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FIELD-FLOW FRACTIONATION: POTENTIAL ROLE IN THE ANALYSIS OF ENERGY RELATED MATERIALS

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ABSTRACT

The general principles and scope of field-flow fractionation (FFF) are presented with descriptions of individual FFF subtechniques and the macromolecular, colloidal, and fine particle systems to which they have been applied. Several specific examples of energy-related materials are presented for which FFF is expected to yield important analytical information.

INTRODUCTION

The production and management of energy is a pervasive subject involving many areas of science and technology. Not surprisingly, the materials used and impacted by energy conversion are enormously varied. These materials include varied forms of fuels, many types of environmental contaminants produced in the fuel cycle, and diverse materials used in the acquisition, processing, and consumption of fuels.

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Optimal energy use requires that energy-related materials be characterized in every important respect. One of the major factors influencing the properties of materials is the underlying state of aggregation and the distribution of aggregate size. The correlation between aggregate size and chemical composition is also important. The state of aggregation influences volatility, fluidity, phase separation, pollution control strategies, combustion efficiency, and a host of important chemical and mechanical properties. As an extreme example, the extended state of aggregation of the hydrogen and its isotopes composing the sun is responsible for the sun acting as a fusion reactor whereas single hydrogen molecules are aggregates of matter too small to undergo spontaneous fusion.

The size of energy-related aggregates ranges from that of simple hydrogen molecules up to macroscopic (and even solar) objects. On the broad scale of aggregation, the two extremes are easiest to characterize: simple molecules like hydrogen and low molecular weight hydrocarbons are easily analyzed by chromatography and other analytical methods while macroscopic objects can be characterized by mechanical tests and visual observations. Intermediate levels of aggregation provide the greatest difficulties. The separation and analysis of molecules and other aggregates in the effective molecular weight range from 10^3 to 10^{15} provide the greatest difficulty and challenge. This molecular weight span corresponds roughly to particle diameters between 10^{-3} and 10 μm. This range includes macromolecules, colloids, and fine particles. These aggregates have a profound impact in many areas of energy technology (see Figure 1 and References (1-33)).

Field-Flow fractionation (FFF) is a relatively new tool capable of separating and characterizing molecules and related aggregates over the entire effective molecular weight range of 10^3-10^{15} and beyond. It provides a high resolution capability for aggregates of matter that are normally difficult to characterize. As a separation method, FFF can provide fractions of material that are generally homogeneous with respect to size,

