. 78.

Table 3.23 Ash Composition of Typical Retorted Oil Shale

Component	TOSCO II ^a	Union B ^b	GCR ^c
	wt%	wt%	wt%
SiO ₂	33.0	31.5	43.8
Fe ₂ O ₃	2.5	2.8	4.6
Al ₂ O ₃	6.8	6.9	12.2
CaO	15.8	19.6	22.1
MgO	5.3	5.7	9.3
SO ₃	-	1.9	2.2
Na ₂ O	8.7	2.2	3.4
K ₂ O	3.3	1.6	2.4

^aRef. 81; data represent Mahogany zone shale (35 gal/ton) from Parachute Creek area.

^bRef. 82; data represent Mahogany zone shale (35 gal/ton) from Parachute Creek area.

^cRef. 83; data represent Mahogany zone shale (30 gal/ton) from Anvil Points.

Retorted shale from the Superior process will have different properties from those of retorted shales from other processes. The raw oil shale found in deep deposits of the Northern Piceance Basin contains sodium and aluminum minerals, and these are slated for recovery, along with pyrolysis products, by the Superior Oil Company. Shale retorted and processed by Superior may be partially "burned," depending on the mode of operation, and will have been stripped of most of the soluble sodium and aluminum salts. Little is known at present about the detailed physical and chemical properties of such processed shales.

Organic Substances in Retorted Shale: The carbonaceous component of processed shales contains organic substances that can be extracted by organic solvents (e.g., benzene), and by water. From 0.01 to 0.1%, by weight, of processed shales are benzene soluble, and substances such as phenols, aromatic acids, and amines are present in the soluble fraction. Compounds belonging to the polycyclic organic matter (POM) class are also present in benzene extracts, including the suspected carcinogen benzo(a)pyrene(BaP).⁸⁴

Trace Metals In Retorted Shale: Distribution and migration of trace metals during retorting of oil shale was analyzed by Shendrikar and Faudel.⁸⁵ Results (see Table 3.24) indicate that the majority (more than 99% in all cases except arsenic) of the trace elements are retained by the retorted shale.

Processed shales contain mineral components that may be partially dissolved by water. Laboratory and field experiments have shown that sodium, calcium, magnesium, potassium, bicarbonate, sulfate, and chloride are present in waters that have contacted freshly processed shale.⁸⁶ Table 3.25 presents the results of laboratory leaching experiments of raw and retorted shales. TOSCO II and USBM retorted shale each contain about 10 kg/tonne (20 lbs/ton) of readily leachable salts, roughly ten times that leachable from raw oil shale. Data for the burned shale from the Union A process (column 4 in Table 3.25) indicate that total soluble salts depend heavily on the extent of carbon burnoff and mineral decomposition that occur in the combustion zone of a gas combustion retort (GCR).

The rate and extent of soluble inorganic salt leaching of retorted shale that will occur under field conditions depend on a number of factors in addition to the type of retorting process employed. Such factors include the amount of water added, the degree of compaction accomplished, the manner in which a pile is laid down (e.g., slope, depth of pile), the extent of preleaching that is accomplished in connection with revegetation, and the age or weathered state of the shale pile. Also, burned shales can form partially cemented barriers to water within a disposal pile that can serve to inhibit further leaching.

3.2.3 Other Shale-Derived Solid Wastes

Retorting and on-site shale oil upgrading can result in the production of shale derived wastes such as coke and oily sludges.

Shale Oil Coke: If the crude shale oil produced by retorting is upgraded on site prior to shipment to market, one of the products may be coke,

Table 3.24 Distribution of Trace Metals During Oil Shale Retorting

Element	Weight (ppm)				% Recovery	% Distribution		
	Raw Shale	Spent Shale	Oil	Water		Spent Shale	Oil	Water
Arsenic	60.0	60.0	21.0	0.0	87.4	95.0	5.0	0.0
Beryllium	1.0	1.2	0.0	0.0	99.6	100.0	0.0	0.0
Boron	63.3	54.0	0.48	0.55	70.9	99.8	0.1	0.0
Cadmium	1.25	1.50	0.00	0.00	99.6	100.0	0.0	0.0
Chromium	41.7	53.8	0.8	0.004	107.3	99.8	0.2	0.0
Cobalt	6.5	8.0	0.26	0.005	102.7	99.5	0.5	0.0
Copper	47.5	55.0	0.25	0.16	96.2	99.9	0.1	0.0
Fluoride	1162.0	1352.0	<1.0	2.6	96.6	99.9	0.0	0.0
Lead	282.3	34.5	0.14	0.0	97.8	99.9	0.1	0.0
Manganese	230.0	275.0	0.05	0.02	99.2	99.9	0.0	0.0
Molybdenum	30.0	37.7	0.50	0.006	104.5	99.8	0.2	0.0
Nickel	23.9	27.5	1.4	0.034	96.2	99.2	0.8	0.0
Selenium	14.6	16.7	0.0	0.1	94.9	99.9	0.0	0.0
Vanadium	57.1	70.6	0.48	0.0	102.7	99.9	0.1	0.0
Zinc	65.0	76.0	1.4	0.045	97.3	99.7	0.3	0.0

Source: Ref. 85.

Table 3.25 Inorganic Ions Leachable from Freshly Retorted Shales^a
(kg/tonne)

Ion	Raw Shale	TOSCO II	GCR (USBM)	GCR (Union A)
K ⁺	0.24	0.32	0.72	6.25
Na ⁺	0.48	1.65	2.25	21.0
Ca ⁺⁺	0.1	1.15	0.42	3.27
Mg ⁺⁺	0.01	0.27	0.04	0.91
HCO ₃ ⁻	0.75	0.20	0.38	0.28
Cl ⁻	0.22	0.08	0.13	0.33
SO ₄ ⁼	0.79	7.3	6.0	62.3
Total (kg/tonne)	1.95	10.96	9.94	94.34
(lb/ton)	3.9	22	20	188

^aBased on laboratory tests.

Source: Ref. 86.

which must be stored prior to sale or will require disposal as a waste. Shale oil coke is expected to have the typical composition shown in Table 3.26. Storage or disposal piles are potentially the sources of salts and organic substances leached to the environment.^{87,88}

API Separator Sludges: Oils and tars separated from wastewaters may constitute a semisolid waste requiring disposal. Such material may contain suspended solids, hazardous organics, and trace elements and may have characteristics similar to separator sludges produced in coal conversion processes and petroleum refineries. Handling options include (1) burial with other solid wastes in the processed shale pile, (2) incineration with air pollution control, and (3) reinjection into the retort or upgrading units.

3.2.4 Non-Shale Solid Wastes

If substantial upgrading operations are conducted at or near the retorting site, non-shale solid wastes will be generated. Such wastes include spent catalysts from hydrotreating, sulfur recovery, and arsenic removal operations, lime sludges and other solids from water and wastewater treatment systems, and spent carbon and diatomaceous earth from gas and oil treating units. Some of these wastes may contain highly toxic substances such as arsenic, and/or may result in emissions of hazardous materials during handling, disposal or reprocessing. Hydrodenitrification catalysts for example, may contain 10-13% carbon, 8-10% sulfur, and up to 7% arsenic after their useful activity has been exhausted and regeneration or disposal is required.⁸⁹

Table 3.26 Typical Composition of Shale Oil Coke

Component	TOSCO II Retorting ^a	Paraho & TOSCO II ^b
Ash, wt %	10-15	12.6
Moisture, wt %	7.0	N/A
Carbon, wt %	91	
Hydrogen, wt %	3.6	82.5
Oxygen, wt %	1.3	
Total Nitrogen, wt %	3.9	4.1
Sulfur, wt %	0.5	0.8
Arsenic, ppm	5-10 (0.3 water soluble)	N/A

^aRef. 87; data are for shale oil produced by TOSCO II retorting.

^bRef. 88; data are for shale oil produced by Paraho and TOSCO II.

3.3 SOLID WASTES ASSOCIATED WITH OTHER ENERGY TECHNOLOGIES

3.3.1 Geothermal Technologies

Geothermal resources of near-term interest are of three types: hydrothermal, geopressured, and hot dry rock.⁹⁰

Hydrothermal Systems: Hydrothermal systems are convective systems of water and steam that are trapped in fractured rocks or permeable sediments by impermeable surface layers. Geothermal fluids may be released when such systems are tapped by drilling. A specific resource is classified as being either vapor- or liquid-dominated, according to the state of the fluid produced.

Hydrothermal resources have high potential for near-term commercial development. For example, vapor-dominated resources are presently being used for the generation of electricity in the United States, Japan, and Italy; liquid-dominated resources are in use in Iceland, Mexico, El Salvador, Russia, and New Zealand.

Geopressured Systems: Geopressured zones consist of highly porous sands saturated with saline water at very high pressure and temperature. The high temperature is thought to be the result of normal heat flow being trapped by uncompact clays, which serve as insulating layers. Water derived from the compaction and dehydration of clays accumulates in the sand and greatly increases the fluid reserve. The marine sediments are under-compacted below depths of 6,500 to 10,000 feet, and the interstitial fluid carries part of the

overburden load (i.e., the fluids are at pressures between the hydrostatic and the lithostatic head). Temperatures up to 290°C and pressures up to 1000 atmospheres have been measured in these systems. In the United States, the principal geopressured formations are located under the Gulf coast of Texas and Louisiana. The magnitude of the resource is substantial, and its economic value is enhanced by the presence of natural gas dissolved in the geopressured fluid; however, difficult technical and economic problems must be solved before geopressured resources can be utilized commercially.

Hot Dry Rock Systems: Hot dry rock resources are those geothermal reservoirs where the heat is contained in rock of low permeability. Hot dry rock systems are potentially the largest and most widely distributed geothermal resource in the nation. A large volume of hot dry rock (normal gradient resource) is located in the earth's crust at depths in excess of 15 km (50,000 ft), which is beyond present drilling capability. However, the volume of hot dry rock at more shallow, accessible depths is also considerable. It is estimated that 95,000 square miles of the Western Heat Flow Province (the 13 Rocky Mountain and Pacific Coast States) are underlain by hot dry rock at temperatures greater than 293°C at depths less than 5 km (16,000 ft). Two specific promising areas are the Valles Caldera, near Los Alamos, New Mexico, and the Coso Hot Springs, near China Lake, California. Other potential sites being evaluated are located on the eastern coastal plain, the midwestern region, and the Pacific Coast.

Development of these resources requires drilling into the rock, inducing fractures, injecting fluid, and removing the resultant heated fluid through separate wells. Technical problems associated with fracturing and maintaining the fractures must be solved before these resources can be developed commercially.

One of the major environmental concerns in geothermal energy utilization has to do with disposal of spent geothermal fluids, which can potentially contaminate surface and subsurface waters. Many geothermal fluids are "junk," containing sodium chloride, sulfates, bicarbonates--compounds normally found in groundwater, but in much higher concentrations. The specific composition of geothermal fluid naturally varies from place to place. In Boise, Idaho, for example, where a major effort to develop geothermal systems for commercial and residential heating is under way, the geothermal fluids contain fluoride at concentrations up to 22 parts per million--12 times the drinking water standard. Arsenic, lead, potassium, and total dissolved solids also run to high levels in some areas.⁹¹

Some geothermal fluids are very saline, for example, the hydrothermal resources in the Salton Sea known geothermal resource area (KGRA) in Imperial Valley, California, produces highly saline fluids, which contain primarily sodium chloride (NaCl) with varying amounts of calcium (Ca). Potassium content is high relative to that in surface water. Sulfate content is low and small amounts of carbonate and bicarbonate are usually present. Boron, lithium, manganese, strontium, and zinc are among the more abundant trace elements in geothermal brines throughout the valley.⁹¹

Table 3.27 summarizes the concentrations of important geothermal constituents in brines from wells in the Salton Sea, Brawley, Heber, and East Mesa KGRA and in areas near Westmorland, California.⁹²

Table 3.27 Average Concentration in Geothermal Brines and in Water Samples (mg/L)

Ion	Average Concentrations in Geothermal Brines					Average Concentrations in Water Samples in Salton Sea KGRA						
	Salton Sea	Westmorland	Brawley	Heber	East Mesa	Vail4 Canal	Sump 120	Sinclair 4	Sump 116	Vail4A Drain	Alamo River	Salton Sea
Na	52,000	10,000	22,000	4,200	2,600	168	1,080	58,442	2,470	970	607	10,600
K	14,000	1,400	3,800	260	190	6.3	20	14,918	247	66	15	195
Ca	24,000	690	8,100	880	130	93	373	26,992	2,050	437	201	850
Mg	106	188	34	5.4	3.4	35	187	736	385	160	120	1,200
Cl	145,000	18,000	46,000	7,900	3,900	158	989	154,590	8,540	1,870	760	14,700
SO ₄	84	57		99	155	357	1,990	19	1,590	1,480	960	8,100
CO ₃	0	130	0	3.3	33	15	<2.5		<2.5	<2.5	<2.5	63
HCO ₃	140	2,900	49	27	490	152	338	0	380	330	205	143
As	11		2.6	<0.1	0.16	0.005	<0.005	10	0.005	0.005	0.007	<0.01
B	350	63	140	14	5.4	0.25	1.1	332	9.7	2	0.76	6.8
Ba	433		363	3.8	2.2	0.09	0.097	1,100	0.54	0.093	0.12	0.07
Cu	4	0.07	0.11	0.53	0.03	<0.005	0.005	3	0.075	0.007	0.014	0.08
F	9	2.24		1.6	2.0	0.5	0.57	14	0.48	0.05	0.66	1.1
Fe	2,300	0.3	65	22	2.2	0.03	0.08	1,240	0.26	0.08	0.045	0.24
Li	211	48.	100	9.5	6.3	0.08	0.31	344	14.3	1.24	0.23	3.2
Mn	1,200	2.8	190	2.7	0.42	0.01	0.30	1,475	47	1.9	0.035	0.08
Ni	<4			0.03	0.01	<0.01	<0.01	<4	0.31	<0.01	<0.01	<0.2
Pb	100	3.6	1.1	1.9	0.09	<0.01	0.01	60	0.29	0.02	0.01	<0.1
Se				1.2	<0.005	<0.005			<0.01	<0.005	<0.005	0.02
Sr	500		340	53	38	1.3	5.0	448	38	6.0	3.2	13.5
Zn	660	0.04	14	0.83	0.07	0.02	0.03	600	7.8	0.12	0.02	0.03
TDS	240,000	37,000	76,000	14,000	7,600	928	5,030	266,560	17,700	5,970	3,000	38,600
pH	5.2	7.5	6.1	6.5	7.3	8.2	7.0	5.3	6.8	7.6	7.7	8.8

Source: Ref. 92.

If the spent fluids are dumped on the ground instead of being reinjected, there is a risk of their seepage into the shallow groundwater system. Though surface water contamination is usually avoided by reinjection, some contamination can still occur. Groundwater is not necessarily isolated from the reinjection point. A change in shallow groundwater quality in those areas would be expected to be influenced by the geothermal system. For example, in one case total dissolved solids in well water are predicted by a computer model to increase over 30 years from 1200 mg/L to 2000-2600 mg/L. Such changes could render unusable irrigation wells that are already on the borderline.⁹¹

In many cases, long-term subsurface injection may not be possible without the treatment of the spent fluids to remove solids that would plug the wellbore or reservoir. If treatment is necessary, large volumes of solid waste may be produced. More tests are needed to define the extent of this problem.

3.3.2 Oil and Gas Extraction

Oil and gas extraction wastes include oil and gas drilling fluids and oil production brines. Oil production brines are coproduced with crude oil from an underground reservoir and consist primarily of brackish waters. Drilling fluids are used in the drilling of oil and gas wells to cool and lubricate the drilling bit, transport drill cuttings to the surface, balance formation pressure, seal the walls of the bore hole, and perform various other related functions.

This section provides a characterization of the oil and gas drill fluids in terms of their composition, volume, and current disposal techniques. Information presented is primarily summarized from a recent report by Fred C. Hart Associates, Inc.⁹³

Composition: The basic drilling fluid predominantly used by the industry is a waterbased bentonitic or attapulgite clay suspension with ferrochrome or chrome lignosulfate added to control fluid viscosity, barium sulfate added to increase fluid density, and a caustic added to maintain an alkaline pH of about 9-11. Oil-based fluids are used for some special applications, but their use is much less common than that of water-based fluids. Also, oil-based fluids are generally saved for reuse rather than being disposed of after a well is completed.

Additives to the basic drilling fluid provide specifically desired properties. Hundreds of compounds are available for use as drilling fluid additives, and about twelve may be used for drilling a given well. Some of the more commonly added materials include detergents, organic polymers, tannin, phosphates, corrosion inhibitors, and bactericides. In addition, fluids may contain asbestos fibers, dissolved metals (e.g., barium, cadmium, chromium, copper, iron, lead, nickel and zinc), salts, and humic acids.

Although water-based drilling fluids consist of over 99% water and other relatively nontoxic components, many of the additives to drilling fluids contain materials that are considered toxic. Of particular concern are the bactericides (e.g., aldehydes, quaternary amines, diamine salts,

sodium pentachlorophenate and other chlorinated phenols), corrosion inhibitors (e.g., arsenites), metals, coal tar derivatives, emulsion breakers, and low molecular weight organic additives (e.g., benzoic acids, dihydroxybenzenes, substituted naphthalenes, amines, and imidazolines). Many drilling fluid additives are water soluble; therefore, leachate from drilling fluid disposal could contain dissolved toxic materials, a high salt concentration, and caustic materials.

Volumes: The quantities of drilling fluids and various fluid components used during a drilling operation vary depending on the requirements of the drilling situation, formation characteristics, and specific drilling practices. The amount of drilling fluid used for a typical 15,000 to 18,000 foot offshore well has been estimated at 690 to 820 tons, with a variability of as much as 50% from well to well. For onshore wells of comparable depth, similar quantities of drilling fluids would be used, and for shallower onshore wells, the quantity of fluid required would be somewhat less. For example, the quantity of fluid used for drilling wells at the Naval Petroleum Reserves Elli Hill field is estimated at 50 to 100 barrels per thousand feet of well depth, for a total of approximately 50,000 barrels per year from approximately 150 wells of 5,000 to 10,000 foot depths.

During some onshore drilling operations, used fluids may be combined with solid cuttings and rig deck wash water, and stored for later disposal. Mixing with wash water greatly increases the total volume of material requiring disposal; typically, 5,000-50,000 barrels may be collected by the end of such a drilling operation. The EPA estimates the quantity of gas and oil drilling muds and oil production brines to be 5 million metric tons per year.

Current Disposal Practices: Only a portion of the drilling fluid is lost to the bore hole during drilling. The remaining fluid must be disposed of or, in the case of oil-based fluids, processed for reuse after completion of a well. In offshore drilling operations, the drilling wastes are typically disposed of in the ocean, following U.S. EPA guidelines as specified in NPDES permits. In onshore drilling operations, used drilling fluids historically have been disposed of on land by such methods as spreading over land surfaces or by evaporation in a diked area, holding pond, or pit. The area used is generally covered after the mud has dried. State governments are becoming increasingly concerned about the land disposal of waste drilling fluids and some, such as California, have opposed surface spreading so that disposal in holding ponds or pits must be used. Oil brines are commonly either reinjected into the reservoir or evaporated in a manner similar to the drilling fluids.⁹³

3.3.3 Tar Sands

Tar sands are mixtures of mineral grains (normally sand grains) and organics (normally called bitumen), which are potential sources of liquid fuels (e.g., gasoline, jet fuel, heating oils). The known tar sand deposits of the world are comparable in size or perhaps larger than the known reserves of conventional oil. The two largest such tar sand deposits are located in Canada and Venezuela. However, the U.S., mostly in the state of Utah, does have substantial tar sand deposits, which may contain 30 million barrels of oil.

Processing of Tar Sands: Tar sands have in the past been used as paving material. However, the production of liquid fuels is currently the use of principal interest. To make liquid fuels from tar sands, it is necessary to remove the bitumen from tar sand and to change its chemical composition.

The methods for removing individual particles of bitumen from the sand grain are by hot-water suspension, cold-water suspension, or with various solvents. In each case, the bitumen, which is barely soluble in water, is separated by gravity and the remaining clean sand rejected.

Once the bitumen has been separated from the sand, it receives further treatment for conversion to a material suitable for use as a liquid fuel. The principal objectives of this process are to remove most of the sulfur from the bitumen, to raise the hydrogen-to-carbon ratio of the liquid fuels above that originally present in the bitumen, and to lower the average molecular weight of the bitumen. Coking followed by hydrotreating of the liquid products has been proven capable of meeting these objectives. Coking is performed by heating the liquid bitumen to a temperature at which it begins to thermally decompose and holding it at that temperature long enough for decomposition to be completed. This decomposition produces a gaseous product, which is easily separated from the remaining material and which, on condensation, is quite similar to ordinary liquid hydrocarbons. The remaining material is a solid coke consisting mostly of carbon but which can contain up to 8% sulfur. Much of the sulfur is immobilized in the coke (which is a by-product of the process) and therefore removed from the valuable liquid fuel. The liquids produced by coking require further hydrotreating to lower their sulfur content to the level which is acceptable in finished liquid fuels.

Characteristics of Solid Wastes: The solid wastes to be dealt with in a major tar sand operation are top soil, over burden, and tailings. Topsoil consists of soil and rocks stripped from the surface and stored for later use in reclamation programs. Over burden is produced if open pit mining is employed. It represents material (soil and rocks) stripped from its location over the ore and deposited either outside the mine area or in the adjacent mined out area of the mine without interfering with current mining operations. Tailings are processed tar sands that are generally pumped in slurry form to the tailing pond and stored for dewatering and revegetation. In addition to these wastes, bitumen conversion processes would produce solid wastes, such as coke and oily sludges.

Potential environmental threats from tar sand-related solid wastes include:⁹⁴

- Air pollution due to wind erosion of the surfaces of storage and disposal piles.
- Pollution of surface and groundwater resources as the result of the leaching of salts and toxic materials from processing wastes, and the picking up of silt or sediment by erosion of the surfaces of disposal piles.
- Mass movement of waste material due to collapse or slumping of unstable piles.

- Visual pollution by scarring the earth and disruption of the natural scenic values of the area and the inherent economic devaluation of surrounding property.

