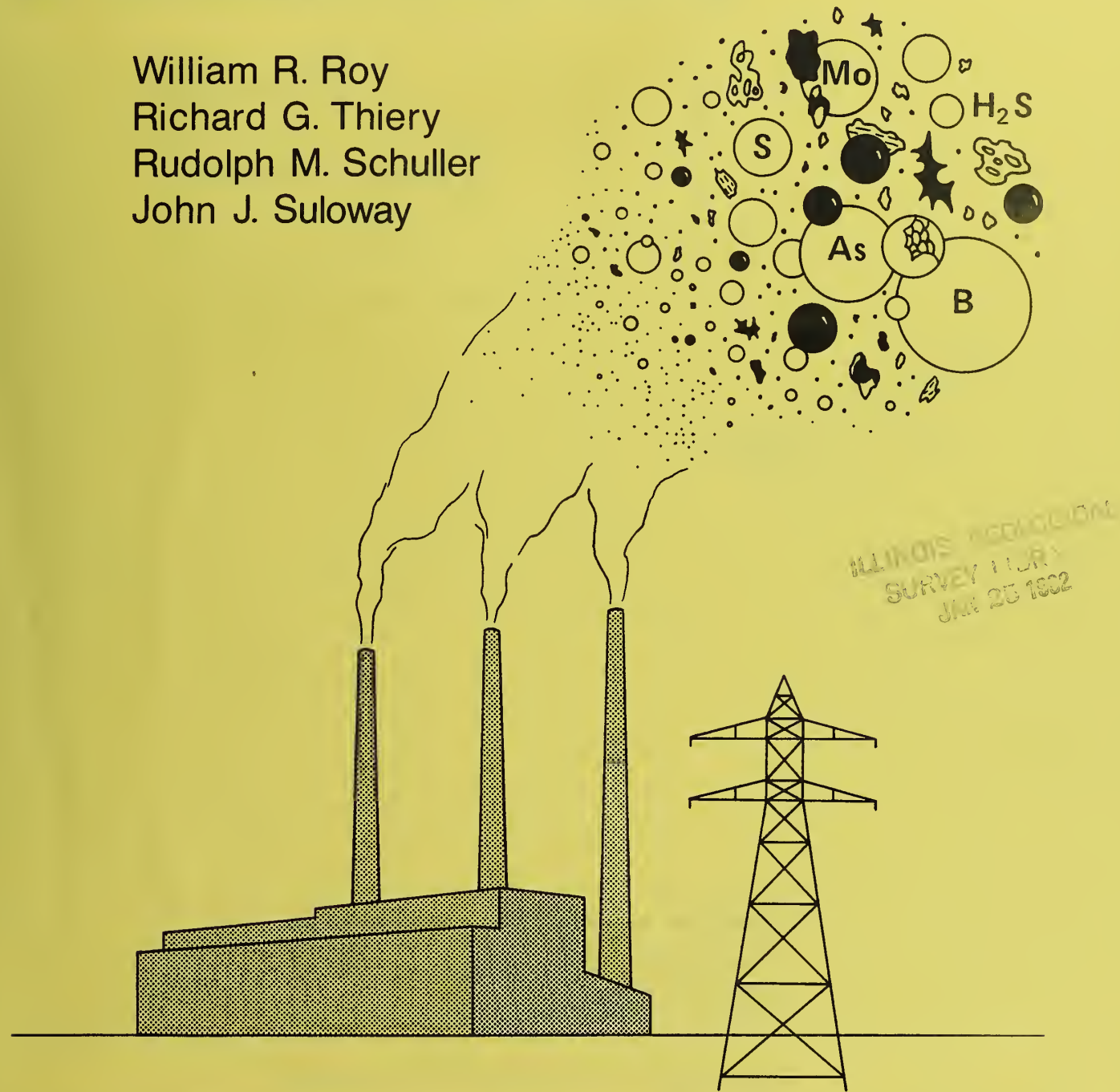
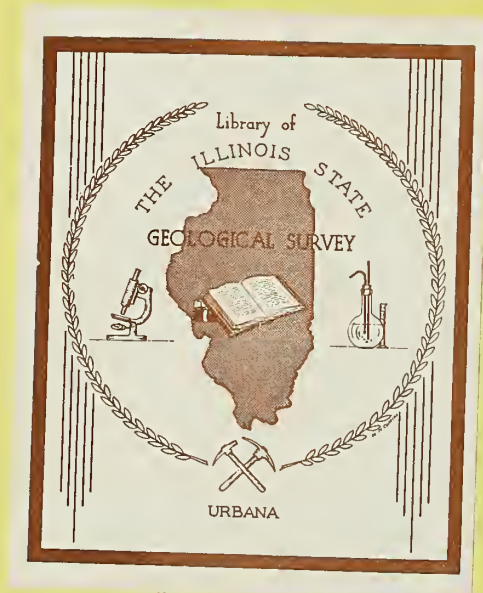


# Coal fly ash: a review of the literature and proposed classification system with emphasis on environmental impacts

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Roy, William R.

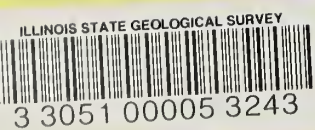
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# Coal fly ash: a review of the literature and proposed classification system with emphasis on environmental impacts

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# CONTENTS

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|  |       |
|--|-------|
| ABSTRACT   | p. 1  |
| INTRODUCTION   | p. 1  |
| ORIGIN OF SOLID WASTES FROM COAL-FIRED POWER PLANTS  | p. 4  |
| PHYSICAL PROPERTIES OF FLY ASH                       | p. 6  |
| Microscopic investigations of fly ash                | p. 6  |
| Mineralogy of fly ash                                | p. 7  |
| CHEMICAL COMPOSITION AND PROPERTIES OF FLY ASH       | p. 8  |
| Fly ash fallout                                      | p. 8  |
| Elemental determinations                             | p. 10 |
| Particle-size relationships                          | p. 13 |
| Organic constituents                                 | p. 17 |
| Radioactivity  | p. 18 |
| Leaching studies                                     | p. 18 |
| EFFECTS OF FLY ASH ON AQUATIC ECOSYSTEMS             | p. 23 |
| EFFECTS OF FLY ASH ON HEALTH                         | p. 29 |
| FLY ASH DISPOSAL AND UTILIZATION                     | p. 32 |
| Disposal methods                                     | p. 32 |
| Fly ash as an additive to construction products      | p. 33 |
| Fly ash as a mineral resource                        | p. 34 |
| Civil engineering applications                       | p. 34 |
| Coal mine reclamation                                | p. 35 |
| Fly ash as a soil modifier                           | p. 35 |
| Ocean disposal                                       | p. 38 |
| Ash pond disposal                                    | p. 38 |
| Landfill disposal                                    | p. 40 |
| Site selection                                       | p. 41 |
| SUMMARY  | p. 41 |
| BIBLIOGRAPHY   | p. 45 |
| APPENDIX A. A PROPOSED FLY ASH CLASSIFICATION SYSTEM | p. 65 |

## FIGURES

---

1. Possible arrangement of solid waste control systems for the removal of slag, bottom ash, and reduction of fly ash emission p. 5
2. Fly ash morphogenesis scheme illustrating probable relationship of opacity to particle combustion and relationship of particle shape to exposure to combustion temperatures p. 7
3. Chromium distribution around a coal-fired power plant p. 9
4. Enrichment factors of various elements in fly ash as related to concentrations in coal p. 16
5. Elemental depth profiles for fly ash particles determined by microprobe techniques p. 17
6. Elemental leaching rates for fly ash p. 21
7. Flow diagram for power plant ash and scrubber sludge waste disposal p. 40
- A-1. Fly ash classification system p. 66

## TABLES

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1. Maximum contaminant concentrations for toxicity classifications p. 3
2. Bibliography of coal fly ash reviews p. 3
3. Variations in mineral composition of fly ashes from three countries p. 8
4. Bibliography of major studies containing results from chemical analyses of fly ashes p. 10
5. Percentages of concentration of the major elements in 13 fly ash samples p. 11
6. Range and average chemical composition of fly ash p. 12
7. Selected analytical data for minor and trace elements in fly ash p. 14
8. Estimated polycyclic aromatic hydrocarbon concentrations in coal ash p. 18
9. Characteristics of discharges through ash ponds p. 24
10. Analyses of ash pond discharges p. 25
11. Elemental concentrations in edible portions of crops grown in pots with soil amended with 10% fly ash p. 38
- A-1. Fly ash groups p. 66
- A-2. Sialic maximum and minimum of the Ferrocalsialic field p. 67
- A-3. pH prefixes p. 68
- A-4. Summary of nomenclature p. 68

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## ABSTRACT

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This comprehensive review of the scientific literature on fly ash generated by coal burning power plants cites studies reported in 284 publications up to September, 1980. General conclusions are formulated, on the basis of data compiled from this review, on the physico-chemical characteristics of the solid waste and the possible environmental impacts of its disposal.

Fly ash is composed of fine-grained particles that have a variable morphology and consist primarily of an amorphous glassy material. The elemental composition of fly ash is highly variable and directly related to compositional variations in the parent coals and to the operational characteristics of the individual power plants. Some elements are concentrated (enriched) on fly ash particle surfaces. While the glass-like particles are essentially insoluble in water, the enriched surface elements may be soluble and therefore available to the environment upon leaching of the solid waste. Fly ash leachates also demonstrate a great deal of variability in chemical composition. Toxicity studies suggest that fly ash leachates may adversely effect aquatic ecosystems, while the solid material may be hazardous to terrestrial ecosystems by direct external reactions (skin, eyes, etc.) or reactions in the respiratory tract or alimentary canal.

The predominant method of fly ash disposal is by wet sluicing to on-site ash ponds. The greatest use of the solid waste is as an additive to concrete mixture; several other schemes for using the solid waste have been proposed. Plants grown in experimental fly ash amended soils have shown enrichment of certain chemical constituents in plant tissues.

A classification system for fly ash is proposed in this paper; this system should aid in systematic fly ash research and in the discussion of fly ash properties.

## INTRODUCTION

---

In response to increasing energy demands, coal will contribute to making up the energy deficits anticipated in the United States during the coming decades. This demand may be increased by the unsure supplies of other fossil fuels and by problems associated with alternate energy sources such as nuclear and solar power. United States coal reserves are estimated at 3.6 trillion metric tons from which 396 billion metric tons (11 percent) can be economically mined under present technological conditions (Swanson et al., 1976). Predictions vary, but the National Coal Association forecasts an increase in coal usage from 787 million metric tons in 1976 to approximately 1.5 billion metric tons by 1985.

The technology of coal utilization produces a number of by-products that must be disposed of in an environmentally safe manner. To achieve this objective,

a series of laws has been passed to provide guidelines for the disposal of utility solid and liquid wastes and to provide criteria for defining hazardous wastes. Although these criteria are still undergoing evaluation, revision, and litigation, the current guidelines were established in the Resource Conservation and Recovery Act (RCRA) of 1976. This legislation had been preceded by the Solid Waste Disposal Act of 1965, the National Environmental Policy Act of 1969, and the Resource Recovery Act of 1970.

The Solid Waste Disposal Act of 1965, an amendment to existing air pollution control legislation, provided funds to generate a survey of municipal solid waste disposal problems. The Resource Recovery Act of 1970 was passed as a first attempt at setting guidelines for hazardous wastes disposal based on the preliminary data base of the previous legislation; further studies were mandated by this Act to augment the data base concerning solid waste management. However, only federal disposal sites were under the jurisdiction of these preliminary guidelines. The Resource Conservation and Recovery Act of 1976 is an amendment to the Act of 1970 based on the expanded data base. Of particular relevancy to coal fly ash is Subtitle C, Section 3001 of RCRA which provides procedures and standards for hazardous waste classification. This section also applies EPA criteria for the identification of hazardous wastes and lists wastes presumed to fall into this classification. A revised version of RCRA was recently published (EPA, 1980) after a period of litigation with industry. Fly ash is currently exempt from the list of Subtitle C or is classified as a nonhazardous waste under the present criteria.

The ramifications of RCRA have focused wide attention on fly ash because of the possibility that this solid waste may in the future be classified as a hazardous waste. As mandated by RCRA, the hazardous waste criteria have been divided into six categories: (1) ignitable, (2) reactive, (3) infectious, (4) corrosive, (5) radioactive, and (6) toxic. The last three categories are potentially applicable to fly ash as well as to most other utility solid wastes.

According to current guidelines, fly ash would be classified as a corrosive waste if, when slurried to a disposal pond, it generates a leachate with a pH less than or equal to 2, or greater than or equal to 12.5. A solid waste would also be classified as a hazardous material if it exhibits a corrosion rate greater than 0.64 mm per year on steel.

Fly ash would essentially be classified as a radioactive waste if the average  $^{226}\text{Ra}$  concentrations exceed 5 picocuries per gram, or if a leachate from a fly ash should exhibit a level of 50 picocuries per liter of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  combined.

The criteria establishing the toxicity of a substance are complex, and involve the generation of a leachate. If this leachate produces (1) gene mutation in bacterial or mammalian somatic cells or (2) DNA damage or modification in bacteria, mammalian cells or yeast, the solid waste is to be considered toxic. A waste can also be classified as toxic if a leachate obtained by the U.S. EPA Extraction Procedure (EP) has a trace metal concentration greater than the primary drinking water standards by a factor in excess of 100. Table 1 lists the maximum allowable contaminant concentrations for toxicity classification based on the U.S. EPA Extraction Procedure. In this procedure, a 6.3 percent slurry is agitated for 24 hours while the pH is held constant (4.9-5.2) during the agitation interval. However, the values (table 1) are currently being revised by the EPA.



TABLE 1. Maximum contaminant concentrations for toxicity classifications (U.S. EPA, 1980).

| Constituent     | Maximum concentration (mg/L) |
|-----------------|------------------------------|
| Ag              | 5.0                          |
| As              | 5.0                          |
| Ba              | 100.0                        |
| Cd              | 1.0                          |
| Cr              | 5.0                          |
| Hg              | 0.2                          |
| Pb              | 5.0                          |
| Se              | 1.0                          |
| Endrin          | 0.02                         |
| Lindane         | 0.4                          |
| Methoxychlor    | 10.0                         |
| Toxaphene       | 0.5                          |
| 2,4-D           | 10.0                         |
| 2,4,5-TP Silvex | 1.0                          |

The main drawback to these criteria is the omission of other potentially hazardous trace elements such as B, Co, Mn, Mo, or V. In the present scheme, even if these trace elements were present in EP extractions at toxic levels, the solid waste could still be disposed of as a nonhazardous waste.

With the onset of environmental legislation, fly ash has been scrutinized by many legislators, especially in the last 10 years. The purpose of this paper is to review the research on coal fly ash with emphasis on its possible effects on the environment. Research on oil fly ash, incinerator fly ash, or metal smelting fly ash is not considered in this review. Although various aspects of coal fly ash research have been previously reviewed (table 2), there has

been no fully comprehensive review covering all the relevant investigations reported in the literature.

A detailed discussion of the physico-chemical properties of fly ash is included to establish a comprehensive data base for environmental considerations. Since the possible generation of toxic leachates from fly ashes is probably the main concern with respect to aquatic ecosystems, leaching studies are treated in detail. Also discussed are disposal and utilization studies, investigations of health effects by fly ash and laboratory and field studies of the effects on terrestrial and aquatic ecosystems by fly ash. The final section deals with disposal and potential utilization studies. A proposed fly ash classification system, derived from information in the literature, is presented in the appendix.

TABLE 2. Bibliography of coal fly ash reviews.

| Source                               | Area of major concern                                      |
|--------------------------------------|--|
| Capp and Spencer, 1970               | Utilization of utility solid wastes                        |
| Torrey (ed.), 1978                   | Physico-chemical characterization of coal ash              |
| Dvorak, Lewis et al., 1978           | Environmental impact of utility solid wastes               |
| EPRI, 1978                           | RCRA and utility solid wastes                              |
| Page, Elsewi,<br>and Straughan, 1979 | Environmental impact and physico-chemical characterization |
| Adriano et al., 1980                 | Utilization and disposal of fly ash                        |

## ORIGIN OF SOLID WASTES FROM COAL-FIRED POWER PLANTS

---

The technology of coal utilization, especially from coal-fired plants, results in several by-products that may pose hazards to the environment. These by-products are derived from (1) coal slurry pipelines, (2) coal cleaning and storage, (3) coal combustion waste products, (4) combustion emission products, and (5) solid wastes generated by emission abatement.

The combustion of coal produces solid wastes composed of noncombustible mineral matter initially present in the coal and to a lesser extent partly combusted coal or uncombusted coal. The mineral matter in coal may be derived from several sources. Detritus may have been deposited in the coal-forming swamps by alluvial processes or may have consisted of marine sediments. Mineral matter may also be derived from the flora that comprised the swamp. Some minerals may be the result of post-depositional agents affecting the composition of the coal deposits (i.e., groundwater, compaction, etc.). While the carbon and some of the other elements in coal may be completely oxidized or volatilized during combustion, a large portion of the mineral matter in the coal is transformed into residual by-products (ash). These by-products include slag, bottom ash, and fly ash.

Slag is a glassy, angular, mostly non-crystalline and sometimes vesicular material that accumulates in the furnace as the ash melts to a viscous liquid and is quenched in water for removal. Bottom ash (also called "cinders") results from ash that is removed in a solid granular form.

The coal residues that accumulate in the furnace (i.e., slag and bottom ash) are periodically flushed out with systems using air and/or water (fig. 1) and then sluiced to settling ponds for disposal. Fly ash is the portion of ash that is small enough, in terms of particle size, to be entrained in the flue gas and carried away from the site of combustion. (Flue gases are the high velocity gases emanating from the furnace.) Fly ash particles are typically derived from the melting of mineral matter or the partial combustion of coal. In general, about 70 to 80 percent of the solid wastes derived from the combustion of coal is fly ash (Dvorak, Lewis et al., 1978; and EPRI, 1979).

Ash production in the U.S. in 1977 resulted in 67.8 million tons, of which about 48 million tons was fly ash (Faber, 1979). Ash production may reach 125 million tons by 1990 and may increase by a factor of four in the next 20 years (Faber, 1979). In Illinois, the three major electric utilities generated an estimated 1,867,000 tons of fly ash in 1979. This estimate does not take into account the smaller electric power companies and state institutions presently using coal. Moreover, the Energy Conservation and Conversion Task Force, responsible for assessing energy options for Illinois, recently recommended that 16 state institutions now using oil be converted to coal. Thus it seems reasonable to predict that the 1979 tonnage of fly ash produced in Illinois will increase substantially during the coming decades.

Devices of various designs are used to remove fly ash from flue gases to abate atmospheric emission of these particles and to collect these wastes for disposal. There are four types of fly ash control systems: fabric filters, mechanical collectors, wet scrubbers, and electrostatic precipitators. Stack-gas cleaning system designs must meet guidelines (New Source Performance) established by the U.S. EPA.

*Fabric filters* simply trap particles on fine threads composing the fabric. Fabric filters are not now often used in the high temperature situations of coal-fired power plants, although some investigators (Carr, Piulle, and Gooch, 1977) favor fabric filtration over other devices.

*Mechanical collectors* utilize centrifugal forces to separate fly ash particles from the flue gases. The particles are thrown to the collector's outside wall where they are removed. Mechanical collectors are not efficient enough to meet U.S. EPA standards but have been used in line with wet scrubbers or electrostatic precipitators, or both, before the final release of the flue gas into the stack.

*Wet scrubbers* remove fly ash particles from the flue gas by: (1) transference to water by inertial impaction (primarily effective for  $>1 \mu\text{m}$  particles); (2) interception (primarily effective for 0.1 to  $1 \mu\text{m}$  particles); and (3) diffusion into collector droplets (for  $>1.0 \mu\text{m}$  particles) (Dvorak, Lewis et al., 1978). The collected fly ash is then sluiced to settling ponds.

