3.2 SOLID WASTES ASSOCIATED WITH OIL SHALE PROCESSING

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

3.2.1 Raw Shale Fines

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

3.2.2 Retorted Shales

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

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

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

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

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

Source: Ref. 78.

Table 3.23 Ash Composition of Typical Retorted Oil Shale

	TOSCO II[a]	Union B[b]	GCR[c]
Component	wt%	wt%	wt%
SiO_2	33.0	31.5	43.8
Fe_2O_3	2.5	2.8	4.6
Al_2O_3	6.8	6.9	12.2
CaO	15.8	19.6	22.1
MgO	5.3	5.7	9.3
SO_3	–	1.9	2.2
Na_2O	8.7	2.2	3.4
K_2O	3.3	1.6	2.4

[a] Ref. 81; data represent Mahogany zone shale (35 gal/ton) from Parachute Creek area.

[b] Ref. 82; data represent Mahogany zone shale (35 gal/ton) from Parachute Creek area.

[c] Ref. 83; data represent Mahogany zone shale (30 gal/ton) from Anvil Points.

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

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

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

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

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

3.2.3 Other Shale-Derived Solid Wastes

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

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

Table 3.24 Distribution of Trace Metals During Oil Shale Retorting

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

Source: Ref. 85.

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

Ion	Raw Shale	TOSCO II	GCR (USBM)	GCR (Union A)
K^+	0.24	0.32	0.72	6.25
Na^+	0.48	1.65	2.25	21.0
Ca^{++}	0.1	1.15	0.42	3.27
Mg^{++}	0.01	0.27	0.04	0.91
HCO_3^-	0.75	0.20	0.38	0.28
Cl^-	0.22	0.08	0.13	0.33
$SO_4^=$	0.79	7.3	6.0	62.3
Total (kg/tonne)	1.95	10.96	9.94	94.34
(lb/ton)	3.9	22	20	188

[a] Based on laboratory tests.

Source: Ref. 86.

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

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

3.2.4 Non-Shale Solid Wastes

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

Table 3.26 Typical Composition of Shale Oil Coke

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

[a] Ref. 87; data are for shale oil produced by TOSCO II retorting.

[b] Ref. 88; data are for shale oil produced by Paraho and TOSCO II.

3.3 SOLID WASTES ASSOCIATED WITH OTHER ENERGY TECHOLOGIES

3.3.1 Geothermal Technologies

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

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

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

Geopressured Systems: Geopressured zones consist of highly porous sands saturated with saline water at very high pressure and temperature. The high temperature is thought to be the result of normal heat flow being trapped by uncompacted clays, which serve as insulating layers. Water derived from the compaction and dehydration of clays accumulates in the sand and greatly increases the fluid reserve. The marine sediments are under-compacted below depths of 6,500 to 10,000 feet, and the interstitial fluid carries part of the overburden load (i.e., the fluids are at pressures between the hydrostatic and the lithostatic head). Temperatures up to 290°C and pressures up to 1000 atmospheres have been measured in these systems. In the United States, the principal geopressured formations are located under the Gulf coast of Texas and Louisiana. The magnitude of the resource is substantial, and its economic value is enhanced by the presence of natural gas dissolved in the geopressured fluid; however, difficult technical and economic problems must be solved before geopressured resources can be utilized commercially.

