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Fly Ash Collected from Electrostatic Precipitators: Microcrystalline Structures and the Mystery of the Spheres

Abstract. *Scanning electron micrographs demonstrate the presence of microcrystalline structures on the surface of coal-derived fly ash samples taken from electrostatic precipitator hoppers. Cenospheres (hollow spheres) were found to be packed with smaller cenospheres, which were also packed with spheres. Microspheres, apparently formed by uneven heating, are encapsulated in the parent sphere. Chemical analyses provide a basis for the postulation of a mechanism of formation for plerospheres (hollow spheres packed with spheres) and microcrystals.*

Elucidation of the potential bioenvironmental effects of various options for the generation of electric power necessitates a physicochemical and biological evaluation of agents released to the environment. As part of our initial efforts to characterize fossil fuel–derived effluents, a detailed investigation of the physical appearance of fly ash was carried out by scanning electron microscopy (SEM). This report describes our findings of microcrystalline structures and cenospheres (hollow spheres) packed with smaller spheres in fly ash collected from electrostatic precipitators (ESP) in coal-fired power plants.

Fly ash samples from two coal-fired power plants, one burning a coal with a low sulfur content (western U.S. coal) and the other burning a coal with a high sulfur content (eastern U.S. coal) were obtained from ESP hoppers. Two fly ash samples from western U.S. coal were collected: one from a hopper at ambient temperatures 30 days after the boiler had been shut down and the second sample from a hopper at about 66°C while the generating unit was in operation. The fly ash sample from eastern U.S. coal was collected from an ESP operating at 125°C.

Fly ash agglomerate composed of spherical particles, shown in the SEM micrograph (Fig. 1A), has been described by a number of investigators as being typical of fly ash derived from coal combustion (*1*). The cenospheres of Fig. 1B are, however, more typical of the particulate aggregates that we have collected. Careful examination of these cenospheres reveals that some of the larger spheres contained within a cenosphere are themselves cenospheres packed with smaller spheres 1 μm in diameter or less. Microcrystals can also be observed on the surface of the large cenosphere as well as on the smaller entrapped spheres. At higher magnification (Fig. 1B, inset) the microcrystals appear to be growing from the surface of the spheres. High local concentrations of crystals (Fig. 1C) could be found in the fly ash sample from western U.S. coal from the generating unit that had been shut down. Although the fly ash from western U.S. coal collected at 66°C also contained a large number of cenospheres with packed spheres (Fig. 1D), microcrystals were not evident. However, in the fly ash agglomerate of Fig. 1E, the lower particle shows a striated surface apparently resulting from initial crystal formation. Spherical cavities in the thick wall of the upper hollow particle were either gas pockets or the remnants of smaller encapsulated spheres. The micrographs in Fig. 1, D and E, were prepared within 2 weeks after collection of the fly ash from western U.S. coal. Subsequent SEM analysis of the fly ash collected at 66°C after it had been stored in closed containers at ambient temperatures for 4 months revealed extensive crystal growth on the surface of the spheres, an indication that the crystal formation occurs gradually after the spherical particles have developed.

The fly ash from eastern U.S. coal contained a larger fraction of amorphous material than that from western U.S. coal, although both contained cenospheres. A typical fly ash aggregate from eastern U.S. coal (Fig. 1F) is composed of spherical particles embedded in an amorphous matrix.

Using light microscopy, we observed unbroken spheres with a "cloudy" interior, as described by McCrone *et al.* (*2*); we found that we could "crack" the spheres by compressing them between two microscope slides and that smaller spheres were contained in the larger spheres. As these spheres are not empty, we suggest that the name "plerosphere" [plero- (from the Greek *plērēs*, full)] be applied to these hollow spheres packed with spheres.