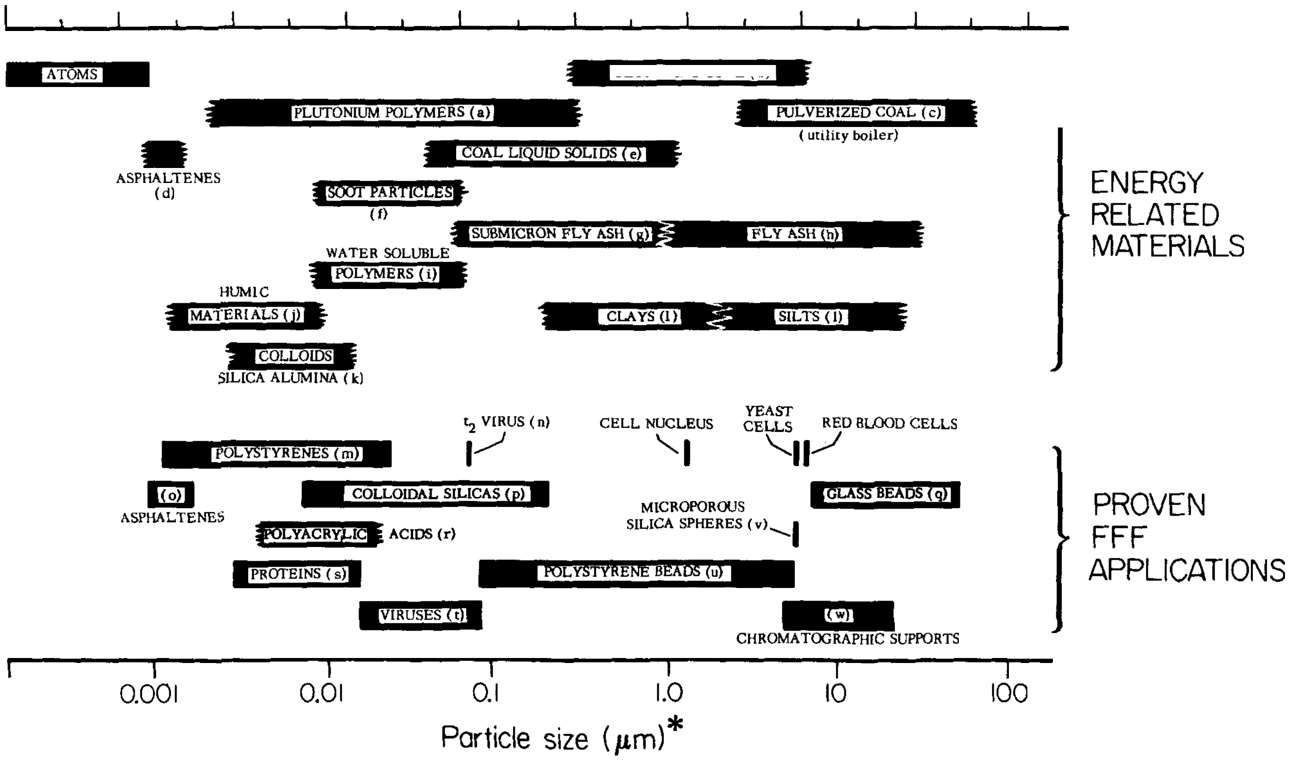

FIGURE 1. Range of aggregate sizes for materials related to energy production and energy impacted environments. a = reference 1, b = 2, c = 3, d = 4, e = 5, f = 6, g = 7, h = 8, i = 9, j = 10, k = 11, l = 12, m = 13-19, n = 20, o = 16, p = 21, q = 22, r = 23, s = 25-27, t = 32, u = 24,27-31, v = 24, w = 33. *Assuming density = 1.5 gm/ml.

mass, or charge. These fractions can be subjected to additional tests to determine composition and other important properties. Furthermore, even without collected fractions, FFF systems can provide aspects of characterization simply through the observations of the spectrum of elution times. FFF therefore promises to have considerable impact in the characterization of energy-related materials.

In the following section we will discuss the principles, applicability, and advantages of FFF. The subsequent section of the paper will be devoted to a discussion of several important areas of energy technology where FFF is expected to have relevance.

NATURE AND SCOPE OF FFF

General Principles of FFF

Field-flow fractionation requires that molecules or particles confined in a narrow channel be subjected to an externally applied force which induces a mean velocity U toward a wall of the channel. At the same time the particles diffuse against the buildup of a concentrated layer near the wall at a rate determined by the diffusion coefficient, D. These two transport processes combine to give a cloud of particles of mean layer thickness ℓ (34,35)

$$\ell = D/U \tag{1}$$

in which the particles are distributed exponentially above the wall

$$c = c_o \exp(-x/\ell) \tag{2}$$

where c and c_o are the solute concentrations at altitude x and at the wall (x = 0), respectively.

When flow is initiated along the axis of the channel the particles are carried along at a rate dependent on the mean layer thickness ℓ because ℓ determines the distance of penetration of the particle cloud into the higher velocity flows away from the channel wall (See Figure 2). This differential displacement by flow is the basis of selective migration (separation) by virtue of the fact that ℓ has a characteristic value for each kind or size of particle or molecule.

We describe the dimensionless parameter λ by (36)

$$\lambda = \ell/w = D/wU = RT/Fw \qquad (3)$$

where R is the gas constant, T is the absolute temperature, and F is the field-induced force per mole. Values of λ less than 0.1 give reasonably good retention (shallow layers). The degree of retention is given by the retention ratio, R, equal to the displacement velocity of the particle cloud relative to the mean flow velocity of carrier (34,35).

$$R = 6\lambda\left[\coth(1/2\lambda) - 2\lambda\right] \qquad (4)$$

When the retention volume V_r is greater than ~ 2 void volumes V^o, which is equivalent to $R < 0.5$, Equation (4) can be closely

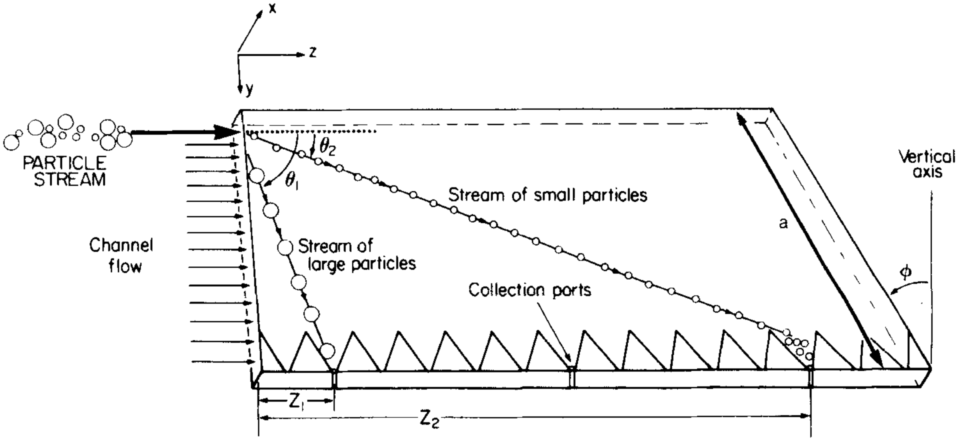

FIGURE 2. Schematic diagram of an FFF channel. Edge view of channel shows parabolic flow profile and mean layer thickness ℓ of two particle clouds.

