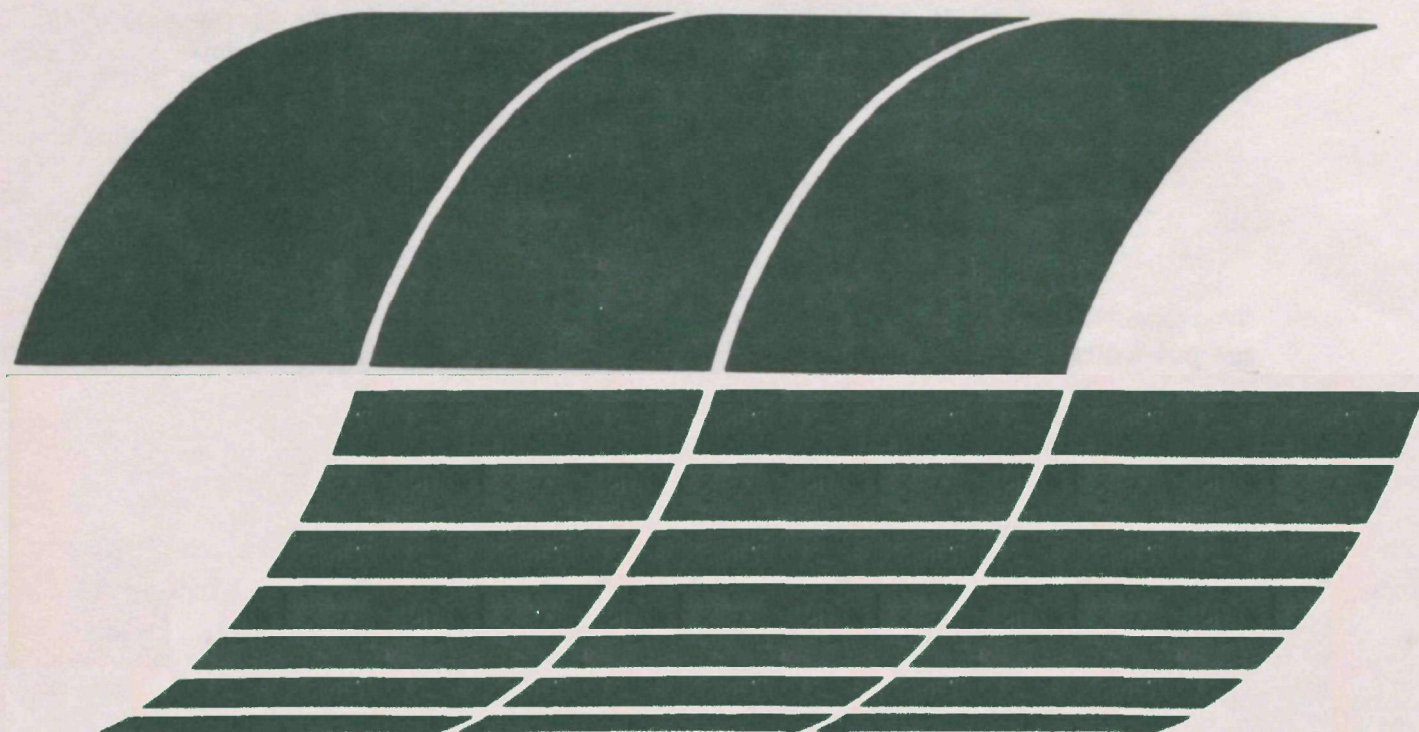




Waste and Water Management for Conventional Coal Combustion Assessment Report-1979 Volume III. Generation and Characterization of FGC Wastes

Interagency
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March 1980

Waste and Water Management for Conventional Coal Combustion Assessment Report-1979 Volume III. Generation and Characterization of FGC Wastes

by

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CONVERSION FACTORS

<u>English/American Units</u>	<u>Metric Equivalent</u>
Length:	
1 inch	2.540 centimeters
1 foot	0.3048 meters
1 fathom	1.829 meters
1 mile (statute)	1.609 kilometers
1 mile (nautical)	1.852 kilometers
Area:	
1 square foot	0.0929 square meters
1 acre	4,047 square meters
Volume:	
1 cubic foot	28.316 liters
1 cubic yard	0.7641 cubic meters
1 gallon	3.785 liters
1 barrel (42 gals)	0.1589 cu. meters
Weight/Mass:	
1 pound	0.4536 kilograms
1 ton (short)	0.9072 metric tons
Pressure:	
1 atmosphere (Normal)	101,325 pascal
1 pound per square inch	0.07031 kilograms per square centimeter
1 pound per square inch	6894 pascal
Concentration:	
1 part per million (weight)	1 milligram per liter
Speed:	
1 knot	1.853 kilometers per hour
Energy/Power:	
1 British Thermal Unit	1,054.8 joules
1 megawatt	3.600×10^9 joules per hour
1 kilowatt hour	3.60×10^6 joules
Temperature:	
1 degree Fahrenheit	5/9 degree Centigrade

GLOSSARY

Cementitious: A chemically precipitated binding of particles resulting in the formation of a solid mass.

Fixation: The process of putting into a stable or unalterable form.

Impoundment: Reservoir, pond, or area used to retain, confine, or accumulate a fluid material.

Leachate: Soluble constituents removed from a substance by the action of a percolating liquid.

Leaching Agent: A material used to percolate through something that results in the leaching of soluble constituents.

Pozzolan: A siliceous or aluminosiliceous material that in itself possess little or no cementitious value but that in finely divided form and in the presence of moisture will react with alkali or alkaline earth hydroxide to form compounds possessing cementitious properties.

Pozzolanic Reaction: A reaction producing a pozzolanic product.

Stabilization: Making stable by physical or chemical treatment.

ABBREVIATIONS

BOD	biochemical oxygen demand
Btu	British thermal unit
cc	cubic centimeter
cm	centimeter
COD	chemical oxygen demand
°C	degrees Centigrade (Celcius)
°F	degrees Fahrenheit
ESP	electrostatic precipitator
FGC	flue gas cleaning
FGD	flue gas desulfurization
ft	feet
g	gram
gal	gallon
gpd	gallons per day
gpm	gallons per minute
hp	horsepower
hr	hour
in.	inch
j	joule
j/s	joule per second
k	thousand
kg	kilogram
kCal	kilocalorie
km	kilometer
kw	kilowatt
kwh	kilowatthour
ℓ or lit	liter
lb	pound
M	million
m ²	square meter
m ³	cubic meter
mg	milligram
MGD	million gallons per day
MW	megawatt
MWe	megawatt electric
MWH	megawatt hour
μg	microgram
mil	milliliter
min	minute
ppm	parts per million
psi	pounds per square inch
psia	pounds per square inch absolute
scf/m	standard cubic feet per minute
sec	second
TDS	total dissolved solids
TOS	total oxidizable sulfur
TSS	total suspended solids
tpy	tons per year
yr	year

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1.0 INTRODUCTION

1.1 Purpose and Content

With increasing coal utilization in industrial and utility boilers, generation of coal ash (fly ash and bottom ash) and flue gas desulfurization (FGD) wastes, which together comprise flue gas cleaning (FGC) wastes, is expected to increase dramatically in the next twenty years. While utilization of FGC wastes is also expected to increase, the anticipated vast increase in generation of FGC wastes indicates that much of the FGC wastes will be discharged for disposal. In any case, these wastes present significant sources of environmental concern and utilization opportunities.

This is the third volume in a five-volume report assessing technology for the control of waste and water pollution from combustion sources. This volume provides an overall review and assessment of generation of the gas cleaning (FGC) wastes and of the characterization of the chemical, physical, and engineering properties of FGC wastes. As such, it serves as the basis for the following two volumes discussing FGC waste utilization and disposal.

The primary focus of this report is on coal-fired power plants; however, many of the characteristics discussed would also apply to wastes from oil-fired boilers. Coal-fired power plants generate the maximum range of wastes and usually the greatest quantity. Thus, they can serve as the logical focus for assessing environmental and technological problems relating to the disposal and utilization of waste materials.

A coal-fired power plant produces two broad categories of coal-related wastes:

- Coal ash, which includes both fly ash and bottom ash (or boiler slag), and
- Flue gas desulfurization (FGD) wastes from the control of sulfur dioxide emissions.

Together, fly ash and FGD wastes are generally referred to as flue gas cleaning (FGC) wastes. In many cases, fly ash and SO₂ emissions are separately controlled and represent separate waste streams. In other cases, fly ash and FGD wastes are combined in a single stream, either through admixture of these wastes or through simultaneous collection of fly ash and SO₂. This review of FGC waste generation and characteristics includes coal ash, FGD wastes, and their combination both as produced directly from FGC systems as well as wastes processed for disposal.

The review and assessment has involved two separate efforts as described below:

- (1) Review of the data and information available as of January 1979 on the generation and chemical, physical, and engineering properties of FGC wastes. The review is based upon published reports and documents as well as contacts with private companies and other organizations engaged in FGC technology development or involved in the design and operation of FGC systems and waste disposal facilities. Much of the information has been drawn from the waste characterization studies and technology development/demonstration programs sponsored by the Environmental Protection Agency (EPA) and the Electric Power Research Institute (EPRI).
- (2) Based upon the review of the data and assessment of ongoing work in waste characterization, identification of data and information gaps relating to waste generation and properties and the development of recommendations for potential EPA initiatives to assist in covering these gaps. The principal purpose of this effort is to ensure that, ultimately, adequate data will be available to permit reasonable assessment of the impacts associated with the disposal and/or utilization of FGC wastes.

Throughout this work, emphasis has been placed upon wastes produced by commercially demonstrated technologies and, where data are available, by technologies in advanced stages of development that are likely to achieve commercialization in the United States in the near future. In terms of FGD wastes, consideration is limited to nonrecovery FGD systems with focus on those producing solid wastes (rather than liquid wastes). There are very few recovery systems in operation or under construction in the United States, and these generally produce a small quantity of waste in comparison to nonrecovery systems.

1.2 Report Organization

This report presents:

- An overview of FGC technology (Chapter 2.5);
- Production trends and disposal/utilization options for FGC wastes (Chapter 3);
- Chemical characteristics of FGC wastes (Chapter 4.0),
- Physical and engineering characteristics of FGC wastes (Chapter 5); and
- An overview of research needs (Chapter 6).

2.0 OVERVIEW ON FGC WASTE GENERATION

2.1 Ash Collection Technology

Coal-fired utility and industrial boilers generate two types of coal ash--fly ash and bottom ash. (Economizer ash and mill rejects are lumped into the two major categories here.) Both constitute the non-combustible (mineral) fraction of the coal and the unburned residuals. Fly ash, which accounts for the majority of the ash generated, is the fine ash fraction carried out of the boiler in the flue gas. Bottom ash is that material which drops to the bottom of the boiler and is collected either as boiler slag or dry bottom ash, depending upon the type of boiler.

The total amount of coal ash produced is directly a function of the ash content of the coal fired. Thus, the total quantity of ash produced can range from a few percent of the weight of the coal fired to as much as 35%. The partitioning of ash between fly ash and bottom ash usually depends upon the type of boiler. Standard pulverized coal-fired boilers typically produce 80-90% of the ash as fly ash. In cyclone-fired boilers, the fly ash fraction is usually less. In some cases bottom ash constitutes the majority of the total ash.

To provide some perspective on ash collected and net particulate emissions, Table 2.1 summarizes available data on fuel use, ash collection, and net particulate emission on a state-by-state basis in 1973. Table 2.2 summarizes data on the 15 largest coal-fired plants in the United States in 1973.

Collection of bottom ash (or boiler slag) does not involve systems outside the boiler itself. The key technology issue is the handling of bottom ash which has been discussed in Volume II.

Fly ash, however, is a major source of particulate emissions and with increasing regulatory stringency has required major collection systems. Control of particulate emissions from pulverized-coal-fired steam generators is rapidly becoming a significant factor in the siting and public acceptability of coal-burning power plants. The particulate

Table 2.1

Ash Collection and Net Particulate Emissions, 1975

LINE NO	GEOGRAPHIC REGION AND STATE	COAL				OIL				GAS		NET PARTICULATES EMISSIONS (1,000 TONS)	ASH COLLECTED (1,000 TONS)
		CONSUMPTION (1000 TONS)	AVERAGE			CONSUMPTION (1000 BBL)	AVERAGE			CONSUMPTION (1000 MCF)	HEATING VALUE (1012/1013)		
			HEATING VALUE (1012/1013)	SULFUR (%)	ASH (%)		HEATING VALUE (1012/1013)	SULFUR (%)	ASH (%)				
1	NEW ENGLAND												
2	CONNECTICUT					21,994.66	144,928	.41		.08	1,000	1.45	4.23
3	MAINE					2,713.40	148,268	2.11				.30	.53
4	MASSACHUSETTS	805.10	11,852	.85	12.59	39,466.52	146,452	.73		1,004.95	1,002	17.21	94.76
5	NEW HAMPSHIRE	978.80	12,138	2.34	9.27	2,213.92	145,958	1.61				1.16	27.79
6	RHODE ISLAND					1,527.21	147,161	.93				.03	
7	VERMONT												
	TOTALS	1,783.90	12,558	1.67	10.77	67,909.91	146,631	.72		1,005.83	1,002	15.15	186.91
8	MIDDLE ATLANTIC												
9	NEW JERSEY	2,248.19	12,329	1.89	11.22	27,569.42	142,792	.36		8,103.05	1,028	3.62	433.00
10	NEW YORK	6,015.96	11,855	2.08	10.12	83,928.07	142,231	1.38		12,043.57	1,025	14.00	1,032.15
11	PENNSYLVANIA	36,716.76	11,591	3.07	10.80	17,105.68	144,083	.43		237.17	1,034	105.51	6,077.21
	TOTALS	44,979.91	11,745	2.08	10.17	123,621.17	144,609	.86		28,234.19	1,026	123.73	7,377.36
12	EAST NORTH CENTRAL												
13	ILLINOIS	32,313.31	10,354	2.47	10.98	7,245.48	145,715	.72		29,169.21	1,029	24.86	3,704.22
14	INDIANA	29,044.00	10,580	2.45	11.76	1,447.14	137,728	.17		10,455.25	1,000	133.01	1,744.05
15	MICHIGAN	21,205.75	11,009	2.42	12.78	15,037.55	141,890	.73		41,402.23	.759	117.93	2,445.64
16	OHIO	46,851.15	10,850	2.45	16.73	1,400.59	141,059	.91		4,649.33	.859	704.71	7,603.15
17	WISCONSIN	9,705.17	10,780	2.44	10.69	245.32	143,917	1.12		13,506.54	1,017	18.11	1,106.25
	TOTALS	139,119.42	10,720	2.40	13.35	25,725.60	142,840	.71		99,182.41	.964	1,001.62	18,005.76
18	WEST NORTH CENTRAL												
19	IOWA	5,048.79	10,202	1.69	10.73	93.20	137,031	.38		41,451.34	1,006	14.72	472.31
20	KANSAS	2,921.56	13,168	1.10	19.12	5,000.38	145,648	.84		137,306.01	.993	110.32	175.64
21	MINNESOTA	7,306.38	9,028	1.45	9.52	807.08	145,796	1.77		16,160.55	.976	122.52	679.97
22	MISSOURI	14,980.79	10,744	3.09	13.46	448.70	145,646	1.28		24,023.14	.578	33.36	1,408.30
23	NEBRASKA	1,265.41	10,505	.95	9.17	624.34	144,462	.78		31,390.36	.982	6.65	106.86
24	NORTH DAKOTA	4,343.03	6,636	.62	8.73	20.12	134,506	.34		76.10	1,054	27.15	362.00
25	SOUTH DAKOTA	1,574.67	6,362	.77	7.33	159.63	149,175	.74		1,714.03	1,002	4.93	115.34
	TOTALS	37,901.03	9,643	2.20	11.78	7,718.45	146,337	.98		224,644.42	.981	319.85	4,328.01
26	SOUTH ATLANTIC												
27	DELAWARE	1,060.60	12,676	3.11	10.87	6,460.09	143,811	.88		4,837.56	1,102	6.03	139.14
28	DISTRICT OF COLUMBIA	110.83	12,774	.70	5.47	2,060.05	146,632	.96				.68	18.00
29	FLORIDA	5,743.90	11,354	2.40	11.18	4,252.35	147,975	1.54		134,511.17	1,069	15.62	627.81
30	GEORGIA	12,468.56	11,665	1.69	12.25	3,733.42	146,687	1.76		38,091.14	1,020	27.60	1,326.10
31	MARYLAND	3,873.25	12,093	1.13	13.80	17,462.22	146,514	1.24				64.82	424.20
32	NORTH CAROLINA	17,554.33	11,766	1.13	13.55	327.34	138,985	.35		16.52	1,031	54.58	2,439.31
33	SOUTH CAROLINA	4,401.08	11,968	1.31	11.90	4,363.51	146,308	1.56		13,252.45	1,028	25.02	496.22
34	VIRGINIA	3,968.34	17,941	.83	14.64	2,431.69	147,932	1.68		397.59	1,119	12.02	546.34
35	WEST VIRGINIA	25,740.02	11,567	2.10	16.33	387.15	138,470	.16		359.63	.947	249.75	1,144.67
	TOTALS	75,367.36	11,702	1.79	13.95	128,443.75	147,443	1.50		192,066.16	1,014	431.30	10,313.48
36	EAST SOUTH CENTRAL												
37	ALABAMA	17,193.70	11,445	2.36	14.79	559.25	137,260	.47		5,958.49	1,033	380.05	2,161.84
38	KENTUCKY	22,326.82	10,740	3.20	15.16	242.61	134,576	.28		1,279.00	1,013	48.54	3,375.59
39	MISSISSIPPI	11,409.74	11,622	2.85	9.67	9,028.58	142,680	1.48		25,950.47	1,032	5.12	13.73
40	TENNESSEE	18,880.60	10,930	2.61	16.36	217.39	137,916	.40				180.76	2,491.60
	TOTALS	59,815.87	11,024	2.82	15.30	10,046.19	147,444	1.82		33,267.96	1,031	612.47	8,517.98
41	WEST SOUTH CENTRAL												
42	ARKANSAS					4,266.56	149,060	1.11		37,124.36	1,011	.72	
43	LOUISIANA					6,171.16	145,450	.60		309,091.17	1,064	1.04	
44	OKLAHOMA					27.81	145,593	1.13		294,091.17	1,039		
45	TEXAS	9,044.30	6,533	.55	12.38	1,652.19	145,027	.66		1,420,122.56	1,023	44.54	1,208.00
	TOTALS	9,044.30	6,533	.55	12.38	12,517.76	146,444	.77		2,024,063.83	1,033	50.30	1,208.00
46	MOUNTAIN												
47	ARIZONA	4,006.20	10,724	.45	9.15	6,925.51	144,277	.83		14,676.40	1,069	12.45	344.00
48	COLORADO	5,771.28	9,549	.52	9.02	743.49	147,432	.92		47,657.50	.952	57.87	525.03
49	IDAHO												
50	MONTANA	1,040.40	7,902	.69	8.65	2.00	146,500	1.74		618.20	1,150	1.05	74.70
51	NEVADA	3,907.57	12,289	.41	9.73	1,257.75	148,144	.71		24,418.50	1,061	6.58	407.57
52	NEW MEXICO	7,329.30	8,422	.57	22.33	1,190.04	141,253	.44		60,331.75	1,074	22.09	1,014.20
53	UTAH	2,017.05	11,868	.50	11.50	32.03	141,327	.32		2,559.424	.940	4.70	1,014.20
54	WYOMING	6,903.41	8,270	.54	10.25	104.01	137,377	.25		11.06	.833	52.31	1,024.30
	TOTALS	30,984.15	9,783	.52	12.71	10,752.00	144,758	.62		150,262.88	1,020	163.05	4,130.15
55	PACIFIC												
56	CALIFORNIA					78,499.31	146,131	.41		273,775.62	1,061	14.02	2.01
57	OREGON												
58	WASHINGTON	4,008.50	7,801	.51	14.92	64.00	137,600	.30				1.02	578.50
	TOTALS	4,008.50	7,801	.51	14.92	78,563.31	146,143	.41		273,775.62	1,061	13.04	580.51
59	NON-CONTIGUOUS U.S.												
60	ALASKA	141.92	8,350	.21	9.66	1.57	135,767	.03				2.67	9.00
61	HAWAII					8,325.40	146,864	.40				1.34	.35
62	PUEBLO ISLAND					17,344.54	146,179	2.10				2.90	.74
63	TOTALS	141.92	8,350	.21	9.66	25,671.81	146,394	1.68				6.91	10.69
64	U.S. TOTALS	402,745.36	10,775	2.19	13.85	490,776.95	147,043	.98		3,019,652.40	1,027	2,738.92	54,642.65

Unit Conversion - .907 metric tons/short ton.

Source: [114]

Table 2.2
Largest Ash-Producing Coal-Fired
Steam Electric Power Plants, 1975

<u>Plant No.</u>	<u>Plant Name/Location</u>	<u>Annual Coal Consumption</u> ('000 metric tons)	<u>Average Ash Content</u> (wt. %)	<u>Annual Ash^a Collection</u> ('000 metric tons)
1	Four Corners/New Mexico	5,510	22.6	1,240
2	Gavin/Ohio	5,230	16.4	840
3	Stuart/Ohio	4,580	19.2	820
4	Paradise/Kentucky	4,280	19.0	800
5	Sammis/Ohio	4,370	17.0	725
6	Monroe/Michigan	5,625	12.9	720
7	Keystone/Pennsylvania	3,780	19.0	710
8	Kingston/Tennessee	3,960	18.5	685
9	Montour/Pennsylvania	3,575	19.2	685
10	Harrison/West Virginia	4,105	14.0	655
11	Conemaugh/Pennsylvania	3,390	18.7	630
12	Shawnee/Kentucky	4,030	15.5	615
13	Monticello/Texas	3,240	15.4	600
14	Marshall/North Carolina	3,720	15.9	595
15	Cumberland/Tennessee	3,570	16.7	590

^aIncludes bottom and fly ash.

Source: [114]

emission limit set by the EPA for large, new coal-fired boilers is 0.043 grams/10⁶ joules (0.1 lb/10⁶ Btu). Some states have requirements more restrictive than this.

Fly ash carried in the flue gas stream can be collected in a number of ways to meet the current particulate emission control limitations as noted above. Typical methods historically employed include mechanical collection, electrostatic precipitation, fabric filtration and wet scrubbing. However, the tightening regulatory requirements support two criteria for fly ash collection systems [118]:

- The collector must be efficient in removing sub-micron size particulate matter. This criterion eliminates from consideration all mechanical collectors and many wet scrubber systems if they are used alone. Mechanical collectors may, however, function as a first unit followed by a more efficient collector.
- The collector must be available commercially and be proven in a utility boiler application. This constraint eliminates, for the immediate future, many hybrid wet scrubber systems and novel collectors that are now under development. In the long run, however, it is conceivable that such advanced systems may be used at least in some instances.

2.1.1 Mechanical Collectors

Settling chambers, cyclones, and impingement separators fall into this category. For a description of mechanical collectors, the reader is referred to references 119 and 120. Such devices are rarely more than 50-80% efficient in particulate collection, particularly at sizes less than two microns. Mechanical collectors alone are not capable of meeting present and future New Source Performance Standards (NSPS) in many cases and in the future are likely to be employed in conjunction with one of the other three methods.

2.1.2 Electrostatic Precipitators

Electrostatic precipitators (ESP's) have been the dominant particulate collection device in the electric utility industry because of their

low capital and operating cost. However, increasingly stringent emission standards have led to substantially higher costs for precipitators. These costs have increased sufficiently that fabric filtration has become a competitive alternative in achieving cost-effective control at least in some cases.

Three general types of electrostatic precipitators potentially are applicable to coal-fired boilers:

- Hot-side ESP (U.S.-style),
- Cold-side ESP (U.S.-style), and
- Cold-side ESP (European-style).

U.S.-style, cold-side ESP's which are designed to treat flue gases downstream of the combustion air preheater are most suitable for easy-to-collect low-resistivity ashes typical of eastern and mid-western medium and high sulfur coals. Hot-side ESP's (which treat flue gases upstream of the combustion air preheater) and European-style, cold-side ESP's were developed to handle the high-resistivity fly ashes typical of low sulfur coals. An alternative to hot-side ESP's and European-style ESP's for some low sulfur coal applications is the use of cold-side ESP's in combination with flue gas conditioning. This usually involves injection of a polar chemical species such as SO_3 into the flue gas to lower the resistivity of the ash through adsorption of the chemical onto ash particles. However, other conditioning agents have been developed which, in addition to reducing ash resistivity, also modify ash particle size and space charge distribution. The applicability of flue gas conditioning is a function of the coal composition, type of boiler (and its operating conditions), ESP design and particulate emissions codes. At present, over 30 different utilities employ some form of flue gas conditioning at one or more of their operating plants [115].

2.1.3 Fabric Filters

Fabric filters do not have the years of utility application compared with ESP's, and only within the past few years have fabric filters been applied to large pulverized-coal-fired boilers. However, results at

several full-scale boiler installations are reported to be encouraging and indicate that high overall efficiency and high sub-micron efficiency can be obtained, with acceptable maintenance and operating costs. The experience of fabric filtration in other industries is probably as great as that of ESP's, and many of the mechanical and process techniques developed for other applications may be applicable to the utility industry; substantial technology transfer is possible.

At present, two types of fabric filters are proved and commercially available for boiler flue gas cleaning:

- Reverse-air systems, and
- Combination reverse-air plus gentle shaking systems.

The first involves fully continuous bag cleaning while the latter uses automatic batch cyclones as a supplementary bag cleaning (i.e., ash removal) device. Use of fabric filters may make dry handling systems for fly ash more competitive. Pulse-jet type bag filters using teflon bags have been tested on boilers [121] but are not commercially proven.

2.1.4 Wet Scrubbers

Most low- and medium-pressure drop scrubbers cannot meet current and future environmental constraints. However, high-pressure (40-80" water column) venturi scrubbers can offer particulate collection efficiencies comparable to ESP's. While these are proven units, the large energy costs associated with such high-efficiency scrubbers will probably make them economically unattractive for most boiler applications. Another possible disadvantage of wet scrubbing is that it necessitates wet slurry handling systems, and hence either ponding of ash or ash dewatering facilities for ultimate dry disposal. However, one special case of wet scrubbing will continue to be employed in ash collection. Such scrubbers use alkalinity of the fly ash to collect SO_x in the flue gas as is discussed in Section 2.2.

2.2 FGD TECHNOLOGY

2.2.1 Introduction

The implementation of flue gas desulfurization (FGD) technology for the control of SO₂ emissions from the combustion of fossil fuels in industrial and utility boilers is rapidly growing in the United States. At present, FGD systems are in operation on over 16,000 megawatts of utility generating capacity at some 30 different plants throughout the country, and more than 40 industrial steam plants are equipped with FGD systems [45,116]. By the end of 1979, the total capacity of FGD systems in operation on utility and industrial boilers is expected to exceed 25,000 megawatts (equivalent). The degree of SO₂ control ranges from less than 50% SO₂ removal efficiency to over 90%, depending upon the type of FGD system, the sulfur content of the fuel, and the applicable SO₂ emissions regulations.

The growth in FGD systems on fossil-fuel-fired boilers in the United States over the next 20 years will be dependent principally upon the growth in utility and industrial boiler capacity, current and future SO₂ emission regulations, and the impact of alternative desulfurization approaches to current and developing FGD technology. An important factor may be the use of existing and enhanced coal-cleaning techniques. In addition to reductions in sulfur content, the potential benefits of coal cleaning include: reduction in ash content; increase in heating value; control of ash fusibility; reduction in quantity (cost) of coal transport; and reduction in boiler operating costs (for coal pulverizing and boiler maintenance). While in many cases the cost of deep coal cleaning may not be justified as an alternative to FGD, physical and low-level chemical coal cleaning may offer substantial overall power cost savings when employed in conjunction with partial or full FGD control. The overall cost savings though must be taken into account--not only the cost of coal cleaning and FGD but also the effects of coal cleaning on ash properties (relative to particulate control), FGD waste characteristics, and the attendant disposal costs for all wastes (coal cleaning, FGD and ash).

A wide variety of FGD processes have been developed for application on utility and industrial boilers. In general, the technology can be grouped into two categories: nonrecovery, or throwaway systems, which produce a waste material for disposal; and recovery systems, which produce a saleable byproduct (either sulfur or sulfuric acid) from the recovered SO_2 . Nonrecovery processes make up the overwhelming majority of the technology. Nine different processes and process variations can be considered to be commercially available, seven of which are nonrecovery systems. These seven processes constitute more than 95% of the capacity currently in operation on utility and industrial boilers, a trend which is expected to continue for the foreseeable future. Table 2.3 summarizes the applications of different FGD process technologies for systems expected to be in operation by the end of 1979; and Table 2.4 summarizes FGD systems for utility boilers that are expected to be operational by 1982 (those now in operation and those in design and under construction).

2.2.2 Nonrecovery Processes

Nonrecovery processes in general can be subdivided into two groups, wet processes and dry processes. Wet processes involve contacting the flue gas with aqueous slurries or solutions of absorbents and produce wastes in the form of solutions or slurries for direct discharge or further processing prior to disposal. In many cases, waste slurries are partially dewatered and further processed to produce a soil-like material for landfill. Dry processes, on the other hand, produce essentially moisture-free waste solids through the use of dry injection of absorbents or spray dryers. All nonrecovery processes now in operation as well as those due to come on line in 1979 involve wet scrubbing. However, a number of contracts have been signed for the application of dry systems to utility boilers which will start up in the early 1980's.

2.2.2.1 Wet Processes

Of the seven different types of nonrecovery processes now in commercial operation on industrial and utility boilers, five involve conversion of the SO_2 to some form of solid waste (sludge) for disposal

Table 2.3
Summary of FGD Systems Expected To Be
in Commercial Operation on Boilers in 1979

	Utility		Industrial	
	Number of Plants	Capacity (MW)	Number of Plants	Capacity (10 ³ scfm)
Nonrecovery				
Direct Limestone-Conventional and Forced Oxidation	19	11,780	1	50
Direct Lime	13	7,305	1	85
Alkaline Ash	2	1,170	0	--
Dual Alkali	3	1,105	8	1,082
Once-Through Sodium	1	510	26	4,954
Ammonia	<u>0</u>	<u>--</u>	<u>7</u>	<u>552</u>
Total	38	21,870	43	6,722 (~3000 MW-eq)
Recovery				
Wellman-Lord	2	735	0	--
Citrate	0	--	1	104
Mag-Ox ^a	<u>0</u>	<u>--</u>	<u>0</u>	<u>--</u>
Total	2	735	1	104 (~50 MW-eq)

^aTwo systems have been commercially operated on utility coal-fired boilers but these are not currently in operation.

Source: [45, 116]

Table 2.4

Summary of FGD Systems Expected To Be in
Commercial Operation on Utility Boilers in 1982

(as of February 1979)

	<u>Utility</u>	
	<u>Number of Plants</u>	<u>Capacity (MW)</u>
Nonrecovery		
Direct Limestone-Conventional and Forced Oxidation	28	21,328
Direct Lime	16	11,445
Alkaline Ash	4	3,597
Dual Alkali	3	1,105
Once-Through Sodium	1	510
Ammonia	0	--
Dry Sorbent - Sodium and Calcium Based	1	450
	<hr/>	<hr/>
Total	53	38,435
Recovery		
Wellman-Lord	3	1,855
Citrate	0	--
Mag-Ox ^a	0	--
Aqueous Carbonate	<u>1</u>	<u>100</u>
Total	4	1,955

^aTwo systems have been commercially operated on utility coal-fired boilers but these are not currently in operation.

Source: Arthur D. Little, Inc.

in either wet ponds or landfills:

- Conventional direct lime scrubbing,
- Conventional direct limestone scrubbing,
- Limestone scrubbing with forced oxidation,
- Alkaline fly ash scrubbing, and
- Dual alkali.

Two systems produce a soluble waste which is discharged as an aqueous liquor to holding ponds or wastewater treatment systems:

- Once-through sodium scrubbing, and
- Ammonia water scrubbing.

As shown in Table 2.3, essentially all utility applications of nonrecovery technology involves solid waste-producing systems. In contrast, a large majority of industrial boiler applications of FGD involve the production of liquid wastes.

Both types of wet scrubbing nonrecovery systems can usually withstand relatively high levels of particulate, and many in the past have been designed for simultaneous SO_2 and particulate removal. Approximately 40% of FGD systems currently in operation on utility boilers and about 80% of those in operation on industrial boilers serve as combined particulate and SO_2 control systems. However, most systems being installed today on utility-scale boilers follow high efficiency electrostatic precipitators in order to ensure reliable service of the FGD system. In fact, all 7,500 megawatts of FGD capacity scheduled to start up on utility boilers in 1979 involve SO_2 removal only. This trend is expected to continue as more stringent particulate emissions control regulations make wet scrubbing for particulates unattractive. For industrial boilers, however, it is likely that a large number of new FGD systems, at least for the next few years, will continue to serve as both particulate and SO_2 control systems. Particulate emissions codes tend to be less stringent at present, and in many cases the range of sizes of particulates encountered is difficult to reliably control with electrostatic precipitators (such as that from combined fuel boilers at pulp and paper plants).

2.2.2.1.1 Solid Waste-Producing Systems

All of the solid waste-producing processes utilize some form of lime or limestone to produce a mixture of insoluble calcium sulfite and calcium sulfate salts as the principal waste product. Four of the five technologies utilize slurry scrubbing (direct lime scrubbing, direct limestone scrubbing, alkaline ash scrubbing, and limestone scrubbing with forced oxidation), and their application is almost exclusively limited to utility boilers. Only one, the dual alkali process, involves solution scrubbing where spent absorbent solution is regenerated using lime to produce a waste solid of calcium-sulfur salts. It is being applied to both industrial and utility boilers.

Conventional direct lime and limestone scrubbing constitute the majority of FGD systems on utility boilers. In these systems, flue gas is contacted with a slurry of calcium salts (calcium sulfite/sulfate and calcium hydroxide or calcium carbonate) and sometimes fly ash at total suspended solids concentrations of 8-16 wt%. Slurries are recirculated through an open venturi or spray-type scrubber at high liquid-to-gas ratios, and the spent liquor is collected in a delay tank to allow completion of the precipitation reactions. Fresh alkali makeup (either slaked lime or a slurry of finely ground limestone) is added to the delay tank, and a slipstream is removed for solids separation. The rate of fresh alkali makeup is controlled on pH with lime systems usually operating at a pH of 6-7, slightly higher than the pH of limestone systems (5-6). Alkaline ash scrubbing systems, which are similar in scrubber configuration and operation, usually operate in a much lower pH range (3.5-5.0) to effect good utilization of the ash alkali content. The waste slurry can be discharged directly to a wet pond (sometimes after thickening) where the solids are settled out and supernate returned to the scrubber system; or it can be thickened and filtered for discharge to a dry impoundment. The latter may require further processing of the wastes.

There are a number of variations on conventional direct lime and limestone scrubbing systems directed toward improving SO₂ removal and overall scrubber system reliability. Many full-scale lime scrubbing

systems, for example, use either carbide lime or a dolomitic (high magnesium content) lime rather than commercial lime. (Dravo Corporation markets a special high magnesium content lime for FGD systems under the name Thiosorbic lime.) The use of these limes effect lower oxidation rates and therefore better control of scrubber scaling. Also, the high magnesium content lime or the addition of magnesium oxide to commercial lime usually results in higher SO₂ removal efficiency and improves lime utilization for high sulfur coal systems (reducing lime stoichiometries from typical levels of 1.1-1.3 to 1.0-1.15).

A principal variation on direct limestone scrubbing involves intentional oxidation of the calcium-sulfite salts formed in the scrubber to calcium sulfate. This is done in order to improve SO₂ removal efficiency, minimize scale and plugging potential, improve solids dewatering properties (by converting the wastes to gypsum), and increase limestone utilization. It is hoped that use of forced oxidation in high sulfur coal applications will reduce limestone stoichiometries from the typical levels of 1.25-1.5 to 1.05-1.1. In the simplest form of the forced oxidation process, air is bubbled through the slurry in a modified delay tank; however, two-stage scrubbing has also been employed to cause intentional oxidation.

Direct lime, direct limestone, and alkaline ash scrubbing systems have demonstrated high availability and reliability in many utility-scale boiler applications. Lime systems have shown good operability in applications to the full range of coal sulfur contents. In low sulfur coal applications, commercial-grade lime frequently is used, since the system chemistry is fairly easy to control and relatively high oxidation rates exist; however, in high sulfur coal applications, magnesium oxide addition with commercial-grade lime or special lime such as dolomitic or carbide lime has been required. Most successful limestone systems to date have been in low and medium sulfur coal applications, again where oxidation rates are relatively high. Forced oxidation using limestone scrubbing, though, offers the potential for broadening the applicability of limestone scrubbing to high sulfur coals.

The dual alkali process is a second generation technology which is just now reaching commercial demonstration in utility-scale applications, although there are a number of successful dual alkali systems in operation on industrial-scale boilers. In dual alkali systems, SO_2 removal is accomplished using solutions of sodium salts which are then regenerated with lime to produce a waste calcium-sulfur salt that is similar in chemical composition to the waste produced from direct scrubbing systems. Dual alkali systems are most appropriate for medium and high sulfur coal applications where relatively high SO_2 removal efficiencies are required and where oxidation rates tend to be relatively low. Waste solids from dual alkali systems are always discharged as washed filter cake; filters are used to recover sodium salts in order to minimize sodium carbonate makeup requirements and reduce the potential adverse environmental impacts from the high TDS levels in the waste material.

2.2.2.1.2 Liquid Waste Systems

Liquid waste-producing systems have achieved a high degree of utilization in industrial-scale boiler applications of FGD technology. Of the two process technologies, once-through sodium scrubbing is the most widely used, accounting for over 70% of the total FGD capacity on industrial boilers. In once-through sodium scrubbing, the flue gas is contacted with a recirculating solution of sodium salts consisting principally of sodium sulfite/bisulfite, sodium sulfate, and sodium chloride. The type of scrubber is dependent primarily upon the degree of SO_2 control required and whether or not particulate is being simultaneously controlled. The pH is controlled in the range of 5-7 through the addition of fresh alkali (e.g. caustic or soda ash). A slipstream of spent liquor is removed for discharge to holding pond and/or wastewater treatment systems. Frequently, the waste liquor is treated prior to discharge. Treatment can involve neutralization and oxidation of sulfite salts to sulfate.

Once-through sodium systems are capable of achieving very high SO_2 removal efficiencies, approaching 99%. However, the high cost of sodium makeup and the problem of liquid waste disposal tend to limit the applicability of once-through sodium systems. Most applications are on low

sulfur fuels (where sodium makeup requirements are relatively low) or in cases where an inexpensive source of alkaline sodium salts is available. Instead of soda ash or caustic, some systems utilize brines, trona (impure soda ash), or other waste process liquors.

There are only a few systems in operation involving ammonia scrubbing. All are on industrial boilers and all utilize ammonia-laden process water. Many of these systems have been installed primarily as wet particulate scrubbing systems where the ammonia water is used to control the pH of the scrubbing water. Spent liquor is usually sent to a settling pond for removal of the particulate and the supernate treated prior to discharge.

2.2.2.2 Dry Processes

As previously indicated, dry nonrecovery processes have not yet been commercially demonstrated in the United States, although at least three systems for full-scale utility applications are in the early stages of planning or design.

Three different approaches to dry scrubbing for producing solid wastes have been actively pursued [57]:

- Injection of solid sorbents into the flue gas stream with collection of sorbents downstream in a particulate control device,
- Injection of solid sorbents into the boiler combustion zone, and
- Contacting of flue gas with alkali sorbent slurries in a spray dryer.

All of these approaches involve simultaneous particulate and SO₂ control, and all offer the advantage of not requiring flue gas reheat, which wet processes generally do require.

The leading approach at present is based on the use of a spray dryer. An aqueous solution or slurry sorbent is injected as a fine mist into the ash-laden flue gas in a spray chamber. The hot gas evaporates the water, and some SO₂ is removed through reaction with the alkali. The gas then passes to a dry particulate collector (fabric filter or electrostatic precipitator) where the fly ash and dry sorbent solids are

removed and further SO₂ removal is achieved. The flue gas is then exhausted directly to the stack without reheat. Reheat is not required since the flue gas is not saturated in the spray dryer.

A number of different sorbents have been tested for dry SO₂ removal including soda ash, trona, nahcolite, lime, and limestone. Soda ash generally provides the highest SO₂ removal capability in excess of 90% at reasonable stoichiometric ratios. Lower SO₂ removal is achieved using lime--60-75% SO₂ removal at stoichiometries of 1.0-1.5. Higher removal efficiencies using lime require unrealistically high stoichiometries. Thus, the application of dry sorbent systems may be limited to low and medium sulfur coals due to the high costs of reagents.

The wastes are discharged as a dry material. The composition will, of course, vary according to the type of reagent used. However, it is expected that the majority of the wastes, aside from fly ash, will consist of sulfate, sulfite, and chloride salts of either sodium or calcium, with sulfates being the predominant species.

One spray dryer system utilizing soda ash is now in design for a utility boiler (a 410-MW unit at Ottertail Power's Coyote Station) and two other contracts have been awarded by Basin Electric Power Cooperative [117]. These latter two will utilize lime as the absorbent. All three of these systems will be installed on low sulfur coal or lignite-fired boilers.

Testing of the other two approaches, injection of sorbents into the flue gas and into the boiler combustion zone, has been ongoing at various levels of activity over the past ten years. Of late, there has been renewed interest in these approaches for low sulfur coal applications. Testing of flue gas injection has focused on the use of sodium bicarbonate nahcolite (impure sodium bicarbonate) and soda ash, all of which have been shown to be effective for SO₂ removal for injection/baghouse collection systems. The most active for SO₂ removal is apparently nahcolite, with removal efficiencies of 60-80% for low and medium sulfur coals at stoichiometries of 0.8-2.0 (based on available alkali). This technology is now being commercially offered.

Boiler combustion zone injection is not being commercially offered, although test work is continuing. The present focus is the mixing of alkali reagents (e.g., lime, limestone, or soda ash) with the coal prior to injection into the boiler. Preliminary results indicate appreciable SO₂ removal efficiencies.

2.2.3 Recovery Processes

As in the case of nonrecovery processes, recovery processes can also be categorized into wet and dry according to the mode of SO₂ removal. They can be further classified according to the type of byproduct produced: concentrated SO₂ for conversion to sulfur or sulfuric acid; sulfur only; or acid only.

At present, only two process technologies have been commercially demonstrated on large industrial- or utility-scale boilers--the Wellman-Lord process and magnesium oxide scrubbing. Another, the citrate scrubbing process, is currently being commercially tested on a large industrial boiler. All three of these are wet scrubbing processes.

The total capacity attributable to these three technologies (including a magnesium oxide system not now in operation) is less than 5% of the total FGD operating capacity in 1979.

2.2.3.1 Wet Processes

Wet scrubbing recovery processes are similar to nonrecovery systems in that solutions or slurries are used in contacting the flue gas for SO₂ removal. Furthermore, the types of scrubbers used are also similar to those for nonrecovery systems. As previously noted, three processes have reached commercial demonstration:

- Wellman-Lord process,
- Magnesium oxide scrubbing, and
- Citrate process.

SO₂ removal capabilities of each of these processes exceeds 90%; however, each involves completely different process chemistry.

The Wellman-Lord process involves absorption of SO_2 by a concentrated aqueous solution of sodium sulfite to produce a solution of sodium sulfite/bisulfite. The scrubber effluent is recovered thermally with steam to produce a sodium sulfite solution for recycle to the scrubber system and a concentrated SO_2 gas for further processing. SO_2 removal efficiencies in excess of 90% can be achieved easily. A small portion of the sulfite absorbent (3-15% of the SO_2 removed) may be oxidized to sulfate. Since sulfate cannot be thermally regenerated, it is purged from the system, preferably as a dry solid for sale or disposal.

The magnesium oxide process involves scrubbing with a slurry of magnesium oxide to produce solid magnesium sulfite and sulfate (from oxidation of sulfite). The solid is removed from suspension by dewatering equipment, dried and roasted in a reducing atmosphere to decompose the magnesium sulfite/sulfate into magnesium oxide and sulfur dioxide. The regenerated magnesium oxide is returned to the scrubbing system, and the sulfur dioxide is processed into its final byproduct form. The regeneration step can be performed at the power plant site or at a remote facility by shipping the magnesium sulfite and oxide, as a dry material, to and from the regeneration facility. Because of the nature of the calcining operation, the concentration of SO_2 in the product gas is relatively low (5-10%), so the gas is most suitable for conversion to sulfuric acid.

In the citrate process the flue gas is scrubbed with a solution of sodium citrate. The sulfur-laden solution is reacted with hydrogen sulfide gas, and sulfur is precipitated. The precipitated sulfur may be separated from the citrate solution by either a kerosene-additive flotation or an air flotation technique. Two-thirds of the product sulfur is reacted with reducing gas to form H_2S for the Claus reactor; the rest of the sulfur is recovered for sale. A bleedstream of the regenerated absorbent is fed to a crystallizer where sulfate formed by oxidation of sulfite is removed as gypsum or Glauber's salt. The process has also been modified to produce concentrated SO_2 gas (for conversion to acid) by thermal stripping of the sulfur-laden citrate solution.

All of these processes have two features in common: first, they have limited tolerance to the buildup of impurities in the absorption/regeneration systems (e.g., chlorides and fly ash); and second, there is a practical limit to the amount of absorbent oxidation that can be tolerated. Thus, they are most appropriate for high sulfur coal application following high-efficiency dry particulate removal systems (ESP's). In most applications to coal-fired boilers, the SO_2 absorbers would be preceded by wet scrubbers to minimize the pickup of fly ash, chloride, and other impurities by the absorbent liquor. The prescrubbing medium is recirculated water, with the only makeup requirement being that required to replenish evaporation losses plus liquor purge. The bleed rate of the purge liquor can be set either by the level of suspended solids to maintain it below about 5 wt%, or by the calcium concentration (from fly ash dissolution) to maintain it below the gypsum solubility product to prevent scaling.

In addition to accomplishing the absorption of chloride and the removal of fly ash, the prescrubber also absorbs some SO_2 from the flue gas. The SO_2 absorption will vary depending upon the liquor bleed rate and the gas composition, but it conceivably can range from a few percent of the inlet SO_2 to as much as 10% or more (especially for low sulfur coal applications). The prescrubber purge, therefore, will be very acidic and will require treatment such as neutralization and solids separation prior to discharge. If neutralization is effected using lime or limestone, then the solid waste ultimately produced will have a chemical composition not unlike the wastes produced from nonrecovery systems.

The Wellman-Lord and citrate processes also produce another secondary waste stream, impure sodium sulfate. The amount will vary according to the extent of absorber oxidation but will typically correspond to about 5% of the SO_2 removed. While magnesium oxide scrubbing does not produce a secondary waste stream of sodium sulfate, it does appear to have an upper limit of about 15% oxidation based upon the ability of the calcining operation to regenerate magnesium sulfate. At higher levels it would probably be necessary to purge some regenerated absorbent to keep magnesium sulfate levels down to prevent scaling in the absorber.

2.2.3.2 Dry Processes

There are presently no dry sorbent systems in operation on utility or industrial boilers; however, there are four in advanced stage of development:

- Aqueous carbonate process,
- Shell/UOP copper oxide adsorption,
- Catalytic/Westvaco dry activated carbon, and
- Bergbau-Forschung/Foster Wheeler process.

The aqueous carbonate process is now being installed on an EPA demonstration unit on a 100-MW utility coal-fired boiler. The process is based upon sodium carbonate scrubbing using a spray dryer for gas contacting, analogous to that discussed with regard to dry nonrecovery processes. Primary particulate removal would be accomplished upstream of the spray dryer using mechanical collectors. Dryer waste solids (principally sulfite/sulfate solids, unreacted carbonate, and some fly ash) are collected and fed to a molten carbonate reactor where the sulfur is reduced to sulfide by carbon (petroleum coke or coal) at a temperature of about 1800°F. A portion of the carbon is combusted to provide heat for the endothermic reduction reactions and system heat losses. The sodium sulfide melt from the reducer is quenched, and the fly ash and unreacted carbon are filtered from the resulting green solution. The CO₂-rich reducer offgas and the green liquor are then reacted to regenerate sodium carbonate. The hydrogen sulfide stream is sent to a Claus plant for sulfur production.

Process wastes include wet filter cake containing mostly fly ash but also residual Na₂S and NaHS and a chloride blowdown stream. In order to achieve a particulate emission of 0.01 gr/scf or less, the process design specifications may include high efficiency particulate collection downstream from the spent absorbent collection device (depending upon the type of device used).

The other three dry processes noted above use dry adsorbents for SO_2 removal. As such, they do not produce any appreciable waste liquor or solid purges other than spent catalysts or adsorbents. These have all been operated either in the United States or Europe on boilers up to about 50 MW in size; however, they have not yet achieved commercial demonstration in the United States.

2.3 Categorization of FGC Wastes

The quantity and characteristics of coal ash and FGD wastes produced from a combustion system depend on a variety of factors including:

- Characteristics (ash and sulfur content) of coal,
- Type of combustion (boiler) system and its operating conditions,
- Type of particulate collection system and its operating conditions, and
- Type of FGD system and its operating conditions.

Categorization of FGD wastes and coal ash requires an understanding of the substances making up FGD wastes.

The principal substances making up the solid phase of FGD wastes are calcium-sulfur salts (calcium sulfite and/or calcium sulfate) along with varying amounts of calcium carbonate, unreacted lime, inerts, and/or fly ash. The ratio of calcium sulfite to calcium sulfate is a key parameter (the latter, usually present as $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ or as gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) will depend principally upon the extent to which oxidation occurs within the system. Oxidation is generally highest in systems installed on boilers burning low sulfur coal or in systems where oxidation is intentionally promoted. Fly ash will be a principal constituent of the waste only if the scrubber serves as a particulate control device in addition to SO_2 removal or if separately collected fly ash is admixed with sludge. The amount of inerts and unreacted raw materials (lime and/or limestone) in sludges depends on the quality and utilization of raw materials (system stoichiometry).