There is, in general, a lack of quantitative information concerning the hazard characteristics of solid wastes from tar sand processing. More tests in this area are definitely needed.

EPA reported sulfur contents of Utah tar sands ranging from 0.14 to 6.27%. An average of 0.4% of sulfur is quoted for the tar sands in the Uinta Basin (80 samples). Average metal concentrations of Utah tar sands are listed as:⁹⁵

Chromium	103 ppm
Cobalt	102
Copper	110
Manganese	547
Nickel	203
Zinc	212

Leachates from tailing piles must be analyzed to determine oil content, salinity, and the concentrations of nitrates, heavy metals and trace organics.

Fish toxicity resulting from seepage from the waste pond at Great Canadian Oil Sands has been reported.⁹⁴ There, the containment dike is built by hydraulic tilling from the waste pond. The water which is carried onto the dike during the filling operation percolates out of the dike; that which is added on the side away from the pond percolates out of that side. In the original design of the project a drainage ditch was cut at the toe of the dike to capture this water and discharge it to the Athabasca River. Subsequently it was discovered that this water is toxic to fish. Currently it is not known which ingredient in the water is toxic to fish, although an organic acid is suspect. As a result, Great Canadian Oil Sands has been obliged to capture this water and pump it into its storage pond.

3.3.4 Nuclear Power Generation⁹⁶

This section presents the types and quantities of radioactive wastes that are generated in the nuclear fuel cycle and identifies several areas of potential risk associated with the disposal of these wastes.

Classes of Nuclear Wastes

Radioactive wastes, which are the by-products of the generation of electricity by nuclear reactors, are encountered at all stages of the nuclear fuel cycle -- in mining and milling, in fuel fabrication, in reactor operation, in spent fuel assemblies, and in the reprocessing of spent fuel. Nuclear wastes can be divided into five classes: high-level waste (HLW), made up of spent fuel and reprocessing wastes; transuranic (TRU) waste; low-level waste (LLW); uranium tailings; and decommissioning/decontamination (D/D) waste.

High-Level Wastes (HLWs): High-level wastes can be either intact spent fuel assemblies removed from a reactor after serving their useful life or the wastes generated as a result of spent fuel reprocessing. A 1000-MW light-water reactor annually discharges about 30 metric tons of spent fuel from the present once-through fuel cycle.⁹⁷ Commercial spent fuel contains about 96% by weight of the uranium originally charged to the reactor as fresh fuel in addition to 3% fission products and 1% TRU elements and daughters.⁹⁸ Most fission products decay to stable elements after several hundred years, whereas TRU elements remain radioactive for thousands of years. Consequently, spent fuel initially generates a great deal of heat and is very radioactive. After a decade, the heat generated decays by a factor in excess of 300, while the radioactivity decays by a factor of 1000.⁹⁹ Currently, commercial spent fuel assemblies are stored at the reactor site until a decision on the question of spent fuel reprocessing is made. If reprocessing is not used in the nuclear fuel cycle, spent fuel will remain the bulk of the waste generated. Twenty-three hundred metric tons of heavy metal already exist from past reactor operations.¹⁰⁰

If the nuclear fuel cycle is closed and spent reactor fuel is reprocessed to recover uranium and/or plutonium, a different type of HLW will become the bulk of the wastes generated. Reprocessing wastes contain 84% by weight of fission products and 16% actinide wastes,¹⁰¹ i.e., elements heavier than actinium. In addition to lessening the volume of wastes that must be disposed of, spent fuel reprocessing reduces the amounts of transuranic elements in the waste. However, the consequent reduction in waste disposal risk achieved by reprocessing and recycling must be balanced against the new risks entailed in using plutonium in the active fuel cycle and in processing large quantities of radioactive materials.

Transuranic (TRU) Wastes: Transuranic wastes, i.e., wastes containing elements heavier than uranium, result primarily from spent fuel reprocessing and fuel assembly refabrication; very little is generated by the once-through fuel cycle. Transuranic wastes are currently defined as material containing more than 10 nanocuries of TRU activity per gram of material.¹⁰² Because of their long half-lives, TRU wastes must be isolated from the biosphere for time periods similar to those for HLWs, i.e., 10^3 to 10^6 years.¹⁰³ However, problems associated with heat generation and temperature increases are absent, and since TRU wastes are easier to handle than HLWs, the operational demands on disposal systems designed for TRU waste alone would be more modest than those associated with an HLW repository. This means that a special TRU repository could precede the development of an HLW repository due to the elimination of concerns about heating effects.

Low-Level Wastes (LLWs): In contrast to TRU wastes, LLWs are defined as containing less than 10 nanocuries of TRU per gram of material or may be altogether free of TRU activity, but LLWs might have potentially hazardous amounts of fission products. LLWs are generated in all phases of the nuclear fuel cycle and other operations that utilize radioisotopes. Disposal of LLWs consists of burial in shallow pits; 14×10^6 of commercial and 46×10^6 metric tons of defense LLWs have already been buried.¹⁰⁰

Uranium Tailings: The residues from the mining and milling of uranium also contain low concentrations of naturally occurring radioactive elements. Uranium mill tailings are generated in large volumes, and 130×10^6 metric

tons are now stored uncovered at various sites of mining and milling operations.¹⁰⁰ Because tailings emit the carcinogenic gas radon-222, the stabilization of these piles from water and erosion is of great concern. According to Victor Gilinsky, nuclear physicist and NRC member, uranium tailings could become the dominant source of radiation exposure to the public from the nuclear fuel cycle, unless the tailings are isolated from the atmosphere.¹⁰⁴

Decommissioning/Decontamination (D/D) Wastes: The final category of nuclear wastes involves those generated upon the retirement of a nuclear facility due to obsolescence or adverse economics of continued operation. D/D is potentially a source of large quantities of radioactive wastes. The volume of LLW (no TRU) that might result after the shutdown of an 1160 MW reactor could vary from 60 m³ under a mothballing procedure, to 23,000 m³ for complete removal/dismantling.⁹⁸ Until retired nuclear facilities and land are decontaminated, such facilities and land must be considered and treated as waste storage sites.

Disposal Technologies and Associated Risks

Many techniques for the disposal of radioactive wastes are under investigation. They include deep geological burial; seabed, ice sheet, and extraterrestrial disposal; transmutation; and disposal by rock melting in deep mined cavities, and in deep drilled holes. Some of these technologies are suitable for one or several types of radioactive waste. However, because some important decisions concerning nuclear energy, namely, spent fuel reprocessing and use of the breeder reactor, have been deferred indefinitely, work is continuing on methods to dispose of all kinds of wastes. Furthermore, many methods need to be researched and developed as a hedge against any of them proving to be technically impossible or environmentally undesirable. Each of the disposal techniques mentioned above and associated advantages, disadvantages, and risks are briefly discussed below.

Burial in Deep Geological Formations: Burial of radioactive wastes in deep geological formations or repositories is the most advocated technique. Of all the candidate rock formations under consideration, e.g., anhydrite (calcium sulfate), granite, shale, flood basalt, tuffs, and unsaturated rocks, rock salt and salt domes are the most studied and the foremost candidates. Rock salt has the favorable characteristic of high pressure. In addition, salt is abundant throughout the United States and salt mining is highly developed. Salt domes are located throughout the Gulf Coast region, and these geological formations are presently being used for the Strategic Petroleum Reserve. Extensive testing of rock salt as a repository medium was made in an abandoned salt mine near Lyons, Kansas, from 1965-1967. The DOE is planning to construct a new salt repository near Carlsbad, N.M., for disposal of TRU military waste and for experimentation with other types of waste.¹⁰⁵ The project, called the Waste Isolation Pilot Plant (WIPP) is scheduled to begin operation in 1985. The costs associated with the waste burial in geologic repositories, the least expensive of any waste disposal technology, are approximately \$50/kg of spent fuel.¹⁰¹

The form of the waste is an important consideration in the success of geological burial. Because of the corrosive nature of groundwater, any container the wastes are placed in will lose its integrity after about 100

years, leaving the wastes themselves subject to groundwater leaching action. Consequently, the wastes must be cast into forms of extremely low solubility and high resistance to the effects of radiation. Liquid wastes must first be solidified and then fixed into a borosilicate glass, ceramic, oxide, or silicate mineral form.

Before large-scale disposal of radioactive wastes in geological repositories can take place, several issues must still be resolved. First, the scientific community is not totally convinced that geological burial is completely safe, because accurate prediction of the fate of buried radionuclides over several hundred to millions of years is unprecedented and risky.¹⁰¹ There is little experience with the long-term effects of heat on rock mechanics, and little information on the leaching and transport of wastes by groundwater and on the tectonic history of the host medium. Second, test facilities are needed in order to fill these gaps in knowledge. Third, criteria for repository site locations must be established so that major population centers and minable resources can be sufficiently isolated from waste repositories.

Seabed Disposal: Disposal of radioactive wastes at sea involves either implanting waste canisters on the ocean floor by means of a free-fall penetrometer (an aerodynamically stable body with a pointed nose and stabilizing fins) or using remotely operated machinery on the ocean floor to drill the holes, emplace the waste canisters, and cover them up.¹⁰¹ The advantages of this waste disposal technology are its remoteness from society, isolation from the biosphere, high heat sink capability, and a large available area. Furthermore, the problem of gaining access and control of terrestrial sites is avoided by using the ocean as a burial site.

The disadvantages involved with seabed disposal include the difficulties of guaranteeing the integrity of the waste container given the corrosiveness of sea water, of monitoring and retrieving the waste canisters, and of the extra ocean transportation and port facilities required. Finally, the issue of the political ramifications of the so-called London Convention must be addressed. This treaty addresses the issue of defining high-level radioactive matter unsuitable for dumping at sea and indicates that wastes should be emplaced only if they have a relatively low radioactive level.¹⁰⁶ Further research is needed to resolve these uncertainties surrounding seabed disposal as well as to estimate the costs of disposal of various candidate wastes.

Ice Sheet and Extraterrestrial Disposal: While these methods have been considered practical, environmental and political considerations will make them rather unlikely candidates.

Transmutation: Transmutation is a process whereby long-lived fission products are converted to shorter lived nuclides by bombarding the nuclei with photons or other subatomic particles. This conversion greatly reduces the long-term risk associated with many fission products and shortens the time over which isolation of the wastes must be assured. Spent fuel reprocessing and plutonium recycling are a necessity in order to partition the wastes for transmutation. Transmutation is accomplished by placing partitioned wastes in any device producing subatomic particles (e.g., accelerators, cyclotrons, or reactors). Commercial nuclear power reactors are favored as transmutation devices because of their demonstrated technology and their availability in large enough numbers to handle the materials being recycled.¹⁰¹

The advantages of transmutation include total irreversibility and simplified disposal, since the transmuted wastes need not be isolated for as long as the original fission products. The disadvantage of transmutation lies mainly in the need to develop the technology to perform the process. A practical partitioning process with a very high degree of recovery of actinides and other long-lived fission products must be developed in addition to an extensive compilation of neutron cross sections for the actinides and fission products. Finally, more research is needed on the reactors and/or accelerators performing transmutation. It is estimated that ten or more years worth of feasibility studies must be performed.¹⁰¹

Disposal by Rock Melting in Deep Mined Cavities and in Deep Drilled Holes: Although these methods have unique advantages and problems, they are essentially variations on the use of geological formations as repositories. Research is needed to determine their environmental acceptability and cost.

4 HAZARD CHARACTERISTICS

The environmental impact of solid wastes from energy-related activities cannot be assessed adequately without consideration of the hazardous characteristics of these wastes. In this section, we explore the hazard potentials of selected waste streams by considering such factors as leachate composition, toxic substances, and biological effects.

The EPA has designated numerous wastes from the industrial sector as potentially hazardous to human health and the environment. For example, the ammonia still lime sludges from the coking industry, and slop oil, API separator bottom, and dissolved air flotation (DAF) float produced in petroleum refineries are considered potentially hazardous and would be subject to appropriate management requirements under subtitle C of the RCRA. In this section, we identify energy-related waste streams that may be closely related to industrial hazardous wastes.

4.1 COAL UTILIZATION WASTES

4.1.1 Ash from Coal Combustion

Trace Elements. Generally, the soluble matter in coal ash includes iron, nickel, and zinc sulfates in the parts per thousand range, as well as trace quantities of chromium, copper, lead, arsenic, and cadmium.¹⁰⁷ The largest quantity of soluble matter, however, consists of calcium, magnesium, potassium, and sodium sulfates, and anhydrous oxides, which raise TDS levels but are not considered toxic pollutants. Flyash typically contains higher concentrations of soluble material than does bottom ash, usually in the range of several percent. Table 4.1 presents recent data on concentrations of various pollutants, including some priority pollutants, found in ash pond liquors and sluicing waters.⁵⁴

The equilibrium concentrations of various trace elements in ash leachates from five different power plants are compared in Table 4.2 with the various water quality standards.⁹⁹ Concentrations that exceed one or more of the standards are indicated by a footnote. Note that the concentrations of arsenic, barium, boron, chromium, mercury, molybdenum, and selenium exceeded one or more of the water quality criteria at one or more of the power plants. The pH of the leachates studied ranged from 8.2 to 12.5.

The American Society for Testing Materials (ASTM) recently evaluated the toxicity potential of trace elements leached from various fossil fuel combustion wastes, including coal fly ash, bottom ash, boiler slag, and fluidized bed combustion residues.¹⁰⁸ Each of the waste materials was tested with three extraction procedures: ASTM Methods A and B, and the EPA's proposed Extraction Procedure (EP). The leachates extracted under each method were analyzed for pH, calcium, and metals including arsenic, barium, cadmium, chromium, mercury, lead, selenium, and silver. Eighteen laboratories participated in the program. The study concluded that (Ref. 108, p. 15)

Table 4.1 Composition of Ash Pond Liquors and Sluicing Waters (mg/L)

Component	Flyash Pond	Bottom Ash Pond	Ash Pond	Ash Pond Overflow	Ash Pond Overflow	Flyash Sluicing Water	Bottom Ash Sluicing Water
Aluminum (Al)	3.6-8.8	0.5-8.0	0.4	0.011-5.3	--	0.57-0.92	1.69-2.31
Antimony (Sb) ^a	--	--	0.007-0.012	--	.003-.03	0.004-0.021	0.034-0.41
Arsenic (As) ^a	<0.005-0.023	0.002-0.015	0.006-<0.12	--	0.003-.02	<0.0001-0.001	0.004-0.008
Barium (Ba)	0.2-0.4	<0.10-0.30	<0.01-<3.0	--	<.3	<0.5-<0.6	<0.5-0.5
Beryllium (Be)	<0.01-0.02	<0.01	<0.002	--	0.001-0.003	<0.002-0.003	0.001-0.002
Boron (B)	--	--	1.0-24.67	--	0.233-1.03	0.5-2.41	0.25-2.46
Cadmium (Cd)	0.023-0.052	<0.001-0.002	0.005-<0.025	--	0.0001-0.04	0.001-<0.002	0.001-0.004
Calcium (Ca)	94-180	23-67	<200-563	--	--	46-114	45-785
Chlorine (Cl)	5-14	5-15	85-189	1-2415	--	14.9-17.2	15.7-27.7
Chromium (Cr) ^a	0.012-0.17	<0.005-0.023	<0.02	0.0005-0.139	<0.0002-0.004	<0.05	<0.05
Cobalt (Co)	--	--	<0.001-<0.7	--	--	<0.003	0.004-0.005
Copper (Cu) ^a	0.16-0.45	<0.01-0.14	<0.003-0.05	0.005-0.06	<0.004-0.09	0.008-0.022	0.011-0.024
Fluorine (F)	--	--	1-14.85	--	0.35-10.4	0.023-0.70	0.25-16.2
Germanium (Ge)	--	--	--	--	0.02-<0.1	--	--
Iron (Fe)	0.33-6.6	1.7-11	<0.05-<0.2	0.001-2.894	--	0.01-1.38	0.31-2.25
Lead (Pb) ^a	<0.01-0.2	<0.01-0.031	0.0028-0.08	--	--	0.006-0.025	0.007-0.024
Lithium (Li)	--	--	0.4-0.08	--	--	--	--
Magnesium (Mg)	9.4-20	0.3-9.3	0.1-102	6-156	--	15.7-24.1	25.8-67.7
Manganese (Mn)	0.29-0.63	0.07-0.26	<0.005-0.49	0.0002-0.102	0.004-1.1	0.016-0.096	0.055-0.77
Mercury (Hg) ^a	<0.0002-0.0006	<0.0002-0.026	<0.001	0.0002	<0.001-<.0022	<0.0004-<0.0005	<0.0004-0.0005
Molybdenum (Mo)	--	--	0.030-0.49	--	0.004-0.10	<0.012-0.015	0.016-0.055
Phosphorus (P)	<0.01-0.06	<0.01-0.23	--	0.1-0.41	--	--	--
Potassium (K)	--	--	6-6.7	--	--	--	--

Table 4.1 (Cont'd)

Component	Flyash Pond	Bottom Ash Pond	Ash Pond	Ash Pond Overflow	Ash Pond Overflow	Flyash Sluicing Water	Bottom Ash Sluicing Water
Selenium (Se) ^a	<0.001-0.004	<0.001-0.004	0.021-<0.05	---	0.003-0.015	0.001-0.004	0.001-0.031
Silicon (Si)	10-15	6.1-8.6	1-51	---	---	---	---
Silver (Ag) ^a	<0.01-0.01	<0.01	<0.02	---	---	<0.0002	<0.0002-0.0004
Sodium (Na)	---	---	170-294	3-982	---	---	---
Strontium (Sr)	---	---	0.8	---	---	---	---
Tantalum (Ta)	---	---	<0.02	---	---	---	---
Titanium (Ti)	---	---	<0.02	---	<0.1	<0.1-0.1	---
Uranium (U)	---	---	---	---	---	0.004-0.005	0.003-0.005
Vanadium (V)	---	---	<0.02	---	<0.1-0.2	<0.005-0.072	<0.005-0.192
Zinc (Zn) ^a	1.1-2.7	0.02-0.16	<0.022-0.09	0.00013-0.17	0.02-2.5	0.008-0.028	0.013-0.075
Zirconium (Zr)	---	---	<0.07	---	---	---	---
Total Hardness (CaCO ₃)	185-520	---	---	25-736	---	---	---
Total Alkalinity (as CaCO ₃)	---	30-160	---	2-443.7	---	---	---
pH	3.6-6.3	4.1-7.9	8.47	---	---	---	---
Dissolved Solids	141-820	69-404	1100-3335	40-3328	---	---	---
Suspended Solids	2-256	5-657	---	1-100	---	---	---
HCO ₃	---	---	31.0	---	---	---	---
SO ₄	---	---	580-2300	2.2-527	---	---	---

^aOn EPA list of 65 priority pollutants.

Source: Ref. 54.

Table 4.2 Equilibrium Concentrations of Trace Elements in Coal Ash Leachate

Component	Station Number					Water Quality Criteria ^a		
	1	2	3	4	5	Surface Water FWPCA (mg/L)	Irrigation FWPCA (mg/L)	Public Water Supply Intake EPA (mg/L)
Bottom Ash (wt %)	20	20	20	50	100			
Precipitator Ash (wt %)	80	80	80	50	---			
pH	12.5	9.5	12.2	12.0	8.2			
Element (ppm)								
Sb	0.006	0.018	0.033	0.022	0.0087	---	---	---
As	<0.002	0.084 ^b	0.015	0.072 ^b	0.006	0.05	1.0	0.1
Ba	40 ^b	<0.3	<0.3	<0.3	<0.3	1.0	---	---
Be	0.003	0.00064	0.0007	0.001	0.00026	---	---	---
B	0.03	16.9 ^b	0.21	1.1 ^b	0.048	1.0	0.75	1.0
Cd	<0.001	0.0025	<0.01	<0.001	0.0011	0.01	0.005	0.01
Cr	<0.001	0.21 ^b	0.11 ^b	1.0 ^b	0.014	0.05	5.0	0.05
F	2.3	1.4	2.0	17.3	1.4	---	---	---
Ge	<0.01	<0.01	<0.01	<0.01	<0.01	---	---	---
Hg	0.0006	0.0005	0.015 ^b	0.0003	0.0003	---	---	0.002
Pb	0.0068	0.0027	0.024	0.0043	0.0063	0.05	5.0	0.05
Mn	<0.002	<0.002	<0.002	<0.002	<0.002	0.05	2.0	---
Mo	0.047 ^b	0.052 ^b	0.05	0.69 ^b	0.010 ^b	---	0.005	---
Ni	<0.05	0.015	0.025 ^b	<0.05	0.046	---	0.5	---
Se	0.009	0.0005	0.033 ^b	0.47 ^b	<0.0005	0.01	0.05	0.01
V	<0.1	<0.1	-0.1	<0.2	<0.1	---	10.0	---
Zn	0.038	0.025	0.19	0.005	0.0175	5.0	5.0	5.0
Cu	<0.005	0.031	0.092	0.013	0.015	1.0	0.2	1.0

^aFWPCA = Federal Water Pollution Control Administration.^bConcentration exceeds one or more of the standards.

Source: Ref. 99.

Analytical test methods and extraction procedures have not been developed to the point where testing can lead to reliable statements regarding classification of materials tested under the program with respect to their toxicity.

Nevertheless, the report reveals that, for many of the residues tested, selenium levels were in excess of then proposed EPA limits (i.e., ten times the EPA Interim Proposed Primary Drinking Water Standards). Other average trace metal concentrations that occasionally exceed the proposed limits were arsenic, cadmium, chromium, and lead. None of the residues yielded a leachate containing excessive concentrations of barium, mercury, or silver.

The EPA has determined that, in the petroleum refining industry, the solid wastes including the API separator sludge, dissolved air flotation (DAF) float, slop oil emulsion solids, heat exchanger bundle cleaning sludge and tank bottoms (lead) may pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, disposed of, or otherwise managed¹⁰⁹ (see Sec. 7.2). The wastewater treatment sludges from the electroplating operations (see Sec. 7.3) and the primary zinc smelting and refining operations (see Sec. 7.8) have also been determined to be potentially toxic. These wastes contain significant levels of toxic heavy metals such as lead and chromium. In addition to being toxic, lead has been shown to be potentially carcinogenic and bioaccumulative. Table 4.3 shows the data on the composition of some of these wastes as well as that of bottom ash and fly ash generated from conventional coal combustion. Some of these values for the two types of waste are quite comparable.