The empirical formula of the major elements in the fly ash from western U.S. coal analyzed by atomic absorption spectroscopy is $Si_{1.00}Al_{0.45}Ca_{0.051}Na_{0.047}Fe_{0.039}Mg_{0.020}K_{0.017}Ti_{0.011}$. When expressed as the associated oxides, the elements are present in the following mass percentages: SiO_2, 65.3; Al_2O_3, 25.2; Fe_2O_3, 3.4; CaO, 3.1; Na_2O, 1.6; TiO_2, 0.98; MgO, 0.89; and K_2O, 0.89. This chemical composition is consistent with fly ash originating from coal with intrusions of clay minerals, probably kaolinite minerals with lesser amounts of quartz (*3*). As calcium does not occur within the lattice structure of these minerals, the calcium present in the fly ash was probably derived from intrusions of calcium carbonate. Electron microprobe analysis of the plerospheres indicated that the surface was predominantly aluminosilicate glass, with intermediate concentrations of iron, calcium, sodium, and magnesium, and minor concentrations of titanium and sulfur. Inclusions with higher concentrations of calcium were found within the surfaces; smaller particles were found in which titanium or iron were the only elements detected. Microprobe analysis of larger crystals (20 μm in length) with a physical appearance similar to those of Fig. 1C indicated high concentrations of calcium and sulfur with no other elements detected. The limits of detectability for other elements in these particles by electron-probe analysis are on the order of 0.1 percent (*4*). The major gases contained within the spheres were H_2O and CO_2 (*5*), as determined by mass spectroscopic analysis after thorough removal of surface-associated gases and repeated crushing of the spheres in a vacuum.

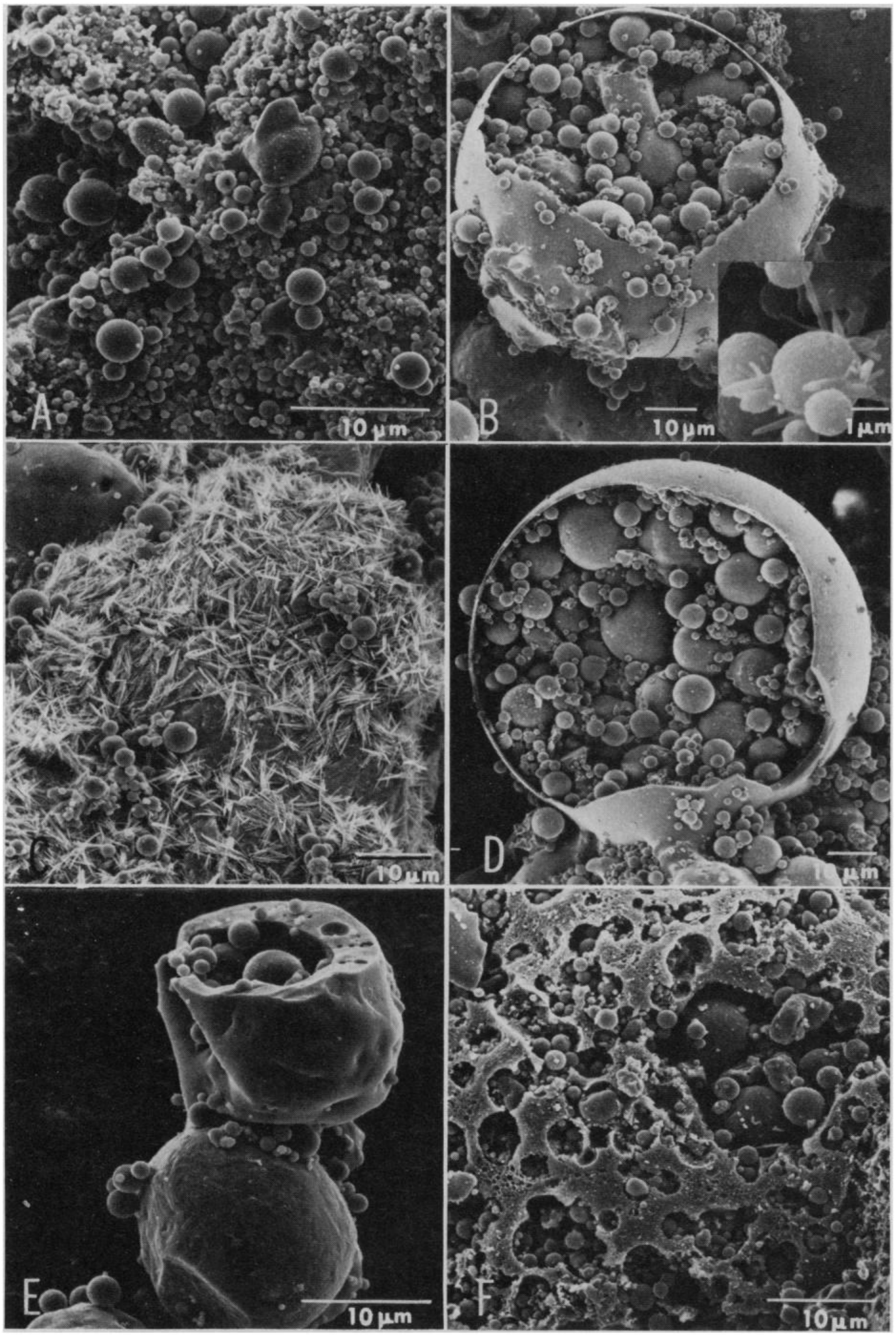
The slow crystal formation process appears to involve the crystallization of soluble substances from liquid condensed on the particle surface. Moreover, the microprobe analysis and the SEM appearance of the larger crystals indicate that these larger crystals are probably anhydrite ($CaSO_4$) or gypsum ($CaSO_4 \cdot 2H_2O$) (*6*). Thus the microcrystals are probably formed by the leaching of metal oxides by condensed