approximated by the limiting form

$$R = 6\lambda = V^o/V_r \qquad (5)$$

The magnitude of λ, which controls retention characteristics through Equations (4) and (5), depends on the strength of the force F applied to the particles. However, both the potential magnitude of the force and its selectivity depend on the type of force or field used to induce lateral migration and consequent layer formation. The use of various fields therefore leads to distinct subtechniques of FFF differing significantly from one another in selectivity, range of applicability, and even in the method of constructing the FFF channel systems. The subtechniques complement one another nicely in applicability, thus providing a highly versatile and broad-based stable of FFF methods. We will briefly review the various subtechniques in the following text.

Sedimentation FFF

A gravitational or centrifugal force can be applied perpendicular to the flow axis by fitting the channel to the inside of a centrifuge basket. This subtechnique is called sedimentation FFF. Particles are eluted in the order of increasing effective mass (real mass minus buoyant mass). The retention parameter is given by various specific forms which differ only in the choice of principal parameters (28,37,38).

$$\lambda_s = D/sGw = RT/GM(1 - \bar{v}_s\rho)w = 6kT/\pi d^3 Gw\Delta\rho \qquad (6)$$

where M is the molecular weight, $\bar{v}_s$ is the partial specific volume, k is the Boltzmann constant, ρ is the solvent density, d is the diameter of an equivalent sphere, Δρ is the difference between particle and solvent density, and s is the sedimentation coefficient. The acceleration G is given by

$$G = \omega^2 r \qquad (7)$$

where ω is the angular velocity and r is the radius of curvature. In that λ is inversely proportional to molecular weight M as shown by Equation (6), retention volume becomes directly proportional to M by virtue of Equation (5).

Flow FFF

In flow FFF the channel is sandwiched between parallel plates consisting of rigid semipermeable membranes. A cross flow directed perpendicular to (and superimposed on) the main channel flow can then be generated by forcing a stream of the carrier through the membrane faces and across the channel. Particles or molecules are fractionated according to their diffusion coefficients or friction coefficients. The retention parameter is given by (21,27)

$$\lambda_F = DV^o/\dot{V}_c w^2 = RTV^o/3\pi\eta N\dot{V}_c w^2 d \qquad (8)$$

where $\dot{V}_c$ is the volumetric cross flow rate, η is the viscosity of the solvent, and N is Avogadro's number. Retention volume is linearly related to the Stokes diameter d for retained components.

Thermal FFF

In thermal FFF the flow channel is a ribbon-like space layered between two metal plates that are maintained at two different temperatures. Fractionation occurs on the basis of differences in thermal diffusion occurring in response to the thermal gradient dT/dx. The basic retention parameter λ is then given by

$$\lambda_T = D/D_T w(dT/dx) = T\alpha w(dT/dx) \qquad (9)$$

where α is the dimensionless thermal diffusion factor (15)

$$\alpha = D_T T/D \qquad (10)$$

and D_T is the thermal diffusion coefficient. For dilute polymer solutions, D varies approximately as $M^{-\frac{1}{2}}$, so retention volume V_r is roughly proportional to the square root of molecular weight.

Electrical FFF

In electrical FFF the channel is formed between semipermeable membranes which are separated by a spacer. The channel is placed between the electrodes of an electrolysis chamber. Particles are fractionated on the basis of their electrical charge. The retention parameter is given by (39)

$$\lambda_E = D/\mu E w \tag{11}$$

where μ is the electrophoretic mobility and E is the electrical field strength.

Steric FFF

Steric FFF is not a subtechnique of FFF produced by yet another kind of field, but rather it is a limiting form of normal FFF realized under well-defined conditions with any of the applicable fields. The principal condition is that the field-particle interactions must be sufficiently strong that the characteristic mean layer thickness ℓ is smaller than the particle radius a (d/2). When this condition is satisfied, the average distance of penetration of the solute particle into the velocity stream of the channel is more a function of the particle size than it is of the rate of diffusion and of the exact magnitude of field-particle coupling. Thus, elution depends mainly on particle diameter and the normal elution order becomes reversed, i.e., large particles elute ahead of small particles. An approximate equation more general than Equation (5) for the retention ratio R which takes the steric effect into account is (40)

$$R = 6\gamma d/2w + 6\ell/w \tag{12}$$

where γ is a factor (<1) accounting for decreased particle velocity due to rotational energy dissipation. When the steric effect predominates, the second term in Equation (12)--which is equivalent to Equation (5)--can be ignored, so that R is directly proportional to the particle diameter (40,41).