Trace Organics. Numerous polycyclic aromatic hydrocarbons have been detected in coal ash (see Table 3.7 in Sec. 3.0), and many chemical species within this class of compounds are considered to be carcinogens. Even in the late 1700's it was recognized that some coal products were carcinogenic, because of the high incidence of scrotal cancer in chimney sweeps working in areas where bituminous coal was used as fuel.

Biological Effects. Limited tests have been conducted to determine the biological effects of coal ashes, and the results indicate that coal ashes can be toxic to certain test animals. Alaire et al.¹¹³ reported that long-term exposure of monkeys and guinea pigs to reaerosolized stack-collected fly ash did not result in pathological changes in the lungs, although light microscopy revealed fly ash in the alveolar macrophage (AM). They did not test the functional integrity of these cells. Aranyi et al.¹¹⁴ demonstrated in vitro that fly ash from conventional coal combustion was cytotoxic to rabbit AMs and that the effect was dependent on particle size. Particles <2 μ m in diameter were more toxic than larger particles. These investigators also found that fly ash coated with heavy metals was much more cytotoxic than uncoated fly ash. More recently, Wehner et al.¹¹⁵ reported mild toxicity in hamster lungs following exposure to fly ash both with and without nickel enrichment. Minimal histological changes were observed after acute (1 exposure of 6 hours) or subchronic (6 hour/day, 5 days a week for two months) exposure. Fly ash was observed in AMs as long as two months after completion of the subchronic exposure. Functional tests on the AMs were not performed. Fisher et al.¹¹⁶ reported that short-term exposure of mice to reaerosolized, mutagenic stack-collected fly ash resulted in decreased AM function, whereas longer exposure to less mutagenic fly ash did not.

Table 4.3 Levels of Chromium and Lead in Solid Residues and Leachates from Coal Combustion and Selected Industries

Process	Waste Composition (mg/kg)		Leachate Composition (mg/L)	
	Lead	Chromium	Lead	Chromium
Petroleum Refining^a				
API sludge	0.25-1290	0.10-6790	--	1.9
DAF float	2.3-1250	28-260	--	3.3
Slop oil emulsion solids	0.25-580	1750	--	--
Bundle sludge	--	310-311	--	--
Tank bottoms	158-1420	--	--	--
Electroplating^a				
Wastewater treatment sludge (segregated zinc)	--	200	--	1.22
Primary Zinc Smelting and Refining^a				
Acid plant blowdown sludge				
Electrolytic	--	--	1.0-2.1	--
Pyrometallurgical plant	--	--	1.3	--
Anode slimes/sludges	--	--	2.0	--
Conventional Coal Combustion^b				
Flyash	4-130	3.7-300	1.6	0.001-1.0
Bottom ash	1-21	3.4-270	--	--
Water Quality Criteria				
Surface water (FWPCA)	--	--	0.05	0.05
Irrigation (FWPCA)	--	--	5.0	5.0
Public water supply intake	--	--	0.05	0.05

^aSources: Refs. 63 and 110.

^bSources: Refs. 111 and 112.

A number of reports have been published on the mutagenicity of coal flyash.¹¹⁷⁻¹¹⁹ Reports from two different groups sampling at seven power plants have concluded that although fly ash leaving the stack to the atmosphere is mutagenic in the Ames Salmonella reversion assay, the ash that is collected as solid waste in the electrostatic precipitator is not mutagenic in this assay. Bonnell and Schilling¹²⁰ also reported no mutagenic activity in fly ash collected in the electrostatic precipitator hoppers from a large British coal-fired power plant. Fisher et al.¹¹⁸ concluded that if there is any mutagenic activity in the collected ash, it must be less than 0.2% of that

in the material emitted to the air. Apparently the mutagenic activity is due to compounds volatilized or formed during combustion and adsorbed on the surface of fine particles--which present the most surface area--as the effluent stream cools. This presumably takes place after the exhaust gases pass through the precipitator. They also conclude that use of low temperature precipitators could lead to contamination of the bulk of the collected flyash with mutagens and recommended high temperature, high efficiency collection of particles followed by cooling of the effluent stream and separate collection of the organic matter. The latter would yield a hazardous solid waste that is much smaller in volume.

Lee et al.¹²¹ reported finding dimethyl and monomethyl sulfate in the particles emitted from a soaker type coal fired heating plant and a large coal-fired power plant. Lesser quantities would be expected in the collected ash. However, there is some question concerning the general applicability of the results.

These studies indicate that there is no risk of mutagenic activity in fly ash collected in current ESP hoppers of large coal-fired utilities. The limited number of plants studied, however, cannot allow this conclusion to be drawn generally with much confidence. Much more testing is needed, and, furthermore, it is particularly important that testing be done when flue gases are apt to be cooled before particle collection. This would include some industrial boilers and facilities with bag houses. The effect of wet scrubbing on mutagenic activity in collected ash must also be evaluated. Finally, the findings of mutagenic activity in ash released to the air may lead to the need for new air pollution control measures, and it is thus necessary to anticipate the potential of collecting mutagenic ash.

4.1.2 Ash and Char from Coal Conversion

Trace Elements. Griffin et al., have conducted a study on the solubility and toxicity of trace elements in coal-related solid wastes.¹²² As part of that study, the chemical composition of coal ash and slurry supernatant solutions of the ash from the Lurgi Gasification process were investigated. The results are presented in Table 4.4. Of the approximately 60 chemical constituents measured in the raw Lurgi ash, 16 were found to be in forms soluble enough to exceed recommended water quality levels in some samples at pH values between three and eight. Table 4.5 lists these 16 constituents. Nine constituents (B, Ca, Cd, K, Mn, NH_4 , Pb, SO_4 and Sb) exceeded the recommended levels in all Lurgi ash solutions over the pH range of three to nine. The authors concluded that these nine constituents pose the highest potential pollution hazard.

Tamura and Boegly⁶³ recently presented the results of research on the impacts of land disposal of coal conversion ash. Included are the results of the batch leaching tests using the EPA Extraction Procedures. Ash samples from several gasification/liquefaction processes were tested. Table 4.6 presents the leaching results along with proposed RCRA criteria (100 times the drinking water standards). None of the wastes listed exceeded the criteria, and of the elements considered, cadmium in one sample came closest to exceeding the RCRA standard.

Table 4.4. Chemical Composition of Lurgi Ash and Slurry Supernatant Solutions of the Ash from an Illinois No.6 Coal at Several pH Levels

Constituents	Chemical Composition of 10% Slurry Supernatant (mg/L)								Recommended Water Levels (mg/L)	Solid Ash Content (mg/kg)
	Air Atmosphere				Argon Atmosphere					
pH	7.55 ^a	5.10	3.82	2.68	8.82 ^a	7.20	5.35	3.79	6.0-9.0	-
Ag	-	-	-	-	-	-	-	-	0.05	<0.4
Al	ND ^b	2	14	132	ND	ND	ND	92	0.1	108,121
Au	-	-	-	-	-	-	-	-	-	0.001
As	ND	ND	ND	ND	ND	ND	ND	ND	0.1	3
B	4.0	4.5	4.5	5.5	4.5	3.0	4.5	8.0	0.75	355
Ba	ND	ND	ND	ND	ND	ND	ND	ND	1.0	950
Be	ND	ND	0.01	0.03	ND	ND	ND	0.01	0.1	12
Br	-	-	-	-	-	-	-	-	-	<1.0
Ca	290	480	400	570	440	370	430	500	50	16,652
Cd	0.02	0.03	0.03	0.06	0.01	ND	0.02	0.05	0.01	<1.6
Ce	-	-	-	-	-	-	-	-	-	140
Cl	ND	ND	ND	ND	ND	ND	ND	ND	250	100
COD ^c	2	2	2	81	2	2	16	140	50	-
MCE ^d	28	28	0	23	10	3	6	4	-	-
Cr	ND	0.02	0.05	0.12	0.01	0.01	0.06	0.16	0.05	212
Co	ND	0.05	0.08	0.19	ND	0 ND	ND	0.17	0.05	34
Cu	0.01	0.02	0.13	0.73	0.01	0.05	0.01	0.05	0.2	57
Cs	-	-	-	-	-	-	-	-	-	11
Eu	-	-	-	-	-	-	-	-	-	1.9
F	0.31	0.30	0.09	0.04	0.51	0.34	0.16	0.02	1.0	<10
Fe ^{Total}	0.06	0.19	0.24	560	0.06	0.11	101	880	0.3	143,780
Ga ⁺²	-	-	-	-	-	-	-	-	-	26
Fe	0.03	0.11	0.10	533	0.13	0.05	110	865	-	-
Ge	-	-	-	-	-	-	-	-	-	7.0

Table 4.4 (Cont'd)

Constituents	Chemical Composition of 10% Slurry Supernatant (mg/L)								Recommended Water Levels (mg/L)	Solid Ash Content (mg/kg)
	Air Atmosphere				Argon Atmosphere					
Hf	-	-	-	-	-	-	-	-	-	6.1
Hg	ND	ND	ND	ND	ND	ND	ND	ND	0.0002	0.5
K	42	49	51	25	39	43	48	61	5	14,611
La	-	-	-	-	-	-	-	-	-	47
Li	1.8	1.9	2.0	2.0	1.6	1.8	1.9	2.1	2.5	42
Lu	-	-	-	-	-	-	-	-	-	1.5
Mg	10.5	14	15	22	9.5	11	13.5	23	50	3,739
Mn	0.45	1.94	2.7	3.8	0.11	0.90	2.3	3.7	0.05	1,859
Mo	ND	ND	ND	ND	ND	ND	ND	ND	0.01	30
Na	34	37	38	40	32	37	37	40	20 ^e	1,929
NH ₄	17	8	12	11	10	10	10	17	0.02	-
Ni	0.03	0.13	0.23	0.50	ND	0.04	0.14	0.42	1	89
Pb	0.1	0.1	0.1	0.2	ND	ND	0.1	0.2	0.03	45
P	-	-	-	-	-	-	-	-	-	87
PO ₄	ND	ND	ND	ND	ND	ND	ND	ND	0.05	-
S _{Total}	-	-	-	-	-	-	-	-	-	6,100
Rb ₂	-	-	-	-	-	-	-	-	-	162
S	ND	ND	ND	ND	ND	ND	ND	ND	0.002	1,500
Sb	0.2	0.2	0.3	0.6	0.3	0.3	0.3	0.3	0.05	4.2
SO ₄	820	943	8089	338	730	735	700	710	250	8,100
Sc	-	-	-	-	-	-	-	-	-	29
Se	-	-	-	-	-	-	-	-	0.01	<1
Si	5	29	60	130	4	9	27	120	-	229,946
Sm	-	-	-	-	-	-	-	-	-	10
Sn	ND	ND	ND	ND	ND	ND	ND	ND	-	-

Table 4.4 (Cont'd)

Constituents	Chemical Composition of 10% Slurry Supernatant (mg/L)								Recommended Water Levels (mg/L)	Solid Ash Content (mg/kg)
	Air Atmosphere				Argon Atmosphere					
Sr	1.8	1.9	2.1	2.9	1.5	1.7	1.9	2.6	50	370
Ta	-	-	-	-	-	-	-	-	-	1.1
Te	ND	ND	ND	ND	ND	ND	ND	ND	-	-
Th	-	-	-	-	-	-	-	-	-	21
Ti	ND	ND	ND	ND	ND	ND	ND	ND	-	6,295
Tl	ND	ND	ND	ND	ND	ND	ND	ND	-	4.6
U	-	-	-	-	-	-	-	-	-	17
V	-	-	-	-	-	-	-	-	0.1	184
W	-	-	-	-	-	-	-	-	-	1.5
Yb	-	-	-	-	-	-	-	-	-	2.9
Zn	.12	5.5	12	17	.01	.11	6.5	20	.2	400
Zr	-	-	-	-	-	-	-	-	-	170
Conductivity (μmho/cm)	1.17	1.50	1.95	5.60	1.20	1.39	1.80	5.20	18	-
Electrode potential (mv)	+233	+246	+407	+349	+109	+161	+102	+243	-	-

^aNatural pH of supernatant.^bNot detectable.^cChemical oxygen demand.^dMethylene chloride extractable.^eFor low Na diet; 250 ppm for taste.

Source: Ref. 121.

Table 4.5 Elements Exceeding Recommended Water Quality Levels

Constituent	Lurgi Ash Solubility	
	pH 3 (mg/L)	pH 8 (mg/L)
Al	132	0.5
B ^a	5.5	4.0
Ca ^a	570	290
Cd ^a	0.06	0.02
Cr	0.12	0.02
Co	0.19	0.10
Cu	0.75	0.01
F	-	-
Fe	560	0.06
Ka	26	42
Mn ^a	3.80	0.45
NH ₄ ^a	11	17
Pb ^a	0.20	0.10
SO ₄ ^a	338	820
Sb ^a	0.60	0.20
Zn	17.00	0.12

^aHighest pollution potential

Source: Ref. 122.

The EPA has determined that certain solid waste effluents from the petroleum refining industry, electroplating industry, and primary zinc smelting and refining industries pose a potential hazard to human health or the environment due to significant levels of the toxic heavy metals lead and chromium (see Sec. 7 of this report). Table 4.7 lists the composition of some industrial hazardous wastes and that of coal ash generated from specific coal conversion processes.

Biological Effects. A considerable amount of information has been accumulated in recent years showing that many organic compounds and trace elements contained in coal ash from conversion processes can produce a wide range of toxic effects. The potential effects of different organic contaminants are of major concern.

Chemical and bioassay tests were conducted on gasifier ash and cyclone dust from a Wellman-Galusha low-Btu coal gasification plant.¹²³ Tables 4.8

Table 4.6 EPA-EP Leaching Results for Five Gasification/
Liquefaction Solid Wastes (ppb)

Element	Waste 1	Waste 2	Waste 3	Waste 4	Waste 5	RCRA Standards ^a
Arsenic	0.27	0.06	<1	<1	0.53	5000
Barium	<200	<500	20	80	<500	10000
Cadmium	0.054	0.97	<1	28	3.4	1000
Chromium	1.6	0.44	<5	<5	0.13	5000
Copper	2.7	3.7	10	10	0.94	b
Lead	<0.3	0.26	<10	<10	1.6	5000
Mercury	0.64	0.03	<1	1	0.191	200
Selenium	<5	2	<1	<1	<1	1000
Silver	<0.03	<0.03	<2	<2	0.07	5000
Nickel	281	219	30	540	758	b
Zinc	63	10	13	2,240	385	b

^aRCRA standards were 100 times the interim primary drinking water standards (5-19-80 regulations).

^bNo primary standards have been established for these elements.

Source: Ref. 63.

and 4.9 present trace elements and organics that were found in potentially hazardous constituents in ash and ash leachate. The major contributors to the hazard potential of ash discharge are trace elements, including barium, chromium, iron, lithium, and nickel. The major contributors for the ash leachate are the unidentified organics. The bioassay health tests (Ames, RAM, and Rodent Acute Toxicity) indicate a low hazard potential. The only ecological bioassay test conducted on the gasifier ash was the soil microcosm test. Although the results from this test cannot be interpreted in terms of low, medium, or high hazard potential, the test did indicate that the gasifier ash was clearly more toxic than the cyclone dust. Tables 4.10 and 4.11 list the compounds found in potentially hazardous concentrations in the cyclone dust and cyclone dust leachates. The major contributors according to the report are the organics, arsenic, barium, chromium, iron, lead, lithium, manganese, nickel, and selenium.

Many of the inorganic components of coal ash are known to be toxic to aquatic biota, and the presence of these compounds in water leaching from coal ash may be a potential hazard to aquatic biota.¹²⁴ Table 4.12 presents acute toxicities to *Daphnia magna* in terms of 48-hr LC₅₀ for three coal ash leachates.¹²⁵ *Daphnia magna* is very sensitive to pH, with a 48-hr LC₅₀ for acidity at pH 6.4 and for alkalinity at pH 10.3. This sensitivity is reflected in the toxicities of the more acidic Illinois #5 and #6 leachate fractions. Probable interactants are also the high trace metal concentrations associated with the more acidic fractions. Many of these trace metals are present in the leachates at concentrations that have been found to be toxic to *Daphnia magna* and other freshwater biota.

Table 4.7 Levels of Chromium and Lead in Solid Residues and Leachates from Coal Conversion and from Selected Industries

Process	Waste Composition (mg/kg)		Leachate Composition (mg/L)	
	Lead	Chromium	Lead	Chromium
Petroleum Refinery^a				
API sludge	0.25-1290	0.10-6790	--	1.9
DAF float	0.23-1250	28-260	--	3.3
Slop oil emulsion solids	0.25-580	1750	--	--
Bundle sludge	--	310-311	--	--
Tank bottoms	158-1420	--	--	--
Electroplating^a				
Wastewater treatment Sludge (segregated zinc)	--	200	--	1.22
Primary Zinc Smelting and Refining^a				
Acid plant blowdown sludge				
Electrolytic	--	--	1.0-2.1	--
Pyrometallurgical plant	--	--	1.3	--
Anode slimes/sludges	--	--	2.0	--
Coal Conversion Ash ^b	40-220	78-800	0.1-0.2	0.02-0.12

^aSources: Refs. 109 and 110.

^bSources: Refs. 53 and 122.

The Rosebud leachate had the highest pH and the lowest toxicity of the three. The first three column volumes leached from the Rosebud ash had pH levels ranging from 6.8 to 9.5 and were nontoxic. The fourth column volume had a pH of 10 and a 48-hr LC₅₀ at a dilution of 49%. Since the 48-hr LC₅₀ for alkaline pH is 10.3 and the Rosebud leachate had the lowest concentration of heavy metals of the three leachates, the toxicity of the leachates was probably caused by their high pH.¹²⁵

The Illinois #5 leachates had pH levels ranging from 4.5 to 5.6 and had heavy metals concentrations between those of the Rosebud and the Illinois #6 leachates. These conditions were reflected in their intermediate toxicities compared with the other leachates.

Plant materials would most likely be exposed to leachates in groundwater, either during revegetation of the landfill site or even perhaps through the use of groundwater for irrigation. Soil and groundwater variables at specific sites will play important roles in the actual hazard potential of

Table 4.8 Chemical and Bioassay Test Results for Gasification Ash

Discharge Severity Range ^a	Compounds Found from Chemical Analysis		Bioassay Test Results	
	Health	Ecological		
10 ³ -10 ⁴	-	-	<u>Health</u>	
10 ² -10 ³	Ba, Cr, Fe, Li, Mn, Ni	-	Ames (RAM) ^b	Negative <1000µL/ml of culture
10-10 ²	Fused polycyclic hydrocarbons ^a , Be, Co, Cu, Pb, Se, Th, V, Zr	Cu, Fe, Ni	Rodent Acute Toxicity (LD ₅₀)	<10 g/kg rat
1-10	Al, As, Bi, Cd, Ca, Hf, Mg, Si, Ag, Sr, Ti, Y	Alkenes, cyclic alkenes and dienes, aromatic amines and diamines, ring substituted aromatics, nitrophenols, ^d phthalate esters, Al, Ba, Cd, Cr, Pb, Li, Mn, Ti, V	<u>Ecological</u>	Soil Microcosm ^c

^aDischarge severity is defined as the ratio of a pollutant's concentration in a stream to its Discharge Multimedia Environmental Goal (DMEG) value.

^bRAM: rabbit alveolar macrophages.

^cThe soil microcosm test results cannot be interpreted in terms of a high, medium, or low potential for hazard, but the gasifier ash was clearly more toxic than the cyclone dust.

^dThese categories of organic compounds are the worst case compounds that provide the largest discharge severity for the 38 µg/g of unidentified organics in the ash. The worst case compounds corresponding to the categories are listed below:

<u>Category</u>	<u>Compound</u>
Fused polycyclic hydrocarbons	7, 12-Dimethylbenz(a)anthracene
Alkenes, cyclic alkenes and dienes	Cyclopentadiene
Aromatic amines and diamines	Aminonaphthalenes
Ring substituted aromatics	Dibromobenzene

Source: Ref. 123.

Table 4.9 Chemical and Bioassay Test Results for Gasification Ash Leachate

Discharge Severity Range	Compounds Found from Chemical Analysis		Bioassay Test Results	
	Health	Ecological		
10 ³ -10 ⁴	Fused polycyclic hydrocarbons ^a	-	<u>Health</u> Ames	Negative
10 ² -10 ³	-	Alkenes, cyclic alkenes, dienes, aromatic amines, diamines, and nitrophenols ^a	WI-38 (EC ₅₀)	<600 µL/ml of culture
10-10 ²	-	phthalate esters, Zn	Rodent Acute Toxicity (LD ₅₀)	< 10 g/kg rat
1-10	-	Cd, Ag	<u>Ecological</u> Soil Microcosm ^b	

^aDischarge severity is defined as the ratio of a pollutant's concentration in a stream to its Discharge Multimedia Environmental Goal (DMEG) value.

^bRAM: rabbit alveolar macrophages.

^cThe soil microcosm test results cannot be interpreted in terms of a high, medium, or low potential for hazard, but the gasifier ash was clearly more toxic than the cyclone dust.

^dThese categories of organic compounds are the worst case compounds that provide the largest discharge severity for the 38 µg/g of unidentified organics in the ash.

The worst case compounds corresponding to the categories are listed below:

<u>Category</u>	<u>Compound</u>
Fused polycyclic hydrocarbons	7, 12-Dimethylbenz(a)anthracene
Alkenes, cyclic alkenes and dienes	Cyclopentadiene
Aromatic amines and diamines	Aminonaphthalenes
Ring substituted aromatics	Dibromobenzene

Source: Ref. 123.