*Electrostatic precipitators* are often used in coal-fired power plants because of their high collection efficiencies and low power requirements. Electrostatic precipitators create a direct-current high voltage corona which ionizes electronegative gas molecules such as  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{SO}_2$ . These ions charge the fly ash particles by colliding with them and transferring the charge. The negatively charged particles of fly ash are then attracted to positively charged collecting electrodes. The collected fly ash is usually sluiced to

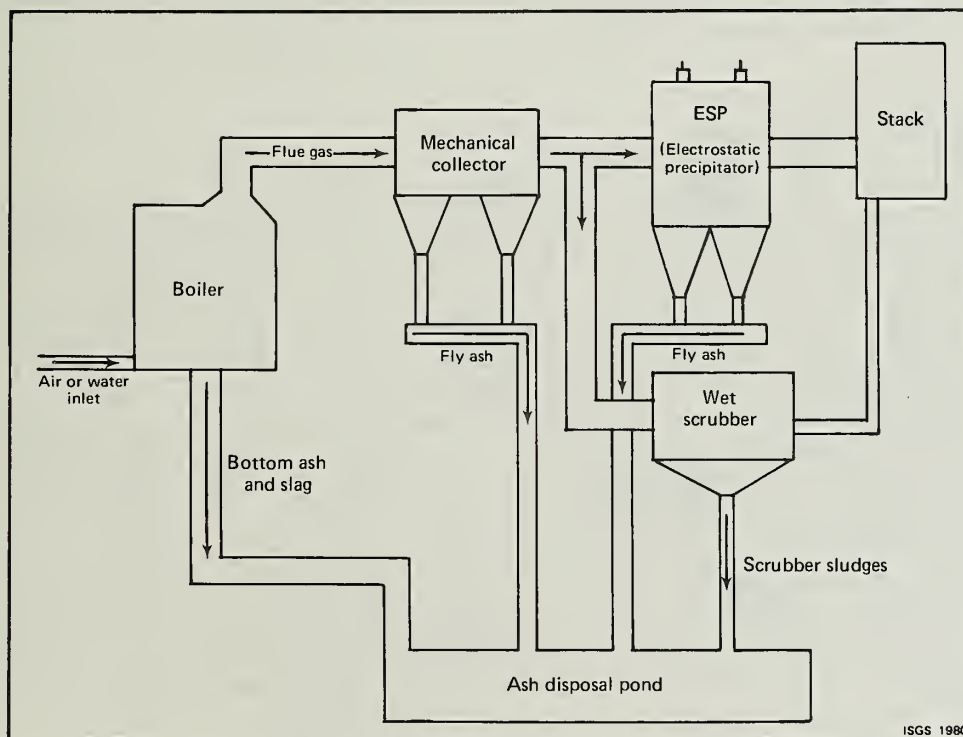


FIGURE 1. Possible arrangement of solid waste control systems for the removal of slag, bottom ash, and reduction of fly ash emission.

settling ponds. Figure 1 shows one possible arrangement of fly ash control systems. The flue gas carrying fly ash particles from the site of combustion enters a mechanical collector where particles ( $>10\ \mu\text{m}$ ) are removed and routed to a disposal area. Assisted by blowers, the flue gas still carrying the remaining fly ash particles ( $<10\ \mu\text{m}$ ) passes through either an electrostatic precipitator or a wet scrubber or both. These devices remove the remainder of the fly ash particles (with a total efficiency of 99.5%) from the flue gas. The collected fly ash is then routed to a disposal area.

## PHYSICAL PROPERTIES OF FLY ASH

---

Fly ash consists of predominantly silt-size particles ranging from grey to tan to reddish brown. Analytical texture data from various investigators (Chang et al., 1977; Page, Elsewi, and Stranghan, 1979; and Townsend and Hodgson, 1973) indicate that, in general, fly ash has a silt loam texture. In a national survey of fly ash produced in 21 states, 60 percent of the samples were described as having a "floury consistency" and 40 percent as having a "fine granular texture" (Furr et al., 1977). Approximately 65 percent to 90 percent of the fly ash is finer than 0.010 mm, depending on the type of removal system and furnace (EPRI, 1979). The fine texture of fly ash reflects its physical properties.

Hydraulic conductivities are variable, but generally are low (Bern, 1976; Dvorak, Lewis et al., 1978; EPRI, 1979; Townsend and Hodgson, 1973), ranging from about 9 cm/day of water through compacted fly ash to 70 cm/day through uncompact fly ash. Also, fly ash characteristically has a low bulk density (Bern, 1976; Cope, 1962; EPRI, 1979; Townsend and Hodgson, 1973). The specific gravity of fly ashes ranges from 2.1 to 2.6 g/cm<sup>3</sup> (EPRI, 1979).

### Microscopic investigations of fly ash

The morphology of fly ash particles has been investigated using scanning electron and light microscopes. Raask (1968) observed thin-walled hollow spheres in coal ash and referred to these particles as "cenospheres." He calculated that they can amount to as much as 20 percent by volume of total fly ash. Ramsden (1968, 1969) reports that various stages characterize the combustion of the coal and the formation of fly ash. Carbon black forms at an early stage, possibly through cracking of volatiles. Many devolatilized coal particles form carbonaceous skeletal structures, while some form vesicular carbonaceous spheres. Small glass-like spheres suggesting formation from a liquid phase were also observed. Ramsden postulates that small droplets of liquid ash coalesce to produce larger droplets. Paulson and Ramsden (1970) describe the presence of (1) black, irregularly shaped particles; (2) angular, transparent and opaque fragments; and (3) glassy spheres and globules ranging in color from black to yellow to red. The spherical particles (cenospheres) are smaller than 5  $\mu\text{m}$  in diameter. Paulson and Ramsden also noted variable particle morphology in some ashes and mentioned that some cenospheres formed agglomerates.

Cenospheres packed with smaller spheres are described by Fisher, Chang, and Brummer (1976), who suggested that the filled spheres be called "plerospheres." They also noted the presence of microcrystal formation in older fly ash samples. Natusch et al. (1977) describe five different morphological classes of fly ash particles: (1) large, irregular particles predominate in the

greater than 74  $\mu\text{m}$  size fraction; (2) solid spherical particles predominate in the size range below 10  $\mu\text{m}$ ; (3) hollow spherical particles (cenospheres) predominate in the 20 to 74  $\mu\text{m}$  size range; (4) hollow spherical particles containing encapsulated particles predominate, as host particles, in the size range from 20 to 74  $\mu\text{m}$ ; and (5) agglomerates of many small (less than 10  $\mu\text{m}$ ) spherical particles form large nonspherical particles that predominate in the size range greater than 74  $\mu\text{m}$ .

Eleven morphological particle types as suggested by Fisher, Chrisp, and Jennings (1978) include: (1) amorphous non-opaque; (2) amorphous opaque; (3) amorphous, mixed opaque and non-opaque; (4) rounded vesicular non-opaque; (5) rounded, vesicular, mixed opaque and non-opaque; (6) angular lacy opaque; (7) non-opaque cenosphere; (8) non-opaque plerosphere; (9) non-opaque solid sphere; (10) opaque sphere; and (11) non-opaque spheres with crystals. According to Fisher et al., the finest fraction was composed of 87 percent non-opaque solid spheres and about 8 percent cenospheres. In contrast, the coarsest fraction was composed of 26 percent non-opaque solid spheres and 41 percent cenospheres. The authors also present a fly ash morphogenesis scheme for fly ash that illustrates the probable relationship of opacity to particle composition and the relationship of particle shape to exposure to the heat in a combustion chamber (fig. 2).

### Mineralogy of fly ash

The mineralogy of fly ash has been studied by x-ray powder diffraction by several investigators. Natusch et al. (1977) state that alpha-quartz, mullite, hematite, and magnetite are present in fly ashes but that amorphous

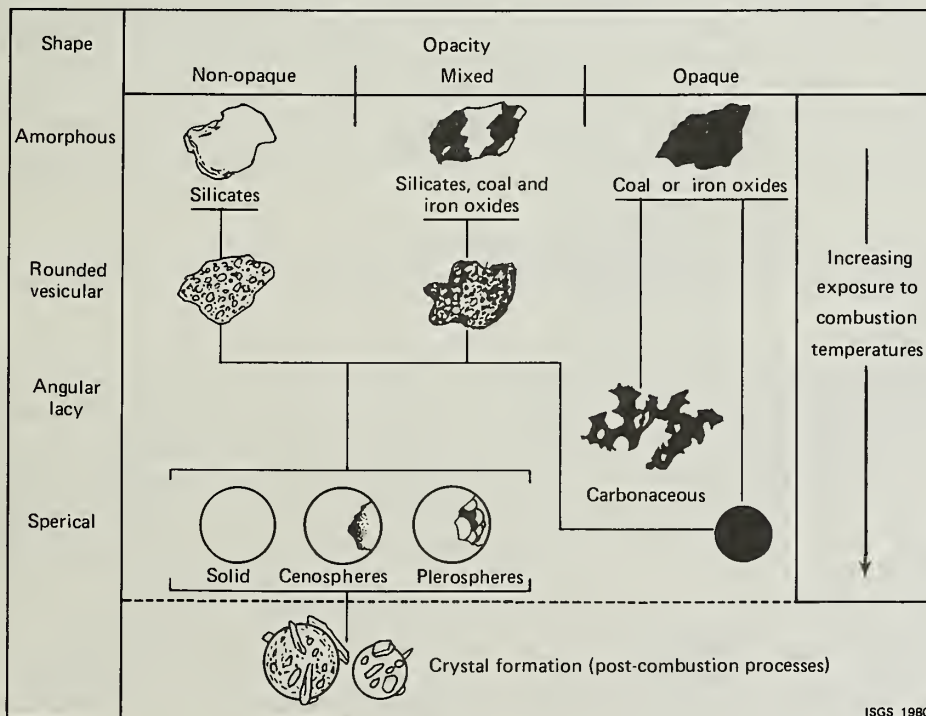


FIGURE 2. Fly ash morphogenesis scheme illustrating probable relationship of opacity to particle combustion and relationship of particle shape to exposure to combustion temperatures (modified from Fisher et al., 1978).

TABLE 3. Variations in mineralogical composition of fly ashes from three countries (Rehsi, 1974).

| Phase composition | United States <sup>a</sup><br>(%) | United Kingdom <sup>a</sup><br>(%) | Japan<br>(%) |
|-------------------|-----------------------------------|------------------------------------|--------------|
| Amorphous glass   | 50-90                             | 50-90                              | 69-84        |
| Mullite           | 0-16                              | 9-35                               | 8-18         |
| Magnetite         | 0-30                              | 5                                  | NA           |
| Hematite          | 1-8                               | 5                                  | 0.5-5.3      |
| Quartz            | 0-4                               | 1.0-6.5                            | 5.4-11.8     |

<sup>a</sup>Simons and Jeffery (1960).

NA = not available.

material predominates in the fly ash matrix. They also found small amounts of gypsum in a few western ashes. Fly ash from eastern coals often displays higher percentages of amorphous material than does fly ash derived from western coals (Fisher, Chang, and Brummer, 1976). Hematite, magnetite, quartz, calcite, and anhydrite were found in other fly ash samples (Schuller et al., 1979). Quartz, gypsum, calcite, Fe and Al oxides, mullite, and chlorite were found in fly ash examined by Page, Elseewi, and Stranghan (1979); they also found that mullite and quartz were more concentrated in the coarse fraction of fly ash and that gypsum and goethite were more concentrated in the fine fractions. A considerable proportion of fly ash consisted of a material shown to be amorphous by x-ray diffraction. Other studies indicate that more than 85 percent of most fly ash is composed of glass (Hurst and Styron, 1979). Mullite, quartz, magnetite, fired illite and other clay, hematite, anhydrite, and in rare instances, periclase and crystalline lime were also detected. In addition to these materials, trace amounts of boron species including borax, rhodium boride, boron arsenite, and boron phosphate were suggested by Adriano et al. (1980). Rehsi (1974) presents data on the mineralogical variation of fly ashes from the United Kingdom, United States, and Japan (table 3). Quantitative mineralogical data such as this is rarely seen in publications.

## CHEMICAL COMPOSITION AND PROPERTIES OF FLY ASH

### Fly ash fallout

The atmospheric dispersion of particulate matter resulting from the combustion of fossil fuels has sparked a number of studies investigating the constituents in fly ash. Preliminary calculations by Bertine (1971) suggest that the combustion of coal and oil could potentially mobilize many elements into the atmosphere at rates comparable to their rates of flow in natural waters during the weathering cycle. The National Academy of Sciences (1979) published estimates of annual atmospheric trace element discharges from three power plants. Estimated discharges of 14 trace elements included As, ranging from 105 to 4,330 kilograms per year; Cd (about 10 kg/yr); Co (11 to 948 kg/yr); Hg (53 to 109 kg/yr); Pb (105-327 kg/yr); and V (210 to 3,265 kg/yr). Another series of estimates suggests that atmospheric Pb emission may be up to 600 kg/yr for one western power plant (Gorden et al., 1977).

The relationship between coal burning and trace element mobilization into terrestrial systems has been documented by a few studies relating the

concentrations of constituents in soils to wind patterns around coal-fired plants. Soils around a coal-fired plant in Michigan were found to be enriched with Ag, Cd, Co, Cr, Cu, Fe, Hg, Ni, Ti, and Zn in the upper 2 centimeters of the soils in the area (Klein and Russell, 1973). Co was found to be about 2.3 mg/kg above background levels and Cd was enriched by about 0.9 mg/kg. Figure 3 illustrates the distribution of Cr concentrations in the surface soils around the power plant. A bimodal distribution of the predominant wind direction (northeast and southeast) may explain the existence of the two distribution lobes.

In a study of a coal-fired power plant in Illinois, trace element enrichment was also documented (Anderson and Smith, 1977). Background levels of Hg averaged about 16 mg/kg in the upper 2 cm of the soils in the area; however, concentrations northeast of the plant (downwind) averaged about 22 mg/kg. Detectable enrichment (correlated with wind direction) may have occurred during the 10 years that the plant had been in operation.

Bradford, Page, and Straughan (1978) found a limited decrease in Ca, Mg, B, Ba, and Sr with increasing distance from a power station; however, measurable enrichment of either soils and plants by fly ash fallout was not detected in their study.

However, Connor et al. (1976a, 1976b) and Gough and Erdman (1976) found selenium in lichen, grass, and sagebrush in concentrations decreasing exponentially with increasing distance from two power plants in Wyoming. Se concentrations in sagebrush, grass, and lichen samples ranged from about 0.5 to 2 mg/kg (dry weight) at about 0.8 to 1.2 km from each of the plants. But in these two studies, as in Bradford et al. (1978), similar trace element patterns were not detected in soil samples. The authors suggested that measurable trace element enrichment in native vegetation rarely extends beyond 10 km downwind from the power plant.

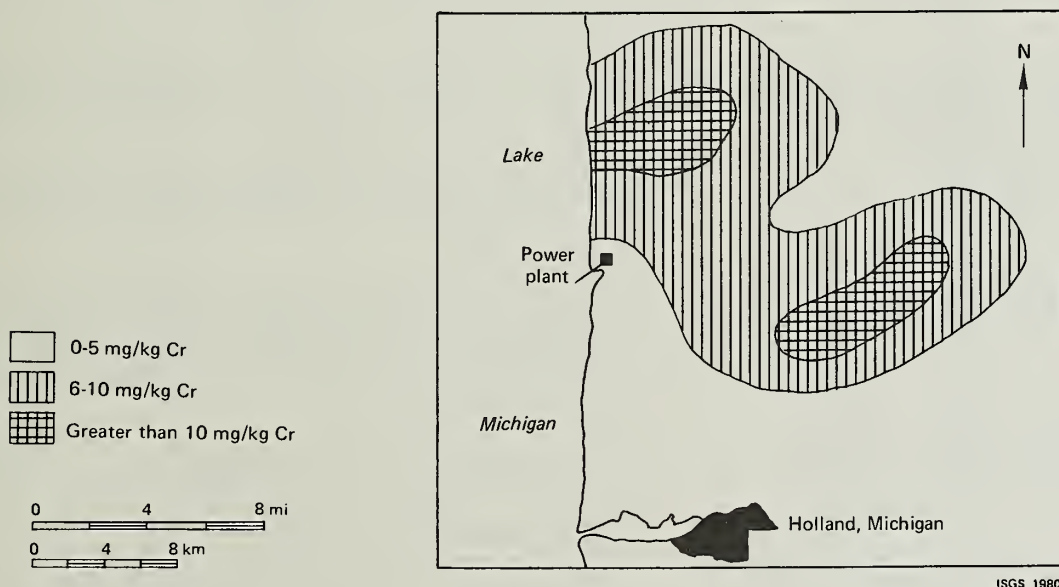


FIGURE 3. Chromium distribution around a coal-fired power plant. Prevalent wind directions were to the northeast and southeast (modified from Klein and Russell, 1973).

Detectable fly ash fallout may not be necessarily toxic. Cannon and Anderson (no date) argued that in some regions fly ash fallout would actually enrich soil deficient in trace nutrients. Some studies, however, indicate that there can be significant accumulation of potentially harmful trace elements. Lindberg et al. (1975), for example, by estimating atmospheric inputs and stream outputs, documented that a terrestrial system near three coal-fired plants contained elevated levels of Pb, Cd, Cu, Zn, Hg, Cr, and Mn. However, it was not possible to isolate the sources of the individual elements. The major source of Pb was probably automobile emissions. Huckabee and Blaylock (1974) showed, in a microcosm experiment, that about half the mercury on fly ash is retained by a terrestrial system while the rest leaches into neighboring aquatic systems.

### Elemental determinations

The elemental composition of fly ash has been characterized in several studies which include analytical data dealing with major, minor, and/or trace components (table 4). Other studies have resulted in the establishment of National Bureau of Standards (NBS) fly ash samples for analytical comparisons (Ondov et al., 1975 and Klein et al., 1975). Studies concentrating on individual elements such as B (Gladney et al., 1978 and Cox et al., 1978); Be (Gladney and Owens, 1976); Hg (Diehl et al., 1972); Se (Andren and Klein, 1975 and Gutenmann et al., 1976); and Zn (Schnappinger et al., 1975) have also been published.

Table 5 is a compilation of selected analytical data for 13 fly ash samples indicating the range of the major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, and S) as reported in their oxide forms. Chemical analyses of fly ash show that the major matrix elements are Al, Fe, and Si with smaller proportions of Ca, K, Na, P, Ti, and S. As discussed by Ode (1963) chemical analyses of ash are commonly reported in terms of oxides. However, the constituents in ash also occur as silicates, sulfates, and smaller quantities of other compounds. The silicon and aluminum oxides are probably derived from silicates

TABLE 4. Bibliography of major studies containing results from chemical analyses of fly ashes.

| Area of major concern       | Reference  |
|-----------------------------|--|
| Major elements              | Bickelhaupt, 1975; Funnell and Johnson, 1976; Nowak, 1974; Roy, Murtha, and Burnett, 1979; and Schuller et al., 1979.  |
| Trace and minor elements    | Coles et al., 1979; Fisher, Crisp, and Raabe, 1979; Kaakinen et al., 1975; Lee et al., 1972, 1975; Lee and von Lehmden, 1973; Natusch et al., 1974a, 1974b; Ondov, Ragaini, and Biermann, 1979a, 1979b; Phung et al., 1979; and Theis and Wirth, 1977.   |
| Detailed analytical studies | Block and Dams, 1975, 1976; Campbell et al., 1978; Chang, et al., 1977; Davison, 1974; Dvorak and Lewis, 1978; Furr et al., 1976a, 1977, 1978; Griffin et al., 1980; Hanson, Carpenter, and Henderson, 1975; Klein et al., 1975; Linton et al., 1976; Morse, 1979; Natusch et al., 1977; Nadkari, 1980; Ondov, Ragaini, and Biermann, 1978; Page, Elsewi, and Straughan, 1979; Ray and Parker, 1977; Santhanam and Ullrich, 1979; Smith, 1979; Smith, Campbell, and Felix, 1979; Smith, Campbell, and Nielson, 1979; and Torrey (ed.), 1978. |



TABLE 5. Percentages of concentration of the major elements (in their oxide forms) in 13 fly ash samples.

| References cited               |                                      |  |   |  |   |                                   |  |                                       |  |  |       |       |       |
|--------------------------------|--------------------------------------|--|---|--|---|-----------------------------------|--|---------------------------------------|--|--|-------|-------|-------|
|                                | Hanson et al. <sup>a</sup><br>(1975) | Natusch<br>et al. <sup>b</sup><br>(1977) | Smith<br>et al. <sup>c</sup><br>(1979a) | Block<br>and Dams <sup>d</sup><br>(1976) | Chu et al. <sup>e</sup><br>(1976, 1978) | Bickelhaup <sup>e</sup><br>(1975) | Ondov<br>et al. <sup>f</sup><br>(1975) | Page<br>et al. <sup>g</sup><br>(1979) | Chang<br>et al. <sup>e</sup><br>(1977) | Block<br>and Dams <sup>d</sup><br>(1975) |       |       |       |
| SiO <sub>2</sub>               | 23.32                                | 50.49                                    | 23.50                                   | 47.06                                    | -                                       | 49.70                             | 18.26                                  | 57.27                                 | 22.00                                  | 44.92                                    | 21.39 | 2.14  | 53.70 |
| TiO <sub>2</sub>               | 0.27                                 | 1.61                                     | 0.79                                    | 1.33                                     | 0.50                                    | 1.27                              | 1.07                                   | 1.05                                  | 0.60                                   | 1.23                                     | -     | -     | 0.75  |
| Al <sub>2</sub> O <sub>3</sub> | 12.79                                | 26.64                                    | -                                       | 20.78                                    | 10.96                                   | 31.19                             | 18.52                                  | 27.16                                 | 14.80                                  | 24.00                                    | 34.01 | 32.50 | 22.67 |
| Fe <sub>2</sub> O <sub>3</sub> | 12.18                                | 3.60                                     | 13.21                                   | 5.00                                     | 8.86                                    | 8.76                              | 20.79                                  | 3.81                                  | 11.20                                  | 8.86                                     | 7.42  | 7.15  | 4.58  |
| MnO                            | 0.10                                 | 0.10                                     | 0.04                                    | 0.12                                     | 0.05                                    | 0.05                              | 0.05                                   | -                                     | -                                      | 0.06                                     | 0.02  | -     | 0.11  |
| MgO                            | 2.24                                 | 0.27                                     | 2.04                                    | 2.98                                     | 1.86                                    | 1.53                              | 1.23                                   | 0.94                                  | 12.75                                  | 2.98                                     | 2.82  | 2.32  | 5.31  |
| CaO                            | 19.03                                | 0.70                                     | -                                       | 6.58                                     | 1.96                                    | 1.82                              | 5.74                                   | 5.18                                  | 31.00                                  | 16.58                                    | 14.41 | 8.68  | 5.29  |
| Na <sub>2</sub> O              | -                                    | -  | -                                       | 1.54                                     | 1.20                                    | 0.32                              | 0.66                                   | 1.83                                  | 1.84                                   | 0.43                                     | 1.62  | -     | 0.54  |
| K <sub>2</sub> O               | 0.79                                 | 3.09                                     | 7.06                                    | 2.55                                     | 0.56                                    | 4.34                              | 3.37                                   | 1.19                                  | 0.20                                   | 2.93                                     | 0.98  | -     | 6.09  |
| P <sub>2</sub> O <sub>5</sub>  | -                                    | -  | 0.14                                    | -  | -                                       | -                                 | -                                      | 0.17                                  | 0.39                                   | -  | 0.09  | 4.12  | 0.92  |
| SO <sub>3</sub>                | -                                    | -  | 1.77                                    | 1.30                                     | -                                       | 0.40                              | 1.55                                   | 0.33                                  | 1.83                                   | -  | 1.83  | -     | 2.75  |

<sup>a</sup>NaOH-Na<sub>2</sub>O<sub>2</sub> fusion and atomic absorption spectroscopy.

