MINI SYMPOSIUM

COAL SLURRY FUELS

COAL SLURRY FUELS
FORWARD

In this age of high technology and incresing demand for fuel, the need
for a substitute energy source for oil is great; thus there is a renew-
ed interest in the abundant coal resources. The economic and political
implications of this development are very important because the coal
reserves can supply the energy requirements for a much longer period
than oil.

It is being demonstrated that coal slurry fuels are an oil substitute
when combusted for the generation of steam in both industrial and util-
ity boilers for the generation of electricity. The production of coal
slurries requires mining, cleaning, grinding and mixing operations.
The fundamentals of surface chemistry are also necessary. This
emerging technology requires the participation of mining and processing
engineers, professions that through their membership, constitute the
SME. The organization of these sessions in the AIME annual meeting and
the preparation of this collection of papers address these topics.

Coal slurry fluids are made up of mixtures of coal and oil or of coal
and water. The coal oil mixtures contain approximately 50% coal ground
to around 80% -200 mesh and the coal water ones around 70% coal ground
to 80% -200 mesh or finer. In both mixtures minor quantities - less
than % of chemical additives are used as surfactants to enhance coal
wetability and stability of the suspension.

During the manufacturing process of the coal slurry fuels, the coal is
finely ground. This operation liberates a large part of the ash allow-
ing a cleaning operation which could be - or not be - integrated to the
coal washery. This fine cleaning operation does not carry the cost of
grinding, thus it is economical.

The coal mining and cleaning technologies were as advanced as any other
technology at the end of the 1920's when coal was used as the main
source of energy. The discovery of oil, its abundances, low cost, ease
of utliization and minimum content of pollutants initiated a
substitution of oil for coal, a substitution which discouraged new
developments in mining or washing technology. Today's oil market
condition has reversed that trend and the substitution of coal for oil
is necessary. The coal technology, which did not progress as rapidly
as that of other branches of engineering, is adopting the advances made
in other areas and as a result very rapid progress is being achieved.
The manufacturing of coal slurry fuels is also adopting the technol-
ogies developed elsewhere. For instance, the grinding technology of
the paint industry and the mixing technology of the plastics industry
are used by some producers of coal slurry fuels.

The coal slurry manufacturers, some with demonstration units in production, and the consumers, the major utility companies, expect to complete the demonstration of their technology in the next two years. Our participation in this new industry is essential. We could be opening new markets for coal and reducing the consumption of very limited oil reserves, thus freeing its use for situations when it can not yet be substituted.

Luis Pommier

Occidental Research Corporation
2100 S.E. Main Street
Irvine, California 92714

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Donald Adams, Island Creek Coal Company, Lexington, KY
Luis W. Pommier, Occidental Research Corporation, Irvine, CA

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H.W. Evans, Old Ben Coal Company, Chicago, IL
George Meisel, El Cerrito, CA

Characterization of Coal/Water Dispersions

E.Z. Casassa

G.D. Parfitt

A. Rao

E.W. Toor

Department of Chemical Engineering
Carnegie-Mellon University
Pittsburgh, Pennsylvania

The coal slurry manufacturers, some with demonstration units in production, and the consumers, the major utility companies, expect to complete the demonstration of their technology in the next two years. Our participation in this new industry is essential. We could be opening new markets for coal and reducing the consumption of very limited oil reserves, thus freeing its use for situations which it can not yet be substituted.

Introduction

There has been a recent revival of interest in concentrated coal/water slurries as a substitute for fuel oil or for coal/oil mixtures, particularly in electric power generation. The idea is not a new one. Coal/water slurries were transported by pipeline in the U.S. in the early nineteen-sixties, and the Black Mesa coal pipeline has been in operation for several years, while in Germany, coal/water slurries were being burnt for power generation in the early nineteen-seventies, as described by Merten and Höner (1972).

Since coal is not a pure substance but a carbonaceous mixture, the different chemical and physical behavior of coal/water dispersions from different deposits must be understood in order to optimize the properties of the resulting slurry fuels. Since minerals which are minor constituents of coal may also strongly affect slurry properties, coal chemistry may vary considerably even within a single deposit. Thus it is unlikely that there will be a single formula for optimizing the slurry properties of all coals, and even the answer for coal from a single source may change with time.

For pipeline transportation a slurry is needed that will flow relatively easily and which will not settle out and plug the pipeline either during pumping or during a hiatus in pumping. The fluid should be neither corrosive nor abrasive and should not be affected by temperature changes. For storage a material is needed which will not settle on standing or which can be kept in suspension or resuspended with minimal stirring. The fluid should be unaffected by temperature changes and storage times up to several months. At the point of combustion, the slurry should flow through an atomizer nozzle, possibly at very high velocity. Coal particles must be small to allow for complete combustion, and must not abrade or corrode the atomizer. Other desired attributes are high heating value, low ash and low air pollution. The maximum possible coal concentration is required both for economic reasons and because water is scarce in some areas where coal is abundant.

Some of these requirements are contradictory. Thus, at the maximum possible coal concentration there may be no settling but high viscosity makes pumping difficult. Reducing particle size to minimize abrasion may also decrease the amount of solid which can be loaded into the slurry, as well as make grinding costs prohibitive. The objective is to balance the conflicting requirements. For a given coal and water supply the factors which can be manipulated are the particle size distribution and the surface chemistry of the slurry, and through these, the particle-particle and particle-fluid interactions which are the basis of all slurry behavior. To optimize slurry properties, then, it is necessary to know how the surface chemistry of a particular coal and the distribution of particle sizes contribute to the rheological and sedimentation behavior in aqueous dispersions.