Table 4.10 Chemical and Bioassay Test Results for Gasification Cyclone Dust

Discharge Severity Range	Compounds Found from Chemical Analysis		Bioassay Test Results	
	Health	Ecological		
10 ³ -10 ⁴	Mn	-	<u>Health</u>	
10 ² -10 ³	Fused Polycyclic Hydrocarbons ^a , As, Ba, Cr, Fe, Pb, Li, Mi, Cu, Fe, Ni Se	-	Ames Cytotoxicity (RAM)	Negative <1000µL/ml of culture <10 g/kg rat
10-10 ²	Be, Cd, Ag, Th, V, Zn	Alkenes, Cyclic Alkenes Dienes, Aromatic, Amines Diamines, Ring, Substi- tuted Aromatics, Nitro- phenols ^a , Cd, Fe, Pb, Mn, Ni, Zn	Rodent Acute Toxicity (LD ₅₀) <u>Ecological</u> Soil Microcosm ^b	
1-10	Al, Sb, Ca, Co, Cu, F, Ga, Hf, Mg, Hg, Si, Sr, Ti, Y, Zr	Phthalate Esters, Al, Sb, As, Ba, Cr, Cu, Li, Mg, Hg, Se, Ti, V		

^aThese categories of organic compounds are the worst case compounds that provide the largest discharge severity for the 622 µg/g of unidentified organics in cyclone dust.

The worst case compounds and their corresponding categories are listed below:

<u>Category</u>	<u>Compound</u>
Fused polycyclic hydrocarbons	7, 12-Dimethylbenz(a)anthracene
alkenes, cyclic alkenes and dienes	Dicyclopentadiene
aromatic amines and diamines	Aminonaphthalenes
ring substituted aromatics	Dibromobenzene
nitrophenols	Dinitrophenols

^bThe soil microcosm test results cannot be interpreted in terms of a high, medium, or low potential for hazard but the cyclone dust was clearly more toxic than gasifier ash.

Source: Ref. 123

Table 4.11 Chemical and Bioassay Test Results for Gasification Cyclone Dust Leachate

Discharge Severity Range	Compounds Found from Chemical Analysis		Bioassay Test Results	
	Health	Ecological		
10 ² -10 ³	Fused polycyclic hydrocarbons ^a	Mn, Zn	Ames	Negative
10-10 ²	Mn	alkenes, cyclic alkenes, dienes nitrophenols, ^a Pb	Cytotoxicity (WI-38)	<500µL/ml of culture
1-10	Pb, Li	Al, Cd, Co, Cu, Fe, Li	Rodent Acute Toxicity	NA ^b
			Soil Microcosm	NA

^aThe 5,400 µg/g of unidentified organics was assumed to contain the worst case compounds that provide the largest discharge severity. The worst case compounds and their corresponding categories are listed below:

<u>Category</u>	<u>Compound</u>
Fused polycyclic hydrocarbons	7, 12- 12-Dimethylbenz(a)anthracene
alkenes, cyclic alkenes and dienes	Dicyclopentadiene
nitrophenolsnes and diamines	Dinitrophenolsnes

^bNA - test was not applied

Source: Ref. 123.

Table 4.12 Acute Toxicities of Lurgi Ash Leachates to *Daphnia magna*

Source Coal	Leachate Column Volume	pH	Heavy Metals Concentration ^a (mg/L)	48-hr LC ₅₀ ^b (%)	95% Confidence Interval	
					Upper	Lower
Rosebud	1	6.8	2.5	no mortality		
	2	8.8	0.3	no mortality		
	3	9.5		no mortality		
	4	10.0		49.1	35.1	82.9
Illinois #5	1	4.5	51.0	45.0	not determined	
	2	5.2	12.4	no mortality		
	3	5.6		no mortality		
	4	5.1		52.4	36.0	264.3
Illinois #6	1	3.2	312.2	5.5	3.7	10.1
	2	3.9		16.8	10.3	33.9
	3	4.3		60.0	26.7	1307.0
	4	5.1		no mortality		

^aIncludes Zn, Fe, Ni, Mn, Cu, Al, Hg, As, Se, Pb, Cd.

^b48-h LC₅₀ = the percent dilution of the leachate in spring water that caused a 50% mortality in 48 hours.

Source: Ref. 125.

these wastes. Table 4.13 compares the phytotoxic effects of various leachate column volumes.¹²⁵ No effects of pH on radish hypocotyl elongation were observed between pH 3.6 and pH 9.3. However, at pH 3.2, growth was slightly inhibited, and a pH of 10 greatly reduced hypocotyl growth. The first column volume of Illinois 6 was the most toxic of all the leachates, causing 62% growth reduction at 10% concentration. At least two of the fractions of all leachates tested cause significant growth reduction of radish hypocotyls. However, only one of the fractions of Illinois 6 produced a growth reduction at the 10% concentration.

4.1.3 FBC Spent Solids

Characteristics and environmental implications of FBC residues were recently reviewed by Henschel.¹²⁶ His findings based on results from EPA's FBC solid residue programs are summarized as follows:

1. The residue, in general, does not appear to be "hazardous" according to the procedures currently proposed under Sec. 3001 of RCRA. None of the trace metals treated exceeded the threshold of 10 times of the NIPDWR (National Interim Primary Drinking Water Regulations) for any of the FBC residues. The residues are expected to be not "corrosive," "ignitable," or "reactive" according to the criteria proposed for hazardous wastes under RCRA. It is possible, however, that in some specific cases, residues from an individual FBC plant may be found to be "hazardous." For example, the specific coal burned, or the specific sorbent used for an individual plant, could result in a residue that might yield a leachate having a high trace metal content and that might thus be found to be "hazardous" using the Extraction Procedure.
2. The primary environmental problem with FBC residue is that the leachate has a high pH and a high total dissolved solids (TDS) content. In addition, sulfate ion concentrations are high.¹²⁷⁻¹²⁹ The levels of pH, TDS, and sulfate are significantly above EPA's proposed NSDWR (National Secondary Drinking Water Regulations), the World Health Organization potable water standards and/or the Public Health Service regulations on drinking water. (These species are not covered by the NIPDWR). When the leaching medium is distilled, deionized water, the pH of the leachate can be 12 or higher (in the range of 10 to 13) if the spent bed material is leached by itself; this pH is well above the NSDWR range of 6.5 to 8.5. TDS levels in FBC residue leachates are typically in the range 1000 to 3000 mg/L or higher, above the NSDWR of 500 mg/L. Sulfate concentrations are generally in the range 1000 to 2000 mg/L, above the NSDWR of 250 mg/L.
3. Trace metal leaching would appear to be of much less concern--in comparison with pH, TDS, and sulfate. When a variety of FBC residues were leached using distilled, deionized water, none of the 15 trace metals,

Table 4.13 Toxicity of Lurgi Ash Leachates to *Raphanus sativus* L^a

Source coal	Leachate column fraction	Concentration (%)	pH	Reduction of growth (%)
Rosebud	1	100	6.5	18
		50	6.5	18
		10	5.5	0
	2	100	9.2	52 ^b
		50	9.2	14
	3	100	9.5	38 ^b
		50	9.5	19
		50	9.3	9
	4	100	10.0	31 ^b
		50	9.8	15
		10	9.5	9
Illinois #5	1	100	4.5	48 ^b
		50	4.5	24 ^b
		10	5.5	0
	2	100	5.2	11
		50	5.2	0
	3	100	5.6	12
		50	5.6	0
	4	100	5.1	86 ^b
		50	5.2	72 ^b
		10	5.4	0
Illinois #6	1	100	3.2	75 ^b
		50	3.2	75 ^b
		10	3.6	62 ^b
		1	3.6	0
	2	100	3.9	45 ^b
		50	4.1	55 ^b
		10	4.5	5
	3	100	4.3	0
	4	100	5.1	9

^aEarly scarlet globe variety.^bIndicates statistical significance at the 0.01 probability level.

Source: Ref. 125.

including silver, arsenic, barium, beryllium, cadmium, chromium, copper, iron, mercury, manganese, nickel, lead, selenium, tin, and zinc exceeded available standards, regulations, or criteria.^{128,129}

4. Substantial heat is released from the residue on initial exposure to water, due to hydration of the CaO content forming calcium hydroxide.^{128,129} This heat release could necessitate some care in handling the residue and could represent an occupational safety concern but is not expected to be a major environmental concern. Heat release may be less of a concern for pressurized FBC systems, since the nonsulfated calcium may, to a greater extent, be in the form of CaCO_3 ; however, even even in residues from pressurized systems, some CaO may be present, and potential heat release problems may exist.
5. The leachate from one sample of spent bed material from one pressurized FBC unit had a low level of toxicity according to one set of fresh-water aquatic bioassays (using algae, fathead minnow, and daphnia as the test organism).¹³⁰
6. Total organic carbon and sulfide are below detection limits in the FBC samples that have been tested and are not expected to be problems.^{128,129}

4.1.4 Sludges from Chemical Treatment of Process Wastewater

Chemical sludges produced from treatment of gas liquor produced in coal conversion may be closely related to the waste stream produced from ammonia stripping during the by-product coke making. EPA has determined that the ammonia still lime sludges from coking industry may pose a potential hazard to human health or the environment and should be subject to appropriate management requirements under Subtitle C of RCRA (see Sec. 7.1). Ammonia still lime sludges from the coking industry contain hazardous constituents such as cyanide, naphthalene, phenols, and arsenic in significant concentrations. Furthermore, cyanide and phenol leached in significant concentrations were detected from an ammonia still lime sludge water sample. Although no leachate data is currently available for naphthalene and arsenic, EPA believes that, based on constituent solubilities, these two constituents are likely to leach from the wastes in harmful concentrations when the wastes are improperly managed.¹⁰⁹

Table 4.14 compares the composition of gas liquor from Synthane, Lurgi, Kloppe-Totzek and SRC-1 with that of coke plant ammonia liquor. With the exception of the Kloppe-Totzek process, other conversion processes appear to produce process wastewater with a composition similar to coke plant ammonia liquor.¹³¹

4.1.5 Tars and Oil Sludges

Oil sludges and tars generated in coal conversion processes are potentially toxic. The counterpart of oil sludge and tars from coal conversion

Table 4.14 Comparison of Process Wastewaters from Coal Conversion and Coke Making Processes (in mg/L)

Component	Coke Plant Ammonia Liquor	Synthane	Lurgi	Koppers Totzek	SRC-1
pH	8.4	8.6	8.9	8.9	8.0
Suspended Solids	4,000	600	5,000	50	300
Phenol	1,000	N.A.	3,500	N.A.	45,000
COD	10,000	150,000	12,500	70	15,000
Thiocyanate	1,000	152	N.A.	N.A.	N.A.
Cyanide	50	N.A.	N.A.	0.7	N.A.
Ammonia	5,000	8,100	11,200	25	5,600
Chloride	6,000	500	N.A.	600	N.A.
Carbonate	N.A.	6,000	10,000	1,200	N.A.
Sulfide	1,250	1,400	N.A.	N.A.	4,000

Source: Ref. 131.

process would be the slop oil, API separator bottoms, and DAF float produced in petroleum refineries. These refinery wastes, which have been classified to be hazardous under RCRA, contain significant concentrations of toxic heavy metals and organics (see Sec. 7.2).

Polycyclic aromatic hydrocarbons (PAHs) are known to be toxic, mutagenic, teratogenic, and carcinogenic. Long-term dermal exposure (1-43 years) to coal tar has been reported to cause malignant tumors on hands, face, and neck of briquette factory workers. When small amounts of coal tar were fed to ducks, the toxicological effect was anemia and extensive liver damage.¹⁰⁹

Bioassay studies have indicated potential mutagenicity of tar samples. Research Triangle Institute has conducted Ames tests for mutagenicity on crude tar samples and their fractions.¹³² The test organism for these bioassay studies was TA-98 Salmonella bacteria strain, which tests for frame shift mutagens. Fractions were obtained from gasification test runs of Western Kentucky No. 9, Illinois No. 6, North Dakota lignite, and Wyoming subbituminous. Bioassay test results are present in Table 4.15. One significant finding is that tar base fractions from coal gasification tests with three coals--Western Kentucky No. 9, Wyoming subbituminous and North Dakota lignite--showed more severe mutagenic effects on strain TA-98 than the crude tar samples from which they were obtained.

The levels of PAHs in coal tar are closely comparable with those in creosote (see Table 4.16). The EPA has determined that the wastewater treatment sludge generated in the production of creosote poses a substantial present or potential hazard to human health or the environment (see Sec. 7.4). The hazardous substances likely to be present in these wastes include creosote

Table 4.15 Bioassay Test Results for Crude Tar Samples and Fractions^a

Sample	Coal	Potential Mutagenicity
Base Fraction	W.Ky. No.9	High
	Wyo. Subbituminous	High
	N.D. Lignite	High
	Ill. No.6	Medium
Acid Fraction	W.Ky. No.9	Negative
	Ill. No.6	Negative
	Wyo. Subbituminous	Negative
	N.D. Lignite	Negative
PNA Fraction	W.Ky. No.9	High
	Ill. No.6	Medium
	Wyo. Subbituminous	Medium
	N.D. Lignite	Medium
Polar Neutral Fraction	Ill. No.6	High
	W.Ky. No.9	Medium
	Wyo. Subbituminous	Medium
	N.D. Lignite	Medium
Nonpolar Neutral Fraction	W.Ky. No.9	Negative
	Ill. No.6	Negative
	Wyo. Subbituminous	-
	N.D. Lignite	Negative
Crude Tar	W.Ky. No.9	High
	Ill. No.6	High
	Wyo. Subbituminous	Medium
	N.D. Lignite	Medium

^aTwo additional Western Kentucky No.9 fractions (Insolubles and XAD-2) both showed negative potential mutagenicity. These same fractions from the other coal types were not tested.
Source: Ref. 132.

and its constituents, benz(a)anthracene, benzo(b)fluoranthene, and benzo(a)pyrene, all of which are alleged human carcinogens. For example, benzo(a)pyrene can induce a cancerous skin tumor in mice when only 0.25 mg is injected subcutaneously.¹⁰⁹

Another PAH-containing industrial effluent determined by the EPA to be hazardous is bottom sediment sludge from wood preserving plants (see Sec. 7.5). In addition to PAHs, it contains chlorinated phenols and volatile organic solvents such as toluene and benzene. PAH levels measured in coal

Table 4.16 PAH Concentration in Creosote and Coal Tar (g/kg)

PAH	Creosote		Coal Tar	
	Sample 1	Sample 2	Sample 1	Sample 2
Anthracene	12.1	12.0	2.88	4.35
Benz(a)anthracene	2.77	2.94	6.24	6.98
Benzo(b)chrysene	0.03	0.06	0.93	0.80
Benzo(j)fluoranthene	0.29	0.29	0.45	
Benzo(k)fluoranthene	0.30	0.11	1.08	1.07
Benzo(g,h,i)perylene			1.23	1.89
Benzo(a)pyrene	0.14	0.22	2.08	1.76
Benzo(e)pyrene	0.18	0.15	1.85	1.88
Carbazole	2.20	1.42	1.32	1.27
Chrysene	1.34	0.94	2.13	2.86
Dibenz(a,h)anthracene			0.30	0.23
Fluoranthene	24.8	22.2	17.7	17.8
Perylene	0.04	0.04	0.70	0.76
Phenanthrene	39.9	33.3	13.6	17.5
Pyrene	9.1	6.8	7.95	10.6

Source: Ref. 53.

tars⁵³ and bottom sediment sludge from a wood preserving plant¹⁰⁹ are fairly close, as can be seen in Table 4.17.

Instead of disposal, coal tars and oil sludges produced in coal conversion processes may be used as a fuel in combustors or feed stock for chemical processes. Under these conditions, the health and environmental effects of tars and oil sludges will, of course, be much different from those previously discussed.

4.1.6 Biosludges

Table 4.18 lists known or suspected carcinogens that may be present in waste streams from coal liquefaction.¹³³

No data are available from chemical and bioassay tests of coal conversion biosludges. The characteristics of the biosludges from coal conversion facilities are expected generally to be similar to those detected in conversion process wastewater or to those of petroleum refinery biosludges and perhaps wood preserving wastewater treatment sludges. Biosludges from refineries have been reported to contain Cr and Zn values of 540 and 200 mg/kg,

Table 4.17 Polynuclear Aromatic Hydrocarbons in Coal Tars and Bottom Sediment Sludge from a Wood Preserving Plant (g/kg)

PAH	Coal Tar ^a	Bottom Sediment Sludge from Wood Preserving Plant ^b
Benz(a)anthracene	6.24-6.98	1.25
Chrysene	2.13-2.86	9.28
Benzo(a)pyrene	1.76-2.08	5.98

^aRef. 53.

^bRef. 109.

Table 4.18 Known or Suspected Carcinogens That May be Present In Waste Streams From Coal Liquefaction

Bicyclic compounds (e.g., (benzidine)	Flouranthene (e.g., benzo (j)-or (b)-...)
Nitrosamines	Cholanthrenes (e.g., 10-methyl...)
Nickel (e.g., nickel carbonyl)	Benzo (e) or (a) pyrenes
Chromium trioxide, Chromate salts	Dibenzo (a,x) pyrene (x=1, n, i, or h)
Salts	Mono- and Dibenzacridines
Beryllium oxide	Mono- and Dibenzocarbazoles
Arsenic (e.g., arsenate salts)	Benzanthrones
Selenium salts	Aminoazobenzenes
Cobalt sulfide	Acenaphthenes
Lead chromate	Naphthylamines
Zinc chromate	Diethyl and Methylethylamines
Mercury	Benzene
Cadmium sulfide	Pyrenes (e.g., cyclopenta pyrene, indeno (1,2,3-c,d) pyrene)
Anthracenes (e.g., 9, 10-dimethyl...)	Fine particulates (e.g., sulfur, coke)
Chrysenes (e.g., 5-methyl...)	
Benzanthracenes	

Source: Ref. 133.

respectively, of dry sludge.¹¹⁰ The sludges generated from the treatment of wastewater from certain wood preserving processes (Sec. 7.5) have been determined to contain significant concentrations of toxic phenolic compounds, polynuclear aromatics, and volatile organic solvents such as benzene and toluene. These wastes have been classified to be hazardous under RCRA.¹⁰⁹

4.2 OIL SHALE PROCESSING WASTES

A major environmental concern with the development of oil shale technology is the potential for long-term health hazards such as carcinogenesis, mutagenesis, and teratogenesis. Exposure to crude shale oils, particulate matter, contaminated aqueous materials, and air pollutants is hazardous to the health of workers. There are additional health and environmental concerns associated with oil shale extraction and processing. Blasting and mining will produce dust, particulate organic matter, CO, NO_x, SO₂, hydrocarbons, silica, and metal salts. Crushing and screening the ore produces more dust, silica, and particulate organic matter. In addition, retort operations can produce polycyclic organic compounds, H₂S, NH₃, and volatiles. Some of these compounds, as well as arsenic and other metals, are produced in the upgrading process and disposal of the solid waste products and are of major environmental concern. Many of these compounds may contaminate not only the atmosphere but the water as well. Since water is a necessary commodity in the oil shale industry, many of these compounds may be found in the waste and runoff waters.

Acute and Chronic Toxicity. Weaver and Gibson¹³⁴ reported on the studies of 134 acute and chronic health effects of four crude shale oils, three raw shales, and four spent shales (Table 4.19). The results do not show that the materials are acutely toxic.

Weaver and Gibson also reported on chronic inhalation studies of two raw shales and two spent shales.¹³⁴ In the study, rats and monkeys were subjected to the inhalation of the respirable dusts at concentrations of 10 and 30 mg/m³. After one year of exposure, no adverse effects were seen in the animals.

Table 4.19 Studies of the Acute Effects of Shale Oil and Shale Oil Products

Sample	Test	Results
Crude Shale Oils (4)	Oral LD ₅₀ (Rat)	8-10 g/kg
Crude Shale Oils (4)	Dermal LD ₅₀ (Rabbit)	5 ml/kg
Crude Shale Oils (4)	Eye Irritation (Rabbit)	Minimal, reversible
Raw Shales (3)	Eye Irritation (Rabbit)	Negative
Spent Shales (4)	Eye Irritation (Rabbit)	Irritating, reversible
Crude Shale Oils (4)	Dermal Irritation (Rabbit)	0.5 g in 72 hour abraded-unabraded
Crude Shale Oils (4)	Sensitization (Guinea Pig)	Negative
Raw Shales (3)	Sensitization (Guinea Pig)	Negative
Spent Shales (4)	Sensitization (Guinea Pig)	Negative

Source: Ref. 134.

Teratogenicity. Spent shale may be used in revegetation of disturbed land, and it is possible that teratogenic agents may be leached from the shale and ingested with plants (or water). Table 4.20 summarizes the results of a study of the potential embryotoxic and/or teratogenic effects of spent shale in New Zealand white rabbits.¹³⁵ Control rabbits given water showed no anomalies except for rudimentary ribs, and four of the 41 rabbit embryos were dead or resorbed after receiving oral doses of spent shale. The animals given carbon or spent shale did not differ from the control group in the number of implants dead or resorbed, and showed only a slight increase in the number of anomalies. The data showed that spent shale does not cause significantly more abnormalities than does inert carbon.

Mutagenicity. Humans may be exposed to materials leached from both raw and spent shale. Adverse human health effects might result particularly from long-term exposure to polycyclic aromatic hydrocarbons and trace elements emitted in various forms from the shale oil. Epler¹³⁶ has selected a group (Table 4.21) of organic compounds in shale oil and evaluated their mutagenic effects on the *Salmonella* histidine-reversion system. Although a number of the compounds may be promoters or modifiers of carcinogenesis (that is, active in co-carcinogenesis, perhaps in some cases as inhibitors), they do not appear to be mutagenic.

Carcinogenicity. Benzo(a)pyrene (BaP) is a readily measurable member of the polynuclear aromatic hydrocarbon class of compounds. Commonly, BaP is used as an indicator compound for potential carcinogenicity of materials in which it is found. BaP levels in oil shale and some natural and industrial materials are given in Table 4.22. Carbonaceous retorted shales contain BaP in concentrations similar to those found in many natural organic materials.¹³⁷ Shale oils, in contrast, contain relatively high levels of BaP.

The search for the carcinogen in Scottish shale eluded many investigators until 1943, when Berenblum and Schoental¹³⁸ identified BaP (Benzo(a)pyrene) in shale oil, but they also observed a fraction of shale oil that was carcinogenic but did not contain detectable quantities of BaP. Later, Hueper and Cahamann¹³⁹ and Bogovsky¹⁴⁰, respectively, reported BaP-free American and Estonian oil shale to be carcinogenic on the basis of mouse skin painting studies. Thus, it is still uncertain which specific compounds in shale oil materials are carcinogenic.