When the sulfate content of the waste solids is low, calcium sulfate can exist with calcium sulfite as a solid solution of hemihydrate crystals ($\text{CaSO}_x \cdot 1/2 \text{H}_2\text{O}$). Data from pilot plant, prototype, and full-scale FGC

system operations indicate that up to 25-30% of the total calcium-sulfur salts can be present as $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ in solid solution with $\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$. At higher calcium sulfate levels, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) becomes the predominant form of calcium sulfate. It is expected that at very high levels of oxidation (greater than 90% oxidation of the SO_2 removed) the calcium sulfite can form a solid solution with gypsum ($\text{CaSO}_x \cdot 2\text{H}_2\text{O}$) analogous to the solid solution of hemihydrate salts formed at low sulfate levels.

Because the differences in the crystalline morphology of hemihydrate and dihydrate solids not only reflect the chemical composition but also to a large extent dictate the physical and engineering properties of FGC wastes, it is convenient to classify FGC wastes on the basis of the calcium sulfate content. Three such categories have been selected, as follows:

<u>Category</u>	<u>Predominant Crystalline Form</u>
Sulfate-rich ($\text{CaSO}_4/\text{CaSO}_x \geq 0.90$)	Dihydrate
Mixed ($0.25 \geq \text{CaSO}_4/\text{CaSO}_x \geq 0.90$)	Dihydrate and hemihydrate
Sulfite-rich ($\text{CaSO}_4/\text{CaSO}_x \leq 0.25$)	Hemihydrate

where CaSO_x is the total calcium-sulfur salt content. This categorization will be employed in the ensuing discussions throughout this report.

Factors which tend to influence the amount of sulfite in FGC wastes (i.e., the extent of oxidation) are:

- Boiler excess air,
- Type of scrubber,
- Use of forced oxidation,
- Presence of oxidation inhibitors or catalysts in fly ash, reagents, or water makeup,
- Type of reagent,
- pH in the scrubber loop, and
- Sulfur content of the coal and the degree of SO_2 removal.

In general, it is possible to relate the three general categories of wastes indicated above and their associated crystalline morphologies with various types of FGC process technologies and their applications according to the coal sulfur content. Such a matrix relationship is shown in Table 2.5. As indicated, dual alkali and conventional direct lime scrubbing systems using either carbide or Thiosorbic lime almost exclusively produce sulfite-rich wastes. Such systems are generally applied to medium and high sulfur coal-fired boilers, and attempts are made to minimize oxidation. On the other hand, alkaline ash and limestone forced oxidation systems produce sulfate-rich wastes almost exclusively. And conventional direct lime (using commercial lime) and limestone systems can produce either sulfite-rich, sulfate-rich, or mixed wastes depending upon the sulfur content of the coal and the manner in which the scrubber systems are operated.

2.4 Dewatering of FGC Wastes

The following review of FGC waste dewatering is restricted to wastes produced from SO₂ scrubbing (both systems for SO₂ control only, and for simultaneous SO₂ and particulate control) and wet particulate scrubbing systems (which also effect a small degree of SO₂ removal). Bottom ash and fly ash are relatively easily dewatered materials in relation to SO₂ scrubbing wastes. Bottom ash and many fly ashes are free draining, and sluiced ash can usually be adequately dewatered to high solids contents by settling or settling with underdrainage. Only a few coal-fired steam or power boilers utilize any means of dewatering beyond gravity sedimentation, including those which ultimately use the ash for fill (where the ash is usually dredged from settling ponds).

2.4.1 State of the Art

Most unthickened slurry wastes produced by FGC systems contain on the order of 5-15 wt% suspended solids. In order to avoid the unnecessary discharge of large amounts of process liquor, these wastes frequently are dewatered mechanically prior to being discharged from the process. Primary dewatering usually is accomplished using thickener/clarifiers or settling ponds. Primary dewatering is virtually universally practiced

Table 2.5

Matrix of Unstabilized FGD Waste
Generation-Nonrecovery Solid Waste Producing Systems

No.	Waste Type ^a	Crystalline Morphology	Low Sulfur Coal ^b				Medium/High Sulfur Coal ^c			
			DL ^d /AA ^e	DLS ^f	LSFO ^g	DA ^h	DL	DLS	LSFO	DA
1	Sulfite-rich ($\text{CaSO}_x \cdot 1/2\text{H}_2\text{O}$)	Needles	-	-	-	-	-	-	-	-
		Platelets	-	-	-	-	✓	✓	-	-
		Agglomerates	-	-	-	-	✓	?	-	✓
2	Mixed Sulfite/Sulfate ($\text{CaSO}_x \cdot 1/2\text{H}_2\text{O} + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	Needles or Platelets + Platy ⁱ	✓	✓	-	✓	✓	✓	-	✓
3	Sulfate-rich ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ +/- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) ⁴	Needles or Platy ⁱ	✓	✓	✓	✓	?	✓	✓	-

^aSulfite-rich = $\text{CaSO}_4/\text{CaSO}_x \leq .25$
Sulfate-rich = $\text{CaSO}_4/\text{CaSO}_x \geq .9$

^bLow sulfur coal <~2% S.

^cMedium/high sulfur coal >~2% S.

^dConventional direct lime process.

^eAlkaline ash scrubbing.

^fConventional direct limestone process.

^gLimestone with forced oxidation.

^hDual alkali process.

ⁱResembling rhombohedral cleavage fragments.

Notes: ✓ Refers to the particular waste type as the common waste product from the type of coal and process.

? Some question on this.

Source: Arthur D. Little, Inc.

in order to reduce sludge volume and conserve water. Secondary methods of dewatering are also sometimes employed. These include vacuum filtration and centrifugation. Secondary dewatering is only employed as a precursor to dry impoundment in order to improve the handling properties of the wastes prior to truck transport or stabilization. Table 2.6 summarizes dewatering practices for full-scale FGC systems in operation on utility boilers as of November 1978.

Table 2.6 shows some interesting trends in dewatering practices in the utility industry:

- No simultaneous SO_2 and fly ash control systems or wet particulate scrubbing systems employ secondary methods of dewatering (i.e., filtration or centrifugation) for FGC waste dewatering, although a number of the plants do dispose of wastes via dry impoundment of wastes reclaimed from secondary settling ponds.
- The overwhelming majority of the FGD capacity for SO_2 removal only involves thickening and filtration or centrifugation for dry impoundment of the wastes. This trend is expected to continue for the foreseeable future. About 6,700 megawatts of new, nonrecovery FGC capacity producing solid wastes are expected to be on-line in 1979, all of which will be devoted to SO_2 control only. Of this total, approximately 85% will utilize some form of dry impoundment for waste disposal, and more than two-thirds of these will employ either filtration or centrifugation for waste dewatering.

The ease and degree of dewatering FGC wastes, which affects not only the cost for transportation and chemical treatment but also the manner in which wastes can be disposed, is highly dependent upon both the chemical composition and the physical properties of the material. The principal chemical properties affecting dewatering are the ratio of calcium sulfite to sulfate, fly ash content, and the presence of unreacted amounts of lime or limestone. The major physical properties are crystalline

Table 2.6
Summary of FGC Waste Dewatering Practices for
Operating Utility Scrubbers^a

Scrubber System Mode	Dewatering Practices Employed				
	<u>Pond Settling^d</u>	<u>Thickening</u>	<u>Thickening/ Pond Settling</u>	<u>Thickening/ Filtration</u>	<u>Thickening/ Centrifugation</u>
	(Number of Plants/Total Capacity, MW)				
• SO ₂ Removal					
- Low Sulfur Coal ^b	3/1570	2/365	--	3/1045	1/1585
- High Sulfur Coal ^c	1/550	3/185	--	6/2515 ^e	--
• SO ₂ + Ash Removal					
- Low Sulfur Coal ^b	2/1085	3/2185	--	--	--
- High Sulfur Coal ^c	2/885	1/1650	--	--	--
• Wet Particulate Removal					
- Low Sulfur Coal ^b	<u>7/1220</u>	<u>3/865</u>	<u>2/1175</u>	<u>--</u>	<u>--</u>
TOTAL	15/5310	12/6250	2/1175	9/3560	1/1585

^aBasis: November 1978.

^bGenerally ≤ 1.5% sulfur.

^cGenerally > 1.5% sulfur.

^dIn addition to dewatering, settling pond acts as final disposal site in 10/3330 of those indicated.

^eIncludes two plants (totaling 920 MW) whose scrubber system removes ash but have ESP's for primary ash removal.

morphology and waste particle size distribution. These properties depend upon a number of factors including:

- Fuel type and composition,
- Boiler type, design, and mode of operation,
- Fly ash and bottom ash removal systems and their relation to sludge disposal,
- FGD system type, design, and mode of operation, and
- Type of reagent used and overall plant water balance considerations.

Because of the numerous variables involved, wastes characteristics (i.e., chemical and physical properties) can vary over extremely wide ranges. Consequently the task of developing generalized correlations between chemical/physical properties of wastes and their degree of dewaterability is difficult, and there is considerable uncertainty in the design of dewatering equipment for full-scale systems. In part this is due to the wide range of operating conditions under which an FGD system must operate; and in part because of the uncertainty in FGD system performance. Hence, dewatering equipment, and filters in particular, are designed with large safety factors.

The dewaterability of FGC wastes can be measured in terms of any number of parameters. The best measures are those which relate directly to the dewatering operations involved. If dewatering is to be accomplished by gravity sedimentation operations--thickening/clarification or pond settling--then one or all of the following parameters could be used as a measure of dewaterability:

- Solids settling rate (cm/second),
- Settled density (grams/cm³), and
- Weight % solids in the settled waste.

However, where thickeners are used, thickening of the waste solids is not always the most important concern in design. In many cases, clarification of the system liquor is the determining factor, and it provides the basis for design. In this regard, a number of FGC systems employ flocculants

to ensure acceptable clarity in scrubber return liquors. If the dewatering is accomplished by either vacuum filtration or centrifugation, the following parameters would be used to design equipment and/or assess performance:

- Filtration rate ($\text{kilograms}/\text{m}^2\text{hr}$),
- Cake density (grams/cm^3), and
- Cake solids content (wt%).

In addition to waste characteristics, the type and design of the filtration equipment (e.g., belt versus rotary drum, scraper discharge versus roller discharge) and the manner in which it is operated can importantly affect the extent of dewatering achieved. In most cases it is necessary to operate filters with relatively thin cake thicknesses (on the order of a few centimeters or less) to prevent cake cracking. Cracking results in loss of vacuum (and thereby poor dewatering) and, where cakes are washed to recover and return FGD system additives (e.g., magnesium or sodium values), loss of wash efficiency. The primary design and operating parameters that can be used to control cake cracking and optimize the overall dewatering performance of the filter include:

- Slurry feed concentration,
- Type of cloth,
- Submergence depth (for a rotary drum filter),
- Vacuum applied,
- Drum speed, and
- Drum cycle times (form time, dry time, etc.).

However, even under the best design and operating conditions the solids content of the filtered cake will still fall short of the optimum dry density for the waste material (solids content at which maximum dry density is achieved on compaction).

In an analogous manner, the design and operation of continuous, solid-bowl centrifuges can importantly affect the extent of dewatering achieved. Important parameters include:

- Feed slurry concentration,
- Feed rate,
- Pool depth, and
- Bowl speed.

In general the dewatering achieved with continuous centrifuges and filters are roughly equivalent, although to some extent, the relative performance is waste-specific. A principal difference is that washing of the wastes, if required is difficult and inefficient using a centrifuge. Also, in some cases with sulfite-rich wastes, centrifuges can produce waste solids contents as much as 5-10% higher than with filters; however, the centrifuge can tend to "masticate" the wastes resulting in a material that can be more difficult to handle and transport than a filter cake even though it has a higher solids content. Thus, to date centrifuges have only been applied to sulfate-rich and/or high fly ash content wastes in full-scale systems.

Table 2.7 summarizes the degree of dewatering reported via filtration or centrifugation for wastes produced by ten full-scale utility FGD systems, six industrial FGD applications, and three prototype installations. Drawing from these data as well as information from EPA-funded pilot plant and laboratory studies [19, 31, 37], some generalizations regarding the dewatering behavior of different types of FGD wastes are possible.

In most direct scrubbing systems producing calcium sulfite-rich wastes, the solids consist of extremely thin, fragile platelets that are formed either as individual crystals or as small clusters of 5-100 crystals. The degree of clustering and the size of the clusters are generally a function of the chemical conditions under which the crystals are formed. It has been suggested that lower sulfur coals form the loosest clusters, so therefore these would be expected to be found in wastes from scrubbing systems on boilers firing low sulfur western coals [2].

Such platelets and small clusters of platelets are generally difficult to dewater and form a loose, structurally unstable material for disposal even after filtration. The platelets and loose clusters can form an open structure of stacked crystals with large voids that trap water. Consequently, such

Table 2.7

Dewatering of FGC Wastes at Utility and Industrial Installations
Employing Filters and Centrifuges

Waste Category	Plant	FGD Capacity (MM)	Type of System	Alkali Used	Coal Composition (wt. %)		Waste Composition		Filter Cake Solids (wt. %)		Centrifuge Cake Solids (wt. %)		References
					Sulfur	Ash	CaSO ₃ /CaSO ₄	Ash (wt. %)	Range	Typical	Range	Typical	
SULFATE-RICH													
o without Ash	Martin Lake	1585	Conventional LS	Limestone	1.0	6-12	sulfate-rich	--	--	--	NR	65-70	123
	R.D. Morrow	180	Conventional LS	Limestone	1.0-1.5	NR	sulfate-rich	--	NR	45	--	--	124
	Scholz (CIC)	20	Acid Scrubbing	Limestone	2.0	14	2.99	--	--	--	NR	85	49
		20	Acid Scrubbing	Limestone	3.6	12	2.99	--	NR	80-85	NR	85	49
	Shawnee	10	Forced Oxidation LS	Commercial Lime	medium-high	NR	2.97	--	NR	80-85	--	--	125, 126
		10	Forced Oxidation LS	Limestone	medium-high	NR	2.97	--	NR	80-90	--	--	125, 126
	Southwest	200	Conventional LS	Limestone	23.5	13	sulfate-rich	--	NR	65	--	--	127
o with Ash	General Motors	(30) ^a	Dual Alkali	Commercial Lime	1.5-3.3	7-12	2.72	6-9	50-65	55	--	--	18
	Milton R. Young	450	Alkaline Ash	Commercial Lime	.7	7.5	2.95	35-70	65-80	75	--	--	128
	Shawnee	10	Forced Oxidation LS	Limestone (+ MgO)	medium-high	NR	2.92	NR	NR	80-85	--	--	126
		10	Forced Oxidation LS	Limestone	medium-high	NR	2.93	NR	NR	80-85	--	--	125, 126
		10	Forced Oxidation LS	Commercial Lime	medium-high	NR	2.96	NR	NR	80-85	--	--	125, 126
SULFITE-RICH													
o without Ash	Coneville	800	Conventional Lime	Thioerbic Lime	4.5-5.0	17	sulfite-rich	--	NR	45-50	--	--	129
	Huntington	415	Conventional Lime	Commercial Lime	.5	13	4.50	--	NR	45-50	--	--	130
	Paddy's Run	65	Conventional Lime	Carbide Lime	3.5-4.0	11.5	5.10	--	NR	60-65	--	--	131
	Petersburg	530	Conventional LS	Limestone	2.5-4.5	12-15	NR	--	NR	NR	--	--	45
	Scholz (CEA)	20	Dual Alkali	Commercial Lime	2.0	14	5.15	--	45-70	50-55	--	--	19
		20	Dual Alkali	Commercial Lime	3.6	12	5.15	--	50-60	55	--	--	19
	Shawnee	10	Conventional Lime	Commercial Lime	2.3-5.5	13-16	5.20	--	40-65	NR	--	--	55, 56
		10	Conventional Lime	Commercial Lime (+ MgO)	2.3-5.5	13-16	5.30	--	45-55	NR	NR	60-65	55, 56
	o with Ash	Caterpillar	(210) ^{a, b}	Dual Alkali	Commercial Lime	2.5-3.5	8-12	sulfite-rich	NR	NR	45-50	--	--
Elrama		510	Conventional Lime	Thioerbic Lime	2.3	21	NR	NR	NR	NR	--	--	45
Firestone		(4) ^a	Dual Alkali	Commercial Lime	2.0-2.5	11	sulfite-rich	45	NR	50	--	--	133
Phillips		410	Conventional Lime	Thioerbic Lime	2.3	21	NR	NR	NR	NR	--	--	45
Scholz (CEA)		20	Dual Alkali	Commercial Lime	3.6	12	5.10	30-40	NR	55-60	--	--	19
		10	Conventional Lime	Commercial Lime	2.3-5.5	15-30	5.30	NR	45-65	50-60	50-65	NR	55, 56
Shawnee		10	Conventional Lime	Commercial Lime (+ MgO)	2.3-5.5	15	5.30	NR	50-65	NR	50-65	NR	55, 56
		10	Conventional LS	Limestone	2.3-5.5	15-30	5.30	NR	55-75	NR	55-65	NR	55, 56
		10	Conventional LS	Limestone (+ MgO)	2.3-5.5	15-30	5.30	NR	30-70	55-65	--	--	55, 56

^a equivalent MM^b total for four plants

NR - not reported

wastes are not easily compacted by normal settling, nor can they be readily filtered to waste cakes containing high solids contents. Further, fragile crystals can break under pressure and may clog filter cloths, resulting in loss of vacuum and poor dewatering [134]. Fracturing also occurs in centrifugation, and the small fractures result in poor dewatering and cloudy supernates.

As a group, sulfite-rich platelets and platelet clusters produced in direct slurry scrubbing systems can generally be thickened to 20-35% solids using conventional open-tank clarifier/thickeners, and can be filtered to 40-55% solids. The degree of dewatering actually achieved within this range appears to vary according to the general type of scrubbing system and reagent (alkali) used. For example, wastes produced from direct lime scrubbing systems using commercial lime tend to fall in the upper end of the range; wastes produced using Thiosorbic lime tend to fall in the medium/upper end of the range; and those produced using carbide lime tend to fall in the low/medium end of the range. Wastes produced from direct limestone scrubbing systems tend to fall in the medium to medium/upper end of the range, although the dewaterability of sulfite-rich and mixed sulfite/sulfate wastes from direct limestone scrubbing systems depend importantly upon the sulfate content of the wastes and the quantity of unreacted limestone present. It should be noted that these are general trends drawn from available data and discussions with FGC equipment suppliers and system operators. Actual dewatering achieved can vary depending upon the scrubber system operating condition and the design and operation of the dewatering equipment as discussed earlier.

In contrast to direct slurry systems, dual alkali processes tend to form needle-like crystals (as opposed to platelets) which generally agglomerate into relatively large spherically-shaped clusters. The extent to which agglomeration occurs depends upon the conditions under which the regeneration of scrubber bleed liquor is carried out. Important factors include the composition of scrubber liquor, the design of the reactor system, and the extent of regeneration (i.e., operating pH). Where a high degree of agglomeration is effected, the solids tend to exhibit better settling and filtration properties in comparison to wastes from

direct slurry scrubbing processes. Using clarifier/thickeners, dual alkali wastes can typically be thickened to 25-45% solids and can be filtered using standard rotary drum vacuum filters to waste cakes typically containing 45-70% solids.

Calcium sulfate-rich wastes are generally much more easily dewatered than are sulfite-rich wastes. The crystalline form of calcium sulfate present as gypsum is blocky, with some tendency toward elongation. Crystals usually grow individually or as twin crystals to relatively large sizes in comparison to sulfite-rich crystals. In general, sulfate-rich wastes thicken to about 40-60% solids via conventional clarifier/thickeners and can be filtered to 65-90% solids.

The presence of fly ash in FGC wastes either through simultaneous collection with SO_2 or admixture with FGD wastes may enhance the dewaterability of the calcium-sulfur salts. The degree of improvement is greatest for wastes exhibiting the poorest dewaterability but it is also dependent on the quantity and properties of fly ash. Fly ash particles tend to be spherical in nature and, hence, more freely draining than platelets. In combination with sulfite-rich platelets and loose clusters, fly ash can fill the void spaces and break the surface tension between the calcium-sulfur particles improving filterability. Laboratory tests performed by Aerospace [31] indicate that more effective dewatering can be achieved when fly ash is added to a freely drained Shawnee lime waste sample. However, fly ash has a much less pronounced effect on dewaterability of tightly packed, spherical-type agglomerates of sulfite-rich crystals and large blocky gypsum crystals. (See Section 2.4.2.1.) In the extreme, fly ash may even slightly decrease dewaterability of large, well-grown gypsum crystals or sulfite clusters.

2.4.2 Research and Development Programs in FGC Waste Dewatering

At present, there are very few programs, completed or ongoing, which focus primarily on the dewatering of FGC waste solids. Table 2.8 lists the major studies having either a principal or limited focus on FGC waste dewatering, and Table 2.9 summarizes the four major EPA- and EPRI-sponsored projects which deal directly with dewatering of FGC wastes. Each of these four programs is discussed briefly below.

Table 2.8

Summary of Past/Present Programs Focusing on the Dewatering of FGC Wastes

<u>Contractor/Agency</u> ^a	<u>Sponsor(s)</u> ^a	<u>Test-Site</u> ^a	<u>Scrubber System Type</u> ^b							<u>Reference Nos.</u>
			<u>C.D.L.</u>	<u>C.D.L.S.</u>	<u>F.O.-L</u>	<u>F.O.-L.S.</u>	<u>D.A.</u>	<u>A.A.</u>	<u>A.S.</u>	
● <u>Laboratory/Pilot Testing (Principal Focus on FGC Waste Dewatering)</u>										
Aerospace	EPA	Aerospace Laboratory	X	X		X	X			31, 37
Auburn University	EPA	Auburn/Shawnee	X							134
Envirotech	EPRI	Not Available (NA)	Not Available							NA
Radian	EPA	Not Applicable (study correlated existing data)	X	X						135
● <u>Pilot/Prototype Testing (Limited Focus on FGC Waste Dewatering)</u>										
ADL	EPA	ADL Pilot Plant					X			19
Bechtel/TVA	EPA	Shawnee	X	X	X	X				55, 56, 136
CEA/ADL	EPA/EPRI	Scholz					X			19
CIC	EPRI/SCS	Scholz							X	49
CIC/Radian,	EPA/EPRI	Scholz				X				NA
EPA	EPA	RTP	X	X	X	X		X		137
GFERC	DOE	GFERC						X		20, 138
GM/ADL	EPA	GM (Parma)					X			18
LG&E/CE	EPA	Paddy's Run	X							139
^a										
ADL	Arthur D. Little									
CE	Combustion Engineering									
CEA	Combustion Equipment Associates									
CIC	Chiyoda International									
DOE	Department of Energy									
EPA	U.S. Environmental Protection Agency									
EPRI	Electric Power Research Institute									
GFERC	Grand Forks Energy Research Center									
GM	General Motors									
LG&E	Louisville Gas and Electric									
RTP	Research Triangle Park									
SCS	Southern Company Services									
TVA	Tennessee Valley Authority									
^b										
C.D.L.	Conventional Direct Lime									
C.D.L.S.	Conventional Direct Limestone									
F.O.-L.	Forced Oxidation with Lime									
F.O.-L.S.	Forced Oxidation with Limestone									
D.A.	Dual Alkali									
A.A.	Alkaline Ash									
A.S.	Acid Scrubbing									

Source: [5]

Table 2.9

EPA- and EPRI-Sponsored Projects Focusing on
the Dewatering of FGC Wastes

<u>Project Title</u>	<u>Contractor/Agency</u>	<u>Sponsor</u>	<u>Project Focus/Status</u>
Disposal of by-product from nonrecovery FGD systems: final report	Aerospace Corporation	EPA	Determine environmentally sound methods for the disposal of wastes from nonrecovery FGD systems. This project involved considerable laboratory testing of FGD wastes to determine their physical and chemical characteristics, along with the evaluation of several dewatering methods for such wastes. (Completed 1978.)
Dewatering of FGC wastes by gravity sedimentation: pilot evaluation	Auburn University	EPA/TVA	Evaluate the performance of a new continuous dewatering system (consisting of a lamina-type clarifier and conventional thickener), proposed by Auburn University, on a pilot scale level on-site at TVA's Shawnee Power Station. (Ongoing.)
Sludge dewatering methods for FGC processes	Envirotech Corporation	EPRI	Evaluate various bench-scale and pilot dewatering devices such as clarifiers, filters, and centrifuges to determine what principal variables in FGD waste affect the design of such devices. Determine capital and operating cost data for these dewatering devices as a function of sludge composition. (Ongoing.)
Development of a mathematical basis for relating sludge properties to FGD-scrubber operating variables	Radian Corporation	EPA	Develop a mathematical basis for relating sludge properties to FGD-scrubber operating variables so as to determine what scrubber operating parameters will increase the average particle size of calcium sulfite enriched sludges in order to increase their dewaterability. (Completed April 1978.)

Source: [5]

2.4.2.1 The Aerospace Corporation

Aerospace has recently completed a four-year study [31, 37] for the EPA to characterize wastes from nonrecovery FGC systems and evaluate environmentally sound methods for waste disposal. In this study, chemical and physical properties of waste samples taken from direct lime, direct limestone, and dual alkali processes at ten different scrubbing facilities were examined. As a part of the characterization effort, waste dewatering properties were investigated in laboratory batch testing using four different methods: settling; settling with underdrainage; centrifugation; and filtration. Wastes tested included both sulfate-rich and sulfite-rich materials with a wide range of ash content.

With a few exceptions, simple gravity settling produced the lowest wet bulk densities (and solids contents), and filtration produced the highest bulk densities (and solids contents). The solids contents achieved with simple settling generally ranged from 40 wt% to 50 wt% solids, while the solids contents achieved with filtration generally ranged from 50 wt% to 55 wt%. In most cases, filtration resulted in about a 10 wt% to 15 wt% increase in solids. Dewatering via settling with underdrainage and centrifugation usually resulted in solids contents between these limits; however, the order of these with respect to dewatering efficiency varied with waste type and composition.

It should be noted that such laboratory testing will not necessarily produce the same results as full-scale operations. First, batch testing by its very nature can be considerably different from continuous operations as would be the case in comparing simple laboratory batch centrifugation versus continuous dewatering using solid bowl centrifuges where the solid and liquid phases are continuously separated and the solids can be physically disturbed by the action of the centrifuge. Second, the small scale of laboratory testing may not account for effects seen in larger scale field operations such as the consolidation and increased solids content of settled wastes in deep disposal ponds. Furthermore, laboratory results may also be affected by sample handling and preparation (e.g., sample storage and aging, sample reconstitution, etc.). It

can be difficult, therefore, to accurately predict the relative effectiveness of different dewatering methods by such tests. However, laboratory batch tests can usually provide a fairly reliable measure of the relative ease of dewatering of different types of FGC wastes.

As expected, the wastes with the coarser particle size distributions were more effectively dewatered by all methods relative to those with finer particle size distributions. In general, sulfate-rich materials tended to dewater to higher solids contents than sulfite-rich materials, although the presence of high concentrations of fly ash and/or unreacted limestone in many samples make even qualitative comparisons difficult.

In an attempt to assess the effect of simultaneous fly ash removal on FGD wastes, samples both with and without fly ash from the Scholz dual alkali prototype system and Shawnee direct lime scrubbing systems were studied. The laboratory dewatering results are presented in Table 2.10. As shown, the effect of fly ash varied depending upon the type of waste, but the effect was generally quite small. The dual alkali waste samples were obtained from operation of the scrubber system for SO_2 removal only and for simultaneous ash and SO_2 removal. The sample of direct lime scrubbing waste containing 40% fly ash, on the other hand, was manufactured in the laboratory by admixing ash to wastes generated from SO_2 scrubbing only. This admixing of ash apparently contributed to the improved dewatering efficiency, particularly of settling with underdrainage. The ash separated from the mix and settled to the bottom of the column and served as a filtering aid to allow better drainage (possibly through prevention of blinding of the filter cloth at the bottom of the column). It is interesting to note that the presence of fly ash in the dual alkali waste (from simultaneous ash scrubbing) did not improve and, in fact, decreased slightly the dewatering efficiency measured in the laboratory tests. However, in actual filter operations at the Scholz plant, the solids content of the waste cake containing ash did increase slightly relative to that without ash (see Table 2.7).

Table 2.10

Effects of Fly Ash on the
Dewatering Properties of FGC Waste Samples
(Laboratory Evaluation)

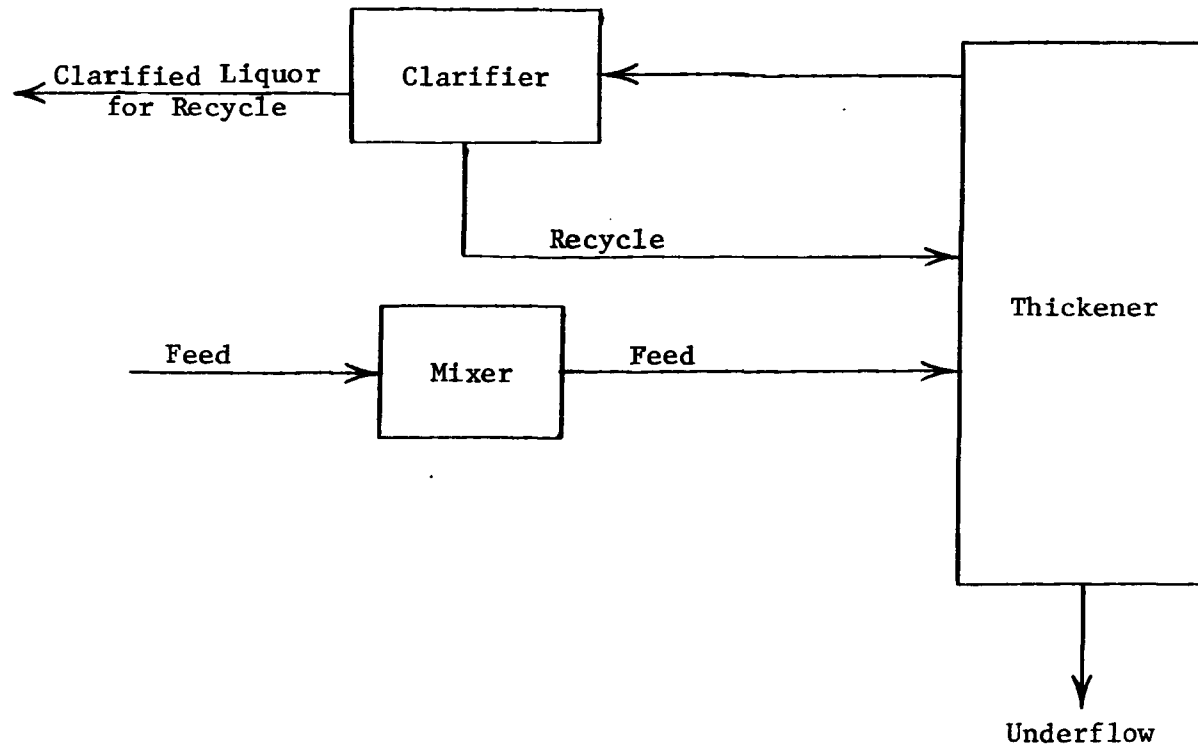
<u>Waste</u>	<u>Approximate Solids Content of Dewatered Waste (wt%)</u>			
	<u>Settling</u>	<u>Centrifugation</u>	<u>Settling with Underdrainage</u>	<u>Filtration</u>
Direct Lime Scrubbing (Shawnee)				
Without Ash	48	49	51	57
With Ash (40 wt%)	45	53	58	61
Dual Alkali (Scholz)				
Without Ash	43	45	51	64
With Ash (30 wt%)	43	45	47	59

Source: [31, 37]

2.4.2.2 Auburn University

Under funding of the EPA, Auburn University is currently conducting a study to improve the dewatering efficiency achievable with available thickening and clarification technology. The work has involved laboratory-scale testing of both batch and continuous thickening using samples of FGD waste obtained from the direct lime scrubbing system at Louisville Gas and Electric's Paddy's Run Station. Based upon the evaluation of several different equipment configurations, a promising dewatering system has been developed. The system shown in Figure 2.1 consists of two separate units: a lamina-type (inclined) clarifier and a conventional (tank) thickener. In this fashion, the clarification and the thickening functions are decoupled as much as physically possible. Consequently, the thickener can be designed to produce a sludge with as high a solids content as possible, without the additional burden of having to produce a very clear overflow. The role of the clarifier is to produce the clear overflow which is then recycled back to the system. In addition, the clarifier produces a moderately concentrated underflow that is returned to the thickener at any desired tank height. In this way, the clarifier enhances the performance of the thickener so that FGD wastes can be thickened to very high solids concentrations with less settling area than that required by conventional-type thickeners. It has been reported [134] that the system yields clear overflows and highly concentrated underflows (30 to 80% solids by weight) as well as offering flexibility of operation, which allows separation of solids at higher efficiencies and solids throughput rates than those possible with conventional systems over a range of scrubber operating conditions.

Auburn University has recently received additional funding from EPA and TVA to evaluate the performance of this dewatering system on a larger pilot scale at TVA's Shawnee facility. This evaluation has a threefold purpose: (1) to confirm and better establish the results obtained from the laboratory-scale tests performed at Auburn; (2) to provide design data for scale-up purposes; and (3) to provide operational data needed to better estimate the potential cost savings offered by this dewatering approach.



Source: [134]

Figure 2.1 Flow Diagram of Proposed Dewatering System

2.4.2.3 Envirotech Corporation

Envirotech has recently completed a study (yet to be published) sponsored by EPRI to provide the utility industry with a sound data base for assisting in selection of dewatering methods for FGC wastes. The program plan focused on the testing of various bench- and pilot-scale dewatering equipment (such as clarifiers, filters, and centrifuges) to evaluate performance and to determine how variations in waste composition affect the design, and capital and operating costs. A follow-on second-phase effort is being planned to field-test pilot dewatering equipment and evaluate the handling and transport properties of the wastes produced.

2.4.2.4 Radian Corporation

Investigators at Radian, under the sponsorship of EPA, examined prospects for increasing the average size of calcium sulfite particles in FGD wastes in order to improve dewaterability [141]. The purpose was to correlate pertinent design and operating parameters of SO_2 removal systems producing calcium sulfite-rich wastes with waste quality, that is, its settling rate, settled bulk density, and particle size distribution. A model for predicting the crystal size distribution of calcium sulfite produced in conventional direct limestone scrubbing systems was developed and used to examine the sensitivity of crystal size distributions to changes in FGD system process variables such as: relative saturation with respect to calcium sulfite; solids residence time in the scrubber recirculation tank; and clarifier overflow maximum particle size. It is believed that the model can be used to interpret actual experimental results as well as predict process conditions for producing an optimum waste.

However, more bench- and pilot-scale work has been recommended to improve the data base for the relationships developed between calcium sulfite particle size distribution and process variables and to verify the model's ability to predict conditions conducive to increased particle size distributions. A pilot-scale test program has been proposed to be

carried out at RTP's pilot plant facility. The major emphasis of the program would be to determine the principal locations of calcium sulfite nucleation in the system. Three possible areas have been identified: the feed pump; the scrubber; and the hold tank. Tests will be performed to determine the effect of (1) the feed pump (i.e., pump tip speed, steel versus rubber-tipped impeller), (2) operating at higher calcium sulfite saturations within the scrubber liquor, and (3) varying both the hold tank agitator speeds and its material of construction (steel versus polypropylene) on the calcium sulfite particle size distribution. Tests also will be performed to determine and correlate any effect that various process variables might have on the nucleation and growth rates of calcium sulfite crystals. These include changes in slurry solids content, scrubbing liquor quality, residence time variations in the scrubber recirculation tank, and the grinding and recycling of clarifier underflow.

3.0 PRODUCTION TRENDS AND HANDLING OPTIONS

3.1 Coal/Waste Relationships

Table 3.1 shows typical coal/ash/sludge relationships for six representative coals and corresponding waste categories according to the basis set forth in Section 2.0. The coal characteristics reflect assumption of some coal cleaning prior to combustion.

3.2 Projected Generation and Trends

Projections of the generation of FGC wastes from coal-fired utility and large-scale industrial boilers (>25 MW-eq) have been estimated through the year 2000. The basis for these projections were the estimates on coal consumption by type developed by Mitre Corporation [140]. Table 3.2 shows the cumulative generation of coal ash and FGD wastes (without fly ash) projected to the year 2000, and Table 3.3 shows the breakdown of ash and FGD wastes by utility and industrial boilers.

The general assumptions used in preparing these estimates were as follows:

- Consumption of coal based on estimates prior to the National Energy Act (NEA) of 1978. NEA is expected to impact future coal utilization.
- All new coal-fired utility boilers are required to meet standards of $0.258 \text{ grams SO}_2/10^6 \text{ joules}$ (0.6 lbs/MMBtu) for Western coal and $0.516 \text{ grams SO}_2/10^6 \text{ joules}$ (1.2 lbs/MMBtu) for all other coals (note that these assumptions were made prior to the revised NSPS of June 1979).
- Coal properties by region roughly equivalent to those given in Table 3.3.
- All FGD systems are nonrecovery.

Obviously, all of these assumptions are oversimplifications; however, the projections do give at least an order of magnitude estimate for waste production and an overall perspective of waste production trends.

It should be stressed that these projections do not take into account the passage of the National Energy Act of 1978, nor the passage

Table 3.1

Coal/Ash/Sludge Relationships (Typical)

Coal Type	Representative Range of Coal Properties ^a				Principal Usage by EPA Federal Region ^b	Predominant FGD Waste Type ^c	Approx. Waste Production (dry tons/MW yr) ^d		% Increase In Waste Due to FGD
	HHV (Btu/lb)	Sulfur (lbs/MBtu)	Ash (lbs/MBtu)				FGD Only ^e	Total FGD ^f	
Appalachian Bituminous	12,500	1.5 ^g	9	1,2,3,4,5	Mixed	270	645	70	
Interior Bituminous	11,500	3.5 ^g	10	4,5,6,7	Sulfite-rich	590	1,005	140	
Texas Lignite	7,500	2.0 ^h	15	6	Mixed	265	890	40	
Western Subbituminous	9,000	1.0 ^g	8	6,7,8	Sulfate-rich	200	530	60	
Western Lignite	6,500	1.0 ^h	12	8	Sulfate-rich	150	650	30	
Mountain Subbituminous	11,000	0.5 ^g	7	7,8	Sulfate-rich	100	390	35	

^aCoal properties are typical for each type of coal. Values used are for illustrative purposes. Actual properties of any specific coal can vary significantly.

^bRegions 9 and 10 are not included due to the very low projections for coal utilization.

^cSulfite-rich: $\text{CaSO}_3/\text{CaSO}_4 < \sim 0.20$ (predominantly $\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$)

Sulfate-rich: $\text{CaSO}_3/\text{CaSO}_4 > \sim 0.90$ (predominantly $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$)

Mixed: FGD systems can be operated to produce a sulfite-rich or a sulfate-rich waste, or possibly a waste with a sulfate content between these two extremes.

^dNumber of dry tons of waste produced for each megawatt-year of operation.

^eAsh-free waste from SO_2 removal only. Based upon: 85% ASO_2 ; 9,500 Btu/kw hr; 3.0 lbs sulfate-rich wastes/lb SO_2 and 2.4 lbs sulfite-rich wastes/lb SO_2 .

^fIncludes all ash.

^g95% sulfur release from coal assumed.

^h65% sulfur release from coal assumed.

Source: Arthur D. Little, Inc.

Table 3.2

Generation of Coal Ash and FGD Wastes

Basis: Estimates prior to National Energy Act.

All numbers are cumulative.

Federal Region	Coal Ash			FGD Waste		
	1975 10 ⁶ Tons	1985 Est. 10 ⁶ Tons (Volume) ^a	2000 Est. 10 ⁶ Tons (Volume) ^a	1975 10 ⁶ Tons	1985 Est. 10 ⁶ Tons (Volume) ^a	2000 Est. 10 ⁶ Tons (Volume) ^a
1	0.3	8.19 (4.10)	28.29 (14.14)	< 0.1	4.94 (3.95)	21.50 (17.21)
2	1.6	27.31 (13.66)	98.28 (49.14)	0.2	14.82 (11.85)	63.98 (51.18)
3	8.4	108.34 (54.17)	317.45 (158.73)	1.2	18.20 (14.56)	60.58 (48.46)
4	13.6	156.10 (78.05)	467.57 (233.79)	1.7	38.74 (34.87)	156.53 (140.88)
5	19.4	232.54 (116.27)	660.29 (330.15)	3.1	51.62 (46.45)	187.90 (169.11)
6	0.6	36.32 (18.16)	253.79 (126.90)	< 0.1	12.00 (9.60)	79.77 (63.81)
7	2.0	36.93 (18.47)	128.84 (64.42)	0.5	14.75 (8.86)	56.65 (33.99)
8	1.7	24.48 (12.24)	68.60 (64.30)	< 0.1	1.29 (0.77)	3.83 (2.30)
9	0.3	10.71 (5.36)	84.23 (42.12)	< 0.1	0.10 (0.05)	0.43 (0.26)
10	0.3	0.81 (0.41)	3.62 (1.81)	0.0	0.02 (0.01)	0.19 (0.12)
Total	48.2	641.73 (320.89)	2,110.95 (1,056.50)	6.8	156.48 (130.97)	631.36 (527.32)

^a Numbers of 1000's of acre-ft are in parentheses.

Numbers may not add up to the last digit due to rounding.

Source: [1]

Table 3.3

Projected Generation of Coal Ash and FGD Wastes
Industrial versus Utility Breakdown

	Annual Rate of Generation			
	<u>1985</u>		<u>2000</u>	
	<u>10³ Tons</u>	<u>% of Total</u>	<u>10³ Tons</u>	<u>% of Total</u>
<u>Coal Ash</u>				
Industrial	9,470	12	21,980	19
Utility	<u>71,010</u>	<u>88</u>	<u>93,450</u>	<u>81</u>
Total	80,480	100	115,430	100
<u>FGD Wastes</u>				
Industrial	1,200	5	5,800	15
Utility	<u>23,200</u>	<u>95</u>	<u>32,900</u>	<u>85</u>
Total	24,200	100	38,700	100

Source: [1]

of any more stringent SO₂ and particulate regulations (NSPS for utility boilers are now being revised and NSPS for industrial boilers are under review).

3.3 Waste Stabilization Technology

3.3.1 General Stabilization of Wastes

There are now more than two dozen "stabilization" processes for solidification/stabilization of many types of wastes. The state of development of these processes ranges from laboratory-scale testing to full-scale, widespread commercialization. Most of the processes have not been commercially applied although most all have been tested at least in the laboratory scale on a number of different types of wastes.

There are basically three methods by which "stabilization" processes can improve the disposability of wastes.

- First, they can improve the physical characteristics of the wastes to the extent that they are more easily handled. This frequently leads to better control/management of the disposal area, resulting in reduced impacts relating to physical stability and contamination of ground and surface waters.
- Second, "stabilization" can decrease the exposure of the wastes by reducing surface area and/or permeability or by encapsulating the wastes, thus limiting the contact of groundwater (or infiltration water) with the waste.
- Finally, "stabilization" can chemically react with the waste, limiting the solubility of chemical constituents that would otherwise be readily accessible either through flushing of interstitial liquor or solubilization.

Different stabilization techniques usually emphasize one or two of these factors. The applicability and "success" of a particular "stabilization" process, therefore, will depend importantly upon the chemical and physical properties of the waste, the disposal site characteristics, and the waste-handling constraints.

At the risk of oversimplification, most all stabilization processes generally can be categorized into one of about six groups, according to the manner in which the wastes are treated. These are discussed briefly below. Table 3.4 lists the principal processes of each type, indicating the vendors and status of the process.

- (1) Lime (Cement)-Based: As the name implies, this approach involves mixing cement or lime with the wastes to produce a material which will harden with time into a more-or-less monolithic mass. The extent of hardening and the strength of the resulting mass will depend importantly upon the waste properties and the amount and type of additives. A number of additives including clay and sodium silicate are often used with cement to increase the curing rate and the ultimate strength attained, and decrease the permeability of the resulting mass. The use of lime is similar to the use of cement in that it relies on the reaction of lime with fine-grained (pozzolanic) material and water to produce a concrete-like mass. Common pozzolanic materials used in waste treatment include blast furnace slag and fly ash from fossil fuel combustion. A pozzolan is a siliceous or aluminosiliceous material that in itself possesses little or no cementitious value, but that in finely divided form and in the presence of moisture will chemically react with alkali and alkaline earth hydroxides at ordinary temperatures to form or assist in forming compounds possessing cementitious properties (ASTM C593-76A, ASTM 1977, Part 13). The products of the reaction of lime and fly ash or lime and slag are basically the same, the principal components being a tobermorite like calcium silicate hydrate with a $\text{CaO}:\text{SiO}_2$ ratio varying between 0.8 and 2 with a hexagonal tetracalcium aluminate hydrate and ettringite type phases also produced [147]. These products are similar to those formed in the hardening of Portland cement.

Table 3.4

Waste Treatment Processes

Process Type	Supplier/Developer	Additives	Degree of Commercialization	Commercial Waste Applications	Level of Testing/Operation with FGD Wastes
Cement (Lime)-Based	IUCS, Inc.	Ash and Lime	Commercial/U. S.	FGD, Fly Ash	Full-Scale
	Dravo Lime Co.	Slag and Lime	Commercial/U. S.	FGD, Fly Ash, Mine Tailings	Full-Scale
	TJK, Inc.	?	Commercial/Japan	Industrial Inorg., Dredge Spoils	Full-Scale (Japan)
	Chem-Nuclear System, Inc. Commonwealth Edison/American Admixtures, Inc. Aerojet Liquid Rocket Sludge Fixation Technology, Inc. Research Cottrell Envirotech (Chemfix)	Cement Lime and Fly Ash Cement ? Lime and Fly Ash Lime and Fly Ash	Commercial/U. S. Laboratory (FGD) Laboratory (FGD) Field (FGD) ?	Utility Radwastes FGD - Industrial Heavy Metal Sludges None None	Unknown Full-Scale None None Reported Field? Lab? Field
Self-Cementing (plaster of paris)	Marston Associates	None	Pilot (FGD)	-	Field
Silicate-Based	Environmental Technology Corp. (Chemfix)	?	Commercial/U. S.	Metal Hydroxide	None Reported
	Envirotech	Silicate + Cement	Commercial/U. S.	Org. & Inorg. Industrial, Sewage	Field
	Ontario Liquid Waste Dispossl, Ltd.	?	Commercial/Canada	Industrial	Field
	United Nuclear Industries Stablex Corporation	Silicate + Cement Silicates	? Commercial/U. K.	(RadWastes) Industrial	None None Reported
Thermoplastic	Werner & Pfeleiderer Corp.	Asphalt	?	RadWastes	None Reported
	Southwest Research Institute	Epoxy Composites Sulfur	Laboratory Laboratory	- -	None None
Organic Polymer	Chem-Nuclear System, Inc.	UF	?	?	None
	ANEFEO Co.	UF	?	?	None
	TRW Systems	Polybutadiene	Laboratory	-	None
	Protective Packaging (Teledyne)	?	?	Nuclear Wastes?	Unknown
Inorganic Precipitation	Industrial Resources, Inc.	Waste Acid + Iron	Field?	?	Lab
Unknown	Mehran Engineering Corp.	-	Laboratory?	?	None

Notes: 1. This is a generic listing for all waste
2. The list is a partial listing

Source: [2,118]

The products formed in mixing fly ash (or slag) and lime with partially dewatered wastes will vary somewhat due to interactions with the waste constituents. For example, in treating FGD wastes, it has been shown [2,146] that the participation of $\text{CaSO}_x \cdot \text{XH}_2\text{O}$ salts present in the waste results in the formation of ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$). The formation of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_3 \cdot 7\text{H}_2\text{O}$ has been hypothesized [2].

In this regard, it should be noted that some wastes, notably FGD wastes, may exhibit self-cementing properties. Fly ash simultaneously collected with SO_2 and/or admixed with the calcium sulfur solids can react with the residual lime (either from the fly ash or calcium sulfur salts), causing hardening of the waste material.

There are numerous suppliers now offering cement or lime-based "fixation" processes. Notable are the processes offered by IUCS (involving the use of fly ash and lime) and Dravo (which uses furnace slag and lime) commercialized in the United States, and by TJK commercialized in Japan.

- (2) Self-Hardening: Marson Associates has been pursuing development of an FGD waste stabilization approach using calcium sulfate contained in the waste to induce hardening. The process involves calcination of a portion of the waste under controlled conditions to produce plaster of Paris. This is then recombined with the waste in a granulator where it hydrates into relatively hard, plaster-like pellets.
- (3) Silicate Based: At least two processes involving silicate chemistry are now being commercially offered--by Chemfix, Inc., and Ontario Liquid Waste Disposal, Ltd. These processes rely on the conversion of the wastes into a relatively stable silicate matrix not unlike the formation of sedimentary rocks. In the case of Chemfix, this is accomplished through the

addition of a soluble silicate gel and a setting agent (usually Portland cement). The amount of each additive varies with the type of waste and its moisture content. The resulting material is usually soil-like in consistency and is amenable to landfilling. Testing and commercial applications indicate that such processes can be effective for inorganic wastes, particularly in tying up heavy metals. However, silicate processes probably are not applicable to most organic wastes, and they appear to be ineffective in tying up chlorides, monovalent cations, and colloidal materials [2].

- (4) Thermoplastic Impregnation/Encapsulation: A number of techniques have been investigated, and a few are being marketed involving impregnating or encapsulating (coating) the wastes with thermoplastic materials. A variety of such materials have been tested including asphalt (or bitumen), paraffin, polyethylene and vinyl resins, and sulfur. Impregnating the wastes usually involves drying and heating the wastes and blending them with the thermoplastic materials at elevated temperatures. The mix is then allowed to cool and solidify. In some cases, such as with the use of bitumen, an emulsified product miscible with the wet sludge is used. Mixing is then accomplished at convenient temperatures; however, heating and drying is still required before the mass is in a suitable form for disposal.