Although some information on the behavior of coal/water dispersions can be found in the literature, most of it quite recent, there is as yet insufficient understanding to allow prediction of the behavior of a particular coal. Indeed the behavior of concentrated dispersions in general is not fully understood. Some concentrated dispersion systems have been extensively studied, such as clays, printing inks and pigments for paints, and also coal/oil dispersions. A general outline of the types of behavior to be expected can be drawn from these studies, but the detailed effects of the surface chemistry must still be investigated for each solid/liquid combination. It may be relatively simple by an empirical approach to optimize the properties of a particular coal/water dispersion without a full understanding of the underlying surface chemistry. However, knowledge of the surface chemistry is required to predict how other coals will behave, or even how that same coal will behave under other conditions. We are characterizing four bituminous coals at present, in the hope of clarifying to some extent the effects of surface chemistry on the behavior of concentrated coal/water dispersions. With additional information on other coals from other laboratories, it may become possible to predict the behavior of dispersions of any coal after a very limited characterization. We are here trying to present an overview of the characterization methods which can be used to build up knowledge of coal/water surface chemistry. It is an oversimplified view, of necessity, and we have indicated sources of more complete information.

Packing of Particles in Suspension

The size distribution and shape of the solid particles set an upper limit to the volume of solid which can be packed into a given volume of any fluid, be it gaseous or liquid. For rigid uniform spheres, the closest array possible is hexagonal close packing with 74% of the volume filled by spheres, while the loosest regular packing is the simple cubic, with 52% of the volume filled by spheres. Uniform spheres randomly packed might thus be expected to fill between 52 and 74% of the total volume initially, and with time, compacting under their own weight or aided by vibration, would tend toward the upper limit. The void space between uniform spheres can be partially filled with additional spheres of smaller diameter, and for a bimodal distribution there will be a particular size ratio which most effectively fills the voids between the larger spheres and gives the most compact packing. Pursuing the idea that the most efficient packing of spheres occurs for a very broad particle size distribution, Hudson (1949) showed that 96% of the volume could be filled by successively adding smaller and smaller sized spheres to fill the void volume remaining after each addition.

Unfortunately, such very flat broad distributions do not normally result from grinding. Instead distributions are found which are narrower with a peak at some intermediate size. Both Yamamura et al. (1982) and Papachristodoulou et al. (1982) have demonstrated that broader particle size distributions pack with greater efficiency in coal slurries, and Funk (1981) has shown that coal having a very flat particle size distribution

can be used to make slurries which contain up to 80% by weight of coal, while the product of ordinary grinding limits slurries to about 60 to 70% by weight of coal. Only by combining materials ground with differing severity or by adding sieved fractions of high and low size can such broad distributions be achieved permitting high solid loadings. Such restrictive tailoring of particle size distributions may not be worth the cost. Observing the effects of different grinding procedures and times on particle size distribution might be of use however in selecting conditions for achieving an optimum distribution.

Maximum loadings of 60 to 70% by weight, well below the densest theoretical packing in terms of volume per cent for even single-sized spheres, are in part due to particles which are not spheres. Although cubes or plates or rods can be packed with less void space than spheres if they are correctly oriented toward each other, when they are packed randomly there is likely to be more void space than for spheres. Even under compaction and vibration they are less likely to fall into an optimum configuration (although they may be oriented by flow). Compact chunky particles which are roughly spherical are likely to pack more efficiently than particles which are far from spherical shape. Another possible reason that maximum theoretical loadings are not obtained is that particles may contain cracks or pores and thus have some internal void space. Particle agglomeration can also increase void space. As we shall see when we consider the effects of increased particle loading on slurry rheology, a slurry at the maximum possible loading from the geometric viewpoint would not be useful in any case.

Fowkes and Fritz (1974) have reviewed the packing of solid particles and Irani and Callis (1963) and Herdan (1953) treat the statistics of particle size distributions.

The Effects of Particle Concentration on Rheology

In dilute suspensions the dependence of the viscosity, η, upon concentration, expressed as the volume fraction, ϕ, can be described by the Einstein equation:

$$\eta = \eta_o (1 + 2.5 \phi) \qquad (1)$$

where η_o is the viscosity of the fluid. The major assumptions in deriving this relationship are that the particles are rigid spheres at a concentration so low that they do not interact. For many materials this relationship holds true up to a volume fraction of about 0.1. Beyond that however, the measured viscosity becomes progressively larger than the Einstein equation predicts, as shown schematically in Figure 1. Introducing higher order terms in ϕ to account for particle-particle interactions permits fitting of the observed curves up to higher concentrations. The Einstein equation, which says nothing about particle size, only particle concentration, and which is applicable to polydisperse materials, fits those of our coal dispersions which we have observed at low concentrations.

Deviations from the Einstein equation may occur even at low concentrations if for some reason the volume fraction of the particles in suspension is larger than supposed. This can occur if the particles hold immobilized an appreciable layer of the liquid. This effect would be larger for smaller particles which have more surface area for a given volume fraction. An increase in effective volume fraction could also occur if the particles form aggregates trapping some of the fluid and carrying it with them.

At higher concentrations not only does the observed viscosity deviate from the Einstein equation but the rheology becomes non-Newtonian, i.e. the viscosity becomes dependent upon the rate of shear. At volume fractions above about 0.3 suspensions frequently show pseudoplastic (shear-thinning) behavior as shown schematically in Figure 2. If particles are deformable or non-spherical, orientation in the flow field under shearing might account for shear-thinning. Another possibility is that at higher concentrations particles are to some extent aggregated, giving viscosities at lower shear rates which diminish at higher shear as the aggregates are broken down.

The onset of pseudoplastic behavior is often accompanied by a yield stress, which also implies the existence of some sort of structure throughout the suspension that must be at least partially broken down before flow can commence. We have observed the development of pseudoplasticity with a yield stress in coal/water dispersions at a volume fraction of .30-.35. It is perhaps not surprising that a randomly packed polydisperse collection of non-spherical particles should begin to develop some sort of structure at that concentration, and that both breaking up of the structure and some alignment of particles along the flow direction could occur at higher shear rates. Both of these explanations of shear-thinning behavior imply that at some still higher shear rate all structure will have been broken down and all possible orientation will have occurred so that the slurry will again become Newtonian.