Table 4.20 The Number and Types of Abnormality Found in Rabbit Embryos After Oral Doses of Spent Shale

	Number of Litters	Number of Implants	Number dead or resorbed	Location of Abnormality				
				Ribs	Skull	Vertebra	Limbs	Others
Control	4	41	4	4				
Carbon 250	8	67	10	8	1			2
Carbon 500	4	50	6	3	1	4	1	1
Spent Shale 250	10	84	9	7	2	8	1	3
Spent Shale 500	15	129	9	17	13	7	1	1

Source: Ref. 135.

Table 4.21 Mutagenic Effect on Salmonella of Chemicals in Shale Oil

Chemical	CAS Registry No.	Strain	Mutagenicity
Phenol and aniline derivatives			
Phenol	108-95-2	98, 100	-
Phenol, dimethyl (xylenol)	1300-71-6	98, 100	-
2.3	526-75-0	98, 100	-
2.4	105-67-9	98, 100	-
2.5	95-87-4	98, 100	-
2.6	576-26-1	98, 100	-
3.4	95-65-8	98, 100	-
3.5	108-68-9	98, 100	-
Phenol, ethyl	25429-37-2	98, 100	-
2	90-00-6	98, 100	-
4	123-07-9	98, 100	-
Phenol, 2,4,6-trimethyl (mesitol)	527-60-6	98, 100	-
Aniline	62-53-3	98, 100	-
Aniline, dimethyl (xylidine)			
2.3	87-59-2	98, 100	-
2.4	95-68-1	98, 100	-
2.5 ^a	-	98	+
Aniline, 2,4,6-trimethyl	88-05-1	98, 100	-
Aniline, ethyl			
2	578-54-1	98, 100	-
3	587-02-0	98, 100	-
Polycyclic fused aromatic hydrocarbons			
Acenaphthene	83-32-9	98, 100	+
Anthracen	120-12-7	98, 100	-
Benz[a]anthracene	56-55-3	100	+
Benz[a]anthracene, 7,12-dimethyl	57-97-6	100	+
Benzo[a]fluorene	238-84-6	100	+
Benzo[a]pyrene	50-32-8	98	+
Chrysene	218-01-8	100	+
Fluoranthene	206-44-0	98	+
Naphthalene	91-20-3	98, 100	-
Phenanthrene	85-01-8	98	+
Pyrene	129-00-0	1537	+
Triphenylene	217-59-4	98	+
1,2,2,4-Dibenzanthracene ^a	-	100	+
1,2,5,6-Dibenzanthracene ^a	-	100	+
Polycyclic fused heterocycles			
Acridine	260-94-6	1537	+
Carbazole	86-74-8	100	-
Isoquinoline ^a	-	98, 100	-
Quinoline	91-22-5	98	+
Quinoline, methyl			
7 ^a	-	100	+
8 ^a	-	100	+
Quinoline, dimethyl			
2.6 ^a	-	98, 100	-

Table 4.21 (Cont'd)

Chemical	CAS Registry No.	Strain	Mutagenicity
Quinoline, hydroxy 8 (sulfate) ^a	134-31-6	100	+
Quinoline, nitro 8 ^a	607-35-2	100	+
Quinoline, amino 8 ^a	578-66-5	1537	+
a-Naphthylamine ^a	-	100	+
2-Acetamidofluorene	53-96-3	98	+

^aCompounds not identified in shale oil, but predicted to occur in the same or modified chemical form.

Source: Ref. 136.

Table 4.23 shows the carcinogenic potency of two crude shale oils from two different processes. The two oils differed very little in tumor incidence and average latency period.¹⁵⁴

Another study determined the BaP content of raw shale oil, upgraded shale oil, processed shale, processed water, native grass, leached water, raw shale and native soil.¹³⁵ The results of these determinations are given in Table 4.24. BaP concentrations found in all samples were considered low.

The results of topical application of raw oil shale and upgraded oil to mouse skin are presented in Table 4.25.¹³⁵ It may be seen that shale oil induced tumors in 86% of the effective number with an average time for appearance of about 30 weeks, whereas the upgraded oil induced tumors in 13% of the effective number with an average latent period of 49 weeks. A solution of 0.05% BaP in toluene resulted in 91% of the effective number of mice developing tumors with an average latent period of 46 weeks. No tumors were observed in the mice treated with toluene alone after eighty weeks of topical application.

Barkley¹³⁵ tested the carcinogenic potential of four shale oils and raw spent shales that Weaver and Gibson studied for their acute and chronic toxicity.¹³⁵ After 60 weeks of topical applications of the materials to the backs of mice, all the animals treated with the shale oils had developed tumors or died. Some results of this study are presented in Table 4.26. No tumors have been observed in the mice receiving raw and spent shale suspended in white mineral oil.

Table 4.22 Levels of Benzo(a)pyrene (BaP) Reported in Oil Shale and Natural and Industrial Materials

Material	Benzo(a)pyrene (ppb)
Coconut oil	43.7
Peanut oil	1.9
Oysters (Norfolk, Va.)	10 to 20
	(based on dry weight)
Forest soil	4 to 8
Farm field near Moscow	79
Oak leaves	300 max
<u>Petroleums and Petroleum Products</u>	
Libyan crude oil	1,320
Cracked residuum (API Smpl 59)	50,000
Cracked sidestream (API Smpl 2)	2,000
West Texas paraffin distillate	3,000
Asphalt	10^4 to 10^5
<u>Oil Shale Related Materials</u>	
TOSCO II retorted shale	13 - 100
GCR retorted shale	15
Raw shale oil (Colorado)	30,000 - 40,000
Crude shale oil (TOSCO II)	3,130
Hydrotreated shale oil (0.25%N)	6,900
Hydrotreated shale oil (0.05%N)	690
<u>Coals</u>	
High volatile bituminous	4,200
Low volatile bituminous	3,150
Lignite	1,200
Coal tar	3×10^6 to 8×10^6

Source: Ref. 137.

Table 4.23 Carcinogenic Potency of Two Raw Shale Oils

Shale Oil	Strain of Mice	Dosage	Number of Mice	Final Effective Number ^a	BaP (%)	Number of Mice Developing Tumors		Average Time of Appearance of Papillomas (weeks)
						Malignant	Benign	
Shale oil #1 Heat transfer process	C3H	50 mg, twice weekly	15	12	<0.00001	8	3	43
Shale oil #2 Retort combustion process	C3H	50 mg, twice weekly	15	12	<0.00001	8	2	43

^aThe final effective number is the number of mice alive at the time of appearance of the median tumor plus those mice that may have died with tumors.

Source: Ref. 135.

Table 4.24 Benzo(a)pyrene Content of Shale Oil Products

Sample	BaP Concentration
Raw Shale Oil	<0.00005%
Upgraded Oil	0.0006%
Processed Shale	<0.000005%
Processed Water	1 ppb
Native Grass	<0.000065%
Leached Water	1 ppb
Raw Shale	<0.000005%
Native Soil	<0.000005%

Source: Ref. 135.

Table 4.25 Carcinogenic Potency of Raw and Upgraded Shale Oil

Sample	Strain of Mice	Dosage	Number of Mice	Final ^a Effective Number	BaP (%)	Number of Mice Developing Tumors		Average Time of Appearance of Papillomas (weeks)
						Malignant	Benign	
Raw shale oil	C3H	50 mg twice weekly	50	45	<0.00005	21	18	30
Upgraded shale oil	C3H	50 mg twice weekly	50	39	0.0006	3	2	49
Positive control (0.05% BaP in toluene)	C3H	50 mh twice weekly	100	92	0.05	75	9	46
Negative control (toluene only)	C3H	50 mg twice weekly	100	91	0	0	0	

^aThe final effective number is the number of mice alive at the time of appearance of the median tumor plus those mice that may have died with tumors.

Source: Ref. 135.

Table 4.26 Carcinogenic Potency of Shale Oils and Shale Oil Products^a

Sample	Strain of Mice	Dosage	Number of Mice	BaP (%)	Number of Mice Developing Tumors		Average Time of Appearance of Papillomas (weeks)
					Malignant	Benign	
Raw oil #1	C3H	50 mg twice weekly	50	0.00018	11	19	28.6
Raw oil #2	C3H	50 mg twice weekly	50	0.00018	30	1	19.1
Raw oil #3	C3H	50 mg twice weekly	50	0.00012	27	10	26.3
Raw shale 101	C3H	50 mg twice weekly	50	0.00042	27	11	24.9
Raw shale 102	C3H	50 mg twice weekly	50	<0.00001	0	0	
Raw shale 103	C3H	50 mg twice weekly	50	<0.00001	0	0	
Spent shale 201	C3H	50 mg twice weekly	50	<0.00001	0	0	
Spent shale 202	C3H	50 mg twice weekly	50	<0.00001	0	0	
Spent shale 203	C3H	50 mg twice weekly	50	<0.00001	0	0	
Spent shale 204	C3H	50 mg twice weekly	50		0	0	
Control - no treatment	C3H	50 mg twice weekly	50	<0.00001	0	0	
Control - mineral oil only	C3H	50 mg twice weekly	50		0	0	
0.05% BaP in mineral oil	C3H	50 mg twice weekly	50	0.05	40	6	37.8
0.15% BaP in mineral oil	C3H	50 mg twice weekly	30	0.15	29	0.1	27.4

^aIncomplete: 54 weeks duration.

Source: Ref. 135.

5 PROBLEMS ASSOCIATED WITH HAZARDOUS WASTE STORAGE AND DISPOSAL

Although a small proportion of the solid waste produced can be used, environmentally acceptable methods of disposal must be found for the rest. This section discusses the available options for solid waste disposal and some of the mechanisms by which containment areas may be breached, thus causing adverse health and environmental impacts. The current waste disposal practices in the industry are also reviewed.

5.1 DISPOSAL OPTIONS

Available options for solid waste disposal and management include the following:

- Tanks and other storage facilities
- Surface impoundments, e.g., ponds
- Waste piles
- Land fills
- Land surface treatment
- Incineration
- Other thermal treatment
- Chemical, physical, and biological treatment
- Underground injection
- Ocean dumping
- Mine backfill

The principal options are described below in light of their applicability for energy-related wastes.

5.1.1 Ponding

This disposal method involves sluicing or trucking of solid waste or sludges or both to on-site disposal ponds, where the sludge solids settle and the overflow liquor is pumped back to the plant (e.g., FGD system) for reuse (closed loop operation) or discharge to bodies of water such as lakes and rivers (open loop operation).

Dumping into on-site shallow ponds or lagoons has been the principal means of ash disposal in the electric utility industry. At present, the most common disposal for FGD is also by ponding. The sludge, normally untreated, is usually mixed with the ash and transported to on-site disposal ponds.

Most of the sludge and ash ponds used to date are unlined. To reduce the possibility of liquors leaching into groundwater, the disposal ponds can be lined with some impermeable material such as clay. Another alternative is to include pond underdrainage.¹⁴¹ This method retains the advantage of

transferring the sludge to the disposal site by liquid transfer. The leachate from the base of the sludge is returned to the scrubber.

The advantages of this method are economic and environmental. By eliminating a supernatant head above the sludge most of the time, and minimizing it for short periods after rainfalls, percolation of sludge leachate into the subsoil can be avoided during the active fill period. Tests have shown drained sludge to have structural qualities adequate to support lightweight construction equipment.

5.1.2 Landfill

Landfill has usually been used by utilities for ash disposal when land was not available on site for ponding. The ash may be ponded and then transported to a landfill site after drying.

Landfill operations range from open dumping of debris to controlled disposal in "secure" landfills. Open dumps, in which wastes are piled on the surface of the terrain, are prohibited in most states and are to be totally phased out under the provisions of RCRA even for nonhazardous waste. Piles that are kept under control, perhaps inside buildings and protected from rain and wind may be suitable for short-term storage. In sanitary landfills, the wastes are usually compacted to confine them to the smallest practical area and are then covered with a layer of soil at regular intervals (usually at the end of a day's operations). Provided that adequate measures are taken to reduce the potential for ground and surface water contamination and to minimize the nuisance associated with landfill operation, sanitary landfilling can be an environmentally acceptable and cost-effective method for solid waste disposal.

To minimize the potential for the contamination of groundwater and surface waters, landfills must be located in areas where the subsurface formation is relatively impervious to infiltration (e.g., dense clays) and where the distance to the groundwater table is significantly large. The landfill surface area should also be properly contoured to divert surface runoff from the site. When the subsurface formations do not provide adequate barriers against leachate infiltration, the use of artificial barriers such as plastic, asphalt, concrete, or clay materials for lining the landfill may be necessary. The intercepted leachate would be pumped to a surface facility for treatment. Observation wells should also be installed downstream of the landfill site (in the direction of groundwater flow) to detect leachate migration.

Controlled landfilling is the most likely method for the majority of energy-related wastes generated from fossil fuel energy industries. For example, virtually all the present proposals for commercial oil shale mining and retorting include plans for disposal of solid waste controlled landfill. All these plans have the objective of creating a stable disposal pile, suitably contoured and revegetated, with provision for protection against leaching of substances into ground and runoff waters.

5.1.3 Mine Disposal

This disposal option encompasses the return of wastes to surface and underground mines. Disposal in surface mines is essentially one form of landfilling where the overburden material is used as the cover material. The operation is subject to the same restrictions as sanitary landfills. When coal is mined by deep mining, there would be a greater time delay before the waste can be deposited in the mine. In the case of deep mining, the physical operation of returning the waste to the mine is also more difficult, requiring certain changes in mine design and operation to accommodate the space and equipment for returning the waste.

Both strip mine reclamation and deep mine filling have been used for ash disposal from power plants for a number of years. It is thus natural to also consider mine disposal for FGD wastes. Evaluations of this form of disposal are being undertaken. Initial assessments have been undertaken by Aerospace¹⁴¹ and Le et al.¹⁴² and are summarized below.

In general, interior region surface-area coal mines appear to be more promising than western (Rocky Mountain and Pacific Coast) surface-coal mines. However, surface-area mines both in the Interior and the West were considered much more promising than eastern surface contour mines, because of the latter's relatively low capacity for FGD wastes, and in many cases, the difficulty for waste placement in contour mines.

Individual interior region surface-area mines have substantial capacity for receiving FGD wastes, and disposal is considered technically feasible within existing mine operations.

Placement and handling techniques for FGD sludge disposal in both surface and underground mines are available and have been demonstrated for disposal of other materials in mines (e.g., coal refuse), although the techniques may require modifications for application of FGD sludge disposal. The FGD wastes will have to be dewatered to the extent necessary for landfill operations.

When transportation costs are not excessive, return of the coal gasification and liquefaction solid wastes and sludges to the coal mines would be an attractive means for the disposal of such wastes, especially when area surface mining is practiced. The designs for proposed commercial Lurgi SNG plants have called for the return to surface mines of all plant solid wastes.

At present, only one of the proposals for oil shale development includes mines disposal of the retorted shale. The Superior process calls for compaction of all process (e.g., leached) shale into a wet cake for disposal underground in the spaces remaining after room-and-pillar mining. It is expected that this commercial operation will dispose of 24,000 tons daily and 4.6 million tons annually of leached spent shale. The leached shale wet cake will be returned to the mine and converted into a slurry, which will be pumped into the empty underground rooms and allowed to drain to approximately 25% moisture content. Because of the dipping beds on the Superior property in the northern Piceance Basin in Colorado, it is claimed that the slurry can be emplaced up to the ceiling, by proper withdrawal of the slurry discharge pipe as each room fills.⁷⁸

5.1.4 Ocean Disposal

Offshore disposal of energy-related solid waste presents itself as a potential disposal option. Disposal of flyash in the ocean has been practiced, particularly on the Atlantic seaboard of the Northeast. Studies have been undertaken of the economic and environmental feasibility of the ocean disposal of FGD sludges.

In a study assessing the ocean disposal of FGD wastes¹⁴¹ various methods of transportation and disposal were examined, including surface craft (e.g., bottom-dump barge and slurry dispersion) and pipeline (outfall). Various chemical and physical forms of the FGD wastes were also considered, e.g., sulfite-rich wastes, sulfate-rich wastes, and chemically treated wastes in both "soil-like" and "brick-like" forms. Both continental shelf and deep ocean disposal of the wastes were examined.

Ocean disposal of solid wastes has many advantages, including moderate cost, and no on-shore impacts. However, because of its potential aquatic impacts, ocean dumping is being discouraged by environmental regulatory agencies.

5.1.5 Deep Well Disposal

Deep well disposal is a method of pumping or injecting liquid waste into a subsurface formation. Many industries that generate large quantities of concentrated waste have used well injection disposal systems, which often have lower capital and operating costs than other available treatment and disposal methods. Concentrated toxic liquid wastes are disposed of in deep wells without treatment, while comparable surface treatment methods could only be accompanied at considerably higher expense. Very little surface area is required except for the well pumping equipment. In the U.S., more than 100 liquid waste disposal wells have been drilled, handling liquid waste capacities of up to 1100 gal/min.

Deep well disposal of wastes is being discouraged because of the uncontrolled nature of pollutant release and the irreversibility of environmental impacts. The method does take advantage of the slow movement of ground water, the ion exchange properties of soil, and if above the water table, the capacity of the unsaturated soil to store moisture. In addition, there is slow dispersion of wastes in the groundwater system. However, any deep well injection methods must be acceptable to, and obtain permits under, the Underground Injection Control Act (PL 95-190).

5.1.6 Soil Application¹⁴³

When large land areas are available and the climate (rainfall, evaporation) and hydrogeological conditions (distance to groundwater; groundwater flow, type of soil, and geological formation) are favorable, some organic and inorganic wastes may be disposed of by application to soil. Waste disposal by application to soils has been used for the disposal of waste sludges from municipal sewage treatment plants. Solid waste/sludge is applied to the soil by "spreading" or "flooding," disked under, and worked into the top soil.

The organic components of the waste undergo biodegradation in the soil and eventually become part of the soil humus. Inorganic sludges and ashes can also be disposed of on land and incorporated into the top soil. Depending on the soil type, such sludges and ashes can improve soil structure, reduce acidity, provide plant nutrients, and decrease the availability and hence toxicity of certain cations. Although tar and oil sludges from petroleum refineries have been shown to be degradable when applied to soils, such sludges from coal gasification plants may be more resistant to degradation in the soil environment due to the highly aromatic nature of the organics in these sludges. Sites for land disposal of sludges can present an odor problem or result in the contamination of surface waters and groundwaters, unless such sites are properly located, designed and operated.

5.1.7 Incineration¹⁴³

Carbonaceous wastes such as tars, oil, chars, and dewatered biosludges can be incinerated before disposal. Depending on the water content of the feed, the combustion may be self-sustaining and also allow for heat recovery. The operation can be combined with on-site power generation or be carried out in a separate waste disposal incinerator. Incineration has proven to be very reliable and efficient and has been widely used for the disposal of a variety of industrial sludges and solids, municipal refuse, and biosludges from the treatment of sanitary sewage. Nearly complete destruction of organics can be achieved in properly designed and operated incinerators. Compared to land disposal methods, incineration requires very little space. Except for potential air pollution problems, which can be controlled by use of good design, afterburners, and particulate control devices, incineration can be the most desirable disposal option (when resource recovery is inapplicable), especially for the destruction of hazardous organics.

5.1.8 Chemical Treatment

The physical and chemical properties of some solid wastes can be altered by chemical treatment to produce useful by-products, and/or to make them easier for handling, and more suited to landfill disposal. For example, the quality of lime/limestone scrubber wastes can be improved by oxidation or by chemical fixation. By oxidation, the precipitated calcium sulfite/sulfate mixtures are oxidized to produce by-product gypsum. Oxidation of FGD sludges has been practiced in Japan where FGD-derived gypsum is marketable. By fixation, materials such as fly ash, lime, silicates, and/or polyvalent metal ions are mixed with wet sludges to form low-grade concretes. The objective of fixation is to solidify the sludges by promoting pozzolanic and other cementitious reactions between lime compounds in additives, alumina/silica in the fly ash, and calcium-sulfur compounds in the sludge. Chemical fixation makes the sludges more suited to landfill disposal and subsequent reclamation and vegetation, reduces the volume of sludge, and minimizes the danger of potential environmental problems from leachates filtering into the groundwater. A number of vendors are currently marketing fixation treatment systems, most of which produce a stable inert material that has high resistance to the release of toxic metals and soluble species and of sufficient compressive strength to support building.

5.2 LONG-TERM ENVIRONMENTAL PROBLEMS

Land disposal of energy-related solid wastes can lead to a number of environmental problems. The primary areas of concern are contamination of groundwater by leachate from disposal ponds and landfills and land use impacts determined by long-term physical and engineering properties. Energy-related solid wastes can result in varying degrees of groundwater pollution depending on chemical composition, solubilities and permeabilities, and the location, hydrogeological characteristics, and design and operation of the disposal site. In terms of land use impact, ponding and landfill may be esthetically objectionable, and food crops may be contaminated by such potentially toxic substances as lead, nickel, cadmium, chromium, arsenic, mercury, and selenium if the reclaimed disposal sites are used for agricultural production. Other potential environmental impacts include surface water contamination by overflow or runoff and air quality deterioration resulting from wind erosion and chemical volatilization at the waste disposal sites.

Little information is available to determine if leachate from operational energy-related solid waste disposal systems (e.g., ash ponds) is a potential source of groundwater pollution. However, this lack of information does not imply that a pollution problem does not exist. The composition of specific solid wastes, the concentration of soluble constituents, the pH of the leaching medium, and/or the lateral water movement in underlying aquifers may be such that the problem areas have not been identified.

Chemical composition data (see Section 3) indicate a potential pollution problem from leaching of many energy-related solid wastes and a need for careful site selection and monitoring. In some cases, installation of special control measures, such as liners, sealants, underdrainage collection system, and devices for routing ground and surface flow may also be needed. Although these control measures are potentially applicable to landfill as well as pond disposal sites, long-term effectiveness is still a matter of concern.

The following subsections discuss some mechanisms by which containment areas may be breached, thus causing surface and groundwater pollution.

5.2.1 Deterioration of Landfill Cover

The list of the functions of landfill cover material includes disease vector and rodent control; containment of odor, litter, erosion, and air emissions; prevention of infiltration by rainwater, thereby decreasing potential leachate generation and surface and underground contamination; and esthetic enhancement of the site during and after use for waste disposal.