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

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

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

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

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

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

	Average Concentrations in Geothermal Brines					Average Concentrations in Water Samples in Salton Sea KGRA						
Ion	Salton Sea	Westmorland	Brawley	Heber	East Mesa	Vail4 Canal	Sump 120	Sinclair 4	Sump 116	Vail4A Drain	Alamo River	Salton Sea
Na	52,000	10,000	22,000	4,200	2,600	168	1,080	58,442	2,470	970	607	10,600
K	14,000	1,400	3,800	260	190	6.3	20	14,918	247	66	15	195
Ca	24,000	690	8,100	880	130	93	373	26,992	2,050	437	201	850
Mg	106	188	34	5.4	3.4	35	187	736	385	160	120	1,200
Cl	145,000	18,000	46,000	7,900	3,900	158	989	154,590	8,540	1,870	760	14,700
SO_4	84	57		99	155	357	1,990	19	1,590	1,480	960	8,100
CO_3	0	130	0	3.3	33	15	<2.5		<2.5	<2.5	<2.5	63
HCO_3	140	2,900	49	27	490	152	338	0	380	330	205	143
As	11		2.6	<0.1	0.16	0.005	<0.005	10	0.005	0.005	0.007	<0.01
B	350	63	140	14	5.4	0.25	1.1	332	9.7	2	0.76	6.8
Ba	433		363	3.8	2.2	0.09	0.097	1,100	0.54	0.093	0.12	0.07
Cu	4	0.07	0.11	0.53	0.03	<0.005	0.005	3	0.075	0.007	0.014	0.08
F	9	2.24		1.6	2.0	0.5	0.57	14	0.48	0.05	0.66	1.1
Fe	2,300	0.3	65	22	2.2	0.03	0.08	1,240	0.26	0.08	0.045	0.24
Li	211	48.	100	9.5	6.3	0.08	0.31	344	14.3	1.24	0.23	3.2
Mn	1,200	2.8	190	2.7	0.42	0.01	0.30	1,475	47	1.9	0.035	0.08
Ni	<4				0.03	0.01	<0.01	<4	0.31	<0.01	<0.01	<0.2
Pb	100	3.6	1.1	1.9	0.09	<0.01	0.01	60	0.29	0.02	0.01	<0.1
Se					1.2	<0.005	<0.005		<0.01	<0.005	<0.005	0.02
Sr	500		340	53	38	1.3	5.0	448	38	6.0	3.2	13.5
Zn	660	0.04	14	0.83	0.07	0.02	0.03	600	7.8	0.12	0.02	0.03
TDS	240,000	37,000	76,000	14,000	7,600	928	5,030	266,560	17,700	5,970	3,000	38,600
pH	5.2	7.5	6.1	6.5	7.3	8.2	7.0	5.3	6.8	7.6	7.7	8.8

Source: Ref. 92.

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

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

3.3.2 Oil and Gas Extraction

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

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

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

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

Although water-based drilling fluids consist of over 99% water and other relatively nontoxic components, many of the additives to drilling fluids contain materials that are considered toxic. Of particular concern are the bactericides (e.g., aldehydes, quaternary amines, diamine salts, sodium pentachlorophenate and other chlorinated phenols), corrosion inhibitors (e.g., arsenites), metals, coal tar derivatives, emulsion breakers, and low molecular weight organic additives (e.g., benzoic acids, dihydroxybenzenes, substituted napthalenes, amines, and imidazolines). Many drilling fluid additives are water soluble; therefore, leachate from drilling fluid disposal could contain dissolved toxic materials, a high salt concentration, and caustic materials.

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

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

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

3.3.3 Tar Sands

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

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

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

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

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

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

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

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

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

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

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

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

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

3.3.4 Nuclear Power Generation[96]

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

Classes of Nuclear Wastes

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

High-Level Wastes (HLWs): High-level wastes can be either intact spent fuel assemblies removed from a reactor after serving their useful life or the wastes generated as a result of spent fuel reprocessing. A 1000-MW light-water reactor annually discharges about 30 metric tons of spent fuel from the present once-through fuel cycle.[97] Commercial spent fuel contains about 96% by weight of the uranium originally charged to the reactor as fresh fuel in addition to 3% fission products and 1% TRU elements and daughters.[98] Most fission products decay to stable elements after several hundred years, whereas TRU elements remain radioactive for thousands of years. Consequently, spent fuel intially generates a great deal of heat and is very radioactive. After a decade, the heat generated decays by a factor in excess of 300, while the radioactivity decays by a factor of 1000.[99] Currently, commercial spent fuel assemblies are stored at the reactor site until a decision on the question of spent fuel reprocessing is made. If reprocessing is not used in the nuclear fuel cycle, spent fuel will remain the bulk of the waste generated. Twenty-three hundred metric tons of heavy metal already exist from past reactor operations.[100]

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

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

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

Uranium Tailings: The residues from the mining and milling of uranium also contain low concentrations of naturally occurring radioactive elements. Uranium mill tailings are generated in large volumes, and 130 x 10^6 metric tons are now stored uncovered at various sites of mining and milling operations.[100] Because tailings emit the carcinogenic gas radon-222, the stabilization of these piles from water and erosion is of great concern. According to Victor Gilinsky, nuclear physicist and NRC member, uranium tailings could become the dominant source of radiation exposure to the public from the nuclear fuel cycle, unless the tailings are isolated from the atmosphere.[104]

Decommissioning/Decontamination (D/D) Wastes: The final category of nuclear wastes involves those generated upon the retirement of a nuclear facility due to obsolescence or adverse economics of continued operation. D/D is potentially a source of large quantities of radioactive wastes. The volume of LLW (no TRU) that might result after the shutdown of an 1160 MW reactor could vary from 60 m^3 under a mothballing procedure, to 23,000 m^3 for complete removal/dismantling.[98] Until retired nuclear facilities and land are decontaminated, such facilities and land must be considered and treated as waste storage sites.