At still higher volume fractions, dilatant (shear-thickening) behavior may be seen. When particles are so numerous that close-packing is approached, particles in adjacent layers cannot move past each other without moving out of close-packed positions. This can only occur by an expansion of the particle packing and consequent sucking of the liquid medium out of some part of the dispersion, causing a volumetric dilatancy which usually is seen at about the same concentration as that at which shear-thickening occurs in a given dispersion. Accordingly it has been suggested by Metzner and Whitlock (1958) that shear thickening occurs at concentrations where void space is sufficient to allow a portion of the particles to move past each other. At low shear rates, a particle can move past particles in an adjacent layer, then fall into a close-packed position, allowing other particles to time-share the available void space. At higher shear rates, where there is insufficient time for this accommodation to occur, flow can only take place by the movement of two-dimensional groups or whole layers of particles past adjacent layers, thus increasing

viscosity at higher shear rates, as the flow mechanism changes. This cannot be the whole story however, for Klimpel (1982) has reported that a bituminous coal/water dispersion showed shear-thickening at 57% by weight solids, and shear-thinning at 68 or 72% by weight, a phenomenon which has also been reported for other systems in the past. Such behavior is difficult to account for by the above explanation of rheological dilatancy, though Klimpel's work indicates the effect is much more marked in narrow size distributions and is therefore probably somehow related to packing efficiency. Most coal/water dispersions have been reported to show shear-thinning, but it is possible that a dilatancy in a narrow concentration range could have been missed in other coals. We have observed dilatant behavior only near the maximum slurry concentrations we have achieved.

Another complication can arise. Shear-thinning at a given shear-rate may increase with time, a phenomenon known as thixotropy, which occurs when the breaking-down of agglomeration achievable at that shear rate does not occur instantaneously, but requires a finite time. This leads to hysteresis in shear stress-shear rate curves, which we have observed in coal/water dispersions.

A more complete discussion of rheology is given in many sources. Among them are Frederickson (1964) and Astarita and Marrucci (1974) who discuss theory, while Van Wazer et al. (1963) describe experimental measurements. Whorlow (1980) describes instrumentation. Frankel and Acrivos (1967) derived an expression for the viscosity of concentrated suspensions of solid spheres which takes into account the maximum packing of the suspension. Farris (1968) considered the effects of particle size distribution on viscosity from the theoretical viewpoint, and Chong et al. (1971) have proposed an empirical relationship taking into account the effects of particle size distribution on the maximum packing. Govier and Aziz (1977) consider concentrated slurries from the viewpoint of pipeline transportation, and Cheng (1980) reviews the rheology of dispersions. Although a variety of equations have been proposed to describe non-Newtonian behavior, that most frequently employed for coal/water dispersions is the power law equation:

$$\tau - \tau_o = K S^n \qquad (2)$$

where τ is the shear stress, τ_o the yield stress, S the shear-rate, K is known as the consistency and n as the flow index. For shear-thinning, n < 1; for Newtonian behavior, n=1; and for shear-thickening n > 1. This is also known as the Ostwald-deWaele Law when τ_o=0 or as the Herschel-Bulkley Law when τ_o is non-zero.

From this overview, it can be concluded that particle size should not affect viscosity (provided the particles are small compared to viscometer dimensions) unless solvation increases the effective volume of fine particles relatively more than that of larger particles. The breadth of particle size distribution can affect the viscosity of concentrated dispersions since at any given volume fraction, a narrow distribution is more nearly close-packed than a broader distribution and should therefore have a higher viscosity, a phenomenon we have observed in coal/water dispersions. If solvation affects fine particles, the decrease in viscosity expected for a broad particle size distribution may not be attained. Orientation under flow of asymmetric particles can cause shear-thinning. The effects of particle aggregation on viscosity are an aspect of surface chemistry which will be considered below. So far as particle packing is concerned, it is clear that whether or not dilatancy occurs, viscosity becomes very high at the highest possible solids concentration in a dispersion. From the viewpoint of rheology a somewhat lower concentration, in the shear-thinning region, is desirable for coal/water dispersions.

The Effects of Particle Concentration on Sedimentation

A single particle of diameter D, falling through a fluid under gravity, will rapidly reach the Stokes velocity, V_s, defined as:

$$V_s = \frac{g(\rho_s - \rho_f) D^2}{18 \eta_o} \qquad (3)$$

where g is the acceleration under gravity, ρ_s is the density of the solid particle, ρ_f is the fluid density and η_o is the fluid viscosity, provided that the particle diameter is not so large that the particle Reynolds number exceeds about 0.1 or, at the other extreme, so small that Brownian motion opposes sedimentation. For coal and water at 25°C this range of D is about 1 to 100 um, or roughly the particle size range of interest for coal/water dispersions.

In a sedimenting suspension of identical monodisperse particles, all fall at the same rate producing a sharp demarcation line between sedimenting particles and supernatant liquid. As the concentration of monodisperse particles becomes larger there is an additonal buoyancy effect introduced by the upward flow of water displaced by the falling particles. The resulting terminal velocity is less than V_s, a condition known as hindered settling. If the particles are not monodisperse, the larger particles fall faster than small ones and there is a gradual clearing of the supernatant in the hindered settling region, with a settled layer visible at the bottom of the column, growing upwards with time. Only at higher concentrations in a polydisperse suspension is there a sharp demarcation line between settling particles and supernatant, when particles are close enough together that larger ones are trapped by smaller ones and cannot fall past them. This is known as mass subsidence. There can be an intermediate range where most particles fall in mass subsidence, but the smallest ones are left behind to settle more slowly, causing both a sharp falling boundary and a gradual clearing of supernatant. The rate of fall of the sharp demarcation line in the mass subsidence region

can be used as a measure of sedimentation veloc-
ity. As particle concentration is increased the
sedimentation rate decreases, since it becomes
more and more difficult for water to move
upward through the falling particles to make
room for settled particles at the bottom. Some
slow further compaction of the settled slurry
under its own weight then occurs. The effects
of concentration on sedimentation rate are
shown in Figure 3. Frequently in intermediate
concentrations in the mass subsidence range the
rate is very slow initially, and then increases
to a steady maximum value before tapering off
during compaction, a phenomenon which may be
caused by the formation of channels for the
upward movement of water.