<sup>b</sup>Spark source mass spectrometry.

<sup>c</sup>X-ray fluorescence and neutron activation.

<sup>d</sup>Neutron activation.

<sup>e</sup>Not stated.

<sup>f</sup>Neutron activation and photon activation gamma-ray detection.

<sup>g</sup>Na<sub>2</sub>CO<sub>3</sub> fusion, spectroscopy, turbidimetrically, colorimetry, and neutron activation.

in the coal. Ferric oxide and sulfur oxides are synthesized by the thermal alteration of pyrite and other iron sulfides. The decomposition of carbonate minerals yields calcium and magnesium oxides, and sulfate compounds may be generated by reactions between carbonates, pyrite, and oxygen. An empirical formula of the chemical composition of the major elements in fly ash as presented by Fisher et al. (1976) is (in percent by weight): SiO<sub>2</sub>, 65.3; Al<sub>2</sub>O<sub>3</sub>, 25.2; Fe<sub>2</sub>O<sub>3</sub>, 3.4; CaO, 3.1; Na<sub>2</sub>O, 1.6; TiO<sub>2</sub>, 0.98; MgO, 0.89; and K<sub>2</sub>O, 0.89. However, a review of the analytical data in the literature suggests that since the chemical composition of fly ash is highly variable this formula should be used with caution.

Analytical determinations of silica (SiO<sub>2</sub>) range from approximately 2 percent to more than 60 percent. Alumina (Al<sub>2</sub>O<sub>3</sub>) and iron (Fe<sub>2</sub>O<sub>3</sub>) have been observed at levels up to 39 percent and 26 percent respectively; this relatively high iron content probably accounts for the reddish colors in some fly ashes. Fly ashes derived from western coals often have greater levels of calcium than fly ashes from eastern coals; this may result from the presence of gypsum, which has not been observed in eastern fly ashes. Swanson et al. (1976) have noted that higher levels of calcium characterize many western coals. Sulfur (SO<sub>3</sub>) determinations range from about 0.1 percent to more than 7 percent. The sulfur content in fly ashes is typically lower than in the feed coals since most of the sulfur is volatilized and discharged in the flue gases. Carbon can also be present in fly ash in levels of from less than 1 percent to more than 20 percent (Capp and Spencer, 1970). Older boilers tend to produce a fly ash with a higher carbon content than do new, more efficient units (EPRI, 1979). The residual carbon content has been related to sulfur retention in fly ash, which in turn has been related to ashing temperature and to the amounts of sulfur and calcium present in the coal (Rees et al., 1966).

Table 6 is a compilation of analytical determinations of the major constituents of fly ash as reported in the publications listed in table 4. Although there is considerable variability, an empirical formula can be calculated based on average constituent concentration. This formula (in percent by weight) is:

TABLE 6. Range and average chemical composition of fly ash (data from publications listed in Table 4).

| Constituent                    | Range (%) | No. of data | Average (%) | Std. dev. (%) |
|--------------------------------|-----------|-------------|-------------|---------------|
| SiO <sub>2</sub>               | 2.19-68.1 | 58          | 44          | 13            |
| TiO <sub>2</sub>               | 0.5-2.55  | 39          | 1.3         | 0.5           |
| Al <sub>2</sub> O <sub>3</sub> | 3.39-39.4 | 60          | 23          | 6.5           |
| Fe <sub>2</sub> O <sub>3</sub> | 3.60-29.2 | 58          | 11          | 6.5           |
| MnO                            | 0.02-0.24 | 14          | 0.1         | 0.1           |
| CaO                            | 0.2-31.0  | 58          | 8.2         | 8.0           |
| MgO                            | 0.4-12.8  | 58          | 2.7         | 2.7           |
| Na <sub>2</sub> O              | 0.2-8.0   | 50          | 1.8         | 2.0           |
| K <sub>2</sub> O               | 0.2-8.1   | 49          | 2.0         | 1.8           |
| P <sub>2</sub> O <sub>5</sub>  | 0.08-6.0  | 34          | 0.8         | 1.7           |
| C                              | 0.1-25.7  | 12          | 4.0         | 7.3           |
| SO <sub>3</sub>                | 0.1-7.28  | 47          | 1.6         | 1.9           |

SiO<sub>2</sub>, 44; Al<sub>2</sub>O<sub>3</sub>, 23; Fe<sub>2</sub>O<sub>3</sub>, 11; CaO, 8.2; C, 4.0; MgO, 2.7; K<sub>2</sub>O, 2.0; Na<sub>2</sub>O, 1.8; SO<sub>3</sub>, 1.6; TiO<sub>2</sub>, 1.3; P<sub>2</sub>O<sub>5</sub>, 0.8; and MnO, 0.1. This formula is broadly comparable to the one developed by Fisher et al. (1976) for Western fly ash.

Elemental determinations of isolated cenospheres (fig. 2) have been reported by Chu, Krenkel, and Ruane (1976 and 1978); Pedlow (1974); Raask (1978); and Zeeus and Abresch (1979). These results reinforce x-ray diffraction data suggesting that the major component of cenospheres is an amorphous glassy matrix. Some of the glassy spheres are filled with nitrogen and carbon dioxide, causing the lightweight particles to float on ash ponds.

Selected analytical data on the concentrations of minor and trace elements in fly ash are presented in table 7, which also demonstrates the variability in the chemical composition of fly ash. However, Natusch et al. (1977) note that ash from midwestern bituminous coals generally exhibits higher trace element levels than those from western subbituminous coals; but Morse (1979) cautions that regional differences in coal composition and coal seam variations complicate generalizations. EPRI (1979) also points out that the composition of the ash will be affected by the design, type, and operation of the power plant so that even when the same feed coal is used, the ash may vary from one plant to another. Other investigators have noted that, in general, fly ashes from western coals often have greater B levels, but lower As, Cd, Co, Cr, Pb, Sb, and Zn concentrations than those from eastern coals (Abernathy, 1969). Concentrations of Ba, Cl, Cu, Sr, and Zn exceeding 0.2 percent in fly ashes have been observed (table 7).

#### Particle-size relationships

The relationship of metal concentration to particle size has also been studied. Work by Davison et al. (1974) indicates that the concentrations of Pb, Tl, Sb, Cd, Se, As, Zn, Ni, Cr, and S increase markedly with decreasing particle size, while V, Mn, and Be exhibit non-uniform dependence on particle size. Bi, Sn, Co, Ti, Ca, K, and Cu concentrations do not correlate with particle size, suggesting that the elemental partitioning observed in fly ash results from the volatilization of certain elements or their compounds in the high-temperature coal combustion zone and their subsequent condensation or adsorption onto entrained particles. In a study by Kaakinen et al. (1975), Al, Fe, Rb, Sr, Y, and Nb were essentially at invariant concentrations in all outlet ashes from a coal-burning power plant (post-aerosol sampling device); Cu, Zn, As, Mo, Sb, Pb, Po, and Se were generally lowest in bottom ash and increased progressively toward the stack in fly ashes collected downstream. A mathematical model for an enrichment mechanism using the vaporization-condensation concept was also developed.

Klein et al. (1975) reported that most Hg, some Se, and probably most Cl and Br from the coal are discharged into the atmosphere as a result of combustion; As, Cd, Cu, Ga, Mo, Pb, Sb, Se, and Zn are concentrated in fly ash relative to the slag and more concentrated in the ash discharged through the stack than in that collected by the precipitator. Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th, and Ti showed little preferential partitioning between the slag and fly ash, whereas Cr, Sc, Na, Ni, U, and V were reported to exhibit inconsistent distributions.

Block and Dams (1975) found the Mg, Al, Ca, Sc, Ti, Cr, Fe, Co, Rb, Ba, Hf, Th, and the rare earths were associated with the larger fly ash particles

TABLE 7. Selected analytical data of minor and trace element composition of fly ash (concentrations in mg/kg).

| Element | References cited                     |  |                                       |  |   |  |  |   |      |      |      |      |      |     |       |   |   |   |   |   |   |
|---------|--------------------------------------|--|---------------------------------------|--|---|--|--|---|------|------|------|------|------|-----|-------|---|---|---|---|---|---|
|         | Smith et al. <sup>a</sup><br>(1979a) | Block<br>and Dams <sup>b</sup><br>(1975) | Page<br>et al. <sup>c</sup><br>(1979) | Ondov<br>et al. <sup>d</sup><br>(1975) | Hanson<br>et al. <sup>e</sup><br>(1975) | von Lehmden<br>et al. <sup>f</sup><br>(1974) | Klein<br>et al. <sup>g</sup><br>(1975) | Furr and Parkinson <sup>h</sup><br>(1977) |      |      |      |      |      |     |       |   |   |   |   |   |   |
| Ag      | 12                                   | 8  | -                                     | -                                      | -                                       | 0.04   | -                                      | -   | -    | -    | -    | -    | -    | -   | -     | - | - | - | - | - |   |
| Au      | -                                    | -  | -                                     | -                                      | -                                       | -  | -                                      | -   | -    | -    | -    | -    | -    | -   | -     | - | - | - | - | - | - |
| As      | 79                                   | 74                                       | 14                                    | 58                                     | 153                                     | 250  | 3                                      | 440                                       | 93   | 0.02 | 312  | 0.02 | 18   | 82  | 0.004 |   |   |   |   |   |   |
| B       | -                                    | -  | 237                                   | -                                      | -                                       | -  | 190                                    | -   | 230  | -    | 42   | -    | 370  | 36  | -     |   |   |   |   |   |   |
| Ba      | 2700                                 | 1  | 3700                                  | 2700                                   | 220                                     | 459  | 110                                    | 750                                       | 1159 | -    | 1068 | -    | 4997 | 974 | -     |   |   |   |   |   |   |
| Be      | -                                    | -  | -                                     | -                                      | 40                                      | 38   | 7                                      | -   | -    | -    | -    | -    | -    | -   | -     |   |   |   |   |   |   |
| Bi      | -                                    | -  | 36                                    | -                                      | 29                                      | 36   | -                                      | -   | -    | -    | -    | -    | -    | -   | -     |   |   |   |   |   |   |
| Br      | 1                                    | 6  | -                                     | 12                                     | -                                       | -  | -                                      | -   | 5    | -    | 11   | -    | 2    | 3   | -     |   |   |   |   |   |   |
| C       | 3000                                 | 4000                                     | -                                     | -                                      | -                                       | -  | -                                      | -   | -    | -    | -    | -    | -    | -   | -     |   |   |   |   |   |   |
| Cd      | 8                                    | 10                                       | 1                                     | -                                      | 0.4                                     | 0.8  | 2                                      | 51  | 2    | -    | 0.3  | -    | 1    | 0.3 | -     |   |   |   |   |   |   |
| Ce      | 170                                  | 180                                      | 108                                   | 146                                    | -                                       | -  | -                                      | 120                                       | 233  | -    | 205  | -    | 169  | 300 | -     |   |   |   |   |   |   |
| Cl      | 530                                  | 480                                      | -                                     | 42                                     | -                                       | -  | -                                      | -   | -    | -    | -    | -    | 16   | -   | -     |   |   |   |   |   |   |
| Cr      | 265                                  | 230                                      | 64                                    | 127                                    | 25                                      | 105  | 330                                    | 900                                       | 171  | -    | 156  | -    | 115  | 172 | -     |   |   |   |   |   |   |
| Co      | 69                                   | 26                                       | 13                                    | 42                                     | -                                       | -  | 45                                     | 65  | 40   | -    | 39   | -    | 26   | 35  | -     |   |   |   |   |   |   |
| Cu      | 650                                  | 500                                      | 50                                    | -                                      | 112                                     | 102  | -                                      | -   | 349  | -    | 99   | -    | 616  | 132 | -     |   |   |   |   |   |   |
| Cs      | 4                                    | 5  | 5                                     | 9                                      | -                                       | -  | -                                      | 27  | 10   | -    | 11   | -    | 8    | 10  | -     |   |   |   |   |   |   |
| Dy      | 20                                   | 8  | -                                     | -                                      | -                                       | -  | -                                      | -   | -    | -    | -    | -    | -    | -   | -     |   |   |   |   |   |   |
| Eu      | 6                                    | 2  | 8                                     | 3                                      | -                                       | -  | -                                      | 1   | -    | -    | -    | -    | -    | -   | -     |   |   |   |   |   |   |
| F       | -                                    | -  | -                                     | -                                      | -                                       | -  | 60                                     | -   | 21   | -    | 2    | -    | 7    | 9   | -     |   |   |   |   |   |   |
| Ga      | 165                                  | 96                                       | 29                                    | -                                      | -                                       | -  | -                                      | -   | -    | -    | -    | -    | 50   | -   | -     |   |   |   |   |   |   |
| Ge      | 33                                   | 30                                       | -                                     | -                                      | -                                       | -  | -                                      | -   | -    | -    | -    | -    | -    | -   | -     |   |   |   |   |   |   |
| H       | 1000                                 | 1000                                     | -                                     | -                                      | -                                       | -  | -                                      | -   | -    | -    | -    | -    | -    | -   | -     |   |   |   |   |   |   |
| Hg      | 5                                    | 5  | -                                     | -                                      | -                                       | -  | 0.1                                    | -   | -    | -    | -    | -    | -    | -   | -     |   |   |   |   |   |   |
| I       | 10                                   | 17                                       | -                                     | -                                      | -                                       | -  | -                                      | -   | 6    | -    | 0.7  | -    | 6    | 1   | -     |   |   |   |   |   |   |
| In      | 11                                   | 15                                       | -                                     | -                                      | -                                       | -  | -                                      | -   | -    | -    | -    | -    | -    | -   | -     |   |   |   |   |   |   |
| Hf      | 27                                   | -  | 1                                     | -                                      | -                                       | -  | -                                      | 5   | 7    | -    | 6    | -    | 8    | 9   | -     |   |   |   |   |   |   |
| La      | 105                                  | 71                                       | 60                                    | 82                                     | 66                                      | 140  | 190                                    | 42  | 76   | -    | 68   | -    | 62   | 99  | -     |   |   |   |   |   |   |
| Li      | -                                    | -  | 1                                     | -                                      | -                                       | -  | -                                      | -   | 1    | -    | 1    | -    | 1    | 2   | -     |   |   |   |   |   |   |
| Lu      | 2                                    | -  | 1                                     | -                                      | -                                       | -  | -                                      | -   | 34   | -    | 32   | -    | 13   | 33  | -     |   |   |   |   |   |   |
| Mo      | 91                                   | 87                                       | 9                                     | -                                      | -                                       | -  | -                                      | -   | -    | -    | -    | -    | -    | -   | -     |   |   |   |   |   |   |
| N       | 3300                                 | 250                                      | -                                     | -                                      | -                                       | -  | -                                      | -   | 19   | -    | 23   | -    | -    | -   | -     |   |   |   |   |   |   |
| Ni      | 90                                   | 190                                      | 50                                    | 98                                     | -                                       | -  | 45                                     | -   | 22   | -    | 11   | -    | 22   | 11  | -     |   |   |   |   |   |   |
| Nb      | 180                                  | 74                                       | -                                     | -                                      | -                                       | -  | -                                      | -   | -    | -    | -    | -    | -    | -   | -     |   |   |   |   |   |   |
| Nd      | 65                                   | 83                                       | 45                                    | -                                      | -                                       | -  | -                                      | -   | -    | -    | -    | -    | -    | -   | -     |   |   |   |   |   |   |
| Pb      | 90                                   | 250                                      | 45                                    | 75                                     | 133                                     | 81   | 180                                    | 650                                       | 18   | -    | 9    | -    | 34   | 15  | -     |   |   |   |   |   |   |

TABLE 7. (continued)

| Element | References cited                     |  |                                       |  |   |  |  |   |     |     |
|---------|--------------------------------------|--|---------------------------------------|--|---|--|--|---|-----|-----|
|         | Smith et al. <sup>a</sup><br>(1979a) | Bloek<br>and Dams <sup>b</sup><br>(1975) | Page<br>et al. <sup>c</sup><br>(1979) | Ondov<br>et al. <sup>d</sup><br>(1975) | Hanson<br>et al. <sup>e</sup><br>(1975) | von Lehmden<br>et al. <sup>f</sup><br>(1974) | Klein<br>et al. <sup>g</sup><br>(1975) | Furr and Parkinson <sup>h</sup><br>(1977) |     |     |
| Pd      | 5                                    | -  | -                                     | -                                      | -                                       | -  | -                                      | -   | -   | -   |
| Ra      | -                                    | -  | -                                     | -                                      | -                                       | -  | -                                      | -   | -   | -   |
| Rb      | 40                                   | 80                                       | 53                                    | 125                                    | -                                       | -  | 190                                    | 116                                       | 205 | 220 |
| Rh      | 5                                    | -  | -                                     | -                                      | -                                       | -  | -                                      | -   | -   | -   |
| Ru      | 6                                    | -  | -                                     | -                                      | -                                       | -  | -                                      | -   | -   | -   |
| Sb      | 9                                    | 50                                       | 4                                     | 7                                      | -                                       | 6  | 55                                     | 3   | 5   | 2   |
| Sc      | 50                                   | 78                                       | 16                                    | 27                                     | -                                       | -  | 36                                     | 16  | 29  | 22  |
| Se      | 15                                   | 80                                       | 19                                    | 10                                     | -                                       | 1  | 88                                     | 6   | 11  | 6   |
| Sm      | 25                                   | 43                                       | 9                                     | 12                                     | -                                       | -  | 9                                      | 12  | 17  | -   |
| Sn      | 60                                   | -  | -                                     | -                                      | -                                       | 2  | -                                      | 93  | 133 | 263 |
| Sr      | 2300                                 | -  | 1800                                  | 1700                                   | 77                                      | 69   | -                                      | 3245                                      | 515 | 794 |
| Ta      | 10                                   | -  | -                                     | 2                                      | -                                       | -  | 2                                      | 2   | 1   | 3   |
| Tb      | 4                                    | -  | 1                                     | -                                      | -                                       | -  | -                                      | -   | -   | -   |
| Te      | 5                                    | -  | -                                     | -                                      | -                                       | -  | -                                      | -   | -   | -   |
| Th      | -                                    | 16                                       | 21                                    | 25                                     | -                                       | -  | 26                                     | 46  | 46  | 68  |
| Ti      | -                                    | -  | -                                     | -                                      | -                                       | -  | -                                      | -   | -   | -   |
| U       | -                                    | -  | 7                                     | 12                                     | -                                       | -  | -                                      | 7   | 7   | 12  |
| V       | 900                                  | 420                                      | 12                                    | 235                                    | 166                                     | 290  | 1180                                   | 276                                       | 247 | 256 |
| W       | -                                    | 6  | -                                     | -                                      | -                                       | -  | -                                      | 4   | 9   | 7   |
| Y       | 115                                  | -  | -                                     | -                                      | -                                       | -  | -                                      | -   | -   | -   |
| Yb      | 11                                   | 17                                       | 4                                     | -                                      | -                                       | -  | -                                      | 4   | 5   | 7   |
| Zn      | 680                                  | 3500                                     | 99                                    | 216                                    | 104                                     | 330  | 5900                                   | 48  | 45  | 20  |
| Zr      | 1400                                 | -  | 183                                   | 301                                    | -                                       | -  | -                                      | -   | -   | -   |

<sup>a</sup>X-ray diffraction and neutron activation.

<sup>b</sup>Neutron activation.

<sup>c</sup>Neutron activation, colorimetry, and atomic absorption spectroscopy of acid extracts.

<sup>d</sup>Neutron activation and gamma-ray detection.

<sup>e</sup>NaOH-Na<sub>2</sub>O<sub>2</sub> fusions and atomic absorption spectroscopy.

<sup>f</sup>Spark source mass spectrometry.