Disposal Technologies and Associated Risks

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

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

The form of the waste is an important consideration in the success of geological burial. Because of the corrosive nature of groundwater, any container the wastes are placed in will lose its integrity after about 100 years, leaving the wastes themselves subject to groundwater leaching action. Consequently, the wastes must be cast into forms of extremely low solubility and high resistance to the effects of radiation. Liquid wastes must first be solidified and then fixed into a borosilicate glass, ceramic, oxide, or silicate mineral form.

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

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

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

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

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

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

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

4 HAZARD CHARACTERISTICS

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

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

4.1 COAL UTILIZATION WASTES

4.1.1 Ash from Coal Combustion

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

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

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

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

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

Table 4.1 (Cont'd)

Component	Flyash Pond	Bottom Ash Pond	Ash Pond	Ash Pond Overflow	Ash Pond Overflow	Flyash Sluicing Water	Bottom Ash Sluicing Water
Selenium (Se)[a]	<0.001-0.004	<0.001-0.004	0.021-<0.05	—	0.003-0.015	0.001-0.004	0.001-0.031
Silicon (Si)	10-15	6.1-8.6	1-51	—	—	—	—
Silver (Ag)[a]	<0.01-0.01	<0.01	<0.02	—	—	<0.0002	<0.0002-0.0004
Sodium (Na)	—	—	170-294	3-982	—	—	—
Strontium (Sr)	—	—	0.8	—	—	—	—
Tantalum (Ta)	—	—	<0.02	—	—	—	—
Titanium (Ti)	—	—	<0.02	—	<0.1	<0.1-0.1	—
Uranium (U)	—	—	—	—	—	0.004-0.005	0.003-0.005
Vanadium (V)	—	—	<0.02	—	<0.1-0.2	<0.005-0.072	<0.005-0.192
Zinc (Zn)[a]	1.1-2.7	0.02-0.16	<0.022-0.09	0.00013-0.17	0.02-2.5	0.008-0.028	0.013-0.075
Zirconium (Zr)	—	—	<0.07	—	—	—	—
Total Hardness ($CaCO_3$)	185-520	—	—	25-736	—	—	—
Total Alkalinity (as $CaCO_3$)	—	30-160	—	2-443.7	—	—	—
pH	3.6-6.3	4.1-7.9	8.47	—	—	—	—
Dissolved Solids	141-820	69-404	1100-3335	40-3328	—	—	—
Suspended Solids	2-256	5-657	—	1-100	—	—	—
HCO_3	—	—	31.0	—	—	—	—
SO_4	—	—	580-2300	2.2-527	—	—	—

[a] On EPA list of 65 priority pollutants.

Source: Ref. 54.

Table 4.2 Equilibrium Concentrations of Trace Elements in Coal Ash Leachate

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

[a] FWPCA = Federal Water Pollution Control Administration.

[b] Concentration exceeds one or more of the standards.

Source: Ref. 99.

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

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

The EPA has determined that, in the petroleum refining industry, the solid wastes including the API separator sludge, dissolved air flotation (DAF) float, slop oil emulsion solids, heat exchanger bundle cleaning sludge and tank bottoms (leaded) may pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, disposed of, or otherwise managed[109] (see Sec. 7.2). The wastewater treatment sludges from the electroplating operations (see Sec. 7.3) and the primary zinc smelting and refining operations (see Sec. 7.8) have also been determined to be potentially toxic. These wastes contain significant levels of toxic heavy metals such as lead and chromium. In addition to being toxic, lead has been shown to be potentially carcinogenic and bioaccumulative. Table 4.3 shows the data on the composition of some of these wastes as well as that of bottom ash and fly ash generated from conventional coal combustion. Some of these values for the two types of waste are quite comparable.

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

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

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

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

[a] Sources: Refs. 63 and 110.

[b] Sources: Refs. 111 and 112.