The concentration of particles in the set-
tled layer is a measure of the maximum packing
density which can be achieved for undisturbed
slurries. A slurry initially at this concentra-
tion will not settle at all, undisturbed. Such
settled layers have fairly large yield stresses
and viscosities of about 1000 centipoise, but
are easily resuspended. Under vibration, how-
ever, further compaction of a sediment to a
concentration several percent higher in solids
produces a layer which has a much higher yield
value and is very difficult to resuspend.

A number of relationships have been proposed
for concentration and sedimentation rate. For
spherical particles Steinour (1944) derived the
relationship:

$$Q = V_s \epsilon^2 \phi(\epsilon) \qquad (4)$$

where Q is the rate of fall of the sharp
interface and ϵ is the volume fraction not
occupied by the solids, that is, the void frac-
tion or porosity of the suspension. $\phi(\epsilon)$ is
a function of particle diameter and becomes
unity at infinite dilution. He found empiri-
cally that $\phi(\epsilon) = 10^{-1.82(1-\epsilon)}$ fits data for
a number of materials over a wide range of
solid concentrations, and that for polydisperse
materials an average particle diameter could be
calculated. To allow for non-sphericity of par-
ticles, the hydraulic radius of the particles
is introduced in place of the radius in Stokes
equation for V_s and the sedimentation equation
then becomes:

$$Q = V_s \frac{\epsilon^3}{(1-\epsilon)} \theta(\epsilon) \qquad (5)$$

where $\theta(\epsilon)$ is called a shape factor. Steinour
found empirically that data for a number of
suspensions could be fitted for $0.3 < \epsilon <
0.7$ with $\theta(\epsilon) = 0.123$. To allow for the
larger effective volume fraction or smaller
effective porosity when a layer of liquid is
immobilized on the particle surfaces Eq. (5)
can be modified:

$$Q = \frac{V_s (\epsilon - W_i)^3}{(1-w_i)^2 (1-\epsilon)} \theta(\epsilon) \qquad (6)$$

where W_i is the ratio of the volume of immobile
liquid to the total volume of solid, and must

be determined empirically. Equation (4) can be
modified similarly.

Another widely used correlation was derived
by Maude and Whitmore (1958):

$$Q = V_s \epsilon^m \qquad (7)$$

where m is a constant depending upon particle
shape and upon particle Reynolds number. For
spheres in laminar flow m has been found to be
about 4.65. A number of other authors had found
empirically that such a relationship fitted
experimental data, including Richardson and
Zaki (1954) by whose names the equation is also
known. Maude and Whitmore point out that the
relationship is not valid at high particle con-
centrations, and neither this nor the various
Steinour equations allow for the fact that at
some concentration the sedimentation rate
becomes zero when the maximum packing density
has been reached. Moreland (1963) found the
Maude and Whitmore relationship satisfactory
for fitting coal/oil dispersion sedimentation
data for particle sizes between 80 and 2000
μm and porosities of 0.6 to 1.0, with values of
m between 6.5 and 7.5. We have found that
neither Eq. (5) nor Eq. (7) will fit our sedi-
mentation data for coal/water dispersions over
the whole mass subsidence range, though either
one will fit data over part of the concentra-
tion range. Values of m of between 10 and 13 were
found for the Maude and Whitmore equation.

We have found the expected effect of median
particle size on sedimentation, that is, for
smaller median particle diameter and therefore
smaller average V_s, the sedimentation rate at a
given volume fraction is lower. We have not
studied the effects of particle size distribu-
tion width upon sedimentation rate but have
observed that for broader distributions, the
final settled height is smaller than for nar-
rower distributions at the same volume
fraction, a consequence no doubt of greater
packing efficiency in the broader distribution.

One effect of particle aggregation is to
increase median size in the suspension, and
therefore sedimentation rate. However if aggre-
gation is extensive, fluid may be trapped
within the aggregates, thus increasing the
effective volume fraction of solid and decreas-
ing the sedimentation rate. Michael and Bolger
(1962) derived equations relating sedimentation
rate and final settled volume to aggregate size
in flocculated kaolin suspensions. Slagle et
al. (1978) have used these equations to analyze
sedimentation data for coal/oil slurries.

There are few reviews of sedimentation in
concentrated dispersions in which a more com-
plete discussion can be found. T. Allen (1975)
has a short description of the subject, while
Bhatty et al. (1982) discuss the interpretation
of sedimentation data using equations (4) to
(7). Fitch (1979) reviews sedimentation as
related to continuous thickening processes for
clarification. The relation between batch sedi-
mentation used for dispersion characterization
and continuous sedimentation processes is of
interest in slurry preparation or dewatering.

As described above, there is a dispersion
concentration above which no sedimentation will
occur. This concentration is not the maximum

possible packing density, since vibration produces further compaction. Even at the lowest concentration which is stable to sedimentation the dispersion viscosity is higher than desirable. If a somewhat lower solids concentration is used to obtain lower viscosity some phase separation will occur. In a storage tank, it is possible to prevent this by stirring, but if flow is interrupted in a pipeline, resuspension may be difficult. By changing the surface chemistry it may be possible to introduce a degree of network structure or aggregation which prevents sedimentation at this lower concentration. If the structure or aggregation breaks down easily under flow and reforms almost instantaneously when flow stops, the requirements of both sedimentation stability and rheology would be compatible, and the dispersion might also be less vulnerable to compaction by vibration. The study of the surface chemistry of the dispersion is essential to achieving such ends.