Systems involving the use of bitumen have been actively researched, particularly for the containment and disposal of radioactive wastes. However, in many cases, the type of waste rules out organic-based encapsulation techniques. Wastes containing organics which are solvents for the encapsulating material obviously cannot be used, and those containing materials which react destructively such as strong oxidizing salts cannot be used in the case of bitumen-based encapsulation.

Thermoplastic materials also have been tested as surface coatings for wastes, particularly wastes already bound in a treated/fixed matrix. No surface coating processes are now being offered for cement-based treated materials due principally to problems with adhesion of the coatings. Surface coatings of polyethylene, however, have been successfully tested in combination with organic polymer and thermoplastic resin impregnation.

- (5) Organic Polymer Impregnation/Encapsulation: A handful of organic polymer techniques have been developed, mostly in response to the need for solidification of radioactive wastes for transportation. These are generally batch processes involving the addition of prepolymers (or monomers) to the wastes, followed by polymerization, which encapsulates the waste particles in a mass rather than chemically combining with the wastes. The required form of the waste and the specific processing conditions will depend upon the type of waste and the specific polymerization technique. When wet wastes are treated, the liquid usually remains after polymerization and requires disposal.

The most thoroughly tested organic polymer solidification process is the urea-formaldehyde system.

- (6) Inorganic Precipitation: An approach to stabilizing sodium sulfate waste from dry sorbent systems is insolubilization by coprecipitation with acidic ferric ions to form $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ (natrojarosite) and $\text{Na}_2\text{Fe}(\text{SO}_4)_2(\text{OH}) \cdot 3\text{H}_2\text{O}$ (sideronatrite) [143]. This would be accomplished by mixing slurried dry sorbent wastes with sulfuric acid and a source of ferric ions (such as waste acid and fly ash). The precipitates are reported to be granular, easily filterable, and relatively free-draining (not sludge-like). The solubilities of these sodium ferric hydroxysulfate compounds are less than those of

calcium sulfate, so the precipitated product may be amenable to landfill without further processing.

3.3.2 Stabilization of FGC Wastes

A number of the above-listed processes have been tested on FGC wastes, mostly in the bench scale. Justification of the use of additives to improve the physical characteristics of FGC wastes has been based on improvement in strength, reduction in compressibility, and reduction in permeability caused by an increase in solids content or the formation of permanent bonds between particles. The additives most advantageous then would be those available at low cost in large quantities (e.g., fly ash) and those effective as cementing agents (e.g., Portland cement). Combinations of additives may produce both types of improvement (e.g., fly ash plus lime). A limited amount of study has been devoted to the evaluation of simple additives such as fly ash, lime, and Portland cement. These studies are discussed later.

At present, there are two approaches which have achieved commercial applicability for calcium-based FGD wastes: addition of lime and fly ash for dry impoundment systems (currently marketed by IUCS); and the proprietary technology developed by Dravo Corporation involving the use of processed blast furnace slag as the additive for stabilization in wet ponds. Other additives and stabilization approaches for calcium-based wastes have been laboratory- and field-tested but are not being actively marketed at present.

The economic evaluation of the use of additives for waste stabilization is site specific, at best, and must take into account not only the applicable disposal regulations, but also the type of waste and the disposal area hydrogeology. In some cases, for example, dry impoundments may be possible to stabilize materials to form containment dikes and basal layers into which unstabilized materials could be placed. This would, of course, depend upon the handling properties of the untreated wastes.

An additive which has received little attention is natural soil. This neglect is justified generally in the case of cohesive soils. Even

though cohesive soils usually contain a significant amount of clay minerals and thus are likely to be almost impervious as well as capable of attenuation of pollutants in flowing groundwater, mixing cohesive soils with FGC waste sludges would be very difficult if not impracticable. On the other hand, less cohesive soils such as clean sands could be added to FGC wastes with little difficulty. Such addition would not decrease the permeability of the wastes or encapsulate it, nor could it provide attenuation capacity. In this regard it would not be considered stabilization. However, addition of sand would increase strength and decrease compressibility.

3.4 Utilization and Disposal Options

Coal ash and FGD wastes together comprising FGC wastes can be disposed of or utilized. At present, most FGC waste is subject to disposal; utilization may be expected to grow in the future, but probably at a rate less than the rate of growth in the total generation of FGC wastes. Following are brief descriptions of disposal and utilization options. These are discussed in more detail in Volumes 4 and 5.

3.4.1 Disposal

There are now a number of methods being employed for the disposal of FGD wastes and power plant coal ash. The most common method of disposal today is impoundment (ponds), although some mine disposal is also being practiced. In the future, in addition to impoundments, landfills (i.e., disposal in which layers of waste are deposited and compacted, ultimately after full use the disposal area is covered with layers of soil) would become a major option. The types of impoundments include both lined and unlined wet ponds and dry pits. In wet impoundments, sluiced ash or FGD waste (often combined with ash) slurry is piped to the pond area where the solids settle out. The supernatant is then collected via overflow weirs and either discharged or recycled to the scrubber or ash sluicing system. Wet impoundments are used almost exclusively for on-site disposal at the power plant. In addition to the disposal of untreated wastes, they are sometimes used for treated materials (admixed lime and fly ash; or admixed lime, fly ash and FGD wastes).

Managed fills (sometimes called dry impoundments or managed landfills) are used for the disposal of dry ash or dewatered (or treated) sludges. They can be either offsite or onsite; however, they are usually located close to the waste source because of the high cost of transportation. In operating a managed fill, the wastes are collected and usually trucked to the disposal area. In the disposal area, the waste is spread on a section of the disposal site at a time in short (1-3 foot or 0.3-0.9 meter) lifts and compacted by wide-track dozer or other conventional compaction equipment. Then another layer of waste is placed on top of the compacted lift and operation proceeds. After filling a section of the disposal site to a predetermined height, the layering and compaction shifts to the next section of the disposal site.

There are three options for surface mine disposal of dry wastes: (1) disposal on the working pit floor prior to return of overburden; (2) dumping in spoil banks prior to reclamation; and (3) mixing with overburden. Sludge or ash would be transported to the mine via rail or truck and then truck-dumped in the disposal area. There is a limited amount of fly ash and/or FGD waste disposal now being practiced using the first two options. Disposal of FGD wastes in active mines leads to fewer fugitive SO_x emissions because active mines are less acidic than inactive or depleted mines; therefore the sulfur compounds in the wastes are less likely to be dissolved (releasing SO_2) in the less acidic environment.

In a few instances, fly ash also has been disposed of in underground mines. The fly ash is sluiced and pumped into mine voids through boreholes. Supernatant can be recovered via dams and sump pumps and returned to a disposal basin or recycled for use in ash sluicing. No commercial scale FGD waste disposal in underground mines is now being practiced.

All of these options undoubtedly will continue to be used in the future. However, based upon the impending regulations prohibiting groundwater contamination, unlined impoundments are expected to decrease in usage. Mine disposal is expected to increase because of the convenience and the elimination of the large tracts of land required for impoundments.

Ocean disposal of treated and sulfate-rich sludges may also be carried out to a limited extent in regions where there are no mines available and disposal sites for land impoundments are scarce. Ocean disposal could take the form of reef construction on the continental shelf (shallow ocean disposal) using treated material or dumping of treated or sulfate-rich material off the shelf (deep ocean disposal). Ocean disposal probably would be more likely to be practiced in Regions 1 and 2. However, should regulations constrain any form of ocean disposal, it is likely that use of regenerable systems would be a strong possibility in areas where land disposal is impractical.

Table 3.5 lists the potential disposal options and sludge types appropriate to each disposal option envisioned for the foreseeable future. Table 3.6 lists the anticipated significance of each disposal option in each federal region. This disposal scenario was compiled based on current trends in regulations, existing data on characteristics of various types of sludges, and expected impacts associated with such operations.

3.4.2 Utilization

There are numerous uses of coal ash that have been developed both in the United States and Europe. However, at present, only about 20% of the total ash produced in the United States is being marketed. Fly ash, bottom ash and boiler slag, all of which comprise coal ash, are used in somewhat different applications. Only fly ash appears to be useful in FGD waste treatment.

Some of the more important markets for ash in the United States include:

- Manufacture of cement and concrete,
- Light aggregate for construction, and
- Areas where availability of disposal options for nonrecovery processes is so constrained that the cost of waste disposal is high.

Table 3.5
Waste Types versus Disposal Scenarios

<u>Disposal Scenario</u>	<u>Requirements</u>	<u>Waste Type</u>
1. Land Disposal		
a. Wet Ponding	Pond	<ul style="list-style-type: none"> ● Any
b. Dry Disposal or Managed Fills ^a	Immediate Workability	<ul style="list-style-type: none"> ● Sulfate-Rich ● Sulfate-Rich + Ash ● Sulfite-Rich + Ash ● Treated Soil
c. Mine Disposal	Dry, Soil-like	<ul style="list-style-type: none"> ● Sulfate-Rich ● (Dry) Sulfite-Rich ● Sulfate-Rich + Ash ● Sulfite-Rich + Ash ● Treated Soil or Brick
2. Ocean Disposal		
a. Shallow Dispersed	No (or low) COD ^b availability	<ul style="list-style-type: none"> ● Sulfate-Rich
b. Shallow Concentrated	Stable, Low COD ^b availability, Non-dispersing	<ul style="list-style-type: none"> ● Treated, Bricklike
c. Deep Condentrated	Low TOS Availability	<ul style="list-style-type: none"> ● Sulfate-Rich ● Treated Soil or Brick

^a Dry disposal refers to dewatered and if necessary stabilized wastes being deposited on ground and compacted.

^b Chemical oxygen demand (COD) is directly related to sulfite concentrations.

Table 3.6
Typical Disposal Scenarios
By Region - 1985 - 2000

<u>EPA Region</u>	<u>Disposal Methods (Significance)^a</u>	
	<u>FGD Waste</u>	<u>Ash</u>
1 and 2	Wet Ponding (H)	Wet Ponding (H)
	Dry Disposal (H) ^b	Dry Disposal (H)
	Ocean (H) ^c	Ocean (L) ^c
	Mine (L)	Mine (L)
3 and 4	Wet Ponding (H)	Wet Ponding (H)
	Mine (H)	Mine (H)
	Dry Disposal (M&H)	Dry Disposal (M&H)
5, 6 and 7	Wet Ponding (H)	Wet Ponding (H)
	Mine (H)	Mine (H)
	Dry Disposal (M&H)	Dry Disposal (M&H)
8, 9 and 10	Wet Ponding (H)	Wet Ponding (H)
	Mine (H)	Mine (H)
	Dry Disposal (L)	Dry Disposal (L)

^a Importance (significance) of each disposal option described in parentheses: (H) = High in importance in the region; (M) = Medium in importance in the region; and (L) = Low in importance in the region. Other options with low importance in a region are not mentioned.

^b Also called managed fills or dry impoundments.

^c If regulations preclude all forms of ocean disposal, then it is likely that ash utilization and the use of regenerable systems would take up the slack where land disposal is impractical.

It is important to note that most recovery systems also produce wastes; e.g., blowdown from prescrubbers (which remove fine particulate matter and chlorides from the flue gas prior to its entering the sulfur dioxide absorber) and blowdown of contaminants from the recovery portion of the process. These were discussed in Section 2 but are not expected to be major factors in the total waste generation in the next few years.

4.0 CHEMICAL CHARACTERIZATION OF FGC WASTES

4.1 Status of Chemical Characterization

The Environmental Protection Agency (EPA), Electric Power Research Institute (EPRI), and a number of other organizations have sponsored studies on the chemical characterization of FGC wastes (fly ash and/or SO₂ removal wastes). Table 4.1 presents the list of major studies funded by government agencies or EPRI which have focused on wastes generated by SO₂ removal systems (with or without simultaneous fly ash removal). In addition, a number of private organizations active in commercial fixation of FGC wastes (for example, Dravo and IUCS and others listed in Table 3.4) and in the marketing of FGC systems as well as utilities have in-house data much of which is not available in the open literature.

There are few extensive, generalized studies that have been published which focus on the characterization of the chemical and physical properties of fly ash and bottom ash. However, there have been numerous, small characterization studies on coal ash, most of which have been tied to site and system specific utilization or disposal options. Examples of these are various projects funded by the Federal Highway Works Administration (FHWA) which emphasize the utilization of coal ash in conjunction with highway construction. As a result, more emphasis is placed in these studies on the engineering properties of coal ash-soil/coal ash-cement road building mixtures than the properties of coal ash alone. One notably large study entitled, "Characterization of Ash from Coal-Fired Power Plants," was performed by the Tennessee Valley Authority (TVA) under an EPA grant [34]. This project involved summarizing existing data from several small, recent coal/ash studies, on both the chemical and physical characteristics of ashes produced by coal burning steam-electric generating plants. The report not only contains information on the physical chemistry of coal ash, coal ash inorganic trace elements, etc., but also examines the particular coal and ash analysis methods used in determining such information.

Attenuation of pollutant concentrations in leachate from deposits of FGC wastes may occur in natural soil strata below and around sludge fills. Studies of pollutant attenuation through surface adsorption and other mechanisms are underway at the U.S. Army Dugway Proving Ground in

Table 4.1

Studies on Chemical Characterization of FGD Wastes^a

<u>Contractor</u> ^b	<u>Plant/ Location</u>	<u>Coal Type</u>	<u>Process Type</u>	<u>Waste Type</u>	<u>Ash/No Ash</u>	<u>Stabilized/ Unstabilized</u>	<u>Studied</u>			<u>Ref.</u>
Aerospace	Shawnee/ Kentucky	H	DLS	M	A/NA	U	MO	MC	TC	31,37
		H	DL	SI	A/NA	U	MO	MC	TC	
		H	DL (ox)	SA	A	U				
	Phillips/ Pennsylvania	M	DL	M	A	U	MO	MC	TC	
	Paddy's Run/ Kentucky	H	DL	SI	NA	U				
	Cholla/Arizona	L/M	DLS/FA	M	A	U	MO	MC	TC	
	Mojave/California	L/M	DLS	SA	NA	U	MO	MC	TC	
	Parma/Ohio	H	DA	SA	NA	U	MO	MC	TC	
	Scholz/Alabama	L/M	DA	SI	NA	U		MC		
		H		M						
	Utah	L/M	DA	SA	NA		MO	MC	TC	
WES	Not reported	Eastern	DLS	NR	NR	T/U	MC	TC	L	16,41
	Not reported	Eastern	DL	NR	NR	T/U	MC	TC	L	
	Not reported	Western	DLS	NR	NR	T/U	MC	TC	L	
	Not reported	Eastern	DA	NR	NR	T/U	MC	TC	L	
	Not reported	Western	DA	NR	NR	T/U	MC	TC	L	
SUNY	Elrama/Duquesne	L/M	DL	M	A	T	MC	TC	L	15
Aerospace/TVA	Shawnee/ Kentucky	H	DL	SI	A/NA	T/U		TC	L (field)	40
		H	DLS	M	A/NA	T/U		TC	L (field)	
		H	DL (ox)	SA	A	T/U		TC	L (field)	
Radian/ ADL/EPA	Not cited	NR	NR	NR	A/NA	U			L	39
	Pilot		DA	SI,M,SA	NA	T/U	MO	MC	TC L	19
	Scholz/Alabama	L/M,H	DA	SI,M	A/NA	U	MO	MC	TC L	18
	Parma/Ohio	H	DA	M,SA	NA	U		MO	MC	
ADL/NEA	Shawnee/Kentucky	H	DLS	M		U	MC	TC	L	39
			DLS	SA		U	MC	TC	L	46
	Scholz/Alabama	L/M,H	DA	SI	N	U	MC	TC	L	
UND/ADL	Square Butte/ North Dakota	L	FA	SA	A	U	MO	MC	TC L (field)	21
DOE/Private Consortium	Square Butte	L	FA	SA	A	U		MC		20
	Pilot/No.Dakota									47
ACE(Dugway)	Six FGD samples and three fly ash samples were leached and soil attenuation measured.									54,55,56
TVA/Bechtel	Shawnee/Kentucky	H	DLS	M	A	U	MO	MC		
			DLS (ox)	SA	A	U	MO	MC		

Table 4.1 (Continued)

Studies on Chemical Characterization of FGC Wastes^a

<u>Contractor</u> ^b	<u>Plant/ Location</u>	<u>Coal Type</u>	<u>Process Type</u>	<u>Waste Type</u>	<u>Ash/No Ash</u>	<u>Stabilized/ Unstabilized</u>	<u>Studied</u>	<u>Ref</u>
LGE/Radian	Paddy's Run/Kentucky	H	DL	SI	NA	U	MO MC TC	51
LGE/CE	Paddy's Run/Kentucky	H	DL	SI	NA	U/T	MC,TC,L(field)	50
SCS	Scholz/Alabama	L/M,H	DA	SI,M	NA/A	T/U	MO MC L	14
EPA(IERL)	Pilot/RTP	L/M,H	DA(ox)	SA	NA/?	T/U	MO MC,TC	52
DOE	GFERC/North Dakota	LM	DL,DLS,DL(OX)	SI,M	A/NA	U	MO	21
	FA,DLS(OX) FA		SA SR	A	U	MO,MC,TC		
Radian (EPRI) 4 FGD samples and 14 fly ash samples were studied.								146
<u>Legend</u>								
Coal Type:	L/M	< 2% S	Ash/No Ash:		A/NA			
	H	> 2% S	Treated/Untreated:		T/U			
Process Type:	DLS;	Direct Limestone	Parameters Studied:		MO; Morphology			
	DL;	Direct Lime			MC; Major Components			
	DA;	Dual Alkali			TC; Trace Components			
	FA;	Fly Ash			L; Leaching			
Waste Type:	SI;	Sulfite Rich			Ox; Oxidation			
	M;	Mixed						
	SA;	Sulfate Rich						

^aStudies included are those partly or fully funded by government agencies (e.g, EPA, DOE, etc.) and utility research groups (EPRI).

^bKey to contractors

ADL Arthur D. Little, Inc.
 ACE Army Corps of Engineers
 Aerospace The Aerospace Corporation
 Bechtel Bechtel Corporation
 CE Combustion Engineering
 CEA Combustion Equipment Associates
 DOE Department of Energy
 EPA Environmental Protection Agency

EPRI Electric Power Research Institute
 GFERC Grand Forks Energy Research Center
 GM General Motors
 MPC Montana Power Company
 NEA New England Aquarium
 Radian Radian Corporation
 SCS Southern Company Services
 SUNY State University of New York
 TVA Tennessee Valley Authority
 UND University of North Dakota
 WES Army Corps of Engineers
 (Waterways Experiment Station)

Dugway, Utah. Results from that study are not available at present. No other comprehensive studies of FGC waste pollutant attenuation in soils have been identified.

Stabilized FGC wastes can be significantly different from unstabilized wastes in physical and chemical characteristics. Hence, as far as feasible, characteristics of stabilized FGC wastes will be separately reported in this chapter.

Data are presented for wastes obtained from non-recovery systems only.

4.2 Principal Components

4.2.1 Principal Components in Coal Ash

When coal is burned, a significant percentage of the weight of the parent material (3-30%) does not burn and remains as ash. Depending on the way in which a particular boiler is fired and the fusion temperature of the ash, as much as 65-95% of the ash passes out of the boiler with the flue gases as fly ash and the remainder is removed as bottom ash. In stoker boilers or other units burning coarsely-ground coal, as little as 10% of the ash can leave as fly ash.

Each year in the United States, more than 60 million tons of ash are collected from stationary combustion sources. Approximately, three-fourths of the collected ash is fly ash. Only about 10% of the collected fly ash is put to further use; the remainder is discarded [5].

The chemical composition of coal ash (bottom ash, fly ash and slag) varies widely, in concentrations of both major and minor constituents. Table 4.2 shows a compilation of chemical composition of fly ash from the firing of a wide range of different coals [6].

Table 4.2

Chemical Composition of Fly Ashes According
to Coal Rank - Major Species (Weight Percent)

Chemical Species ^a	Eastern Bituminous			Western Bituminous			Western Lignite		
	Range	Median	Total No. of Observations	Range	Median	Total No. of Observations	Range	Median	Total No. of Observations
Sodium Oxide, Na ₂ O	0.05-2.04	0.53	21	0.15-2.14	1.04	8	0.60-8.10	1.45	8
Potassium Oxide, K ₂ O	0.92-4.00	2.53	20	0.50-1.80	0.99	8	0.20-1.02	0.50	8
Magnesium Oxide, MgO	0.50-5.50	1.24	23	1.10-5.90	2.96	12	3.3-12.75	6.79	10
Calcium Oxide, CaO	0.26-13.15	2.88	21	1.80-30.40	13.81	12	11.7-35.44	22.29	10
Silicon Dioxide, SiO ₂	36.00-57.00	48.76	22	31.00-64.80	49.69	9	2.20-46.1	30.69	8
Aluminum Oxide, Al ₂ O ₃	16.25-30.30	23.26	22	18.70-37.00	23.04	12	10.7-25.3	15.48	10
Iron Oxide, Fe ₂ O ₃	3.88-35.40	16.44	23	3.07-21.50	6.48	12	2.9-14.15	8.87	10
Titanium Dioxide, TiO ₂	1.00-2.50	1.45	19	0.68-1.66	1.09	11	0.52-1.60	0.74	8
Phosphorous Pentoxide P ₂ O ₅	<0.02-0.42	2.73	16	1.19-0.70	0.38	6	<0.02-0.76	0.25	5
Sulfur Trioxide, SO ₃	0.09-3.30	0.78	17	0.10-5.23	1.66	12	0.32-7.20	3.14	8

^a Composition reflects only element breakdown of constituents and reported as their oxides and is not meant to indicate actual compounds present.

Source: [144]

The principal factor affecting the variation in the composition is the variability in the mineralogy of the coal. However, differences in composition can exist between fly ash and bottom ash (or boiler slag) generated from the same coal due to differences in the degree of pulverization of the coal prior to firing, the type of boiler in which the coal is fired, and the boiler operating parameters and combustion efficiency. For both fly ash and bottom ash more than 80% of the total weight of the ash is usually made up of silica, alumina, iron oxide, and lime.

It should be noted that the compositional breakdown shown in Tables 4.2 and 4.3 reflects only the elemental breakdown of the constituents reported as their oxides and is not indicative of the actual compounds present. A sampling of available data on a number of fly ashes and bottom ashes is presented in Table 4.3.

As much as 20% of fly ash can be water soluble, so the potential exists for release of contaminants through leaching. The principal soluble species are usually calcium, magnesium, potassium, sulfate, and chloride. Leachates resulting from ash are usually alkaline due to the presence of calcium oxide and other alkaline species, although some ashes have been found to be inherently neutral or even acidic. A high, available alkalinity is particularly characteristic of the ash from low sulfur western sub-bituminous and lignite coals. Coal ash can also contain sulfate compounds (expressed as percent SO_3) which are partly due to occluded sulfate minerals, but also the result of the reaction of SO_2 produced during combustion with the alkaline cations and its subsequent oxidation.

An important property of coal fly ash is its pozzolanic potential. The pozzolanic reaction involving fly ash occurs either because of the lime contained in the fly ash itself or is induced by addition of lime (and water). The reaction causes the fly ash to aggregate and harden when moistened and compacted.

Bottom ash can be collected either dry or in a molten state (generally referred to as bottom slag). Dry collected bottom ash has a different particle size distribution from fly ash and its bulk density

Table 4.3

Major Constituents in Fly Ash and Bottom Ash
from Various Utility Plants

Compound or Element ^a	Plant 1		Plant 2		Plant 3		Plant 4		Plant 5		Plant 6	
	FA	BA	FA	BA	FA	BA	FA	BA	FA	BA	FA	BA
SiO ₂ , %	59.	58.	57.	59.	43.	50.	54.	59.	NR	NR	42.	49.
Al ₂ O ₃ , %	27.	25.	20.	18.5	21.	17.	28.	24.	NR	NR	17.*	19.
Fe ₂ O ₃ , %	3.8	4.0	5.8	9.0	5.6	5.5	3.4	3.3	20.4	30.4	17.3	16.0
CaO, %	3.8	4.3	5.7	4.8	17.0	13.0	3.7	3.5	3.2	4.9	3.5	6.4
SO ₃ , %	0.4	0.3	0.8	0.3	1.7	0.5	0.4	0.1	NR	0.4	NR	NR
MgO, %	0.96	0.88	1.15	0.92	2.23	1.61	1.29	1.17	NR	NR	1.76	2.06
Na ₂ O, %	1.88	1.77	1.61	1.01	1.44	0.64	0.38	0.43	NR	NR	1.36	0.67
K ₂ O, %	0.9	0.8	1.1	1.0	0.4	0.5	1.5	1.5	NR	NR	2.4	1.9
P ₂ O ₅ , %	0.13	0.06	0.04	0.05	0.70	0.30	1.00	0.75	NR	NR	NR	NR
TiO ₂ , %	0.43	0.62	1.17	0.67	1.17	0.50	0.83	0.50	NR	NR	1.00	0.68

^aAnalysis is performed for the individual elements and then expressed as their oxides.

Legend: FA - Fly Ash, BA - Bottom Ash, NR - Not Reported

Source: [112]

is higher than that of fly ash. It has a similar chemical composition to that of fly ash, although with less pozzolanic activity.

Boiler slag is a black glassy substance composed chiefly of angular or rod-like particles, with a particle size distribution ranging from fine gravel to sand. Boiler slag is porous, although not as porous as dry bottom ash. It is generally less reactive in terms of its pozzolanic properties than either dry bottom ash or fly ash. Fly ash is the only coal ash employed in stabilization of FGC wastes.

Partly because of the historical practice of combined handling, bottom ash and fly ash have been grouped together in terms of considerations relative to environmental impact assessment. Both bottom ash and fly ash frequently are disposed of in a pond disposal area. Typically, bottom ash and fly ash are sluiced to a central disposal pond where the ash is allowed to settle out and the overflow liquor discharged or returned for sluicing. Analyses of pond liquors indicate total dissolved solids levels on the order of hundreds of mg/l (ppm), with the major constituents being calcium, magnesium, sodium, sulfate, and chloride, and lesser amounts of silicates, iron, manganese, and potassium.

4.2.2 Principal Components in Unstabilized FGC Wastes

4.2.2.1 Wet Processes

4.2.2.1.1 Solid Wastes

The chemical composition of the wastes produced in any FGC system will depend upon a variety of factors including:

- the composition of the coal burned,
- the type of boiler and its operating conditions,
- the method of particulate control employed, and
- the type of FGD system and the way in which it is operated.

Waste characteristics, and in particular the chemical composition, can vary over extremely wide ranges. The principal substances making up the solid phase of FGD wastes are calcium-sulfur salts (calcium sulfite and/or calcium sulfate) along with varying amounts of calcium carbonate, unreacted lime, inerts and/or fly ash. The ratio of calcium

sulfite to calcium sulfate (the latter present as $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ or as gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) will depend principally upon the extent to which oxidation occurs within the system.

Oxidation, and consequently, the calcium sulfate-to-calcium sulfite ratio, is usually greater in systems burning low sulfur western coal. Less oxidation usually takes place in direct lime than in direct limestone systems. However, it is possible to promote oxidation in either of these types of systems (or in dual alkali systems) to produce wastes with a high calcium sulfate-to-calcium sulfite ratio, where essentially all of the calcium sulfate is present in the form of gypsum. When high sulfur coal is burned and the boiler and FGD systems are operated in a conventional manner, the calcium-sulfur salts can consist primarily of calcium sulfite.

Table 4.4 contains examples of different types of wastes from conventionally operated FGD systems. Some of the wastes contain only very small amounts of calcium sulfate (Paddy's Run--high sulfur coal, direct lime scrubbing), and others contain essentially no calcium sulfite (Mohave--low sulfur coal, direct limestone scrubbing). Scrubbing under conditions of forced oxidation has been tested at the Shawnee Test Facility [13] for a direct lime system and a limestone system; and at both Parma and Gadsby using a dual alkali system.

Fly ash is the other major component which can occur in FGC wastes and its concentration in the waste can vary over a wide range. Fly ash will be a principal constituent of the waste only if the scrubber serves as a particulate control device in addition to SO_2 removal or if separately collected fly ash is admixed with the FGD waste. The amount of inerts and unreacted raw materials (lime and/or limestone) in the wastes will depend upon the quality and utilization of raw materials (system stoichiometry). In some systems, e.g., Paddy's Run, Mojave, or Scholz, fly ash is collected separately in electrostatic precipitators or in mechanical collectors ahead of the FGD scrubber. Such fly ash collection is usually very efficient and little, if any, fly ash is found in the

Table 4.4

Major Components in Selected FGC Waste Solids

Plant	System Size ^a	Location	Process	% S	Percent by Weight					Source (Ref. No.)
					$\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	CaCO_3	Fly Ash	Other	
Shawnee	PR	Eastern	Limestone	2.9 ^c	19-23	15-32	4-42	20-43		13
Shawnee	PR	Eastern	Lime	2.9 ^c	50	6	3	41		13
Shawnee	PR	Eastern	Lime (Ox.) ^b	(2.3) ^c	(3)	52-65	2-5	30-40		13,14
Phillips	FS	Eastern	Limestone(Ox.) ^b	1-2.8 ^c	(3)	47-62	5-10	30-40	8.2 Unk. ^d	13,15
			Lime		13	19	0.2	60		
Paddy's Run	FS	Eastern	Lime	3.5-4 ^c	94	2	0	4		16
Cholla	FS	Western	Limestone	0.44-1 ^c	11	17	2.5	59	10.7 Unk. ^d	13,15
Mojave	FS	Western	Limestone	<2 ^c	2	95	0	3		17
Parma	FS	Eastern	Dual Alkali	2-3	14	72 ^b	8	7		18
Scholz	PR	Eastern	Dual Alkali	1-4	65-90	5-25	2-10	nil		19
Gadsby	PP	Western	Dual Alkali	0.55 ^c	0.2	82 ^c	11	9		13
Colstrip	FS	Western	Fly Ash	0.8	0-5	5-20	nil	40-70	5-30% MgSO_4	20

^aFS = Full Scale PR = Prototype PP = Pilot Plant

^bForced Oxidation

^cRef. 45

^dPortion (20% of sludge) reportedly $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$

^ePortion (18% of sludge) reportedly CaSO_4

^fUnknown soluble salt; quantity determined by difference

Table 4.4 (Continued)

Major Components in Selected FGC Waste Solids

<u>Plant</u>	<u>System Size^a</u>	<u>Location</u>	<u>Process</u>	<u>% S</u>	<u>Percent by Weight</u>					<u>Source (Ref. No.)</u>
					<u>CaSO₃ · 1/2H₂O</u>	<u>CaSO₄ · 2H₂O</u>	<u>CaCO₃</u>	<u>Flyash</u>	<u>Other</u>	
Milton R. Young	PP	Western Lignite	Fly Ash	0.6	Nil	40	-	60		21
Black Dog	PP	Western	Limestone (Ox.) ^b	0.8	Nil	20 40	← remainder →			22
La Cygne	FS	Eastern	Limestone	5.4	20	15	41	24		23
Lawrence	FS	Western	Limestone	0.5-1	0.2-7	11 - 31	2-22	(40-60)		24

^aFS = Full Scale PR = Prototype PP = Pilot Plant^bForced Oxidation

waste. In other systems, the SO_2 scrubber also functions as a particulate control device and the collected fly ash can comprise from 20-60% of the FGD waste solids. Even in installations where fly ash is collected separately, it can be admixed with ash-free waste in an attempt to improve the handling properties of the waste.

Varying amounts of unreacted limestone (CaCO_3) can be found in the wastes from direct limestone processes. Direct lime and dual alkali processes utilizing lime for regeneration usually operate with amounts of lime only slightly in excess of that required for liquor regeneration. However, lime is often contaminated with some limestone which passes through the system unreacted and ends up in the waste, and lime can also react with CO_2 forming small amounts of CaCO_3 . Some dual alkali processes employ sodium carbonate softening to reduce dissolved calcium levels in order to minimize scrubber scaling. The softening reaction produces calcium carbonate, which leaves with the waste.

In certain systems operating with a very tight water balance, relatively soluble substances, e.g., MgSO_4 in the Montana sludge, can build to sufficiently high levels that they can crystallize out and appear as solids in the waste. Scrubbers collecting large amounts of fly ash from low sulfur coals are most likely to produce such wastes.

The samples characterized in most studies usually consist of a few samples taken from different FGC systems on particular days. It must be noted that the compositions of samples taken from any one system could be quite different on different days. Similarly, the same type of FGC system installed on another boiler and run under a different set of operating conditions can produce a waste with entirely different properties. Thus, the data cited in this section should be viewed as illustrative of the effects of various considerations which can influence waste composition rather than as defining the composition of waste produced by a particular process or process type. Furthermore, in all cases (fly ash, and stabilized and unstabilized FGC wastes), few data are available on speciation of various elements reported recently.

A critical problem in environmental impact assessment is identifying the chemical form of constituent elements in waste. SCS Engineers initiated a study for the EPA on chemical speciation of contaminants in FGD wastes and wastewater [14].

4.2.2.1.2 Liquid Wastes

Waste Liquors

Untreated FGC solid wastes (and some stabilized wastes) carry with them occluded and/or free liquor which contains a wide variety of dissolved substances ranging from trace amounts of various heavy metals, some of which are toxic at even very low concentrations, to substantial quantities of commonly occurring species such as sodium, calcium, magnesium, chloride, and sulfate. The amount of liquid phase present depends upon the degree to which the solids are dewatered prior to discharge and can range from as much as 90% of the total weight of the waste to as little as 10%.

Early studies on FGC wastes performed by Aerospace [31,37] and the U.S. Army Waterways Experiment Station (WES) [16,41] under the sponsorship of the EPA, included the compositional analyses of liquors in a variety of FGC waste samples taken from different pilot, prototype, and full-scale systems. Table 4.5 summarizes the reported concentrations of the major constituents measured in the waste liquors and their principal sources.

The major constituents are considered to be those which can be present at concentrations up to 100 ppm or more. For commercially available, calcium-based nonrecovery FGD technology, these include: calcium, chloride, magnesium, sodium, sulfate and sulfite. Because of the extensive data on these components from analyses performed in waste characterization programs and operating data from organizations developing, testing and operating FGC systems, their concentrations are fairly predictable.

Broadly speaking, the concentrations of different species in solution will be dictated either by equilibrium solubilities or, for the

Table 4.5

Waste Liquor Phase - Major Constituents

<u>Species</u>	<u>Concentration (mg/l)</u>	<u>Principal Source</u>
Calcium	150-3,000	Process Makeup
Chloride	400-50,000	Flue Gas
Magnesium	nil-3,000	Ash, Process Makeup
Potassium	nil-200	Ash, Process Makeup
Sodium	10-30,000	Ash, Process Makeup
Sulfate	500-30,000	Flue Gas, Ash, Process Makeup
Sulfite	nil-3,000	Flue Gas
Total Dissolved Solids	2,500-100,000	---

Source: [30,37]

most highly soluble species, by the rate at which they enter the FGC system. Thus, the levels achieved in the waste liquor will depend upon the type of FGC system and its operating conditions as well as the coal composition and reactant impurities.

Compounds of sodium and chloride are generally highly soluble and their solubilities do not vary appreciably with pH. The concentrations of these ions in solution tend to rise to a point where the rate at which they are rejected from the system is in balance with the rate at which they enter the system from the flue gas, fly ash, (if collected with FGD waste), and process makeups.

The primary source of chloride is usually the coal, and the soluble chloride concentration is principally a function of the chloride and sulfur contents of the coal and the rate of water discharge with the wastes. Chlorides in coal are highly volatile and enter the system in the flue gas from which the chloride (present as HCl vapor) is effectively scrubbed by relatively alkaline scrubber liquors. While chloride concentrations in liquors are generally less than about 5,000 ppm, levels as high as 43,000 ppm have been reported [37] for systems burning low sulfur western coal where a very tight system water balance is maintained (low water discharge rate) and where cooling tower blowdown (a major source of chlorides) is used for process makeup water.

In most direct lime and limestone scrubbing systems sodium concentrations are generally low, less than a few hundred ppm. However, in alkaline fly ash scrubbing systems where there are high levels of soluble sodium in the fly ash and in sodium based dual alkali systems where sodium compounds are added to replace losses in the wastes, sodium levels in waste liquors can range up to 10,000 ppm or more depending on the degree of dewatering and the extent of washing of filtered wastes [18, 19, 20]. For example, during the sampling of the dual alkali systems at Gadsby (pilot) and Parma, Ohio (industrial full-scale) for the Aerospace [37] and WES [16] programs, the filter cake was not washed well and sodium levels (primarily Na_2SO_4 and NaCl) exceeded 20,000 ppm. In contrast, during periods of proper cake wash, samples of wastes from the

Scholz dual alkali system showed 4,000-8,000 ppm of sodium in the waste liquor [19].

Concentrations of calcium, sulfate, and sulfite are generally limited by the solubility products of the respective salts and the ion activities. Ion activities and hence solubilities of these salts depend importantly upon ionic strength. Thus the ultimate concentrations achieved in the waste liquors usually vary with the type of system and the manner in which it is operated.

In general, calcium sulfite and sulfate salts are relatively insoluble and calcium concentrations usually do not exceed a few thousand ppm (and are typically on the order of 1,000 ppm or less). Sulfate concentrations are limited by the solubility product of gypsum and the level of calcium present. In conventional direct lime and limestone systems where calcium concentrations are also dictated by the solubility of gypsum (where there is no appreciable sulfite present), sulfate levels generally do not exceed the range of 5,000-8,000 ppm. However, when soluble alkali or alkaline earth compounds are added to such systems to improve performance, and in dual alkali systems where there are high process liquor TDS levels, the changes in ion activities and the higher levels of sulfite (which decrease calcium levels) can result in sulfate concentrations in waste liquors well in excess of 10,000 ppm.

Magnesium sulfite and sulfate are considerably more soluble than the respective calcium salts and the levels of magnesium achieved are usually dictated by the rate at which it enters the system. In cases where it is intentionally added to the system or enters in appreciable quantities via fly ash significant levels can be attained. The magnesium concentrations are pH sensitive and if the pH is raised to higher than about 10.5, precipitation of $Mg(OH)_2$ will reduce magnesium levels to negligible levels.

Lunt et al. [30] point out that the leaching of sulfite or total oxidizable sulfur (TOS) from wastes is also of concern. Since it is readily oxidized to sulfate, TOS represents an immediate oxygen demand to groundwaters and receiving waters. Total oxidizable sulfur (TOS) may

also be potentially toxic to aquatic life. The amount of sulfite in liquor will depend upon the degree of oxidation in the scrubber system and the manner in which the waste is processed (e.g., further dewatered, admixed with ash, etc.) and handled prior to and during disposal. Sulfite levels initially in the liquor phase of FGC wastes as they are discharged can range from nil to hundreds of ppm, and the amount of sulfite in the waste solids can vary from nil to greater than 95% of the total calcium-sulfur salts present. Sulfite levels can change during waste processing and handling prior to disposal resulting from contact with air and oxidation of the sulfite. Since dissolution of $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ solids would normally be relatively low and would be limited by equilibrium conditions (unless the wastes were acidified), it can be expected that soluble sulfite levels would not exceed the initial liquor concentrations.

4.2.2.2 Dry Processes

As mentioned earlier in Section 2, a number of dry sorbent processes are under investigation. These processes can be divided into two categories. The nonrecovery dry sorbent FGD processes use an alkaline solid sorbent to react with the SO_2 and produce a sulfate or a sulfite salt as a final product. A listing of the chemical compounds being tested as sorbents and the final waste products is given in Table 4.6. Extensive chemical characterization of any of the waste products has not been published. Of the sorbents listed in Table 4.6, the use of dry nahcolite and the spray drying of sodium carbonate and lime slurries have received greatest attention. The major components present in the final product may be inferred from the postulated gas-solid reactions. For nahcolite the reactions which are thought to occur are decomposition of the solid sodium bicarbonate to solid sodium carbonate, reaction of gaseous SO_2 with either of these two solids to form solid sodium sulfite and then partial oxidation of the solid sodium sulfite to sodium sulfate by oxygen.

The relative chemical compositions of the raw nahcolite and after exposure to simulated flue gas are shown in Table 4.7 and indicate the presence of these reactions.

Table 4.6

Major Dry Solvents Under Investigation in the
United States and Their Reaction Products

<u>Dry Sorbent</u>	<u>Reaction Process</u>	<u>Major Sulfur Products</u>
<u>Sodium Based</u>		
Nahcolite (70% NaHCO_2)	{ solid injection into gas stream or spray drying of a slurry	{ Na_2SO_4 Na_2SO_3
Commercial NaHCO_3)		
Na_2CO_3		
Trona $(\text{Na}_3\text{HCO}_3)_2 \cdot 2\text{H}_2\text{O}$		
<u>Calcium Based</u>		
$\text{Ca}(\text{OH})_2$		CaSO_4 , CaSO_3

Source: [57]

Table 4.7

Chemical Composition of Raw and Spent
Nahcolite Ore

<u>Component</u>	<u>Raw Composition (% by wt)</u>	<u>Spent Composition (% by wt)</u>
NaHCO_3	77.7-84.7	1.4-5.9
Na_2CO_3	2.1-2.7	1.6-32.3
Na_2SO_3		33.4-51.3
Na_2SO_4		8.7-24.5
Moisture ^a	2.0-2.3	0.8-1.0
Water Insolubles	8.7-12.3	11.4-14.4
Organics ^a	2.5-5.0	3.3-5.9
Wt Ratio Na_2SO_4 to Na_2SO_3	-	2.1-5.7

^aDetermined by differential heating and gravimetric analysis.

Source: [58]

In some of the processes, fly ash is separated prior to contact of the flue gas with the dry sorbent. In others, such as the spray-dried sodium carbonate or calcium hydroxide slurries, the flue gas leaves the spray dryer containing both the dry reacted sorbent and boiler fly ash. The ash and sorbent are removed simultaneously. Thus, depending on the system, the waste can contain significant amounts of fly ash.

The solids produced from the calcium hydroxide spray dry system, being mainly CaSO_4 and CaSO_3 , are similar to other FGD wastes now disposed. Yet sufficient differences in some properties may occur due to the different mode of interaction of the SO_2 and the absorbing species to warrant investigation of the characteristics of this product. Since the waste is produced from direct reaction of a solid with a gas as opposed to other FGD systems where absorption and subsequent reaction occurs in the liquid phase, the morphology of the product may be extremely different. In addition, the utilization of $\text{Ca}(\text{OH})_2$ may be quite different in these systems and may lead to greater alkalinity in the waste product. An additional difference may occur in the trace element content of the waste. Since the dry sorbent systems operate at higher temperatures than other FGD systems, and since no liquid phase exists, some trace elements which occur as volatile species may not be absorbed as efficiently on the solid sorbent as they would with an aqueous scrubbing media. Thus, for a dry sorbent system where fly ash is collected separately, the waste product conceivably could contain fewer trace elements than other FGD systems.

4.2.3 Stabilized FGC Wastes

As discussed earlier in Section 3, a significant number of generic and proprietary processes have been proposed whereby FGC wastes would be "stabilized" by a combination of mechanical or chemical modifications and the addition of materials to increase strength and decrease permeability and compressibility. A partial listing of such processes was presented in Section 3. Two of these (offered by IUCS and Dravo) are now offered commercially for treating FGC wastes from utility plants.

The alumina and silica which are primary components of coal ash are slightly soluble in alkaline solutions producing silicate and aluminate ions. If a source of calcium is present, a reaction producing calcium silicate and calcium aluminate can occur. Those reactions also occur during the setting and curing of Portland cement and tend to form cementitious bonds in particulate matter that is present. These intermediate products of this pozzolanic reaction reportedly can react further with sulfate to produce ettringite, $(3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O})$ [2].

Ashes that are sufficiently alkaline and contain enough leachable calcium can be auto-pozzolanic, either alone or in combination with calcium sulfur salts produced during scrubbing. This phenomenon has been observed for wastes produced in alkaline fly ash scrubbing systems operating on low sulfur western coal. This same chemistry is the basis of the treatment process reportedly practiced by IUCS in which lime is added, and fly ash if necessary, to scrubber wastes in order to stabilize them.

The Dravo process uses a proprietary material named Calcilox, which is a product derived from basic, glassy, blast-furnace slag and hydrated lime. It has been reported [2] that the Chemfix process involves addition of a soluble silicate, a setting agent such as Portland cement, and lime, if necessary, to the material being stabilized. In all these stabilization processes, the formation of cementitious calcium silicates and aluminates is a key step.

Reduction in waste permeability accompanying the stabilization reactions is probably the primary factor which reduces pollutant mobility from treated materials. Such reduction in pollutant mobility is one of the primary objectives of stabilization. Ease of handling in disposal is another advantage accruing from stabilization. Inclusion of soluble sulfate into the insoluble mineral ettringite has been mentioned above, and the high alkalinity which sometimes results from stabilization theoretically should reduce the solubility of trace metals in the waste. However, very little conclusive data demonstrating the chemical immobilization of pollutants by treatment have been developed.

At present, some limited data are available in the open literature concerning complete chemical analysis and mineralogy of wastes treated by any stabilization process. Limited analysis of some stabilized materials has been attempted at SUNY [15] and WES [16]. A recent paper by Weeter [25] reviews results obtained by using several methods including scanning electron microscopy (SEM), x-ray diffraction (XRD), and energy dispersive x-ray analysis (EDXRA). All these methods are useful in evaluating the structure of stabilized and unstabilized FGC wastes. IUCS [26] concludes that stabilization leads to a decrease in $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ and increase in ettringite. Other investigators [27] report formation of calcium sulfoaluminate hydrate in systems with lime, fly ash and sulfate.

Very limited data are available on stabilization processes and properties of stabilized wastes produced from dry sorbent processes. Both sodium sulfate and sodium sulfite produced in the sodium based dry systems are extremely water soluble and may have significant environmental impact via leaching. Limited laboratory experiments have been performed [59] which demonstrated how sodium sulfate is rendered insoluble by coprecipitation with acidic ferric ion to form insoluble double salts $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ (natrojarosite) and $\text{Na}_2\text{Fe}(\text{SO}_4)_2(\text{OH}) \cdot 3\text{H}_2\text{O}$ (sideronatrite). These experiments were performed with nahcolite filter cake after separation of the water insolubles and fly ash.

4.3 Composition Ranges for Trace Components

4.3.1 Trace Components in Coal Ash

A variety of trace elements find their way to coal ash waste principally from coal and possibly, to a small extent, from water used for handling. Coal contains a large number of trace elements present either in minerals occluded within the coal or as organometallic compounds (compounds of arsenic and selenium, in particular) distributed throughout the coal itself. The Illinois Geological Survey [28] conducted a survey of trace elements in coal. From a statistical analysis, they conclude that:

1. Elements that have relatively large ranges in concentration and that have standard deviations larger than the arithmetic means (for example, As, Ba, Cd, I, Pb, Sb, and Zn) include those that are found in coals within sulfate and sulfide minerals or those that would be expected to be found in that association. Elements that occur in organic combination or that are contained within the silicate minerals have narrow ranges and smaller standard deviations. Many of the silicate minerals are thought to be emplaced in the coal very early in the period of coal formation as detrital or as syngenetic minerals. The sulfides and some sulfates, although syngenetic in part, have a major portion emplaced in the coal by epigenetic mineralization.
2. In general, elemental concentrations tend to be highest in coals from eastern United States, lowest in coals from western United States, and intermediate in value in coals from the Illinois Basin.
3. Many elements are correlated positively in coals. The most highly correlated are Zn:Cd ($r = 0.94$ for coals of the Illinois Basin). Chalcophile elements (As, Co, Ni, Pb, and Sb) are all mutually correlated, as are the lithophile elements (Si, Ti, Al, and K). Other significant correlations are Ca:Mn ($r = 0.65$) and Na:Cl ($r = 0.48$) [28].

The above study [28] also concludes that only four elements are, on the average, present in coals in concentrations significantly greater than the Clarke of those elements (average concentration in the earth's crust). These are boron, chlorine, selenium, and arsenic. Not all are concentrated in each of the samples analyzed from the three geographic groups (eastern U.S., western U.S., and the Illinois Basin).

Typical ranges of concentrations for some trace elements in coal ash obtained from power plants are presented in Table 4.8. For comparison, ranges for some trace elements in coal ash obtained from ashing coal samples at 600°C (1140°F) are given in Table 4.9. While the major constituents of bottom ash and fly ash are generally similar, there is

Table 4.8

Trace Elements in Coal Ash

<u>Element</u>	<u>Concentration Range (ppm)</u>
Antimony	ND - 200
Arsenic	ND - 1,000
Barium	50 - 10,000
Beryllium	ND - 200
Boron	15 - 6,000
Cadmium	ND - 0.5
Chromium	5 - 500
Cobalt	5 - 400
Copper	20 - 3,000
Fluoride	---
Lead	10 - 1,500
Manganese	50 - 10,000
Mercury	.01 - 100
Molybdenum	5 - 1,500
Nickel	15 - 70
Phosphorous	5 - 10,000
Selenium	1 - 50
Vanadium	10 - 1,000
Zinc	25 - 15,000

Source: [28]

Table 4.9

Concentration
Range of Trace Species Present in Coal Ashes^a

Element ^b	Concentration Ranges (ppm)		
	Lignites and Subbituminous	Anthracites	Bituminous
Ag	1-50	1	1-3
As	9-45		11-990
B	320-1900	63-130	74-2800
Ba	55-13900	540-1340	96-4660
Be	1-28	6-11	4-60
Br	2-3		2-4
Ce	<95-130		<53-250
Cl	41-90		76-270
Co	11-310	10-165	10-440
Cr	11-140	210-395	36-490
Cu	53-3020		30-850
F	16-1000		30-380
Ga	10-30	30-71	10-135
Ge	20-100	20-20	20-285
La	34-90	115-220	19-270
Li	56-1-0		48-500
Mn	310-1030	58-365	31-4400
Mo	6-11		12-17
Nb	21-34		31-78
Ni	20-420	125-320	20-610
Pb	20-165	41-120	23-1500
Rb	17-43		29-<1000
Sc	2-58	50-82	7-155
Se	5-16		10-37
Sn	10-660	19-4250	10-825
Sr	230-8000	80-340	40-9600
Th	21-43		26-54
V	20-250	210-310	60-860
W	7-14		16-30
Y	21-120	70-120	29-460
Yb	2-10	5-12	3-23
Zn	50-320	155-350	50-1200
Zr	100-490	370-1200	115-1450

^aAtomic absorption data on coals ashed at 600°C (1140°F). Concentrations are ppm.