A number of reports have been published on the mutagenicity of coal flyash.[117-119] Reports from two different groups sampling at seven power plants have concluded that although fly ash leaving the stack to the atmosphere is mutagenic in the Ames Salmonella reversion assay, the ash that is collected as solid waste in the electrostatic precipitator is not mutagenic in this assay. Bonnell and Schilling[120] also reported no mutagenic activity in fly ash collected in the electrostatic precipitator hoppers from a large British coal-fired power plant. Fisher et al.[118] concluded that if there is any mutagenic activity in the collected ash, it must be less than 0.2% of that in the material emitted to the air. Apparently the mutagenic activity is due to compounds volatilized or formed during combustion and adsorbed on the surface of fine particles--which present the most surface area--as the effluent stream cools. This presumably takes place after the exhaust gases pass through the precipitator. They also conclude that use of low temperature precipitators could lead to contamination of the bulk of the collected flyash with mutagens and recommended high temperature, high efficiency collection of particles followed by cooling of the effluent stream and separate collection of the organic matter. The latter would yield a hazardous solid waste that is much smaller in volume.

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

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

4.1.2 Ash and Char from Coal Conversion

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

Tamura and Boegly[63] recently presented the results of research on the impacts of land disposal of coal conversion ash. Included are the results of the batch leaching tests using the EPA Extraction Procedures. Ash samples from several gasification/liquefaction processes were tested. Table 4.6 presents the leaching results along with proposed RCRA criteria (100 times the drinking water standards). None of the wastes listed exceeded the criteria, and of the elements considered, cadmium in one sample came closest to exceeding the RCRA standard.

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

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

Table 4.4 (Cont'd)

Constituents	Chemical Composition of 10% Slurry Supernatant (mg/L)								Recommended Water Levels (mg/L)	Solid Ash Content (mg/kg)
	Air Atmosphere				Argon Atmosphere					
Hf	-	-	-	-	-	-	-	-	-	6.1
Hg	ND	ND	ND	ND	ND	ND	ND	ND	0.0002	0.5
K	42	49	51	25	39	43	48	61	5	14,611
La	-	-	-	-	-	-	-	-	-	47
Li	1.8	1.9	2.0	2.0	1.6	1.8	1.9	2.1	2.5	42
Lu	-	-	-	-	-	-	-	-	-	1.5
Mg	10.5	14	15	22	9.5	11	13.5	23	50	3,739
Mn	0.45	1.94	2.7	3.8	0.11	0.90	2.3	3.7	0.05	1,859
Mo	ND	ND	ND	ND	ND	ND	ND	ND	0.01	30
Na	34	37	38	40	32	37	37	40	20[e]	1,929
NH_4	17	8	12	11	10	10	10	17	0.02	-
Ni	0.03	0.13	0.23	0.50	ND	0.04	0.14	0.42	1	89
Pb	0.1	0.1	0.1	0.2	ND	ND	0.1	0.2	0.03	45
P	-	-	-	-	-	-	-	-	-	87
PO_4	ND	ND	ND	ND	ND	ND	ND	ND	0.05	-
S_{Total}	-	-	-	-	-	-	-	-	-	6,100
Rb_2	-	-	-	-	-	-	-	-	-	162
S	ND	ND	ND	ND	ND	ND	ND	ND	0.002	1,500
Sb	0.2	0.2	0.3	0.6	0.3	0.3	0.3	0.3	0.05	4.2
SO_4	820	943	8089	338	730	735	700	710	250	8,100
Sc	-	-	-	-	-	-	-	-	-	29
Se	-	-	-	-	-	-	-	-	0.01	<1
Si	5	29	60	130	4	9	27	120	-	229,946
Sm	-	-	-	-	-	-	-	-	-	10
Sn	ND	ND	ND	ND	ND	ND	ND	ND	-	-

Table 4.4 (Cont'd)

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

[a] Natural pH of supernatant.

[b] Not detectable.

[c] Chemical oxygen demand.

[d] Methylene chloride extractable.

[e] For low Na diet; 250 ppm for taste.

Source: Ref. 121.

Table 4.5 Elements Exceeding Recommended Water Quality Levels

Constituent	Lurgi Ash Solubility pH 3 (mg/L)	pH 8 (mg/L)
Al	132	0.5
B[a]	5.5	4.0
Ca[a]	570	290
Cd[a]	0.06	0.02
Cr	0.12	0.02
Co	0.19	0.10
Cu	0.75	0.01
F	-	-
Fe	560	0.06
Ka	26	42
Mn[a]	3.80	0.45
NH_4[a]	11	17
Pb[a]	0.20	0.10
SO_4[a]	338	820
Sb[a]	0.60	0.20
Zn	17.00	0.12

[a]Highest pollution potential

Source: Ref. 122.

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

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

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

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

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

[a] RCRA standards were 100 times the interim primary drinking water standards (5-19-80 regulations).