A special case of steric FFF is represented by the continuous steric FFF apparatus, which utilizes a wide tilted channel with a collection system along one side (24). The distance Z the particles travel before deposition is given by

$$Z = 54\eta \langle v \rangle a\gamma / 980 dw \Delta\rho \cos\phi \qquad (13)$$

where a is the channel breadth, <v> is the mean channel flow velocity, and ϕ is the angle of tilt of the channel (see Figure 3).

Advantages and Applications of FFF

FFF has been called one-phase chromatography (42). The absence of a stationary phase and attendant packing is advantageous in several respects. There is less adsorption than with packed columns which expose solute to a large surface area. Also, the dynamics of flow are much simpler, leading to behavior that can be theoretically correlated and predicted.

FFF is complementary to more conventional separation

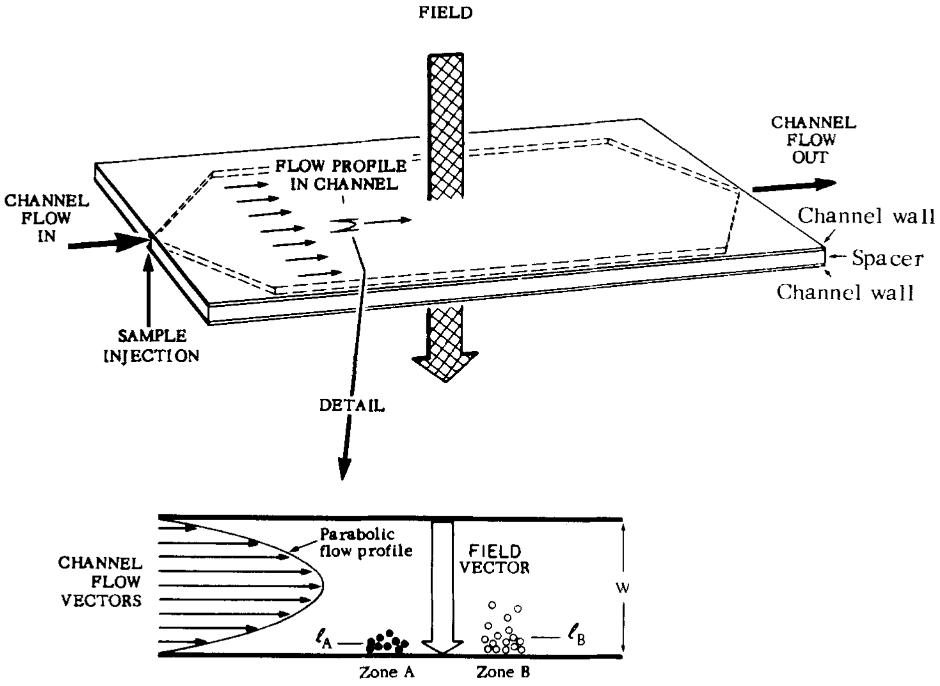

FIGURE 3. Diagram of a continuous steric FFF device which uses a field of one gravity to separate particles.

techniques because it performs well for molecular weights or particle sizes that are too large for techniques such as gas and liquid (including exclusion) chromatography and extraction and for particles that are smaller than those that can be fractionated by cascade impaction. It has the advantage of physically separating the particles according to size or other parameters unlike non-fractionating techniques such as light scattering, electronic counting or microscopy which are often used to measure size distributions of fine particles. Standard liquid chromatography detectors (for example, refractive index, infrared, or ultraviolet absorption) can be used with FFF. These detectors are nondestructive so that the fractions can be collected and examined by other techniques (such as electron microscopy or spectroscopy) if information other than that derivable from retention data is required.

The conditions of FFF are extremely gentle. Even in thermal FFF where the solvent at the hot wall may be near the boiling point, the solute normally layers at the cold wall away from danger. FFF is therefore applicable to materials of a sensistive nature such as biological fractions and cells.

Since the force causing retention in FFF is externally applied, programming can be employed to extend the useful range of particle size fractionation in a convenient time frame. Field programming has been used in a variety of FFF subtechniques (14,17,29,43). Other programming techniques such as flow programming (31) and gradient elution (29) have been employed.

Sedimentation FFF can be used to fractionate materials that have a density different from that of the solvent. The lower size limit of particles that can be retained is determined by the maximum rotation rate of the centrifuge. Fields of 10^3 gravities are obtainable which extend the useable range down to molecular weights of 10^7 or particles 0.02 to 0.03 μm in diameter. Systems with higher rotation speeds are under development. Upper limits on particle size (normally about 1 μm) are determined by the onset of steric effects. Equation (12) can be used to predict the steric transition (40).