According to the EPA,¹⁴⁴ hazardous waste landfill operations should specify what soils are to be used as cover material, where they are to be obtained, and how they are to be placed over the waste in order to meet the aforementioned objectives. If the cover is to be exposed longer than one year, a 3-foot soil cover is recommended by the EPA for sanitary landfills, for isolation of wastes from the environment.¹⁴⁵ Even so, the effectiveness of landfill cover could decrease over time as a result of numerous natural phenomena, including erosion, cracking, landslides and subsidence.

Erosion results from detachment and movement of soil by water, wind, ice, or gravity. Cracking is caused by volume changes in cover soils; shrinkage upon loss of water, and expansion at additions of water. Erosion and cracking can deteriorate the structure of a landfill and increase the likelihood of water entering the site. Subsequent infiltration and development of the hydraulic head can hasten the vertical migration of pollutants from the site.

Landslides, along with floods and erosion, are common occurrences due to weather, the nature of solids, and gravity. Any of these occurrences, however, can produce a change in a site, thereby directly affecting the rate at which contaminants reach the environment. Subsidence of a landfill could breach the landfill containment system by causing depression of landfill surfaces in which surface water can accumulate and by enhancing infiltration and hastening vertical movement of pollutants.

5.2.2 Limited Soil Attenuation Capacity

Landfills in most cases are underlain with natural soils. The contaminants in leachates can be attenuated when passing through soils by physical-chemical, mechanical, and/or biological processes. The mechanisms of these processes include filtration, ion exchange, absorption, chemical precipitation, biodegradation and complexing. For acidic or neutral leachates, soil attenuation of trace contaminants usually occurs through absorption/ion exchange mechanisms. In this case, soil properties, such as texture (e.g., clay content or particle size distribution), surface area, percentage of free ion oxides, and pH, are the most important controlling factors.¹⁴⁶⁻¹⁴⁸ Other factors such as percentage of hydrated oxides of manganese, aluminum oxides, and silicates as well as organic contents in the soils and competing ions in the soil solution are also important factors.

Attenuation of the leachate contents by percolation through soil has been shown, in many cases, to provide substantial protection against trace elements reaching an aquifer. Laboratory attenuation (percolation) data obtained on soils at utility stations indicate that after 10 years of continuous flow, the levels of chromium and selenium (at soil depths of 30-50 feet) would still be 95% less than they were in the original ash leachate. Boron and arsenic were also significantly absorbed by the same soil.

The absorption/ion exchange capacities of soils are limited, however, and the migration of pollutants from disposal sites to the environment will occur. Estimation of the capacity of absorption/ion exchange can be approximated by using the Cation Exchange Capacity (CEC). In general, high CEC values usually indicate high clay content, high surface area, and thus higher attenuation capacity. For a specific site condition, (e.g., soil permeability, cation exchanger capacity, and depth), soil attenuation capacity can be quantitatively expressed as "breakthrough time," which refers to the years the specific site is capable of attenuating metal species in the leachate. The soil depths required for 20-year breakthrough of leachate concentrations of up to 1020 meq/ft³ have been estimated for six different soils. The results indicate that leachate attenuation capacity of individual soils may be ranked in the following order: clay>loam>loam-silt loam>sandy clay loam>silt loam-silty clay loam>loam-clay loam>loamy sand. In addition, approximately

two feet of clay can provide 20-year breakthrough for leachate concentrations of up to 100 meq/ft³.¹¹²

Since most metals may be leached from coal residues over a long (hundreds of years) period of time, and soil attenuation capacities are limited, long-term protection of groundwater supplies may require the utilization of control methods in addition to soil attenuation.

5.2.3 Long-Term Reliability of Impervious Liners

The use of liners to isolate hazardous waste from the environment is a possible solution when impervious basins are needed at a landfill site and the existing soil is not suitable. Liners may be natural or synthetic, or a combination of both. Natural impermeable barriers consist of clay and fine-grained soils; synthetic liners range from asphaltic and concrete compositions to various polymeric membranes.

The EPA's proposed standard set under RCRA allows for the use of either of two basic designs (I and II) for the construction of a landfill liner in conjunction with a leachate collection system(s).^{149,150} Design I requires a soil barrier (liner) of at least 1.5 meters in thickness composed of natural in-place soil or imported amended, recompacted, or reworked soil with a permeability of 1×10^{-7} cm/sec. Design II is more complex, involving a double liner system with leachate collection and removal. The liner system of Design II consists of a 1 meter (3-foot) soil liner with a permeability of 1×10^{-7} cm/sec. It overlies a synthetic membrane liner that meets the specification in Section 250.45-2 and is protected on both sides with a minimum of 14 cm (6") of clean sand or soil. In addition, a leachate detection and removal system will be required beneath the membrane liner of Design II.

Numerous artificial pond liners have been proposed, including both flexible films of rubber or various plastics and nonflexible liners such as asphalt, cement, or even stabilized FGD wastes. The useful lifetimes of potential liners, which are determined by the aging characteristics of the material and by chemical interactions with the sludge and soil, are a matter of concern. Flexible liners are generally guaranteed for 20-25 years, and nonflexible liners are expected to have a somewhat longer life, but long-term service data for sludge containment are not yet available for either type of liner.

The possible chemical reactions between the soil liner and a waste can result in decomposition of liner material. For example, some natural impermeable soils may fail when exposed to strong acids. Also, artificial liners and synthetic membranes may fail if not properly installed or constructed, or when exposed to some hydrocarbon solvent. The organic compounds have been shown in experiments to affect some types of disposal site liners, resulting in failure, loss of strength, or increase in permeability.^{151,152}

Following are some of the observations regarding potential deterioration of liner materials:

- Clay soils, including bentonites, can lose their impermeability when impounding strong acids, strong bases, or brine.

- Exposure of liner to sunlight can cause some polymers, such as polyvinyl chloride to become brittle and to crack. Butyl rubber is susceptible to cracking from ozone attack.
- Soil liners may be damaged by drying or by freeze/thaw of exposed areas.

6 SOLID WASTE UTILIZATION

Commercial use of solid waste is clearly an attractive alternative to disposal, as a means of reducing both environmental impacts and costs. At present only a portion of coal ash from utilities is used; possible uses for other wastes such as FGD sludge and fluidized-bed material are being evaluated. The major areas for use are in building materials, road construction, and agriculture. Each of these areas will be discussed with regard to the possible extent to which different solid wastes could be utilized and the possible environmental consequences. Two commercial products that might be obtained from some waste streams are elemental sulfur and sulfuric acid and the possibilities of producing and selling such products will be discussed. A comprehensive picture of trends in the use of energy waste is not intended. Estimates have been made for individual uses or individual waste streams. The information on ash use is most complete. The various uses are described below by major use category and waste type. This is followed by a general discussion of the extent of and trends in utilization of solid waste.

6.1 BUILDING MATERIALS

6.1.1 Ash from Conventional Boilers

Ash is used in a number of ways for building materials and construction, and these uses are summarized below.⁶⁸

6.1.1.1 Cement and Concrete

Blended cements are usually made by intergrinding cement clinker with industrial by-products such as fly ash or granulated blast-furnace slag. Fly ash is attractive for this purpose because it is widely produced in large amounts and in a form that is usually immediately suitable for this purpose.

Research by the Bureau of Reclamation showed the replacement of 15-30% of cement in normal density concrete by fly ash improves sulfate resistance of test specimens by an average of 50-100% and prevents or greatly retards corrosion of the reinforcing steel.

There are several economic and ecological advantages to utilizing fly ash as a substitute for part of the cement used in concrete construction.

1. Cost - whereas the delivered price of cement is about \$30/ton, fly ash will cost \$6-\$7/ton.
2. Convenience - ash requires less pouring time and less finishing time than does standard concrete.
3. Conservation - there is a considerable savings in processing energy: 1,300 kWh/ton for cement and nominal kWh/ton for waste fly ash.
4. Expansive production - plant capacity is extended with practically no investment in new facilities.

6.1.1.2 Aggregates for Lightweight Concrete

A considerable quantity of fly ash was utilized in 1975 for producing lightweight concrete, and this use is expected to expand rapidly. Its resistance to freezing and thawing makes the lightweight aggregate prepared from sintered fly ash more valuable to roadbuilders and to the concrete construction industry.

6.1.1.3 Load-Bearing Fill

Because of its high load-bearing capacity, fly ash is often used as load-bearing structural fill for structures such as industrial buildings and schools. Its lightweight and self-hardening properties make fly ash an ideal construction raft for building developments on poor ground. Settlement is reduced to a minimum. The hardened fly ash raft forms a monolithic structure that can then bridge weak spots in the subgrade and thus reduce differential settlement.

6.1.1.4 Brick

Extensive R&D has been conducted on fly-ash brick by the Coal Research Bureau of West Virginia University (CRB/WVU). A fly-ash brick plant designed to produce 35 million bricks yearly, using a process developed at the CRB/WVU, is operating at Edmonton, Alberta. The demand for fired products from fly ash has led to the construction of a second plant for the manufacture of paving tile. Further expansion is reportedly being considered for this plant. However, efforts to expand the use of fly ash in the manufacture of ceramic brick in the U.S. have not resulted in consumption of substantial quantities of the waste.

6.1.2 FGD Sludges

Using FGD sludges in the production of aerated and poured concrete appears at present to be an attractive possibility.¹⁵³ Experiments on the potential use in wallboard are being conducted by the EPA, and Southern Services Wallboard has been manufactured using a 50/50 blend of natural and FGD sludge-derived gypsum. However, evaluations of FGD gypsum used for manufacturing wallboard are not available.¹⁴¹

6.1.3 Fluidized Bed Material

One of the uses considered for spent sorbent is in the manufacturing of gypsum board (wallboard). The TVA conducted a detailed assessment of the production and market potential, including its use for wallboard manufacture, of abatement gypsum. It does not seem likely that spent limestone sorbent, which usually contains only about 25-35% CaSO_4 , or dolomite spent sorbent, with its high content (20%) of magnesia, could meet the industry's chemical specifications or displace the much-favored natural gypsum.⁶⁸

The Coal Research Bureau of West Virginia University has investigated the use of spent lime sorbent plus fly ash for the manufacture of cement or cinder block, facing-quality brick mineral wool, cracking beds, ceramic castings, and glaze-coated materials. Of these, mineral wool production seems to have some promise.⁶⁸

6.1.4 Other Solid Wastes

Early investigations have suggested that spent oil shale could be used in concrete blocks, building brick, and portland cement.¹⁵⁴ Ash from gasification and liquefaction plants could also be used for the production of brick.¹⁴³

6.2 ROAD CONSTRUCTION MATERIAL

6.2.1 Ash⁶⁸

6.2.1.1 Lime- and Cement-Stablized Fly-Ash Pavements

The use of lime/fly-ash aggregate (LFA) and lime/cement/ fly-ash aggregate (LCFA) mixtures in pavement construction has increased substantially during recent years.

6.2.1.2 Asphalt Pavements

In general, power plant aggregates (ash and slag) can be successfully used in asphaltic compositions. The advantages of fly ash as mineral filler in asphalt paving are lower cost, acceptable size, size gradation without processing, and superior resistance to water.

6.2.1.3 Road Fill

The light weight of fly ash makes it extremely attractive as road fill, especially when embankments have to be constructed over poor ground, such as alluvial clay or silt, where excessive weight might cause settlement beyond the allowable limits and, in the worst case, could produce a complete failure of the subsoil.

The wet weight of fly ash compacted to one cubic yard is between 0.9 and 1.1 tons, depending on the source and moisture content of the material. This compares very favorably with the weight of traditional filling material.

6.2.2 FGD Sludge

Synthetic aggregates composed of lime, fly ash, and scrubber sludge have been tested as substitutes for the natural aggregate used in paving mixtures. These synthetic aggregates appear to be useful for road-base construction but not suitable for wearing surfaces.⁶⁸

6.2.3 Fluidized Bed Material

Substitution of fluidized-bed residues for part of the aggregate in asphalt has been found neither to significantly benefit nor to adversely affect the asphalt compression strength. Tests have shown that up to 92% of the aggregate could be replaced, and this would result in a 5% cost reduction.¹⁵³

6.2.4 Other Solid Wastes

Possible uses for spent oil shale would be as asphaltic concrete, highway lightweight aggregate road base, and sub-base, materials.¹⁵³

6.3 AGRICULTURAL USES

6.3.1 FGD Wastes

The use of lime/limestone wastes as a filler material and source of sulfur in granular fertilizers is being investigated at pilot-plant scale by the TVA in the Interagency Energy-Environment Program. In addition to process development, the program includes field tests, economic/marketing studies, and comparison of trace element contents with those of conventional fertilizers.

The use of natural gypsum as a calcium source for peanuts is fairly well established in the U.S., and the growth of peanuts and soybeans in mixtures of soils and Chiyoda-produced gypsum is being evaluated at the University of Florida Agricultural Center in Quincy. Early results indicate the feasibility of applying up to 20 tons of the derived gypsum per acre.⁶⁸

6.3.2 Fluidized Bed Material

Although further evaluation will be needed, initial results indicate promising applications for fluidized bed wastes in agriculture. Rather favorable results have been obtained with limestone spent sorbent as a nutrient for peanut growing. When applied to plots planted with peanuts, spent limestone sorbent from the small (about 0.7 MW) Pope, Evans, and Robbins pilot plant improved yields by about 10% over those obtained with no fertilizer. These results were equal to, or slightly better than the improvements afforded by land plaster (natural gypsum).⁶⁸

Initial studies by Ralph Stone and Co.¹⁵³ have shown that fluidized-bed residues can be used beneficially as a soil conditioner when soils are acidic, high in heavy metals, or deficient in trace metals. The height of tomato plants increased from 15 to 70% with the application of the residue. They also conclude that substitution of FBC residues for calcium carbonate as a source of calcium can be economically feasible for selected crops grown in alkaline soils containing a very high sodium ratio.

6.4 ENVIRONMENTAL IMPACTS

The major causes of potential impacts from ash utilization are fugitive dust and leachate. Control of dust will always be necessary wherever dry fly ash is handled. Hauling waste ash, even dampened fly ash, in open-bodied dump trucks is unlikely to be tolerated much longer. Tank trucks would minimize the dust problem.

Dust is also a threat in the sintering of fly ash for use in synthetic aggregates. However, this nuisance can be controlled by spraying with water; by adjustment of flow, pressure, and moisture; and by dust collection systems.

The leaching of compositions containing ash may cause environmental concern, although ash compositions can be stabilized (rendered less soluble and/or unavailable) by cementitious reactions. However, the leaching aspect certainly needs to be more fully investigated both for ash and for other wastes such as FGD sludge and fluidized-bed material.

One concern with the agricultural use of the fluidized-bed waste is the possibility of contamination of vegetables by such potentially toxic substances as lead, nickel, cadmium, chromium, arsenic, mercury, and selenium. Preliminary analysis indicates that lead, nickel, cadmium, and chromium may be present in sufficiently high concentrations to be of concern in the production of certain crops.⁶⁹ Cadmium, in particular, is a problem since it can accumulate in a leafy vegetable in high levels, although nontoxic to the plant. However, concentrations are high enough to cause toxic effects in animals, including humans.

6.5 EXTENT OF UTILIZATION

European countries utilized a major fraction of their national production of fly ash in 1971 (79% in the Federal Republic of Germany, 65% in France, 54% in the United Kingdom, 44% in Belgium, and 44% in Poland. At least in the case of the UK, this is largely due to a strong marketing effort by the Central Electricity Generating Board.¹⁵⁵

In contrast, U.S. utilization is only around 20%. However, it is encouraging to note the growth in actual tonnage of ash consumed in beneficial end uses (Table 6.1). The tonnage used in 1977 was over four times that used in 1966 (14.0 compared to 3.1 million tons), even though the percent utilization less than doubled (from 12.1 to 20.7%). As production of ash expands over the next few years, a greater tonnage may be utilized--but not necessarily a higher percentage.¹⁵⁶

Enough technically sound applications have been developed so that the annual quantity generated could be absorbed. However, it is not likely to occur in the near future because of customer uncertainties about reliability, technical complexity of application, uniformity, and quality of the new product.¹⁵³ Many of these barriers may be overcome with time and then the extent of utilization will depend on economic considerations.

For the past 10 years, the National Ash Association (NAA) has fostered development of markets for power plant ash and promoted its use for new applications. The NAA is a trade association sponsored by 30 of the electric

Table 6.1 Electric Utility Ash Utilization

	1966	1973	1974	1975	1976	1977
Ash Collected						
Fly ash	17.1	34.6	40.4	42.3	42.8	48.5
Bottom ash	8.1	10.7	14.3	13.1	14.3	14.1
Boiler slag		4.0	4.8	4.6	4.8	5.2
Total ash collected - 10 ⁶ tons	25.2	49.3	59.5	60.0	61.9	67.8
Ash Utilized						
Fly ash	1.4	3.9	3.4	4.5	5.7	6.3
Bottom ash	1.7	2.3	2.9	3.5	4.5	4.6
Boiler slag		1.8	2.4	1.8	2.2	3.1
Total ash utilized - 10 ⁶ tons	3.1	8.0	8.7	9.8	12.4	14.0
Percent of Ash Utilized						
Fly ash	7.0	11.4	8.4	10.6	13.3	13.0
Bottom ash	21.0	21.9	20.3	26.7	31.5	32.6
Boiler slag		44.3	50.0	40.0	45.8	60.0
Percent of total ash utilized	12.1	16.3	14.6	16.4	20.0	20.7

Source: Ref. 156.

utility companies of the nation, some coal companies and the National Coal Association, some university faculty members, and an impressive number of industrial firms active in utilizing ash and/or doing research on its uses.

The outlook for the use of other wastes is very uncertain. Researchers at Argonne National Laboratory estimated that little FGD waste will be used in the near future.⁶⁸ Major deterrents to utilization of lime/limestone scrubber wastes are their variable physical and chemical properties, high transportation costs, dewatering requirements for many applications, and their inability to compete economically with other materials. Although some applications appear to be technically and economically feasible, the potential use is so limited that only a small fraction of the expected sludge production could be marketed. At least for the near term, disposal of wastes by ponding or landfill will continue to be the major alternative.

Ralph Stone and Co.¹⁵³ concluded that although there may be customer resistance to a new residue, the commercial potential of fluidized-bed waste is greater than that of ash (in terms of ratio of waste used to waste product) because of the high calcium and magnesium contents.

Depending on the type of SO₂ control employed, a number of the technologies could produce elemental sulfur or sulfuric acid. Regenerable FGD systems such as magnesium oxide and the Wellman-Lord process, which produce sulfur or sulfuric acid, are available. Although their cost has to date prohibited the use of these systems by utilities, they may be used in the

future by utilities and industry where land is not readily available for solid waste disposal.

In order to reduce the solid wastes from fluidized-bed combustion and reduce the cost of sorbent, studies are being conducted into the feasibility of regenerating the bed material. This would release SO_2 , which would be converted to sulfur or sulfuric acid. Gasification and liquefaction plants will almost certainly employ sulfur emission control systems, such as the Claus or Stretford processes which produce elemental sulfur.

Routes for elemental sulfur resale include production of sulfur-containing fertilizers to slow the release of urea, sulfur-based paving material as a bulk aggregate limestone substitute, sulfur foams for pavement subsurfaces, and thermal and acoustical insulation. New uses for sulfur include plastics, surface bonding structural materials, mortar and brick panels, asphalt paving mixes and binders, soil stabilizers, and electrodes for lithium batteries. Potential agricultural uses of sulfuric acid include reclamation of sodic soils to increase plant nutrient availability; treatment of alkaline or ammoniated irrigation water; control of certain weeds and pathogens; and improvement of range grass establishment.

Use of recovered sulfur is limited, however, since the potential supply exceeds the total demand for sulfur in the U.S. Development of either new sulfur uses or acceptable methods of environmental sulfur disposal is essential.⁵³ This is illustrated in Table 6.2, which gives the approximate amount of sulfur that could be produced by a single plant in one year compared to the total quantity of sulfur which was sold in the U.S. in 1976.

Quantitative estimates or projections of trends in use for wastes other than ash are not available.

Table 6.2 Sulfur Produced by Individual Energy Technologies and Sulfur Sold in the U.S.

Technology	Sulfur Production per Plant per Year (tons)
Coal utility with regenerable FGD	42,000 ^a
AFBC with bed regeneration	36,000 ^b
Gasification	150,000 ^c
Liquefaction	120,000 ^d
Total U.S. sulfur sales (1976)	10,768,000 ^e

^aRef. 141, p. 134, 1000 MW plant using magnesium oxide scrubbers.

^bRef. 69, Vol. 1, Section 5, 600 MW plant.

^cRef. 157, p. 672, Lurgi process producing 250×10^9 Btu/day.

^dRef. 157, p. 539, SRC II process producing 250×10^9 Btu/day.

^eRef. 158, p. 1287.

7 CHARACTERIZATION OF SELECTED HAZARDOUS WASTES FROM THE INDUSTRIAL SECTOR

This section provides the background information on selected industrial solid wastes designated by the EPA as potentially hazardous to human health and the environment. Waste streams from eight industries are included: coking, petroleum refining, electroplating and metal finishing, creosote production, wood preserving, phenol/acetone production, secondary lead smelting, and primary zinc smelting and refining. Industrial profiles and manufacturing processes are described, and hazardous constituents in waste streams are identified. The information presented is primarily based on the EPA background document.¹⁰⁹

Potential problems associated with certain waste streams from energy production are identified on the basis of information on industrial hazardous wastes. Some examples are given below:

- Waste sludges from treatment of process wastewater from certain coal conversion processes (e.g., Synthane, Lurgi, and SRC-I) are potentially hazardous. These wastewater streams have been determined to contain similar pollutants (i.e., cyanide, ammonia, phenolics, and arsenic) at levels comparable to those of coke plant ammonia liquor. The EPA has determined that ammonia still lime sludges from the coking industry are hazardous to human health and the environment because they contain significant levels of toxic substances.
- Slop oil, API separator bottoms, and DAF float produced in petroleum refineries contain significant concentrations of toxic heavy metals and organics. They have been designated as hazardous wastes under the RCRA. Their counterparts in coal conversion facilities, such as oil sludges, and tar may have similar characteristics.
- The composition of biosludge from coal conversion and oil shale retort facilities could resemble those of petroleum refinery biosludge and wood preserving wastewater treatment sludges. The latter have been determined to be hazardous because they contain significant concentrations of toxic phenolic compounds, polynuclear aromatics, and volatile organic solvents such as benzene and toluene.
- Certain solid waste streams from petroleum refining, electroplating, and secondary lead smelting industries have been included in the EPA hazardous waste listing due to significant concentrations of lead and chromium.
- Available analytical data for these wastes infer that some coal utilization wastes, such as ash and char, may potentially be classified as hazardous.