^bElements whose concentration are <2¹ppm include Ru, Pd, Re, Os, Ir, Rt, Au, Rh, Te, Bi, W, Hf, Lu, I, Cd.

Source: [7, 29, 81, 112]

usually an enrichment of trace elements in the fly ash as compared with the bottom ash based upon the total quantity of trace elements in the coal fired as shown in Table 4.10. A few of the elements originally present in the coal (notably sulfur, mercury, and chlorine) are almost completely volatilized and leave the boiler as gaseous species which are not collected downstream in dry ash collection equipment. However, these can be collected in wet scrubber systems (i.e., FGD system). The substantial enrichment of fly ash with antimony, selenium, and lead in comparison to concentrations in the coal (after correcting for weight loss due to combustion) is shown in Figure 4.1.

It appears that the condensation of elements including volatile trace elements resulting in a higher concentration of these elements in the fine particulates of fly ash can occur for two reasons:

1. Condensation occurs either by nucleation or by deposition on previously formed particles. Since residence times between volatilization and condensation are relatively low, any nucleation will produce relatively small particles.
2. Deposition occurs on the particle surface and is, therefore, dependent on particle surface area. Since surface area is greater for finer particles, small particulates display increased concentrations of elements which tend to recondense [34].

The distribution of various trace elements with fly ash particle size is shown in Table 4.11 for one sample of fly ash.

4.3.2 Trace Elements in Unstabilized FGC Wastes

4.3.2.1 Total Wastes

The level of trace elements in the FGC waste depends primarily upon three factors:

- The level of various trace constituents in the coal relative to its sulfur content and in any FGD process additives;
- The amount of ash, if any, collected with or admixed with the sludge; and
- The efficiency of the scrubber system in capturing volatile trace constituents.

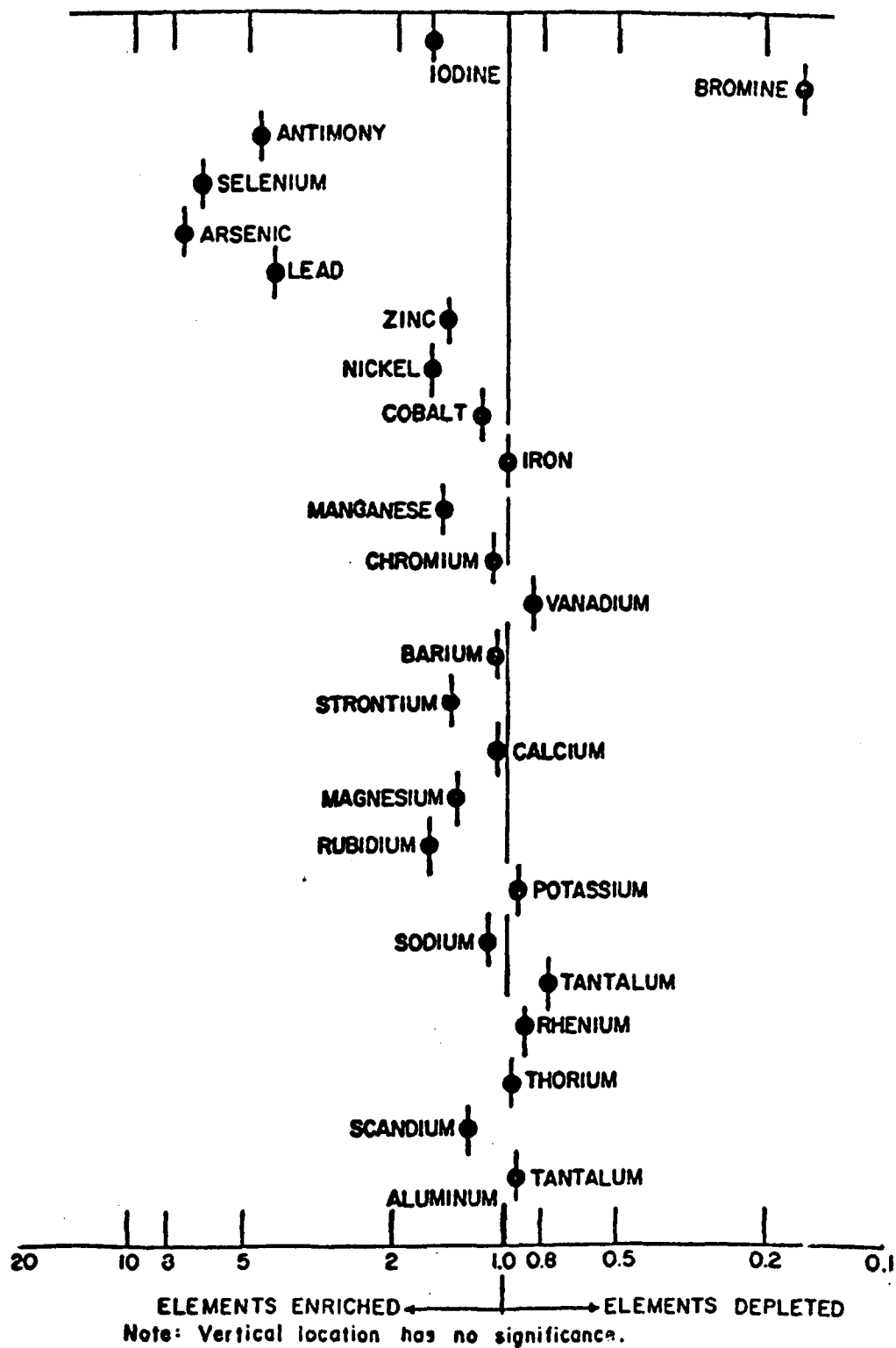
Table 4.10

Trace Constituents in Fly Ash and Bottom Ash
From Various FGC Units^a

Element	Plant 1		Plant 2		Plant 3		Plant 4		Plant 5		Plant 6	
	FA	BA	FA	BA	FA	BA	FA	BA	FA	BA	FA	BA
As, ppm	12.	1.	8.	1.	15.	3.	6.	2.	8.4	5.8	110.	18.
Be, ppm	4.3	3.	7.	7.	3.	2.	7.	5.	8.0	7.3	NR	NR
Cd, ppm	0.5	0.5	0.5	0.5	0.5	0.5	1.0	1.0	6.44	1.08	8.0	1.1
Cr, ppm	20.	15.	50.	30.	150.	70.	30.	30.	206.	124.	300.	152.
Cu, ppm	54.	37.	128.	48.	69.	33.	75.	40.	68.	48.	140.	20.
Hg, ppm	0.07	0.01	0.01	0.01	0.03	0.01	0.08	0.01	20.0	0.51	0.05	0.028
Mn, ppm	267.	366.	150.	700.	150.	150.	100.	100.	249.	229.	298.	295.
Ni, ppm	10.	10.	50.	22.	70.	15.	20.	10.	134.	62.	207.	85.
Pb, ppm	70.	27.	30.	30.	30.	20.	70.	30.	32.	8.1	8.0	6.2
Se, ppm	6.9	0.2	7.9	0.7	18.0	1.0	12.0	1.0	26.5	5.6	25.	0.08
V, ppm	90.	70.	150.	85.	150.	70.	100.	70.	341.	353.	440.	260.
Zn, ppm	63.	24.	50.	30.	71.	27.	103.	45.	352.	150.	740.	100.
B, ppm	266.	143.	200.	125.	300.	70.	700.	300.	NR	NR	NR	NR
Co, ppm	7.	7.	20.	12.	15.	7.	15.	7.	6.0	3.6	39.	20.8
F, ppm	140.	50.	100.	50	610.	100.	250.	85.	624.	10.6	NR	NR

^aFA = Fly Ash, BA = Bottom Ash, NR = Not Reported

Source: [112]



Source: [34, sic]

Figure 4.1 Enrichment Factors of Various Elements on Suspended Particles in the Stack with Respect to the Concentrations in the Ash

Table 4.11

Elements Showing Pronounced Concentration
Trends With Decreasing Particle Size
(ppm unless otherwise noted)

Particle diam, μ	Pb	Tl	Sb	Cd	Se	As	Ni	Cr	Zn	S, wt%	Mass Frac %
A. Fly Ash Retained in Plant											
Sieved fractions											
74	140	7	1.5	10	12	180	190	100	500	...	66.30
44-74	160	9	7	10	20	500	140	90	411	1.3	22.89
Aerodynamically sized fractions											
40	90	5	8	10	15	120	300	70	730	0.01	2.50
30-40	300	5	9	10	15	160	130	140	570	0.01	3.54
20-30	430	9	8	10	15	200	160	150	480	...	3.25
15-20	520	12	19	10	30	300	200	170	720	...	0.80
10-15	430	15	12	10	30	400	210	170	770	4.4	0.31
5-10	820	20	25	10	50	800	230	160	1100	7.8	0.33
5	980	45	31	10	50	370	260	130	1400	...	0.08
Analytical method											
	a	a	a	a	a	a	b		a	a	
B. Airborne Fly Ash											
11.3	1100	29	17	13	13	680	460	740	8100	8.3	
7.3-11.3	1200	40	27	15	11	800	400	290	9000	...	
4.7-7.3	1500	62	34	18	16	1000	440	460	6600	7.9	
3.3-4.7	1550	67	34	22	16	900	540	470	3800	...	
2.1-3.3	1500	65	37	26	19	1200	900	1500	15000	25.0	
1.1-2.1	1600	76	53	35	59	1700	1600	3300	13000	...	
0.65-1.1	48.8	
Analytical method											
	d	a	a	d	d	d	d	d	a	c	
(a) De arc emission spectrometry. (b) Atomic absorption spectrometry. (c) X-ray fluorescence spectrometry. (d) Spark source mass spectrometry.											

Source: [112]

Unlike the data on FGC wastes and those on trace elements in coal ash (which refer to the solid phases in those wastes), available data on trace elements in FGC wastes are the sum total of those elements in the solid and liquid phases of these wastes (or sludges).

Many of the elements are not highly volatile and will be retained in the ash (fly ash and bottom ash) matrix. The extent to which fly ash is a part of the waste composition determines the presence of the least volatile elements in FGD waste but has little impact on the presence of highly volatile elements. On the other hand, the concentrations of such highly volatile elements as arsenic, mercury, and selenium which appear in the waste will depend upon the extent to which they are present in and released from the coal and, as importantly, the efficiency with which they are captured in the scrubber. Mercury and selenium are likely to be present in the flue gas as elemental vapors that might not be scrubbed efficiently.

Assuming that the limestone, lime, and process water makeup to the system are not contaminated with trace elements and that all highly volatile species and fly ash are captured in the scrubber, then the FGD system would increase the concentration of trace elements proportionate to the coal weight lost upon combustion. Since the burning of one metric ton of coal typically produces 0.05-0.20 metric tons of dry scrubber waste without fly ash (depending upon the sulfur content and SO₂ removal efficiency) and up to 0.4 tons of scrubber waste with fly ash, theoretically it could be expected that many trace element concentrations in the sludge could increase by a factor of 2.5X to 20X over those found in coal.

In addition to changes in concentration of trace constituents in waste as compared to coal, there is also a change in the form and availability of these constituents. Important differences in trace element chemistry and availability between the original coal material and the FGD waste are as follows:

Original Coal	FGC Waste
Trace elements contained in highly insoluble mineral matrix.	Trace elements dispersed in potentially soluble CaSO_4 and CaSO_3 matrix.
Undisturbed geological material compact, relatively non-porous with low leaching rates.	Sludge composed of fine particles, with finite permeability.
Trace elements usually present as organometallics, sulfides or carbonates [6].	On combustion, trace elements containing compounds are converted to oxides and in certain cases, elemental forms.

A number of the important trace elements which have been found in FGC wastes containing up to 60% ash are listed in Table 4.12 along with the range of concentrations at which they have been detected in conjunction with measurements performed on many samples and a comparative listing of ranges of trace metal levels which have been measured in a variety of coal samples.

The observed concentrations range over as much as three orders of magnitude, primarily because the levels of trace elements in coal can vary by that same extent. The measured concentrations of a given element in the waste samples studied generally fall within the same broad range as do typical concentrations in coal.

Additional data on trace element levels in total FGC wastes are available from the sampling and testing program performed by Radian for EPRI [39]. In this program, three power plants with FGC systems (one with direct lime and two with direct limestone) were studied. Trace element levels were measured in the coals fired, ash produced (bottom ash and fly ash), makeup water, reactant feed, total waste, and waste liquors. The results are given in Tables 4.13, 4.14, and 4.15.

The Radian data indicate that there is no direct general correlation between the levels of a trace element in the coal with those in the wastes. This is to be expected even in cases where all of the ash is simultaneously removed with the SO_2 or admixed with the waste calcium-sulfur salts. An appreciable quantity can enter the system through the reactant feed (lime, limestone, soda ash, etc.) and, in some cases, the process makeup water (concentrations in makeup water can be magnified by factors as large as ten to twenty in systems with tight water balances).

Table 4.12

Concentrations of Trace Metals in FGC Wastes and Coal

<u>Elements</u>	<u>FGC Waste Solids (ppm)</u>	<u>FGC Waste Liquor (ppm)</u>	<u>Range in Coal (ppm)</u>
Antimony	---	0.09-1.6	---
Arsenic	0.6-63	<0.004-1.8	3-60
Beryllium	0.05-11	<0.001-0.18	0.08-20
Cadmium	0.08-350	0.004-0.11	---
Chromium	3-250	0.001-0.5	2.5-100
Copper	1-76	0.002-0.6	1-100
Lead	0.2-21	0.001-0.55	3-35
Manganese	11-120	<0.01-90	---
Mercury	0.001-6	<0.001-0.07	0.01-30
Molybdenum	---	0.9-5.3	---
Nickel	6-27	0.005-1.5	---
Selenium	0.2-19	<0.001-2.7	0.5-30
Zinc	10-430	0.01-27	0.9-600

Source: [30, 37]

Table 4.13

Trace Element Content of Samples from Station 1

Element	Coal (ppm)	Bottom Ash (ppm)	Ppt. Ash (ppm)	Lime (ppm)	Waste (ppm)	Scrubber Liquor (mg/l)	Makeup Water (mg/l)
Antimony	.43	<.48	1.0	5.3	4.3	.02	.008
Arsenic	.26	2.3	3.2	3.0	4.0	.011	.017
Barium	300.	2200.	3600.	<30.	500.	<.3	<.5
Beryllium	.44	4.6	5.2	3.0	1.5	.008	.001
Boron	27.9	41.9	179.	6.45	68.7	11.7	2.1
Cadmium	.028	.19	.39	.28	.40	.006	.0004
Chromium	1.5	3.4	5.6	1.2	1.6	.01	<.001
Copper	7.6	29.	43.	5.8	38.9	.53	.35
Fluorine	54.	50.0	377.	105.	1017.	62.7	5.1
Germanium	<1.0	<.1	1.2	<1.0	<1.0	.015	.015
Lead	.90	2.3	6.4	1.3	1.6	.015	.014
Manganese	16.0	181.	157.	29.8	56.	2.2	.07
Mercury	.140	.027	.126	<.010	<.010	<.001	.0015
Molybdenum	<.13	15.	7.0	150.	81.	.56	.08
Nickel	2.3	15.6	34.2	4.3	13.	.330	.062
Selenium	4.2	.36	1.7	.08	4.13	.44	.019
Vanadium	<13.	<24.	<50.	<50.	<50.	.2	.2
Zinc	40.	35.	92.	9.6	13.9	.92	1.0

Note: Values represent the average of duplicate determinations.
Solid samples are reported on a dry basis; water and liquor
samples on an as-sampled basis.

Source: [39]

Table 4.14

Trace Element Content of Samples from Station 4

Element	Coal (ppm)	Bottom Ash (ppm)	Ppt. Ash (ppm)	Lime- stone (ppm)	Waste (ppm)	Ash Pond Liquor (mg/l)	Scrubber Liquor (mg/l)	Makeup Water (mg/l)
Antimony	.08	<1.0	4.4	1.3	7.5	.007	.009	<.002
Arsenic	.87	4.4	61.	.66	12.	.004	.0006	.006
Barium	440.	5600.	15,000	<30.	4400.	<.3	<.3	<.3
Beryllium	.29	.40	5.2	.37	2.0	.002	.002	.001
Boron	37.7	83.2	1040.	10.8	211.	.41	2.10	.25
Cadmium	.11	1.1	4.2	.90	1.1	.001	.002	<.001
Chromium	1.8	15.6	8.9	.57	4.0	.004	.003	.09
Copper	5.2	68.	238.	15.6	104.	.090	.032	.16
Fluorine	78.5	44.6	2880.	103.	950.	.43	3.85	2.72
Germanium	.48	<.1	9.2	<.1	2.4	<.1	<.1	<.1
Lead	.15	1.0	4.0	14.	2.4	.018	.009	.02
Manganese	26.2	56.7	374.	20.3	147.	.10	.21	.19
Mercury	.131	<.010	<.010	<.010	.46	<.001	<.001	.013
Molybdenum	.87	3.2	12.	8.9	8.0	.012	.010	.01
Nickel	3.67	14.5	92.9	<6.0	26.0	.078	.072	.16
Selenium	.98	.14	16.4	.30	3.8	.0030	.042	.0017
Vanadium	<13.	<100.	<100.	<24.	<100.	<.2	<.2	<.2
Zinc	16.2	<8.0	386.	28.0	169.	.12	.02	.40

Note: Values represent the average of duplicate determinations.
Solid samples are reported on a dry basis; water and liquor
samples on an as-sampled basis.

Source: [39]

Table 4.15

Trace Element Content of Samples from Station 5

Element	Coal (ppm)	Bottom Ash (ppm)	Lime- stone (ppm)	Waste (ppm)	Ash Pond Liquor (mg/l)	Scrubber Liquor (mg/l)	Makeup Water (mg/l)
Antimony	.33	3.4	3.2	6.7	.03	.06	.005
Arsenic	4.6	3.9	2.7	6.7	.004	<.0004	.002
Barium	100.	300.	<30.	<20.	<.3	<.3	<.3
Beryllium	.16	4.5	.17	1.8	.001	.004	.001
Boron	96.9	53.8	17.4	41.8	1.03	6.17	.414
Cadmium	7.9	1.6	.65	25.	.04	.009	.0007
Chromium	.45	5.5	<.80	5.2	<.0002	<.0002	<.0002
Copper	41.5	130.	2.4	65.	.01	.01	.006
Fluorine	372.	95.7	117.	266.	10.4	15.9	.66
Germanium	4.5	.25	.11	5.9	.07	.39	.02
Lead	41.	21.	13.	290.	.008	.010	.014
Manganese	142.	491.	290.	340.	1.1	2.0	.15
Mercury	.322	<.010	.020	0.10	.0015	.002	<.001
Molybdenum	.41	1.4	12.	9.6	.10	.27	.02
Nickel	51.7	187.	6.20	75.2	.11	.25	<.01
Selenium	3.2	.51	.22	2.1	.015	.18	.0012
Vanadium	<12.	<24.	<160.	<100.	.2	.2	.2
Zinc	780.	798.	48.	2050.	2.5	4.2	.04

Note: Values represent the average of duplicate determinations.
Solid samples are reported on a dry basis; water and liquor
samples on an as-sampled basis.

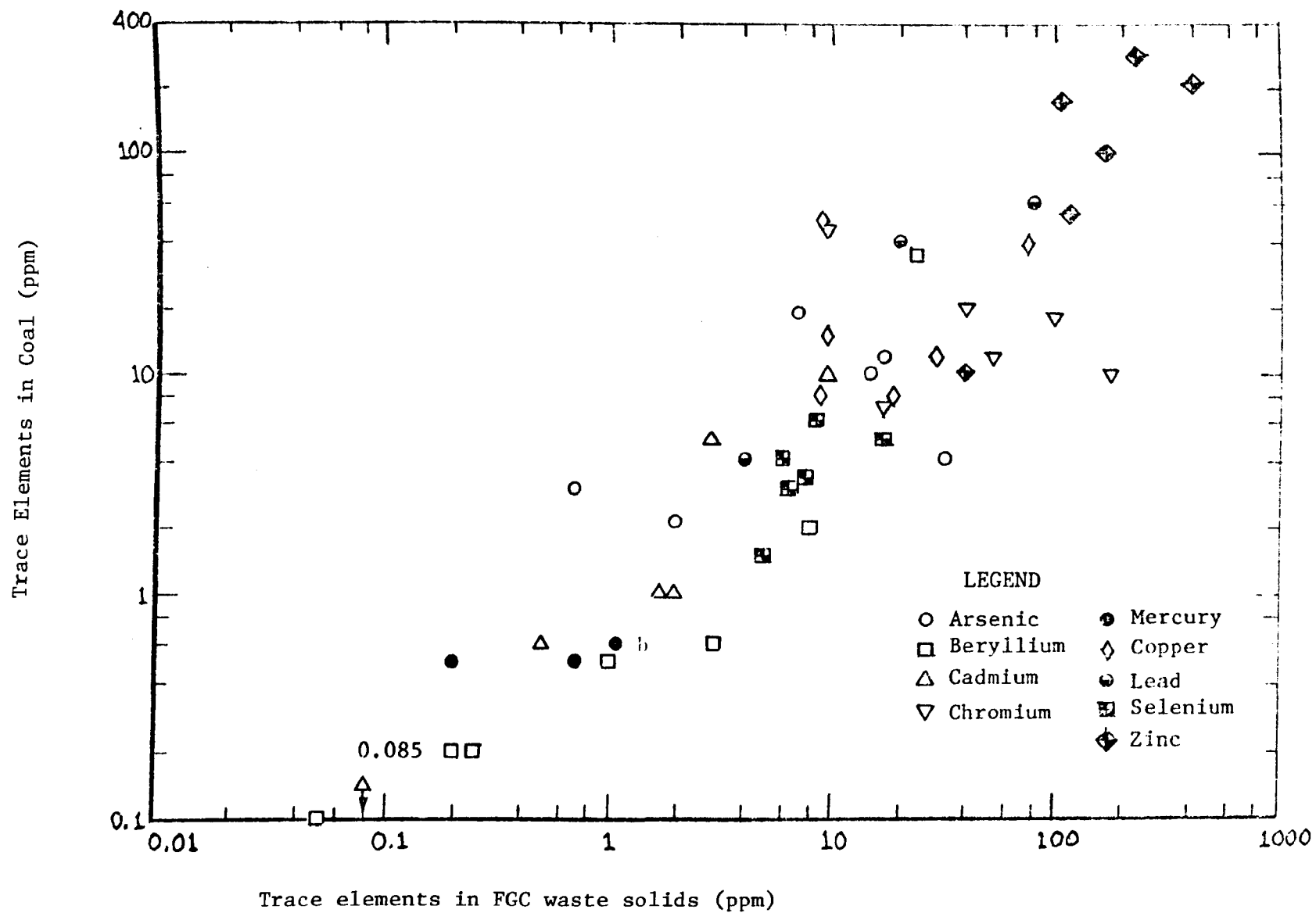
Source: [39]

Furthermore, some elements which are highly volatile may not be efficiently collected in the scrubber system. Mercury and selenium, for example, are likely to be present in the flue gas as elemental vapors that might not be effectively scrubbed or completely condensed on fly ash particles.

The fact that a direct generalized correlation does not seem to exist between trace metal levels in coal and FGC wastes is also confirmed by analyses performed by Aerospace [31]. Aerospace [31] compared total trace element content of FGC waste measured in solids with the trace element content of the parent coal being fired for a large number of waste samples. The samples were taken from wet scrubbing systems with simultaneous SO_2 and ash removal and the ash content of the samples varied over wide range. The relationship between the concentration of trace elements in the coal and the concentration in the waste solids (corrected for contributions from the absorbent) is shown in Figure 4-2 when all the elements are taken into account, inspection of data for individual elements shows varying degrees of correlation. Of the nine elements studied, general relationships are apparent for only four - beryllium (both 7 data points) and cadmium (6 data points) over the range of 0.1 to 10 ppm, lead (3 data points) over the range of 1 to 100 ppm and zinc (6 data points) over the range of 30 to 300 ppm. For arsenic, copper, mercury and selenium, there is no clear correlation; and for chromium, there appears to be an inverse relationship. Figure 4.3 shows plots of concentrations of nine trace elements measured in coals versus concentrations in corresponding FGC liquors. In no case is a clearcut correlation evident. The lack of correlation for most of the elements is not surprising in view of the fact that the amount of fly ash in the samples is variable and that the FGC waste analyzed in many cases is not obtained from a unit which collects all of the fly ash produced. Analytical error and in some cases the limited range of the data may also be contributing factors.

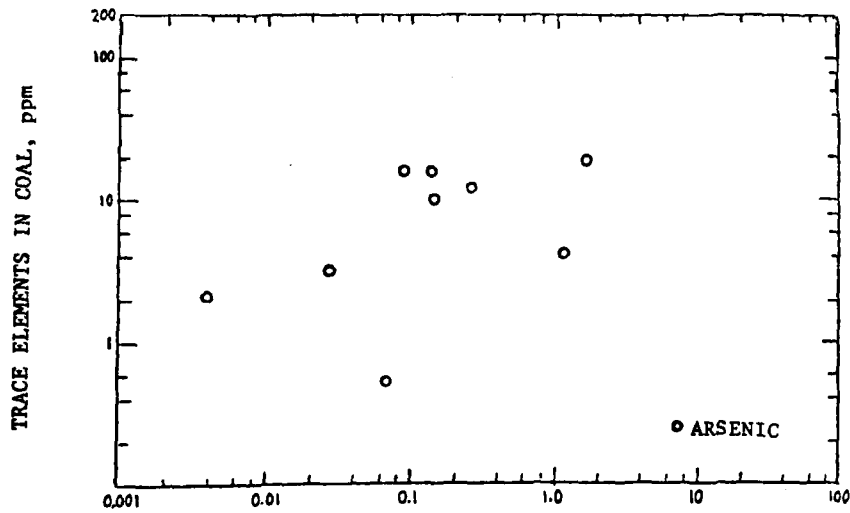
In all of the above cases, trace elements are reported as total values; no speciation data are available for unstabilized or stabilized FGC wastes.

There are no data available on the trace element content of dry sorbent FGD wastes. For dry sorbent processes which include simultaneous fly ash removal, the waste is expected to contain the trace element contribution from the fly ash.

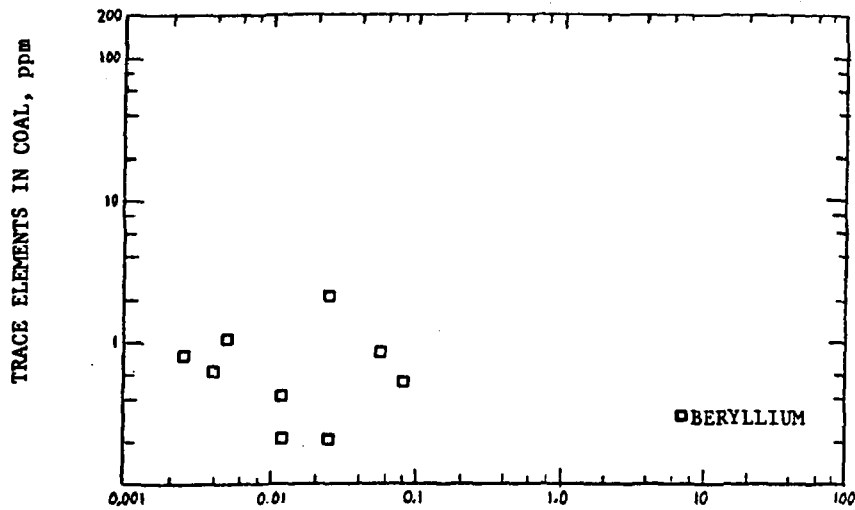


Source: [31]

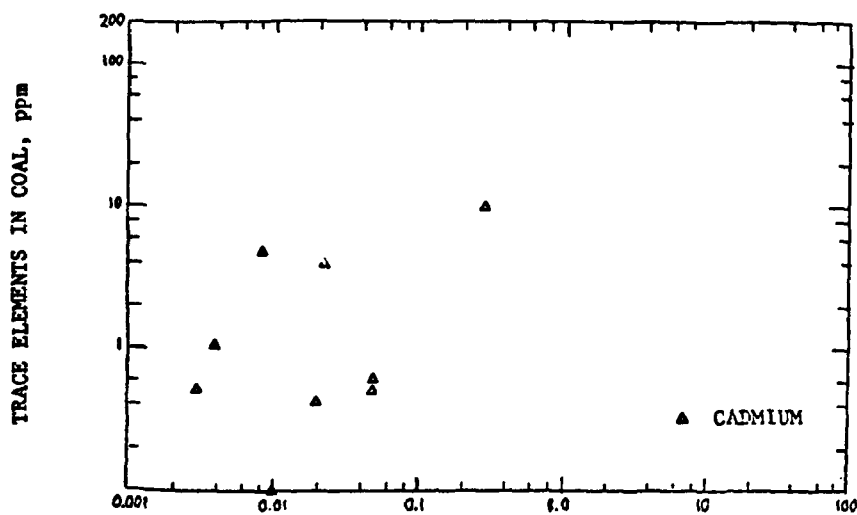
Figure 4.2 Correlation of Trace Element Content in Parent Coal and FGC Wastes



(a)

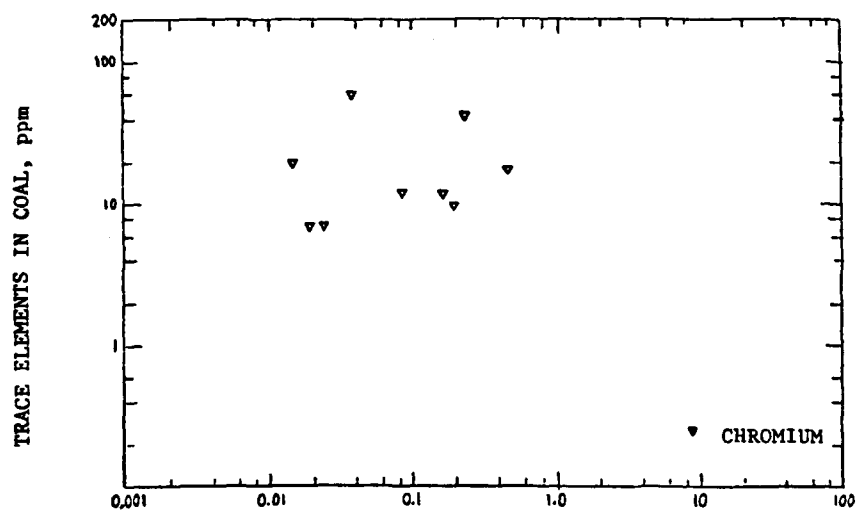


(b)

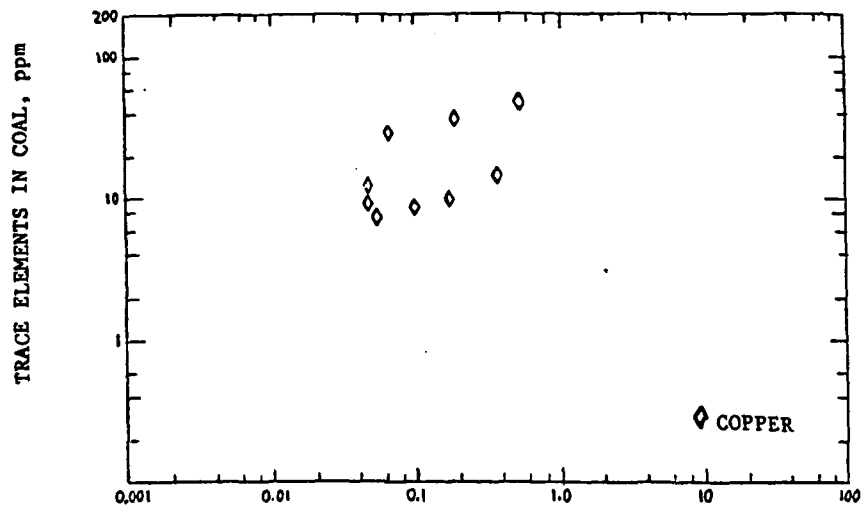


(c)

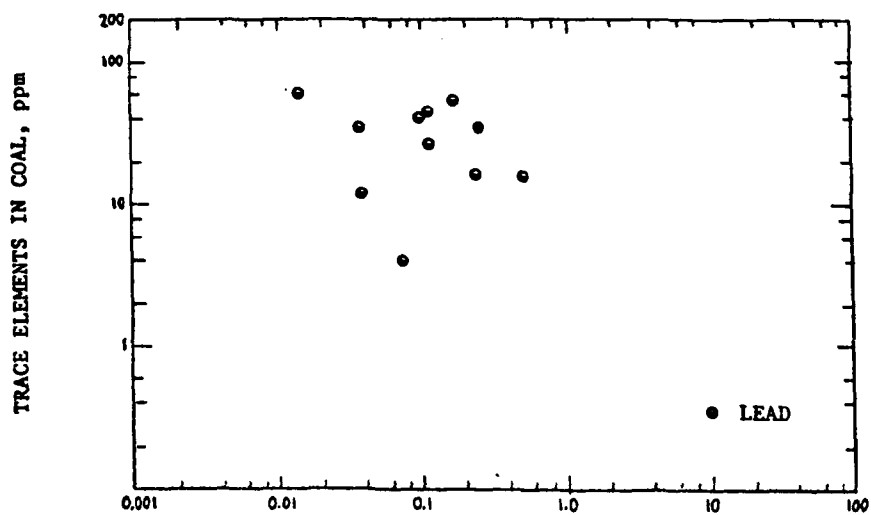
Figure 4.3 Average Trace Element Content of Sludge Liquor (mg/l)



(d)

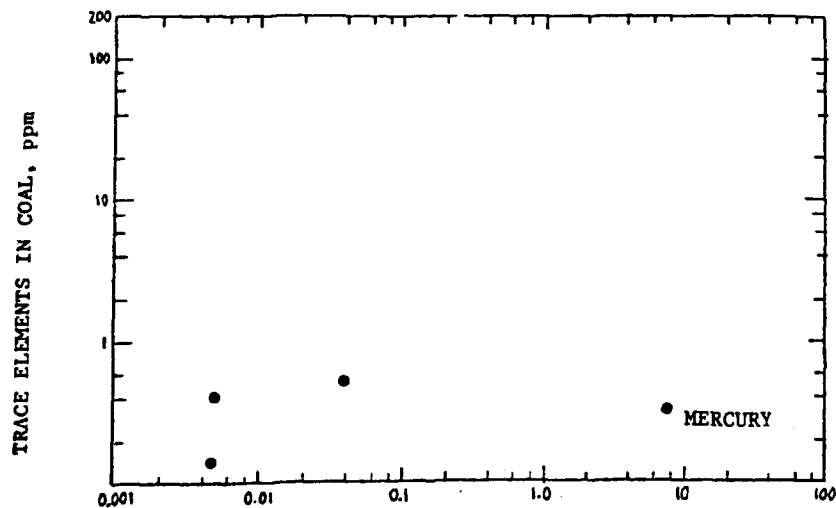


(e)

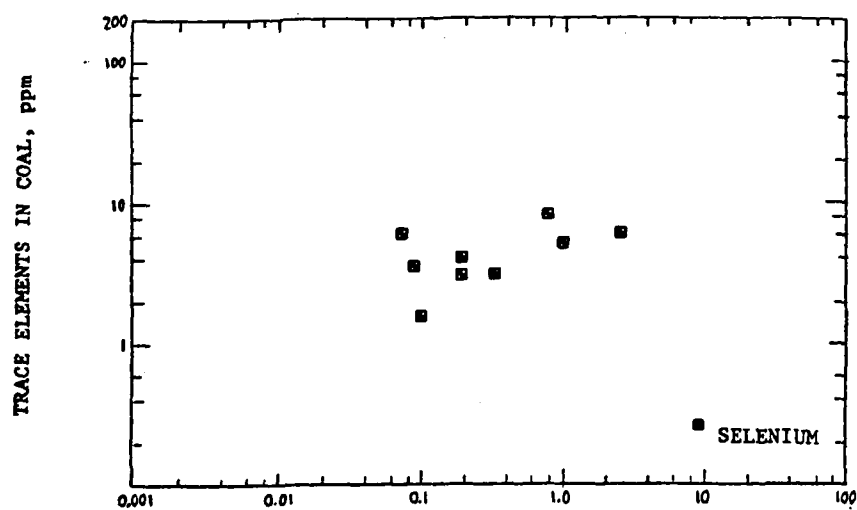


(f)

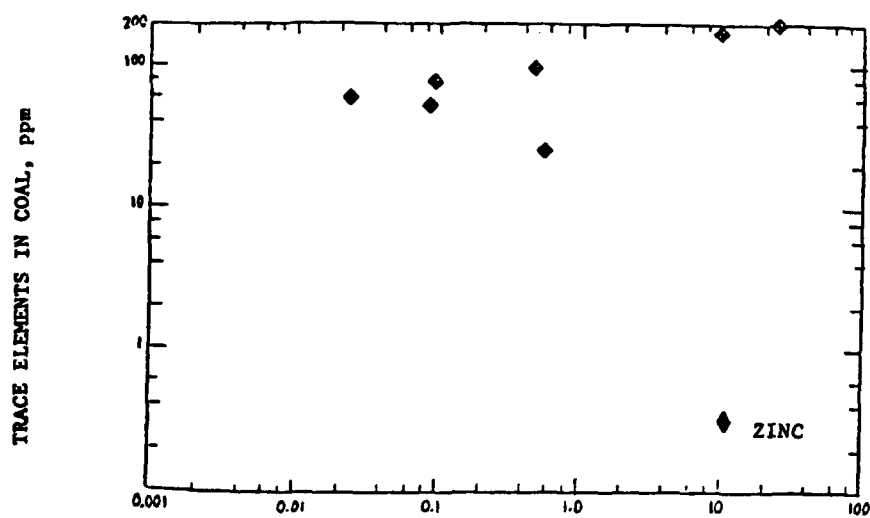
Figure 4.3 (Continued)



(g)



(h)



(i)

Figure 4.3 (Continued)

Source: [31]

In addition to heavy metals, other chemical constituents that can potentially cause concern even in small concentrations include polycyclic aromatics and radionuclides. When coal containing trace radionuclides is combusted, the radionuclides not volatilized remain with the ash as do other non-volatilized trace substances. Because of the reduction in solid mass accompanying combustion, the specific activity of the radionuclides in the ash increases over that observed in the coal. In conjunction with the evaluations of the environmental impact of radioactivity released from nuclear power plants, a number of comparisons of radioactive discharges from fossil-fuel plants to those of nuclear power plants have been made. Radioactive discharges were reviewed in one of the most recent studies by Coles, et al. [32], where samples of coal and ash from two power plants burning low sulfur coal were characterized. One, Plant A, was burning a low ash (9.2%) coal and was equipped with electrostatic precipitators (ESP's). A second plant, Plant B, was firing 23.3% ash coal and had three boilers equipped with Venturi scrubbers and two units equipped with ESP's. Measurements of concentrations of uranium, thorium, and potassium, as well as specific activities for a number of radionuclides in the coal and samples of bottom and fly ash are shown in Table 4.16. Also included in the table are ranges of average values for several important radionuclides, ^{40}K , ^{226}Ra , and ^{238}U taken from Eisembud [33]. An examination of Table 4.16 shows first that in both coals which were being fired, the ^{40}K , ^{226}Ra , and ^{238}U levels were in fact within the normal range for various rocks. Observed increases in specific activity in the ash over the coal are as expected. Further, an examination of the specific activities of the four size fractions of post-ESP fly ash shows an enrichment with decreasing particle size for all of the radionuclides which is typical of the behavior of the trace elements having significant volatility at combustion temperatures; the possible exceptions to such behavior are ^{40}K and ^{228}Th .

The activity of ^{226}Ra measured in fly ash is of particular interest because ^{226}Ra activity is one of the measurements specified in Draft RCRA methods for assessing waste hazard. (^{226}Ra activity is not to

Table 4.16
Contents of Various Radionuclides
in Coal, Bottom Ash, and Fly Ash

(n)	ppm			pCi/g						
	U	Th	K ^a	⁴⁰ K	²³² Th	²²⁸ Ra	²¹⁰ Pb	²²⁶ Ra	²³⁸ U	²³⁵ U
Plant A ^b										
Coal (12)	0.71	1.6	860	0.73	0.17	0.17	0.26 ^c	0.21	0.24 ^c	0.012 ^c
ESP fly ash (9)	5.6	15	9440	8.1	1.7	1.7	1.4 ^c	2.3	1.9	0.093
Bottom ash (7)	4.6	14	7900	6.8	1.5	1.5	0.58 ^c	1.9	1.5	0.072
Plant B ^c										
Coal (3)	2.6	5.0	1660	1.4	0.56	0.55	0.68 ^c	0.64	0.85 ^c	0.037
ESP fly ash (6)	11	22	7400	6.3	2.4	2.4	2.2 ^c	2.9	3.5 ^c	0.14
Bottom ash (10)	8.4	19	7200	6.2	2.2	2.1	0.84 ^c	2.5	2.8 ^c	0.11
Scrubber ash (7)	11	22	7200	6.2	2.5	2.5	2.8 ^c	3.0	3.6	0.14
Plant B ^c										
Post-ESP (stack)										
fly ash (mmd) ^d										
18.5 μ m (2)	16	25	8200	7.0	2.8	2.7	4.3	3.3	5.4	0.17
6.0 μ m (2)	20	31	8600	7.3	3.3	3.5	10	4.6	6.8	0.28
3.7 μ m (2)	30	36	8600	7.4	3.3	4.0	14	5.3	10	0.39
2.4 μ m (2)	38	38	8100	7.0	3.3	4.2	17	5.9	12	0.50

^a Errors 20% with*, 10% without* (1 σ error from the mean or counting statistics, whichever is larger). ^b Samples from Plant A; input coal contains 11.3% H₂O, 9.2% ash, and 0.52% sulfur. ^c Samples from Plant B; input coal contains 6.8% H₂O, 23.2% ash, and 0.46% sulfur. ^d mmd = mass median diameter determined by centrifugal sedimentation.

Range in Rocks	--	--	--	2.2-22	--	--	--	0.4-1.3	0.4-1.3	--
(sedimentary)										

Source: [32, 33]

exceed five pCi/g.) The ^{226}Ra activities measured in the referenced [32] work lie between the average range in sedimentary rocks and the RCRA limits.

Measurements of radioactivity in samples of FGD waste have not been made or are not readily available from published reports. However, by analogy with other trace elements, it would be expected that since the radionuclides are relatively non-volatile and tend to follow fly ash, they would tend to be found in FGD waste in proportion to the amount of ash collected.

One of the measurements that has not been reported is a determination of the level of radionuclide activity in leachates from fly ash and/or FGD wastes. Lead and radium are not particularly soluble so one might expect to find that the mobility of those substances via leaching would be rather low.

Although the organic matrix of coal itself is primarily a polycyclic aromatic structure, and copious quantities of polynuclear aromatic compounds (PNA's) are produced when coal is liquefied or destructively distilled, the amounts of such PNA's on fly ash or in FGD wastes have not been determined. Certain of the PNA's are known or suspected carcinogens. Ray and Parker [34] present results from attempted measurements of PNA's in samples of ash obtained from the Widow's Creek steam plant. In only a very small proportion of the samples analyzed were measurable quantities of PNA compounds detected.

Making measurements of PNA's at sub-part-per-million levels has been possible only recently; and measurements on samples of FGD waste and fly ash are currently underway in a program being carried out by TRW [35] for the EPA.

4.3.2.2 Trace Elements in Waste Liquors

The range of trace elements observed for FGD waste liquors are shown in Table 4.17, and in many cases, the concentrations cover two

Table 4.17

Typical Levels of Chemical Species in FGD Waste Liquors and Elutriates

Species	Eastern Coals			Western Coals		
	Range in Liquor (ppm)	Median (ppm)	Total No. of Observations	Range in Liquor (ppm)	Median (ppm)	Total No. of Observations
Antimony	0.46-1.6	1.2	4	0.09-0.22	0.16	2
Arsenic	<0.004-1.8	0.020	15	<0.004-0.2	0.009	7
Beryllium	<0.0005-0.05	0.014	16	0.0006-0.14	0.013	7
Boron	41	41	1	8.0	8.0	1
Cadmium	0.004-0.1	0.023	11	0.011-0.044	0.032	7
Calcium	470-2,600	700	15	240-(~45,000) ^b	720	6
Chromium	0.001-0.5	0.020	15	0.024-0.4	0.08	7
Cobalt	<0.002-0.1	0.35	3	0.1-0.17	0.14	2
Copper	0.002-0.4	0.015	15	0.002-0.6	0.20	7
Iron	0.02-0.1	0.026	5	0.42-8.1	4.3	2
Lead	0.002-0.55	0.12	15	0.0014-0.37	0.016	7
Manganese	<0.01-9.0	0.17	8	0.007-2.5	0.74	6
Mercury	0.0009-0.07	0.001	10	<0.01-0.07	<0.01	7
Molybdenum	5.3	5.3	1	0.91	0.91	1
Nickel	0.03-0.91	0.13	11	0.005-1.5	0.09	6
Selenium	<0.005-2.7	0.11	14	<0.001-2.2	0.14	7
Sodium	36-20,000 ^a	118	6	1,650-(~9,000) ^a	--	2
Zinc	0.01-27	0.046	15	0.028-0.88	0.18	7
Chloride	470-5,000	2,300	9	1,700-43,000 ^b	--	2
Fluoride	1.4-70	3.2	9	0.7-3.0	1.5	3
Sulfate	720-30,000 ^a	2,100	13	2,100-18,500 ^a	3,700	7
TDS	2,500-70,000 ^a	7,000	--	5,000-95,000 ^b	12,000	3
pH	7.1-12.8	--		2.8-10.2	--	

^a Levels of soluble sodium salts in dual alkali sludge (filter cake) depend strongly on the degree of cake wash. The highest levels shown reflect single measurements on an unwashed dual alkali filter cake. (See text.)

^b Levels of soluble chloride components in sludges are dependent upon the chloride-to-sulfur ration in the coal. The highest levels shown are single measurements for a western limestone scrubbing system operating in a closed-loop using cooling tower blowdown for process makeup water.

Source: [31,37]

orders of magnitude or more. One may expect that dilution associated with elutriate tests could have reduced concentration of trace elements by a factor or as much as five to ten. However, significantly different concentrations of these elements in elutriates and direct liquors were not observed. This may be due, at least in part, to the relatively large reservoirs of trace elements for dissolution from the solids (as discussed below).

It should be emphasized that only a small fraction of the total amount of trace elements present in FGC wastes is found dissolved in the waste liquor; the major portion of trace elements is found in the solid phase.

The trace element levels in waste liquors measured by Radian, shown earlier in Tables 4.13 through 4.15, generally agree with the ranges shown in Table 4.16. The WES/Aerospace and Radian data also agree on the partitioning of trace elements between the waste liquor and solids. It is apparent from a comparison of the levels reported for waste liquors versus total wastes, as given in Tables 4.17 and 4.12, respectively, and in Tables 4.10 through 4.12, that only a small fraction of the total amount of almost every trace metal is found dissolved in the sludge liquor. In fact, taking into account the relative quantities of liquor and solids in the waste, in almost all cases well over 90% of the trace elements appear in the solid phase. This is probably due to the very low solubilities of the trace metal hydroxides, oxides, and carbonates.

If trace element levels in solution are limited by solubility, as would be expected by the trace element partitioning, then no direct generalized correlation would be expected between trace metal levels in the parent coal and in the waste liquors. The lack of evidence for such a relationship existing is evident from the Radian data and is also confirmed in analyses performed by Aerospace [31] which were discussed earlier.

However, the data do not show any upper bound on the soluble concentration corresponding to an obvious solubility limitation (as might be expected based upon the levels of trace elements in the solid phase). There could be any number of explanations for this including: data scatter, displacement of the solution chemistry from actual equilibrium, and changes in solution chemistry made possible by the presence of complexing ions. Unfortunately, there are no data at present on trace element speciation that could shed some light on the system chemistry. Work has been initiated in this regard by SCS [14].

4.3.3 Trace Elements in Stabilized FGC Wastes

There are some data on concentration ranges of trace elements in leachates from treated sludges which will be discussed later. However, no data are available on trace elements in treated wastes.

4.4 Leaching Behavior

The potential for groundwater and surface water contamination from the disposal of FGC wastes varies with the waste characteristics, the method of disposal, and the site conditions. Potentially, there are two routes by which such contamination can occur:

- Direct release of occluded waste liquors, and
- Leaching of FGC waste constituents.

Leaching can be envisioned as involving two different mechanisms:

- Surface leaching in which diffusion and waste dissolution are usually limiting, and
- Flow through waste pores, in which case the mass permeability strata can be limiting.

In leachate formation via water flow through the wastes, it would normally be expected that the water will first flush the interstitial waste liquors from the deposit; and leachate concentrations would be roughly equivalent to the composition of the occluded liquor. In successive pore volume displacements, leachate concentration would then

approach the equilibrium (or steady state) concentrations due to dissolution of the solids. The rate of leachate production would be defined by the limiting mass permeability coefficient (the waste or the surrounding strata) and the hydraulic potential (i.e., head of water) present.

The dissolved species in FGC wastes are frequently more readily available for impacting the environment than are substances associated with the solid phase which are not highly soluble. The dissolved species can be released directly, with the waste liquor, via runoff and/or drainage accompanying natural settlement, or by forced displacement of liquor via compaction; and indirectly through flushing or mixing of the liquor with permeating water. This potential for greater immediate impact and, perhaps, the fact that undisturbed waste liquors samples are more easily obtained than pure solid phase samples have resulted in considerably more detailed analysis of the composition of waste liquors than that of the solids.