Surface Chemistry of Aqueous Coal Dispersions

The behavior of dilute dispersions of charged colloidal particles can be considered in light of the Deryaguin, Landau, Verwey and Overbeek (DLVO) theory of colloid stability described by Verwey and Overbeek (1948). Particles experience a van der Waals attraction toward each other which can be expressed as a negative potential energy diminishing with distance between the particles, as shown in curve 1 in Figure 4. The electrostatic charge on the particle surfaces, however, gives rise to a repulsive potential energy, as shown in curve 2. This also decays toward zero as the separation between particles increases, but usually somewhat more rapidly than the attractive potential. The stability of a dispersion depends upon the relative magnitudes of these two potential energies, and curve 3 shows schematically the result of combining the two curves. At small separation there occurs what is called the primary minimum, while at greater separation there may be a secondary minimum, separated from the primary minimum by an energy barrier. If the energy barrier is small or non-existent, as when the repulsive energy is small compared to the attractive one, the net force of attraction pulls the particles together into the primary minimum, and they are flocculated, or act as a single unit. If, however, the energy barrier is high, particles are prevented from flocculating in the primary minimum. Depending upon the depth of the secondary minimum, particles may or may not flocculate in it, but even if they do, the aggregates are less tightly held together and more easily broken apart.

The attractive potential energy, which depends on the chemical nature of the solid particles, is relatively insensitive to electrolytes in the liquid. However, the repulsive potential energy can be greatly altered by electrolytes. First, increasing either the concentration or the charge of the ions in solution reduces the distance over which the repulsive potential decays. This has the effect of lowering the potential energy barrier to flocculation in the primary minimum. Coals

often contain soluble inorganic electrolytes as contaminating minerals, which can act in this way. Second, some "potential determining" ions may be adsorbed at the particle surface, thus changing the repulsive potential. Surfaces with acid-base character, for example, may develop a positive charge at low pH owing to adsorbed hydrogen ions. At high pH, such surfaces may become negatively charged through loss of hydrogen ions to the solution. In between there exists a point of zero charge. The repulsive potential will be high at low or high pH, thus increasing the energy barrier, but will go through a minimum near the point of zero charge where the particles will be very vulnerable to flocculation in the primary minimum. Coals contain acidic groups and do show this type of behavior. If the surface chemistry of coal/water dispersions can be controlled to achieve a high barrier to primary flocculation but also weak flocculation in a secondary minimum, the desired balance of sedimentation and rheological requirements might be achieved.

It should be noted that the upper limit of the colloidal particle size range is usually considered to be about 1 μm and most coal particles are larger than that. The same stability principles apply to larger particles, although with increasing particle size the lower ratio of surface area to volume means that surface effects become less important. A larger proportion of colloidal size particles in powdered coal might make it easier to apply surface chemistry to achieve the desired properties; it could, however, also make the slurry more vulnerable to unwanted flocculation in a primary minimum. Alternatively it may be possible to use a colloidal additive which will form a weak network structure, even at low concentrations, and prevent sedimentation of the coal powder in that way. For example, Sparks and Sawyer (1982) have reported such stabilization of coal/water dispersions by the use of small amounts of clay.

Hydrophobicity is another important aspect of surface chemistry. Many coals, particularly higher rank ones, are so hydrophobic that water will not spread on the coal surface. Although the powder can be mechanically mixed into a slurry, many of the particles, especially smaller ones with high surface areas, may stick together rather than become fully dispersed. The particle size distribution in the slurry will then be less broad than expected and the packing efficiency lower. A wetting agent can counteract this tendency. Surfactants used for this purpose may adsorb on the surface and make it more hydrophilic in addition to promoting wetting by lowering the surface tension of the water.

It is thus possible that for optimal performance a coal/water dispersion will require the addition of a wetting agent, a stabilizing agent, and a chemical to adjust the pH. In the choice of these agents it is necessary to consider also their effects on corrosion and on ash formation and air pollution at the point of combustion. The surface chemistry of each coal must be studied to determine what additives would be helpful and how much of each to use.

Many sources are available for a detailed treatment of the surface chemistry of colloidal dispersions. Among them are "Principles of Col-

loid and "Surface Chemistry" by Hiemenz (1977),
"Physical Chemistry of Surfaces" by Adamson
(1982), a review of the "Characterization of
Aqueous Colloids" by James and Parks (1982),
and "Dispersion of Powders in Liquids", edited
by Parfitt (1981).

Characterization Methods for Coal Powders

a) <u>Particle Size Distribution</u>: Coal powders
for coal/water dispersions are typically pre-
pared to be 100% less than 100 mesh (150 μm)
and 70 to 90% less than 200 mesh (75 μm).
The smallest particles present in any signifi-
cant weight are likely to be about 1 to 5 μm.
A number of methods of analysis are available
for this size range, most of them described in
detail in "Particle Size Measurement" by Allen
(1975). Sieve analyses of particle size distri-
bution are particularly useful since various
size fractions are separated for subsequent mea-
surement of other properties which may vary
with size, such as density, wettability, or
surface area. Although sieves with openings
down to 5 μm are available, below about 40
μm special sieving equipment is required. Siev-
ing may yield an underestimate of the finer
particles which may stick to larger particles
or to the undersides of sieves, and may be lost
as dust during repeated handling. Such losses
may be reduced by using an air jet or oscillat-
ing air column to combat sieve blinding, or by
wet sieving of particles well dispersed in a
liquid.

Microscopy, either optical or electron, is a
sizing method which reveals particle shape as
well. Sizing particles under the microscope or
in photographs is a tedious operation which
commercial optical instruments perform electron-
ically. Careful preparation of fully dispersed
samples is necessary since the instruments can-
not distinguish between individual particles
and aggregates.