7.1 COKE INDUSTRY

The EPA Administrator had determined that ammonia still lime sludge may pose a present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of, or otherwise managed, and therefore should be subject to appropriate management requirements under subtitle C of RCRA. This conclusion was based on the following considerations:

1. These wastes contain the hazardous constituents cyanide, naphthalene, phenolic compounds, and arsenic, which adhere to the lime flocs and solids in significant concentrations.
2. Cyanide and phenol leached in significant concentrations from an ammonia still lime sludge water sample, which was tested by a distilled water extraction procedure. Although no leachate data is currently available for naphthalene and arsenic, the EPA strongly believes that, on the basis of constituent solubilities, the high concentration of these constituents in the wastes, and the physical nature of the waste, these two constituents are likely to leach from the wastes in harmful concentrations when the wastes are improperly managed.
3. It is estimated that a very large quantity, 963,000 tons of ammonia still lime sludge (5% solid by weight) is currently generated annually, and that this quantity will gradually increase to 1.45 million tons (5% solid by weight) per year as the remaining coke plants add fixed ammonia removal capability to comply with Best Practical Technology (BPT) limitations. There is the likelihood of large-scale contamination of the environment if these wastes are not managed properly.
4. Coke plant operators generally dispose of these sludges on-site in unlined sludge lagoons or in unsecured landfill operations. These management methods may not be adequate to impede leachate migration.

7.1.1 Industry Profile and Process Description

The stripping of ammonia during the by-product cokemaking process is currently practiced at 39 facilities, distributed across 17 different states, with about half of the operating plants located in Pennsylvania, Ohio and Alabama. These plants are currently producing 45 million tons of coke per year. Of the 39 plants which practice ammonia recovery, 31 use lime, generating in the processes an ammonia still lime sludge. Eight plants currently use sodium hydroxide as their alkali and produce about 1/5 of the sludge volumes common to lime systems. These eight plants tend to be smaller in capacity, with smaller volumes of process wastewater to treat. The EPA believes that this sludge will be similar in composition to the ammonia still lime sludge and plans on collecting additional data to determine whether this waste should also be listed.

During the recovery of chemical by-products from the cokemaking process, excess ammonia liquor is passed through stills to strip the NH_3 from solution for recovery as ammonium sulfate, phosphate, or hydroxide. About half of the ammonia originally present (5000 mg/L) strips readily, but the remaining fraction can only be recovered by elevating the pH of the waste liquor to 10-12 through the addition of lime and passing additional steam through the solution. This stripping transfers some of the contaminants to the gas stream, but enough remains behind for the lime sludge to contain high levels of hazardous constituents (e.g., cyanide, naphthalene, phenol, and arsenic).

Cyanide, naphthalene, phenol, and other organic constituents are formed as a result of the destructive distillation of coal and are present in the ammonia liquor. Arsenic, on the other hand, is present along with other naturally occurring metallic contaminants in coal and is also present in ammonia liquor. Although other metals are present in the waste, only arsenic is deemed present in sufficient concentrations to present a problem.

Review of the chemical mechanisms, pH, and operating temperatures at which the ammonia stripping process is conducted indicates that cyanide, naphthalene, phenol, and arsenic tend to remain relatively chemically unreactive in the ammonia still stripping process. As a result, the presence of these four pollutants in the ammonia still lime sludge is predictable. Sludges are typically settled out in sedimentation basins, from which settled material is periodically removed from disposal.

7.1.2 Hazardous Properties of the Waste

Data collected by the EPA from the process wastewater samples taken before and after the addition of lime in coking operations reveal the differences in pollutant mass before and after the lime addition: 13,640 ppm of cyanide, 4,770 ppm of naphthalene, 680 ppm of phenols (the mass of phenolic compounds present in the sludge is estimated and has been adjusted for partial volatilization of the phenol in the stripper), and 1,086 ppm of arsenic are present in the ammonia still lime sludge.¹⁰⁹ A separate study of ammonia still lime sludge indicated that phenol and cyanide concentrations ranged from 670 ppm to 1910 ppm, and 343 ppm to 1940 ppm, respectively.¹⁰⁹

Cyanide, phenol, naphthalene, and arsenic tend to remain chemically unreactive in the ammonia still lime sludge. Since lime is a relatively porous substance, constituents in the lime sludge will themselves tend to be released when the waste sludge is exposed to a leaching medium.

The waste constituents appear capable of migrating from the waste in harmful concentrations. These constituents are chemically persistent, and thus have an increased likelihood of reaching an environmental receptor. Arsenic, as an element will persist indefinitely in some form. Cyanides also tend to persist after migration. Cyanides and phenols have been implicated in actual damage incidents as well, again confirming the ability of these waste constituents to be mobile, to persist, and to cause substantial harm.

The concentrations of cyanide in the leachate is far in excess of the concentrations in water considered harmful to human health and the environment. The proposed EPA Water Quality Criteria limit the level of cyanide at

0.2 mg/L and phenol at 1 ppm for domestic water supply. The EPA is not using these standards as absolute benchmarks but is citing them to give some indication that very low concentrations of these contaminants may give rise to a substantial hazard.

Although no leachate data are currently available for naphthalene and arsenic, the EPA believes that these constituents will leach in harmful concentrations from these wastes if not properly managed. Some compounds of arsenic are quite soluble. Arsenic trioxide has a solubility of 12,000 mg/L at 0 °C, and arsenic pentoxide has a solubility 2,300 mg/L at 20 °C. The solubility, the high concentrations of arsenic in the ammonia still lime sludge, and arsenic's extreme toxicity make it likely that it will leach from the wastes in harmful concentrations (i.e., a small quantity of arsenic is sufficient to present a problem to human health and the environment) if the wastes are not properly managed.

Naphthalene exhibits water solubility ranging from 30,000 mg/L to 40,000 mg/L. The solubility of naphthalene in water and its presence in such high concentrations in the waste make it likely that it will leach from the wastes in harmful concentrations if the wastes are not properly managed.

Process wastes similar in composition to coke plant ammonia still lime sludge can be produced in coal conversion and oil shale retort facilities. A study compared the process wastewater of coke plant ammonia liquor and the coal conversion processes including Synthane, Lurgi, Koppers-Totzer and SRC-I. Except for the low pressure and high temperature gasification processes (e.g., K-T process), other gasification and all coal liquefaction processes appear to produce process wastewaters with similar pollutants and composition ranges¹³¹ (see Table 4.14 of Sec. 4).

7.2 PETROLEUM REFINING INDUSTRY

The EPA has determined that API Separator Sludge, Dissolved Air Flotation (DAF) Float, Slop Oil Emulsion Solids, Heat Exchanger Bundle Cleaning Sludge and Tank Bottom (leaded) in the petroleum refining industry are solid wastes that may pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, disposed of, or otherwise managed, and therefore should be subject to management under Subtitle C of RCRA. This conclusion is based on the following:¹⁰⁹

1. The wastes contain significant concentrations of the toxic heavy metals lead and chromium. In addition to being toxic, lead has been shown to be potentially carcinogenic and bioaccumulative.
2. Current disposal methods such as land-filling, landfarming, lagooning, and incineration, if not properly designed and operated, can lead to the contamination of surface water and groundwater either by overflow of wastes or the leaching of harmful constituents from the disposal sites into the environment, thereby constituting a potential substantial hazard to human health and the environment.

Lead in the waste streams comes predominantly from the use of tetraethyl lead in the blending of leaded products. Chromium in the waste stream comes predominantly from cooling tower blowdown that uses a chromium base corrosion inhibitor.

7.2.1 API Separator Sludge

The API Separator provides for primary refinery wastewater treatment. The Separators are usually connected to the oily water plant sewer. As a result, the API Separator bottoms contain a mixture of all sewered waste, including tank bottoms, boiler blowdown, desalter wastes, and also traces of all chemical elements that enter the refinery process.

Refineries usually use gravity separation as the first step in the treatment of oily wastewaters for the removal of bulk separable oil and suspended solids. API separators, which are gravity separators designed in accordance with the criteria suggested by the American Petroleum Institute, are widely used in petroleum refineries for this purpose. Gravity separation is also used following biological and chemical floccs. In gravity separation, the wastewater is allowed to undergo "quiescent settling" in a basin. The oil globules, which are lighter than water, float to and are collected at the surface; the settleable solids settle to the bottom and are recovered as sludge. The settling basins are usually rectangular or circular in shape with accessories for introducing a raw wastewater collection of effluent, sludge, and/or oil. To maximize the use of space, the settling basin design may incorporate the use of inclined parallel plates/tubes, each representing a "mini basin" within which solids-liquids separation takes place. The efficiency of gravity separation brings finely divided oil and solid particles to the surface where they are skimmed for disposal.

Water typically constitutes 82% by weight of this waste stream, whereas oil and solids constitute approximately 12.5% and 5.5%, respectively. The solids are generally fine silts that did not have sufficient residence time in primary separators to settle, but the waste also contains the heavy metals chromium and lead.

The oil in the petroleum refinery sludge will most likely be present in the form of heavy tars, since the surface oil is skimmed periodically from the API separator. Oil content of the sludge is approximately 23% by weight whereas water and solids constitute approximately 52% and 23%, respectively. Most of the solids are silt and sand, but significant amounts of heavy metals (Cr and Pb) are also present in the sludge.

The characteristics of the organic fraction of the sludge in petroleum refineries would be similar to the bulk tars and oils produced in a coal gasifier. Because tars and oils are removed from the raw gas in a quenching operation, tar and oily sludge would contain high levels of coal-derived organic and inorganic particulate matter.

In oil shale, oil and tarry materials separated from wastewaters may constitute a semi-solid waste requiring disposal. Such material may contain suspended solids, hazardous organics, and trace elements. Handling options include incineration with air pollution control, burial with other solid

wastes in the process shale pile, and reinjection into the retort or upgrading units.

7.2.2 Dissolved Air Flotation Float

Some refineries utilize dissolved air flotation (DAF) following primary separation in the API Separator to remove additional oil and solids. The process depends on the wastewater characteristics and the hydraulic ("surface area") loading of the basin. The following ranges or removal efficiencies have been reported for the API separators in refinery oil-water separation applications; 10%-50% suspended solids; 50%-99% free oil, 5%-35% BOD and 5%-30% COD.

Although also applicable to and used for the separation of solids heavier than water, dissolved air flotation is most widely used in lieu of or as a supplement to conventional gravity separation for the removal of separable oils from oily wastewaters. Air is dissolved under pressure in a portion of the raw or untreated wastewater or in the entire volume of the raw wastewater. In all cases, the total wastewater volume is subsequently discharged to an open basin (the flotation basin) where minute air bubbles attach themselves to the oil particles and float them to the surface at a faster rate than would be achieved otherwise. The reported data for refinery applications indicate that without the addition of chemicals, flotation can result in 70%-90% removal of separable oils and 5%-25% BOD removal.

Chemicals such as iron and aluminum salts and polymeric organics are often added as coagulants or coagulant aids to improve the efficiency of gravity separation and flotation operations. When added to wastewaters, these chemicals can destabilize colloidal particles and agglomerate fine particles into larger flocs that settle or rise at a faster rate. Particle growth is often facilitated by gentle mechanical mixing (flocculation). When used in conjunction with API separators or air flotation units, coagulation/flocculation can increase removal efficiencies and/or enable higher throughput rates.

When extensive removal of oil and suspended solids is desired (e.g., for certain reverse applications), the conventional treatments such as gravity separation and chemical treatment may be followed by filtration through a bed of inert solids such as sand, diatomaceous earth, or anthracite. The suspended solids trapped in the filter are periodically removed through filter backwashing. As a polishing step for the API separator effluent, sand filtration has been reported to achieve the following removal efficiencies: 70%-75% suspended solids, 52%-83% free oil, 25%-44% COD, and 36% BOD.¹¹⁰

The wastewater treatment in the coal conversion plant at Sasol, South Africa, uses (a) API separators for the treatment of the gas reforming plant condensate; (b) tar/oil separators that operate on the flotation principle; (c) sand filtration for the treatment of the trickling filter effluent; and (d) flocculation of oily wastewaters from the Fisher-Tropsch oil production and refining units. The designs of high BTU gasification plants that have been proposed for the U.S. incorporate gravity settling of ash quench water and air flotation of the API separator effluent (in the Wesco, New Mexico plant).

7.2.3 Slop Oil Emulsion Solids

The third hazardous solid waste generated by oil refineries is slop oil emulsion solids. The skimming from the API separator generally consists of a three-phase mixture of oil, water, and a third emulsified layer. The oil is returned to crude storage, the water is discharged to the wastewater treatment system, and the emulsion (oil, water, and solids) becomes a process waste stream. A typical combination of the waste streams by weight is 40% water, 43% oil, and 12% solids.

The counterpart of the refinery slop oil in a coal conversion plant would be the product or by-product oils/tars separated from quench waters or condensates. In most coal conversion facilities, the separated oil/tar stream would be further refined (e.g., in hydrotreating of the COED oil), recycled to the gasifier (e.g., in the Lurgi process), combusted on-site for heat recovery, or sold.

7.2.4 Heat Exchanger Bundle Sludge

The fourth type of solid waste from petroleum refineries is from heat exchanger bundles that are cleaned during plant shutdown to remove deposits of scale and sludge. Depending on the characteristics of the deposits, the outside of the tube bundles may be washed, brushed, or sandblasted, whereas the inside of the tube can be wiped, brushed, or rodded out. Sludge resulting from the cleaning process has approximately 53% water, 11% oil, and 36% solids.

These solids are composed largely of silt precipitated from the water. The metals present are mostly corrosion products or scale deposits from the exchange bundle. Chromium is present in the waste in substantial concentrations, and the waste is thus listed as hazardous.

7.2.5 Tank Bottoms

The fifth type of solid waste produced by oil refineries comprises tank bottoms. After being separated in the distillation column, the petroleum products (or fractions) have to be cooled in product storage tanks before they are sent out or used for other by-products. As cooling occurs, the water separates from the hydrocarbon phase and is continually drained from the tanks to the refinery water treatment system. The solid products of corrosion in the tanks contain toxic heavy metals and are periodically removed. Such waste is listed as hazardous because it contains lead.

Data on two of the waste streams (API separator sludge and DAF float) are shown in Table 7.1 for a study in which a water-washing step was conducted to simulate leaching.¹¹¹ Chromium concentrations were in excess of 100 times the National Interim Primary Drinking Water Standard. In many cases, off-site waste disposal is implemented and these sites may be characterized by acidic environments (for instance, if they contain domestic refuse or other acidic wastes), in which case even more of the hazardous constituents would be released to the environment. Levels of chromium in coal ash leachate may be comparable to that in API sludge and DAF float.

Table 7.1 Levels of Chromium (mg/L) in Leachate for Two Petroleum Refinery Solid Wastes and Coal Ash

Petroleum Refinery ^a		Coal Ash ^b	Irrigation Water (FWPCA)	Public Water Supply Intake (EPA)
<u>API Sludge</u>	<u>DAF Float</u>			
1.9	3.3	.001 - 1.0	5	0.05

^aSource: Ref. 109.

^bSource: Ref. 111.

Although leaching data for the other three waste streams are not presently available for the petroleum refineries, the EPA believes that, because of their solubility, the contaminants found in the waste would also tend to migrate from the waste. An additional factor supporting this belief is that chromium and lead have been shown to migrate in significant concentrations from the API separator sludge and DAF float, and since the three remaining waste streams are of roughly similar composition and are generated as part of the same production process, migration patterns of these similar waste streams can be readily anticipated. Table 7.2 shows leaching data for five refinery waste streams and those for bottom ash and fly ash from conventional coal combustion.

7.2.6 Biosludges

When biological processes are employed for the treatment of aqueous wastes, the degradation of organics and the physical entrapment and settling of suspended particles occur as a result of the production of the biosludge. Sludges produced in the activated sludge and trickling filtration processes are settled in the "final" clarifiers that follow the aeration tank or the filter. In the activated sludge process, a portion of the settled sludge that is recycled from the final clarifiers typically contains 2% to 5% solids, which, in turn, generally containing 50% to 70% "volatile" matter. When lagoons and stabilization basins are used for biological treatment, the biological sludge produced and the settleable matter in the raw wastewater settle to the bottom, and the degradable material in the settled sludge undergoes aerobic and/or anaerobic decomposition. Depending on the nature and quantity of the solids in the raw wastewater and the lagoon design, periodic cleaning of the lagoons to remove the settled sludge may be necessary.¹¹⁰

Certain elements (e.g., heavy metals and refractory organics that may be present in the raw wastewater) at relatively low concentrations tend to concentrate in the biosludges. High concentrations of such substances in the sludge may eliminate certain options for sludge disposal (e.g., use as fertilizer on agricultural soils). Biosludges from refineries have been reported to contain Cr and Zn values of 540 and 200 mg/kg of dry sludge, respectively. Heavy metal concentrations are especially pronounced when anaerobic digestion is used for the stabilization and thickening of "primary" and "secondary" sludges.

Table 7.2 Levels of Chromium and Lead (mg/kg) in the Effluents of Petroleum Refinery Solid Waste Streams and Conventional Coal Combustion Solid Residues

	Petroleum Refinery ^a					Conventional Coal Combustion ^b	
	API Sludge	DAF Float	Slop Oil	Bundle Sludge	Tank Bottoms	Bottom Ash	Fly Ash
Cr	0.10 - 6,790	28 - 260	1,750	310 - 311	-	3.4 - 270	3.6 - 300
Pb	0.25 - 1,290	2.3 - 1,250	0.25 - 580	-	158 - 1,420	1 - 21	4 - 130

^aSource: Ref. 110.

^bSource: Ref. 112.

The characteristics of the biosludges from coal conversion facilities are generally expected to be similar to those of petroleum refinery biosludges. However, coal conversion biosludges may contain refractory organics that are chemically different from those in petroleum biosludges. The inorganic component of coal conversion biosludges (e.g., trace elements) may also be different.¹¹⁰

7.2.7 Spent Catalyst

Some of the catalysts used in coal conversion are the same as those used in refining operations. For example, cobalt-molybdate catalysts are used in the hydrotreating of product oil in the COED process and in refinery hydrotreating. The contaminants, which will be present on the spent hydrotreating catalysts, would differ considerably between coal conversion systems and refineries because of feedstream differences.

7.3 ELECTROPLATING AND METAL FINISHING INDUSTRY

The wastewater treatment sludge from electroplating operations has been determined by the EPA to pose a substantial hazard to human health and the environment. This conclusion is based on the following considerations:¹⁰⁹

1. Wastewater treatment sludge from electroplating operations contains significant concentrations of the toxic heavy metals chromium, cadmium, and nickel, and highly toxic cyanide.
2. Leaching tests using the extraction procedure (used in determining the toxicity characteristic) have shown that these metals leach out in significant concentrations, with some samples failing the extraction procedure toxicity characteristic. Therefore, the possibility of groundwater contamination via leaching will exist if these waste materials are improperly disposed of.
3. A large quantity of this waste is generated annually and amounts are expected to increase substantially

when the pretreatment standards for these sources become effective. Damage incidents (i.e., contaminated wells, destruction of animal life, etc.) that are attributable to the improper disposal of wastewater treatment sludge from electroplating operations have been reported, thus indicating that the wastes may be mismanaged in actual practice and are capable of causing substantial harm.

7.3.1 Process Description

Electroplating includes a wide range of production processes that utilize a large number of raw materials. Production processes include common and precious metals, electroplating, anodizing, chemical conversion, coating (e.g., coloring, chromating, phosphating, and immersion plating), electrodeless plating, chemical etching and milling, and printed circuit board manufacturing. The primary purpose of electroplating operations is to apply a surface coating, typically by electrode decomposition, to provide protection against corrosion, to increase wear or erosion resistance, or for decorative purposes. The operation itself involves immersing the article to be coated/plated into a bath consisting of substances such as acids, bases, and salts. A plating line is a series of unit operations conducted in sequence in which one or more coatings are applied or a base material is removed.

The metals used in electroplating operations (both common and precious metal plating) include cadmium, lead, chromium, copper, nickel, zinc, gold and silver. Cyanides are also extensively used in plating solutions and in some stripping and cleaning solutions. Electrodeless plating often uses copper, nickel, and tin complexed with cyanide. Etching solutions are commonly made up of strong acids or bases with spent etchants containing high concentrations of spent metal. The solutions include ferric chloride, nitric acid, ammonium persulfate, chromic acid, cupric chloride, and hydrochloric acid. Anodizing is usually performed on aluminum parts using solutions of sulfuric or chromic acid often followed by a nickel acetate seal. Chemical conversion coating most commonly involves the use of chromate or phosphate-containing baths. A number of acids can also be used (as in passivating) but are not as common as the phosphate/chromate baths.

7.3.2 Waste Stream Description

The spent plating/coating solution and rinse water are chemically treated to precipitate the toxic heavy metals and to destroy the cyanide. The extent to which plating solution carry-over or drag-out adds to the wastewater and enters the sludge depends on the type of article being plated and the specific method employed.

The composition of these sludges will vary because of the number of processing sequences that exist in the industry. However, it is expected that since most platers conduct a number of different electroplating operations, all sludges will contain significant concentrations of toxic heavy metals, as well as complexed cyanides in high concentrations if the cyanides are not properly isolated in the treatment process.

Cyanides have been shown to be extremely mobile in the soil environment and have been shown to move from soils to groundwater. Thus, cyanide is also available for potential release and transport to environmental receptors. Cyanide has been found in several different waste streams from coal technologies.

Significant levels of chromium have been detected in solid residues from various coal processes. Table 7.3 shows the chromium concentrations in leachate from certain wastes from primary plating processes. These concentrations may be comparable to those found in leachate from coal ash.