[b] No primary standards have been established for these elements.

Source: Ref. 63.

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

Many of the inorganic components of coal ash are known to be toxic to aquatic biota, and the presence of these compounds in water leaching from coal ash may be a potential hazard to aquatic biota.[124] Table 4.12 presents acute toxicities to *Daphnia magna* in terms of 48-hr LC_{50} for three coal ash leachates.[125] *Daphnia magna* is very sensitive to pH, with a 48-hr LC_{50} for acidity at pH 6.4 and for alkalinity at pH 10.3. This sensitivity is reflected in the toxicities of the more acidic Illinois #5 and #6 leachate fractions. Probable interactants are also the high trace metal concentrations associated with the more acidic fractions. Many of these trace metals are present in the leachates at concentrations that have been found to be toxic to *Daphnia magna* and other freshwater biota.

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

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

[a] Sources: Refs. 109 and 110.

[b] Sources: Refs. 53 and 122.

The Rosebud leachate had the highest pH and the lowest toxicity of the three. The first three column volumes leached from the Rosebud ash had pH levels ranging from 6.8 to 9.5 and were nontoxic. The fourth column volume had a pH of 10 and a 48-hr LC_{50} at a dilution of 49%. Since the 48-hr LC_{50} for alkaline pH is 10.3 and the Rosebud leachate had the lowest concentration of heavy metals of the three leachates, the toxicity of the leachates was probably caused by their high pH.[125]

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

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

Table 4.8 Chemical and Bioassay Test Results for Gasification Ash

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

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

[b] RAM: rabbit alveolar macrophages.

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

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

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

Source: Ref. 123.

Table 4.9 Chemical and Bioassay Test Results for Gasification Ash Leachate

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

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

[b] RAM: rabbit alveolar macrophages.

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

[d] These categories of organic compounds are the worst case compounds that provide the largest discharge severity for the 38 µg/g of unidentified organics in the ash.

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

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

Source: Ref. 123.

Table 4.10 Chemical and Bioassay Test Results for Gasification Cyclone Dust

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

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

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

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

[b] The soil microcosm test results cannot be interpreted in terms of a high, medium, or low potential for hazard but the cyclone dust was clearly more toxic than gasifer ash.

Source: Ref. 123

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

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

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

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

[b] NA - test was not applied

Source: Ref. 123.

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

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

[a] Includes Zn, Fe, Ni, Mn, Cu, Al, Hg, As, Se, Pb, Cd.

[b] 48-h LC_{50} = the percent dilution of the leachate in spring water that caused a 50% mortality in 48 hours.

Source: Ref. 125.

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

4.1.3 FBC Spent Solids

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

1. The residue, in general, does not appear to be "hazardous" according to the procedures currently proposed under Sec. 3001 of RCRA. None of the trace metals treated exceeded the threshold of 10 times of the NIPDWR (National Interim Primary Drinking Water Regulations) for any of the FBC residues. The residues are expected to be not "corrosive," "ignitable," or "reactive" according to the criteria proposed for hazardous wastes under RCRA. It is possible, however, that in some specific cases, residues from an individual FBC plant may be found to be "hazardous." For example, the specific coal burned, or the specific sorbent used for an individual plant, could result in a residue that might yield a leachate having a high trace metal content and that might thus be found to be "hazardous" using the Extraction Procedure.

2. The primary environmental problem with FBC residue is that the leachate has a high pH and a high total dissolved solids (TDS) content. In addition, sulfate ion concentrations are high.[127-129] The levels of pH, TDS, and sulfate are significantly above EPA's proposed NSDWR (National Secondary Drinking Water Regulations), the World Health Organization potable water standards and/or the Public Health Service regulations on drinking water. (These species are not covered by the NIPDWR). When the leaching medium is distilled, deionized water, the pH of the leachate can be 12 or higher (in the range of 10 to 13) if the spent bed material is leached by itself; this pH is well above the NSDWR range of 6.5 to 8.5. TDS levels in FBC residue leachates are typically in the range 1000 to 3000 mg/L or higher, above the NSDWR of 500 mg/L. Sulfate concentrations are generally in the range 1000 to 2000 mg/L, above the NSDWR of 250 mg/L.

3. Trace metal leaching would appear to be of much less concern—in comparison with pH, TDS, and sulfate. When a variety of FBC residues were leached using distilled, deionized water, none of the 15 trace metals,

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

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

[a] Early scarlet globe variety.

[b] Indicates statistical significance at the 0.01 probability level.

Source: Ref. 125.