H_2SO_4 with subsequent crystallization of metal sulfates.

The mechanism of formation of the plerospheres containing plerospheres that contain microspheres is not known with certainty. Formation of these spheres within spheres was not caused simply by gas bubbles blown from the surface of a burning coal particle because such a low-temperature (200° to 300°C) process (*2*) is inconsistent with the high temperatures of a large boiler designed for the utilization of pulverized coal. Furthermore, the melting points of the fly ash particles are well above the range of 200° to 300°C.

The sphere-within-sphere structure may, however, result from a similar bubbling process occurring in the high-temperature combustion zone. As a noncombustible parent particle is progressively heated from its outer surface, a temperature gradient develops, which permits the surface layer of the particle to become molten while the interior remains, for a time, either highly viscous or solid. Thermal decomposition or dehydration of certain minerals (for example, $CaCO_3$ or clay minerals) provides a source of gas (either CO_2 or H_2O) forming a bubble around the core, which remains attached to the interior of the spherical shell. Because the thermal conductivity of the gas is less than that of the liquid shell in contact with the core, the core continues to heat most rapidly at this point of contact. Additional gas formation causes the core to boil away from the interior surface, possibly forming small solid microspheres in the process. The process can be repeated on smaller spheres boiled from the core, as suggested in Fig. 2, until the interior of the plerosphere is filled with other plerospheres containing microspheres or until the particle is carried out of the high-temperature combustion region and freezes.

On the basis of dimensional reasoning (*7*), the characteristic time required to heat a homogeneous solid particle about 10 μm in diameter to a uniform temperature is about 100 μsec. If gas expands the outer shell to a diameter of 50 μm



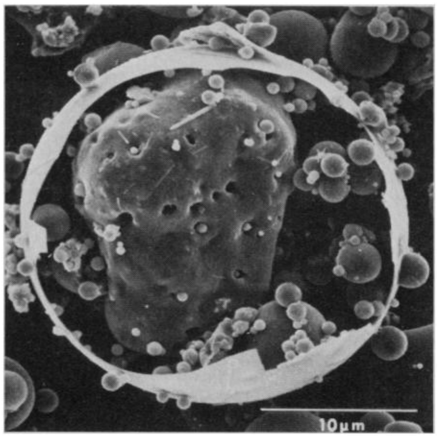


Fig. 1 (left). Scanning electron micrographs of ESP fly ash samples collected from power plants fired with western U.S. coal (A through E) and eastern U.S. coal (F). Although fly ash agglomerates composed of spherical particles (A) were observed, the plerospheres (B, D, and E) were more typical of the particulate aggregates of the fly ash from western U.S. coal samples. In the fly ash samples from the stack that had been shut down, microcrystals are evident on the spheres (B) and appear (B, inset) to be growing from the surface of the fly ash, although high local concentrations were also observed (C). Microcrystals were not observed in the samples collected from the operating plants (D, E, and F), although the striated surface of the lower particle in (E) may have resulted from initial crystal formation. The samples of fly ash from eastern U.S. coal (F) contained a larger fraction of amorphous material than the samples from western U.S. coal. Fig. 2 (right). Plerosphere containing an amorphous core with smaller spheres which appear to have been formed from boiling within the core. This sample was collected from a plant burning western U.S. coal which had been shut down for 30 days.

and insulates the core, the entire heating process would take about 1000 μsec. The mean velocity of the flue gases in pulverized coal units is the order of 15 m/sec (*8*). We believe that the short time interval for formation and freezing of the particles precludes the alternative hypothesis of plerosphere formation by mechanical interaction with surrounding gases. In addition, the spherical nature of the plerospheres suggests that pressure and surface tension are the predominant forces acting on the particles.