<sup>g</sup>Neutron activation, x-ray diffraction, atomic absorption spectroscopy, and isotope dilution spark source mass spectroscopy.

<sup>h</sup>Neutron activation, colorimetry, anodic stripping voltammetry, specific ion electrode, x-ray diffraction, and furnace atomic absorption.

and occurred in lower concentrations relative to the original coal. Cl, Cu, Zn, As, Se, Br, In, Sb, I, and Hg were reported to be associated with the organic fraction of coal and were found to have a maximum concentration in the small fly ash particles. Na, K, V, Mn, Ni, Ga, Mo, Ag, Cd, Cs, W, and Au displayed an inconsistent distribution between the large and small fly ash particles.

Similar investigations by Coles et al. (1979) suggest that the concentrations of Al, Ca, Cs, Fe, Hf, K, Mg, Mn, Na, Rb, Sc, Ta, Th, Tl, and the rare earths Ce, Dy, Eu, La, Nd, Sm, Tb, and Yb showed little or no enrichment with decreasing particle size while As, Cd, Ga, Mo, Pb, Sb, Se, W, and Zn concentrations increased with decreasing particle size. They also state that Ba, Be, Co, Cr, Cu, Ni, Sr, U, and V displayed an intermediate behavior. Further work demonstrating trace metal concentrations and particle size relationships are found in Fisher, Chrisp, and Raabe (1979), Smith, Campbell, and Felix (1979), and Smith, Campbell, and Nielson (1979). Figure 4 gives enrichment factors of various elements in fly ash produced by two power plants in a study summarized by Torrey (1978). It should be noted that some investigators (Carr and Teixeira, 1977) do not believe that trace element enrichment necessarily exhibits monotonically increasing concentration as particle size decreases. Their work suggests that trace element concentrations reach a maximum in the 0.1 to 1.0  $\mu\text{m}$  diameter range; however, they do advocate that further research is needed. Problems in defining particle-size distributions of atmospheric aerosols, an integral part of evaluating trace metal dependency studies, have been described by Cheng and Yeh (1979), and by Dzubay, Hines, and Stevens (1976).

To summarize, many elements (As, B, Ba, Br, Cd, Cl, Co, Cu, Cr, Fe, Ga, Hg, I, In, Mg, Mn, Mo, Ni, Pb, Po, Rb, S, Sb, Sc, Se, Sr, Tl, W, V, and Zn) have been reported as being enriched in fly ash in varying degrees of magnitude, showing increasing concentrations with decreasing particle size.

Surface analytical techniques, ion microprobe mass spectrometry and Auger electron spectrometry have been used to demonstrate surface predominance of trace elements in fly ash. These elements are concentrated in a thin layer (about 1,000  $\text{\AA}$  in thickness) forming a shell around some particles (Linton et al., 1975). Linton et al. (1976), Linton, Williams, and Evans (1977), and Natusch et al. (1977) present elemental depth profiles (fig. 5) which establish that a number of potentially volatile elements are concentrated on the particle surface, but show that the more refractory species such as Al, Fe, and Si and the minor elements Mg and Ca do not exhibit surface predominance. The mechanism for this surface layer enrichment is not known with certainty, and

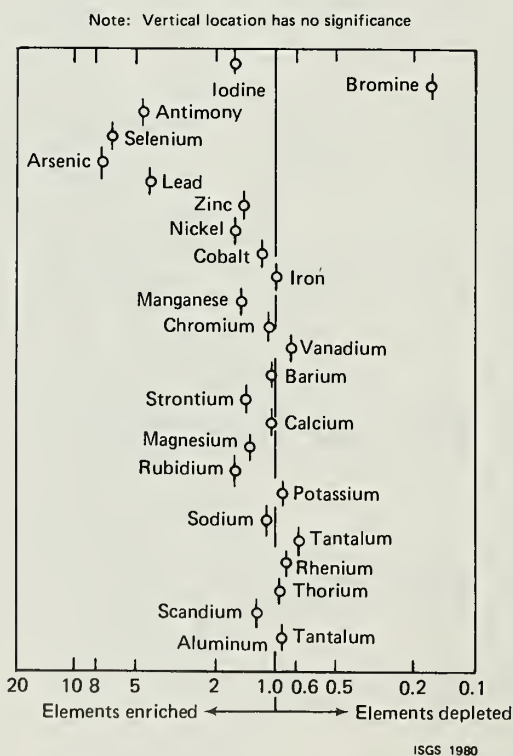


FIGURE 4. Enrichment factors of various elements in fly ash as related to concentrations in coal (from Torrey [ed.], 1978).

warrants further study. A mathematical volatilization-condensation model presented by Smith, Campbell, and Felix (1979) and Smith, Campbell, and Nielson (1979) relates the bulk concentration of the particles to their diameter, matrix composition, surface layer thickness, and surface concentration. Investigations of surface layer composition suggest that the outermost layer on the surface of some fly ashes is composed chiefly of  $H_2SO_4$ , which permits surface condensation of certain trace elements (Swaine, 1977). The presence of sulfuric acid on some particle surfaces may be the causative agent in post-combustion crystal formation of metal and/or ammonium sulfates (Fisher, Chang, and Brummer, 1976; Fisher, Chrisp, and Jennings, 1978). How this crystal formation affects the physico-chemical form of the enriched constituents has not been studied.

### Organic constituents

Trace inorganic constituents are not the only potentially hazardous substances in fly ash. Various complex organic molecules are also present, including such known carcinogens and/or mutagens as dimethyl and monomethyl sulfate (Lee et al., 1980) and the polycyclic hydrocarbons (PAH) dibenzofuran and benzo(a)pyrene (Masek, 1976). There are undoubtedly a large number of such organic molecules yet to be identified (Griest, Yeatts, and Laton, 1980).

The study of organic molecules in fly ash is complicated by the possibility of chemical changes during atmospheric transport. Utsumi, Lakas, and Elkind (1979) showed that light and the PAH dimethyl benzanthracene could interact to produce toxic substances. Korfmacher et al. (1980) found that organic molecules could oxidize spontaneously at a rate apparently dependent upon the fly ash composition. In either case, there is potential for post-emission chemical changes; therefore fly ash collected in the stack may not give realistic toxicity estimates. In fact, Natusch (1978) believes that a majority of organics do not condense onto fly ash until after emission.

One study (EPRI, 1978) found a total hydrocarbon content of about 9 mg/kg, with  $C_{17}$ ,  $C_{18}$ ,  $C_{21}$ , and  $C_{27}$ - $C_{31}$  hydrocarbons at concentrations in the range of 500 to 900  $\mu\text{g}/\text{kg}$ . Table 8 presents polycyclic aromatic hydrocarbon concentrations found in coal ash. The concentrations of these constituents were low, ranging from less than 0.2  $\mu\text{g}/\text{kg}$  to about 37  $\mu\text{g}/\text{kg}$ .

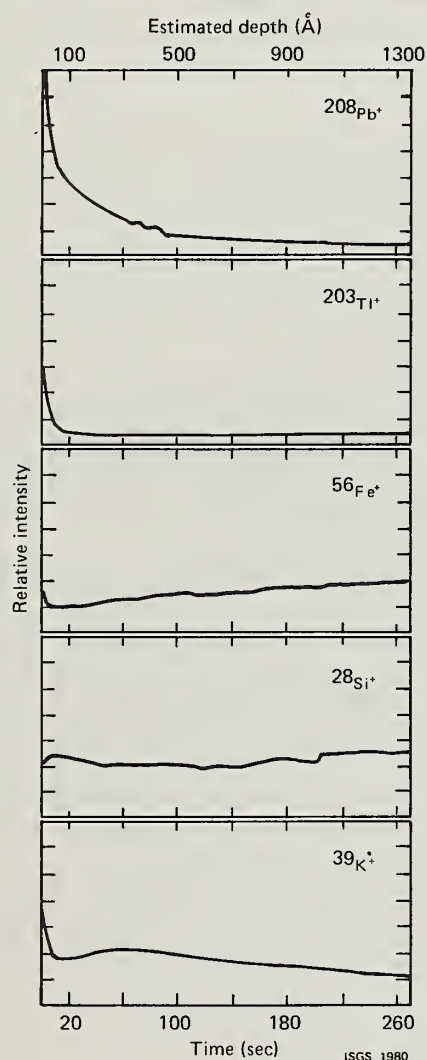


FIGURE 5. Elemental depth profiles, determined with microprobe techniques, for fly ash particles (Natusch, 1977).

TABLE 8. Estimated polycyclic aromatic hydrocarbon (PAH) concentrations in coal ash (from EPRI, 1978).

| PAH                                 | Concentration (µg/kg) |
|-------------------------------------|-----------------------|
| 1,2-Benzofluorene                   | 36.8                  |
| Phenanthrene                        | 17.6                  |
| 9,10-Dihydroanthracene              | 12.6                  |
| 2,3-Benzofluorene                   | 11.8                  |
| Biphenyl                            | 10.3                  |
| 2-Methylantracene                   | 9.1                   |
| Napthalene                          | 8.3                   |
| 1-Methylnaphthalene                 | 5.2                   |
| 2-Methylnaphthalene                 | 5.0                   |
| 1,6- and/or 1,3-Dimethylnaphthalene | <0.2                  |
| 2,6-Dimethylnaphthalene             | <0.2                  |
| 1,5- and/or 2,3-Dimethylnaphthalene | <0.2                  |
| 1-Methylpyrene                      | <0.2                  |
| Picene                              | <0.2                  |
| 1-Methylphenanthrene                | <24.8                 |
| Pyrene                              | <19.0                 |
| Fluoranthene                        | <13.4                 |

## Radioactivity

Radioactivity in fly ash has also been studied. However, there are few publications containing radio-nuclide concentration data. Coles, Ragaini, and Ondov (1978) describe the behavior of  $^{40}\text{K}$ ,  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$ ,  $^{228}\text{Th}$ ,  $^{228}\text{Ra}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$  in coal-fired power plants. They showed that significant to slight enrichment of these nuclides characterized the finer fly ash particles in the stack. The order of enrichment was  $^{210}\text{Pb} \gg ^{238}\text{U} \gg ^{226}\text{Ra} > ^{228}\text{Ra} > ^{228}\text{Th}$ . Gamma radiation detected in 23 fly ash samples ranged from 3.9 to 14.4 pCi/g above background, averaging  $6.4 \pm 2.3$  pCi/g (Furr et al., 1977). Morris and Bobrowski (1979) list gamma radiation ranges for 18 fly ash samples. They report that  $^{226}\text{Ra}$  varied from 2.4 to 10.0 pCi/g;  $^{214}\text{Pb}$  varied from 1.9 to 5.0 pCi/g; and  $^{214}\text{Bi}$  varied from 1.6 to 4.8 pCi/g. For comparisons, they included  $^{226}\text{Ra}$  activities of selected geological samples including limestone (0.29-0.42 pCi/g); sandstone (0.32-0.71 pCi/g); igneous rock

samples (1.02-2.06 pCi/g); and other specimens. EPRI (1978) concluded, on the basis of available data, that fly ash approaches but does not exceed the 5 pCi/g level of  $^{226}\text{Ra}$  that would classify it as a radioactive waste. However, available data are limited, and since there may be potential radiation hazards, future studies are needed.

The potential radiation hazards have been discussed by several researchers. For instance, the radioactive emission from coal-fired plants may exceed that of nuclear plants of similar size (Eisenbud and Petrow, 1964 and Kolb, 1978). Enhanced levels of U, Th, and Ra have been documented in the soils of industrial regions (Jaworowski and Gryzbowska, 1977). These studies to date have concluded that no direct health hazard exists (Styron, 1978, and Krieger and Jacobs, 1978); but if the use of fly ash (as a concrete additive) in building materials increases, there may be a problem. Pensko (1975) calculated that the average human radiation dose of 100 mrad/year may be increased to 130-300 mrad/year by habitation in buildings constructed with building materials impregnated with fly ash. Pensko has also projected the potential increases in leukemia, thyroid tumors, and lung carcinoma, and found the increases to range from 10 percent to 100 percent.

## Leaching studies

As discussed in Linton et al. (1976) and Linton, Williams, and Evans (1977), conventional bulk chemical analyses of particles that are essentially insoluble



aluminosilicate glasses provide little information on the mobility of potentially toxic trace metals in the aquatic ecosystem. The surface of the glassy spheres of fly ash particles may contain easily exchangeable or adsorbed molecules which may dissolve in the presence of a liquid, producing a potentially toxic leachate (EPRI, 1979). The toxicity of these leachates to aquatic organisms may be partly due to the release of toxic trace elements typically enriched on the surfaces of fly ash particles. To evaluate the potential for the contamination of water and soils from the leaching of fly ash, several different extraction methods, including various distilled water/ash slurries, cold and hot extractions with different acids, organic solvents, and bases, have been proposed. The overall results of these studies indicate the extreme variability of leachates generated from fly ash. This variability is directly related to the processes within the individual plants generating the ash, the coals being burned and the leaching procedures used. As shown by Gluskoter et al. (1977), coals from different regions possess diverse chemical compositions and, in fact, the chemical composition may change from seam to seam or even within a seam.

Jones and Lewis (1960) used constant head leaching columns and analyzed the leachates generated from fly ashes of different ages for P, Fe, Al, B, K, and Ca concentrations. They concluded that the leachability of these elements from fly ashes decreased as the age of the material increased.

The principle cations in water extracts of four fly ashes from lignite coal were Ca and Na (Shannon and Fine, 1974). Considerable variability in concentrations of Ca and Na were observed. Also, Mg and Fe were solubilized at rates roughly one to two orders of magnitude less than Ca and Na. As the ratios of water to ash were increased, the concentrations of Ca, Mg, and Fe increased proportionally, while Na acted inversely. Shannon and Fine found that about half of the aqueous species existed in the leachate as sulfates.

Hot extractions with concentrated  $\text{HNO}_3$  were used by Hanson, Carpenter, and Henderson (1975) to represent "extreme conditions" or worst case conditions for fly ash dissolution. Cold extractions with dilute HCl were used to represent biological conditions. Although the rationale for using a dilute acid as an extractant is not well explained, it may be based on the underlying principle that metabolic processes generate acidic conditions (i.e., dissolved  $\text{CO}_2$  in lung fluids). Dimethyl sulphoxide (DMSO) was used to represent analogous complexing agents found in lung tissues. Many elements require nitric acid for appreciable dissolution to occur, and fly ashes from different sources exhibit differences in elemental solubility in  $\text{HNO}_3$  and HCl, making generalizations difficult. DMSO extractions indicate that Bi, Sr, Ca, and K were concentrated in the precipitate that formed after the addition of water to the DMSO and that a large number of elements were soluble in DMSO. Therefore, dissolution of fly ash may occur by the complexing agents in lung fluids.

Chu, Krenkel, and Ruane (1976) and Chu, Ruane, and Krenkel (1978) used ratios of 30 g of fly ash to 1 L of water to make slurries which were shaken for 24 hours. The slurries were then filtered and the fly ash discarded. Fresh fly ash was again mixed in the same proportions with the filtered water and the shaking and filtration procedures were repeated. This procedure was designed to represent successive cycles of ash sluicing. Results of these investigations indicated that the rate of chemical leaching was influenced by ash particle size, agitation of the mixture, pH, and the temperature of the water. Specific conductance and pH generally reached equilibria within four

hours after contact of the ash with the water. The leachability of trace elements was governed by the surface concentration of each trace metal in the ash matrix, its chemical bonding in the ash, and the pH of the water it contacts. The authors concluded that low pH water favors the leaching of trace metals. The ranking of trace metal concentrations in alkaline ash sluice water after numerous cycles was: B > Ba > Al > Cr > Se > As and in neutral ash sluice water: B > As > Zn > Mn > Ni > Ba > Se > Cu > Cd. Moreover, the ranking of the amount leached in comparison to the total available (matrix concentration) was: Se > B > Cr > Ni > Cu > Ba > As > Zn > Al for alkaline fly ash and B > Cd > As > Se > Zn > Ni > Mn > Cu > Ba for the neutral fly ash. An acidic fly ash was not used in this study.

However, an acidic fly ash was studied by Griffin et al. (1980). A 10 percent slurry was stirred for six months. A 10 percent slurry was believed to best simulate ash ponding environments, and the long-term approach of this study was an attempt to generate a leachate at chemical equilibrium with the solid waste. After the leaching interval, the ranking of inorganic constituent concentration in the liquid phase was:  $SO_4 \gg Ca > Na > Al > B > Mg > Si > Zn > Fe > Mn > F, Sr, Ni, K > Li, Cd, Co > Cu, Pb > Be$ . The ranking of the amount leached in comparison to the matrix concentration was:  $B \gg Zn > Ca, F > Na > Mg, Co > Ni, Sr > Be > Cu, Pb, Al \gg Si, Fe, K$ . Griffin et al. also generated a series of leachates using the same acidic fly ash in which the pH of each solution was maintained at about 3, 8, or 9 by the additions of NaOH or  $HNO_3$ . Experiments were carried out in both aerobic and anaerobic conditions.

Samples of 0.2 g to 5.0 g of fly ash from different particle size fractions were equilibrated by continuous shaking with 24 mL deionized water in 35 mL-centrifuge tubes by Phung et al. (1979). Twice daily the pH was adjusted in the respective tubes with HCl to either 6.0 or 9.0. After three days, the volume in the tubes was brought to 30 mL, the tubes were centrifuged, and the supernatant filtered. Results of this study also indicated that solubility increased with decreasing pH. At pH 6.0, the relative solubilities of trace elements were suggested as  $B \gg Pb > Co > Cr > Ni > Mn > Zn > Cu > Cd$ .

Various dilutions of  $HNO_3$ , 1.0 M HCl, distilled  $H_2O$ , and 0.1 M  $NH_4OH$  were used as extractants with 25 percent (wt/vol) slurries by Dreesen et al. (1977). B, F, Mo, and Se were found to be typically most extractable by water and As, B, Cd, F, Mo, and Se by acidic extractants.

Fly ashes collected by electrostatic precipitators from eleven different plants were leached by three extraction procedures (Theis and Wirth, 1977). Amorphous oxides of Fe, Al, and Mn were determined by ammonium oxalate extractions. Solubility studies were performed by a series of experiments involving 20 percent slurries with distilled water in which the pH of the solutions (pH 3, 6, 9, and 12) were maintained with NaOH or  $HClO_3$  during a 24-hour shaking time. This work suggests that desorption of metals in leachates follows a predictable pattern of increasing release with decreasing pH (with the exception of As, which demonstrates amphoteric characteristics).

Natusch et al. (1977) used three extraction procedures in solubility studies of fly ash:

1. Three to four grams of ash in 200 mL of distilled water were sonically agitated for 30 minutes, then allowed to stand for 48 hours. This procedure was chosen to represent turbulent flow that might occur in sluicing.

2. Ten grams were placed in a pre-extracted Soxhlet thimble and refluxed for 24 to 48 hours with 300 mL solvent. This procedure was chosen to minimize the common ion effect on solubility.
3. Ten grams were continuously leached with a 400 mL stream of solvent circulated by a rotary pump. This procedure was chosen to represent in situ leaching of fly ash piles by rain or groundwater.

The extraction rates of different elements during continuous leaching of fly ash from western subbituminous coal is shown in figure 6. The behavior of most of the elements depicted is consistent with the idea that material in the surface layer is mostly soluble and that elements go into solution progressively as the solvent reaches their region of predominance—that is, the chemical form or physical location conducive to leaching. The surface layer appears to be almost completely solubilized within 24 hours, but Ca, Cu, Fe and Zn will be continuously leached from the glassy matrix for longer periods. Fe, Si, Ba, Ca, Mg and Ti exhibit very low solubility, but elements which predominate in the surface layer (i.e., Cd, Co, Li, Mn, P, Tl, and Zn) exhibit substantial solubility. Elements that are enhanced in the surface layer but have most of their mass in the particle interior (e.g., K and Na) are partially soluble.

James, Janghorbania, and Baxter (1977) studied the leachability of neutron-irradiated fly ash. Although their paper is basically concerned with the method, they do briefly point out some solubility trends. Rapid early dissolution

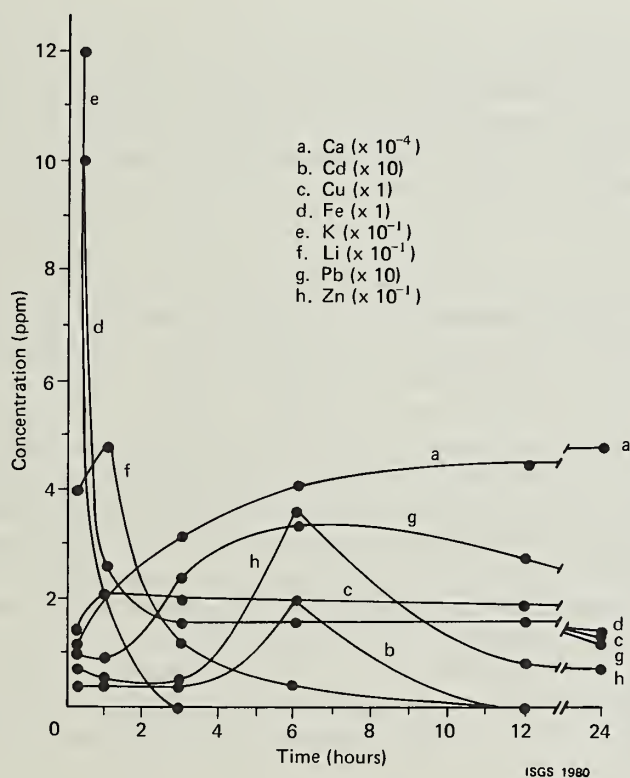


FIGURE 6. Elemental leaching rates for fly ash (Natusch et al., 1977).

characterize Cr and Mo, while Sb, As, Ba and, in some cases Se, leached out at slower rates. The oxyacids of Cr and Mo are water soluble whereas the intermetallic compounds of Sb, As and Se are much less leachable. There were no consistent inter-element patterns for different leaching media.