Numerous studies have been undertaken to evaluate the potential for contamination due to leaching from FGC wastes and to characterize the leaching behavior of different types of wastes. Most of these have been laboratory studies involving various leaching column tests at accelerated flow rates and/or elutriate (shake) tests. These tests attempt to either simulate actual or "worst case" field leaching conditions or to obtain the potential maximum leachate concentrations. A few programs have included pilot-scale field testing in an attempt to corroborate laboratory results. However, to date, there has been no large-scale field monitoring of full-scale, commercial operations, although a few demonstration projects are now in planning or early stages of monitoring (as will be discussed later).

Table 4.18 summarizes the major programs funded by the government and the utility industry which have been undertaken to characterize the general leaching behavior of FGC wastes. Only those studies and programs which have been completed, are currently underway, or have been funded, but not yet started have been included. All of the demonstration

Table 4.18

**Principal Programs Funded by the Government and Utility Industry
to Evaluate Leaching Behavior of FGC Wastes**

<u>Sponsor</u>	<u>Contractor</u>	<u>Waste Type</u>	<u>Program Focus</u>	<u>Status</u>	<u>References</u>
EPA/IERL	Aerospace	Unstabilized & Stabilized	Laboratory	Underway	31,37
	ADL	Unstabilized & Stabilized	Laboratory	Completed	30
	Aerospace/TVA	Unstabilized & Stabilized	Laboratory/Pilot (Impoundment)	Underway	40
	LGE/CE	Unstabilized & Stabilized	Laboratory/Pilot (Impoundment)	Underway	
	ADL/UND	Unstabilized	Demonstration (Mine)	Underway	21
	ADL/NEA	Unstabilized & Stabilized	Laboratory/Pilot (Ocean)	Underway	30,48
	LGE/Bachtel	?	Demonstration (Impoundment)	Planned	---
EPA/NERL	WES	Unstabilized & Stabilized	Laboratory	Underway	16
	ACE (Dugway)	Unstabilized	Laboratory (Land Disposal)	Underway	47
EPRI	Radian	Unstabilized	Laboratory	Completed	39
	Southern Services (Scholz)	Unstabilized	Pilot (Impoundment)	Completed	49
	Radian	Stabilized	Laboratory	Underway	---
DOE/ERDA	GFERC	Unstabilized	Laboratory	Underway	---
NYERDA	SUNY/IVCS	Stabilized	Laboratory/Pilot (Ocean)	Underway	15

Source: Arthur D. Little, Inc.

projects and the pilot work performed by Louisville Gas & Electric and Combustion Engineering at Paddy's Run involve waste from a single system. All others involve wastes generated by two or more different systems. Furthermore, the demonstration programs will include laboratory and possibly some small-scale field testing to "calibrate" the full-scale monitoring data and evaluate different waste conditions.

In addition to data obtained in these programs a considerable amount of data has been developed in testing performed or funded independently by specific utilities, FGD equipment suppliers, companies offering commercial treatment systems, and universities.

Unfortunately, at present no standard laboratory leaching test has been developed. Testing procedures have varied widely in the methodology. Variations have included:

- Sample preparation (dried vs. as received material),
- Degree and method of drying,
- Extent of sample grinding, etc.,
- Characteristics of the leach solution used (distilled and/or deionized water, simulated groundwater, buffered solutions, etc.), and
- The manner of contact of leach water and the sample (simple column leaching, single elutriate, multiple elutriate, etc.).

To compound the problem, few organizations have tested the same waste sample. In a few cases, though, different methods have been used with the same samples in an attempt to determine the effects of test methods on results. A review of the many leaching tests that have been used by various organizations on many different wastes has been published recently [113].

This situation has resulted in considerable disagreement and controversy over the proper method(s) for performing leaching tests. At present, both the EPA (via RCRA) and ASTM are attempting to establish standardized procedures. However, some argue that the leaching test most applicable will have to take into account both the waste characteristics and the disposal scenario. For example, IUCS has developed

in-house leach tests and advocates the use of a shake test and/or a combination runoff/leaching test, particularly where treated materials are concerned.

4.4.1 Leachates

4.4.1.1 Coal Ash

The chemical composition of ash pond effluents varies over a wide range, depending on the chemical composition of the ash, the variations in flow and quality of the raw water supply used for sluicing the ash and the other waste streams discharged into the pond. The concentrations of the various constituents in the case where only fly ash is disposed depend only on the fly ash composition, the flow rate and the quality of the initial water used for sluicing.

A recent survey of ash pond effluents of over 800 plants has been performed by Hittman Associates. The data have not been published [118].

The characteristics of coal ash leachate vary greatly since some ashes, upon contact with water, yield acidic solutions while others yield neutral or greatly basic solutions. Basic leachates occur when the metal oxides (primarily Ca, Mg, K, and Na) come in contact with water. On the other hand, when the metal oxide content of the ash is very low, an acidic leachate will occur due to hydrolysis of the transition metal ions (such as Fe^{3+} , Al^{3+}) and oxidation of sulfides. The extent of trace element dissolution from the ash will vary greatly, depending on the leaching media pH. Generally, the greater the acidity of the liquor, the greater the solubility and rate of solubilization of most of the trace elements.

The TVA [61] has been monitoring discharges from ash ponds since 1973 for 17 trace elements and 14 other parameters. A typical profile of a once-through discharge of a fly ash pond is given in Table 4.19. The values represent not only the materials leached out from the ash but also include background concentrations of the raw water supply.

Laboratory experiments have been performed on leaching of fly ash. Radian [62] conducted leaching experiments using deionized water for

Table 4.19
Characteristics of Once-Through Fly Ash Pond Discharges

<u>Parameters</u>	<u>TVA Plant A</u>	
	<u>1973</u>	<u>1974</u>
Flow (lit./min.)	23.8	23.2
pH*	4.5	4.3
Total Hardness (mg/l as CaCO ₃)*	241	280
Conductivity (μmhos/cm)*	807	814
Total Dissolved Solids (mg/l)*	508	508
Suspended Solids (mg/l)*	67	38
Phosphorus (mg/l)	0.07	0.02
Ammonia (mg/l as N)	0.16	0.70
Sulfate (mg/l)	383	333
Chloride (mg/l)	8	6
Cyanide (mg/l)	<0.01	<0.01
Silica (mg/l)	13.8	11
Calcium (mg/l)	170	102
Magnesium (mg/l)	13.4	14.6
Aluminum (mg/l)	6.6	7.8
Arsenic (mg/l)	0.01	<0.006
Barium (mg/l)	0.2	0.3
Beryllium (mg/l)	<0.01	0.01
Cadmium (mg/l)	0.037	0.037
Chromium (mg/l)	0.03	0.11
Copper (mg/l)	0.30	0.30
Iron (mg/l)	0.74	2.13
Lead (mg/l)	0.04	0.08
Manganese (mg/l)	13.38	0.46
Mercury (mg/l)	<0.0002	<0.0002
Nickel (mg/l)	0.12	0.09
Selenium	<0.002	<0.002
Silver (mg/l)	<0.01	<0.01
Zinc (mg/l)	1.4	1.63

* Note: All numbers are averages of quarterly grab samples collected during the indicated year, except those parameters shown with an asterisk are averages of weekly grab samples. The reported values include background concentrations in the raw water supply.

Source: [61]

24 hours in 28% slurry samples. The ash samples were various mixtures of bottom ash and fly ash from five stations. The natural pH of all the samples was greater than 7. The concentrations of the trace elements observed are given in Table 4.20. It is difficult to draw conclusions from these data due to the variability in pH of the final slurry. The effect of pH on the leachability of the trace elements was also investigated for the ash obtained from Station 1. The pH was varied between 8.5 and 11.0 by introducing CO₂ into the slurry. The concentrations of As, F, Se, Cr and Cu in the leachate were unaffected by variation in this pH range. Passage of the ash leachates through cation and anion exchange resins indicated that most of the Cr is present in a cation form and most of the Se is present in an anion form.

Laboratory experiments on cation solubilities from lignite fly ash [63] have been made to determine effects of water-to-ash ratio and leaching percentage with subsequent washings. These results have shown that between 78% and 91% of the soluble sodium is leached in the first wash, and variations in the water to ash ratio have little effect on the total leached. A pH effect (over the range 11.8-9.7) on the solubility of Mg and Fe from the ash was suggested. Laboratory experiments on boron leaching from southern Illinois fly ash and bottom ash [64] indicate that up to 50% of the boron in fly ash leaches in the pH region of 6-8. Leaching was pH independent and occurred within two hours. Results of ESDA indicated that the boron was present in two chemical states. Little leaching of boron from bottom ash occurred (<0.1%) where the boron was present in only one chemical state. Heat treatment (1200°C) rapidly converted the boron in fly ash to the less leachable form found in bottom ash.

4.4.1.2 Unstabilized FGC Wastes

One of the earliest programs undertaken to characterize the leaching behavior of different FGC wastes was initiated by the EPA in 1975. This study, performed by the Aerospace Corporation, is now nearly completed. At the outset, work focused on untreated FGC wastes. Accelerated leaching column tests were performed on samples of untreated FGC

Table 4.20

Equilibrium Concentrations of Trace Elements
in Coal Ash Leachate

	<u>Station Number</u>				
	1	2	3	4	5
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
<u>Element (ppm)</u>					
Antimony	.006	.018	.033	.022	.0087
Arsenic	<.002	.084	.015	.072	.006
Barium	40	<.3	<.3	<.3	<.3
Beryllium	.003	.00064	.0007	.001	.00026
Boron	.03	16.9	.21	1.1	.048
Cadmium	<.001	.0025	<.01	<.001	.0011
Chromium	<.001	.21	.11	1.0	.014
Fluorine	2.3	1.4	2.0	17.3	1.4
Germanium	<.01	<.01	<.01	<.01	<.01
Mercury	.0006	.0005	.015	.0003	.0003
Lead	.0068	.0027	.024	.0043	.0063
Manganese	<.002	<.002	<.002	<.002	<.002
Molybdenum	.047	.052	.05	.69	.010
Nickel	<.05	.015	.025	<.05	.046
Selenium	.009	<.0005	.033	.47	<.0005
Vanadium	<.1	<.1	<.1	<.2	<.1
Zinc	.038	.025	.19	<.005	.0175
Copper	<.005	.031	.092	.013	.015
OH	800				
CO ₃	70				
Cl	10				
SO ₄	10				
Ca	900				
Na	72				
K	4				
Mg	1				
Fe	1				
NO ₃	2				

Source: [62]

wastes obtained from five pilot and full-scale systems [37]. Columns containing each waste were leached with acidified, neutral, and basic solutions saturated with oxygen. A single column containing a portion of each sample was leached with deaerated, neutral solution to simulate anaerobic conditions. Leaching was continued until 40-50 pore volume displacements (PVD's) were collected. In Table 4.21 concentrations of substances measured in a sample of the leachate collected at the end of the leaching experiment (40 or 50 PVD's) during aerated leaching tests on four materials, are compared to the corresponding concentrations in the liquor occluded within the waste solids when they were discharged from the FGD process. No significant differences which could be attributed to the pH of the leach solutions were observed, and the values of final leachate concentration represent the median of the three values obtained. The results in Table 4.21 show that concentrations of sulfate and chloride as well as TDS, measured in the leachate after 50 PVD's of leached liquor had passed through the waste, had reached similar levels even though the initial concentrations in sludge liquors were significantly different. In all cases, TDS had fallen to about 1,500-2,500 mg/l and sulfate had fallen to about 1,200 mg/l. These levels probably reflect the equilibrium solubility of the calcium sulfate component of the waste. The other chemical species showed the same tendency to level off to similar concentrations after 50 pore volumes of leaching had taken place.

Recent work reported by Aerospace [31] on additional samples of unstabilized FGC wastes from three different prototype/test systems is summarized in Tables 4.22 through 4.25 and corresponding Figures 4.4 through 4.6. Table 4.22 and Figure 4.4 show comparative laboratory leaching data on waste produced from direct lime scrubbing at the Shawnee test facility, both with and without simultaneous fly ash removal. Table 4.23 and Figure 4.5 show similar data for waste from a different direct lime scrubbing system, the Louisville Gas & Electric plant at Paddy's Run which operates with high efficiency ESP's. Finally, Table 4.24 and Figure 4.6 provide laboratory data on dual alkali waste filter cake from

Table 4.21

Comparison of the Chemical Constituents in Sludge Liquors
With Leachate After 50 Pore Volume Displacements
(Concentrations in mg/liter)

	Eastern Limestone Shawnee (Clarifier Underflow) ^a		Western Limestone Cholla (FDS Tank Discharge) ^a		Eastern Dual Alkali Parma (Unwashed Filter Cake) ^a		Western Limestone Mojave (Centrifuge Cake) ^a	
	<u>Liquor</u>	<u>Leachate</u>	<u>Liquor</u>	<u>Leachate</u>	<u>Liquor</u>	<u>Leachate</u>	<u>Liquor</u>	<u>Leachate</u>
As	0.14	0.01	< 0.004	< 0.004	< 0.004	< 0.002	0.03	< 0.004
Be	0.054	0.004	0.18	0.004	< 0.005	< 0.004	0.02	0.004
Cd	0.003	< 0.001	0.0009	< 0.001	< 0.02	< 0.001	0.05	< 0.001
Cr	0.09	0.003	0.21	0.002	< 0.02	< 0.001	0.25	0.003
Cu	0.01	0.010	0.20	0.01	0.06	< 0.01	0.6	0.010
Pb	0.25	0.01	0.01	< 0.001	0.52	< 0.01	0.04	< 0.001
Hg	< 0.05	< 0.00005	0.13	< 0.00005	0.0005	< 0.00005	< 0.005	< 0.00005
Se	--	0.006	2.5	0.05	0.075	0.010	0.12	0.004
Zn	--	0.045	0.07	0.04	0.59	0.04	0.18	0.045
Cl	2,250	120	1,430	110	5,200	95	28,000	130
F	6.2	< 0.2	0.7	6.1	58	0.2	30	< 0.2
SO ₃	80	25	0.9	9.0	140	30	1.5	0.3
SO ₄	10,000	1,200	4,400	1,150	35,000	1,100	25,000	1,300
pH	8.3	5.0	4.3	5.9	12.7	6.1	6.7	4.5
TDS	15,000	2,400	9,100	1,900	65,000	1,650	92,500	2,100

^aLiquor analysis for liquor occluded with sludge solids as disposed.

^bAfter 40 pore volume displacements.

Source: [31, 37]

Table 4.22

Chemical Analysis - Shawnee Lime Waste Liquor and Leachates

Constituent ^a	Without Fly Ash			With 40% Fly Ash	
	Filtrate	Leachate		Leachate	
		First Pore Volume	Fifth Pore Volume	First Pore Volume	Seventh Pore Volume
pH	8.0	8.3	7.1	7.9	7.4
TDS	10260	4480	1770	4330	2430
Arsenic	0.058	----	0.120	----	0.360
Beryllium	<0.001	----	<0.001	----	<0.001
Boron	76	35	3	65	16
Cadmium	0.013	----	0.013	---	0.010
Calcium	650	690	450	600	640
Chromium	0.011	0.025	0.010	0.010	0.004
Copper	0.005	0.011	<0.002	<0.002	<0.002
Lead	0.010	<0.002	<0.002	<0.005	<0.005
Magnesium	1730	400	30	310	10
Mercury	<0.00006	----	<0.00006	----	0.00024
Potassium	24	14	2	7	4
Selenium	0.078	----	<0.0004	----	0.051
Sodium	137	75	47	72	42
Zinc	<0.001	0.007	0.01	0.003	0.02
Chloride	1320	550	128	400	130
Fluoride	1.9	2.6	2.5	6	1.2
Sulfate	4500	2150	1100	2700	1450

^aSampling date - 9/8/76; concentrations in mg/l as appropriate.

Table 4.23

Chemical Analysis Paddy's Run - Carbide Lime
FGC Waste Liquor and Leachates
12% Ash

<u>Constituent</u>	<u>Filtrate</u>	<u>Leachate ^a</u>	
		<u>First Pore Volume</u>	<u>Tenth Pore Volume</u>
pH	8.9	7.4	8.1
TDS	24230	5240	1650
Arsenic	0.011	---	0.023
Beryllium	< 0.001	---	< 0.001
Boron	18	2	< 0.5
Cadmium	0.025	---	0.004
Calcium	515	410	260
Chromium	0.054	< 0.0008	< 0.0008
Copper	0.0045	0.004	< 0.002
Lead	< 0.005	< 0.002	< 0.002
Magnesium	3400	470	70
Mercury	0.00006	---	0.00006
Potassium	760	125	21
Selenium	0.0028	---	0.006
Sodium	260	40	3
Zinc	0.003	0.015	0.005
Chloride	5600	410	157
Fluoride	< 1	< 0.1	< 0.1
Sulfate	15000	2800	920

^a Concentrations in mg/l as appropriate.

Source: [31]

Table 2.24

Chemical Analysis - Plant Scholz Dual Alkali FGD Waste Liquor and Leachates

Constituent	6/20/76 Run with No Fly Ash			6/27/76 Run with 30% Fly Ash		
	Leachate ^a			Leachate ^a		
	Filtrate ^b	First Pore Volume	Sixth Pore Volume	Filtrate ^b	First Pore Volume	Ninth Pore Volume
pH	12.1	12.5	12.3	12.0	10.4	9.1
TDS	155700	9140	3550	162700	17330	2140
Arsenic	---	---	<0.004	---	---	0.019
Beryllium	---	---	<0.001	---	---	<0.001
Boron	43	5	<0.5	40	<0.5	<0.5
Cadmium	---	---	0.016	---	---	0.010
Calcium	12	1000	1100	7	550	800
Chromium	---	---	0.0025	---	---	0.024
Copper	---	---	<0.002	---	---	<0.002
Lead	---	---	0.005	---	---	<0.002
Magnesium	0.1	<0.01	<0.01	0.1	0.2	0.3
Mercury	---	---	0.00030	---	---	0.00024
Potassium	320	43	1	380	74	11
Selenium	---	---	<0.0004	---	---	<0.0004
Sodium	53600	2260	12	55300	4720	82
Zinc	---	---	0.007	---	---	0.013
Chloride	5000	1070	310	4900	1050	134
Fluoride	24	48	13	4	3	0.9
Sulfate	80000	3700	1160	84000	10100	1415

^aConcentrations in mg/l as appropriate^bIncomplete analyses for filtrate samples is a consequence of insufficient sample quantity.

Source: [31]

Table 2.25

Mass Balance, Charge Balance, and Gypsum Solubility
Ratio of Waste Liquors and Leachates

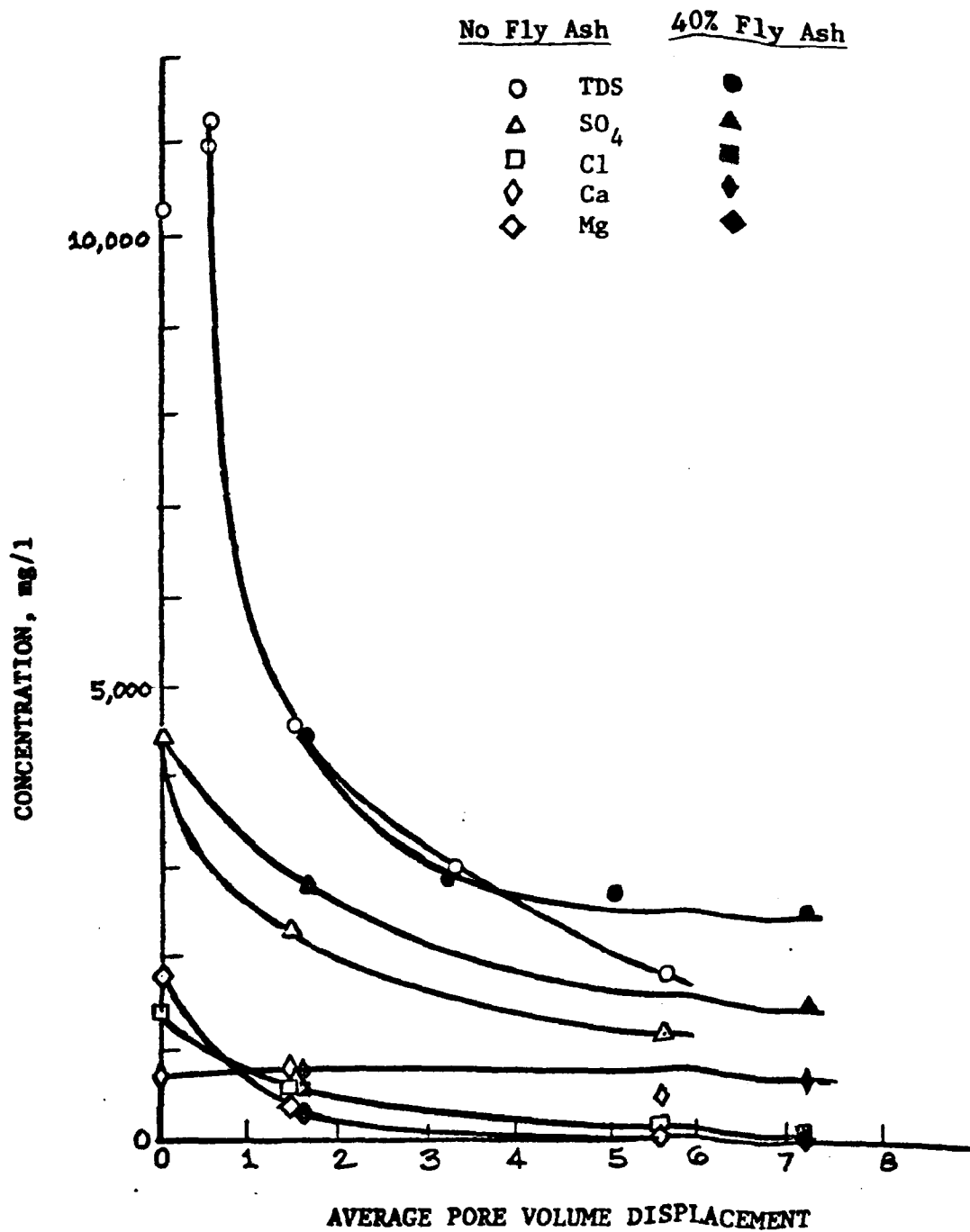
Sample	Mass Ratio ^a	Charge Ratio ^b	Ionic Strength	Solubility Ratio ^c
<u>TVA/Shawnee Waste</u>				
Run E Filtrate	1.01	1.29	0.14	0.97
Run F Filtrate	0.88	1.38	0.27	0.85
Run F Leachate (No Fly Ash):				
First Pore Volume	0.93	1.18	0.12	1.07
Sixth Pore Volume	1.03	1.02	0.05	0.82
Run F Leachate (40% Fly Ash):				
First Pore Volume	1.01	0.87	0.12	1.20
Seventh Pore Volume	0.97	1.03	0.07	1.23
<u>Gulf/Scholz Waste</u>				
Filtrate (No Fly Ash)	0.91	1.29	2.91	1.19
Leachate (No Fly Ash):				
First Pore Volume	1.01	1.08	0.21	1.46
Sixth Pore Volume	0.86	1.08	0.09	1.22
Filtrate (30% Fly Ash)	0.90	1.27	3.03	0.91
Leachate (30% Fly Ash):				
First Pore Volume	0.98	0.98	0.36	1.17
Ninth Pore Volume	1.17	1.32	0.07	1.36
<u>L.G. & E. /Paddy's Run Waste</u>				
Filtrate	1.19	0.71	0.71	0.86
Leachate:				
First Pore Volume	0.85	0.92	0.13	0.80
Tenth Pore Volume	0.91	0.82	0.04	0.48
Average Mass Ratio	0.97(±0.10)			
Average Charge Ratio		1.08(±0.20)		
Average Solubility Ratio				1.04(±0.26)

^a Mass Ratio = Σ All Ion Concentrations/TDS (corrected for water in $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ not lost in drying).

^b Charge Ratio = Σ Equivalent Concentrations of Cations/ Σ Equivalent Concentrations of Anions.

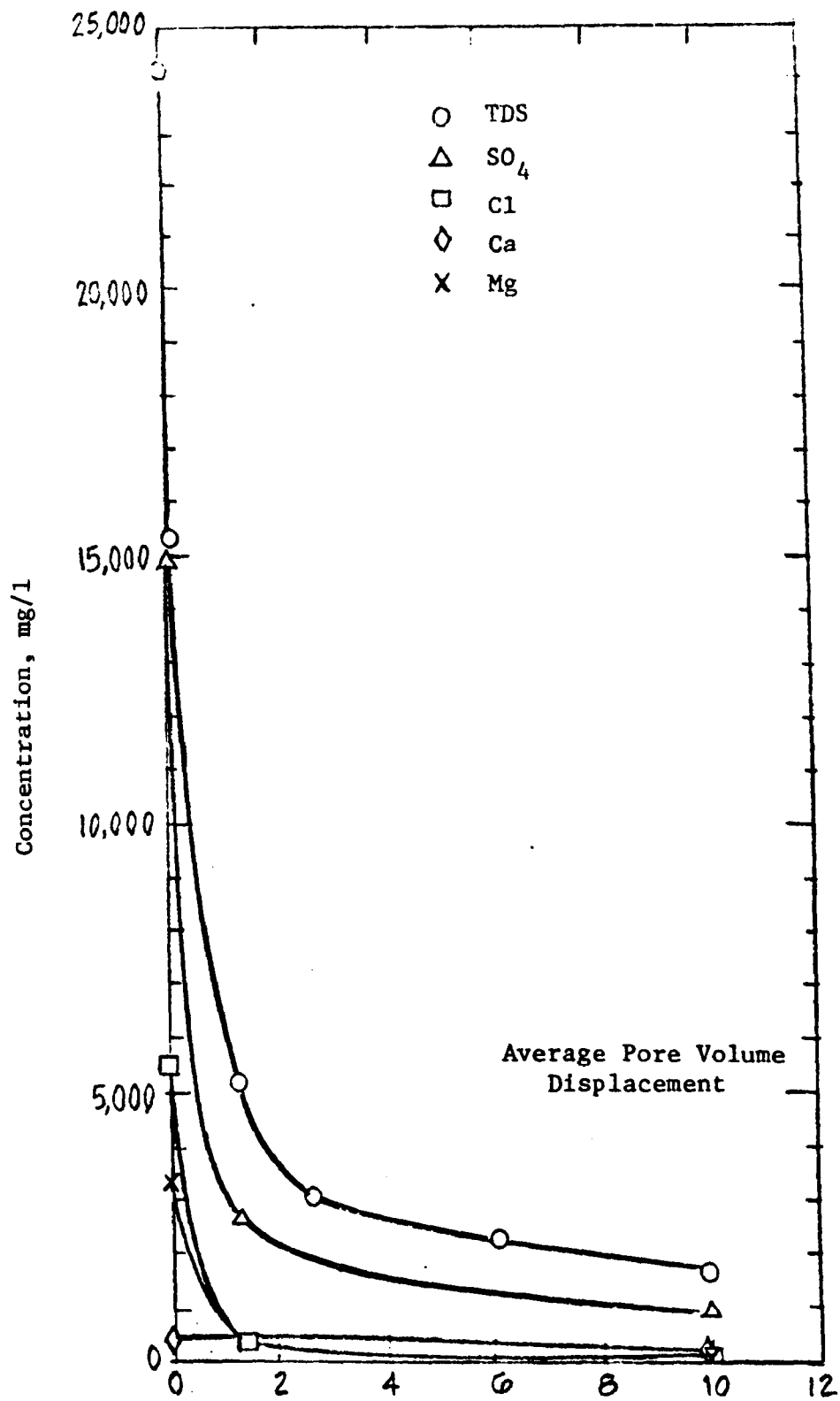
^c Solubility Ratio - Measured Calcium Concentration x Measured Sulfate Concentration/ K_{sp} (Solubility Product Constraint Corrected for Ionic Strength).

Source: [31]



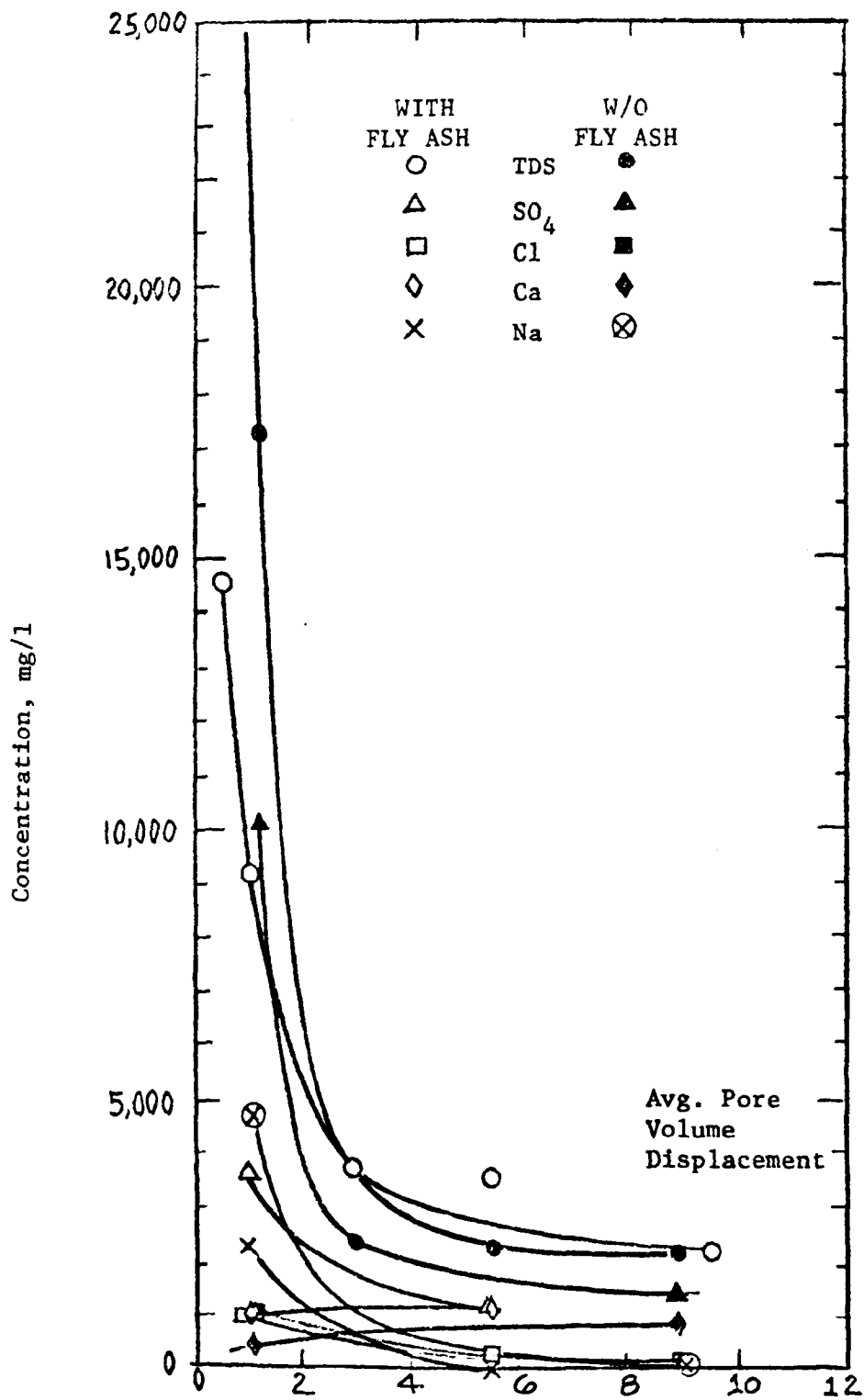
Source: [31]

Figure 4.4 Concentration of Major Species and TDS in Leachate Lime FGD Waste with and without Fly Ash from Shawnee, Run F



Source: [31]

Figure 4.5 Concentrations of Major Species and TDS in Filtrate and Leachate FGD Waste from LG&E Paddy's Run



Source: [31]

Figure 4.6 Concentration of Major Species and TDS in Leachate of FGD Dual Alkali Waste and Mixed Waste and Fly Ash from GPC Scholz Station

the Southern Co. Services prototype system at the Scholz Steam Plant. Again, data are shown for wastes generated from SO₂ removal only and from combined fly ash and SO₂ removal.

In general, the results for TDS and sulfate levels for these samples roughly agree with those of earlier tests. Except for the dual alkali material without fly ash, TDS levels fell to the range of 1,650-2,430 mg/l. (The dual alkali materials with their higher initial TDS level may require a few more displacements to achieve the same steady-state TDS levels.) Sulfate concentration levelled off in the range of 920-1,420 mg/l. However, it is interesting to note that in the case of the Paddy's Run waste (a material consisting almost entirely of calcium sulfite) the TDS and sulfate concentrations did not level off at the saturation concentrations corresponding to gypsum--they were much lower. This subsaturation with respect to gypsum is shown in Table 4.25 in which the charge and mass balances and gypsum solubility ratios for these liquors and leachates are tabulated.

Presumably, the gypsum subsaturation is due to the almost complete absence of calcium sulfate in the waste. Dissolution of calcium sulfite (in conjunction with oxidation of the dissolved sulfite in the aerated leach water) may therefore be limiting. This would also be expected in other sulfite-rich wastes such as the Scholz dual alkali material, particularly where leaching occurs under anaerobic conditions. Under the aerated conditions of these tests, though, there may be sufficient sulfite oxidation that continuing formation of sulfate combined with the higher levels of calcium sulfate dissolving results in saturation with respect to gypsum (the Scholz material contained ~20% calcium sulfate vs. <5% for the Paddy's Run waste).

The leaching of sulfite from FGC wastes may be a concern, as pointed out by Lunt, et al., [30]; however, there are very few data on sulfite levels in leachate under different conditions. As previously noted, sulfite (or total oxidizable sulfur, TOS) is readily oxidized and therefore represents an immediate oxygen demand to groundwaters or receiving waters. TOS may also be potentially toxic to aquatic life. Under contract

to the EPA, Arthur D. Little, Inc., is studying the question of sulfite availability and leaching as a part of their program to evaluate the disposal of FGC wastes in mines and the ocean [30].

The data on the levels of trace metals in the leachates for comparable wastes with and without fly ash differ for the Scholz and Shawnee sample materials. In the Shawnee materials, arsenic, boron, mercury, selenium, and possibly zinc are significantly higher in the waste containing fly ash after more displacement washes. The rest of the trace element concentrations are about the same except for chromium and magnesium which are slightly lower in the ash-containing waste. It is also interesting to note that, of the data reported, arsenic and zinc concentrations in the leachate are higher than in the original liquor, whereas the concentrations of other trace elements in the leachate are about the same or lower than in the original liquors.

For the Scholz wastes, the concentrations of arsenic, chromium, magnesium, and possibly zinc in the leachates are higher in the waste containing ash than in those with no ash, although the wastes containing ash had undergone more PVD. The higher levels of magnesium in the leachates of the ash-containing sludge can be attributed to the lower pH of these leachates. The fluoride concentration in the leachate of the ash-containing waste is also significantly lower.

Using a different type of test procedure, Radian in a study funded by EPRI analyzed trace elements in leachates from untreated FGC wastes produced at three different power plants. The test procedure involved air-drying the waste followed by 24-hour extraction with deionized water using 20 wt.% slurries. Results are shown in Table 4.26. The trace element levels observed generally fall within and to the lower end of the range of concentrations for waste liquors and elutriates measured by WES and Aerospace and shown in Table 4.16. The measurements of boron concentrations range from 1 to 6 ppm compared with the two values of 8 ppm and 41 ppm in Table 4.17. Fluoride was also found at substantial levels, but the several measurements of molybdenum were all less than 0.1 ppm--substantially below the two concentrations reported in Table 4.13.

Table 4.26

Equilibrium Concentrations of Trace Elements
In FGC Waste Leachate

	<u>Station Number</u>		
	<u>1</u>	<u>4</u>	<u>5</u>
pH	8.5	9.7	8.4
<u>Element (ppm)</u>			
Sb	0.014	0.013	0.035
As	<0.002	<0.002	0.03
Ba	2	<0.3	<0.3
Be	0.002	0.001	0.002
B	2.6	6.3	0.96
Cd	0.0005	<0.001	0.002
Cr	0.001	0.011	<0.001
F	31.5	8.7	7.6
Ge	<0.01	<0.01	0.02
Hg	0.0005	0.001	0.0008
Pb	0.0056	0.0033	0.0061
Mn	<0.002	<0.002	<0.002
Mo	0.063	0.061	0.075
Ni	<0.05	<0.05	<0.05
Se	0.045	0.0096	0.016
V	<0.1	<0.1	<0.1
Zn	0.005	0.052	<0.005
Cu	0.031	0.045	<0.005

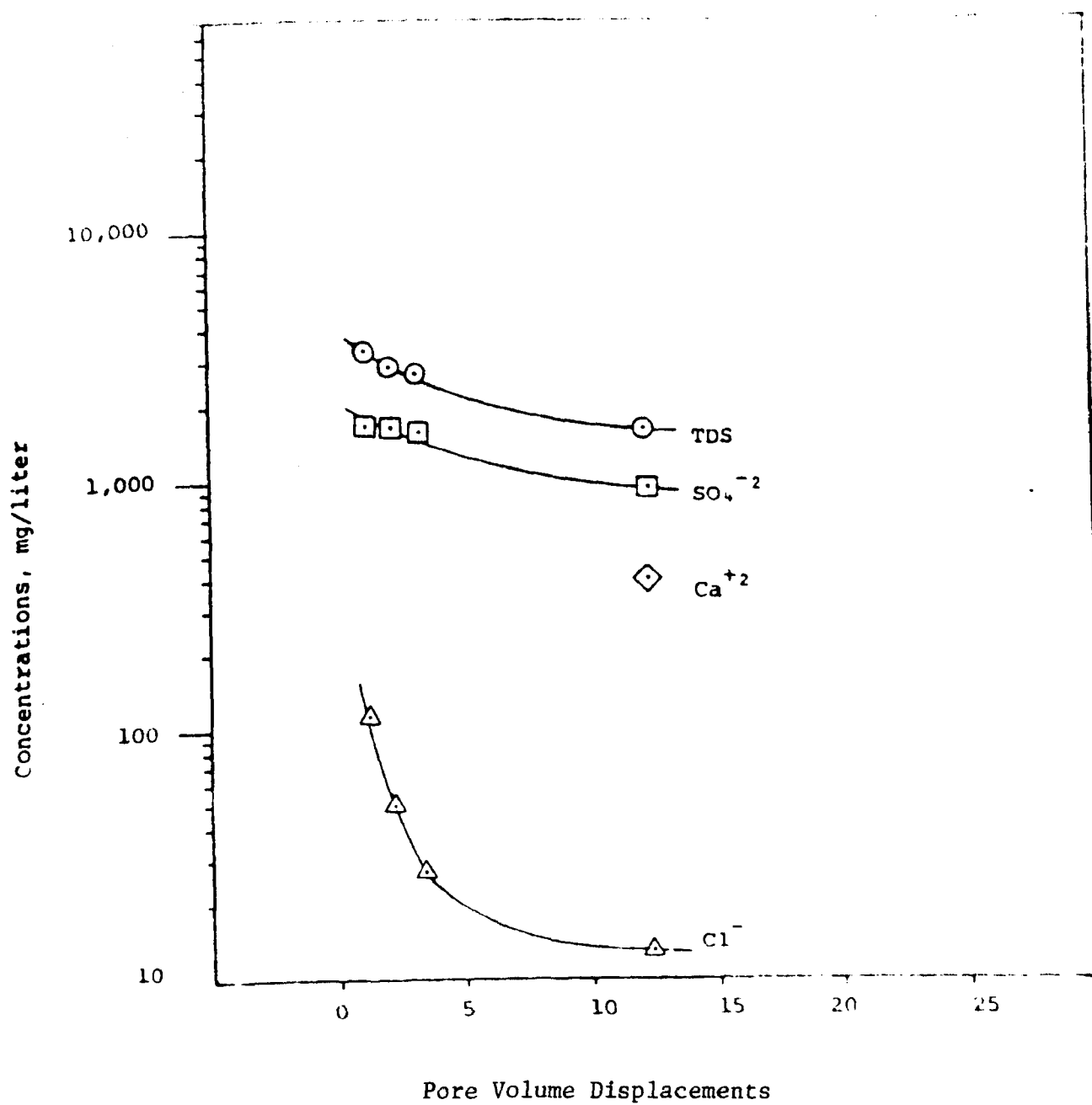
Source: [39]

Radian noted that the sludge from Station No. 5 contained a substantial amount of fly ash, whereas the sludges from Stations No. 1 and 4 were quite clean. Interestingly, only arsenic was present at a substantially higher level in the Station No. 5 ash-containing sludge leachate as compared to the other two which did not contain ash.

Limited data on leachate concentration of sulfate-rich FGC wastes are available. Radian [146] has performed laboratory leaching experiments in a permeability measuring apparatus on the Shawnee forced oxidation scrubber waste and on waste from the Four Corners fly ash scrubber. The concentration of major and trace species in these leachates are shown in Figures 4.7 and 4.8 and Table 4.27.

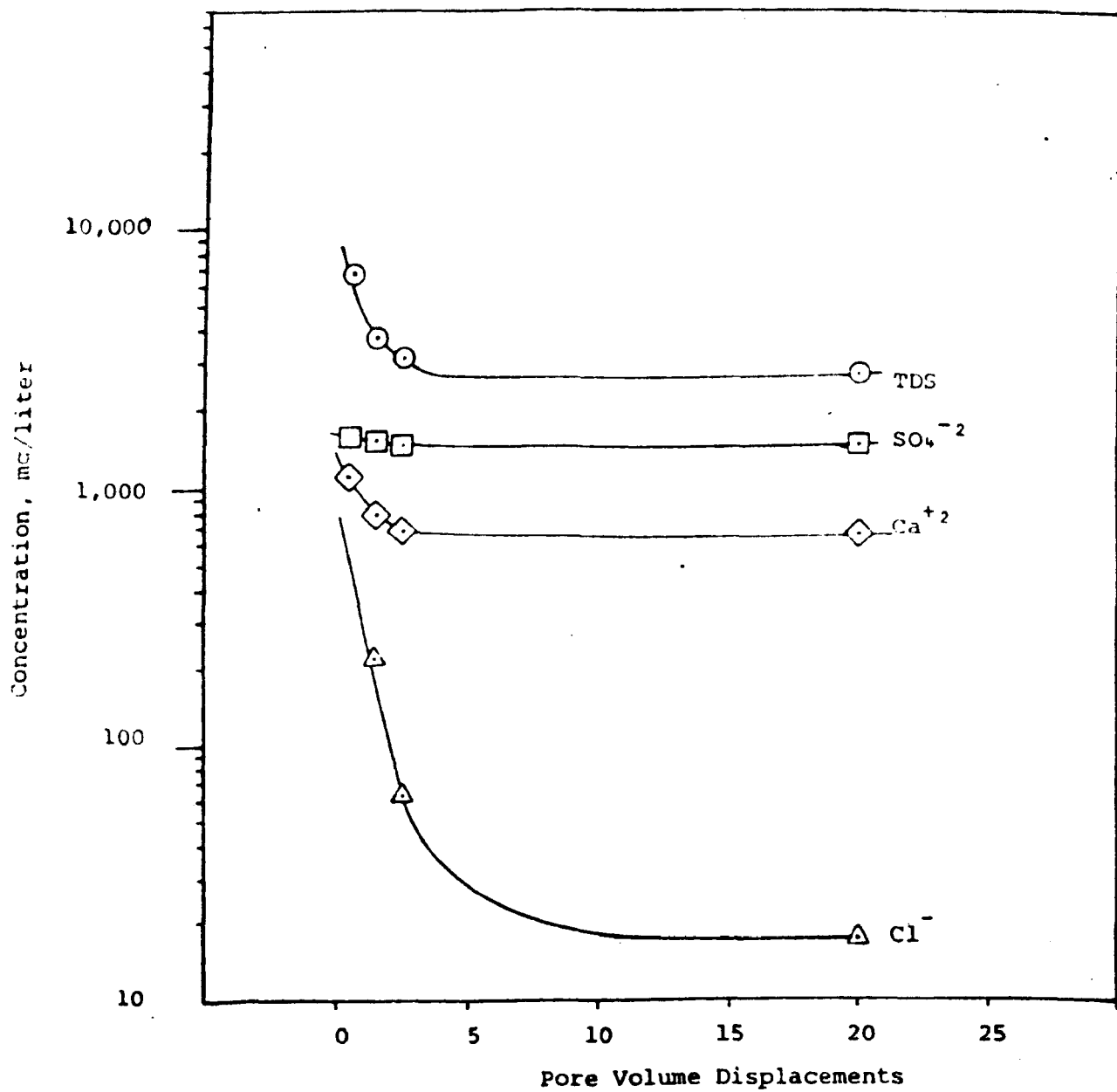
These data reported by Aerospace and Radian are representative of the results obtained in other laboratory studies of the leaching behavior of untreated wastes. The changes in leachate concentrations (for most constituents) with successive PVD's and the range of concentrations observed are generally confirmed in elutriate data reported by Arthur D. Little [19], preliminary results of leaching column tests performed by WES [16], and many other investigations of leaching with water. While these studies are certainly not conclusive, there are definite trends in laboratory leaching behavior:

- The concentrations of major soluble species and trace elements in waste liquors vary considerably with the type of FGC system, the composition of the coal burned, and other factors including the impurities in process makeups (reactants and water).
- The initial flush of leachate from the wastes (first pore volume or less) has concentrations approximating those in the interstitial (occluded) liquor.
- Successive displacements of occluded pore water show rapidly decreasing levels in TDS and certain highly soluble species (e.g., Na^+ and Cl^-).
- The initial concentrations of trace elements in leachate are generally quite low, although many (depending on the waste characteristics) can exceed levels prescribed in drinking water standards. Most trace element levels tend to decrease with successive PVD's. There are a few notable exceptions, such as



Source: [146]

Figure 4.7 Concentration of Major Species in Leachate from Four Corners Scrubber Waste



Source: [146]

Figure 4.8 Concentration of Major Species in Leachate from Shawnee Forced Oxidized Scrubber Waste

Table 4.27

Concentration of Trace Elements in Leachate
From Sulfate-Rich Wastes (First Pore Volume)^a

	<u>Four Corners(μg/ml)</u> (Fly Ash Scrubber)	<u>Shawnee (μg/ml)</u> (Forced Oxide)
Li	0.05	0.002
B	0.9	0.01
F	~0.5	~2
Na	>4	2
Mg	1	0.7
Al	1	0.1
Si	3	>10
P	0.5	0.1
S	>9	>4
A	0.8	0.2
K	2	0.9
Ca	>10	>10
Ti	0.3	0.08
V	0.05	0.04
Cr	0.03	0.02
Mn	0.01	0.009
Fe	1	0.2
Co	<0.002	<0.001
Ni	0.01	0.01
Cu	0.02	0.01
Zn	2	0.06
Ga	0.05	0.002
Ge	0.003	0.007
As	0.01	0.01
Se	0.02	0.02
Rb	0.005	
Sr	1	
Sn	0.01	0.004
Sb	0.02	<0.001
Ba	1	0.2
Pb	0.05	0.009
U	0.02	0.02

^aLiquid sample thermally ashed at 350°C for one hour prior to analysis by Spark Source Mass Spectrometry.

Source: [146]

arsenic and zinc, which have been observed to remain relatively constant, at least over the first ten pore volumes.

- Concentrations of constituents tend to level out after 5-10 PVD's with TDS concentrations in the range of 1,500 to 2,500 ppm and calcium and sulfate concentrations, in most cases, corresponding to the gypsum solubility product. This suggests that essentially all of the occluded waste has been displaced and that dissolution of the solid phase (with the release of any trapped liquor) is controlling.

The results of laboratory leaching tests have yet to be confirmed by monitoring programs of full-scale field disposal operations. There are a number of factors which may alter the leaching behavior which have not been adequately tested, including:

- The effects of microbial activity,
- Variations in the composition of the leaching water and conditions (e.g., high buffering capacity),
- High TDS levels,
- Anaerobic conditions for sulfite-rich wastes (complete submersion in seawater, etc.), and
- Management of the disposal sites.

Considering the variations in the types of disposal and disposal management, and the site conditions, such laboratory leaching studies need field corroboration.

A limited amount of pilot field testing related to impoundments of untreated wastes has been performed which has yielded some leaching data. EPRI funded a study of the impoundment of the wastes generated from two of the three prototype systems tested at the Scholz Steam Plant [49]. The wastes were dumped in a one-acre, artificially-lined pit with a leachate collection system. The pond was allowed to sit open without control of surface water so that the surface of the wastes was covered with water. Leachate samples were then taken from the pond underdrainage.

Leachate compositions measured from the dual alkali waste pit over a period of approximately a year and a half (7/75-12/76) are shown in Table 4.28. Because of the low flow rates through the wastes, there

Table 4.28

Summary of Leachate Concentrations from Dual Alkali Wastes
Generated During Prototype Testing at the Scholz Steam Plant

<u>Species</u>	<u>Concentration Range Measured in Field Leachate Samples^a</u>	<u>Laboratory First PVD</u>	<u>Leach Test^b Sixth PVD</u>
Al	0.12 - 29.0	---	---
As	<0.01 - 0.25	---	<0.004
B	0.9 - 2.5	5	<0.5
Be	---	---	<0.001
Ca	211 - 420	1000	1100
Cd	<0.01 - 0.018	---	0.016
Cr	<0.01 - 0.06	---	0.0025
Cu	<0.01 - 0.23	---	<0.002
Fe	0.03 - 4.5	---	---
Hg	<0.0002 - 0.0026	---	0.00030
K	17 - 165	43	1
Mg	0.019 - 5.2	<0.01	<0.01
Mn	<0.01 - 0.07	---	---
Na	2460 - 7880	2260	12
Ni	<0.01 - 0.11	---	---
Pb	<0.01	---	0.005
Se	<0.002 - 0.190	---	<0.004
Zn	<0.01 - 0.07	---	0.007
TDS	8540 - 24,050	9140	3550
Cl	169 - 887	1070	310
F	3.6 - 110	48	13
SO ₃	54 - 500	---	---
SO ₄	5200 - 13,100	3700	1160
pH	11.0 - 12.8	12.5	12.3

^aSamples taken from pit underdrain from 7/75 to 12/76, and includes disposal of waste with inadequate or no filter cake wash. Performed by Southern Company Services. Source: [49]

^bLaboratory leaching test performed by Aerospace on sample taken at 6/20/76.