7.4 CREOSOTE PRODUCTION INDUSTRY

The EPA has determined that solid wastes from creosote production may pose a substantial present or potential hazard to human health or the environment because of the following considerations:¹⁰⁹

1. The hazardous substances likely to be present in the wastes include creosote and its constituents, benz(a)anthracene, benzo(b)fluoranthene, and benzo(a)pyrene, all of which are carcinogens. Several reported cases of cancer in humans have been attributed to creosote exposure.
2. If the lagooning/landfilling of these wastes is improperly conducted, the contamination of soil, land, and ground

Table 7.3 Levels of Chromium (mg/L) in Leachate from Electroplating Sludges and Coal Ash

Primary Plating Process ^a	
Segregated Zinc	1.22
Multiprocess Job Shop	0.2
Multiprocess with Barrel or Vibratory Finish	0.32
Printed Circuits	0.12
Coal Ash Leachate ^b	0.014 - 1.0
Water Quality Criteria	
Surface Water (FWPCA)	0.05
Irrigation Water (FWPCA)	5.0
Public Water	0.05

^aSource: Ref. 109.

^bSource: Ref. 112.

and surface water is likely to result. Since creosote is highly mobile and persistent, there is increased likelihood of hazardous waste constituents reaching environmental receptors. There is a reported incident of surface water contamination due to improper disposal of creosote wastes, demonstrating that creosote is mobile and persistent and capable of causing substantial harm if improperly managed.

3. It is estimated that 60-115 million lb/year of creosote is contained in the listed wastewater treatment sludge. Thus, substantial amounts of waste constituents are potentially available for environmental release.

7.4.1 Process Description

Creosote is produced by the distillation of coal tar, which is produced by the high temperature carbonization of bituminous coal. The two waste streams generated in the production of creosote are: 1) the process wastewater and 2) the sludge resulting from the wastewater treatment plant.

During the distillation process, an appreciable quantity of the water contained in the coal tar (1-2% of the total volume) is boiled off and disposed of along with other process waters. This aqueous waste from the distillation step in the process is the source of hazardous constituents. Creosote wastewater is either discharged to publicly owned treatment works (at smaller facilities) or treated on site in holding ponds (at larger plants). Where on-site treatment is used, ponds are dredged periodically. According to the waste disposal practice prevalent in the chemical industry, these wastewater treatment sludges are transferred to a landfill for final disposal.

On the basis of the estimated annual production of 1,150 million lb/yr of creosote, generation of 1 lb of creosote/12 lb coal tar, and a 1-2%, by volume, water content in coal tar, which is boiled off in the distillation process and disposed of as wastewater, it is estimated that 60-115 million lb of creosote per year are present in the raw process wastewater sent to treatment. Obviously, such large quantities of this waste have the propensity for large-scale environmental harm.

7.4.2 Hazardous Components of the Waste

The raw wastewater from the production of creosote is expected to contain varying amounts of creosote, the creosote constituents benz(a)anthracene, benz(b)fluoranthrene and benzo(a)pyrene, all of which are polycyclic aromatic hydrocarbons, and other distillation intermediates. The actual composition of the constituents in the wastewater from creosote production depends on the source of the coal used to produce the tar, the design and attendant operating conditions (temperature, coking time, gas collection systems) of the coke ovens, and the design and operating parameters of the still (e.g., the feed rate, temperature, and the blending of various tar distillation fractions). As a result of these factors, the fractional distillation is ordinarily incomplete and a certain amount of creosote residue is present in the raw wastewater.

These waste components could be released from holding ponds into the environment, unless proper management is assured. The migratory potential via ground and surface water, as well as the persistence of creosote have been demonstrated. Creosote and the other waste constituents may thus reach humans and animals in concentrations sufficient to pose a substantial hazard.

The wastewater treatment sludges that remain after biological treatment are also hazardous. The carcinogenic constituents of creosote, namely benz(a)anthracene, benzo(b)fluoranthene and benzo(a)pyrene, are especially likely to be present in the treatment sludge since these constituents adsorb to sediments at very high levels. Where treatment is incomplete, creosote (which is, however, somewhat amenable to biodegradation), is projected to be present in the sludge. If these sludges are placed in a leaking landfill, an unlined holding pond, or an improperly sited facility (e.g., as in an area with permeable soil) the waste constituents may be released.

7.5 WOOD PRESERVING INDUSTRY

Wood preserving processes that use creosote or pentachlorophenol as preserving agents generate a wastewater that contains toxic phenolic compounds including penta- and tetrachlorophenol, volatile organic solvents such as benzene and toluene, and polynuclear aromatic (PNA) components of creosote. Treatment of this wastewater results in the generation of a bottom sediment sludge that must be removed for ultimate disposal. The EPA Administrator has determined that wastewater from these wood preserving processes and the resulting bottom sediment sludge are solid wastes that may pose a substantial present or potential hazard to human health or the environment.

The EPA's conclusion is based on the following considerations:⁶³

1. The wastewater generated from wood preserving processes using pentachlorophenol as a preservative and the sludge generated from the treatment of this wastewater will contain significant concentrations of toxic phenolic compounds and volatile organic solvents such as benzene.
2. The wastewater from wood preserving processes that use creosote and the sludges generated from the treatment of this wastewater will contain significant concentrations of toxic polynuclear aromatic components of creosote and volatile organics such as toluene. Wastewater and resulting sludges from wood preserving operations that use both creosote and pentachlorophenol as preservatives will generate waste streams that contain all or most of the above contaminants.
3. Polynuclear aromatics, as a group, are known to be toxic, mutagenic, tetratogenic, and carcinogenic. Phenolics are toxic and, in some cases, bioaccumulative and carcinogenic substances. Benzene and toluene are relatively toxic, and benzene is carcinogenic.
4. Approximately 200 million gallons of wastewater are generated annually. About 90% of this wastewater is

treated by treatment methods that generate a bottom sediment sludge.

5. Treatment of wastewater in evaporation ponds or lagoons could lead to the environmental release of hazardous constituents and result in substantial hazards via groundwater or surface water exposure pathways. Evaporation of wastewater in ponds, lagoons, or by other treatment methods, if mismanaged, could lead to the release of hazardous constituents into the atmosphere and result in substantial hazard via an air exposure pathway.
6. Off-site disposal in landfills is the most commonly used disposal method for these sludges. This presents the possibility of the toxic components in the sludge migrating to nearby underground drinking water sources, if the landfill is improperly designed or operated.
7. The EPA has been informed that incineration is another (though less frequently used) disposal method for these sludges. If improperly managed, incineration could result in the release of hazardous vapors to the atmosphere, presenting a substantial hazard.

7.5.1 Industry Profile

There are approximately 415 wood preserving plants operated by about 300 companies in the United States. The plants are concentrated in two areas, the Southeast from east Texas to Maryland and along the Northern Pacific coast. These areas correspond to the natural ranges of the southern pine and Douglas fir-western red cedar, respectively.

Approximately 250 million cubic feet of wood are treated each year, principally for railroad ties, utility poles, and lumber for construction materials. Of this amount, it is estimated that approximately 85% is treated with creosote or pentachlorophenol-based preservatives. The total quantity of preservative consumed in 1975 during these treatment cycles exceeded 200 million pounds.

7.5.2 Process Description

At plants using creosote or pentachlorophenol-based preservatives, wood products are treated by chemical processes to increase their resistance to natural decay, attack by insects, microorganisms, or fire. Briefly, the treatment consists of debarking, forming, drying, impregnation of preservatives, and storage.

The two major wood preserving processes, producing large quantities of wastewater and sediment sludge, are called steaming and boultonizing. Both of these processes are pressure processes and differ mainly in the way the wood is conditioned before or during the application of the preservative.

Steaming is used principally on southern pines. In this process, the stock is normally steamed for 1 to 16 hours at about 120°C to reduce the

wood's moisture content and render it more penetrable to preservatives. After steaming, the preservative is added to the same retort. Condensate removed from the retort after steaming is contaminated with entrained oils, organic compounds, and wood carbohydrates.

In the boulton process, used principally on Western Douglas fir, the wood is already immersed in the preservative, placed under vacuum, and then heated in the retort at approximately 100°C. The vapor removed is composed of water, oils, organic compounds, and carbohydrates from the wood. Contaminated vapors from both the steaming and boultonizing processes are condensed and transported to an oil/water separator to reclaim any free oils and preserving chemicals before treatment and/or disposal of the wastewater, usually an oil/water emulsion.

7.5.3 Hazardous Waste Constituents

Bottom sediment sludge from wood preserving plants contains primarily creosote, polynuclear aromatics (creosote compounds), chlorinated phenols, and volatile organic solvents such as toluene and benzene.

EPA has tested samples of bottom sediment sludge and found that it contains polynuclear aromatic hydrocarbons (see below). Many wood processing plants may use both creosote and pentachlorophenol-based processes and thus treat the wastewater generated by these processes in a combined treatment system. Thus, sludge samples from one plant may contain both creosote compounds and phenolic compounds, as shown in the following table:

<u>Polynuclear Aromatic Hydrocarbons (PAH)</u>	<u>Bottom Sediment Dry Weight (mg/kg), Aerated Lagoon</u>
Benz(a)Anthracene	1250
Chrysene	9280
Benz(a)pyrene	5980

The following table shows that benzo(a)pyrene may be found in lower concentrations in both oil shale and some coals.⁷⁸

<u>Oil Shale Materials</u>	<u>(ppb)</u>
TOSCO II retorted shale	13 - 100
GCR retorted shale	15
Raw shale oil (Colorado)	30,000 - 40,000
Crude shale oil (TOSCO II)	3,130
Hydrotreated shale oil (0.25% N)	6,900
Hydrotreated shale oil (0.05% N)	690

Coals	ppb
High volatile bituminous	4,200
Low volatile bituminous	3,150
Lignite	1,200
Coal tar	3×10^6 to 8×10^6

The formation of PAHs in coal conversion processes has been well documented, and several studies have been undertaken for PAH identification and characterization in a number of waste streams at pilot gasification plants.⁵³ Mass spectroscopic analysis of tars produced in a synthane gasifier have indicated the presence of PAHs. In general, the quantities, chemical structures, and fate of PAHs in coal conversion operations are not well defined and are expected to vary among different plants, depending on the type of coal used, coal conversion process employed, and operating conditions.

Benzo(a)pyrene has been determined to be carcinogenic to experimental animals. It can induce a cancerous skin tumor in mice when 0.25 mg is injected subcutaneously.¹⁰⁹ Benzo(a)pyrene is the most widely accepted indicator of PAH content and biological activity.

7.6 PHENOL/ACETONE PRODUCTION INDUSTRY

Distillation bottom tars from the production of phenol/acetone from cumene (heavy tars) contain toxic and potentially carcinogenic organic substances, including phenol and polycyclic aromatic hydrocarbons. EPA's determination of this solid waste as hazardous is based on the following considerations:¹⁰⁹

1. Approximately 100-200 million pounds of these wastes containing phenol and PAHs from tars are generated annually at 11 plants in the United States.
2. Tars containing PAHs are demonstrated carcinogens and mutagens as well as being toxic. Phenol is a suspected carcinogen and is toxic.
3. There is potential for mismanagement of the waste by leakage during transport or storage, by improper disposal allowing leaching, or by incomplete incinerator combustion.
4. The waste tars persist in the environment, and phenol can spread rapidly in ground or surface water, posing a risk of exposure to these hazardous compounds to humans.

7.6.1 Process Description

There are two steps in the manufacturing process: 1) oxidation of cumene to cumene hydroperoxide; and 2) cleavage of the hydroperoxide to form phenol and acetone. Cumene hydroperoxide is the first main reaction product when cumene is oxidized with air at 130 °C in an aqueous sodium carbonate

medium. The reaction mix is circulated to a vacuum column where unreacted cumene is separated from the mix and a cumene hydroperoxide concentration of about 80% is obtained in the bottom product. Recovered cumene is recycled to the reactor. Any α -methylstyrene contained in the recovered cumene is separated by distillation and sold or incinerated. However, not all of the α -methylstyrene may be separated at this point. The 80% cumene hydroperoxide cumene mixture is then reacted with 10-25% sulfuric acid at 60 °C and co-mixed with an inert solvent (such as benzene) to extract organic material from the aqueous acid. The mixture is allowed to settle. The acid phase is separated out and recycled to the process. The remaining organic layer is neutralized with dilute sodium hydroxide. The resultant aqueous waste stream containing sodium sulfate, sodium phenate, phenol, acetone, and sodium stearate is separated and sent to wastewater treatment. The crude, neutralized organic layer is then sent to a series of distillation columns where acetone, cumene, phenol, and acetophenone and the solvent are recovered. The first column separates a crude acetone product overhead that is further purified by distillation. The bottoms from the acetone distillation column pass through a waste scrubber to remove residual acetone and inorganic salts. They then pass to a series of columns where the lower boiling hydrocarbons, solvents, cumene, and α -methylstyrene are successively removed, then recovered and sold or recycled and disposed of. The bottoms from the last of the series of columns contain crude phenol, which is refined in the next distillation column from which the purified phenol is removed overhead.

7.6.2 Hazardous Properties of the Waste

The bottoms from the phenol still contain phenol, acetophenone, cumyl phenol, phenyl dimethyl carbinol, higher boiling phenolic compounds, and polymers. This mixture may be further distilled to recover the acetophenone. The still bottoms remaining at the completion of distillation are the waste streams of concern.

The distillation bottoms are a tarry solid in physical form. An EPA study states that these wastes (i.e., the tars generated at the bottom of the acetophenone distillation column) amount to 50-110 g tar/kg of phenol product (100-220 lb tar/ton of phenol).

The waste tars are expected to contain large concentrations of polycyclic aromatic hydrocarbons for the following reasons. Cumene (the essential feedstock material) is itself a polynuclear aromatic hydrocarbon. In the successive steps of hydroperoxidation and acid cleavage, the aromatic ring can open, and other polyaromatic ring structures formed. These are high-boiling substances and will be found in the distillation bottom tars.

7.7 SECONDARY LEAD SMELTING INDUSTRY

The emission control dust/sludge from reverberatory furnace smelting of secondary lead products is generated when lead, cadmium, and chromium contaminants found in the source materials are entrained in the furnace fumes during the smelting process and subsequently collected by air pollution control equipment. Dry collection methods generate a dust as a solid residue; wet collection methods generate a sludge as a solid residue. The sludge is

usually disposed of on land; the dust is usually recycled for further lead smelting. Before recycling, however, the dust may be leached with acid for zinc recovery, and the resulting waste acid leaching solution containing lead, cadmium, and chromium is disposed of on land. The EPA has determined that these dusts and sludges are solid wastes that may pose a substantial present or potential hazard to human health or the environment. This conclusion is based on the following considerations:¹⁰⁹

1. The emission control dusts and sludges contain significant concentrations of the toxic heavy metals lead, cadmium, and chromium.
2. Waste leaching solutions from acid leaching of the emission control dusts and sludges contain significant concentrations of lead, cadmium, and chromium, since the acid leaching medium dissolves these heavy metals.
3. The hazardous constituents of these waste streams may migrate from the waste in harmful concentrations, since distilled water extraction procedures performed on samples of the emission control dust and sludge leached significant concentrations of lead, cadmium, and chromium from the dust.
4. The emission control sludge and the waste leaching solutions are typically disposed of in unlined lagoons, thus posing a realistic possibility of migration of lead, cadmium, and chromium to underground drinking water sources. Further, these metals persist in the environment, thereby posing a real danger of long-term contamination.
5. Very large quantities of these emission control dusts and sludges are generated annually (7,151,600 metric tons of sludge and 127,158,000 metric tons of dust in 1977) and are available for disposal as solid waste. There is thus greater likelihood of large-scale contamination of the environment if these wastes are not managed properly.

7.7.1 Process Description

Emission control dust and sludge are generated from the manufacture of refined lead, lead oxide, and lead alloy in reverberatory furnaces. In the production process, "soft lead" (low antimony lead) is smelted in a reverberatory furnace from lead residues, scrap lead. In the case of lead alloy, recycled secondary lead emission control dust is a source material. The soft lead is then further processed to either refined lead or lead oxide. In the scrubbing of reverberatory furnace emissions, cadmium, chromium, and lead entrained in the fumes are collected by either wet scrubbing or by baghouse, resulting in a sludge or dust that may be discarded. The EPA attributes the presence of lead, cadmium, and chromium in the waste stream to their presence in the source materials.

7.7.2 Hazardous Waste Constituents

The EPA presently does not have data for this industry on the heavy metal concentrations in the waste leaching solution from an operational land-fill. Concentrations of these heavy metals in the waste leaching solution, however, can be expected to be significant since the acid leaching medium will readily dissolve heavy metals. Since lead is more soluble in acid than in distilled water, the concentrations of these constituents in the dilute sulfuric acid leaching solution can be expected to be at least as great as, and more likely higher, than concentrations in the distilled water extract. Lead can be bioaccumulated and passed along the food chain but not biomagnified.

Some states are currently operating hazardous waste management programs specifically to regulate cadmium, chromium, and lead compounds as hazardous wastes. Maryland, Minnesota, New Mexico, Oklahoma, and California have final regulations, and Maine, Massachusetts, Vermont, and Louisiana have proposed regulations.

7.8 PRIMARY ZINC SMELTING AND REFINING INDUSTRY

The primary zinc industry is composed of plants that employ one of two major zinc manufacturing processes -- electrolytic or pyrometallurgical processing -- to recover zinc metal from ore concentrates. Cadmium and lead contaminants found in the raw materials are carried through numerous processes and are subsequently found in high concentrations in the wastewater treatment sludge generated by the treatment of process wastewater and/or acid plant blowdown, in the electrolytic anode slimes and sludges, and in cadmium plant leach residues (iron oxide). These wastes have been determined to be potentially hazardous to human health or the environment. The EPA's conclusions are based on the following considerations:

1. The wastes contain significant concentrations of the toxic heavy metals cadmium and lead.
2. Cadmium and lead have been shown to leach from samples of these wastes in significant concentrations when the samples were subjected to a distilled water extraction procedure.
3. These wastes are currently stockpiled on site and/or hauled off site to landfills in a manner that could allow the lead and cadmium wastes to leach to groundwater.

7.8.1 Process Description

Pyrometallurgical processing entails the following steps: sintering, retorting, refining, and casting. Sintering develops the desired characteristics for pyrometallurgical smelting of the calcine by processing the calcine in a sinter machine where the calcine burns automatically and is fused into hard, permeable sinter. Retorting consists of reducing the calcine in the sinter with carbon in a retort to produce zinc metal. Preheated feed of

sinter and coal or coke are fed into the top of the retort; the inside temperature reaches 1300 °C - 1400 °C. Because of zinc's low boiling point (906 °C), it is volatilized as soon as it is formed. In this way, the zinc is purified by separating it from the gangue in the calcine. Zinc from the retort smelting may need further purification for some commercial uses and is purified by distillation in a graphite retort. Molten zinc from the graphite retort is either poured into bars or blocks or is alloyed with other metals and cast.

The sources of hazardous solid waste generated by the pyrometallurgical process are: 1) collection and treatment of acid plant blowdown; and 2) leaching of high-cadmium dusts in the cadmium plant.

In pyrometallurgical plants, roaster off-gas is treated in sulfuric acid plants to control sulfur dioxide emissions. The acid plants produce a salable sulfuric acid bleed stream that must be neutralized. The plant neutralizes the blowdown with lime, which leads to the generation of settled sludge. The sludge contains significant concentrations of cadmium and lead.

The sources of solid waste generated by the electrolytic process are: 1) treatment of preleach residue (this operation occurs at only one plant), 2) the collection and treatment of acid plant blowdown and miscellaneous slurries, 3) the cleaning of the electrolysis cells (anode slimes and sludges), and 4) the filtration of the leach solution.

All zinc concentrations received at zinc plants are roasted to drive off sulfur and convert the zinc sulfide in the concentrate to an impure zinc oxide called calcine. The conversion to calcine in the roaster produces a roaster off-gas stream containing enough sulfur dioxide to permit sulfur recovery as sulfuric acid. The acid production results in a weak acid waste stream from the scrubbing columns that clean the off-gas. This waste is referred to as a bleed stream or acid plant blowdown. The acid plant blowdown is neutralized and thickened, and the solids are recycled or disposed of. Treatment of acid plant blowdown generates sludge that has been designated as hazardous.

All electrolytic plants also generate a waste of anode slimes or sludges from cleaning of the electrolytic cells. Anode slimes/sludges have been designated as hazardous.

7.8.2 Hazardous Properties of Waste

Current solid waste control practices are fairly uniform throughout the zinc industry. Of the total solid waste generated, about 90% is controlled through on-site stockpiling, 7% is removed by private and municipal organizations and individuals for various uses (such as winter road sand), and the remaining 3% is hauled and landfilled by private contractors.

Water extractions of the wastes have shown that the wastes could leach potentially hazardous concentrations of toxic metals. This indicates that under the mildest environmental conditions (e.g., neutral pH rainfall) at a mono-disposal site, the wastes may leach contaminants to the groundwater in.

concentrations that could be harmful to human health and the environment. Where conditions tend to be acidic, the release of heavy metals over the lifetime of a landfill is expected to be even higher than indicated by the water extraction data, since Pb solubilities increase with a decrease in pH. Lead is poisonous in all forms; it is one of the most hazardous of the toxic metals because it accumulates in many organisms, and the deleterious effects are numerous and severe. Lead may enter the human system through inhalation, ingestion, or skin contact. Ingestion of contaminated drinking water is a possible means of exposure to humans as a result of improper management of their wastes.

Table 7.4 compares the levels of lead leaching from coal ash those from solid wastes from the primary zinc smelting and refining industry. These levels appear to be comparable.

Table 7.4 Levels of Lead (mg/L) In Leachate From Coal Ash and Zinc Smelting Processes

Coal Ash Leachate ^a		Sludges from Acid Plant Blowdown (Electrolytic) ^b	Sludges from Acid Plant Blowdown (Pyrometallurgical Plant) ^b	Anode Slimes and Sludges ^b
Spent Solids Residue	Fly Ash			
1.1	1.6	1.0 - 2.1	1.3	2.0

^aSource: Ref. 112.

^bSource: Ref. 109.

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