Churey et al. (1979) stirred 1-gram samples of 22 fly ashes for 2 hours in 200 mL distilled water. They analyzed the supernatants for As, B, Mo, P, and Se. B and Mo were found to be very soluble in ashes derived from soft coals (low carbon content) as well as Se in ashes from lignite coals.

The American Society for Testing and Materials (ASTM) evaluated three leaching tests using fly ash, bottom ash, and slag as samples. The three leaching tests were the ASTM methods "A" and "B" (ASTM, 1978) and the EPA Extraction Procedure (EPA, 1980). The ASTM "Method A" involves mixing 700 g of sample with 2800 g of deionized water by a constant shaking motion for 48 hours. A second procedure ("Method B") follows the same experimental design as "Method A" but uses an acidic sodium acetate buffer as an extractant. The third leaching procedure used was the EP test, which consists of mixing a ratio of one part sample to 16 parts water (by weight) by a constant shaking motion for 24 hours. Throughout the leaching interval, the pH of the leachate is maintained at pH 5 by 0.5N acetic acid additions. Although this section of the study was primarily concerned with evaluating the procedures, analytical results are reported in EPRI (1979). These results indicated variable pH (4.38-12.5 by "Method A") and calcium content (37-1708 mg/L) characterized the fly ash samples tested. In all three procedures Ag, As, Ba, Cd, Cr, Hg, Pb, and Se concentrations were typically less than about 5 mg/L, but concentrations of 7 mg/L As and 79 mg/L Ba were reported for the leachates from some samples.

During a study of leachability of As from coal ash, Auerbach and Reichle (1980) found that while increasing pH favors the extraction of As, anomalously low extractions of As characterized some alkaline leachates. This was thought to result from the formation of a precipitate of barium arsenate in leachates from coal ashes from western coals, which generally have greater Ba content than eastern coals.

Little research has been done on the prevalent geochemical characteristics of fly ash that determine the ultimate pH of fly ash leachates. Shannon and Fine (1974) suggest that alkaline leachates are the result of considerable portions of Ca, Mg, and Na existing in the ash in oxide form. Theis and Wirth (1977) and EPRI (1979) state that the pH may be controlled by the proportion of free lime to iron present. Elsewi, Page, and Grimm (1980) generated alkaline pHs from fly ashes from western coals with high CaO matrix concentrations. They found that the solutions were composed of more than 90 percent of Ca and OH ions; they also found that the highest Ca and OH concentrations when compared to the theoretical maximum solubility of  $\text{Ca}(\text{OH})_2$  in water indicated a near-saturated solution of lime. Chu, Krenkel, and Ruane (1976) and Chu, Ruane, and Krenkel (1978) also suggest a relationship between pH and the alkaline metal oxide (mainly CaO) in addition to the  $\text{SO}_3$  content. Some acidic leachates may be attributed to the hydration of  $\text{SO}_3$  forming  $\text{H}_2\text{SO}_4$ . Sulfuric acid has been observed as a condensate on the surfaces of particles in some fly ashes (Swaine, 1977).

Other results indicate that the principle ions in leachates produced by fly ashes are calcium and sulfate, with smaller quantities of Mg, Na, K and Si (EPRI, 1979). Free lime (CaO) accounts for part of the soluble calcium.

Studies of ash pond effluent have been reported. Chu, Krenkel, and Ruane (1976) and Chu, Ruane, and Krenkel (1978) point out that ash pond chemistry is a function of: (1) the chemical and physical character of the ash; (2) quantity and chemical composition of the water used for sluicing; and (3) the performance characteristics of the settling pond. Table 9 presents chemical data on ash ponds used by the Tennessee Valley Authority. The ponds are used for the disposal of fly ash, bottom ash, or mixtures of the two. The pH of these effluents varied from 3.3 to 12; half of them were alkaline.

Table 10 is a summary of chemical determinations of waters from disposal ponds used for the storage of fly ash, bottom ash, and combinations of both waste products. Further studies are summarized in Dvorak, Lewis, et al. (1978), Morse (1979), and Torrey (1978).

To summarize, it is difficult to make generalizations about the relative solubilities of the constituents in fly ash. Such generalizations are complicated by the variable nature of the solid waste. Leachates may vary greatly in pH, which in turn is the dominant factor controlling the solubility of many constituents. The data base for relative solubilities is not adequate and cannot be used as a basis for making detailed generalizations. Several studies have reported only observed concentrations in laboratory-generated leachates or ash ponds, with no comparisons to matrix concentrations. However, B consistently appears to be soluble in water. Limited data also suggest that Li, Cr, Co, P, and Tl are soluble in water extractions. Al, Ba, Mg, Si, and Sb appear to be relatively insoluble in water extractions, and limited data suggest that Fe is characterized by a low leachability. Ca, Cd, Cu, K, Mn, Na, Ni, Pb, and Zn exhibit either intermediate or inconsistent leachabilities.

However, the potential for the leaching of other toxic constituents cannot be ignored. Natusch (1978) claims that only the surface portion of each particle is significantly soluble and that, therefore, material bound in the glassy matrix is essentially unavailable. Linton et al. (1976) estimate that mobile elements are extractable to a depth of 100 Å from the surface of a particle. For a small particle (<1 micron) as much as 80 percent of a substance will be available for extraction. Natusch (1978) properly points out, however, the distinction between concentration of a substance and the total amount extracted: high localized concentrations of a constituent in living tissues may be capable of causing damage in a restricted region by the leaching of body fluids, even though the total amount of substance released is very low.

Therefore, the actual concentrations at the point of contact between a particle and living tissue are substantially higher than would be estimated by simple bulk chemical analysis of the particles. In addition, Hayes, Pawley, and Fisher (1978) have shown that some elements are not homogeneously distributed among particles of a given size, but instead vary in concentration from particle to particle. This means that the concentration at a point might exceed that predicted even by an analysis of size-fractionated particles.

## EFFECTS OF FLY ASH ON AQUATIC ECOSYSTEMS

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Prior to the discussion of research on the disposal and utilization of fly ash (in the final section of this review), the possible biological and physiological ramifications of fly ash exposure will be considered. This review contains data which suggest that the physico-chemical properties of fly ash

TABLE 9. Characteristics of discharges through ash ponds,<sup>a</sup> from Chu, Ruane, and Krenkel, 1978 (all concentrations in mg/L unless noted otherwise).

| Water quality constituent                | Plant A (fly ash pond) |  | Plant B (fly ash pond) |  | Plant C (com-bined ash pond) |  | Plant D (com-bined ash pond) |  | Plant E (com-bined ash pond) |  | Plant F (com-bined ash pond) |  | Plant G (com-bined ash pond) |  | Plant H (com-bined ash pond) |  | Plant I (com-bined ash pond) |  | Plant J (com-bined ash pond) |  | Plant K (com-bined ash pond) |  | Plant L (com-bined ash pond) |  |
|--|------------------------|--|------------------------|--|------------------------------|--|------------------------------|--|------------------------------|--|------------------------------|--|------------------------------|--|------------------------------|--|------------------------------|--|------------------------------|--|------------------------------|--|------------------------------|--|
|  | Avg                    |  | Avg                    |  | Avg                          |  | Avg                          |  | Avg                          |  | Avg                          |  | Avg                          |  | Avg                          |  | Avg                          |  | Avg                          |  | Avg                          |  | Avg                          |  |
| Total alkalinity <sup>c</sup>            | -                      |  | 54                     |  | 71                           |  | 58                           |  | 154                          |  | 113                          |  | 47                           |  | 70                           |  | 150                          |  | 41                           |  | 96                           |  | 92                           |  |
| Phenolphthalein alkalinity <sup>bc</sup> | 0                      |  | 3                      |  | 0                            |  | 5                            |  | 114                          |  | 96                           |  | 22                           |  | 14                           |  | 126                          |  | <1                           |  | 75                           |  | 44                           |  |
| Conductance, umhos/cm <sup>b</sup>       | 810                    |  | 242                    |  | 495                          |  | 264                          |  | 817                          |  | 855                          |  | 394                          |  | 406                          |  | 618                          |  | 312                          |  | 469                          |  | 314                          |  |
| Total hardness                           | 260.5                  |  | 108                    |  | 208                          |  | 124                          |  | 288                          |  | 301                          |  | 196                          |  | 114                          |  | 209                          |  | 105                          |  | 174                          |  | 239                          |  |
| pH                                       | 4.4                    |  | 8.0                    |  | 7.1                          |  | 8.6                          |  | 11.2                         |  | 11.2                         |  | 9.6                          |  | 8.5                          |  | 11.3                         |  | 6.3                          |  | 10.8                         |  | 10.5                         |  |
| Dissolved solids                         | 508                    |  | 142                    |  | 363                          |  | 151                          |  | 380                          |  | 452                          |  | 279                          |  | 268                          |  | 270                          |  | 197                          |  | 232                          |  | 219                          |  |
| Suspended solids                         | 62.5                   |  | 64                     |  | 42                           |  | 21                           |  | 12                           |  | 39                           |  | 20                           |  | 18                           |  | 22                           |  | 140                          |  | 14                           |  | 18                           |  |
| Aluminum                                 | 7.2                    |  | 1.8                    |  | 1.8                          |  | 1.4                          |  | 2.4                          |  | 2.0                          |  | 1.8                          |  | 1.6                          |  | 1.6                          |  | 2.7                          |  | 1.7                          |  | 2.1                          |  |
| Arsenic                                  | 0.010                  |  | 0.03                   |  | 0.013                        |  | 0.03                         |  | 0.005                        |  | <0.005                       |  | 0.029                        |  | 0.10                         |  | 0.005                        |  | 0.038                        |  | 0.012                        |  | 0.036                        |  |
| Barium                                   | 0.3                    |  | 0.1                    |  | 0.2                          |  | 0.2                          |  | 0.2                          |  | 0.2                          |  | 0.2                          |  | 0.2                          |  | 0.2                          |  | 0.2                          |  | 0.2                          |  | 0.1                          |  |
| Beryllium                                | 0.01                   |  | <0.01                  |  | <0.01                        |  | <0.01                        |  | <0.01                        |  | <0.01                        |  | <0.01                        |  | <0.01                        |  | <0.01                        |  | <0.01                        |  | <0.01                        |  | <0.01                        |  |
| Cadmium                                  | 0.037                  |  | 0.001                  |  | 0.005                        |  | 0.001                        |  | 0.001                        |  | 0.001                        |  | <0.001                       |  | <0.001                       |  | <0.001                       |  | 0.001                        |  | <0.001                       |  | 0.001                        |  |
| Calcium                                  | 136                    |  | 142                    |  | 82                           |  | 32                           |  | 129                          |  | 115                          |  | 78                           |  | 47                           |  | 103                          |  | 37                           |  | 87                           |  | 55                           |  |
| Chloride                                 | 7                      |  | 6                      |  | 12                           |  | 4                            |  | 6                            |  | 5                            |  | 4                            |  | 14                           |  | 6                            |  | 3                            |  | 12                           |  | 6                            |  |
| Chromium                                 | 0.067                  |  | 0.02                   |  | 0.005                        |  | 0.004                        |  | 0.019                        |  | 0.043                        |  | 0.012                        |  | 0.006                        |  | 0.024                        |  | 0.006                        |  | 0.021                        |  | 0.008                        |  |
| Copper                                   | 0.31                   |  | 0.023                  |  | 0.03                         |  | 0.01                         |  | 0.08                         |  | 0.02                         |  | 0.03                         |  | 0.05                         |  | 0.05                         |  | 0.06                         |  | 0.05                         |  | 0.04                         |  |
| Cyanide                                  | 0.01                   |  | 0.01                   |  | 0.01                         |  | 0.01                         |  | 0.01                         |  | 0.01                         |  | 0.01                         |  | 0.01                         |  | 0.01                         |  | 0.01                         |  | 0.01                         |  | 0.01                         |  |
| Iron                                     | 1.44                   |  | 1.93                   |  | 2.1                          |  | 0.25                         |  | 0.30                         |  | 0.23                         |  | 0.95                         |  | 0.63                         |  | 0.29                         |  | 2.3                          |  | 0.24                         |  | 0.69                         |  |
| Lead                                     | 0.06                   |  | 0.01                   |  | 0.02                         |  | 0.01                         |  | 0.014                        |  | 0.01                         |  | 0.01                         |  | 0.01                         |  | 0.01                         |  | 0.02                         |  | 0.015                        |  | 0.01                         |  |
| Magnesium                                | 14                     |  | 3.9                    |  | 10                           |  | 8.3                          |  | 0.4                          |  | 2.0                          |  | 2.5                          |  | 7.4                          |  | 0.4                          |  | 6.5                          |  | 1                            |  | 3.1                          |  |
| Manganese                                | 0.48                   |  | 0.13                   |  | 0.22                         |  | 0.03                         |  | 0.01                         |  | 0.01                         |  | 0.05                         |  | 0.05                         |  | 0.01                         |  | 0.39                         |  | 0.01                         |  | <0.01                        |  |
| Mercury                                  | 0.0003                 |  | 0.001                  |  | 0.015                        |  | 0.0002                       |  | 0.0002                       |  | 0.038                        |  | 0.0008                       |  | 0.0006                       |  | 0.0002                       |  | 0.0003                       |  | 0.0004                       |  | 0.0003                       |  |
| Nickel                                   | 1.1                    |  | 0.05                   |  | 0.031                        |  | 0.05                         |  | <0.05                        |  | <0.05                        |  | <0.05                        |  | 0.05                         |  | <0.05                        |  | 0.05                         |  | 0.07                         |  | <0.05                        |  |
| Total phosphate as P                     | 0.02                   |  | 0.08                   |  | 0.05                         |  | 0.03                         |  | 0.01                         |  | 0.03                         |  | 0.05                         |  | 0.12                         |  | 0.02                         |  | 0.05                         |  | 0.02                         |  | 0.07                         |  |
| Selenium                                 | 0.002                  |  | 0.015                  |  | 0.014                        |  | 0.065                        |  | 0.009                        |  | 0.016                        |  | 0.010                        |  | 0.013                        |  | 0.004                        |  | 0.003                        |  | 0.011                        |  | 0.010                        |  |
| Silica                                   | 12.6                   |  | 8                      |  | 7                            |  | 3.7                          |  | 6.6                          |  | 6.1                          |  | 4.8                          |  | 4.8                          |  | 8.1                          |  | 6.2                          |  | 7.4                          |  | 5.6                          |  |
| Silver                                   | <0.01                  |  | <0.01                  |  | 0.01                         |  | <0.01                        |  | <0.01                        |  | <0.01                        |  | <0.01                        |  | <0.01                        |  | <0.01                        |  | <0.01                        |  | <0.01                        |  | <0.01                        |  |
| Sulfate                                  | 358                    |  | 209                    |  | 155                          |  | 59                           |  | 136                          |  | 156                          |  | 133                          |  | 88                           |  | 76                           |  | 122                          |  | 87                           |  | 85                           |  |
| Zinc                                     | 1.51                   |  | 0.06                   |  | 0.12                         |  | 0.03                         |  | 0.05                         |  | 0.04                         |  | 0.03                         |  | 0.04                         |  | 0.08                         |  | 0.05                         |  | 0.05                         |  | 0.04                         |  |

<sup>a</sup>The reported values include background concentrations in the raw water supply. To assess environmental impacts that may be attributed to ash pond effluents, these background concentrations would have to be subtracted from the above values.

<sup>b</sup>For those cases in which a minimum value was less than detectable, the average was calculated by using a substituted value equal to one-half the value of the detectable limit.

<sup>c</sup>As CaCO<sub>3</sub>.

TABLE 10. Analyses of ash pond discharges (in mg/L), from Weeter and Bahor (1979).

| Substance | Fly Ash Pond      |        |          |
|-----------|-------------------|--------|----------|
|           | Range             | Avg    | Data Pts |
| Arsenic   | 0.01 - 1.1        | 0.38   | 3        |
| Barium    | 0.02 - 0.3        | 0.25   | 2        |
| Cadmium   | 0.001 - 0.037     | 0.019  | 2        |
| Chloride  | 6 - 7             | 6.5    | 2        |
| Chromium  | 0.02 - 0.067      | 0.044  | 2        |
| Copper    | 0.02 - 2.4        | 0      | 3        |
| Iron      | 1.44 - 630        | 211.12 | 3        |
| Lead      | 0.01 - 0.91       | 0.33   | 3        |
| Manganese | 0.13 - 0.48       | 0.31   | 2        |
| Selenium  | 0.02 - 0.33       | 0.12   | 3        |
| Sulfate   | 209 - 358         | 283.5  | 2        |
| Zinc      | 0.06 - 2.2        | 1.26   | 3        |
| Substance | Bottom ash pond   |        |          |
|           | Range             | Avg    | Data pts |
| Arsenic   | 0.006 - 0.018     | 0.012  | 2        |
| Barium    | 0.1 - 0.2         | 0.15   | 2        |
| Cadmium   | 0.001 - 0.003     | 0.002  | 2        |
| Chloride  | 7 - 8             | 7.5    | 2        |
| Chromium  | 0.009 - 0.01      | 0.095  | 2        |
| Copper    | 0.041 - 0.065     | 0.053  | 2        |
| Iron      | 5.29 - 5.98       | 5.64   | 2        |
| Lead      | 0.02 - 0.02       | 0.02   | 2        |
| Manganese | 0.16 - 0.58       | 0.37   | 2        |
| Selenium  | 0.002 - 0.011     | 0.007  | 2        |
| Sulfate   | 49 - 139          | 94     | 2        |
| Zinc      | 0.09 - 0.14       | 0.12   | 2        |
| Substance | Combined ash pond |        |          |
|           | Range             | Avg    | Data pts |
| Arsenic   | 0.005 - 0.038     | 0.038  | 9        |
| Barium    | 0.01 - 0.02       | 0.19   | 10       |
| Cadmium   | 0.001 - 0.005     | 0.002  | 6        |
| Chloride  | 3 - 14            | 7.2    | 10       |
| Chromium  | 0.004 - 0.043     | 0.015  | 10       |
| Copper    | 0.01 - 0.08       | 0.042  | 10       |
| Cyanide   | 0.01 - 0.05       | 0.03   | 3        |
| Iron      | 0.23 - 2.3        | 0.8    | 10       |
| Lead      | 0.01 - 0.025      | 0.014  | 10       |
| Manganese | 0.01 - 0.39       | 0.09   | 9        |
| Selenium  | 0.003 - 0.065     | 0.01   | 10       |
| Sulfate   | 59 - 156          | 109.7  | 10       |
| Zinc      | 0.03 - 0.12       | 0.053  | 10       |

could pose environmental problems and have toxic effects on organisms. All current fly ash disposal or utilization schemes would expose the solid waste to the biosphere.

This section discusses (1) research on ash ponds and fly ash and their effects on aquatic ecosystems, and (2) health effects observed in different organisms (i.e., mice, hares, sheep, etc.) that have been exposed in a variety of ways to fly ash.

The toxicity of fly ash to aquatic organisms has largely been studied in connection with the accidental or intentional discharge of large quantities of fly ash into aquatic systems. Cairns, Crossman, and Dickson (1972), for example, described the effects of a fly ash pond spill on a small river. Approximately 490 million liters of alkaline leachate (pH 12) entered a small watershed via a dike failure. After a rapid initial flow, the alkaline effluent moved downstream for four days at a rate of about 1.4 km/hr. The populations of bottom-dwelling fish were drastically reduced as far as 124 km downstream from the spill. More than 200,000 fish died in a 144 km section downstream from the power plant. Insects were essentially eliminated for 4.8 km and molluscs for 18 km. The authors suggested that the principle lethal agent was the high pH level, which was composed of 90 percent hydroxide alkalinity. Two years after the spill, the insect community was able to support a productive fish community. Molluscs had not completely recovered, apparently because of their weak dispersal powers, and some fish species were still repopulating in an upstream direction. Overall, it appeared that no permanent damage to the biota had occurred.

Shelton (1973) discussed the effects of the disposal of coal cleaning wastes and fly ash 6.5 km off the east coast of England. He stated that these materials are not acutely toxic to marine animals. The major impacts of fly ash disposal result from increased turbidity, which inhibits the growth of benthic algae, and the filling in of rocky crevices, which reduces the microhabitat available to crabs and lobsters.

Wasserman, Chung, and Rubin (1974) reported that runoff from alkaline ash settling ponds was lethal to catfish because the runoff raised the pH, causing precipitation of ferric hydroxide. This precipitate may have clogged the gill mucus, resulting in asphyxiation.