Particle size distributions may also be
determined from the rate of sedimentation of a
very dilute suspension. If the change in concen-
tration with time can be measured at some point
near the bottom of the sedimentation column,
the particle size distribution can then be
determined using the Stokes relation, equation
(3). The change in concentration can be fol-
lowed by removing small samples for gravimetric
analysis, by measuring specific gravity with
hydrometers, or by observing the attenuation of
a beam of visible light or x-rays on passage
through the suspension. Alternatively the
weight of material settling onto a balance pan
at the bottom of the column can be recorded as
a function of time. Sedimentation may be
carried out under gravity or centrifugation.
The effective diameter during sedimentation
refers to a plane normal to the sedimentation
direction, so highly asymmetric particles will
have effective sizes in settling which differ
from those obtained by other methods.

Another type of sizing instrument is the
electronic particle counter. Particles in
dilute suspension in an electrolyte flow
through a small aperture between two elec-
trodes. The change in resistance as a particle
passes through the aperture is proportional to
the particle volume. The results are expressed

as diameters of spheres of equivalent volume,
so here too particles deviating markedly from
sphericity can appear to have particle size
distributions different from those found by
other methods. The method is rapid, but the
range of particle sizes which can be handled is
about 20 to 1, so that more than one measure-
ment may be required to cover the 1 to 150
μm particle size range which may occur in pow-
dered coals for coal/water dispersions. Other
instruments measure the light scattered from
individual particles in a very dilute suspen-
sion in a gas or liquid, tabulating such data
to build up a particle size distribution, a
method which can be very rapid.

Most methods for obtaining particle size dis-
tributions in the range above 1 μm are un-
usable for smaller particles. Electron
microscopy, however, can be used over a wider
range, and can give an estimate of the number
of sub-micron particles present. Otherwise it
is usually necessary to separate sub-micron par-
ticles from the larger particles by filtration
and then to resort to methods of sizing such as
centrifugation, light scattering or hydrody-
namic chromatography to obtain information on
the distribution of sub-micron particles. What-
ever the method used for obtaining particle
size distributions, it is advisable to compare
the result from at least one other method and
to resolve any discrepancies which may be found.

b) <u>Wettability</u>: Effective dispersion of pow-
dered coal in water requires that water or
slurry supernatant spread on the coal surface,
i.e. wet it, a phenomenon of importance also in
froth flotation, dewatering, or dust
suppresion. One method of quantifying the wet-
ting of a solid by a liquid is to measure with
a goniometer the contact angle of a drop of the
liquid placed on a smooth clean solid surface,
as in the work on coal by Bailey and Gray
(1958). With a natural material like coal, the
contact angle may vary from place to place on
the surface owing to chemical heterogeneity,
some of which is native and some the con-
sequence of oxidative attack. Surface roughness
or cracks can affect the contact angle, but
polishing the surface should be approached with
caution as it may result in contamination of
the surface. For all these reasons, obtaining
reproducible results which can be related to
the behavior of powdered material can be very
difficult. A more representative value of the
contact angle may be obtained upon a compressed
powder sample instead of a solid lump. Kossen
and Heertjes (1964) and Carino and Mollet
(1975) discuss this method, which has been
applied to coals by Murata (1981). Preparing
such compacted powders reproducibly may also be
very difficult.

Washburn (1921) and Bartell (1942) developed
a method for determining contact angles of pow-
ders by infusion or capillary rise. The powder
is packed in a tube with a porous barrier at
the bottom. When the tube is placed in the test
liquid the rate of rise through the powder is
measured. This method has the drawbacks that
powders with different particle size distribu-
tions will not pack in the same way, wet or
dry, and that the liquid may dissolve material
as it rises, so that the liquid may change from

sample to sample or from point to point in a single sample.

Another method, which has been applied to powdered coals by Vargha-Butler et al. (1981), is the observation under a microscope of the engulfment or rejection of single particles of a powder by the solidification front of a molten organic compound. If the critical velocity of the solidification front required for engulfment of a particle is measured, it is possible then to calculate contact angles for the particle in other liquids. The method was devised by Omenyi et al. (1976, 1980, 1981a, 1981b) and can be used in a simplified form to qualitatively rank the wettability of different coals or of different particle sizes of one coal.

A qualitative method of comparing the wettability of different coal powders, developed by Walker et al. (1952), has been used by Papic and McIntyre (1973) and by Glanville and Wightman (1979) to compare the effectiveness of different surface active agents in wetting coal dust. In this test a series of solutions of increasing concentrations of a surfactant are employed. A known weight of the powder is dropped gently into a mound on the surface of a standard volume of each solution. The time required for all the powder to pass through the surface is then measured and the wetting rate in mg/sec is plotted versus surfactant concentration. Placing the powder on the liquid surface in the same way each time requires practice. Leaching of soluble contaminants which could affect wetting does occur, but the effect is minimized by using a small amount of powder in a large volume of solution. We have found that ranking different coals by this method agrees qualitatively with results of contact angle measurements on lump coal or on compacted powders. Glanville and Haley (1982) have found that this method and the infusion method show poor correlation. Papic and McIntyre (1973) found no significant difference in wetting rates for different coals when they were dried to the same moisture content, but found a strong dependence of wetting time on moisture content. Both they and Glanville and Haley (1982) found that wetting time was inversely dependent upon particle size. The Walker test furnishes a useful comparison of the ease of wetting of different coal powders used for dispersions, even if the effects observed are only the consequence of moisture content and particle size distribution. It is also a useful method for comparing the effectiveness of different dispersing agents. Glanville and Wightman (1979) have employed a variant of this method using a series of alcohol-water mixtures of known surface tensions to find the critical surface tension for wetting of a coal powder, that is, the liquid-vapor surface tension above which the powder remains on top of the liquid surface indefinitely.