Microcrystals, if present on stack-emitted particles, as described for fly ash collected from ESP hoppers may have important biologic implications. The health hazard associated with inhalation of the crystalline particles, with their increased surface areas and potentially different chemical compositions, may be greater than that expected for the plerospheres. The crystals may preferentially concentrate metals, some of which may be toxic, by processes similar to that described for calcium. Thus, deposition of microcrystals in macrophages, for example, could subsequently result in high local concentrations of toxic elements. Furthermore, the existence of microcrystals may be responsible in part for the recent reports of the association of increased concentrations of heavy metals with smaller particles (*9*).

This initial study indicates that fly ash may exhibit a variety of shapes (predominantly spherical) and surfaces. Because the surface serves as the interface for biological interaction, it is essential to further define the surface characteristics of fly ash in toxicologic studies.

Note added in proof: For example, surface predominance of trace elements in fly ash has been demonstrated in a recent report (*10*).

G. L. FISHER
Radiobiology Laboratory, University of California, Davis 95616
D. P. Y. CHANG
Department of Civil Engineering, University of California, Davis
MARGARET BRUMMER
California Primate Research Center, University of California, Davis

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$$\tau \sim \ell^2 \rho c_p k^{-1}$$
For the solid particle, k was assumed to be the thermal conductivity of clay. For the spherical shell surrounding the solid core, k was taken to be the thermal conductivity of air, as the gas would be the limiting component for heat transfer. Values used in the calculation were taken from A. J. Chapman [*Heat Transfer* (Macmillan, New York, 1967), pp. 556–567].
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Eleven-Year Variation in Polar Ozone and Stratospheric-Ion Chemistry

Abstract. *A mechanism for producing an 11-year oscillation in ozone over the polar caps is the modulation of galactic cosmic rays by the solar wind. This mechanism has been shown to give the observed phase in ozone oscillations and the correct qualitative dependence on latitude. However, the production of nitrogen atoms from cosmic-ray collisions seems inadequate to account for the ozone amplitude. Negative ions are also produced as a result of cosmic-ray ionization, and negative-ion chemistry may be of importance in the stratosphere. Specifically,* NO_x^- *may go through a catalytic cycle in much the same fashion as* NO_x*, but with the important distinction that it does not depend on oxygen atoms to complete the cycle. Estimates of the relevant rates of reaction suggest that negative ions may be especially important over the winter polar cap.*

Strong evidence has been offered for an 11-year variation in the total O_3 at high latitudes, and especially at high altitudes (*1*). To account for this effect, Ruderman and Chamberlain (*2*) proposed a physical mechanism based on the well-documented 11-year modulation of galactic cosmic rays (GCR's) by magnetic fields in the solar wind. The cosmic rays were shown to produce free N atoms, which in turn react with O_2 or O_3 to form NO_x, a catalytic destroyer of odd oxygen (O, O_3). Recent estimates that the density of ambient NO_x is as high as 10 parts per billion at the important altitudes (*3*) make it appear less likely that this mechanism by itself will produce enough variation in NO_x to account for the reported 11-year O_3 cycle. However, the Ruderman-Chamberlain mechanism gives approximately the correct phase of the O_3 variation and its dependence on latitude.

Crutzen *et al.* (*4*) have noted that bursts of solar cosmic rays, which are responsible for the intense polar-cap absorption (PCA) of radio waves, would also be a strong source of NO_x in the upper stratosphere. The incidence of PCA events, however, tends to be in phase with sunspots, so that any NO_x generated would be expected to be nearly opposite in phase to that from GCR's, which fits the O_3 observations. In addition, most PCA ionization is deposited much higher in altitude than that from GCR's.

The striking increase of the amplitude of the 11-year O_3 variation with latitude and its phase make it likely, in our opinion, that the mechanism responsible for the effect is associated with the periodic component of the cosmic-ray ionization, which is limited to high latitudes. One must then understand how the ionization affects O_3 and why GCR ionization effects should dominate those from PCA events.

It is possible that important direct catalytic destruction of O_3 can result from the chemical reactions of positive or negative ions, in spite of their low densities (less than 10^4 cm^{-3} at the altitudes of interest). Thus in the conventional O_3-destroying reactions involving oxygen species only (*3*) or NO_x, the rates for destruction of O_3 by O or NO are of the order of only 10^{-14} cm^3/sec; reaction rates with ions are typically 10^3 to 10^4 times faster. [In addition, the production of NO from N_2O depends on the presence of the extremely rare, short-lived $O(^1D)$ state.] But most important at polar