Birge (1978) designed a bench scale plexiglass settling pond to investigate the aqueous leaching characteristics and toxicity of precipitator-collected fly ash. Continuous flow bioassays were performed on the simulated ash effluent to evaluate toxicological properties of the aqueous effluents. Eggs of the goldfish (*Carassius auratus*), readear sunfish (*Lepomis microlophus*), Leopard frog (*Rana pipiens*), and Fowler's toad (*Bufo fowleri*) were used as test organisms. The bioassays were initiated after 522, 1,033, and 1,775 hours of continuous aqueous leaching of the precipitator-collected fly ash. Total mortality occurred in the bioassays of undiluted effluent using frog eggs and eggs of readear sunfish. Moderate mortality (greater than 40 percent) occurred in bioassays of undiluted effluent using toad eggs and goldfish eggs. In addition, mortality was noted in bioassays of diluted effluents using readear sunfish eggs and goldfish eggs.

An early toxicity study (Thompson, 1963) examined the mortality thresholds of marine fish in fly ash polluted water. Most species had thresholds of



about 10 g/L, but estuarine species generally exhibited greater tolerance. The leaching of Pb, Zn, and Cu was also investigated in this study, but data were not included in the report. Thompson believed that death was caused by asphyxiation due to clogging of the gill mucus by ash particles rather than by leached chemical constituents.

Griffin et al. (1980) conducted 96-hour static bioassays using 1- to 6-day-old fathead minnow fry (*Pimephales promelas*) and leachate generated from an acidic fly ash (pH 4). A 100 percent mortality response was observed. Attempts were made to decrease the mortality rate resulting from the acidic pH by adding NaOH. However, total mortality was still observed. As suggested by the investigators, the high total ion concentration observed in the neutralized solution was probably responsible for the observed toxicity. The LC-50 value for the leachate generated from this particular fly ash was 9.0 mL/100 mL: that is, it was predicted that a test solution of 9.0 mL of leachate diluted with 91.0 mL of reconstituted water will statistically be lethal to 50 percent of the fathead minnow fry exposed in a 96-hour interval. However, the authors pointed out that it was not possible from these experiments to determine which specific chemical constituents were directly responsible for the observed mortality. They suggest performing additional chemical and biological analyses which include organic compound determinations of fly ash and leachate as well as bioassays of particular chemical constituents found in fly ash leachates.

Apparently not all aquatic organisms are detrimentally effected by ash effluent. At least one freshwater fish, the mosquitofish (*Gambusia affinis*) is very tolerant to ash effluent (Cherry et al., 1976). In fact, high temperature (39°C) appeared to have a greater effect on *Gambusia* distribution than did high turbidity or elevated elemental concentrations known to be lethal to other species. The pH of the effluent was not discussed but Fe, Al, Si, Na, K, and Mg were in a concentration range of 4 to 17 mg/L. Potentially toxic trace elements such as As, Cd, Co, Hg, and V were observed at levels in the range of 43 µg/L to 0.123 mg/L.

Guthrie, Cherry, and Singleton (1978) studied the changes in a heterotrophic bacterial community due to a lowering of pH by ash effluent. They found an overall decrease in bacterial diversity and abundance and an increase in chromogenic (color-producing) bacteria. They were unable to characterize these changes as indicating either beneficial or detrimental change in the environment.

The concentration or bioaccumulation of trace elements in living tissues must be considered with respect to both the contaminated organism and its predators (as with fish and man). There are three examples of biological concentration in aquatic organisms in which fly ash is known to be the source of the elements. Ryther et al. (1979) demonstrated in laboratory experiments that many elements, including As, Co, I, Se, V, and Zn, are concentrated in sandworms (*Nereis virens*) and three species of marine bivalves (*Mya arenaria*, *Mercenaria mercenaria*, and *Crassostrea virginica*). Depending on the organism and constituent, these elements were concentrated by factors ranging from about 1.2 to nearly 14. Typical enrichment was approximately in the range of 1.2 to 1.6. The ultimate Co concentration observed in the sandworms was 6.2 mg/kg while V was 22 mg/kg, and As was about 19 mg/kg. Enrichment of Al, B, Br, Ca, La, and Sn was also documented. Cherry et al. (1976) noted that Se, Br, Zn, Cl, and Ca were concentrated in the mosquito fish, *Gabusia affinis*. The content of Se, the constituent most elevated, was 9.4 mg/kg in mosquito fish muscle.

The environmental impact of thermal discharge and combustion by-products (including fly ash) on the aquatic ecosystem of a cooling lake in central Illinois (Lake Sangchris) has been documented. Although the final report was not available in time to be included in this review, this interdisciplinary study includes investigations of water quality, plankton, benthos, fish, clams, water fowl, aquatic macrophytes, and pesticides; also included is a partial physico-chemical characterization of lake sediment, slag, fly ash, and coal samples.

Cumbie and Van Horn (1978) found that fish population of Belews Lake, North Carolina, declined during the period of operation of the Belews Creek Steam Station. Reproduction of fish in the main lake was almost completely absent in 1976 and 1977. The authors found that selenium concentrations were elevated in the Belews Lake water, and that fish in the lake had accumulated unusual ( $>3\text{mg/kg}$  wet weight) amounts of selenium. Selenium entered the lake in soluble form via the power plant fly ash sluice water return. Selenium concentrations in the lake water were not high enough to be directly toxic to fish. Uptake by plankton introduced selenium into the food chain, where it ultimately reached elevated levels in the fish because of bioaccumulation. Cumbie and Van Horn believe that selenium accumulation, perhaps associated with other dissolved constituents, was the probable cause of reduced fish reproduction in Belews Lakes.

Fly ash can alter aquatic ecosystems even when no toxic effects are produced. Fly ash can be a source of Si which may change the distribution of Si in aquatic ecosystems. Gallup and Hickman (1975) showed how an accumulation of fly ash on the winter ice of a lake near a power plant led to an abundance of dissolved Si near the surface of the lake at spring thaw; this was unlike the pattern in most lakes, in which the highest values of Si are found near the bottom due to the leaching of Si from clays.

Fly ash can reduce phosphorous levels in water, which may lower the productivity of an aquatic system. Fly ash adsorbs phosphorus to such an extent that its use in the treatment of waste water has been investigated. The capacity of fly ash to adsorb phosphorus is directly related to its carbon content (Johnson et al., 1966). Fly ash adsorbs more phosphorus than some alumina compounds used in such applications (Gangoli and Thodos, 1974) but not as well as activated carbon (Bhargava et al., 1974; Hung, 1976; Froneberger and Pollock, 1976). Fly ash also may (Ballance, Capp, and Burchinal, 1966) or may not (Nelson and Guarine, 1969) help reduce suspended solids, biological oxygen demand (BOD), and chemical oxygen demand (COD), depending upon the chemical character of both the fly ash and the waste water.

Fly ash has been used to reduce phosphorus levels in lakes (Tenney and Eichelberger, 1970; Theis and DePinto, 1976; and Theis and McCabe, 1978). When fly ash is deposited in lakes, a portion of the solid waste will begin to settle out. During sedimentation, Ca may be leached from the fly ash while P in the lake water is adsorbed; the net effect is the precipitation of  $\text{CaHPO}_4$ . When the fly ash settles to the bottom it forms a layer which may reduce the rate of phosphorus influx from bottom sediments. There are also indications that fly ash may remove other algal growth factors or perhaps add an inhibiting substance (Higgins, Mohlegi, and Irvine, 1976). Cherry et al. (1976), however, found that orthophosphate concentrations were higher in areas of a stream influenced by ash effluent than they were in unpolluted areas.

Researchers have found that even when fly ash addition does reduce phosphorus availability, the processes of sedimentation soon create a new layer of lake sediments over the fly ash layer (Theis and McCabe, 1978); the new layer may insulate the fly ash from the water just as the fly ash layer sealed off the original sediment. This highlights a serious problem with the use of fly ash to control lake eutrophication: this practice largely ignores work demonstrating that lake trophic status is controlled not by the total amount of phosphorus in the system, but by the input rate of phosphorus (Schindler, Lean, and Fee, 1975). Since phosphorus input is often continuous, phosphorus removal must also be continuous. If the fly ash layer is sealed off by later sedimentation, the lake will eventually revert to its former condition.

Nevertheless, in most lakes the difference between oligotrophic and eutrophic P-input rates is so small (Schindler, Lean, and Fee, 1975) that it is conceivable that a continuous input of fly ash particles from the atmosphere could reduce a lake's trophic status. Lake Michigan, for example, receives an estimated  $10^6$  to  $10^7$  particles/cm<sup>2</sup>/year (Alberts et al., 1977).

## EFFECTS OF FLY ASH ON HEALTH

Many elements (Se, As, V, Mn, Zn, Cr, Co, Cd, etc.) are extremely toxic to many organisms via a variety of mechanisms (Waters et al., 1975; Eichorn et al., 1973; Browning, 1969; Hartung, 1973). Their introduction into the environment via fly ash could therefore be a significant health hazard.

Fly ash can be hazardous in three different ways by (1) direct action on external surfaces (skin, eyes, etc.); (2) action in the respiratory tract; and (3) action in the alimentary canal (either through direct ingestion or via fly ash expelled from the lungs).

Many trace elements show higher levels of concentration with decreasing particle size. This gradational effect of particle size and trace element concentration is important for three reasons:

1. Smaller particles have longer atmospheric residence times and can be expected to disperse at greater distances from their source.
2. Electrostatic precipitators decline in efficiency with decreasing particle size; therefore, some of the potentially most toxic particles are most likely to escape, and studies using stack collected fly ash may underestimate its toxicity.
3. Smaller particles penetrate further into, and remain longer in, lung tissues. Large particles come to rest in the nasopharyngeal and tracheobronchial regions of the lung where they can be expelled by cilia; however, smaller particles deposited in the pulmonary region (where ciliary action is much less effective) may remain there for weeks or longer (Natusch and Wallace, 1974; Bice, 1980). In addition, the lung wall is thinnest in the alveoli, making adsorption rapid.

Bencko and Symon (1970) exposed hairless mice (to reduce ingestion of material via grooming) to aerosol arsenic-enriched fly ash. The fly ash was moistened with an arsenic trioxide solution synthesizing fly ash with about one percent As. The mice were exposed to the fly ash in dust chambers at 1-, 2-, 4-, and

6-week intervals. The researchers found elevated concentrations of As in the liver and kidney, but these levels subsequently returned to near background concentrations. However, skin concentrations of As remained high. Their explanation was that increased arsenic levels activated excretion mechanisms in the liver and kidney, but that the skin, directly exposed to the aerosol, was unable to eliminate the As. No examinations for pathological effects were made, but the implication that skin lacks effective clearance mechanisms for fly ash could be significant.

Sixteen months after the commencement of a power plant in Montana, enriched levels of fluoride in the femurs of deer mice were documented in a preliminary report by Gordon et al. (1977). Attributing these levels to atmospheric emissions, they also cited enrichment (up to a factor of 2) of fluoride in honeybees (*Apis mellifera*).

Mikova and Novakova (1979) studied hares living in areas contaminated by industrial emissions and found changes in corneal glycosaminoglycan values similar to changes brought on by senescence. These changes appeared to be more severe in areas exposed to coarse fly ash than in areas of fine fly ash contamination, but no controlled laboratory experiments were done.

Bilek, Fiker, and Janeckova (1976) found that acid (HCl and H<sub>2</sub>SO<sub>4</sub>, neutralized) extracts of fly ash caused positive reactions in 20 percent of the people given skin-prick (allergy) tests; water and ethyl alcohol extractions caused no reactions. Epicutaneous tests with all three extracts were negative as were tests on rabbit corneas.

There is more data on the effects of ingestion of fly ash than of integumentary effects (skin, eyes, etc.). Pujman et al. (1972) demonstrated that mice that ingested up to 1 percent fly ash in drinking water showed reduced neutrophil count and enhanced red blood cell production. They concluded, however, that these were general reactions to foreign substances in the body not attributable to fly ash specifically. Hogue et al. (1980) fed sheep a ration of 10 percent fly ash for 135 days. Selenium in the blood rose by a factor of three but no adverse effects on the animals were noted. Mandisodza et al. (1979) monitored Se in pigs raised on clover grown on fly ash. The Se level in the clover averaged about 70 mg/kg. In one experiment, the pigs were fed corn-soybean meal diets containing 5 or 10 percent clover. In the second phase, the pigs were fed the same corn-soybean base with 0, 1, 3, 4, or 8 percent fly ash (containing 6 mg/kg Se) added. After 61 days, selenium levels in blood samples were elevated, but there was no effect on weight gain and no pathological damage to the heart, liver, kidney, pancreas or skeletal muscle. In the first experiment, Se levels in the kidney tissue ranged from 4 to 17 mg/kg. On the meal-fly ash mixture, Se levels in kidney tissues ranged from 5 to 9 mg/kg.

In a series of studies by Furr and his co-workers (1975, 1978a, 1978b), various test animals were also fed white sweet clover grown in fly ash. Sheep were fed up to 6.5 percent by weight clover for 124 days. Of 34 elements characterized, only Se was concentrated in the blood. The observed concentrations of Se in blood averaged 1.75 mg/kg (dry weight) while sheep fed a diet composed of 7.5 percent fly ash exhibited Se levels averaging 1.98 mg/kg. No elevated Se levels were observed in brain, heart, kidney, liver, spleen, thyroid, adrenal, lung, pancreas, or bone tissues; moreover, no effects on growth were observed. Lambs and goats were fed a diet composed of 24 percent clover grown on fly ash. After 173 days, high concentrations of Se were found

in both animals as measured in tissue, fecal, and urine samples. In the tissue sampled (bone, brain, liver, etc.) Se levels were greater than control groups by factors ranging from 6 to 65. Se concentrations in kidney tissues were about 35 or 29 mg/kg greater than the control animals. Elevated concentrations of Ru, Mo, and sometimes Br were also observed, but no pathological damage was found.

Pharr and Andrews (1977) experimented with fly ash as a replacement for limestone (a calcium source) in chicken feed. They observed no changes in growth or in the breaking strength of the chickens' bones.

Most studies concerning the toxicity of fly ash have concentrated on the respiratory tract. It is generally believed that since the ash remains longer in the respiratory tract than in the alimentary canal, there is greater opportunity for absorption of toxic materials in the respiratory tract. For example, approximately 70 percent of the lead is extracted from particles deposited in the lung but only about 10 percent from those particles passing through the stomach (Patterson, 1965). Bencko and Symon (1970) however, found that the increased solubility of arsenic salts in the acidic conditions of the stomach allow greater absorption than in the lungs. Thus, the possibility of significant gastrointestinal absorption for certain substances should not be ignored.

Despite the plethora of toxic substances found in fly ash, studies actually demonstrating the respiratory toxicity of fly ash are relatively few. But fly ash has been found to be mutagenic. Chrisp, Fisher, and Lampert (1978) used horse serum, saline, and cyclohexane extracts of fine fly ash (collected downstream from the electrostatic precipitator in the stack) in the Ames test for mutagenicity. Study results indicated that at least one organic and one inorganic mutagen were present. The extract of horse serum, which is very similar to alveolar fluid, had the highest mutagenicity. Fisher et al. (1979) demonstrated that fine fly ash was more mutagenic than coarse fly ash, and in their study, the fly ash collected by an electrostatic precipitator was not mutagenic. They also found that heating to 350°C removed all mutagenic activity. This was believed to indicate that the mutagenic activity was due to organic compounds. Clark, Hanson, and Sanchez (1978) reported that mutagenicity of fly ash varied with the operating conditions of the combustor. Methyl phenanthrene was the suspected carcinogen in their study.

Schnapperelle and Fenske (1976) injected up to 500 mg of fly ash into the trachea of chickens. No detrimental effects on growth, feed conversion, or blood cell count were observed; a decline in hemoglobin was the only change noted. Alarie et al. (1975) exposed monkeys and guinea pigs to mixtures of fly ash, sulfur dioxide, and sulfuric acid mist. Although no experiments were done with fly ash alone, the authors concluded that exposure of up to 0.05 mg/m<sup>3</sup> fly ash for one year was not harmful. MacFarland et al. (1971) exposed monkeys to fly ash and after 18 months found no change in health or pulmonary function. Microscopically, the worst condition found (at an exposure of 0.45 mg/m<sup>3</sup>) was the occurrence of small nodules in the alveolar wall, some of which showed a slight fibrotic response.

Hamsters have been exposed to nickel-enriched fly ash (9000 mg/kg Ni). The two-month exposure to approximately 185 µg/L of aerosol produced an increase in lung weight by about 5.7 mg, dark discoloration, and a greater density of alveolar macrophages with dust particles (Wehner et al., 1979). However, no

effects on body weight or life span were observed. Moreover, both acute and chronic toxicities were low.

Gil'denskiold (1976) found that rats could be exposed to up to  $0.05 \text{ mg/m}^3$  fly ash aerosol for 96 hours without toxic effects. Higher aerosol concentrations produced a variety of symptoms including low erythrocyte and high leucocyte counts and pathological damage in the lungs, liver, and kidney.

In all these studies accumulations of fly ash were found in the alveoli. Brummer and Schwartz (1977) found that rats exposed to  $150 \text{ mg/m}^3$  of fly ash aerosol for 90 days showed little clearance after an additional 90 days. This reinforces the earlier point that small fly ash particles can have long residence times in the lung and that chronic long-term experiments are needed to show if there are any toxic effects due to fly ash inhalation.

There are several *in vitro* studies demonstrating toxic effects of fly ash. Aranyi et al. (1979) exposed alveolar macrophages to particle size fractionated fly ash. (*Macrophages* are cells that characteristically engulf and remove foreign particles.) The fly ash was fractionated into less than 2-micron, 2- to 5-micron, and 5- to 8-micron size ranges. The particle surfaces were coated with  $\text{PbO}$ ,  $\text{NiO}$ , or  $\text{MnO}$ . Metal concentrations ranged from about 2.6 to 3.9 percent Pb, Ni, or Mn for all particle sizes. For each size class, macrophages exposed to enriched fly ash (especially Pb) were less viable than were the macrophages exposed to typical fly ash (with smaller amounts of trace metal concentrations).

Within each type of fly ash, increased particle size required greater concentrations to reduce viability to a given level. Similarly, Hill and Mitchell (1978) found that macrophage toxicity was related to particle size and the number of particles ingested. In addition, lower molecular weight aromatic compounds were more toxic than heavier compounds.

## FLY ASH DISPOSAL AND UTILIZATION

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### Disposal methods

It is axiomatic that increased consumption of coal will produce an increase in quantities of ash requiring disposal. Because of the chemical and physical nature of fly ash, environmentally acceptable methods of disposal have been studied as well as the potential for fly ash utilization as a useful by-product of coal-fired power plants.

Four basic methods are now used to dispose of fly ash: (1) cement mixtures; (2) asphalt additives; (3) soil modifiers in agriculture; and (4) various schemes for temporary and permanent on and off site disposal in mines, basins or landfills.

Only 8.4 percent of the fly ash generated in the United States in 1974 was utilized as construction materials or in structural products; 20.3 percent of the bottom ash and 50.0 percent of the boiler slag generated were utilized (Faber, 1976). The problems and the potential of ash marketing have been studied by various investigators (Brackett, 1967, 1974; Blocker et al., 1974; Capp and Spencer, 1970; Faber, Eckard, and Spencer, 1973; Faber, 1976, 1979; Hyland, 1974; Minnick, 1974a, 1974b; Zimmer, 1967; and many others).

## Fly ash as an additive to construction products

Utilization of fly ash in concrete, concrete block manufacture, precast concrete products and mortar has constituted the largest single market for the material in recent years. Some fly ashes act as a pozzolanic material that in the presence of water will react with alkali and alkaline earths to produce cementitious products. The addition of certain types of fly ash to concrete improves the concrete by imparting certain properties, including strength (compressive strength, resistance to slump, etc.), resistance to sulfate reaction with the hydrated lime and calcium aluminate, workability (increasing plasticity) and reduction of permeability. It also helps to control shrinkage and lowers the heat of hydration during setting (after Capp and Spencer, 1970).

A relationship between viscosity and the compressive strength of fly ash as cement grouting mixes may exist. Further research to determine the optimum water/cement ratio for high strength pumpable grouts has been advised (Hempling and Pizella, 1976). Fly ash-concrete mix containing 4 parts fly ash (1137 kg) to 1 part portland cement (284 kg) has been found to have a compressive and flexural strength comparable or superior to concrete containing 1034 kg of portland cement (Akin and Fon, 1979). This data suggests that fly ash/concrete mixes (made with cement, sand, and aggregate, and conformities) can save as much as \$3.67 per cubic yard of concrete (over concrete made with cement, sand, and aggregate).

Jain (1979) states that some fly ash concrete mixtures have greater strength than conventional concrete at ages of 180 and 365 days. He also concludes that:

1. Fly ash/cement mixes (with fly ash replacing from 10 to 20 percent of the cement normally used) have a lower 7-day compressive strength than conventional concrete; but at later ages, these mixes have equal and even higher strengths than conventional concrete.
2. Upon loading, the creep of fly ash concrete was lower than conventional concrete, irrespective of the fly ash content.
3. In experimental determination (modulus of elasticity, creep time curves, and logitudinal pulse velocity), concrete with fly ash consistently gave lower coefficients of variations than plain concrete.