Sedimentation FFF has been demonstrated in the high resolution fractionation of submicron polystyrene beads (28-31) as shown in Figure 4 and in the molecular weight determination of the T2 virus (20). More recent work has been done involving characterization of the gypsy moth nuclear polyhedrosis virus, characterization of emulsions to follow rates of degradation, and characterization of submicron PVC particles used in coatings. Although aqueous systems

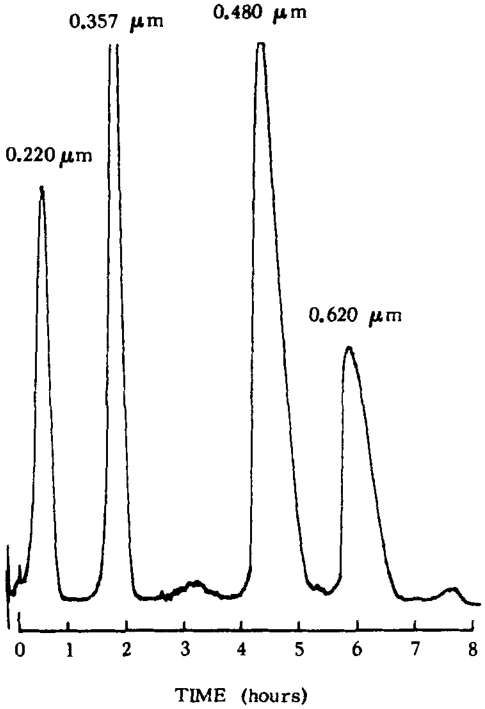

FIGURE 4. Fractionation of four samples of Dow polystyrene latex beads by sedimentation FFF. Flow rate = 12 ml/hr, channel thickness $w = 0.0127$ cm and void volume $V^{o} = 2.0$ ml and field strength was 193.7 gravities.

have been studied most frequently, we have used sedimentation FFF with organic solvents as well.

Flow FFF is theoretically the most universal of all FFF techniques. It has been used to fractionate a variety of materials that are soluble or dispersible in aqueous solutions or buffers. Organic solvents are presently avoided because of the properties of of the membranes available, but there is no fundamental reason to exclude such solvents. The lower limit of molecular weight is determined by the pore size of the membrane material and the tolerable pressure drop. The onset of steric effects at high cross flow rates or gravitational interferences determine the upper particle size limits of the system. Materials in the molecular weight range of 10^4 and 10^{10} have been fractionated including proteins (26,27), polystyrene latex beads (27), Qβ, P22, f2, ϕx174 viruses (32), colloidal silica and paint pigments (21), and the water soluble polymers sulfonated polystyrene and polyacrylic acid (23). Flow FFF has thus proven to be one of the most versatile of the FFF subtechniques. The flow FFF channel can also be used as a dialysis cell (44).

Thermal FFF can be used to fractionate any material that exhibits strong thermal diffusion effects. Molecular weights from 10^3 to 10^7 can be fractionated, all in a single run with the aid of programming (17). The lower molecular weight limit is determined by the maximum temperature drop, which is often limited by boiling at the hot wall and solidification at the cold wall. By using pressurized systems to raise the boiling point, it is possible to extend the lower molecular weight limit to 600 (16). Thermal FFF has been shown applicable to polystyrenes in a variety of solvents (13-15,18,19), asphaltenes, crude oil and asphalt (16), Blue Dextran in DMSO-water (15), polyisoprene, polytetrahydrofuran, and polymethylmethacrylate in ethyl acetate and THF (19). Although thermal FFF does not work well for aqueous solutions (15), it is complemented by flow FFF which performs well in such cases.

Electrical FFF can be used to advantage where the solutes are charged. It is subject to some of the same limitations as flow FFF because the channel is formed between semipermeable membranes in both cases. This subtechnique has been used to fractionate proteins (25).

Steric FFF is expected to be applicable to particles in the 1-100 μm diameter range (22). The technique is relatively fast (5-30 minutes). Separations have been demonstrated using primarily the force of gravity on glass beads in the 10 to 30 μm range (22), 3 to 20 μm spherical and irregularly shaped chromatographic supports (33), 5 to 14 μm silica beads (45), red blood cells, and yeast cells. If the magnitude of the field strength is adjusted to higher values (as by centrifugation) the technique is expected to be applicable to a wider range of materials at increased speed (45). In the continuous mode, steric FFF has semipreparative as well as analytical applications. The continuous system has been used in the fractionation of silica beads (24).