c) Density: In rheological and sedimentation rate equations the solids concentration is expressed as the volume fraction; hence the density of the coal powder is required for conversion of the measured weight fraction. The density of the solid also appears in the Stokes relationship which is used to determine particle size distribution from sedimentation. The density of the powder immersed in water can be measured by standard methods. However, coals can be quite hydrophobic, and gas bubbles may be trapped between incompletely wetted particles or in pores. Subjecting the sample to reduced pressure or to ultrasonic vibration may free at least a part of the trapped gas. A more reliable figure for the true density of the solid is given by the helium density measured with the dry powder. Since dissolution of denser minerals may decrease the density of the coal, and lowering the surface tension of the liquid may increase the apparent powder density because of better dispersion and increased wetting of pores, and because both of these effects may depend upon the particle size distribution of the powder, it appears that only by measurement under carefully standardized conditions can the effective density of the solid in a particular dispersion be determined.

d) Other Methods of Powder Surface Characterization: A number of methods exist for the chemical analysis of the surface layers of solids, such as Auger electron spectroscopy (AES) or electron spectroscopy for chemical analysis (ESCA). Elemental analyses of particle surfaces can reveal what ash components are there, and whether the distribution of these materials changes with particle size. The advantages and disadvantages of a variety of techniques are discussed in "Methods of Surface Analysis," edited by Czanderna (1975), and "Chemistry and Physics of Solid Surfaces" edited by Vanselow and Tong (1977) devotes several chapters to surface analysis. All such methods have the disadvantage that the sample must be evacuated, with possible accompanying disruption of the original surface. With some of the more sophisticated instruments, data gathering and interpretation requires highly trained operators who are often understandably reluctant to introduce a "dirty" material like coal into their instruments for fear of permanent contamination by powder or by volatile components.

The measurement of powder surface area by gas adsorption, another characterization technique which might be employed, is discussed in many sources including the textbooks by Adamson (1982) and by Hiemenz (1977), while Fuller (1981) discusses its application to coals. The usual method of pre-treatment of the sample by evacuation to remove moisture, however, may change the surface considerably. Surface area measurements can be used to give information on changes in the porosity of the material with particle size.

Although these methods may not be absolutely required for the characterization of coal/water dispersions, they may be of value when the slurry characterization methods described next are insufficient to explain observed dispersion behavior.

Dispersion Characterization Methods

a) Chemical Analysis: Analysis of the fluid separated from a coal/water dispersion will reveal the presence in the coal of contaminating

minerals which are soluble in the fluid. An elemental analysis of the coal ash can suggest which inorganic ions are likely to be present. If appreciable amounts of dissolved inorganic materials are found, it may be desirable to compare dispersions made from the original material with one made from the powder after washing to remove soluble contaminants. In this way the effects of the soluble minerals on dispersion stability can be gauged. Variations in the content of inorganic ions in the water supply should also be noted.

b) Measurement of Zeta Potential: As described above, the combined effects of attractive and repulsive potentials govern the behavior of suspended particles. The repulsive potential may vary with the concentration of hydrogen ion and other electrolytes in solution, an effect which is most readily observed by measuring the zeta potential, ζ. When a charged particle moves through a liquid in an electric field, an immobilized liquid layer at its surface is transported with it. The rate at which the particle with associated liquid layer moves in a given field depends upon the ζ potential defined as the potential at the surface of shear. This potential is not the same as ψ_o, the repulsive potential at the particle surface, but is the potential at some small, and unknown, distance from the particle surface. By measuring the rate v at which a particle moves through the medium under a known applied electric field E, the electrophoretic mobility $u=v/E$, can be determined for the particle. The sign of the charge on the particle is revealed by the direction in which it moves. For spherical particles with size greater than 1 μm and electrolyte concentration greater than $\sim 10^{-3}$ M, the ζ potential is related to the electrophoretic mobility by the Helmholtz-Smoluchowski equation:

$$u = \frac{\epsilon \zeta}{4 \pi \eta} \qquad (8)$$

where ϵ is the dielectric constant of the medium and η the viscosity of the medium. This relationship should apply to coal particles in the 1-150 μm range. For colloidal particles there is a more complex relationship between electrophoretic mobility and ζ potential. Either electrophoretic mobility as measured, or ζ potential calculated from it may be used to infer changes in ψ_o, the repulsive potential. A detailed discussion of electrophoresis is given in Chapter 11 of the book by Hiemenz (1977), or in "Zeta Potential in Colloid Science" by Hunter (1981).

Both simple and elaborate commercial instruments are available for measuring electrophoretic mobility of particles in dilute suspension. At least one instrument is also available for measuring gravimetrically the mass transfer occurring in concentrated slurries subjected to an electric field, from which an average mobility can be determined, though the interpretation of this average value may be difficult.

When the electrophoretic mobility of particles is measured at different pH values, regions of high positive or negative charge can

be found, where repulsive forces make the particles most stable toward flocculation. Also found may be points of zero charge where they are most vulnerable to flocculation in a primary minimum. Several coals we have observed show the same general pattern as that in the solid line in Figure 5, which suggests the presence of two types of ionizing groups on the coal surface, possibly carboxylic acid and phenolic groups. When the electrophoretic mobility is measured in slurry supernatant, the mobility-pH curve can be modified by the adsorption of dissolved contaminants onto the coal surface, to something like the dashed line in Figure 5. Slurry supernatant probably better represents the electrolyte environment of the particles in a concentrated dispersion.