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

4. Substantial heat is released from the residue on initial exposure to water, due to hydration of the CaO content forming calcium hydroxide.[128,129] This heat release could necessitate some care in handling the residue and could represent an occupational safety concern but is not expected to be a major environmental concern. Heat release may be less of a concern for pressurized FBC systems, since the nonsulfated calcium may, to a greater extent, be in the form of $CaCO_3$; however, even even in residues from pressurized systems, some CaO may be present, and potential heat release problems may exist.

5. The leachate from one sample of spent bed material from one pressurized FBC unit had a low level of toxicity according to one set of fresh-water aquatic bioassays (using algae, fathead minnow, and daphnia as the test organism).[130]

6. Total organic carbon and sulfide are below detection limits in the FBC samples that have been tested and are not expected to be problems.[128,129]

4 1.4 Sludges from Chemical Treatment of Process Wastewater

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

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

4.1.5 Tars and Oil Sludges

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

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

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

Source: Ref. 131.

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

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

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

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

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

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

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

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

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

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

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

Source: Ref. 53.

tars[53] and bottom sediment sludge from a wood preserving plant[109] are fairly close, as can be seen in Table 4.17.

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

4.1.6 Biosludges

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

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

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

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

[a] Ref.53.

[b] Ref. 109.

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

Bicyclic compounds (e.g., (benzidine)
Nitrosamines
Nickel (e.g., nickel carbonyl)
Chromium trioxide, Chromate salts Salts
Beryllium oxide

Arsenic (e.g., arsenate salts)
Selenium salts
Cobalt sulfide
Lead chromate
Zinc chromate

Mercury
Cadmium sulfide
Anthracenes (e.g., 9, 10-dimethyl...)
Chrysenes (e.g., 5-methyl...)
Benzanthracenes

Flouranthene (e.g., benzo (j)-or (b)-...)
Cholanthrenes (e.g., 10-methyl...)
Benzo (e) or (a) pyrenes
Dibenzo (a,x) pyrene (x=1, n, i, or h)
Mono- and Dibenzacridines

Mono- and Dibenzocarbazoles
Benzanthrones
Aminoazobenzenes
Acenaphthenes
Naphthylamines

Diethyl and Methylethylamines
Benzene
Pyrenes (e.g., cyclopenta pyrene, indeno (1,2,3-c,d) pyrene)
Fine particulates (e.g., sulfur, coke)

Source: Ref. 133.

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

4.2 OIL SHALE PROCESSING WASTES

A major environmental concern with the development of oil shale technology is the potential for long-term health hazards such as carcinogenesis, mutagensis, and teratogenesis. Exposure to crude shale oils, particulate matter, contaminated aqueous materials, and air pollutants is hazardous to the health of workers. There are additional health and environmental concerns associated with oil shale extraction and processing. Blasting and mining will produce dust, particulate organic matter, CO, NO_x, SO_2, hydrocarbons, silica, and metal salts. Crushing and screening the ore produces more dust, silica, and particulate organic matter. In addition, retort operations can produce polycylic organic compounds, H_2S, NH_3, and volatiles. Some of these compounds, as well as arsenic and other metals, are produced in the upgrading process and disposal of the solid waste products and are of major environmental concern. Many of these compounds may contaminate not only the atmosphere but the water as well. Since water is a necessary commodity in the oil shale industry, many of these compounds may be found in the waste and runoff waters.

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

Weaver and Gibson also reported on chronic inhalation studies of two raw shales and two spent shales.[134] In the study, rats and monkeys were subjected to the inhalation of the respirable dusts at concentrations of 10 and 30 mg/m^3. After one year of exposure, no adverse effects were seen in the animals.

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

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

Source: Ref. 134.

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

Mutagenicity. Humans may be exposed to materials leached from both raw and spent shale. Adverse human health effects might result particularly from long-term exposure to polycyclic aromatic hydrocarbons and trace elements emitted in various forms from the shale oil. Epler[136] has selected a group (Table 4.21) of organic compounds in shale oil and evaluated their mutagenic effects on the Salmonella histidine-reversion system. Although a number of the compounds may be promoters or modifiers of carcinogenesis (that is, active in co-carcinogenesis, perhaps in some cases as inhibitors), they do not appear to be mutagenic.

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

The search for the carcinogen in Scottish shale eluded many investigators until 1943, when Berenblum and Schoental[138] identified BaP (Benzo(a)pyrene) in shale oil, but they also observed a fraction of shale oil that was carcinogenic but did not contain detectable quantities of BaP. Later, Hueper and Cahamann[139] and Bogovsky[140], respectively, reported BaP-free American and Estonian oil shale to be carcinogenic on the basis of mouse skin painting studies. Thus, it is still uncertain which specific compounds in shale oil materials are carcinogenic.