Methods and procedures for evaluating the performance of fly ash concrete and recommendations for applications have been published (Funnell and Johnson, 1976; Meyers, 1976; Mielenz, 1967, 1974, 1979; Nicolescu, 1979). A historical overview (Elfert, 1974) of fly ash concrete applications (retaining walls, drain pipes, and miscellaneous small pipe contracts) by the U.S. Bureau of Reclamation also comments on strength, heat generation (by drying concrete), permeability and other physical properties of fly ash concrete. Other papers summarizing current research and potential utilization of fly ash/cement mixes in concrete have been presented (Belot, 1967; Chropa et al., 1979; Lovewell, 1974; Meyers, Kapples, and DiGiola, 1976; Rehsi, 1974; and many others).

Morse (1979) acknowledges the potential environmental problems of using fly ash in concrete, recognizing the phenomena of enrichment of potentially toxic trace elements. He concludes that trace elements would be trapped or "fixed" within the hardened concrete matrix, reducing their accessibility to leachants.

Furthermore, the cement would "dilute" the specific concentrations of the trace elements in the fly ash. He concludes that trace element leaching would present no environmental problem. Unfortunately, the postulation was not tested by actual leaching experiments using fly ash concrete.

Fly ash has also been used as an additive to lightweight aggregate. Barenberg (1967) points out that lime/fly ash/aggregate mixtures have the necessary physical properties to produce a pavement that has a high bearing capacity and is stable to weathering. The materials are economical because local aggregates can be used with fly ash, which, if not utilized, can pose an expensive disposal problem.

Problems in using fly ash in lightweight aggregates stem from the preparation or sintering of fly ash. (Sintered fly ash or Edicrete is produced by heating ash to temperatures conducive to agglomeration into more useful forms.) These problems are derived mostly from variations in chemical composition, particularly in carbon content, since carbon is a necessary component for fly ash sintering. Variation in carbon content is difficult to contend with in terms of equipment operation and product specification compliance (Barenberg, 1967; Capp and Spencer, 1970; and Pearson, 1967).

Bricks using fly ash as a raw material have been manufactured on a pilot scale using about 74 percent fly ash mixed with 23 to 24 percent coarse bottom ash and 3 percent sodium silicate as a binder (Capp and Spencer, 1970; Shafer, 1967). Slonaker (1979) points out since fly ash is largely a fused amorphous glass that has already been subjected to power plant furnace temperatures, little additional heat, as compared to conventional clay bricks, is required to form the ceramic bonds necessary to produce quality brick. Since fly ash brick can be fired in approximately one-half or less the time required for firing clay brick, there would be a savings in energy costs and a reduction of other costs when firing fly ash-based brick.

### **Fly ash as a mineral resource**

Other less-used methods for fly ash utilization have been proposed. Fly ash has been considered as a potential mineral resource. Beneficiation of iron by magnetic separation from fly ash has been done for a number of years (Nowak, 1974; Stirling, 1970).

Morrison (1976) speculates that fly ash could, assuming total recovery, provide substantial quantities of Si, Al, Ca, S, P, Ti, Mg, Na, as well as Fe. In addition to the major elements, fly ash could also serve as a source of Th, Cr, Mn, V, Ni, Co and Zn (Seeley et al., 1979). The potential for recovering aluminum from fly ash has received the greatest attention, but currently aluminum extraction from fly ash does not compare favorably with its recovery from bauxite. Various aluminum extraction procedures have been designed and compared (Canon, Seeley, and Watson, 1979; Seeley et al., 1979).

### **Civil engineering applications**

Engineering applications using fly ash have been designed and tested. Soil stabilization using a western coal high in calcium was studied by Thornton, Parker, and White (1976) and Thornton, Parker, and Yang (1979) who found that



fly ash can effectively stabilize sandy organic-rich clay soils when compacted following recommended procedures. Bacon (1976) evaluated the suitability of fly ash for bridge and highway construction and discovered fly ash to be an acceptable material to use as an embankment material above the water table; in some cases it was found to be a superior structural material. Culley and Smail (1979) and Head and Seals (1979) recognized the feasibility of fly ash application in subsurface preparation when the construction procedures and designs are modified so as to be compatible with the physical and chemical characteristics of fly ash (as opposed to conventional aggregate-base designs). Lamb (1974) summarizes his observations by suggesting that it is possible to utilize ash to construct structural fills, embankments, dams, and dikes. However, special care must be taken to ensure against possible liquefaction as a result of sudden loading. A study on the feasibility of using fly ash as a construction material in water retaining structures found the incorporation of fly ash could be suitable and would reduce construction costs (Lamb et al., 1979). However, the leaching of potentially hazardous substances from fly ash used in all these constructional applications may be a concern.

### **Coal mine reclamation**

Some studies have discussed the feasibility of using fly ash for coal mine reclamation. Magnuson and Malenka (1970) and Ryan (1976) suggest using dry ash or water slurries injected through boreholes to fill voids left by underground mining to attempt to reduce spontaneous combustion in abandoned coal mines. Alkaline fly ashes have been used to neutralize acidic coal cleaning wastes (Capp and Spencer, 1970). Some test spoil bank plots with pH values of about 3.5 were raised to about 5.2 by the application of alkaline fly ash. Capp and Gillmore (1974a and 1974b) experimented with mixing fly ash with coal cleaning wastes to produce a substrate conducive to plant growth. By mixing alkaline fly ash with spoil, they reduced the bulk density of the mixture; greater pore volume and higher field capacity resulted, and hence better conditions for root penetration and growth.

### **Fly ash as a soil modifier**

The most extensively studied biological aspect of fly ash is the utilization of the solid waste as material suitable for plant growth. Gonsoulin (1975) has noted that local vegetation will colonize abandoned fly ash piles but that the alkaline pH, characteristic of many fly ashes, may cause different successional sequences of vegetation than adjacent abandoned croplands.

In developing new utilization schemes for fly ash, researchers have approached fly ash as: (1) a "soil," i.e., as particulate matter forming a substrate for plant growth; and (2) an additive or modifier mixed with soils. If these approaches are found to be ecologically and economically feasible, it would greatly facilitate the utilization of fly ash in soils.

Thompson and Cope (1962) summarized the characteristics of fly ash that make it an undesirable "soil": (1) characteristic alkaline pH; (2) poor aggregate stability; (3) susceptibility to wind and erosion; (4) N deficiencies and low availability; and (5) a very low cation-exchange capacity (2 to 4 milliequivalents per 100 g) and therefore a low cation nutrient retention capacity. The concentration of many elements in fly ash exceeds typical levels in soils

(Cope, 1962); however, many of these constituents are essential plant nutrients (Martens, Schnappinger, and Zelazny, 1970). To overcome the adverse physical and chemical properties, Cope recommends using boron tolerant crops, heavy applications of phosphates, and smaller doses of nitrogen.

Studies of fly ash amended soils have received the greatest attention. Such studies deal with the physical and chemical changes brought about by mixing various proportions of fly ash with soils and the vegetative response in these mixtures.

Chang et al. (1977) mixed fly ash with two forest-grassland transitional soils, a desert soil, a grassland soil, and a gleyed soil. The fly ash was mixed with the soils at rates of 0.2, 0.5, 5.0, 10.0, and 50.0 percent by volume. Their work demonstrated that the addition of fly ash generally reduced the bulk density of the soil. One soil with a bulk density of 1.60 g/cm<sup>3</sup> was mixed with 50 percent fly ash by volume. The bulk density of the mixture was 1.27 g/cm<sup>3</sup>. Similar observations were noted by Patterson et al. (1967). Chang et al. (1977) also found that the mixtures had a greater water retaining potential, and the same conclusion was reached by Nebgenl et al. (1979), Patterson et al. (1969), and Plank, Martens, and Hallock (1975). However, the actual availability of the increased water supply to plants is uncertain (Jones and Amos, 1976; Dougherty and Holzen, 1976).

The hydraulic conductivity of a soil may increase when fly ash is added, but may also reach a maximum conductivity followed by a decrease as additional fly ash is mixed with the soil. Chang et al. (1977), postulated that the pozzolanic property found in some fly ashes may make the soil/ash mixture less permeable. The cementation of the soil particles may eventually partly block the water movement through the soil. The maximum increase in hydraulic conductivity was about 2 cm/hr greater than in the soil alone where fly ash additions of 5 to 20 percent by volume were made.

Evaluation of the success of plant growth in fly ash amended soils is difficult because of the variable composition of fly ashes and soils and the diverse edaphic requirements of many flora. The mobility of many plant nutrients is influenced by pH; therefore, the relative pHs of the fly ash and the soil could determine the available concentrations of these constituents and the beneficial or harmful levels predominating. Rees and Sidrak (1956) indicated that only manganese and aluminum appear at toxic levels to barley and spinach grown in fly ash amended soils while the weed *Atriplex* is more tolerant. However, Holliday et al. (1958) suggested that boron is the dominant toxin leached from fly ash and not aluminum or Mn as suggested by Rees and Sidrak. Jones (1961) also found that *Atriplex*, white clover and mustard grown in fly ash alone were tolerant to the high aluminum levels in a fly ash.

Corn (*Zea may* L.) displayed reduced yields due to B toxicity in fly ash mixed with a well-leached residual soil (Martens, Schnappinger, and Zelazny, 1970); also, the application of certain fly ashes increased magnesium uptake, which possibly suppressed potassium uptake by corn. Alfalfa (*Medicago sativa* L.) grown in alkaline fly ash mixed with a forest soil displayed lower yields with increasing pH. This was attributed to the addition of the alkaline fly ash which may have reduced the mobility of Zn, resulting in a deficient nutrient level (Mulford and Martens, 1971). However, in other cases using alfalfa (*Medicago sativa* L.) grown in a fly ash amended forest soil, the waste product alleviated a boron deficiency, producing a greater yield than control plots

(Plank and Martens, 1974). Moreover, greenhouse studies also suggested that the application of fly ash corrected molybdenum deficiencies of alfalfa, and zinc deficiencies of corn (*Zea mays* L.) while partially correcting phosphorus and potassium deficiencies of corn.

Plank, Martens, and Hallock (1975) used mixtures of weathered fly ash (exposed for 3 years in a disposal lagoon) and forest soils as a substrate for corn (*Zea mays* L.). The weathered ash may have been subjected to leaching of many of the possible toxins present. The authors concluded that: (1) weathered fly ash may be disposed of in acid soils without adversely affecting the growth of corn; and (2) concentrations of aluminum, Mn, and B in the plant tissues were not present at sufficient levels to cause plant damage. The selected use of weathered fly ash has also been advised by other researchers (Cope, 1962; Townsend and Hodgson, 1973). However, Plank and his co-workers (1975) caution that further studies comparing the effects of weathered versus unweathered fly ash on plants as well as long-term effects are needed before more definitive conclusions can be made. Further elucidation of the effects of fly ash on plants is given by Adriano et al. (1980).

Even if vegetation is not adversely affected by the trace elements from fly ash, the constituents may be concentrated in the tissues of the plants with time. White sweet clover (*M. alba*) concentrated Se exceeding the levels in fly ashes by a factor of five (more than 200 mg/kg Se). Furr and his co-workers (1976, 1978) examined a number of vegetables, grains, and forages grown in fly ash amended soils. Forty-two elements were determined in beans, cabbage, carrots, millet, onions, potatoes, and tomatoes grown in potted soil amended with 10 percent fly ash (by weight). Compared to control groups grown in soil without fly ash, 32 constituents were present at elevated concentrations in the plants grown in the treated soil. As, B, Ca, Cu, Fe, Hg, I, K, Mg, Mo, Ni, and Sb were observed at increased levels in the edible portions of some of the plants (table 11). Field tests with alfalfa, birdsfoot trefoil, brome, field corn, millet, orchard grass, sorghum, and timothy in addition to the vegetables previously listed also demonstrated trace element enhancement. Of 41 elements studied, As, B, Mg, and Se were in greater concentrations in crops grown in fly ash amended soils (45.5 metric tons/acre) than in control plots.

A recent study by Furr and his co-workers (1979) suggests that enhanced absorption of B, Cu, Co, Fe, Mg, Mn, Mo, Se, and Zn occurs in a variety of vegetables, millet, and apple trees. These plants were grown in potted soils mixed with fly ash (100 tons/acre). Mo levels in cabbage grown in fly ash mixtures were 23 mg/kg which was 22.3 mg/kg greater than the control group. Se levels were enhanced in all of the plants by factors ranging from 30 to 120 times the concentrations in the control plants. Se concentrations in cabbage grown in fly ash mixtures averaged about 3.1 mg/kg.

Si, Sr, Ba, and V have also been found at elevated levels in the leaves, stems, and roots of bean plants (*Phaseolus vulgaris*). The beans were grown for 14 days in cultures with fly ash added. However, the experimental design of this study did not represent typical field conditions (Wallace, Romney, and Alexander, 1977).

Recent studies (Gutenmann and Lisk, 1979) demonstrate that B, Se, and Mo were still concentrated in alfalfa, birdsfoot trefoil, brome, orchard grass, and timothy after five successive cuttings of each crop. However, it should be

TABLE 11. Elemental concentrations (mg/kg, dry weight) in edible portions of crops grown in pots with soil (control or fly ash) amended with 10% (by weight) fly ash. (Furr et al., 1976)

| Element | Beans   |         | Cabbage |         | Carrots |         | Millet  |         |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|         | Control | Fly ash | Control | Fly ash | Control | Fly ash | Control | Fly ash |
| As      | 0.01    | 0.2     | 0.1     | 0.2     | 0.01    | 0.2     | 0.2     | 1.0     |
| B       | 16      | 24      | 23      | 24      | 19      | 21      | 17      | 22      |
| Ca      | 2,670   | 2,900   | 4,500   | 4,950   | 1,650   | 2,280   | 3,700   | 2,090   |
| Cu      | 3.2     | 1.3     | 3.0     | 1.1     | 2.0     | 2.4     | 2.4     | 2.8     |
| Fe      | 108     | 92      | 78      | 267     | 143     | 170     | 49      | 85      |
| Hg      | 0.2     | 0.1     | 0.1     | 0.3     | 0.1     | 0.2     | 0.7     | 0.2     |
| I       | 0.7     | 0.5     | 0.3     | 0.7     | 0.9     | 0.9     | —       | 0.1     |
| K       | 16,300  | 19,500  | 31,200  | 27,200  | 25,300  | 29,400  | 20,500  | 12,200  |
| Mg      | 1,340   | 1,590   | 2,160   | 1,320   | 730     | 1,020   | 3,100   | 2,550   |
| Mo      | 0.9     | 3.2     | 1.0     | 2.2     | 0.2     | 0.4     | 0.3     | 1.2     |
| Ni      | 3.9     | 4.3     | 1.9     | 1.3     | 2.7     | 2.8     | 1.4     | 0.7     |
| Sb      | 0.4     | 0.4     | 1.4     | 2.0     | 0.9     | 0.4     | 1.1     | 0.6     |

noted that trace element accumulation is often not a major consideration since the objective of most reclamation efforts is only to revegetate fly ash piles or coal-cleaning wastes mixed with fly ash and not to raise crops.

#### Ocean disposal

Seligman and Duedall (1979) investigated the possibility of ocean disposal of fly ash by using a stabilized mixture of scrubber sludge and fly ash cured into solid cylinders. Leaching studies indicated minimal release of Cu, Fe, and Ni from the cylinders. Subsequent study showed the structural strength of the test cylinders was maintained during prolonged periods in seawater.

#### Ash pond disposal

The prevalent method for fly ash disposal is by wet-sludging from electrostatic precipitators to on-site ash ponds. Wet disposal systems are designed to dispose of bottom and fly ash in the form of a slurry. The slurry is pumped into some type of natural or man-made basin where the ash settles, leaving a supernatant. The advantages of ash pond disposal are economic considerations, dust and noise minimization, and simplicity (Chu, Krenkel, and Ruane, 1976; Chu, Ruane, and Krenkel, 1978; EPRI, 1979). However, the EPA has stated that ponding will be unacceptable, since the process may produce a supernatant water with levels of dissolved solids and heavy metals exceeding permissible limits for discharge, which may pose potential ground water contamination problems (Smith, 1979).

The two federal laws that have the greatest impact on ash disposal techniques are the Resource Conservation and Recovery Act of 1976 (RCRA) and the Clean Water Act of 1977 (CWA), which set effluent limitations for point source discharges to surface waters. The effluent guidelines and standards for

TABLE 11. (continued)

| Element | Onions  |         | Potatoes |         | Tomatoes |         |
|---------|---------|---------|----------|---------|----------|---------|
|         | Control | Fly ash | Control  | Fly ash | Control  | Fly ash |
| As      | 0.1     | 0.03    | 0.1      | 0.1     | 0.1      | 0.1     |
| B       | —       | 22      | 6        | 10      | 4        | 15      |
| Ca      | 4,210   | 7,150   | 237      | 200     | 780      | 980     |
| Cu      | 3.4     | 2.0     | 3.1      | 5.5     | 2.2      | 3.3     |
| Fe      | 100     | 120     | 49       | 63      | 173      | 114     |
| Hg      | 0.3     | 0.3     | 0.1      | 0.2     | 0.1      | 0.3     |
| I       | 0.7     | 2.6     | 0.1      | 0.3     | 0.4      | 0.6     |
| K       | 14,900  | 16,300  | 21,500   | 23,800  | 22,200   | 25,100  |
| Mg      | 1,480   | 1,160   | 740      | 1,200   | 880      | 1,080   |
| Mo      | 0.7     | 0.4     | 0.2      | 0.6     | 0.5      | 0.8     |
| Ni      | 2.2     | 2.9     | 0.6      | 0.7     | 0.5      | 0.8     |
| Sb      | 0.8     | 2.2     | 0.4      | 0.7     | 2.5      | 1.1     |

coal-fired power plant ash disposal ponds require that by 1983, the "Best Available Technology Economically Achievable" (BATEA) standard be implemented. The impact of the RCRA on future disposal sites as well as suggestions for methodologies complying with RCRA regulations are discussed in EPRI (1979).

Ash pond design is varied, depending on site conditions. Some ponds are made by simply damming valleys, which results in large irregular basins; other ponds are made by constructing dikes on flat ground. Ash disposal ponds may be lined or unlined. Several materials have been used as liners, including compacted earth, clay, synthetics, etc. Dvorak, Lewis, et al. (1978) summarize the nature and utility of six different liner approaches. EPA guidelines state that new disposal-pond type impoundments above usable aquifers must have a liner meeting specific permeability and thickness criteria depending on the nature of the material used (Ellison and Shapiro, 1979; EPRI, 1979).

As noted by Dzurinkol and Lin (1979), many factors (including turbulence, hydraulic distribution and loading, liquid retention time, and the settling characteristics of the suspended particles) affect the efficiency with which suspended solids are removed (by sedimentation) in ash ponds. These factors must be considered in the design of ash ponds. To enhance sedimentation the authors recommend that: (1) where possible, ash ponds should be long, narrow, rectangular basins; (2) the amount of discharge water should be reduced (by using denser slurries) to reduce hydraulic loading; (3) the operating depth of disposal ponds should be increased to augment retention time; (4) distribution systems should be installed to impart uniform effluent flow so that there is even sedimentation in the ash disposal basins.

A report by Miller, Chu, and Ruane (1979) describes procedures for designing water quality monitoring programs for ash pond effluents. Based on statistical treatment and theoretical considerations, the proposed methods are applied to two ash pond systems to demonstrate their effectiveness.

## Landfill disposal

Dry disposal procedures involve transporting the ash, often by truck, to landfills. The ash may be compacted to reduce the overall volume. Ash stored dry usually retains its chemical properties and thus provides ash stockpiles for future utilization.

The major environmental concern in dry storage is minimizing leachate production upon burial of the ash. Landfill design and operational procedures to abate soil and water contamination are beyond the scope of this paper. However, several general precautions should be observed: (1) the compacted wastes should be stored with minimal water content; (2) surface water should be diverted away from the site; (3) the site should be located away from topographic depressions; and (4) the stored ash should be covered with soils characterized by low permeabilities.