Source: [31]

was standing water on the pond at all times. These conditions would favor a plug flow mechanism (initial flush) for leachate production and the concentrations in the leachate may be expected to be similar to those in the liquor.

During the period of testing (3/75-7/76), the system was operated with a wide range of conditions (including different coals) including periods where there was no filter cake wash, so that no direct correlations can be made. However, the results are illustrative of the range of leachate concentration that can be achieved with one type of system operating under slightly different conditions at one power plant firing three different coals. For comparison purposes, the leachate data from laboratory testing performed by Aerospace on one sample of these wastes is also included in Table 4-28. The concentrations reported for the pond leachate correspond more closely to the first PVD data than the sixth.

Aerospace and the TVA are also jointly evaluating leaching from three small ponds of untreated wastes and a number of ponds containing treated wastes at Shawnee as a part of the EPA's program to test the effects of waste treatment. Results of this program are discussed later.

To date there has been no monitoring of full-scale disposal operations of untreated wastes which provide data on leaching behavior. However, two demonstration projects funded by the EPA are planned--one at the Baukol-Noonan mine to evaluate strip mine disposal of wastes from an alkaline fly ash scrubbing system and one at Louisville Gas & Electric's Cane Run Station to evaluate the impoundment of dual alkali wastes.

4.4.2 Effects of Stabilization on Pollutant Migration from FGC Wastes

The impact on the environment of the pollutants contained in a mass of FGC waste depends not only on the concentration of species in the liquid and solid phases of the waste, but also on the rate that the materials dissolve from the solid into the interstitial liquor and the rate that they are transported out of the sludge mass. In earlier sections, it was noted that chemical stabilization of a waste can affect

the permeability of the waste in addition to improving its physical properties for disposal. Reductions in permeability directly reduce the rate at which interstitial liquor is flushed from the sludge and for equal concentration in the interstitial liquor, directly reduce the flux of constituents emerging. Chemical stabilization may also affect the concentration of substances which are dissolved in the interstitial liquor by chemical reaction and/or encapsulation. However, in studies conducted to date it has been difficult to experimentally separate the effects on solubility and permeability.

In an attempt to evaluate the effect of waste stabilization on pollutant mobility, Aerospace [40] had samples of waste stabilized chemically by each one of three commercial processors--Chemfix, IUCS, and Dravo. After the stabilized samples had cured, they were ground into a fine powder and subjected to accelerated leaching tests similar to those used for the untreated sludges. Samples were ground to minimize the effects of restricted diffusion of pollutants from impermeable, large particles. The results of one such set of tests which is typical of results obtained for the three stabilization processes are shown in Table 4.29. With some exceptions, the concentrations of substances in the first pore volume were somewhat lower for the unstabilized waste than for the stabilized material. Concentrations of the major soluble species, sulfate and TDS, were reported to be reduced by 30-50%. A reduction in chloride concentrations was not observed in this experiment; however, substantial reductions were observed in tests of other stabilized material. In this experiment, concentrations of lead and fluoride were substantially lower in the first PVD sample from the stabilized material. However, levels of copper and chromium in the first pore volume were somewhat higher for the stabilized materials than for the unstabilized material.

The accelerated leaching tests were designed primarily to determine the final equilibrium concentrations of pollutants in leachate after the major soluble substances had been flushed out. The fact that the first PVD concentrations in the unstabilized material were somewhat less than those in the interstitial liquor suggests that perhaps because of the

Table 4.29

Comparison of the Chemical Constituents in
Eastern Limestone Waste Leachate with Chemfix
Chemically Stabilized Waste Leachate

	<u>Waste - Aerobic</u>		<u>Chemfix - Aerobic</u>	
	<u>1st Pore Vol.</u>	<u>50th Pore Vol.</u>	<u>1st Pore Vol.</u>	<u>50th Pore Vol.</u>
As	0.06	0.01	0.04	0.006
Cd	0.002	<0.001	0.003	<0.001
Cr	0.025	0.003	0.04	<0.001
Cu	0.007	0.010	0.05	0.005
Pb	0.12	0.01	<0.035	<0.001
Hg	0.05	<0.00005	<0.005	<0.0005
Se	0.03	0.006	0.01	0.002
Zn	0.85	0.045	0.5	0.065
Cl	1350	120	1400	60
F	2.7	<0.2	0.9	0.2
SO ₄	6500	1200	3000	250
TDS	10,500	2400	7000	500
pH	4.7	5.0	4.70	6.01

Source: [40]

rapid rate of elutriation, concentrations of substances measured at early stages of leaching may not have been representative of those which would have been obtained if lower leach rates, more representative of an actual disposal situation, had been employed.

In 1973, WES [41] began an extended leaching column study of samples of five unstabilized FGD wastes and corresponding samples treated by one or more of several commercial treatment vendors. By means of stop-cocks at the bottom of each leaching column, leachate flow was to be controlled so that downward flow would approximate permeation through a sludge mass having a permeability of 10^{-5} cm/sec. A large number of substances, both trace and major constituents, are being monitored in the leachate collected from the leaching columns. At this time, only preliminary data are available and the results are inconclusive. In some cases, there is evidence that treatment may not have reduced the concentration of dissolved solids in the leachate over the first few PVD's while in other instances, there appears to be a definite reduction in leachate concentrations. Preliminary data also suggest that concentrations of trace elements are reduced; however, with a few stabilized wastes, concentrations of some trace elements in the leachate were relatively unchanged or increased, possibly because of the addition of fly ash or other additives not present in the stabilized wastes.

Jones and Schwitzgebel [42] performed column leaching studies on mixtures of fly ash and commercial gypsum or a synthetic calcium sulfite/sulfate co-precipitate prepared in the laboratory. Leaching tests were also performed on waste samples obtained from four full-scale FGC systems; two contained significant amounts of ash. Based on measured permeabilities and unconfined compressive strengths, some of the fly ash containing sludges had undergone considerable pozzolanic reaction. The compositions of corresponding fractions of leachate collected from a variety of samples were quite similar regardless of the nature of the sample. Chloride ion concentration fell very rapidly to about 10 mg/l. Concentrations of TDS, calcium, and sulfate fell to equilibrium concentration levels in the range of 1,000-3,000 mg/l. The similarities in the leaching behavior

of the materials tested suggested that the curing reactions which resulted in reduced permeability had not significantly changed the actual solubility of the solid phase.

Chu, et al., [43] studied a number of the physical and chemical properties of mixtures of fly ash/FGD waste with hydrated lime. They reported very large decreases in the concentrations of a variety of substances in leachates from wastes containing lime and fly ash as compared with unstabilized sludges. Ten-fold reductions in the concentrations of major soluble anions like sulfate and choride were reported to be the result of treatment. The concentrations of certain trace substances such as boron, fluoride and arsenic were reduced by stabilization; many were not significantly altered; and a few like molybdenum and chromium were higher in the treated leachates. The reductions in major soluble components, in particular, are striking. However, the flow rates used in the experiments and the extent to which the leach liquor was forced to pass through the waste matrix were not stated, so the reductions in concentration might be largely due to reduced diffusion from within the pieces of stabilized material.

IUCS has been using a "shake test" to characterize the leaching behavior of the stabilized FGC wastes produced by the IUCS process [44]. Although very few experimental results have been reported in the literature, these tests provide some evidence that in the IUCS process, pollutant immobilization is probably more a result of physical entrapment than chemical insolubilization. In the IUCS shake test, which is quite analogous to the elutriate test performed by WES and others, a quantity of stabilized material, usually 400 grams, is immersed in about 2 liters of doubly distilled water and shaken very gently for two days. The water is decanted, replaced with fresh water, and shaking is resumed for two more days. The process is repeated until a total of five "surface washes" have been performed. The elutriate liquors are then analyzed for TDS and trace metals. Very few useful data on trace metal analyses are available. Concentrations of TDS measured by IUCS in five successive elutriates of a sample of stabilized FGC waste obtained from a Shawnee

test pond are shown in Table 4.30. The fact that TDS concentrations declined markedly in the first several leach solutions and then appeared to be levelling off at a constant value is interpreted to mean that the first wash is really a wash of the surface and the high TDS is due to the dissolution of solids on or near the surface. Successive washes involved dissolution of solubles from within the relatively impermeable pieces of material and the amount leached became limited by slow diffusion from within the piece. Unfortunately, IUCS did not report the amount of sample taken for leaching, or provide an estimate of the total solubles potentially leachable. Without such data it is not possible to speculate as to whether or not increased chemical insolubility had accompanied stabilization.

The best test of the effect of chemical treatment on pollutant mobility would be a field test conducted on a sufficiently large scale and over a sufficient length of time so that actual samples of permeate and solid cores could be obtained for study and analysis. To that end, Aerospace, on behalf of EPA, initiated a field study at the TVA Shawnee Power Station at Paducah, Kentucky. Initially, five 0.1-acre containments were constructed; two were filled with unstabilized FGC wastes and three with FGC wastes stabilized by Dravo, IUCS, and Chemfix processes, respectively [36,37]. All of those wastes contained fly ash. During 1976, a program of studies of ash-free lime waste, ash-free limestone waste, and gypsum waste (produced by forced oxidation in a direct limestone system) in three additional ponds were undertaken. Test samples of stabilized and unstabilized waste, groundwater, surface water, leachate and soil cores were analyzed in conjunction with the study.

An example of the behavior of measured values of TDS and three other major components in the leachate from one of the ponds containing unstabilized material is found in Figure 4.9. This behavior, which was reported to be typical of the unstabilized ponds, showed all of the substance concentrations rising rapidly after filling and reaching concentrations approximating those in the interstitial liquor of the dissolved wastes. Although there are temporal variations, after about one year of

Table 4.30

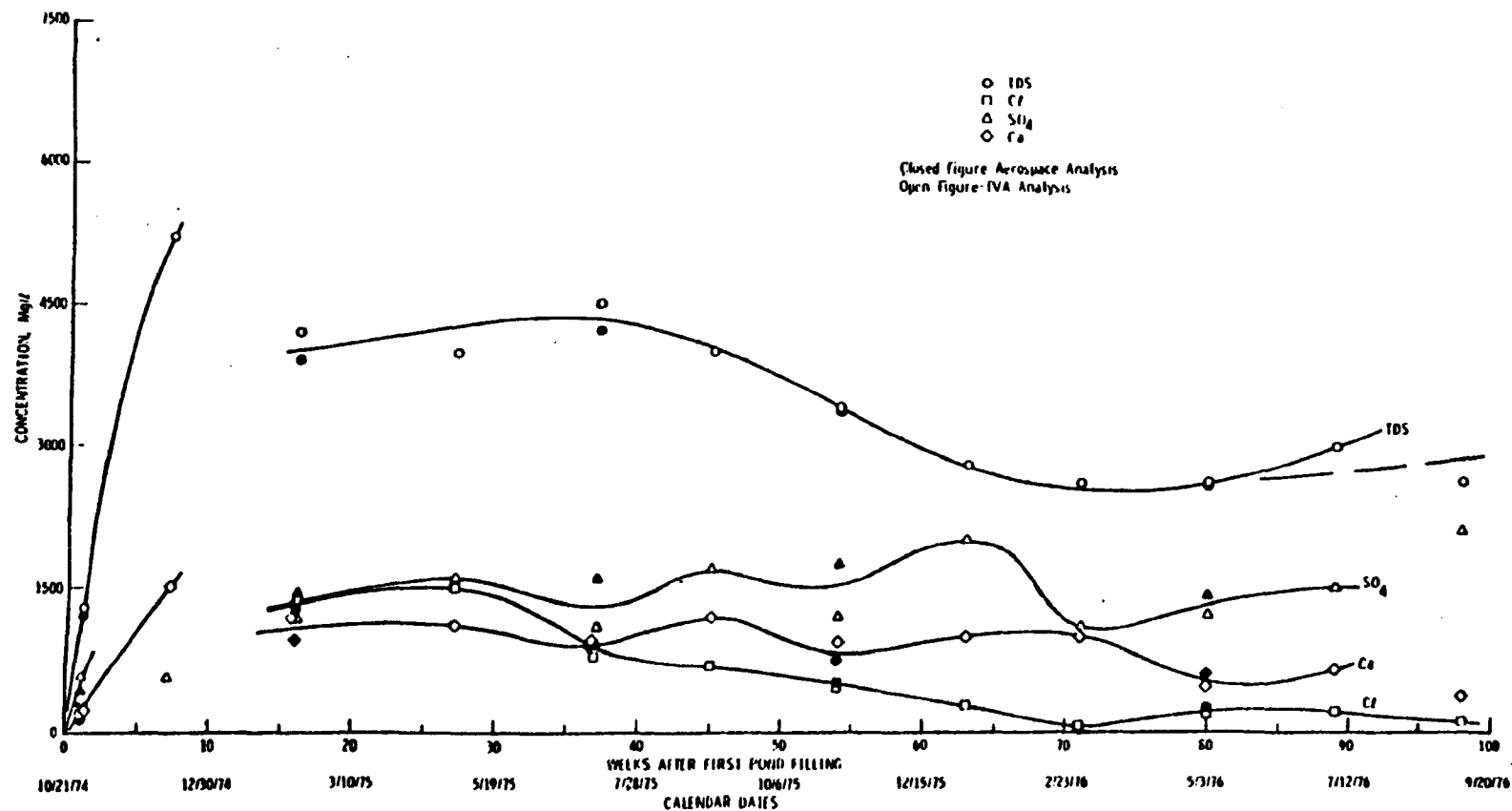
Concentrations of TDS in Leachate from Successive
Shake Tests of Stabilized FGC Waste Sample^a

<u>TDS</u> <u>(ppm)</u>	<u>Grams</u> <u>Leached</u>	<u>Grams</u> <u>(in.²)</u>
974	1.948	.046
338	.676	.015
268	.536	.012
194	.388	.009
214	.428	.010

^aSurface area of sample exposed to leaching solution
273 cm² (42.4 in²)

Ratio of surface area to volume of leaching solution
137 cm²/ (21.2 in²/

Source: [44]



Source: [37]

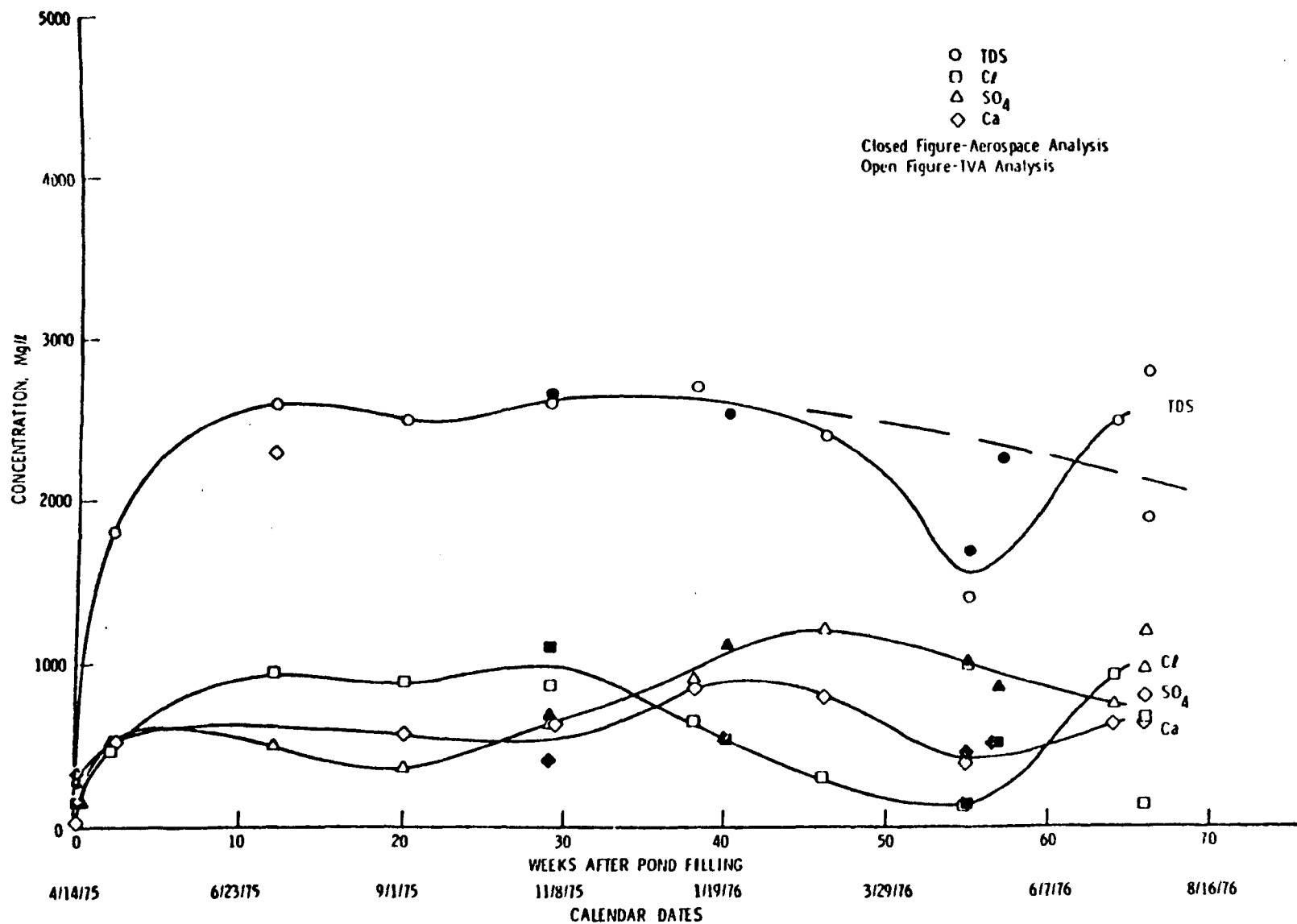
Figure 4.9 Concentration of Total Dissolved Solids and Major Species in Pond D Leachate

leaching the concentrations seem to have begun to decline. For comparison, the concentrations of the same substances measured in the leachate from the same FGC waste after chemical stabilization are shown in Figure 4.10. The general rise in concentration was observed to be similar to that in the waste from the unstabilized pond. However, the maximum concentrations observed were only about 60% of those measured for the unstabilized material.

The general behavior described above was reported by Aerospace to be typical of the other stabilized or unstabilized materials as well. Concentrations of major substances in the leachate from unstabilized materials rose rather rapidly to about the levels present in the interstitial waste liquor. For stabilized materials, concentrations of the same substances rose to about 1/3-2/3 of the levels observed for the unstabilized ponds. Significantly, Aerospace reported that levels of trace substances in pond leachates seemed, for the most part, to be unaffected by chemical stabilization, probably because the trace elements do not participate in the fixation reactions.

Another field study of stabilized wastes is being conducted by Louisville Gas & Electric, Combustion Engineering and the University of Louisville at the Cane Run Station. This ongoing study focuses on the effects of stabilizing wastes from a direct carbide lime scrubbing system with fly ash and lime. Both physical properties and leaching behavior are being studied.

Testing is also underway to evaluate the disposal of stabilized wastes in the ocean. Although companion tests on the unstabilized material were not performed, Duedall, et al. [15], performed elutriate tests using seawater to leach four samples of FGC waste treated by IUCS as a part of its program to study the feasibility of using stabilized FGC wastes for ocean reef construction. Two of the stabilized materials had a high sulfate/sulfite ratio. Of particular interest in that work was the observation that except for a few scattered cases, the concentrations of nearly all of the trace substances measured in the elutriates were less than those measured in the starting seawater, which was used



Source: [37]

Figure 4.10 Concentrations of Total Dissolved Solids and Major Species in Pond B Leachate

to perform the elutriation. Duedall, et al. [15], attributed the decrease to adsorption of the trace elements from the seawater onto the stabilized FGC waste. Additional testing of both unstabilized and stabilized wastes in regard to ocean disposal is being performed by Arthur D. Little, Inc. and the New England Aquarium under EPA funding [48].

Data included in a recent EPRI summary of the state of the art of FGC waste fixation [2] suggest that in other stabilization processes, such as the Chemfix process, constituents might in fact be chemically bound within the stabilized material, thus reducing their solubility. The results of one laboratory leaching study performed by Chemfix are shown in Table 4.31. Chemfix [15] has observed that their process will not immobilize certain soluble substances like chloride and monovalent cations. The details of leaching studies which Chemfix has performed are not presented; however, a comparison of the concentrations measured in the first leachate fraction with the concentrations in the unstabilized waste showed that essentially all of the other constituents were reduced to a greater extent than was chloride. This suggests that a chemical insolubilization was probably occurring in addition to possible immobilization due to permeability reductions.

The IUCS shake test is of general interest because a test of that sort may be a good way to characterize and compare the leaching behavior of stabilized materials relatively quickly and inexpensively. The alternative to a shake test is a leaching column test which must be run for months or years to provide meaningful data.

A recent study on the effect of stabilization on leaching behavior of dry sorbent FGC waste has been made by the University of Tennessee [117]. The Extraction Procedure (see Section 4.4.5) was applied to calcium based dry sorbent process wastes before and after fixation using commercially available processes. The results have not been published.

4.4.3 Soil Attenuation

If the supernatant liquor from a disposal pond is allowed to permeate

Table 4.31

Chemfix Preliminary Leaching Study on Waste From
Shawnee Plant, TVA
Test Number One

Constituents ^a	Unstabilized Waste ^b	<u>Inches of Leachate Water^c</u>			
		0-25	25-50	50-75	75-100
Cadmium	1.0	< 0.10	< 0.10	< 0.10	< 0.10
Total Chromium	20	< 0.10	< 0.10	< 0.10	< 0.10
Copper	24	< 0.10	< 0.10	< 0.10	< 0.10
Iron	8,700	.06	.02	< 0.10	< 0.10
Lead	54	.09	< 0.10	< 0.10	< 0.10
Nickel	23	< 0.10	< 0.10	< 0.10	< 0.10
Zinc	56	< 0.10	< 0.10	< 0.10	< 0.10
Phenol and related	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
Cyanide and related	0.15	.002	< 0.10	< 0.10	< 0.10
Sulfate	9,000	285	250	135	90
Chloride	1,500	110	45	30	20
Alkalinity	600	100	125	75	65
Chem. Oxy. Dem.	6,500	550	500	500	

^aAll results in ppm.

^bSample from turbulent contact absorber (without upstream fly ash removal), centrifuged to 56% solids.

^cEach 25" of leachate represents approximately 800cc of distilled water.

The above data are supplied for information purposes only. Since unstabilized wastes vary considerably, other samples of this waste may yield somewhat different results.

down through the settled waste and into the underlying soil, the leachate will carry with it dissolved contaminants, initially, at levels as high as in the interstitial liquor of the wastes. The same percolation could occur through a landfill disposal site that was insufficiently graded and sufficiently permeable so that a significant amount of the rainfall it received percolated directly down into, and through, the waste mass. However, if the soil underlying such a disposal site has a sufficiently high ion exchange capacity or is a sufficiently active adsorbent for dissolved ions, potential contaminants in the permeate can be retained by the underlying soil, thereby purifying the permeate and effecting containment of these species.

Radian [39] studied the retention of a number of trace elements and species on soil types ranging from sand to loam. Test solutions were prepared to simulate fly ash leachate and FGC waste leachate by initially leaching samples of fly ash and waste, and then, because the levels of trace elements in the actual leachate were quite low, the leachate samples were spiked with concentrated metal solutions of the sort used for standardizing atomic absorption spectrometry measurements. The spiked leachates were allowed to percolate through columns packed with each of the soil types. Fractions were collected from the effluent and analyzed for trace element concentrations in order to detect the breakthrough or point at which the column had become saturated with a particular trace element. The relative retentions for the trace elements tested on each of the soil types are shown in Tables 4.32 and 4.33. The relative retentions are presented as values of a parameter, K , which is the number of interstitial column volumes of leachate which could pass through the column before the concentration of the emerging trace element had risen to 5% of its concentration entering the column. The waste leachate differed from the ash leachate not only in trace elements and their levels, but also in pH--the fly ash leachate being very alkaline ($\text{pH} = 12$), while the waste leachate was nearly neutral. Trace elements like copper, arsenic, and zinc were uniformly well retained on most soils from both types of leachate. Conversely, fluoride was poorly

Table 4.32

Values of K for Spiked Ash Leachate^a

	<u>Cu</u> <u>(0.075)</u> ^b	<u>Cr</u> <u>(1.0)</u>	<u>As</u> <u>(0.4)</u>	<u>Se</u> <u>(1.0)</u>	<u>F</u> <u>(0.9)</u>	<u>Soil T</u>
Plant 1	>300	~10-20	>300	25	0	
Plant 3	>300	~300	>300	225	<20	
Plant 4	>1000	550	>1000	100	<20	silt loam
Plant 5	c	<20	>600	200	~25	loam
Soil 6	>300	0	>300	<10	0	
Soil 7	>200	50	>200	25	<10	
Soil 8	c	200	>200	~300	--	loam
Soil 9	>300	150	>300	150	150	silt loam

^aK is the number of interstitial column volumes leachate would pass through before 5% of the initial concentration would emerge from the column.

^bConcentration (ppm) of element in spiked leachate is in parentheses with each element.

^cInitial large values, decreasing.

Source: [39]

Table 4.33
Values of K for Spiked Waste Leachate^a

	<u>Cu</u> <u>(1.0)</u> ^b	<u>Cr</u> <u>(1.0)</u>	<u>F</u> <u>(12.6)</u>	<u>Hg</u> <u>(1.2)</u>	<u>Zn</u> <u>(1.0)</u>
Plant 1	1800	10	10	40	1000
Plant 3	>500	20	50	>500	>500
Plant 4	>1200	40	25	>700	>1200
Plant 5	1700	20	20	1000	1000
Soil 6	>1000	10	20	300	350
Soil 7	250	0	<10	20	
Soil 8	>150	0	10	>150	>150
Soil 9	>150	0	30	>150	>150

Source: [39]

^aK is the number of interstitial column volumes leachate would pass through before 5% of the initial concentration would emerge from the column.

^bConcentration (ppm) of element in spiked leachate is in parentheses with each element.

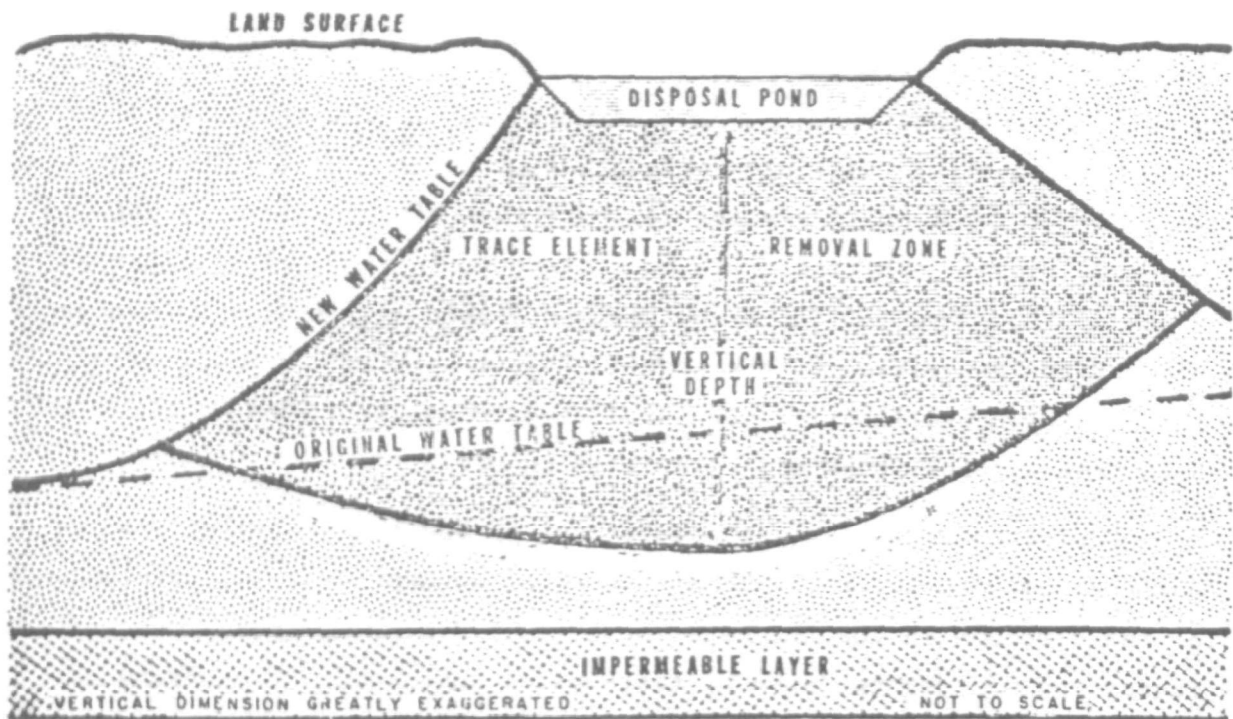
attenuated in almost every case; chromium was poorly attenuated under conditions of neutral pH. Retention of selenium was quite variable depending on the soil type.

The practical significance of soil attenuation in a disposal site can be seen in Figure 4.11. The capacity of the underlying soil to absorb elements (determined by soil texture, mineralogy, and organic content), the concentrations and speciation of the elements and the rate of permeation of the leachate through the soil all combine to influence pollutant transport from the pond. The Radian data suggest that if homogeneity of the underlying soils is assumed and if the single species column attenuation tests are representative of the interaction that would occur for a multi-element leachate then certain elements such as arsenic, copper, and zinc would be attenuated in most soils within a depth of 15 meters (50 ft) below the waste pond for as long as ten years after first deposition of the waste. However, other trace elements like chromium and fluoride were predicted to penetrate hundreds of feet below the disposal pond with little attenuation.

Soil attenuation is, as pointed out by Radian, a complex process composed of both ion exchange and physical adsorption. The speciation of the elements in the leachate is variable depending upon pH and other factors as was demonstrated by tests using anion and cation exchange resins by Radian. Because of the variabilities in the leachate and the complexity of the interactions with soil, predictions of attenuation are difficult and column tests are necessary.

One of the most important limitations to the degree to which soil attenuation can contain pollutants from FGC waste is the fact that major soluble components like sodium, chloride, and sulfate are very poorly attenuated and pass readily through the underlying soil into the receiving groundwater. In addition, the higher concentration of these species in the FGC waste relative to rainwater may interact with the soil to displace some of the trace elements in the soil and mobilize them.

Under an Interagency Agreement between EPA and the U.S. Army Dugway Proving Ground, a study of the leaching of trace levels of potential



Source: [39]

Figure 4.11 Removal of Trace Elements from
Pond Leachate by Soil Attenuation

pollutants from FGC wastes and their subsequent attenuation by soil columns has been carried out at Dugway. A series of column tests were set up to study the leaching of selected trace species from six samples of FGD wastes and three samples of fly ash. The FGC waste samples were from limestone scrubbers (low and high sulfur coals), lime scrubbers (low and high sulfur coal and dolomitic lime), and a dual alkali waste (medium sulfur coal). All of the fly ash samples were from electrostatic precipitators (low and high sulfur coals). The leaching column effluents subsequently were passed through columns filled with six different types of soil. The experimental design permitted samples of both the influent to, and effluent from, the soil attenuation column to be taken for analyses. Preliminary results indicate that the FGC waste leachates contained little zinc but that a substantial increase in concentration was observed after the leachate was passed through various soils. Evidently, displacement and solubilization of the naturally occurring zinc in the soil occur by passage of the waste leachates. The concentrations of boron and fluoride in the wastes and their leachates were highest compared to all the other trace elements of interest (e.g., As, Cu, Cd, Cr, Pb, Ni, Zn) and indicate that these two elements deserve greater attention. These elements were, however, well attenuated by most of the soils tested. Arsenic was also found in substantial amounts in some of the wastes but was well attenuated by most soils. Solubilization of in situ arsenic also occurred from one soil by passage of the leachate solution. The species of Cd, Cr, Cu, Pb, and Ni, which were found in very low concentrations in the waste leachates, were only partly attenuated by the soils.

4.4.4 Impacts of Weathering on FGC Wastes

Weathering of FGC wastes, both stabilized and unstabilized, has been observed to produce several important physical and chemical changes.

Of most importance is the potential for structural deterioration of stabilized materials which can occur when they are subjected to freeze/thaw and wet/dry cycling. Increased pollutant mobility may result from the breakup of the less permeable stabilized structure. WES has carried

out some preliminary lab tests of wet/dry and freeze/thaw behavior on stabilized FGC waste specimens. Breakup has also been noticed on some of the ponds at Shawnee.

Oxidation of calcium sulfite at the surface of high sulfite wastes can increase the dissolved solids present in surface runoff following a rain. Alternate wet/dry cycling can cause recrystallization with the resultant formation of a hard surface layer which could reduce wind erosion. Such crustation has been observed at Scholz and by Radian in their EPRI work.

A further discussion of the effects of weathering on FGC wastes properties is presented in Section 5.

4.4.5 RCRA Implications for FGC Waste Leachates

Recently, provisions of the Resource Conservation and Recovery Act (RCRA) of 1976 have raised the possibility that FGC wastes may be declared hazardous materials. The draft regulations place utility wastes in a "special" waste category under Section 3004 (hazardous wastes). Until further data become available, FGC waste disposal will require waste analysis, monitoring, site selection, recordkeeping, security and requirements of Section 3004 (Hazardous Wastes) will apply.

The tentative categories under which a waste may be defined as hazardous are: ignitable, reactive, infectious, corrosive, radioactive, and toxic, phytotoxic, mutagenic and teratogenic.

Considering the available data on the characteristics of FGC wastes (fly ash, bottom ash, scrubber sludge, and leachate) there is no evidence to suggest that any of these wastes are either ignitable or reactive. The infectious criteria pertain only to health care facilities and, thus, are not applicable to any of these wastes. The major concern which may lead to the placement of FGC wastes in the group of hazardous waste is the toxic category criteria. The pertinent section of the draft regulations determining the potential toxicity is Section 3001 of the draft regulations. According to the proposed draft regulation [46] a solid waste is toxic if the elutriate obtained when the waste is applied to

the Extraction Procedure (EP) has certain properties as determined by various testing methods specified in the regulation. The properties tested include gene mutation, DNA damage, bioaccumulation potential, presence of "special chemicals" as defined by RCRA, or presence of concentrations of various species which exceed various applicable thresholds.

In the latest Extraction Procedure (EP) protocol [46], a sample of the waste is placed in a polyurethane foam sample holder. The sample holder is then placed in a compaction tester and subject to a compactive action. A weight of 0.33 kg is dropped 15 times from a height of 15.2 cm on the sample. The sample may remain intact or be pulverized by this action. The sample is then placed together with an amount of water 16 times its weight in a stainless steel container equipped with a low RPM stirrer. The pH of the slurry is adjusted to 5.5 using 0.5 N acetic acid and the sample is stirred for 24 hours with continual adjustment of pH. Aliquots of the liquid phases are then taken for biological and chemical testing.

The lack of available data on many of the above specified properties (mainly due to the need to use specific test methods, some of which have only recently been defined) prevents the determination of the degree of hazard of FGC wastes at this time.

However, the available data on characteristics of these wastes suggest some areas of concern. The presence of many trace metals and sodium disulfite (which has been shown to be mutagenic) may yield mutagenic activity for the waste leachate. In addition, these trace elements are known to accumulate in the food chain to a significant degree and thus may yield positive results on the bioaccumulation tests. The presence of compounds in the wastes which were also on the "special chemicals" list was not noted [116] so that it is not likely to fall in this category. Concentrations of some species in the EP elutriate may exceed threshold values (such as 10 times the EPA Human Health Water Quality Criteria) since it is known that the concentrations of some species in waste liquors exceed these values. FGC waste may also be classified as hazardous under the corrosive criteria. One such criterion is that of an aqueous waste having a pH of less than or equal to 3 or greater than or equal to 12. Certain fly ash slurries may exhibit pH values at these extremes.

The last criterion by which FGC wastes may be classified as hazardous is radioactivity. The criterion is defined by a waste for which the Radium-226 concentrations exceed 5 pci/g of solid or 50 pci/l of liquid waste, or a total of 10 μ C for a single discrete source. The single source of data presented in Section 4.3 on the radionuclide concentrations is fly ash and bottom ash indicating that this criterion may be of concern.

The applicability of various liquors used in laboratory leaching experiments towards predicting environmental impact for FGC wastes needs to be determined. Adjustment of the pH of the final slurry, as is called for in procedures of ASTM and the Extraction Procedure may produce leaching conditions which are not representative due to the significant buffering action that some FGC wastes have from their limestone and other alkali content.

Oak Ridge National Laboratory under contract to the EPA has begun to evaluate the toxicity of various power plant wastes and the complete extraction procedure. Initial results have indicated that the procedure extracts little material with organic character and that the metals analyses are extremely sensitive to the blank values. Among the samples being tested are fly ash, bottom ash, and scrubber waste from the Shawnee Power Plant. Bioassays using *Daphnia magna*, mutagenicity assays using the Ames Salmonella/microsomal activation assay, seedling studies and chemical characterization of the extracts, including chromatography after preconcentration on XAD-2 resin, are being carried out. Preliminary results have shown that Shawnee fly ash extracts pass nearly all of the criteria mentioned above.

A recent assessment on the potential impact of RCRA on utility solid wastes by Fred Hart Associates for EPRI [108] concludes that ash, scrubber sludge and other wastes might approach or exceed EPA criteria in toxicity, radioactivity and corrosiveness. While ash and scrubber sludges present the most important issues, other utility wastes including metal cleaning wastes, both blowdown and coal pipe drainage may also present

potential problems. The economic impact of RCRA on utility solid wastes are under study by the Department of Energy. Results of this study are expected later in 1979.

4.5 Data Gaps and Research Needs - Chemical Properties

The major data gaps could be subdivided into those relative to wastes from:

- Dry sorbent systems (whose importance will increase in the future), and
- Wet scrubber systems.

Dry sorbent systems have not reached significant commercial use now but are expected to by the early 1980's. Lack of chemical and physical data on these wastes are major data gaps.

The following data gaps and research needs for wet scrubbed FGD wastes and coal ash have been identified:

(1) Field Data - There is an important need to characterize the chemical and physical properties and behavior of unstabilized and stabilized wastes in actual field disposal operations. Data are needed on changes in FGC waste composition and properties resulting from waste aging, weathering (rewetting and freezing/thawing), handling, processing (stabilizing) and the disposal environment; and the associated changes in the pollutant mobility. This information is needed covering the ranges of: basic FGC system types (direct lime, direct limestone, alkaline ash, and dual alkali) and/or waste types (sulfite-rich vs. sulfate-rich and pH level); methods of processing (unstabilized, blended, stabilized); and types of handling and disposal (ponding, landfill, mine disposal, ocean). While a limited number of data do exist or are being developed from EPA-funded projects (e.g., Square Butte demonstration project, Louisville Gas & Electric/Combustion Engineering, TVA/Aerospace) or studies are being planned (Louisville Gas & Electric/Bechtel/Combustion Equipment Associates/Southern Services), more extensive field testing is recommended. This would involve monitoring of a number of representative full-scale systems not now studied via waste sampling, corings, and leachate wells.

(2) Laboratory Test Procedures - Presently available leachate (elutriate) and toxicity test procedures do not as yet confidently predict dissolution and toxicity constituents of FGC wastes. It is important to be able to perform tests in the laboratory quickly and cost effectively, which will characterize the mobility and impact potential of FGC wastes. A number of different procedures need to be developed and tested. The current extraction procedure developed under RCRA needs to be tested on its ability to characterize these properties in FGC wastes. Limited data in this regard are currently being generated at Oak Ridge National Laboratory.

(3) Ash/Waste Co-Disposal - There is the distinct possibility that the practice of co-disposal of fly ash and FGD waste as a mixture currently done at many locations could have certain advantages over the disposal of each separately. However, there is a lack of fully definitive data correlating the levels of trace elements in the coal, fly ash and bottom ash, FGD waste, and ash/waste admixtures - either in the waste materials or their leachates. More laboratory and field testing needs to be carried out to determine such correlations if possible and identify and assess pollutant mobility and toxicity.

(4) Stabilization Requirements - Many fly ashes have appreciable pozzolanic activity and when admixed with FGD waste (and possibly lime) will result in a material which hardens with time. The extent of hardening reactions occurring will be dependent to a great extent upon the ash characteristics but also on the waste type (sulfite vs. sulfate-rich), the presence of high levels of TDS, and the conditions of ash mixing (methods and relative quantities). This area still remains somewhat of an art, and more studies are needed to determine the effects of different types of wastes and waste/ash mixtures not only on physical properties but also major and trace elements mobility and toxicity.

(5) Trace Element Focus and Speciation - A number of trace elements present in FGC wastes are of particular interest because they have been observed in waste liquors at levels which in some situations may deleteriously impact on plants or animals. Certain of the elements, e.g., boron,

fluoride, and molybdenum have been studied in only a few samples. Others, such as arsenic, antimony, selenium, manganese, and cadmium, are difficult to measure precisely and accurately at the levels at which they are present in wastes. This warrants a continuing focus. It is recommended that as additional samples are obtained from FGC systems for characterization, these trace elements in particular should be measured by techniques offering state-of-the-art accuracy and precision in order to extend the base of good data describing their occurrence in FGC wastes. That list of key elements should be re-evaluated from time to time based on an assessment of the potential impacts on plants and animals so that relatively expensive analytical efforts are focused on the most important parameters.

Since the chemical form (oxidation state, and existence as a cationic, neutral or anionic complex) of a pollutant affects its solubility, toxicity, and attenuation by soil, it is recommended that experimental and theoretical studies of the chemical species of trace pollutants in FGC wastes and leachates be continued. The trace elements of arsenic, selenium, antimony, chromium, and boron either exhibit amphoterism or highly variable attenuation by different soils and would be good candidates for speciation studies. In addition, selenium reportedly can exist as the free element, and as such its mobility has not been well characterized.

The ability to measure trace (ppm and ppb) levels of pollutants has only recently been developed and is still an active area of research. Speciation of a trace constituent into its various chemical forms in a complicated mixture is still only a research area. Some techniques are currently available which will allow a limited degree of speciation of metals in solution. For example, separation of a particular metal into its kinetically inert anionic, cationic or neutral species is possible using ion exchange resins and the use of polarographic techniques will allow determination of oxidation state in solutions under limited conditions. The combination of ion chromatography and electrochemical detection (conductivity or polarographic) may be a useful tool in the future.

(6) Reactions Producing Gaseous Species - Studies of the reduction reactions, e.g., Se to H_2Se or As to arsines, that might occur in an anaerobic region of an FGC waste disposal landfill or pond should be conducted. Tests should also be conducted to determine if any species which may be present in a volatile state (i.e., elemental Hg and Se) is released upon exposure of the waste to environmental conditions. These experiments are important because they would yield data on gaseous products which could be transported into the atmosphere.

Measurement and identification of trace gases in air is a very active area of research. Measurement of total species in air samples is currently possible for many species. Separation and quantification of the individual chemical forms (such as various methylated arsines) of one group of volatile species is a more difficult problem and still under investigation for many species.

(7) Radionuclides and PNA's - Although it is not expected that radionuclides and polynuclear aromatic (PNA) organic compounds will be present at levels that are of concern, and even more unlikely that they will leach from the waste at substantial levels, measurements of radionuclide activity (^{226}Ra , ^{210}Pb , and ^{238}U , etc.) should be made for a representative set of FGC wastes and their leachates. The wastes should be chosen to include those with no ash, those with ash, stabilized materials and unstabilized materials. In this regard, the results of ongoing PNA measurements at TRW should be evaluated and additional measurements made, if necessary, to ascertain if any potential problem could arise due to their presence.

A measurement of radionuclide activity in FGC wastes and their leachates is complicated by the expected low level of activity. However, such measurements have been performed for many years and should not require a substantial research effort. The ability to analyze trace levels of PNA's, on the other hand, is the result of more recent research. However, techniques are currently available for analyses of these species at the ppm to ppb region.

5.0 PHYSICAL CHARACTERIZATION OF FGC WASTES

5.1 Introduction

This section describes the current status of physical testing of FGC wastes and summarizes the results of appropriate tests conducted to date on unstabilized and stabilized FGC wastes. The critical properties which relate to the handling characteristics, placement and filling characteristics, long-term stability, intrinsic pollution potential, and potential for stabilization are described. A brief summary of the status of physical testing is given together with the available data on important physical properties. Deficiencies in the body of existing knowledge of these properties are identified and future areas of research are suggested.

5.2 Critical Properties

It is probable that for some time into the future, the bulk of the fly ash collected in the United States will be discarded, but the physical and chemical characteristics of ash (particularly fly ash) make it suitable for a variety of uses. Such utilization is likely to grow in the future [69].

Disposal of FGC wastes involves handling and transport, field placement at a disposal site, long-term stability of the deposit, and the pollutant mobility in the disposal site environment [65]. Each of these characteristics can be evaluated on the basis of selected parameters as listed below:

- Handling Characteristics
 - dewaterability
 - consistency versus water content
 - viscosity versus solids content
 - compaction parameters
- Placement/Filling Characteristics
 - dewaterability
 - compaction parameters
 - compressibility
 - strength parameters

- Long-term Stability in Fills
 - erodibility
 - durability under weathering
 - strength parameters
 - compressibility
- Pollutant Mobility
 - erodibility
 - water retention
 - permeability

Some fundamental physical properties importantly govern many of the characteristics described above. These properties are the grain properties which include particle size distribution, particle morphology and specific gravity. The relationship between these and other properties given above and the characteristics important for FGC waste disposal are discussed in the following sections.

5.2.1 Handling Characteristics

Handling characteristics have a major bearing on the choice of transport; e.g., tanker truck vs. pipeline vs. conveyor. It is necessary to develop quantitative parameters to describe handling characteristics of wastes before alternative transport systems can be evaluated.

The following parameters appear to be diagnostic with respect to the handling characteristics of FGC wastes:

- The relations between waste consistency and moisture content, analogous to the Atterburg Limits of natural soils;
- The viscosity of the FGC wastes as a function of water content (or solids content);
- The dewatering characteristics of the waste as measured by the equilibrium water content under gravity drainage and as a function of applied vacuum;
- The compaction characteristics of the waste as quantified by the compaction moisture--dry density relations for

various compactive efforts (Standard Proctor Compaction Test and Modified Proctor Compaction Tests); and

- The sizes of the waste particles, as determined by a standard hydrometer grain size analysis.

The tests listed above are not considered sufficient to provide all the data required for the design of an FGC waste handling system. For example, pumping tests on various mixes and consistencies of wastes and additives may be required for selection of transport equipment and design of pipe networks. Such detailed tests would be required, in any case, for a site-specific design. However, the tests listed above should be adequate for comparison and differentiation between various wastes on the basis of handling characteristics.

5.2.2 Placement and Filling Characteristics

The general feasibility of land disposal of FGC wastes is to a great extent determined by the economics of disposal compared to FGC waste utilization. Thus, physical parameters which describe the conditions of waste placement in fills or ponds need to be identified and related to economic considerations.

The economics of depositing FGC waste on land depend on the mode of deposition. Land area required for disposal is directly related to the weight of FGC waste solids per unit volume of disposal space. The final dry density of the deposited material depends upon the dewatering and compaction properties of the wastes. The total amount of waste solids placed on any unit of area of a disposal site depends not only on the dry density of the waste, but also on the mode of placement: ponding, filling inside containment dikes, or construction of a fill composed entirely of waste. If a fill is to be composed only of waste, or waste plus stabilizing agent, then material of sufficient strength is needed for construction of starter dikes. However, starter dikes can be made of different materials with a general increase in economic considerations. The physical parameters of greatest significance in evaluation of various modes of filling include the moisture-density (compaction) properties of the waste, the compressibility of the placed material, and the strength

of the waste to resist slope/bearing failures. The compressibility, quantified by the results of laboratory consolidation tests, describes the change in waste density under the influence of its own weight and any external loads. Compressibility values may be used in settlement prediction computations. The strength of the waste is described best by the results of triaxial compression tests. Strength for granular materials such as waste can be stated according to a Mohr-Coulomb criterion as:

$$s = c + p (\tan \phi)$$

where s = shear strength;

c = cohesion or that portion of the strength unrelated to changes in external confining pressure; and

$\tan \phi$ = the angle of internal friction, which is the coefficient of proportionality between increase in shear strength and corresponding increase in intergranular pressure, p .

Thus, values of c and ϕ characterize the strength of waste materials and can be used in design of FGC waste ponds or fills.

5.2.3 Long-term Stability

Closely associated with parameters which describe the placement characteristics of FGC waste are those parameters which describe the relative stability of a waste deposit or landfill. For example, compaction characteristics may determine the bulk density of waste which can be obtained in a fill and thereby may affect fill economics, but the long-term strength and durability of the waste govern the feasibility of the filling operation and dictate the uses to which the sludge fill may be put in the future.

The overall technical feasibility of any given mode of land disposal of FGC waste, as well as the economics of such disposal, are dependent on the long-term stability of the deposited waste under relevant static and dynamic loadings, and on the durability of the waste under weathering forces such as freeze-thaw cycles, wet-dry cycles, and erosion by wind and water. Erodibility does not appear to be of prime importance. On

the other hand, cycles of freezing and thawing and cycles of wetting and drying, with consequent swelling, shrinking, and distortion of deposited material, may have significant effects on grain structure, intergranular cementation (fixation), and mass stability. Obviously, stability under loading can be evaluated by means of the strength parameters c and ϕ . However, the stability of deposits of waste under dynamic loading (machinery vibrations, blast impacts, earthquake vibrations, etc.) will depend upon the relative density, degree of saturation, and effective confining pressure in the deposit undergoing vibratory loading, as well as on the strength parameters c and ϕ . A loose deposit under low confining pressure may lose shear strength under dynamic loading. Thus, long-term stability also is related to compaction characteristics and placement techniques. Finally, the ability of a waste deposit to support external loads will be dependent on the compressibility of the sludge and on the limitations on settlement created by the nature of the external load source (cover soil, building foundation, roadway sub-base, etc.). The ability to support external loads will govern future use of the disposal site; thus, this characteristic has great economic significance.