FFF AND ENERGY RELATED MATERIALS

The capability of FFF to fractionate macromolecules, colloidal dispersions and particles suggests a number of important applications in the characterization of energy-related materials. The applications proposed below constitute only a sampling of potential uses, intended to illustrate the interface between FFF and materials of energy relevance.

Coal Liquids

Economic factors and shortages have resulted in recent interest in the production of substitutes for petroleum. Conversion of coal to petroleum-like liquids can be accomplished by solvent refining where the coal is reduced from a high molecular weight insoluble form through a series of pyridine soluble then benzene soluble (asphaltene) and finally pentane soluble (oil and resin) fractions (46). The structure of coal itself is complex and varies according to source and its geological history.

The nature of the initial product of the conversion process is not well known. Data on molecular weight distribution would be valuable in determining the effectiveness of process parameters, catalysts, solvents, etc. The benzene soluble fraction has been studied (4,47) and although the asphaltenes are of low enough molecular weight to be candidates for gel permeation chromatography, they tend to adsorb on the gel to such an extent that adsorption is the basis of a method for the separation of aliphatic and aromatic chemical classes on Sephadex LH-20 (48). Asphaltenes have been retained by thermal FFF in our laboratory (36,43).

Colloidal particles are formed in the liquefaction processes, but the conditions leading to their formation are unknown (49). Particles can consist of unchanged mineral solids from the coal, asphaltene micelles, and graphite-like particles from undissolved coal or char. Solids removal can present a serious technological problem since most of these aggregates are in the submicron size range and tend to be difficult to filter (5). The characterization of particulates in coal liquids is an area where FFF could contribute vital information leading to improved processing.

Ultrafine Coal Production

The use of coal in an ultrafine state (less than 1 μm particles) has several advantages. The mineral inclusions can be removed when coal is in the finely divided state to provide control of pollutants normally resulting from ash and pyrite components. Also, this form of fuel has a large surface area which results in high reactivity in coal conversion processes (2).

Sizing submicron particles is an area where sedimentation and flow FFF have been successfully applied. Another possibility for characterizing the fine powders or evaluating the effects of beneficiation is the use of solvent density programming (29) in sedimentation FFF since the ash constituents have a density of approximately 3 gm/cm^3 and the coal itself has a density in the range 1.2 to 1.4 gm/cm^4 (50).

There is evidence that fly ash resulting from combustion of coal has a bimodal distribution (7). The large fraction has been found to consist of particles in the 1 to 10 μm size range for which the concentration of volatile trace elements is inversely related to particle size (51) and in the submicron range where concentrations are independent of particle size (52). This would seem to indicate that there exist at least two separate mechanisms of fly ash formation (53).

Air Particulate Characterization

Fossil fuel (particularly coal) combustion results in the introduction of particulate matter to the atmosphere. Combustion particles have been recognized as sources of reduced visibility, acid rain, health damage, and perturbations of the earth's climate. Fly ash has been found to concentrate toxic volatile trace elements in a particular size range (51) that includes the respirable fraction. Carbon or soot particles from power production, automobile exhaust, or refining constitute a form of particulate matter that is in the submicron range. Sulfuric acid can condense on the carbon nuclei with detrimental effects to the respiratory system when the particles are inhaled (54,55).

Submicron particles are difficult to characterize (often the collected sample must be examined by electron microscopy and individual particles measured) and extremely difficult to fractionate by methods other than FFF. Particles ≥ 1 μm in diameter could also be better characterized by improved methodology. Since the particle size governs the site of deposition in the respiratory system and persistance in the atmosphere, particle size distributions are of great importance.

Water Soluble Polymers in Petroleum Recovery Applications

Ultrahigh molecular weight water soluble polymers have been suggested as compounds capable of enhancing the recovery of petroleum from underground formations (9,56). Determination of molecular weight distribution in these materials would provide a capability for following the degradation processes of the polymers during use and in subsequent displacements where the polymers could possibly spill into aquifers used as municipal and industrial water sources. Water soluble polymers are also used as an agent to increase the viscosity of drilling fluids used in oil exploration. Two polymers, polyvinylacetate-malic anhydride copolymer and zanthate gum, have been found to be toxic to rainbow trout (57) in the 400-600 mg/l range. The possibility of determining which polymers will biodegrade most quickly under field conditions (by following the molecular weight distribution) would ensure proper choices for the least biological impact and the greatest effectiveness in the oil recovery.