Several combinations of wet and dry disposal techniques are possible. As summarized in Dvorak, Lewis, et al. (1978), common disposal schemes of fly

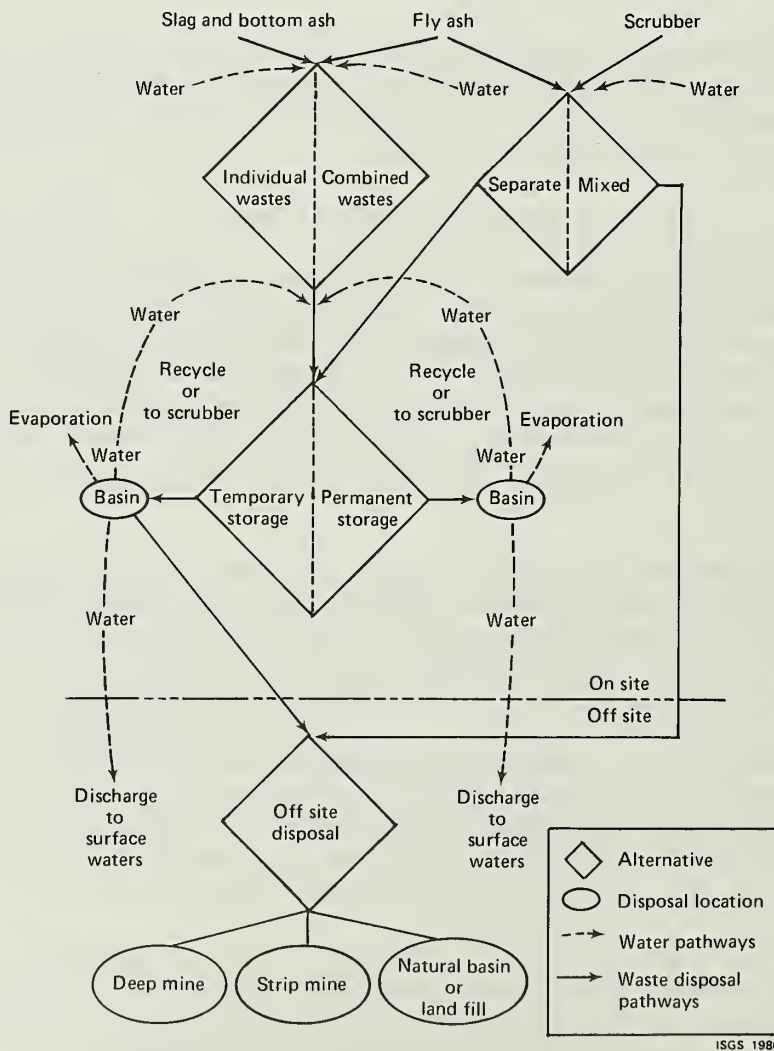


FIGURE 7. Flow diagram for power plant ash and scrubber sludge waste disposal (From Dvorak, Lewis, et al., 1978).

ash disposal in temporary or permanent storage sites include: (1) combining bottom ash with fly ash; (2) layering the coarser bottom ash over compacted fly ash to reduce runoff and wind dispersal of fly ash; and (3) combining alkaline scrubber sludges (flue gas desulfurization by-products) to neutralize acidic fly ashes. Figure 7 presents a flow diagram illustrating several options or methods for the disposal of fly ash, bottom ash, slag and scrubber sludges.

### Site selection

Site selection for ash disposal can be the result of multidisciplinary studies. Delwiche, Digiola, and Niece (1970) presented a case history of the evaluation of ash storage sites for a power plant in Wisconsin in which the feasibility of both wet and dry methods in four different sites were explored. Each site was characterized in terms of topography, bedrock stratigraphy and weathering, soil formation and unconsolidated deposits, hydrology, aesthetics, physiography, vegetation, wildlife, and aquatic life. After presenting environmental and economic analyses, the authors evaluated the suitability of each site for several proposed methods of fly ash disposal.

A systematic approach for determining ash disposal sites has been proposed by EPRI (1979); the methodology was developed using several criteria including ash character (physical and chemical) and to a greater extent, the legal and environmental ramifications of potential ash disposal sites. They use the case study discussed by Delwiche and his co-workers (1979) to demonstrate their disposal site methodology.

### SUMMARY

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On the basis of currently available data, the following conclusions were made:

1. Coal ash is predominantly a noncombustible mineral-derived by-product resulting from coal combustion. Fly ash is produced when fine-grained ash particles are entrained in the flue gases.
2. To abate atmospheric emission of fly ash from coal-fired power plants, fly ash particles are collected from the flue gases by various control systems, most commonly electrostatic precipitators.
3. The morphology of fly ash particles is variable but the finest fraction is predominately composed of non-opaque solid spheres resembling glass-like beads.
4. These glassy spheres are predominately amorphous material (lacking distinct crystalline structure); the crystalline phases are typically magnetite, mullite, hematite and quartz.
5. Fly ash fallout may be a source of trace elements to terrestrial ecosystems.
6. The elemental composition of fly ash is highly variable and directly related to elemental variations in the parent coals and to the characteristics and operational procedures within the individual plants

generating the ash. The major constituents present (each approximately greater than 1 percent by weight) are typically  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$ ;  $\text{TiO}_2$ ,  $\text{MnO}$ , and  $\text{P}_2\text{O}_5$  are generally at levels less than 1 percent by weight. The  $\text{SO}_3$  level is typically less than 3 percent in fly ash, and carbon levels may range from less than 1 percent to more than 20 percent. Ba, Cl, Cu, Sr and Zn concentrations exceeding 0.2 percent have been observed but are uncommon.

7. Elemental partitioning occurs during the formation of fly ash, possibly as a result of volatilization-surface condensation mechanisms. A number of elements have been found to be more concentrated in fly ash relative to the (ash of) parent coals. These elements are As, B, Br, Cl, Hg, I, In, Pb, Po, S, Sb, Se, and Zn. In contrast, Al, Bi, Ca, Ce, Cs, Dy, Eu, Hf, K, La, Na, Nb, Nd, Sc, Si, Sm, Sn, Ta, Tb, Th, Ti, Y, and Yb have been described as demonstrating little or no enrichment. On the basis of the literature, Ag, Au, Ba, Cd, Co, Cu, Cs, Fe, Ga, K, Mg, Mn, Mo, Ni, Rb, Sc, Sr, Tl, U, V, and W demonstrate nonuniform distributions.
8. Organic compounds are present in fly ash. Available analyses suggest that total hydrocarbon contents are less than 10 mg/kg and total polycyclic aromatic hydrocarbon concentrations are less than 0.2 mg/kg. To date the organic compounds present in fly ash have been inadequately characterized.
9. While fly ash particles are, in terms of mass, essentially insoluble aluminosilicate glasses, the enriched surface elements may be soluble. The chemical composition of fly ash leachates demonstrates a great deal of variability, which is a function of the physico-chemical character of the fly ash and the leaching conditions. However, B consistently appears to be soluble in water. Al, Ba, Mg, Si, and Sb appear to be relatively insoluble in water extractions. Ca, Cd, Cu, K, Mn, Na, Ni, Pb, and Zn exhibit either intermediate or inconsistent leachabilities.
10. Toxicity studies of fly ash to aquatic ecosystems are limited, but available data suggest that certain species of fish may be more adversely affected by the alkaline pH (characteristic of many fly ash leachates) and the physical presence of the particles (as turbidity) rather than by leached metals.
11. Several elements have been found to be concentrated by some marine organisms subjected to fly ash leachates. These elements are Al, As, B, Br, Ca, Cl, Co, I, La, Se, Sm, V, and Zn.
12. Besides direct toxicity to organisms, fly ash may affect aquatic ecosystems by altering nutrient cycles. Fly ash may serve as a phosphorous sink to reduce the phosphorous level in lakes or as a silicon source.
13. Fly ash may be hazardous (1) by direct external reactions (skin, eyes, etc.) or (2) by reactions in the respiratory tract or alimentary canal. Uptake of toxic materials is greatest via the respiratory system. Mice, hamsters, and rats exposed to various fly ash aerosol concentrations have demonstrated pathological damage to the lungs. Moreover, since fly ash particles can have long residence times in the lung, chronic



long-term studies are needed to characterize the effects of fly ash inhalation. Animals (sheep, lambs, goats, etc.) fed diets containing plants grown in fly ash amended soils have exhibited elevated levels of Se in the blood, but no pathological effects have been observed.

14. The predominant method of fly ash disposal is by wet sluicing to on-site ash ponds. The greatest utilization of fly ash as a useful material is as an additive to concrete mixtures. The use of fly ash as a soil additive shows promise but must be tailored to the specific chemical properties of the soil and the fly ash, and to the diverse edaphic requirements of plants.
  15. Numerous field and laboratory experiments have demonstrated that some elements are enriched in plants grown in fly ash amended soils. As, B, Ba, Ca, Cu, Fe, Hg, I, K, Mg, Mn, Mo, Ni, Sb, Si, V, and Zn have been found concentrated in plant tissues.
  16. A fly ash classification scheme should be developed to establish a common language for geologists, chemists, biologists and others concerned with fly ash research to aid in the organization of analytical data and to ensure that basic fly ash properties are recognized, investigated, and reported.
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## APPENDIX A. A PROPOSED FLY ASH CLASSIFICATION SYSTEM

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The Resource Conservation and Recovery Act (RCRA) of 1976—and its implications for health and environment—have focused wide attention on the need to develop environmentally sound methods of utilizing and disposing of utility solid wastes and have provided the impetus for many studies investigating coal fly ash as a health hazard, soil modifier, concrete additive, and mineral resource.

These studies have been carried out by geochemists, environmentalists, engineers, and ecologists and investigators in related fields. In many of the published investigations of fly ash, fundamental properties such as particle size, chemical composition, and leachate pH are only briefly mentioned or omitted altogether: this oversimplification of a complex material makes comparisons between studies difficult. Part of the problem is that there is still no uniform physico-chemical definition of the selected fly ashes used in the various studies, which probably results from the different priorities and research emphasis by investigators in different disciplines.

The rudimentary classification system proposed in this section is an attempt to establish a uniform language, applicable to most disciplines, that would (1) facilitate communication between investigators with dissimilar backgrounds and priorities; (2) make organization of analytical data easier; and (3) increase the likelihood that basic fly ash properties (such as particle-size) will be identified and investigated.

A system for the classification of fly ash was first proposed by Kocuvan (1979). The taxa of his classification scheme is essentially particle-size parameters and empirical ratios derived from  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{SO}_3$ , and  $\text{MgO}$  concentrations. Although Kocuvan attempted to organize some fly ash data, his system was designed primarily to suit the needs of fly ash-concrete studies. Moreover, an integral part of the system is based on abstract ratios which are conceptually difficult to deal with in describing a given fly ash system. Another difficulty with this system is that the particle-size parameters are cumulative size fractions; the particle-size classes defined by the Soil Conservation Service (1975) are simpler and easier to use for defining textures.

The seven basic units (groups) of this classification system are based on chemical composition; they are formed by the intersections of three end members in a triangular graph (figure A-1). These end members are the Sialic group ( $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2$ ), the Calcic group ( $\text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$ ) and the Ferric group ( $\text{Fe}_2\text{O}_3 + \text{MnO} + \text{SO}_3 + \text{P}_2\text{O}_5$ ). These elements are usually major constituents of fly ash with Si, Al, Fe, or Ca predominating in the matrix composition. Combinations of the sialic, calcic, and ferric components yield the Ferrosialic, Ferrocalsialic, Calsialic, and Ferrocalcic groups. For example, the Ferrocalsialic group would represent fly ashes predominantly composed of  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2$ , with smaller proportions of  $\text{Fe}_2\text{O}_3 + \text{MnO} + \text{SO}_3 + \text{P}_2\text{O}_5$  and  $\text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$ . A Calcic fly ash would be composed mainly of  $\text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$ , with smaller proportions of the ferric and sialic components. The exact numerical values defining the chemical fields are given in table A-1.

The rationale for deriving these numerical values is based partly on the analytical data reported in the publications cited in this review. Some of

TABLE A-1. Fly ash groups

| Group          | Sialic component (%) | Calcic component (%) | Ferric component (%) |
|----------------|----------------------|----------------------|----------------------|
| Sialic         | >88                  | 0-12                 | 0-12                 |
| Ferrosialic    | 48-88                | 0-29                 | 23-52                |
| Calsialic      | 48-<29               | >29-52               | 0-23                 |
| Ferrocalsialic | >48-88               | 0-29                 | 0-23                 |
| Ferric         | <48                  | 0-29                 | >23                  |
| Calcic         | <48                  | >29                  | 0-23                 |
| Ferrocalcic    | <48                  | 29-77                | >23-71               |

the divisions are arbitrary because of the lack of more definitive criteria. As a preliminary datum, 479 analytical determinations for the major elements were compiled from the literature cited and averaged to derive an empirical formula for fly ash composition. Although there is wide variation, this approach may establish a preliminary norm for fly ash composition. The empirical formula for major elements (in percent by weight) is SiO<sub>2</sub>, 43.9; Al<sub>2</sub>O<sub>3</sub>, 22.7; Fe<sub>2</sub>O<sub>3</sub>, 10.7; CaO, 8.2; Na<sub>2</sub>O, 1.8; MgO, 2.7; K<sub>2</sub>O, 2.00; TiO<sub>2</sub>, 1.3; SO<sub>3</sub>, 1.6; P<sub>2</sub>O<sub>5</sub>, 0.8; MnO, 0.10; and carbon, about 4. This formula is broadly comparable to the empirical formula presented by Fisher et al. (1976) for western fly ashes (see p. 12). The sialic component of this preliminary norm is 67.9 percent, while the ferric component is 13.7 percent and the calcic component is 14.7 percent. Therefore, this hypothetical fly ash would plot in the field proposed as a Ferrocalsialic. The standard deviation of the 479 analytical determinations of each chemical constituent was used to define the boundaries of each field in figure A-1. For example, to establish the lower and upper boundary of the sialic component of the

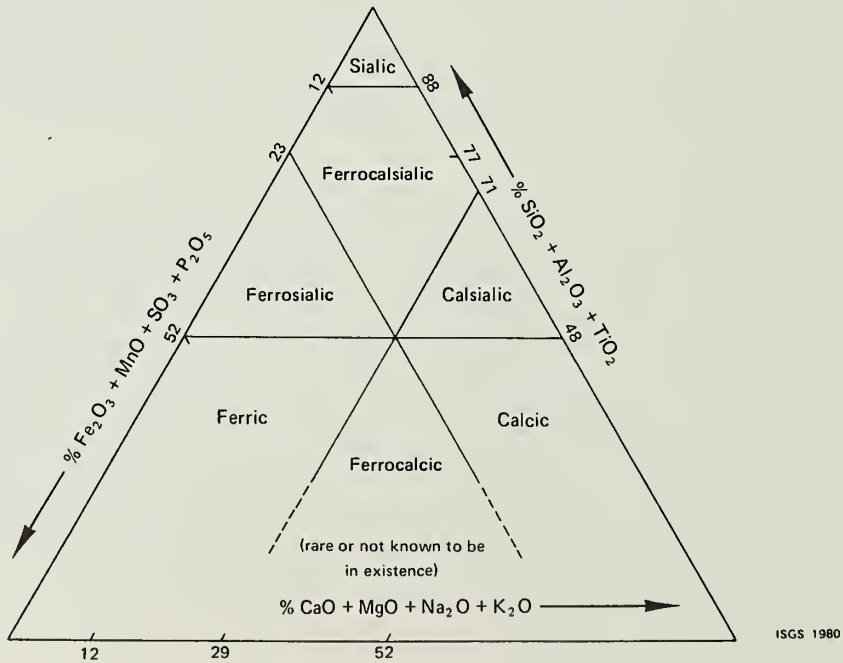


FIGURE A-1. Fly ash classification system.



TABLE A-2. Sialic maximum and minimum of the Ferrocalsialic field

| Constituent                    | Average | Std. dev. | Range ( $\bar{x} \pm \sigma$ ) |
|--------------------------------|---------|-----------|--------------------------------|
| SiO <sub>2</sub>               | 43.88   | ±12.87    | 31.01-56.75                    |
| Al <sub>2</sub> O <sub>3</sub> | 22.69   | ±6.45     | 16.24-29.14                    |
| TiO <sub>2</sub>               | 1.25    | ±0.51     | 0.74- 1.76                     |
|                                |         |           | SUM 47.99-87.65                |

Ferrocalsialic field, the range of each constituent was calculated and summed to yield minimum and maximum values as shown in table A-2.

Thus, the sialic boundaries for the Ferrocalsialic field range from 48 to 88 percent SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> + TiO<sub>2</sub>. A fly ash with a sialic proportion greater than 88 percent falls into the Sialic field. The same rationale was used for determining the calcic and ferric maximum and minimum boundaries for the Ferrocalsialic field; therefore, a fly ash with a calcic component exceeding 29 percent and a ferric component less than 23 percent would be classified as a Calsialic. (The boundaries defining each field will probably need to be modified as new data becomes available.)

This classification system could be used as an aid in determining what utilization method might be best suited for particular types of fly ash. Iron beneficiation of fly ash may become a cost-efficient process with further development of extraction procedures; therefore, Ferric and Ferrosialic fly ashes may best serve as likely candidates for iron sources. Ferrocalsialics, Calsialics, Ferrosialics, and Sialics may broadly correlate with Class F fly ashes, defined by ASTM procedures as having cementitious and pozzolanic properties (Mielenz, 1979). The chemical requirements of an F fly ash as a mineral admixture for concrete include: (1) a SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub> concentration equal to or exceeding 70 percent and (2) a SO<sub>3</sub> content less than or equal to 5 percent and a Na<sub>2</sub>O + K<sub>2</sub>O content less than or equal to 1.5 percent. Because most Calcic fly ashes would exhibit cementitious abilities and lack pozzolanic properties, they would not be suitable for the concrete industry, but could be very useful in acid mine reclamation because of their high CaO (in the form of CaO, CaOH, and CaCO<sub>3</sub>) concentrations. Studies have demonstrated that high calcium fly ashes can neutralize acidic coal-cleaning wastes in various co-disposal schemes. Fly ashes fitting into the proposed Ferrocalsialic Group may be extremely uncommon. Because of the apparent scarcity of fly ashes with extremely high ferric and calcic components, the lower area of the triangular field may also have limited applicability.

To indicate leachate pH, a prefix is used to modify each group name (table A-3). The pH is to be measured on a 1:1 mixture of fly ash to distilled water (wt/vol) or by any one of the methods currently used to determine soil reaction. Therefore, a fly ash with a SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> + TiO content greater than 80 percent and a Fe<sub>2</sub>O<sub>3</sub> + MnO + SO<sub>3</sub> + P<sub>2</sub>O<sub>5</sub> + CaO + MgO + Na<sub>2</sub>O + K<sub>2</sub>O content of less than 10 percent which generates a leachate with a pH less than 5 would be called an Adsialic. A fly ash with a calcic component of 37 percent and a sialic percentage of 50 percent which produces a leachate greater than pH 9 would then be referred to as an Alcalcic.

More than 96 percent of the matrix composition of many fly ashes consists of the three end members of the classification fields (Sialic, Calcic, and Ferric);

but concentrations of Ba, Cl, Cu, Sr, and Zn exceeding 0.2 percent have also been reported in the literature. Although such levels may be uncommon, this classification system accommodates fly ashes with such levels by providing for the inclusion of the name of the constituent exceeding 0.2 percent before the formal

name. For example, an Alcalcic with a Sr concentration of 2261 mg/kg would be written as a Strontium Alcalcic (or Sr-Alcalcic) to call attention to the elevated level of a given constituent (strontium) in a single name which also suggests the major elemental character and pH. The same rationale would be applied to fly ashes having a carbon content exceeding 5 percent. If the fly ash in the previous example exhibited a C value of 5.2 percent, the waste would be designated as a Carbon Strontium Alcalcic (C, Sr-Alcalcic). These special compositional properties are to be listed in alphabetical order if more than one is required. Obviously, some constituents may be at levels exceeding what may be considered as "typical" yet still be below 0.2 percent of the total composition. It might be possible to derive classification guidelines for these elements as more data becomes available; such guidelines could then be included in a revision of this classification system. A summary of the nomenclature used in this classification system (including examples) is given in table A-4.

TABLE A-3. pH prefixes

| pH      | Prefix to group     |
|---------|---------------------|
| <5.0    | ad (after acidic)   |
| 5.0-9.0 | nu (after neutral)  |
| >9.0    | al (after alkaline) |

TABLE A-4. Summary of nomenclature

| Group          | pH character<br>(prefix to group name)                   | Special compositional<br>properties<br>(examples)                   |
|----------------|--|---|
| Sialic         | Adsialic<br>Nusialic<br>Alsialic                         | Ba-Adsialic<br>Ba, C-Nusialic<br>C, Zn-Alsialic                     |
| Ferrocalsialic | Adferrocalsialic<br>Nuferrocalsialic<br>Alferrocalsialic | Ba, Zn-Adferrocalsialic<br>C-Nuferrocalsialic<br>C-Alferrocalsialic |
| Ferrosialic    | Adferrosialic<br>Nuferrosialic<br>Alferrosialic          | Sr-Adferrosialic  |
| Calsialic      | Adcalsialic<br>Nucalsialic<br>Alcalsialic                | Zn-Nucalsialic  |
| Ferric         | Adferric<br>Nuferric<br>Alferric                         | Cl-Alferric   |
| Calcic         | Adcalcic<br>Nucalcic<br>Alcalcic                         | Ba, Cu, Zn-Adcalcic   |
| Ferrocaltic    | Adferrocaltic<br>Nuferrocaltic<br>Alferrocaltic          | Ba, C, Cu-Nuferrocaltic   |

As noted earlier, the textural classification used for soils by the Soil Conservation Service could be used in conjunction with the classification system described here to define fly ash textures. Complete discussion of this texture classification system is found in Soil Conservation Service (1975). We are not necessarily advocating that this textural classification be used in lieu of other currently used schemes; we are simply urging that the texture of a given fly ash under study be well-characterized by some accepted system.

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