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

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

Source: Ref. 135.

Table 4.21 Mutagenic Effect on Salmonella of Chemicals in Shale Oil

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

Table 4.21 (Cont'd)

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

[a] Compounds not identified in shale oil, but predicted to occur in the same or modified chemical form.

Source: Ref. 136.

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

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

The results of topical application of raw oil shale and upgraded oil to mouse skin are presented in Table 4.25.[135] It may be seen that shale oil induced tumors in 86% of the effective number with an average time for appearance of about 30 weeks, whereas the upgraded oil induced tumors in 13% of the effective number with an average latent period of 49 weeks. A solution of 0.05% BaP in toluene resulted in 91% of the effective number of mice developing tumors with an average latent period of 46 weeks. No tumors were observed in the mice treated with toluene alone after eighty weeks of topical application.

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

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

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

Source: Ref. 137.

Table 4.23 Carcinogenic Potency of Two Raw Shale Oils

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

[a] The final effective number is the number of mice alive at the time of appearance of the median tumor plus those mice that may have died with tumors.

Source: Ref. 135.

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

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

Source: Ref. 135.

Table 4.25 Carcinogenic Potency of Raw and Upgraded Shale Oil

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

[a] The final effective number is the number of mice alive at the time of appearance of the median tumor plus those mice that may have died with tumors.

Source: Ref. 135.

Table 4.26 Carcinogenic Potency of Shale Oils and Shale Oil Products[a]

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

[a] Incomplete: 54 weeks duration.

Source: Ref. 135.

5 PROBLEMS ASSOCIATED WITH HAZARDOUS WASTE STORAGE AND DISPOSAL

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

5.1 DISPOSAL OPTIONS

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

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

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

5.1.1 Ponding

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

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

Most of the sludge and ash ponds used to date are unlined. To reduce the possibility of liquors leaching into groundwater, the disposal ponds can be lined with some impermeable material such as clay. Another alternative is to include pond underdrainage.[141] This method retains the advantage of transferring the sludge to the disposal site by liquid transfer. The leachate from the base of the sludge is returned to the scrubber.

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

5.1.2 Landfill

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

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

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

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

5.1.3 Mine Disposal

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

Both strip mine reclamation and deep mine filling have been used for ash disposal from power plants for a number of years. It is thus natural to also consider mine disposal for FGD wastes. Evaluations of this form of disposal are being undertaken. Initial assessments have been undertaken by Aerospace[141] and Le et al.[142] and are summarized below.

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

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

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

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

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

5.1.4 Ocean Disposal

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

In a study assessing the ocean disposal of FGD wastes[141] various methods of transportation and disposal were examined, including surface craft (e.g., bottom-dump barge and slurry dispersion) and pipeline (outfall). Various chemical and physical forms of the FGD wastes were also considered, e.g., sulfite-rich wastes, sulfate-rich wastes, and chemically treated wastes in both "soil-like" and "brick-like" forms. Both continental shelf and deep ocean disposal of the wastes were examined.

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

5.1.5 Deep Well Disposal

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

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

5.1.6 Soil Application[143]

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

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

5.1.7 Incineration[143]

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

5.1.8 Chemical Treatment

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

5.2 LONG-TERM ENVIRONMENTAL PROBLEMS

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

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

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

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

5.2.1 Deterioration of Landfill Cover

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

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

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

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

5.2.2 Limited Soil Attenuation Capacity

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

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

The absorption/ion exchange capacities of soils are limited, however, and the migration of pollutants from disposal sites to the environment will occur. Estimation of the capacity of absorption/ion exchange can be approximated by using the Cation Exchange Capacity (CEC). In general, high CEC values usually indicate high clay content, high surface area, and thus higher attenuation capacity. For a specific site condition, (e.g., soil permeability, cation exchanger capacity, and depth), soil attenuation capacity can be quantitatively expressed as "breakthrough time," which refers to the years the specific site is capable of attenuating metal species in the leachate. The soil depths required for 20-year breakthrough of leachate concentrations of up to 1020 meq/ft^3 have been estimated for six different soils. The results indicate that leachate attenuation capacity of individual soils may be ranked in the following order: clay>loam>loam-silt loam> sandy clay loam>silt loam-silty clay loam>loam-clay loam>loamy sand. In addition, approximately two feet of clay can provide 20-year breakthrough for leachate concentrations of up to 100 meq/ft^3.[112]