Engine Oil Additives

One approach to conserving energy has been to reduce fuel consumption of automobiles by improving engine efficiency. The introduction of 10 to 15% by weight of colloidal size lubricating particles (e.g., MoS_2 or graphite) to engine oil has been shown to reduce fuel consumption by 2% (58). These additives appear to reduce engine friction and are most effective for urban-style driving, light loads and low speeds. FFF methods which give size distribution of the colloidal particles should be useful in product development and testing, quality control, degradation studies, shelf life, and the introduction of particles of metal generated by wear in the lubricating system. More recently polytetrafluoroethylene colloids have also been tested for effectiveness in reducing friction. Particle size and uniformity were found to have significant effects on performance (59).

Nuclear Waste Disposal

The use of nuclear energy to supplement the energy extracted from fossil fuels has become embroiled in controversy. One of the major areas of conflict concerns the disposal of radioactive wastes. There is evidence that migration of actinides from disposal sites may take place when they become associated with small soil particles (60) or colloidal silicate hydrolysis products (61). Conventional sieving or sedimentation separations are difficult to perform on small (submicron) soil components. The ability of FFF to size small particles and provide fractionated samples for further characterization is expected to contribute greatly to the understanding of the seriousness of this problem.

Other Potential FFF Applications

Other energy-related applications of FFF can be suggested. For example, FFF might aid emulsion characterization for the water-fuel emulsions proposed as alternative fuels for diesel engines and turbines as well as for emulsions encountered in the processes of oil recovery from shale and tar sands and in petroleum refining. Particle characterization beyond that already detailed could be important in studies of solid fuels undergoing transportation as slurries and in sizing catalyst particles. In general, gains in particle and polymer characterization can be expected to lead to improvements in materials being developed for fuel processing equipment, solar collectors, lighter weight vehicles, better insulation, and many others.

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REFERENCES

1. J. M. Cleveland, The Chemistry of Plutonium, Gordon and Breach, New York, 1970, p. 88.

2. J. A. Herbst, personal communication.

3. L. D. Smoot, Pulverized Coal Combustion and Gasification, Plenum Press, New York, 1979, p. 131.

4. B. C. Bockrath, K. T. Schroeder, and F. W. Steffgen, Anal. Chem., 51, 1168 (1979).

5. D. E. Briggs, et al., ERDA Report NSF-AER-7515213, September 1977.

6. L. D. Smoot, Pulverized Coal Combustion and Gasification, Plenum Press, New York, 1979, p. 184.

7. J. M. Ondov, R. Ragaini, A. H. Bierman, Environ. Sci. Technol., 13, 946 (1979).

8. H. J. White, J. Air Poll. Control Assoc., 27, 15 (1977).

9. E. F. Herbech, H. C. Heintz, and J. R. Hasting, Petroleum Engineer, July 1976, p. 48.

10. W. Flaig, H. Beutelspacher, and E. Reitz, Soil Components, Vol. 1, Organic Components, (J. E. Gieseking, ed.,) Springer-Verlag, New York, 1975, p. 164.

11. M. Fieldes and G. G. C. Claridge, Soil Components, Vol. 2, Inorganic Components, (J. E. Gieseking, ed.), Springer-Verlag, New York, 1975, p. 352.

12. Handbook of Chemistry and Physics, 52nd Ed. (E. C. Weast, ed.), Chemical Rubber Co., Cleveland, 1971-72, p. F-218.

13. G. H. Thompson, M. N. Myers, and J. C. Giddings, Sep. Sci., 2, 797 (1967).

14. G. H. Thompson, M. N. Myers, and J. C. Giddings, Anal. Chem., 41, 1219 (1969).

15. M. N. Myers, K. D. Caldwell, and J. C. Giddings, Sep. Sci., 9, 47 (1974).

16. J. C. Giddings, L. K. Smith, and M. N. Myers, Anal. Chem., 47, 2389 (1975).

17. J. C. Giddings, L. K. Smith, and M. N. Myers, Anal. Chem., 48, 1587 (1976).

18. J. C. Giddings, M. Martin, and M. N. Myers, J. Polymer Sci., (submitted).

19. J. C. Giddings, M. N. Myers, and J. Janca, J. Chromatogr., (submitted).

20. J. C. Giddings, F. J. F. Yang, and M. N. Myers, Sep. Sci., 10,133 (1975).

21. J. C. Giddings, G. C. Lin, and M. N. Myers, J, Colloid 65, 67 (1978).

22. J, C. Giddings and M. N. Myers, Sep. Sci. Technol., 13, 637 (1978).

23. J. C. Giddings, G. C. Lin, and M. N. Myers, J. Liq. Chromatogr., 1, 1 (1978).

24. M. N. Myers and J. C. Giddings, Powder Technology, 23, 15 (1979).

25. K. D. Caldwell, L. F. Kesner, M. N. Myers, and J. C. Giddings, Science, 176, 296 (1972).

26. J. C. Giddings, F. J. Yang, and M. N. Myers, Science, 193, 1244 (1976).

27. J. C. Giddings, F. J. Yang, and M. N. Myers, Anal. Chem., 48, 1126 (1976).

28. J. C. Giddings, F. J. F. Yang, and M. N. Myers, Anal. Chem., 46, 1917 (1974).

29. F. J. F. Yang, M. N. Myers, and J. C. Giddings, Anal. Chem., 46, 1924 (1974).

30. F. J. Yang, M. N. Myers, and J. C. Giddings, J. Colloid Interfac. Sci., 60, 574 (1977).

31. J. C. Giddings, K. D. Caldwell, J. F. Moellmer, T. H. Dickinson, M. N. Myers, and M. Martin, Anal. Chem., 51, 30 (1979).