5.2.4 Pollutant Mobility

Another set of characteristics of great importance are those which physically govern the mechanisms for pollution of the air and water in the vicinity of the power plant, transport system, and final disposal (or reuse) location. For example, an integrated evaluation of FGC waste permeability, host soil permeability, waste and soil water retention characteristics, groundwater flow regime and soil-waste interaction would be required for an assessment of potential groundwater pollution at a specific disposal site. Such an evaluation could not be made without a knowledge of physical parameters which quantitatively describe the flow of water through FGC wastes.

In order to evaluate the intrinsic potential of any FGC waste to cause air or water pollution, it is necessary first to differentiate between the characteristics of a site which led to pollution and the characteristics of a waste which would lead to (or inhibit) pollution

of any given site. The properties of a waste of interest in this regard are those which describe the potential for the material itself to be transported from a disposal site or other location and those which quantify the potential for toxic constituents to be removed (leached) from the mass of the waste. Transport of FGC wastes from a disposal site could occur by erosion caused by wind or water. It is presumed that erosion would occur only during construction or filling of a disposal site; after filling, the waste deposit would be protected by proper grading and drainage and by some sort of cover layer. Erosion is often a relatively minor source of pollution; however, in some cases water erosion of landfill materials has been significant and design of a collection basin for runoff is generally considered. Erosion potential can be related to grain size distribution and interparticle cohesion; an extensive body of literature exists in which erodibility of materials by wind or water has been expressed in terms of grain size distribution and interparticle cohesion. Pollution of surface waters and groundwater by leaching of pollutants from waste deposits is a more important potential problem than erosion-related pollution. The physical characteristics of an FGC waste which affect the potential for leachate pollution include the permeability of the waste, the water retention of the waste, expressed in terms of water content (i.e., degree of saturation) and any interactions which occur between the waste and adjacent soil or rock to limit the flow of leachate from the waste into the surrounding media. Permeability and water retention will vary with the relative density or void ratio of the waste. FGC waste-soil interactions will vary from one soil to the next, and only general indications of possible interactions could be obtained from laboratory tests using a given FGC waste and soils of various textures and mineralogical character. Thus, FGC waste permeability and water retention will be the most consistent physical parameters for measuring pollution potential of FGC wastes.

The feasibility of land disposal of FGC waste may be affected seriously by improvements in waste characteristics achieved through treatment of the waste with some additive or stabilizing agent. Physical parameters must be selected which describe the ease of waste stabilization

with additives and which will provide quantitative indicators of the effects, on physical properties, of waste stabilization treatment with additives.

Preliminary evaluations of the physical characteristics of many FGC waste samples have indicated the desirability of improving the properties of these materials. It would be advantageous to decrease waste permeability, increase its strength and decrease its compressibility if these improvements could be made in a cost-effective way. Some degree of improvement in these parameters can be achieved through dewatering and/or densification. It appears that further improvements may be made by adding stabilizing materials to the wastes. In some instances, other wastes (e.g., fly ash) may be mixed with FGD wastes to yield materials with characteristics superior to (or no worse than) the individual constituent characteristics. The physical characteristics of resultant mixtures may be evaluated by measuring the physical parameters mentioned previously in connection with unstabilized, unmixed wastes. It is appropriate, however, to consider evaluating the FGC wastes themselves with regard to the relative ease or difficulty of preparing a "stabilized" mix. In other words, the wastes should be tested and characterized in some way to indicate the potential for physical stabilization. The best indications of possible mixing or handling problems may be obtained from evaluation of waste grain sizes, grain size distribution (uniformity and texture), and water content-consistency relationships.

5.3 Status of Physical Testing

A brief summary of the status of physical testing of FGC wastes is shown in Table 5.1.

The tests listed below with appropriate references/standards have been standardized on the basis of experience gained in evaluating natural soils, mineral aggregates, and other particulate materials.

Table 5.1

Summary of Physical Testing - FGC Wastes

<u>Waste Type</u>	<u>Physical Tests</u>	<u>Investigators^a</u>	<u>Remarks</u>
Sulfite-Rich ($\text{CaSO}_x \cdot 1/2\text{H}_2\text{O}$)	Grain-Size Analysis	ADL [19], Aerospace [37], Dravo [93,94], PMC [90,91], UL [71], WES [100]	Adequate coverage
	Atterberg Limits	Dravo [92-94], PMC [90,91], UL [71]	Not diagnostic
	Proctor Compaction	ADL [19], PMC [90,91], UL [71], WES [100]	Field Correlation needed
	Permeability	ADL [19], Aerospace [37], UL [71], WES [100], Radiam [146]	Serious data gaps
	Consolidation	Dravo [93], PMC [91], UL [96]	PMC: mixed with fly ash
	Unconfined Compression	ADL [19], Radiam [146]	Marginally useful
	Triaxial Compression	PMC [90,91], UL [71], Radiam [146]	Serious data gaps
	Dynamic Loading	UL [97]	Scarce data
	Dewatering-Viscosity	ADL [19], Aerospace [37,122], UL [95]	Limited extent
	Field Compaction	SCS [49,99]	Serious deficiency in data
Mixed Sulfite/Sulfate ($\text{CaSO}_x \cdot 1/2\text{H}_2\text{O} + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	Grain Size Analysis	Aerospace [37], BAL [4], K&D [88], UL [71], WES [100]	Adequate coverage
	Atterberg Limits	BAL [4], K&D [88], UL [71]	Not diagnostic
	Proctor Compaction	BAL [4], K&D [88], UL [71], WES [100]	Field correlation needed
	Permeability	Aerospace [37], K&D [88], WES [100]	Serious data gaps
	Consolidation	UL [96,98]	UL: mixed with fly ash
	Unconfined Compression	BAL [4], K&D [88]	Marginally useful
	Triaxial Compression	BAL [4], K&D [88]	Serious data gaps
	Dewatering-Viscosity	ADL [19], Aerospace [37,122], Dravo [92]	Limited extent
Sulfate-Rich ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} + \text{or} \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	Grain-Size Analysis	ADL [19], Aerospace [37], UL [71], WES [100], Radiam [146]	Adequate coverage
	Atterberg Limits	UL [71,84,95-97]	Not diagnostic
	Proctor Compaction	ADL [19], TCT [89], UL [71], WES [100]	Field correlation needed
	Permeability	ADL [19], Aerospace [37], WES [100], Radiam [146]	Serious data gaps
	Consolidation	UL [97,98]	Limited extent
	Unconfined Compression	ADL [19], TCT [89], Radiam [146]	Marginally useful
	Triaxial Compression	UL [71,84,95-97], Radiam [146]	Serious data gaps
	Dewatering-Viscosity	ADL [19], Aerospace [37,122]	Limited extent
Other (mixed)	Liquefaction	Crowe [102]	3/4 inerts and fly ash

^aADL = Arthur D. Little, Inc.
Aerospace = Aerospace Corporation
Dravo = Dravo Corporation
PMC = Factory Mutual Corporation
BAL = Buss and Ladd

K&D = Klynn and Dodd, Ontario Hydro
SCS = Southern Company Services
TCT = Twin City Testing
UL = University of Louisville
WES = U.S. Army Waterways Experimental Station
Radiam = Radiam Corporation

<u>Test</u>	<u>Reference/Standard</u>
Index Properties	
● Grain Size Analysis	ASTM D422-63
● Specific Gravity	ASTM D854-58
● Atterburg Limits	ASTM D423-66, D424-59
Soil Classification	ASTM D2487-69
Compaction Behavior	ASTM D698-70
Field Compaction	ASTM D1556-54, D2167-66
Permeability	ASTM D2434-66
Consolidation	ASTM D2435-70
Unconfined Compression	ASTM D2166-66
Triaxial Compression	ASTM D2850-70

Available values for critical parameters and other information from previous studies of physical characteristics of FGC wastes are presented below.

5.4 Available Information

The properties on which information is available are given in the following sections:

- 5.4.1 Index Properties
- 5.4.2 Consistency-Water Retention
- 5.4.3 Viscosity vs. Water (Solids) Content
- 5.4.4 Compaction Behavior
- 5.4.5 Dewatering Characteristics
- 5.4.6 Strength Parameters
- 5.4.7 Permeability
- 5.4.8 Weathering

The index properties discussed in Section 5.4.1 are in a different class than the other properties discussed in this chapter since they are more fundamental to the material and are not dependent, as are the other properties, on the parameters used in the specific testing procedures.

5.4.1 Index Properties

5.4.1.1 Fly Ash

Properties of individual fly ash grains include specific gravity, shape, mean size, and size range. Specific gravity ranges widely, from about 2.1 to almost 2.9, and is influenced primarily by iron oxide content increasing with increasing iron oxide content [66].

As much as 70% by weight of a given fly ash may consist of hollow spherical particles. Typically, fly ashes consist of silt-size particles with a very narrow grain size distribution [67,81]. Grain size analyses for fly ashes are given in Table 5.2 and described in detail below. A comparison of grain size distribution for fly ash and bottom ash is shown in Figure 5.1.

5.4.1.2 FGC Wastes

The properties of particulate masses most commonly used for purposes of description are the specific gravity of individual particles and the sizes of individual grains and grain size distribution.

FGC wastes, as discussed in Chapter 4, are composed mainly of calcium sulfate and calcium sulfite salts. In stack gas cleaning operations in which fly ash and sulfur dioxide are removed simultaneously, FGC wastes may contain significant amounts of fly ash particles. The specific gravities of typical FGC wastes are also listed in Table 5.2. It may be seen from this tabulation that specific gravity values of wastes composed almost entirely of calcium sulfate salts range between 2.30 and 2.40. Specific gravity values of clean calcium sulfite wastes range between 2.4 and 2.7. FGC wastes containing significant amounts of fly ash may exhibit specific gravity values below 2.3 or above 2.6, depending on the specific gravity of the fly ash. As mentioned previously, the specific gravity of fly ash depends mainly on the iron oxide content and ranges between 2.10 and 2.90, with the high values being those having a higher iron oxide content [71].

Values of specific gravity for FGC wastes higher than values listed in the ranges given above have been reported by various investigators. Many of these anomalous values might be explained by the method used to

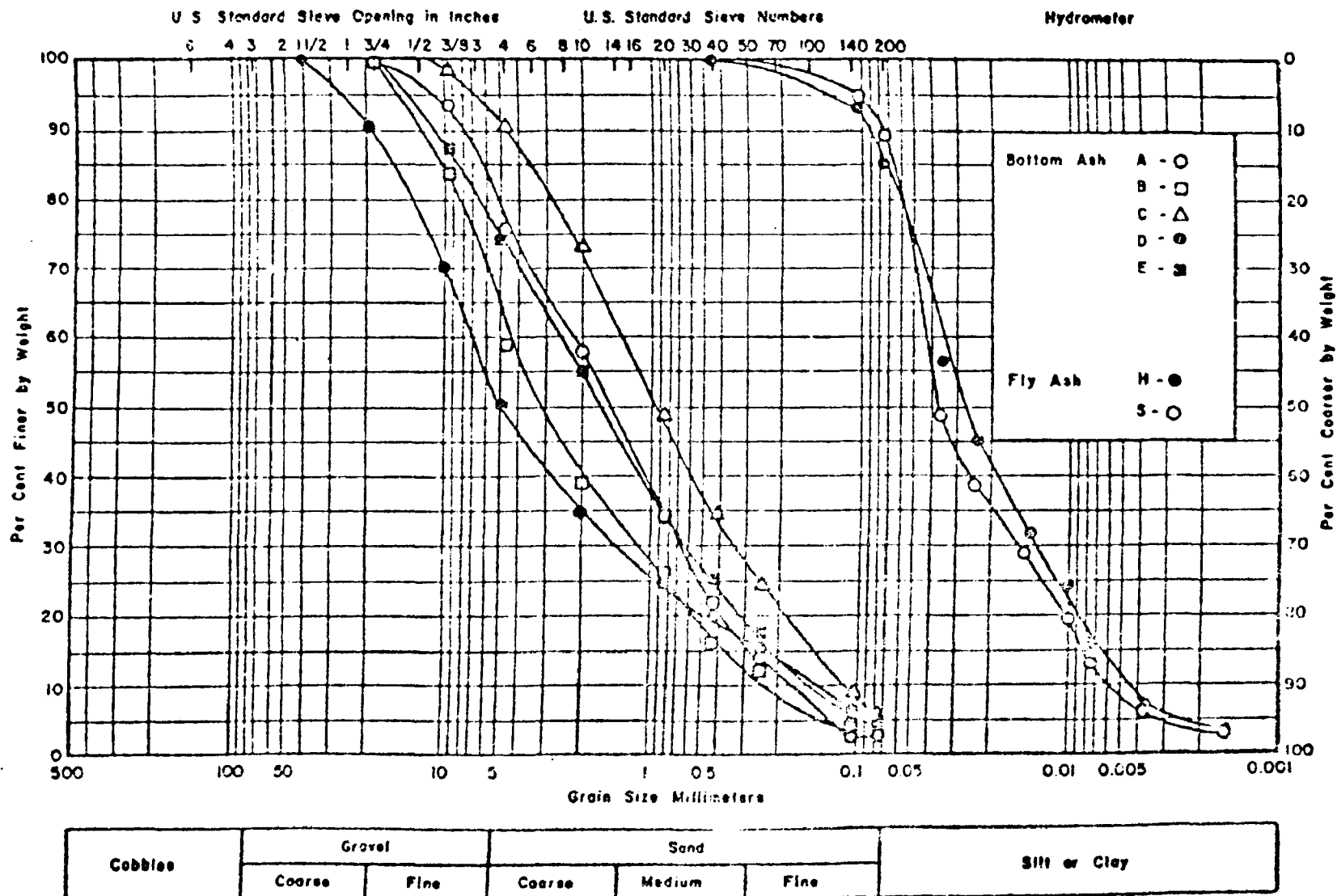


Table 5.2

Physical Properties of FGC Wastes

WASTE TYPE	SPECIFIC GRAVITY (G _s)	GRAIN SIZE DISTRIBUTION (Wt %)			COEFFICIENT OF UNIFORMITY (Cu)	ATTERBURG LIMIT		REFERENCE
		>74µm	2-74µm	<2µm		W _L ^a	W _P	
FLY ASH								
Bituminous	1.97-2.59	—	—	—	—	—	—	—
Subbituminous	1.97-2.47	—	—	—	—	—	—	146
Lignite	2.76-2.85	—	—	—	—	—	—	146
Scholz (Bituminous)	2.32	9%	91%	—	1.3	NP	—	71
LG&E (Bituminous)	2.67	7%	93% (<74)	—	1.4	NP	—	71
Gaston	2.16	12%	88%	—	1.2	NP	—	71
SULFITE-RICH								
• Without Ash								
Harrington Station (Southwestern)	2.86	8	88	4	1.5	—	—	88
Lake View (Ontario Hydro)	2.68	38	62	—	3.4	NP	—	96
Paddy's Run (LG&E)	2.49	7	91	2	1.3	65%	48%	95
Scholz (CEA/ADL)	2.56	4	93	3	1.5	NP	—	96
Range	2.49-2.86	4-10	85-93	2-3	1.3-3.4			
• With Ash								
Double Alkali (FMC, 30-50% Ash)	2.54	10	85	5	—	45	—	91
Paddy's Run (50% Ash)	2.59	3	97	—	1.3	36	—	71
Paddy's Run (33% Ash)	2.58	6	94	—	1.2	37	—	71
Paddy's Run (10% Ash)	2.48	4	96	—	1.2	45	—	71
Scholz (CEA/ADL, 50% Ash)	2.60	7	93	—	1.2	NP	—	71
Scholz (CEA/ADL, 33% Ash)	2.57	5	95	—	1.2	NP	—	71
Scholz (CEA/ADL, 10% Ash)	2.51	6	94	—	1.3	56	—	71
Elrama	—	9	91	—	—	—	—	145
Bruce Mansfield	—	26	74	—	—	—	—	145
• With Ash and Lime								
Paddy's Run (50% Ash, 5% Lime)	2.57	3	97	—	1.2	33	—	95
Paddy's Run (50% Ash, 10% Lime)	2.55	4	96	—	1.3	33	—	95
Scholz (CEA/ADL, 50% Ash, 5% Lime)	2.58	6	94	—	1.3	39	—	95
Scholz (CEA/ADL, 50% Ash, 10% Lime)	2.56	5	95	—	1.3	34	—	95
Elrama (IUCS Process, Cured)	—	3	66	30	—	—	—	145
Range	2.55-2.58		66-96		1.2-1.3			
SULFATE-RICH								
• Without Ash								
Scholz (CIC)	2.35	18	76	6	2.5	—	NP	96
Japanese Gypsum	2.34	27	71	2	2.4	—	NP	96
German Gypsum	2.34	30	66	4	2.3	—	NP	96
Range	2.34-2.35	18-30	66-76	2-6	2.3-2.5			
• With Ash								
Gaston (Fly Ash Scrubber)	2.68	38	62	0	3.4	—	NP	95
German Gypsum (50% Ash)	2.24-2.51	7-12	88-93	—	1.5-1.8	—	NP	91

a W_L = Water content where waste transforms to viscous fluid (moisture content dry basis).

b NP = Nonplastic (ASTM D424-59).

c Cu = Coefficient of uniformity.

Source: [71, 90, 91, 94, 98, 99, 123, 124]

determine specific gravity: the weight and volume of about 40 grams of FGC waste are experimentally measured. The volume is determined by a displacement technique, and the weight is determined by oven-drying and weighing the specimen. In laboratory soils testing, the conventional drying temperature is 105°C. However, calcium sulfate and calcium sulfite salts contain chemically bound water which is driven off by temperatures exceeding 75-80°C [96]. ASTM Specification D2216 states that soils containing large quantities of gypsum should be dried at 60°C. Drying of calcium sulfate at 105°C yields an apparent specific gravity of about 3 (CaSO_4 ; $G_s = 2.96$), while use of the 60°C drying temperature yields the appropriate specific gravity of gypsum solids ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), 2.32.

Grain size analyses of FGC wastes have been performed by a number of investigators [71,19,4,88,90,95,96]. Particles of any one waste tend to be extremely uniform in size and morphology [96]. Studies to date indicate that sulfite wastes resemble in size uniform silts, whereas sulfate wastes resemble in size sandy silts. Coefficients of uniformity (C_u) of wastes (without additives) listed in Table 5.2 are generally less than 2.5, which is indicative of the extremely uniform nature of FGC waste particle size distribution. The coefficient of uniformity is defined as the particle size corresponding to 60% finer by weight divided by the particle size corresponding to 10% finer by weight. The coefficient of uniformity of a waste composed entirely of particles of a single size is 1. Sulfate-rich FGC wastes appear more well-graded (containing many different particle sizes) than sulfite-rich FGC wastes.

Specific gravity values and grain size distributions of various combinations of waste/fly ash and waste/lime/fly ash are also listed in Table 5.2 [71,95]. It should be noted that these mixtures are also generally quite uniform in nature, having C_u values of 1.2-1.3.

5.4.2 Consistency-Water Retention

5.4.2.1 Fly Ash

Fly ash is a non-plastic material; i.e., it is transformed from a semi-solid granular mass to a viscous slurry over a very narrow range in moisture content and exhibits no significant plasticity during this transformation.

Water flow through fly ash occurs more rapidly than through natural soils of similar grain sizes and water retention in fly ash should be equal to or less than water retention in fine sands [70,76,81,82,83]. Thus, most fly ashes are freely-draining materials.

5.4.2.2 FGC Wastes

Consistency is generally defined in terms of stiffness or strength and is a function of water content. The consistency of cohesive soils (clays) is defined in terms of unconfined compressive strength. For a given soil type, as the water content increases, the unconfined compressive strength decreases. Clays possessing unconfined compressive strengths less than $2.4 \times 10^{+4}$ Pa (3.5 psi) are termed "soft," whereas strength values exceeding $1.91 \times 10^{+5}$ Pa (28 psi) indicate "stiff" materials.

Atterburg Limits tests are of great use in soils engineering because the results of these simple tests relate to cohesive soil properties used in design, such as strength and compressibility. That is, Atterburg Limits tests are a measure of consistency. The liquid limit is defined as the value of water content above which a material behaves as a viscous fluid. The plastic limit is defined as the value of water content below which a material behaves as a semi-solid. For values of water content between the liquid limit and plastic limit, a material behaves as a plastic, or remoldable material. The water content of most in-place cohesive soils is such that they exhibit plastic characteristics.

Granular soils, such as sands and silts, are nonplastic in nature; that is, at a certain water content value a granular soil transforms from a friable semi-solid material to a viscous liquid. As mentioned previously, FGC wastes are similar in size to silts and sandy silts. Therefore, it is to be expected that FGC wastes would exhibit little

or no plasticity. As shown in Table 5.2, only one (Paddy's Run) of the several wastes tested exhibited plastic behavior [90]. Liquid limit values are tabulated for other wastes in Table 5.2, but these values indicate water contents at which behavior transforms from that of a semi-solid to that of a viscous liquid.

Liquid limit and plastic limit values are useful only to the extent that they correlate with engineering properties used in design. In this context, Atterburg Limits values apply only to cohesive soils and are not applicable to silts or sands. The relationship of liquid limit and plastic limit values to the compressibility and strength of FGC wastes has not been demonstrated.

5.4.3 Viscosity vs. Water (Solids) Content

5.4.3.1 Fly Ash

The spherical nature of many fly ash particles causes the apparent viscosity of fly ashes to be much lower than that of soils or mineral aggregates of similar grain size. This has led to the widespread use of fly ash in cement grouts to improve penetration of grout into voids in pervious media. Viscosity tests on one fly ash have been done by Coones [84]. In general, fly ash viscosity is lower than the viscosity of other materials at equal solids content and in similar grain size ranges.

5.4.3.2 FGC Wastes

One of the earliest parametric studies of FGC waste viscosity and pumpability was done by the Colorado School of Mines Research Institute (CSMRI) for the Dravo Corporation [92]. The FGC waste slurries studied consisted of a basic composition of FGC waste/fly ash to which additional fly ash, slaked lime, grits and Calcilox were added. The FGC waste/additive slurry contained approximately 30% solids by weight.

Two waste samples labeled "C" and "D" were tested in preliminary studies to determine solids concentrations, specific gravities, viscosities, and pH [92].

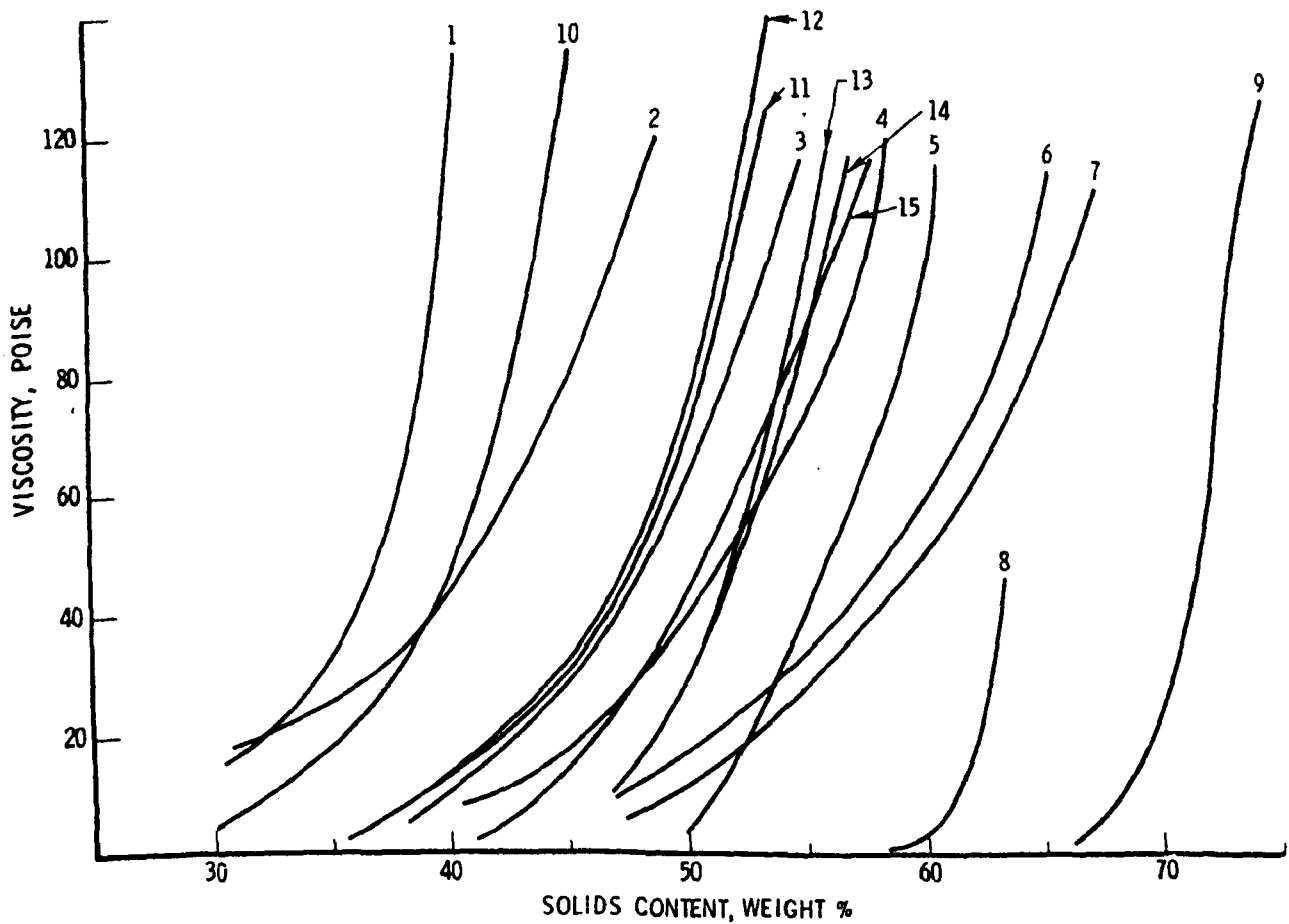
Pipeline loop pumping studies were done on the waste/additive slurry described above using a 6-inch diameter pipe loop. Head loss vs. velocity and relative pipe wear observations were made. Samples were collected from the loop for rheological testing and slurry concentration measurements.

On the basis of these studies, CSMRI concluded that FGC waste slurries are excellent materials for pipeline transport. It was concluded that the wastes studied behaved as nonsettling slurries. A critical velocity was found below which turbulent flow could not be maintained. CSMRI recommended that pipelines be designed to give turbulent flow with values of Reynolds Number greater than 4000. Results of friction head loss tests were inconclusive since slurry weight percent solids varied in the narrow range from 28% to 35%. No significant pipe wear was observed in these tests. Shutdown of the pumping system for 30 to 40 hours did not result in restart problems; slurry solids concentrations of 30% to 40% were measured after this time.

The Aerospace Corporation also conducted a series of viscosity measurements on FGC wastes in an EPA-sponsored study [37]. Viscosity measurements were conducted on nine FGC waste slurries at varying values of water content at room temperature using a commercial viscometer (range, 3 to 150 poise). The results of these viscosity tests are shown in Figure 5.2. The Aerospace Corporation suggested that waste slurries possessing viscosities less than 20 poises could be easily pumped; as shown in Figure 5.2, one waste (curve 9) could be pumped at solids contents of up to 70%, whereas another waste (curve 1) could not be pumped at solids contents exceeding 32%. Results of these tests were too limited to indicate the effects of particle shape, size, and distribution on viscosity; however, it was apparent that the addition of fly ash to waste increases the fluidity of the slurry. Also, high values of pH appeared to increase viscosity.

In a recently completed study done at the University of Louisville by Coones [84], viscosity tests, liquid limit tests, and pipe loop pumping tests were done on a series of sulfite waste, dual alkali FGC waste, sulfate waste, and waste/additive slurries.

Curve	Waste	Fly Ash, %
1	GM Parma Dual Alkali	7.4
2	UPL Gadsby Dual Alkali	8.6
3	TVA Shawnee Lime	40.5
4	DLC Phillips Lime	59.7
5	TVA Shawnee Limestone	20.1
6	TVA Shawnee Limestone	40.1
7	TVA Shawnee Limestone	40.9
8	SCE Mohave Limestone	3.0
9	APS Cholla Limestone	58.7
10	LG&E Paddy's Run Carbide Lime	12.4
11	TVA Shawnee Lime	<1.0
12	TVA Shawnee Limestone	<1.0
13	GPC Scholz Soda Ash Dual Alkali	<1.0
14	GPS Scholz Soda Ash Dual Alkali	30.0
15	TVA Shawnee Lime	40.0



Source: [37]

Figure 5.2 Viscosity of FGC Wastes

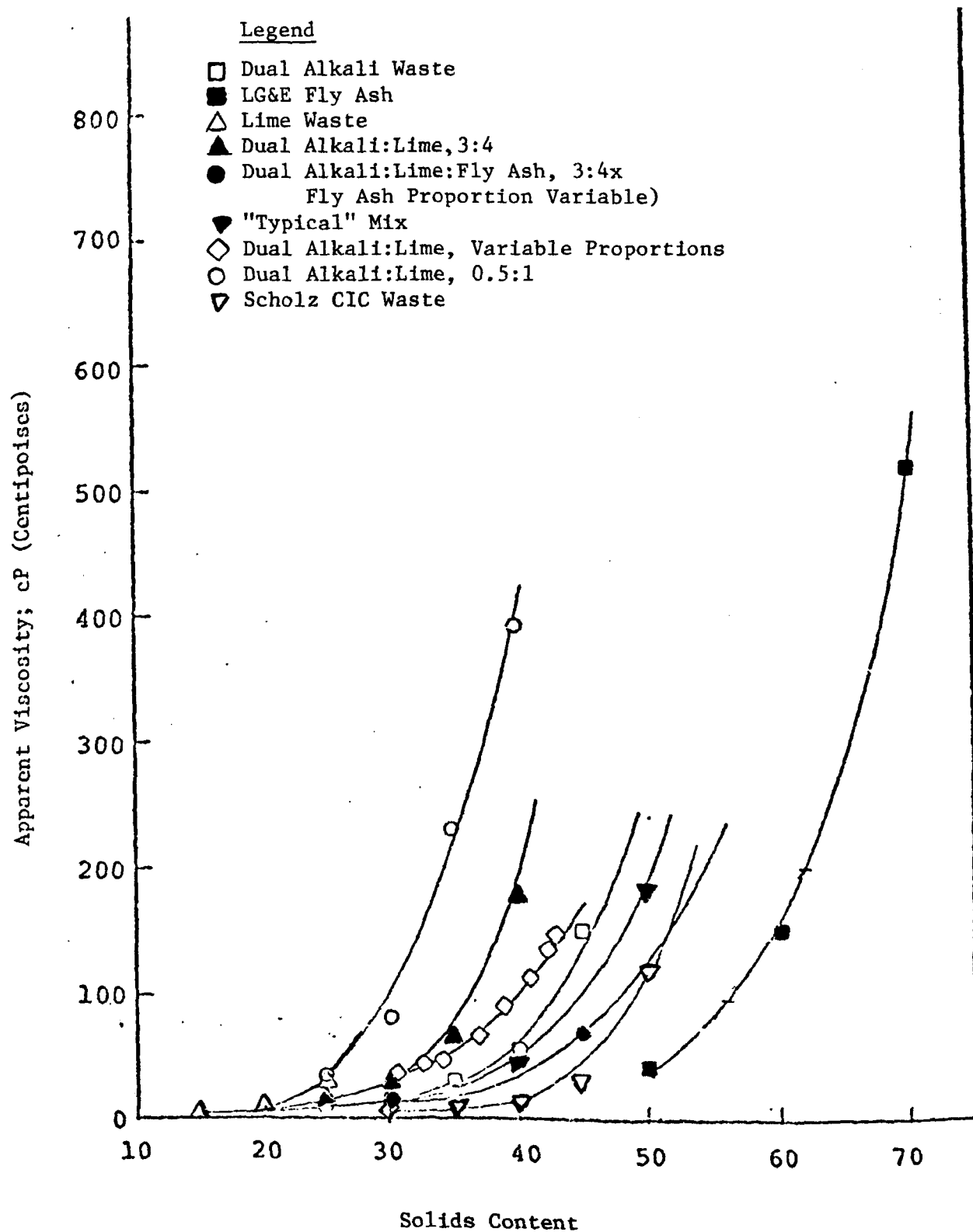
Viscosity tests were done with a Brookfield Synchroelectric viscometer (range, 0 to 100 poise). Slurry water contents were varied so that curves of viscosity vs. percents solids could be plotted. Results of viscosity testing are shown in Figure 5.3. Test results indicated the following:

- 1) Paddy's Run and Cane Run sulfite-rich FGC wastes from direct lime scrubbing have very similar viscosity-solids content relationships;
- 2) The viscosity characteristics of the dual alkali waste tested are very similar to those of the other sulfite wastes; however, the dual alkali waste is less viscous, at a given solids content, than are the other sulfite wastes;
- 3) The Scholz CIC (sulfate) waste is much less viscous, at a given solids content, than either the dual alkali waste or the other sulfite wastes;
- 4) At a given solids content, fly ash is the least viscous of all the materials tested, thus this material could be tested at much higher solids content than the other FGC wastes.

Various mixtures of wastes and additives were also tested; mixtures of dual alkali waste and the other sulfite waste with varying proportions were tested for viscosity. Also, a 3:4 mix of dual alkali waste to sulfite waste was tested; in these tests, the proportion of added fly ash was varied. Results of viscosity tests on waste/waste and waste/additive mixtures are shown in Figure 5.3.

Coones performed liquid limit tests on each of the wastes and waste/additive mixtures tested for viscosity. Atterburg Limits tests were particularly difficult to perform and gave unreliable results. However, a modification of the standard liquid limit test was correlated with viscosity test results. Although this correlation is based on limited data, it does indicate that results of a relatively simple liquid limit test might be used as an index to viscosity.

Additional pipe loop pumping tests were conducted in 1978 at the University of Louisville on sulfite waste/dual alkali waste mixtures and on other sulfite waste/dual alkali waste/fly ash mixtures. From limited results of pumping tests it was concluded that FGC wastes may be pumped at solids contents as great as 60%, as recommended by The Aerospace Corporation [37]. The first pumping tests in this study



Source: [84]

Figure 5.3 Viscosity Versus Solids Content

were done using a relatively slow flow velocity with a high viscosity material. For a material with lower viscosity, pumped at a higher velocity, the mass handling capacity might be very large. Coones also noted that, in his tests, the rate of settling of materials was not high; he suggested that temporary reductions in velocity, which might be expected in a prototype pumping operation, would not greatly affect the flow of material. These tests are being continued using different waste/additive mixtures and pumping velocities.

5.4.4 Compaction/Compression Behavior

5.4.4.1 Fly Ash

Compaction tests yield data on the optimum water content of the waste, which is an important consideration for placing of the waste materials at the maximum density in the disposal site. These properties also influence the degree of settlement, permeability and strength of the material. Laboratory and field compaction data have been reported by a number of investigators [68,70,71,72,82,83]. Typically, as disposed of, fly ash has a bulk dry density of 0.8-1.28 g (50-80 lb) of dry solid per cm³ (ft³) with a mean value of about 0.96 g/cm³ (60 lb/ft³). Field compaction may increase the density to an average of 1.12 g/cm³ (70 lb/ft³) while controlled compaction may increase the average value to 1.2 g/cm³ (75 lb/ft³) [70]. Compaction by vibratory rollers has been shown to be more effective in increasing fly ash density than that by a static pneumatic-tired roller or a sheepfoot roller [68,70]. The optimum moisture content of fly ash ranges between 16-31% with a corresponding maximum dry density of 1.14-1.65 g/cm³ (71-103 lb/ft³) [144]. The corresponding values for bottom ash are 14-25% and 1.17-1.87 g/cm³ (73-117 lb/ft³) [144].

Volume change under load has been reported for fly ash by several investigators but test results tend to be highly site specific [68,70, 82,83,86]. Compacted to 90-95% of Standard Proctor maximum dry density (ASTM D698-70), fly ash has a compressibility similar to that of medium stiff clays [68,70,82]. The dry density of fly ash is lower than compacted natural soils and thus may cause less settlement when placed over soft subsoils of equal fill stiffness.

5.4.4.2 FGC Wastes

The compaction characteristics of some FGC wastes and mixtures of FGC wastes and fly ash and lime are summarized in Table 5.3. This data, obtained using Standard and/or modified Proctor compaction test shows a range of $1.15\text{--}1.36\text{ g/cm}^3$ ($72\text{--}83\text{ lb/ft}^3$) for the maximum dry density of ash-free, sulfite-rich wastes with a median of 1.28 g/cm^3 (80 lb/ft^3). Maximum dry densities for ash-free sulfate wastes are in the $1.12\text{--}1.52\text{ g/cm}^3$ ($70\text{--}95\text{ lb/ft}^3$) range with a median of 1.28 g/cm^3 (80 lb/ft^3). The results of these tests on sulfate-rich materials may not be meaningful since in some tests (not included in Table 5.3), no well defined maxima appeared [90]. The moisture content at the maximum dry density for sulfate wastes has a wider and lower range than the sulfite wastes (13–41% vs. 32–43%). The degree of saturation at the optimum moisture content appears to be lower for the sulfate wastes. The compaction characteristics of mixtures of sulfate and sulfite wastes with fly ash and lime are significantly affected by the particle morphology, grain size distribution and specific gravity of each of the components in the mixture and, thus, the results are highly dependent on the characteristics of the materials used. Generally, however, addition of fly ash to sulfite-rich waste increases maximum dry density while decreasing the moisture content and percent saturation at the maximum dry density (Table 5.3). Addition of lime to the sulfite-rich waste/fly ash mixture generally produces further increases in maximum dry density and further decreases in moisture content and percent saturation at the maximum dry density.

Addition of fly ash to sulfate-rich wastes also generally increases their maximum dry density and decreases their moisture content at the maximum dry density. However, the percent saturation at the maximum dry density is generally not decreased. Repeated impacts on sulfite-rich waste appear to cause progressive breakdown in the waste particles [49,71,99]. The maximum dry density of fresh CEA/ADL waste sample was 1.15 g/cm^3 (72 lb/ft^3) vs. 1.28 g/cm^3 (80 lb/ft^3) for the same sample which was subjected to impacts in a previous Proctor compaction test [71]. The optimum moisture content of the sample was lowered from 33% to 30% by the previous impacts.

Table 5.3

Standard Proctor Moisture-Density Parameters
for Selected FGC Wastes

<u>Waste</u>	<u>Maximum Dry (lb/ft³)</u>	<u>Density (g/cc)</u>	<u>Optimum Moisture Content^a</u>	<u>% Saturation at Optimum Moisture Content</u>	<u>Reference</u>
<u>Sulfite-Rich</u>					
● <u>Without Ash:</u>					
Harrington Station	83	1.33	32%	-	4
Lakeview	85	1.36	35	91%	88
Paddy's Run	80,65	1.28	33,52	88	96,146
Scholz (CEA/ADL)	72,80	1.15-1.25	33,43	69,89	19,71
Range:	65-85	1.15-1.36	33-52	69-91	
Median:	80	1.28	33		
● <u>With Ash:</u> ^b					
Paddy's Run					146
Paddy's Run (50% Ash)	81,92	1.30,1.47	26,29	80,91	71
Paddy's Run (33% Ash)	82	1.31	32	86	71
Scholz (CEA/ADL, 50% Ash)	86	1.38	27	89	71
Scholz (CEA/ADL, 33% Ash)	93	1.49	23	79	71
Will County	87	1.39	29	-	146
Range:	81-93	1.30-1.49	23-32	79-91	
● <u>With Ash and Lime:</u>					
Paddy's Run (50% Ash, 5% Lime)	93,93	1.49,1.49	25	81,82	71
Paddy's Run (50% Ash, 10% Lime)	94	1.50	25	85	71
Scholz (CEA/ADL, 50% Ash, 5% Lime)	92,92	1.49,1.49	23,24	73,77	95
Scholz (CEA/ADL, 50% Ash, 10% Lime)	91	1.46	25	79	95
Range:	91-94	1.46-1.50	23-25	73-85	

Table 5.3 (Continued)

Standard Proctor Moisture-Density Parameters
for Selected FGC Wastes

<u>Waste</u>	<u>Maximum Dry (lb/ft³)</u>	<u>Density (g/cc)</u>	<u>Optimum Moisture Content^a</u>	<u>% Saturation at Optimum Moisture Content</u>	<u>Reference</u>
<u>Sulfate-Rich</u>					
● <u>Without Ash:</u>					
Shawnee (Forced Oxide)	82	1.32	32	-	146
Scholz (CIC)	95	1.52	13	56	96
Dual Alkali Gypsum (ADL Pilot Plant)	79	1.26	33	89	19
Range:	79-95	1.26-1.52	13-33		
● <u>With Ash:</u>					
Milton R. Young	78-82	1.26-1.32	35-41	-	89
Gypsum (Fly Ash Scrubber)	86,97,103	1.38-1.64	23	80	96
Gypsum (Fly Ash Scrubber)	97,103	1.55,1.64	14,17	64,72	96
Gaston (50% Ash)	78,89	1.25,1.42	28,25	73,81	71
Gaston (33% Ash)	83	1.33	31	85	71
Four Corners	76	1.25	24	-	146
Range:	76-103	1.12-1.55	14-41	64-85	
Median:	86	1.38			

^a Grams of water per gram of dry solid x100.^b Not aged

Very little information is available on field compaction behavior of FGC wastes. The limited data available from Scholz on the effect of four, eight or twelve passes of a rubber-tired roller on mixtures of waste and fly ash (1:0.75 ratio) and waste, fly ash and lime mixture (1:0.75:0.02 ratio) have indicated no substantial difference in the dry density of the materials after the various roller passes. There are no data available to attempt to correlate field and laboratory moisture-density relationships.

The compression indices determined at various consolidation loads of a variety of wastes and waste, fly ash and lime mixtures are shown in Table 5.4 [93,95,96]. The compression index of sulfite-rich wastes depends to a great extent on their water content and degree of compaction with materials compacted to their optimum moisture content having the lowest values. Sulfate wastes are much less compressible, due in part to the different particle morphology, and the compression index is much less dependent on the water content.

Decrease of the moisture content by addition of a dry filler (e.g., fly ash) to sulfite wastes results in a decrease in compressibility with the most dramatic effect occurring with fly ash added to the sulfite waste containing the greatest initial water content. Addition of a small amount of lime to the sulfite waste and ash mixtures causes no appreciable change in compressibility in the absence of the pozzolanic reaction (unaged conditions, Table 5.3). Allowing the samples to cure for 28 days generally leads to materials which are much less compressible approaching those properties observed for the sulfate waste.

5.4.5 Dewatering Characteristics

The dewatering properties, like most physical properties, are primarily a function of the crystalline morphology and distribution of crystalline phases and the particle size distributions. These, in turn, are principally dependent upon the type of FGD system (and alkali used), the calcium sulfite to sulfate ratio in the waste, and the amount of fly ash and unreacted alkali present.

Table 5.4

Compression Indices for Some FGC Wastes

WASTE	INITIAL WATER CONTENT, %	% SOLIDS	COMPRESSION INDEX			
			STRESS RANGE	2.4-4.8 (3.5-7)	9.6-24 (14-35)	48-91 (x10 ⁴ Pa) (70-140 psi)
SULFITE-RICH						
• Without Ash						
Paddy's Run	200	33%		0.3	0.85	1.21
Paddy's Run	315 (123-60)	24 (45-63)		0.72	1.12	1.21 0.84d 0.66d
Paddy's Run	31c	76c		0.04	0.08	0.16
Scholz (CEA/ADL)	86	54		0.12	0.26	0.58
Scholz (CEA/ADL)	27	79		0.02	0.06	0.10
Lime Scrubber	135	43		0.3	0.85	1.15
• With Ash						
Paddy's Run (50% Ash)	90	53		0.18	0.37	0.62
Paddy's Run (50% Ash)	128	44		0.26	0.50	0.72
Paddy's Run (50% Ash)	25c	80		0.02	0.05	0.11
Will County	32	76				0.14d
• With Ash and Lime (Uncured)						
Paddy's Run (50% Ash, 5% Lime)	77-80	56	0.13-0.17	0.43-0.48	0.77-0.87	
Scholz (CEA/ADL, 50% Ash, 5% Lime)	53-54	65	0.10-0.23	0.33-0.48	0.73-0.70	
• With Ash and Lime (Aged 28 days Under Light Consolidation Pressure)						
Paddy's Run (50% Ash, 5% Lime)	77	56	0.13	0.43	0.83	
Scholz (CEA/ADL) 50% Ash, 5% Lime)	53-54	65	0-0.1	0.08-0.33	0.57-0.70	
Lime Scrubber	110	48	0.01	0.02	0.04	
SULFATE-RICH						
• Without Ash						
Shawnee (Forced Oxid)	40	71	0.01	0.06	0.04d	
Scholz (CIC)	33	75	0.02	0.01	0.12	
Scholz (CIC)	14	88	--		0.03	
• With Ash						
Four Corners	45	69	--		0.17d	
Four Corners	33	75	--		0.06d	

a Water added to simulate filter coke moisture.

b Water added to simulate thicker underflow moisture.

c Compacted at optimum moisture content (Proctor).

d 3.2 - 6.4 tons/ft² range

Source: [93, 95, 96, 146].

While much of the research and characterization work performed to date on wastes from FGC systems has not focused on dewatering, some data are available from pilot and prototype testing [19,49,55,56,125,126] and full-scale operations [18,123,124,127-133]. A few studies have also been undertaken sponsored by EPA and EPRI to characterize waste dewaterability [1,37,135] and improve dewatering performance [134].

In general, sulfite-rich wastes do not dewater as readily as sulfate-rich wastes. Sulfite-rich wastes typically can be thickened in conventional open-tank thickener/clarifiers to 20-45% solids and filtered to 40-70% solids. Sulfate-rich wastes, on the other hand, typically can be thickened to 40-60% solids and filtered to 65-90% solids. The presence of fly ash and unreacted alkali (especially limestone) can also affect dewatering. The presence of these materials can improve the dewaterability of wastes with initially relatively poor dewatering properties; however, unreacted alkali and fly ash may even decrease dewaterability for waste with inherently good dewatering properties.

A more detailed discussion of waste dewatering characteristics and a review of studies on waste dewatering are provided in Section 2.4.

5.4.6 Strength Parameters

5.4.6.1 Fly Ash

Unconfined compressive strength measurements of cohesive wastes and triaxial shear tests of cohesionless wastes are useful in determining load bearing capacity of these materials. The shear strength of fly ash depends to a great extent on its density. The angle of internal friction, a measure of the shear strength, typically ranges from 28° to 38° as the density goes from 0.8 g/cm³ (50 lb/ft³) to 75 g/cm³ (75 lb/ft³) [70]. Aged fly ash may exhibit a great deal of cohesion due to pozzolanic cementation [68,70,82,83,85]. Angle of internal friction may increase to as much as 43° and cohesion to more than 6.9×10^5 Pa (100 psi) [68,70,85]. The extent of cementation depends on the lime content and surface area and is affected detrimentally by unburned carbon. Pozzolanic potential of fly ash can be determined by adding water (and/or lime) and measuring strength parameters of the final cured product.

5.4.6.2 FGC Wastes

Unconfined and triaxial compression tests on FGC wastes without additives have been performed by various investigators [4,19,88,89,98,104-106]. Both sulfite- and sulfate-rich wastes resemble micaceous silts and very fine sands in shearing behavior and possess insignificant (~ 0 Pa, ~ 0 psi) effective cohesion and angles of internal friction of from 25° to 35° (Table 5.6). If these wastes are compacted to their maximum dry density (Proctor compaction) and dried, unconfined compression strengths on the order of $7-14 \times 10^4$ Pa (10-20 psi) are observed. Liquefaction upon vibration has also been observed for a sulfite-rich waste [27,43]. The values of the unconfined compression strength are sensitive to changes in moisture content and, depending on the waste, age of the waste [89,104].

Shear strength parameters for uncured wastes, fly ash and lime mixtures are shown in Table 5.5. Addition of fly ash and lime generally results in an increase in shear strength for sulfite-rich wastes derived both from an increase in the angle of internal friction and in the effective cohesion. Effective cohesion increases from zero to $2-11 \times 10^4$ Pa (2.4-15.3 psi).

Unconfined compression strength values for uncured and cured sulfite-rich wastes, fly ash and lime mixtures are given in Table 5.6. These results illustrate the substantial gain in strength of the waste/additive mixtures upon curing. Increases in strength of $9-24 \times 10^4$ Pa (10-34 psi) are observed. Addition of only lime to these ash-free sulfite wastes produces no time-dependent increase in strength.