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

5.2.3 Long-Term Reliability of Impervious Liners

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

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

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

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

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

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

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

6 SOLID WASTE UTILIZATION

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

6.1 BUILDING MATERIALS

6.1.1 Ash from Conventional Boilers

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

6.1.1.1 Cement and Concrete

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

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

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

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

6.1.1.2 Aggregates for Lightweight Concrete

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

6.1.1.3 Load-Bearing Fill

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

6.1.1.4 Brick

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

6.1.2 FGD Sludges

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

6.1.3 Fluidized Bed Material

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

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

6.1.4 Other Solid Wastes

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

6.2 ROAD CONSTRUCTION MATERIAL

6.2.1 Ash[68]

6.2.1.1 Lime- and Cement-Stablized Fly-Ash Pavements

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

6.2.1.2 Asphalt Pavements

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

6.2.1.3 Road Fill

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

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

6.2.2 FGD Sludge

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

6.2.3 Fluidized Bed Material

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

6.2.4 Other Solid Wastes

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

6.3 AGRICULTURAL USES

6.3.1 FGD Wastes

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

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

6.3.2 Fluidized Bed Material

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

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

6.4 ENVIRONMENTAL IMPACTS

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

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

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

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

6.5 EXTENT OF UTILIZATION

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

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

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

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

Table 6.1 Electric Utility Ash Utilization

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

Source: Ref. 156.

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

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

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

Depending on the type of SO_2 control employed, a number of the technologies could produce elemental sulfur or sulfuric acid. Regenerable FGD systems such as magnesium oxide and the Wellman-Lord process, which produce sulfur or sulfuric acid, are available. Although their cost has to date prohibited the use of these sytems by utilities, they may be used in the future by utilities and industry where land is not readily available for solid waste disposal.

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

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

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

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

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

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

[a] Ref. 141, p. 134, 1000 MW plant using magnesium oxide scrubbers.

[b] Ref. 69, Vol. 1, Section 5, 600 MW plant.

[c] Ref. 157, p. 672, Lurgi process producing 250 x 10^9 Btu/day.

[d] Ref. 157, p. 539, SRC II process producing 250 x 10^9 Btu/day.

[e] Ref. 158, p. 1287.

7 CHARACTERIZATION OF SELECTED HAZARDOUS WASTES FROM THE INDUSTRIAL SECTOR

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

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

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

7.1 COKE INDUSTRY

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

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

7.1.1 Industry Profile and Process Description

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

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

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

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

7.1.2 Hazardous Properties of the Waste

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

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

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

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

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

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

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

Process wastes similar in composition to coke plant ammonia still lime sludge can be produced in coal conversion and oil shale retort facilities. A study compared the process wastewater of coke plant ammonia liquor and the coal conversion processes including Synthane, Lurgi, Koppers-Totzer and SRC-I. Except for the low pressure and high temperature gasfication processes (e.g., K-T process), other gasification and all coal liquefaction processes appear to produce process wastewaters with similar pollutants and composition ranges[131] (see Table 4.14 of Sec. 4).

7.2 PETROLEUM REFINING INDUSTRY

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

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

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

7.2.1 API Separator Sludge

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

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

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

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

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

In oil shale, oil and tarry materials separated from wastewaters may constitute a semi-solid waste requiring disposal. Such material may contain suspended solids, hazardous organics, and trace elements. Handling options include incineration with air pollution control, burial with other solid wastes in the process shale pile, and reinjection into the retort or upgrading units.

7.2.2 Dissolved Air Flotation Float

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

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

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

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

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

7.2.3 Slop Oil Emulsion Solids

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

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

7.2.4 Heat Exchanger Bundle Sludge

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

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

7.2.5 Tank Bottoms

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

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

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

Petroleum Refinery[a]		Coal Ash[b]	Irrigation Water (FWPCA)	Public Water Supply Intake (EPA)
API Sludge	DAF Float			
1.9	3.3	.001 - 1.0	5	0.05

[a]Source: Ref. 109.

[b]Source: Ref. 111.

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

7.2.6 Biosludges

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

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

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

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

[a] Source: Ref. 110.

[b] Source: Ref. 112.

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

7.2.7 Spent Catalyst

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

7.3 ELECTROPLATING AND METAL FINISHING INDUSTRY

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

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

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

7.3.1 Process Description

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

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

7.3.2 Waste Stream Description

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

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