32. J. C. Giddings, F. J. Yang, and M. N. Myers, J. Virol., 21, 131 (1977).

33. J. C. Giddings, M. N. Myers, K. D. Caldwell, and J. W. Pav, J. Chromatogr., (accepted).

34. J. C. Giddings, J. Chem. Ed., 50, 667 (1973).

35. E. Grushka, K. D. Caldwell, M. N. Myers, and J. C. Giddings, Separation and Purification Methods, Vol. 2, (E. J. Perry, C. J. Van Oss, and E. Grushka, eds.), Dekker, New York, 1974, p. 127.

36. J. C. Giddings, S. R. Fisher, and M. N. Myers, American Laboratory, 10, 15 (1978).

37. J. C. Giddings, M. N. Myers, and J. F. Moellmer, J. Chromatogr., 149, 501 (1978).

38. J. C. Giddings, M. N. Myers, F. J. F. Yang, and L. K. Smith, Colloid and Interface Science, Vol. IV, (M. Kerker, ed.), Academic Press, New York, 1976.

39. L. F. Kesner, K. D. Caldwell, M. N. Myers, and J. C. Giddings, Anal. Chem., 48, 1834 (1976).

40. J. C. Giddings, Sep. Sci. Technol., 13, 241 (1978).

41. J. C. Giddings and M. N. Myers, Sep. Sci. Technol., 13, 637 (1978).

42. J. C. Giddings, J. Chromatogr., 125, 3 (1976).

43. J. C. Giddings, M. N. Myers, G. C. Lin, and M. Martin, J. Chromatogr., 142, 23 (1977).

44. J. C. Giddings, F. J. Yang, and M. N. Myers, Sep. Sci., 12, 499 (1977).

45. K. D. Caldwell, T. T. Nguyen, M. N. Myers, and J. C. Giddings, Sep. Sci. Technol., 14, 935 (1979).

46. H. W. Sternberg, Scientific Problems of Coal Utilization, (B. Cooper, ed.), DOE Symposium Series No. 46 (1978) p. 46.

47. F. W. Steffgren, K. T. Schroeder and B. C. Bockrath, Anal. Chem., 51, 1164 (1979).

48. B. R. Clark, C. H. Ho, and A. R. Jones, Analytical Chemistry of Liquid Fuel Sources, Adv. in Chemistry Series, 170, 1978, p. 288.

49. D. M. Bodily, L. Anderson, R. Pugmire, University of Utah Fuels Engineering Dept., personal communication.

50. A. Davis, Scientific Problems of Coal Utilization, (B. R. Cooper, ed.), DOE Symposium Series 46, 1978, p. 17.

51. D. F. S. Natusch, J. R. Wallace, C. A. Evans, Jr., Science, 183, 202 (1974).

52. R. D. Smith, J. A. Campbell, K. K. Nielson, Environ, Sci. Technol., 13, 553 (1979).

53. P. C. Malti and D. P. Rees, Pulverized-Coal Combustion and Gasification, (L. D. Smoot and D. T. Pratt, eds.), Plenum press, New York, 1979, p. 198.

54. J. D. Fenters, J. N. Bradof, C. Aranyi, K. Ketels, R. Ehrlich, and D. E. Gardner, Environmental Research, 19, 244 (1979).

55. L. Schiff, M. M. Byrne, and J. D. Fenters, Environmental Research, 19, 339 (1979).

56. W. B. Gogarty and W. C. Tosch, J. Petroleum Technol., December 1968, p. 1407.

57. J. B. Sprague and W. J. Logan, Environ. Pollut., 19, 269 (1979).

58. J. E. Bennington, D. E. Cole, P. F. Ghirla, R. K. Smith, SAE Report No. 750677, (1975).

59. F. G. Reick, American Laboratory, March 1978, p. 57.

60. J. C. Sheppard, M. J. Campbell, J. A. Kittrick, and T. L. Hardt, Env. Sci. Technol., 13, 680 (1979).

61. L. L. Ames, Report 1974, BNWL-1812, p. 66.