The effect of admixing various additives with sulfite-rich and fly ash waste mixtures is shown in Table 5.7. Addition of only soil to the sulfite waste does not significantly alter its strength initially, but a gain in strength is observed over a period of time. Addition of soil and fly ash to sulfite waste produces the same effect but with a marked increase in strength with time. Addition of cement to sulfite waste causes an increase of strength with time with highest strengths obtained for highest percentage of cement added. The strength obtained for cement,

Table 5.5

Shear Strength Parameters of FGC Wastes

<u>Waste</u>	<u>Angle of Internal Friction, ϕ</u>	<u>Effective Cohesion, C</u>	
		(10 ⁺⁵ Pa)	(lb/in ²)
<u>Sulfite-Rich</u>			
● <u>Without Ash:</u>			
Paddy's Run	30.5°	0.3	4.6
Scholz (CEA/ADL)	36	0	0
● <u>With Ash:</u>			
Paddy's Run (50% Ash)	35,32	0.2,0.6	2.4,8.3
Paddy's Run (33% Ash)	33	0.6	8.3
Scholz (CEA/ADL, 50% Ash)	36,33	0.3,0.7	4.9,10.7
Scholz (CEA/ADL, 33% Ash)	36	0.8	11.1
● <u>With Ash and Lime:</u>			
Paddy's Run (50% Ash, 5% Lime) ^a	31,35	0.5,0.3	7.6,4.3
Scholtz (50% Ash, 5% Lime) ^a	35	0.6	7.9
Elrama (IVCS Process) ^b	0	1.2	1.6
<u>Sulfate-Rich</u>			
● <u>Without Ash:</u>			
Scholz (CIC)	42	0	0
● <u>With Ash Added:</u>			
Gypsum (Fly Ash Scrubber, 50% Ash)	32,37	1.1,0	15.3,0
Gypsum (Fly Ash Scrubber, 33% Ash)	35	0.8	10.9

^a Uncured^b Cured

Source: [71,95,98]

Table 5.6

Unconfined Compressive Strength Values as a
Function of Time for Some FGC Wastes

<u>Waste</u>	Water Content %	Strength (10^5 Pa)			(lb/in ²)		
		0	7	28	0	7	28 days
<u>Sulfite-Rich</u> ^a							
● <u>With Lime</u>							
Paddy's Run (10% Lime)	94-98	0.16	0.16	0.44	2.4	2.3	6.4
Scholz (CEA/ADL, 10% Lime)	61-62	0.2	0.2	0.2	3.6	3.2	3.1
● <u>With Lime and Fly Ash</u>							
Paddy's Run (50% Ash, 5% Lime)	70	0.05	0.27	0.94	0.8	3.9	13.8
Paddy's Run (50% Ash, 10% Lime)	68	0.22	0.19	1.43	3.2	2.8	21.0
Scholz (CEA/ADL, 50% Ash, 5% Lime)	-	0.4	0.4	1.5	6.1	6.4	21.6
Scholz (CEA/ADL, 50% Ash, 10% Lime)	50-52	0.4	0.5	2.8	6.7	7.4	41.5

^a FGC wastes without any additives generally flow as viscous fluids and thus do not have sufficient consistency for an unconfined compression test.

Source: [95]

Table 5.7

Strength Parameters for FGC Wastes

WASTE CATEGORY	Strength ^d (x 10 ⁺⁵ Pa)				Strength (psi)			
	0	Cure Time		>28 Days	0	Cure Time		>28 Days
(Sulfite-Rich Wastes)		7	14			7	14	
• Without Additives								
Double Alkali (Pilot Plant)				0.7-1.0				10-15
Limestone		1.5			22			
• With Fly Ash ^a								
Limestone (20-66% Ash)	1.0-1.8				14-16			
Limestone (40-50% Ash)		0.7-2	1.3-1.4	1.3-1.6	10-29	19-20		19-23
• With Fly Ash and Lime								
Limestone (Shawnee, IUCS)								410-510 ^e
Limestone (Elrama, IUCS)								43 ^f
• With Fly Ash and Soil ^b								
Limestone (20% Ash, 50-80% Soil)		1.5-2.5		>4.6-7.1	18-36			>62-96
• With Fly Ash and Cement ^c								
Limestone (30-50% Ash, 7-22% Cement)		2-18	7.33	6-57	29-257	100-473		93-814
Double Alkali (50% Ash, 33% Cement)				12-17				165-244
• With Soil								
Limestone (50-80% Soil)		1.2-1.8		1.1-3.5	17-26			16-52
• With Cement								
Limestone (7-15% Cement)		1.1-1.9	2.5-3.0	4.6-5.2	16-27	34-44		62-72
• With Additive								
Limestone (Shawnee, Calcilox)								26-33 ^e
Limestone (Bruce Mansfield, Calcilox)								6 ^f
Limestone (Shawnee, Chemfix)								24-260 ^e

^a Ash Source

^b Soil is gravelly, silty clay

^c Cement is Portland cement

^d Unconfined strength

^e Field data

^f Cured in tap water

Source: [4, 19, 24, 27, 37, 88, 96]

fly ash and waste mixtures after curing 28 days suggest that at higher fly ash ratios cement may be more effective than lime in producing increased strengths.

Limited comparison of laboratory and field strength data has been performed. Field vane shear tests and continuous sampling were done on ten waste-additive mixtures contained in 15 impoundments (5 pits and 10 pools) at Cane Run Station (LG&E). Laboratory permeability and unconfined compression tests were done on samples obtained from the field. In general, it was found from the vane shear measurements that undrained compressive strength increased with time for all impoundments, and that measured strength values of commercial lime wastes were much higher than those of carbide lime wastes. Average vane shear strength values determined at various times after placement are listed in Table 5.8 for carbide lime wastes and in Table 5.9 for commercial lime wastes. These values are considered representative of in-situ shear strength. In other cases laboratory unconfined compressive strength tests done on field samples yielded strength values less than 50% of vane shear strength values. The reason for the differences between vane shear measurements and laboratory unconfined compressive strength values was sample disturbance. Sample disturbance was severe for frozen waste samples and for frozen-thawed materials in the summer because the mixture structure was brittle and sensitive. Many samples were found to be friable and others contained numerous voids and discontinuities. Thus it was felt that vane shear strength values were better indicators of in-situ shear strength than were laboratory unconfined compressive strength values.

Unconfined compressive strength values have been reported for laboratory-prepared samples of waste/additive mixtures identical to those contained in the LG&E field impoundments [101]. The unconfined compressive strength values reported in this reference are for intact samples cured 60 days under saturated conditions. These values are also listed in Tables 5.8 and 5.9. Comparison of strength values of laboratory-prepared samples with strength values measured in-situ

Table 5.8

Shear Strength and Permeability Values
Waste-Carbide Lime-Fly Ash Impoundments

Mix ^a	Impoundments	Undrained Compressive Strength (In-Situ Vane Shear Measurements)				Laboratory Permeability of Field Specimens	Unconfined Compressive Strength (Laboratory-Prepared Specimens)
		0-Days	30-Days	90-Days	180-Days		
0.5 Waste: 0.5 Fly Ash + 5% Carbide Lime	Pit #1	Negl.	0.3×10^5 Pa (4.2 psi)	0.3×10^5 Pa (4.2 psi)	0.5×10^5 Pa (7 psi)	3×10^{-5} cm/sec	Negl.
	Pool #1	Negl.	Negl.	--	--	--	Negl.
0.5 Waste: 0.5 Fly Ash + 5% Carbide Lime	Pit #2	0.5×10^5 Pa (7 psi)	0.7×10^5 Pa (10.4 psi)	0.7×10^5 Pa	0.9×10^5 Pa (13.9 psi)	7×10^{-6} cm/sec	7.8×10^5 Pa (114 psi)
	Pool #3	0.4×10^5 Pa (5.5 psi)	2.4×10^5 Pa (34.7 psi)	2.8×10^5 Pa (41.7 psi)	$> 2.8 \times 10^5$ Pa (> 42 psi)	7×10^{-6} cm/sec	7.8×10^5 Pa (114 psi)
Waste + 5% Carbide Lime	Pool #2	0.6×10^5 Pa (8.3 psi)	0.7×10^5 Pa (10.4 psi)	1.4×10^5 Pa (20.8 psi)	0.9×10^5 Pa (13.9 psi)	1×10^{-5} cm/sec	4.0×10^5 Pa (57 psi)
0.5 Waste: 0.5 Fly Ash + 3% Carbide Lime	Pool #4	0.7×10^5 Pa (10.4 psi)	23×10^5 Pa (33.3 psi)	0.1×10^5 Pa (1.4 psi)	0.2×10^5 Pa (2.8 psi)	2×10^{-5} cm/sec	2.4×10^5 Pa (349 psi)

^aWaste is a product of a lime process using carbide lime.

Source: [10]

Table 5.9

Shear Strength and Permeability Values
Waste-Commercial Lime-Fly Ash Impoundments

Mix ^a	Impoundments	Undrained Compressive Strength (In-Situ Vane Shear Measurements)		Laboratory Permeability of Field Specimens	Unconfined Compressive Strength (Laboratory-Prepared Specimens)	
		0-Days	30-Days			
Waste + 0.5 Fly Ash + 3% CaO	Pit #3	0.4x10 ⁵ Pa (7 psi)	>2.8x10 ⁵ Pa (>42 psi)	3x10 ⁻⁶ cm/sec	6.9x10 ⁵ Pa	(100 psi)
	Pool #6	0.9x10 ⁵ Pa (1.4 psi)	>2.8x10 ⁵ Pa (>42 psi)	--	6.9x10 ⁵ Pa	(100 psi)
0.5 Waste: 0.5 Fly Ash + 3% Ca(OH) ₂	Pit #4	1.9x10 ⁵ Pa (27.8 psi)	>2.8x10 ⁵ Pa (>42 psi)	--	12.9x10 ⁵ Pa	(190 psi)
	Pool #8	1.9x10 ⁵ Pa (27.8 psi)	>2.8x10 ⁵ Pa (>42 psi)	3x10 ⁻⁶ cm/sec	12.9x10 ⁵ Pa	(190 psi)
0.5 Waste: 0.5 Fly Ash + 3% CaO	Pit #5	>2.8x10 ⁵ Pa (>42 psi)	>2.8x10 ⁵ Pa (>42 psi)	5x10 ⁻⁶ cm/sec	8.0x10 ⁵ Pa	(118 psi)
	Pool #7	0.4x10 ⁵ Pa (7 psi)	>2.8x10 ⁵ Pa (>42 psi)	8x10 ⁻⁶ cm/sec	8.0x10 ⁵ Pa	(118 psi)
0.5 Waste: 0.75 Fly Ash + 3% CaO	Pool #5	0.6x10 ⁵ Pa (8.3 psi)	>2.8x10 ⁵ Pa (>42 psi)	5x10 ⁻⁶ cm/sec	11.8x10 ⁵ Pa	(174 psi)
0.5 Waste + 0.5 Fly Ash + 3% Portland cement	Pool #9	2.8x10 ⁵ Pa (42 psi)	>2.8x10 ⁵ Pa (>42 psi)	--	5.1x10 ⁵ Pa	(75 psi)
0.5 Waste + 0.5 Fly Ash	Pool #10	0.7x10 ⁵ Pa (9.7 psi)	>2.8x10 ⁵ Pa (>42 psi)	--	2.8x10 ⁵ Pa	(42 psi)

^aWaste is a product of a lime process using carbide lime.

Source: [10]

indicates that unfavorable curing conditions in the field and field placement procedures have resulted in in-situ strength values much lower than those expected on the basis of tests done on laboratory-prepared samples.

As previously noted, the cohesionless granular nature of FGC wastes is similar to the character of fine sands and nonplastic silts. Such materials may be affected by vibrations. If silty or sandy soils in a loose (low density) condition are subjected to vibratory loading of appropriate intensity and frequency, they will tend to densify, particularly if they are characterized by a uniform particle size distribution. If the silt/sand is saturated the tendency for volume decrease creates positive pressure in the water between particles. The positive water pressure decreases the contact pressure between particles; a "buoyant" effect is created. Since the strength of the material (resistance to distortion) is due to interparticle forces, including friction, the mass of particles temporarily loses stability. The unstable mass may flow like a liquid; this behavior is known as liquefaction. Generally, excess water is expelled and a denser, more stable structure is produced, although this effect may be localized in a liquefaction zone.

Several investigators, including Crowe of TVA [102], Edwards of Southern Services, Inc. [99], and Twin City Testing [89] have reported instances of instability of FGC wastes subjected to vibrations. However, disposal of sulfate (gypsum) slurries (from other industries, not flue gas cleaning) on land in deposits many feet high has been done for years with no instability.

To resolve this paradox, a series of tests [36] were carried out in which model embankments of FGC wastes were subjected to vibratory loading. A dual alkali process waste and a lime process waste were tested. The model embankment was approximately 10 centimeters high by 90 centimeters long, with a base width of 64 centimeters and a crest width of 21 centimeters (side slope angles of 25°). These dimensions were chosen to yield a shape stable under static loading. The models were prepared by compacting the waste in layers about 1 centimeter thick, with a

compaction energy about 20% of Standard Proctor compaction. Models were prepared at solids contents bracketing the optimum solids content determined from compaction tests. Horizontal vibratory motion of the models was achieved by use of a shake table. The amplitudes and frequencies used were characteristic of ground motions caused by earthquakes, blasting, or similar disturbances. All of the results of the tests cannot be given here. In brief, dual alkali process waste behaved as a brittle material if compacted at solids contents of 75% or greater. Frequencies of 15 Hz or greater and accelerations of 1.5g or more were required to fail models of such material. However, the models compacted at 70% solids content developed failure planes after several seconds shaking at a frequency of 1 Hz; 7.5 Hz induced slumping and 10 Hz caused flow of material. For comparison, a lime process waste model compacted at 51% solids content failed completely by flow after only a few cycles of motion at 10 Hz. Since the models were not saturated, cessation of shaking caused cessation of slumping or flow. Saturated material may continue to flow after external disturbance ceases.

These results indicate the need for conducting further tests on the susceptibility of FGC wastes to vibrational instability. The results may not be as pertinent to the assessment of stability in existing gypsum waste fills because such fills almost always exhibit a significant degree of cementation between grains. This cementation is believed to be caused by the migration of saturated leachate down through the fills with deposition of secondary gypsum between grains in the lower portions of the fill. It appears to be worthwhile, however, to evaluate the dynamic behavior of fills of sulfate-rich wastes which are placed by dumping after filtration rather than in a slurry as is done in most existing waste gypsum disposal operations.

The loss of strength under vibration shown by FGC wastes has led some investigators to state that these wastes are thixotropic. A truly thixotropic material would soften and flow under finger pressure. FGD wastes, when tested for thixotropic behavior by placing a nearly saturated sample in a small dish and tapping the dish lightly on a table, release excess water which appears atop of the densified sludge, and when a finger groove is made in the waste, the material behaves as a stiff mass and breaks

apart. Renewed tapping of the dish containing the waste which has been broken apart causes the waste to flow again and close the groove left by the finger. Extensive testing of FGC wastes has produced no evidence of true thixotropic behavior or a tendency to "rewet." FGC wastes liquefy under vibration repeatedly only as long as sufficient water exists in the waste mass for the creation of positive water pressure and consequent loss of strength. Drainage of excess water during vibration will prevent or greatly diminish liquefaction potential for subsequent vibratory loading.

5.4.7 Permeability

5.4.7.1 Fly Ash

The mass permeability of fly ash deposits has been studied by several investigators [70,82,83]. Typically, values of coefficient of permeability range from 5×10^{-5} cm/sec to 5×10^{-4} cm/sec. Field permeabilities may be higher (10^{-4} cm/sec) than laboratory values (10^{-5} cm/sec) because of compaction problems [83]. Laboratory tests have shown that treatment with lime is effective in reducing fly ash permeability to values which depend highly on the treatment conditions [82].

5.4.7.2 FGC Wastes

Permeability tests have been performed on FGC wastes and mixtures of wastes and additives by a number of investigators [19,37,88,98,100,145]. The coefficient of permeability for particulate materials (such as natural soils) varies in magnitude more than any other engineering property. For example, a sand with no fine particles may have a coefficient of permeability of 0.01 cm/sec, while a clay may have a coefficient of permeability as low as 10^{-11} cm/sec (one billionth of the value for the sand). The permeability of material samples tested in the laboratory is extremely sensitive to sample disturbance. Also, passage of water around a sample in a laboratory permeameter is a common source of erroneous data. Finally, because of sample disturbance, stratification of deposits, and short-circuiting of water around low-permeability soils in permeameters, laboratory values of coefficient of permeability may not relate to field permeability. For these reasons, permeability determinations should be made by several methods on samples with minimal disturbance, and should be complemented with field determinations of mass permeability. However, available data can be summarized.

with minimal disturbance, and should be complemented with field determinations of mass permeability. However, available data can be summarized.

The Aerospace Corporation [37] measured laboratory permeability values for seven unstabilized FGC waste samples. Laboratory permeability values were also measured for four FGC wastes stabilized by one or more of three commercial fixation processes. Results of these tests indicate that the coefficient of permeability of unstabilized FGC wastes generally falls in the range of 2×10^{-4} to 1×10^{-5} cm/sec. Similar permeability values were obtained for samples of crushed stabilized wastes. However, permeability values for intact samples of stabilized wastes were two or more orders of magnitude smaller than those of unstabilized FGC wastes.

The U.S. Army Corps of Engineers-Waterways Experiment Station (WES) has conducted a laboratory physical characterization study of five FGC waste samples [100,142]. Unstabilized wastes and wastes stabilized by use of five procedures were tested for permeability. In general, permeability values of unstabilized wastes were in the range of 1×10^{-4} cm/sec to 1×10^{-5} cm/sec. Permeability values of stabilized wastes were, in many cases, several orders of magnitude lower than those of unstabilized wastes.

The results of a number of laboratory permeability tests on FGC wastes are shown in Table 5.10. In some instances, the investigators did not describe the test method they used, but in most cases, the data in this table were derived from falling-head permeability tests. The influence of waste composition and morphology is evident from a comparison of the values of permeability for the various classes of wastes.

In general, sulfite wastes are less permeable than sulfate wastes although close control of gypsum formation in a dual alkali plant may yield a low permeability FGC waste. Addition of stabilization additives such as fly ash and cement reduce the total waste permeability by about 50%. However, a much more pronounced decrease in permeability was found for increases in solids contents of the wastes; for example, the addition of only fly ash may produce a decrease in permeability proportional to

Table 5.10

Coefficients of Permeability for FGC Wastes

WASTE CATEGORYSULFITE-RICH

	<u>% Solids^a</u>	<u>Permeability Coefficient (cm/sec)</u>
• Without Ash		
Lake View (Ontario Hydro)	77	9×10^{-6}
Paddy's Run	52	8×10^{-6}
Scholz (CEA/ADL)	63	4×10^{-5}
Range:		$(0.9-4) \times 10^{-5}$
• With Ash		
Bruce Mansfield	59	2×10^{-5}
Elrama	50	7.5×10^{-6}
Lake View (Ontario Hydro) -65% Ash	79	7.2×10^{-6}
Paddy's Run -50% Ash	63	1×10^{-5}
Phillips	--	$.74-1.2 \times 10^{-4}$
Mohave	--	$1.6-5.0 \times 10^{-4}$
Range:		$(.07-5.0) \times 10^{-4}$
• With Additive		
Bruce Mansfield + Calcilox (Dravo) ^c	47	1.8×10^{-5}
Lake View (Ontario Hydro) -39% Ash, 5% Cement	75	4.0×10^{-6}
Shawnee + Calcilox (Dravo)	--	$3.8-14.0 \times 10^{-5b}$
Range:		$(.4-14.0) \times 10^{-5}$
• With Ash and Lime (Cured)		
Elrama (IUCS Stabilization) ^c	58	3×10^{-5}
Shawnee (IUCS Stabilization)	--	$.5-55.0 \times 10^{-7b}$
Range:		$(.5-300) \times 10^{-7}$

SULFATE-RICH

• Without Ash		
Scholz (CIC)	82	5×10^{-5}
Cholla	--	$1.1-2.7 \times 10^{-5}$
Gadsby	--	$1.2-9.8 \times 10^{-4}$
Shawnee (Forced Oxidation)	--	$.59-2.3 \times 10^{-4}$
Range:		$(0.1-9.8) \times 10^{-4}$

^a % solids by weight for saturated waste.^b Cured in the field.^c Cured in the presence of tap water.

Source: [19, 37, 88, 98, 145]

the resultant decrease in the square of the void ratio. Thacker [98] also reported substantial decreases in permeability with increasing values of solids content. As an example, the permeability of Paddy's Run waste decreased from 1×10^{-5} cm/sec to 5×10^{-6} cm/sec as the solids content increased from 50% to 55%.

Laboratory permeability tests have been performed by the University of Louisville on samples of direct-lime FGC waste obtained from field impoundments at the Louisville Gas and Electric Company Cane Run Station and those results have been shown in Tables 5.8 and 5.9. Pits 1 and 2 and Pools 1 through 4 contained waste/additive mixtures utilizing carbide lime; Pits 3 through 5 and Pools 5 through 8 contained mixtures utilizing commercial lime additives. Field vane shear testing and continuous sampling of each impoundment were done on a schedule of 0-days, 30-days, 60-days, 180-days and 360-days after filling.

Laboratory permeability tests were performed on waste/additive samples obtained from field impoundments by the falling-head technique (ASTM D2434). Results of permeability tests were quite variable, mainly because of sample characteristics. Many of the impounded FGC waste/additive mixtures exhibited distinct layering due to incomplete mixing. In addition, many samples contained numerous voids and discontinuities due to the compaction procedures used in placement. Non-homogeneity of FGC waste/additive mixtures placed in impoundments was encountered as a result of freezing and thawing and because of interruptions in the filling operations. Finally, sample disturbance was inevitable and severe when frozen FGC waste was sampled; brittle frozen-thawed materials were also particularly sensitive to sampling. Therefore, because of these circumstances, changes in field permeability due to curing were masked by sample variability. However, average permeability values are given for the various impoundments in Tables 5.8 and 5.9; these values reflect estimates of the maximum in-situ permeability as determined in laboratory tests performed on disturbed samples. It is noteworthy that maximum permeability values range between 3×10^{-6} cm/sec and 3×10^{-5} cm/sec. In-situ values of permeability may be determined by multiple well pumping tests. Field permeabilities are probably an order of magnitude lower than maximum values given in Tables 5.8 and 5.9.

Permeability tests were performed by Combustion Engineering on intact, laboratory-prepared samples of waste/additive mixtures identical to those contained in the LG&E field impoundments, [101]. FGC waste mixtures were cured under saturated conditions before permeability testing. The permeability values of samples of the various mixtures were determined by the falling-head technique. Results of these tests indicate values of permeability between 2×10^{-7} cm/sec and 8×10^{-5} cm/sec. Comparison of permeability values determined on laboratory-prepared samples with results of permeability tests done on field samples reveal that field sample values were from one-half to two orders of magnitude greater than those of laboratory-prepared samples.

IUCS [26,107] has reported permeability values of 10^{-6} and 10^{-8} cm/sec for an anonymous FGC waste-lime-fly ash admixture. The samples studied reportedly exhibited unconfined compressive strength values of $(12 - 23) \times 10^5$ Pa (180-344 psi). Triaxial compression tests yielded cohesion values of $(0.72 - 23.9) \times 10^5$ Pa (10.4-347 psi) and an angle of internal friction of $>40^\circ$.

Some indications have been seen in field studies at the Louisville Gas and Electric Company Cane Run Plant that physical blinding may occur at the contact zone between FGC waste and soil layers. Apparently, fine sludge particles are carried into voids between soil grains to form a zone of very low permeability. The importance of such action cannot be evaluated on the basis of the limited data currently available.

Further laboratory determinations of waste permeability are needed and such determinations must be correlated with field determinations of mass permeability.

Permeability measurements in addition to all of the physical properties described in previous sections are planned for Milton R. Young Plant (fly ash scrubbing) wastes by the University of North Dakota for the EPA as part of their evaluation of disposal of this high alkalinity fly ash in a decoaled mine seam.

5.4.8 Weathering

5.4.8.1 Fly Ash

Very little attention has been given to the effects of weathering (freeze-thaw cycles and/or wet-dry cycles) on fly ash durability because

the individual grains are highly durable, disposal practices do not rely on cohesion or cementation between grains, and, when fly ash is used as a material filler, weather effects are more severe on the material matrix rather than the filler. Durability of fly ash-stabilized soils [72] and other media has been investigated because of the frost susceptibility [76] of the fly ash (uniform, silt-size grains), and durability of waste-fly ash mixtures should be investigated.

Because of its texture (uniform size spherical grains), fly ash is readily eroded by water and/or wind [68,86]. Fugitive dust emissions and surface erosion by water are problems in fly ash disposal areas, particularly in dried sections of disposal ponds.

5.4.8.2 FGC Wastes

Another area of research which has received little consideration is weather effects on the physical properties of deposits of waste and/or waste plus additives. Of particular interest are the effects of freeze-thaw cycles and wet-dry cycles. Freezing of wastes and waste-additive mixtures soon after placement is certain to occur if land disposal of FGC wastes is continued year-round in many parts of the United States. Freezing has been demonstrated to be of some significance in dewatering of wastes placed in lagoons and ponds (e.g., water treatment wastes). Field studies at the Louisville Gas and Electric Company Cane Run Plant have indicated that freezing may cause dewatering of wastes to some extent (after subsequent thawing), but freezing also produced layering in waste deposits. Frozen zones that formed on the surface of waste deposits did not thaw when more waste was added over the surface of the fills; some layers remained frozen for four to five months. Further, stabilization of FGC waste with additives was impaired drastically by freezing. In some deposits, anticipated pozzolanic reactions were delayed; in other fills such reactions never occurred. In one particular instance, a mixture of carbide lime process waste, fly ash, and carbide lime (1:1:0.03 weight proportions) emerged from a mixing truck as spheres 2.5 to 15 centimeters (1 to 6 inches) in diameter. These stiff balls froze to rock-like hardness within hours after placement, and remained

rock-like for more than three months. However, with the advent of warm weather, the balls thawed, dried, and, in many cases, crumbled. Such behavior indicates the need for more evaluation of freeze-thaw effects.

Of less significance than freeze-thaw effects are the effects of wet-dry cycles. Field compaction studies at Plant Scholz have shown that FGC wastes deposited in relatively thin layers 15-45 centimeters (6-18 inches) may dry appreciably in a hot, dry climate. Experience with waste sludge disposal at the Reid Gardner Station near Las Vegas, Nevada also indicated that field drying may be feasible; experience with the waste from the Trona scrubbing operation at Reid Gardner may not be directly applicable to disposal of calcium-sulfur salt wastes, but general behavior may be extrapolated. Drying effects would occur only under conditions existing at a limited number of sites only during certain seasons. Intermittent periods of wet weather may increase the potential for leachate generation and surface erosion of waste deposits. As mentioned previously, wetting of waste does not appear to cause detrimental changes in strength, compressibility, or permeability.

Laboratory tests on the effects of freeze/thaw cycles on fly ash/laboratory samples of CaSO_3 and CaSO_4 /lime mixtures have been performed by Radian [146]. Twenty-four mixtures were tested for unconfined compressive strengths after freezing and thawing ten times. In general, slightly higher strengths were observed for the frozen/thawed sample than those cured at room temperature. Similar effects are also noted for Calcilox stabilized waste [146].

Erosion of surface layers of waste deposits has been addressed briefly by Radian Corporation [39]. This problem is not a major hindrance to land disposal of wastes since permanent cover layers of soil probably would be placed over any waste deposit and, during construction of waste fills, surficial drainage management would minimize area exposed for erosion as well as prevent contamination of water bodies by eroded materials. The "silty" nature of FGC wastes, however, makes them prone to water and air transport. In the Radian study, plots of a clay loam soil, a fly ash and a scrubber waste were tested. Artificial rainfall

on plots with varying slopes produced sediment yields 3 to 10 times as great from the waste plots as from the clay loam soil plots. The fly ash yielded only about 10-70% as much sediment as did the soil, depending on slope. Radian investigators applied these results in the Uniform Soil Loss Equation developed by Wischmeier and Smith [103], for a hypothetical disposal site location in Central Illinois, assuming exposed slope lengths of 61 meters (200 ft) at an 8% grade. Their analysis yielded an estimate of loss of 269 tons/hectare (120 tons/acre) per year. This figure, four to five times greater than the loss anticipated for silty soils under natural conditions, indicates that surface erosion must be considered in the design of disposal areas for FGC wastes. In contrast, wind erosion experiments showed little susceptibility of waste to wind transport, because of the protective action of a surface crust on the waste plots tested. The results of the experiments were not conclusive and indicate the need for further investigation.

5.5 Data Gaps and Future Research Needs

The major data gaps in physical characteristics of FGC wastes can be subdivided into those relative to wastes from:

- dry sorbent systems (whose importance will be greater in the future), and
- wet scrubber systems.

Dry sorbents have not reached significant commercial use now but are expected to by the early 1980's. Lack of physical characterization data on these wastes is a major data gap.

A review of the state-of-the-art of FGC wastes characterization indicates that any program to fill deficiencies in existing data should be structured in the following priority ranking:

(1) Laboratory and Field Permeability Data - A comprehensive laboratory and field permeability testing program of FGC wastes and waste additive mixtures (particularly sludge-fly ash mixtures) is needed. These tests are required since many of the data on permeability which have been reported are of dubious value, particularly for "fixed" sludges.

(2) Freeze/Thaw and Dry/Wet Cycles Effects - An aspect of stability which has emerged as significant as a result of field testing is the possible deterioration of waste and waste/additive mixtures under influence of freezing. This behavior requires comprehensive investigation. A laboratory study of the effects of freezing on waste and waste/additive mixtures is appropriate. Physical and chemical changes, including cementation by fixatives, should be studied in tests where mixing and compaction are done in freezing temperatures and in tests where the onset of freezing is delayed for various time periods. The effects of cycles of freezing and thawing, with various durations of freezing and thawing, should be determined. These effects are relevant especially in the case of mixes of sludges and additives in which chemical reactions are anticipated. These tests should be supplemented with field testing to verify that field conditions have been simulated accurately in the laboratory.

A limited number of tests should be conducted to determine the effects of periods of intense heat and low humidity alternating with periods of heavy rainfall. These tests would be intended to ascertain if high temperatures and low humidity may accelerate chemical fixation reactions, and if such acceleration is beneficial or detrimental. Alternating exposure to intense rainfall not only would simulate climate conditions in some areas of the United States, but also would serve to test the hypothesis that wastes and mixtures do not reslurry upon rewetting.

(3) Laboratory and Field Compaction Tests - Laboratory and field compaction testing of FGC wastes and mixtures is needed to "calibrate" the relation between lab and field tests and to determine the most effective compaction equipment and techniques. Laboratory determinations of compaction characteristics have been made; these tests must be correlated with field studies of waste compaction. Various compaction methods and equipment should be evaluated: sheepsfoot rollers; pneumatic rubber-tired rollers; steel drum rollers; and vibratory rollers. Lift thickness (depth of layer before compaction), number of roller passes, and compaction moisture content are variables to be evaluated. The

energy and economic trade-offs between dewatering with better subsequent compaction and poor compaction of wetter materials should be examined. Optimum compaction conditions may be achieved through addition of dry solids (e.g., fly ash) and this alternative also merits evaluation. In any field evaluation of compaction techniques, mixtures of additives plus waste should be studied, as well as unstabilized wastes.

One additive which has received only limited study is natural soil. In some locations, cohesionless soils may be available at low cost in quantities sufficient for use as a waste/additive. Mixing of dry sand with FGC wastes probably would have minimal effect on the permeability of the mixed components, but the strength of the mix should be far superior to that of waste alone, and similar improvements in stiffness (less compressible) should be realized. Handling and compacting of a waste-sand mix or a waste-fly ash-sand mix may be easier than similar processing of raw waste and the resultant fill should be much stronger and more stable than a mass of ponded waste. Mixing and compacting of waste-sand and waste-fly ash-sand blends should be evaluated in laboratory tests and in field demonstrations.

(4) Dewatering Characteristics - Tests are needed of dewatering characteristics of FGC wastes and mixtures, including those of drying with underdrains in field and laboratory. These tests are needed because of the important connection between dewatering and subsequent mixing and/or compaction of wastes in land disposal sites. Dewatering techniques for FGC wastes are being investigated by a team of research personnel at Auburn University.

(5) Comprehensive Triaxial Compression Tests and Consolidation Tests - The evaluation of strength and compressibility of FGC wastes and waste-additive mixtures, although claimed by many, has been accomplished by few. It is necessary to perform a full suite of triaxial compression tests and consolidation tests on a representative number of FGC wastes and waste/additive mixtures after various durations of curing and in various conditions (compacted, uncompacted, "fixed").

(6) Mixing Characteristics - Transport and handling characteristics are extremely important since they are at the beginning point in the generation-to-disposal route of FGC wastes. To date, it appears that insufficient attention has been given to the mixing characteristics of FGC wastes and pertinent additives. Further examination of the mixing characteristics of FGC wastes, including examination of field deposits and ponds for evidence of heterogeneity or stratification is needed. Attention should be given to settling of solids in pipelines and any changes in apparent pumping characteristics after periods of interrupted flow. This study should include an examination of the mixing properties of FGC wastes and likely additives. Field tests have shown that such mixing may be difficult and that segregation of additives may be a serious problem under certain conditions. Samples of sludge-additive mixtures from the EPA-TVA demonstration site at the Shawnee Steam Plant in Paducah, Kentucky, have exhibited distinct stratification of mix components, and mixing of fixatives in sludge at the Phillips Station of the Duquesne Light Company has not always been uniform. Mixing tests appear to be appropriate.

(7) Hydrologic and Soil Attenuation Studies - Field studies also appear to be required for the evaluation of the water pollution potential of leachate from FGC waste deposits. Leachate collection and testing has been done at Plant Scholz, the Phillips Station, the Shawnee Steam Plant, the LG&E Cane Run Plant and elsewhere. However, more attention should be given to hydrologic studies to quantify water flow in, around and under waste lagoons and fills. Additionally, attenuation of leachate by in-situ soils should be studied to provide correlative data for soil attenuation studies being done at the Dugway Proving Ground. Several field disposal sites should be monitored to determine overall water balance (net precipitation or evapotranspiration, infiltration, temporary storage, etc.), mass permeability within waste deposits and at soil contact zones, and chemical characteristics of leachate after passage through natural soil strata.

(8) Viscosity and Pumping Characteristics - To date, insufficient attention has been given to the pumping characteristics of FGC wastes and pertinent additives. Viscosity tests should be performed on a representative number of sludges, and mixtures of wastes and fly ash or other non-cementing additives. It appears ill-advised to consider pumping mixtures which could react and cement in pipelines and pumps; however, non-alkaline fly ash, lime and some soils, used as single additives with FGC waste, should be examined. The relations between apparent viscosity and solids content, and between apparent viscosity and flow rate (shear rate) should be investigated.

Standard tests and equipment are available to determine all of the properties listed above as current data gaps. With regard to planning and design of an FGC system for electric power utilities and other combustion sources, the first five items are of greater ranking than the last three.

6.0 RESEARCH NEEDS

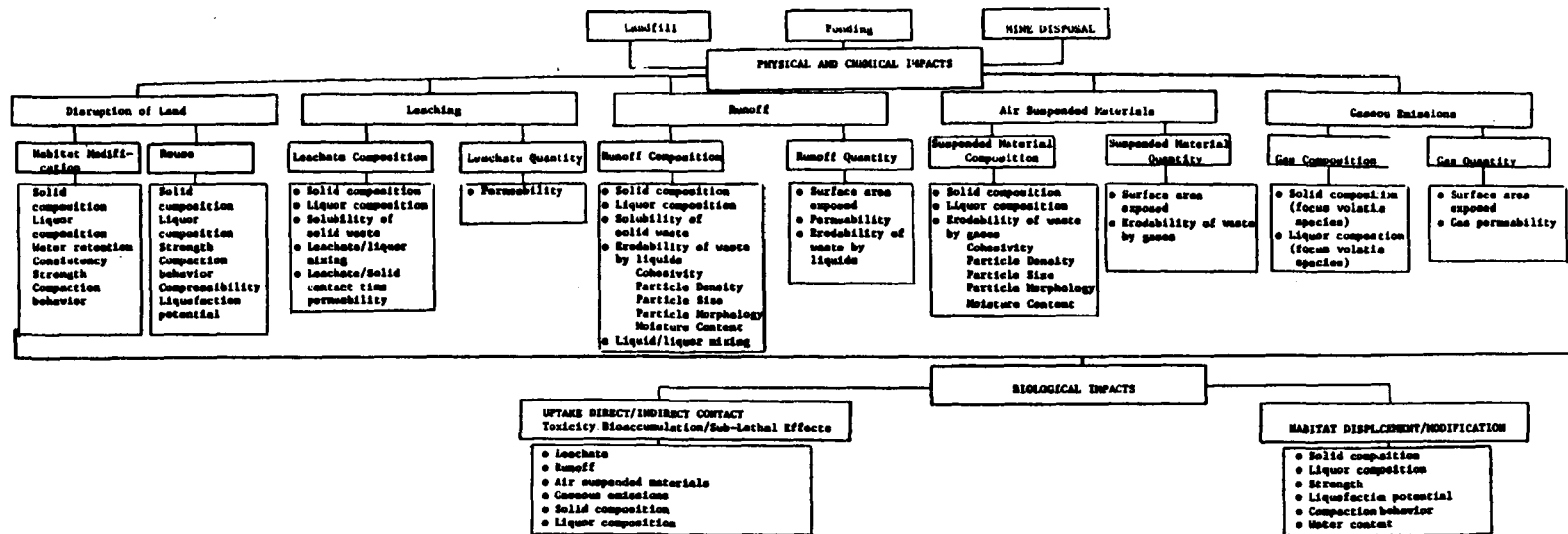
6.1 Waste Properties Relation to the Disposal Process

Knowledge of the handling properties and the behavior of FGC wastes prior to, during and after disposal in relation to their possible environmental impacts are necessary for the design and operation of disposal systems. The chemical and physical properties discussed previously aid in determining handling methodology and in assessing possible environmental impacts leading to the choice of the disposal site design. Determination of these properties may be accomplished by performing laboratory experiments which are designed to simulate disposal site conditions or by monitoring disposal sites. Generally, however, laboratory experiments cannot always be designed which accurately simulate a specific disposal environment because of the many possible variables involved. It is then more beneficial to perform experiments which give insights on the mechanisms of environmental impact and how specific waste properties relate to these mechanisms in producing the impact. The relationship of some of the previously discussed waste properties to possible routes of environmental impact for land disposal is shown in Table 6.1.

The mechanisms of environmental impact (e.g., leaching) are separated under headings of physical and chemical impact and those related to biological impacts. The physical and chemical impacts are prerequisites for any biological impacts to occur, but they may occur without any subsequent biological impacts. The extent that these mechanisms contribute to the total impact is governed both by waste properties and site considerations. Only the properties relating to the waste are included in Table 6.1, and they are separated into those which affect the identity and concentration of the species exiting the waste into the environment and those which affect the total quantity exiting. For example, the composition of the leachate exiting the waste depends on the solid and liquid portions of the waste and how much of these species dissolve or mix with the leaching solution. The total quantity coming out of the waste depends on the rate that the leachate flows (permeates) through the waste (waste volume, also a factor in determining quantities, is not considered to be a waste property).

Table 6.1

FGC Wastes Properties and Possible Routes of Important Environmental Impacts (Land Disposal)



The extent of disruption of existing conditions and biological effects are less defined by quantitative parameters than the other mechanisms and are not done so in Table 6.1. It is impossible to quantify, for example, the suitability of the waste for habitation or the impact of leachate on biological organisms. In this regard, the other FGC waste properties listed can give insight into the extent of each mechanism occurring but, at this time, are no substitute for actual exposure tests.

The extent of biological impacts is not only related to specific waste properties, but is also dependent on the extent with which the chemical and physical impacts are modified by interaction with the surrounding environment (see below) prior to interaction with the ecology. Thus, for example, actual biological impact of leachate may occur only after it has passed through several underlying strata and has been diluted by underground water flows. These may contribute to modification of both concentration and species in the leachate with which biological interaction may occur.

The waste properties listed in Table 6.1 may be modified during the course of the disposal process and the lifetime of the disposal site. These modifications may occur due to the specific site conditions, interaction with the environment as well as handling and placement factors. A listing of these variables is given in Table 6.2. In addition to modifying the waste properties, some of these variables affect the overall environmental impact by modification of the composition and quantity and resulting effects of the pollutants that may enter the environment. Specific in-site conditions such as age of the waste after placement may alter waste properties for materials which are not at thermodynamic equilibrium (e.g., uncured stabilized wastes). Interaction of groundwater with the waste may, for example, produce gaseous products (e.g., acid mine drainage interacting with sulfite wastes) or deterioration of waste (e.g., reversal of the stabilization process). Hydrology is also important in determining the final concentration and species entering the environment (e.g., via leaching). Geological effects may range from restriction of leachate flow by an impermeable underlying strata and removal of trace pollutants by soil attenuation to the act of breaking up a stabilized waste by a seismic disturbance.

Table 6.2

Variables Affecting FGC Waste Properties
And The Resulting Environmental Impact

TIME (WASTE AGE)

WASTE VOLUME

SITE CONDITIONS

- Hydrology
 - Surface Water
 - Groundwater
- Geology
 - Soils
 - Topography
 - Seismicity
- Climate
 - Wet/Dry Cycles
 - Freeze/Thaw Cycles
 - Light
 - Air Flow
- Ecology
 - Biological Interactions

HANDLING/PLACEMENT FACTORS

- Additives
 - Stabilization
 - Co-Disposal
 - Admixing
- Dewatering
 - Moisture Content
- Compaction

Climactic conditions may effect waste properties and quantity of pollutants. Examples are the possible deteriorating effects of freeze/thaw cycles and the quantity of rain governing extent of leaching or runoff. One example of ecological effects is the possible formation of gaseous products from bacteriological reduction of sulfites and sulfates.

Other variables shown in Table 6.2 involve handling and placement effects produced during the disposal process. Examples of these effects include changing initial waste properties by addition of various substances or chemical reactions and compaction of the waste (which may change the effective permeability).

In addition to their importance in assessing environmental impact some of the waste properties discussed previously are important in determining handling methodology in the disposal process. Important waste properties which affect the handling of the waste are listed in Table 6.3. These are separated into those which aid in determining the storage transport process and those relating to placement of the waste. Properties which relate to the fluid properties of the waste provide information on the mode of storage and mode of transport. Strength and compaction properties relate to the ability of the waste to support compaction equipment. A more detailed discussion of these properties in relation to handling of the waste was presented in Section 5.0.

6.2 Overview on Research Needs

A number of programs have have been undertaken sponsored by the EPA, EPRI and others to develop and demonstrate FGD technology and assess waste disposal and utilization options. Many of these are still in progress. Continuation of these programs will provide additional data and information on the characterization of FGC wastes.

The EPA program for control of waste and water pollution from combustion sources has among its overall objectives development of additional information on the characterization of FGC wastes, thereby permitting better environmental assessment. Such characterization studies are part of the overall environmental assessment program initiated by the EPA which includes:

Table 6.3

Important Properties of FGC Wastes
Affecting Handling of the Waste Prior to
and During Disposal

STORAGE/TRANSPORT

- Dewaterability
- Pumpability
 - Viscosity
 - Density
 - Consistency
 - Moisture Content
 - Atterberg Limits
- Physical Stability
 - Consistency
 - Density
 - Liquefaction Potential
 - Atterberg Limits
 - Dewaterability
- Compaction Behavior
 - Strength
 - Compressibility

PLACEMENT

- Volume Related Properties
 - Density
 - Compaction Behavior
 - Dewaterability
 - Consolidation
- Strength Parameters
 - Compressibility
 - Intrinsic Strength
 - Compaction

- FGC waste characterization studies,
- Laboratory and pilot field studies of disposal techniques for chemically treated wastes,
- Characterization of coal pile drainage, coal ash and other power plant effluents, and
- Studies on the attenuation of FGC waste leachate by soils.

Many data gaps in the physical and chemical characteristics of FGC wastes have been identified in Sections 4.5 and 5.5. These provide a fairly comprehensive list and could serve as a reasonable starting point for any program planning in this area. In order to assist in this program planning in each of the above list of data gaps, a priority rating for each one of the data gaps has been suggested.

Dry sorbents have not reached significant commercial use now but are expected to by the early 1980's. Since very little chemical and physical data is available in wastes from this type of process, this area represents a major research need.

Testing of FGC wastes should not be limited to solid-producing non-recovery FGC systems but should also include fly ash and bottom ash, both dry and wet collected as well as wastes produced from recovery system prescrubbers and waste liquor producing systems.

Research needs that would be particularly useful are presented below in the order of priority.

6.2.1 Field Data

There is an important need to characterize:

- Chemical properties and leaching behavior of stabilized and unstabilized wastes in actual field disposal operations, and
- Permeability of untreated FGC wastes and waste/additive mixtures (particularly, FGD waste-fly ash mixtures) in the field.

Data are needed on changes in waste composition and the associated pollutant mobility resulting from waste aging, weathering (erosion,

rewetting and freeze/thaw), handling, processing (treatment) and the disposal environment. Information is needed covering the ranges of: basic FGC system types (direct lime, direct limestone, alkaline ash, and dual alkali) or waste types (sulfite-rich vs. sulfate-rich); methods of processing (untreated, blended, treated); and types of handling and disposal (ponding, landfill, mine disposal). While a limited amount of data do exist or are being developed from EPA funded projects (e.g., Square Butte mine disposal demonstration project, Louisville Gas & Electric/Combustion Engineering/University of Louisville, testing at Paddy's Run, and the TVA/Aerospace Project at Shawnee) or studies are being planned (e.g., LG&E dual alkali demonstration program), more extensive field testing is needed. This would involve monitoring of a number of representative full-scale systems not now studied via sludge sampling, corings, and leachate wells. Field tests, particularly on physical characteristics, should be done along with lab tests on a suite of FGC wastes to "calibrate" the relation between lab and field tests and to determine most effective compaction equipment and techniques.

6.2.2 Laboratory Test Procedures

Presently available leachate (elutriate) and toxicity test procedures do not as yet confidently predict dissolution and toxicity of constituents from FGC wastes. It is important to be able to perform tests in the laboratory quickly and cost-effectively, which will characterize the mobility and impact potential of FGC waste components. A number of different procedures need to be developed and tested. The current toxicant extraction procedure developed under RCRA needs to be tested on its ability to characterize these properties in FGC wastes.

6.2.3 Ash/FGD Waste Co-disposal and Treatment Requirements

(a) Ash/FGD Waste Co-disposal

There is the distinct possibility that co-disposal of fly ash and FGD waste as a mixture could have certain advantages over the disposal of each separately. However, there is a lack of definitive data correlating the levels of trace elements in the coal ash, fly ash (bottom ash),

FGD waste, and ash/waste admixtures--either in the waste materials or their leachates. More laboratory and field testing needs to be carried out to determine such correlations if possible and identify/assess pollutant mobility and toxicity.

(b) Treatment Requirements

Many fly ashes have appreciable pozzolanic activity and when admixed with FGC waste (and possibly lime) will result in a material which hardens with time. The extent of hardening reactions will be importantly dependent upon the ash characteristics but may also depend on the FGD waste type (sulfite vs. sulfate-rich), presence of high levels of TDS, and the conditions of ash mixing (methods and relative quantities). This area still remains an art, and more studies are needed to determine the effects of different types of sludges and sludge/ash mixtures not only on physical properties but also trace element mobility and toxicity.

6.2.4 Physical Characterization of FGC Wastes

In light of the research needs identified in items (1) and (3) above, appropriate physical characterization programs need to be undertaken. This should include:

- Triaxial compression tests on a suite of FGC wastes and mixtures (after various durations of curing),
- Consolidation tests to determine compressibility of wastes and mixtures at various solids contents and in various conditions (compacted, uncompacted),
- Further examination of the mixing characteristics of FGC wastes, including examination of field deposits and ponds for evidence of heterogeneity or stratification,
- A limited number of tests of the viscosity and pumping characteristics of FGC wastes, and

- Tests of dewatering characteristics of waste and waste mixtures, including drying with underdrainage.

6.2.5 Trace Element Focus and Speciation

A number of trace elements which are present in FGC wastes are of particular interest because they have been observed in waste liquors at levels where a deleterious impact on plants or animals could be possible in some situations. Certain of them, e.g., boron, fluoride and molybdenum, have been studied in only a few samples. Others, such as arsenic, antimony, selenium, manganese and cadmium, are difficult to measure precisely and accurately at the levels at which they are present in waste; this warrants a continuing focus. It is recommended that as additional samples are obtained from FGC systems for characterization, these trace elements in particular should be measured by techniques offering state-of-the-art accuracy and precision in order to extend the base of good data describing their occurrence in FGC wastes. That list of key elements should be reevaluated from time to time by those assessing impacts on plants and animals so that relatively expensive analytical efforts are focused on the most important parameters.

Since the chemical form (cation, neutral, anion, and oxidation state) of a pollutant affects its solubility, toxicity, and attenuation by soil, it is recommended that studies of the oxidation state of trace pollutants in FGC wastes and leachates be continued. The trace elements arsenic, selenium, antimony, chromium, and boron either exhibit amphoterism or highly variable attenuation by different soils and would be good candidates for speciation studies. In addition, selenium can reportedly exist as the free element, and as such, its mobility has not been well characterized.

6.2.6 Anaerobic-Induced Reduction Reactions/Volatile Species

Studies of the reduction reactions, e.g., Se to H_2Se or As to arsines that might occur in an anaerobic region of an FGC waste disposal landfill or pond should be conducted. Such reactions are important because they could produce gaseous products which could be transported

into the atmosphere. The presence of volatile species (Hg, Se) initially in the waste material needs to be determined in order to assess if these species can be released to the atmosphere upon disposal of the waste.

6.2.7 Radionuclides and Trace Organics

Although it is unlikely that radionuclides and polynuclear aromatic (PNA) organic compounds will be present at levels that are of concern, and even more unlikely that they will leach from the waste at substantial levels, measurements of radionuclide activity (^{226}Ra , ^{210}Pb , and ^{238}U , etc.) activity should be made for a representative set of FGC wastes and their leachates. The wastes should be chosen to include those with no ash, those with ash, treated materials and untreated materials. In this regard, the results of ongoing PNA measurements at TRW should be evaluated and additional measurements made, if necessary, to ascertain if any potential problem could arise due to their presence.

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16. ABSTRACT The report, the third of five volumes, focuses on trends in generation of coal ash and FGD wastes (together comprising FGC wastes) and the characteristics of these wastes. With increasing use of coal, the generation of FGC wastes is expected to increase dramatically: to about 115 million tons of coal ash and 38.7 million tons of FGD wastes by the year 2000. Most of these wastes will be disposed of on land. Data on the chemical characteristics of fly ash, bottom ash, and both treated and untreated FGD wastes in this report include data on principal components, composition ranges for trace components, and leaching behavior. Based on the characteristics of FGD wastes, a categorization of these wastes is also presented. Ongoing programs on chemical characterization are assessed. The fundamental physical properties of FGC wastes are density, size, and crystal morphology. The critical physical and engineering properties are those relating to handling characteristics, placement and filling characteristics, long-term stability, and pollutant mobility. The report includes information on index properties, consistency-water retention, viscosity vs. water content, compaction/compression behavior, dewatering characteristics, strength parameters, permeability, and weathering characteristics. Further efforts in this area are recommended: key is data from full-scale disposal sites.		
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