c) The Effects of Inorganic Electrolytes: Some of the same information can be obtained without measuring electrophoretic mobility, by making use of the fact that as ionic strength is increased repulsive potential decays toward zero over a shorter distance from the particle surface, lowering the energy barrier toward flocculation. The higher the valence of the ions of charge opposite to that of the particles, the more effective is the flocculation. This effect of added electrolyte on dilute colloidal suspensions has been known empirically for many years, and is called the Schulze-Hardy rule. In dilute colloidal suspensions, flocculation can be observed by the settling out of the suspension. However, in coal/water dispersions where the sedimentation rate in dilute suspension is in any case high because of the larger particle size, it is easier to observe the effects of added electrolyte at higher concentrations where sedimentation rates are lower. At these concentrations, weak flocculation can then increase sedimentation rate, perhaps as particles form doublets or triplets. If flocculation is extensive, however, and larger groupings are formed, part of the fluid is trapped, making the effective volume fraction of the solid larger, which has the opposite effect of decreasing the sedimentation rate. Figure 6 shows the effects on sedimentation rate at different pH's of adding the same concentration of 1-1, 2-1, and 3-1 electrolytes to suspensions of Pittsburgh Seam #8 coal. The decrease in sedimentation rate in the presence of La^{+3} ions becomes very marked at about the pH at which microelectrophoresis measurements in the same coal in slurry supernatant, shown in Figure 5, indicate that the charge on the particles changed from positive to negative. On the other hand, in the presence of K^{+1} ions, there is an increase in sedimentation rates at the same pH, indicating only very mild flocculation, and an intermediate effect for Mg^{+2} ions, where increased flocculation size and increased volume fraction are roughly balanced.

Thus it is possible to discover the pH range in which the particles have a high surface charge, and the approximate location of a point of zero charge, by observing the effects of added electrolytes on sedimentation rate.

d) Sedimentation: In the mass subsidence region, it is possible to measure sedimentation rates and final settled heights for coal/water

dispersions, by visually observing the falling boundary between the dispersion and its supernatant liquid in a graduated cylinder. More elaborate means of following the falling boundary could be devised, but it is not clear that there would be much saving of time or effort, or increased precision, for the rates in the range of 0.1 to ~40 cm/hr which we have found for coal/water dispersions in the mass subsidence region. During the compaction stage of sedimentation, the settled height in the column slowly decreases to its final value over a period which may vary from a few hours to about a week in the coal/water dispersions we have observed.

Measurements of sedimentation rate and final height as a function of solid concentration are useful to compare the effects of varying particle size distribution and average particle size. The sedimentation rate depends upon the average particle size, while the final height depends upon the distribution width and the consequent packing efficiency, as shown in Figure 7. When the rate versus concentration curve has been established for a given powder, the effects of pH and added electrolytes can be observed at a single solids concentration, as described in the previous section.

Column height and diameter can affect sedimentation rates. Comparisons of sedimentation rates under different conditions can be made in columns of a single size, but additional information on particle aggregation can be extracted from comparisons of sedimentation rates under one set of conditions in columns of different sizes, following the method of Michael and Bolger (1962). The additional effort may be well worthwhile as a final step for complete characterization of dispersions.

e) Rheology: Concentric cylinder viscometers are generally the most suitable type for use with dispersions which have some particles as large as 100–150 µm. The gap size in the viscometer should be at least ten times the diameter of the largest particle in the dispersion. It may also be necessary to use special ridged cylinders to prevent slip at the cylinder surface. Since concentrated dispersions exhibit non-Newtonian behavior, the viscometer chosen should allow observation of the shear stress-shear rate relationship over as wide a range as possible. It may be sufficient for practical purposes to study rheology only at high dispersion concentrations, but additional information can be extracted on degree of aggregation by observing deviations from the Einstein equation at lower concentrations. The viscosity over the entire concentration range may vary from 1 to about 10,000 centipoise, increasing rapidly at high volume fraction of coal, a factor to be considered in choosing a suitable viscometer.

Laboratory measurements have been compared to bench scale pipeline pressure drop tests for coal/oil dispersions by Al Taweel et al. (1982) with reasonable agreement found between the two. Cen et al. (1982) also found that the pressure drop predicted from laboratory rheological data on coal/oil and coal/water dispersions agreed with observed values in bench scale pipeline tests. Funk and Funk (1982) found that yield stress could be related to starting pressure drop while the apparent viscosity was related to the running pressure drop in a bench scale pipeline system. They also found that particle comminution could occur during pumping, changing the particle size distribution and flow properties. While it appears that laboratory viscometry can thus be extrapolated to pipeline flow conditions, it is probably not possible to predict behavior at the very high velocities and non-laminar flow which may be encountered in atomizer nozzles at the point of combustion.

f) Temperature Effects: For both sedimentation and rheology the range of possible ambient temperatures which might be encountered during transportation and storage is of interest. We have observed one coal between 8°C and 48°C and have found that the observed variation in both sedimentation rate and in rheological behavior is proportional to the variation in the viscosity of water over the same temperature range. Faddick (1974) found the same effect of temperature in flow behavior for coal/water slurries. However, since the dissolution of soluble material from the coal into the liquid or subsequent reactions of the dissolved material may be strongly temperature dependent, and the dissolved material may affect slurry properties, it cannot be assumed that the temperature variation in the viscosity of water will be the only effect on slurry behavior.

g) Time Effects: We have found that both sedimentation behavior and rheology may change with time. For the one coal we have so far observed over a period of time, about two weeks are required to reach equilibrium, an effect which is apparently related to the presence of soluble materials in the coal. The time dependence may be owing to slow dissolution of the soluble material, to slow chemical transformation of material once dissolved, or both. Iron, for instance, could be dissolved as the sulfite and then be oxidized and precipitated as a hydrous oxide, at a rate which depends upon temperature and pH. Such possibilities must be investigated, for should they prove important in a given coal, the dispersion emerging from a long pipeline may have rather different properties from that which went into it two weeks earlier.

Summary

Extensive characterization of the behavior of water dispersions of a particular coal, by means of all the methods we have described, provides the understanding needed to make an informed choice of additives for optimizing the properties of slurries of that coal, to foresee interactions of the additives, and to safeguard slurries against unexpected changes in conditions. When much more information on the behavior of a variety of coals in slurries has been published, it will become possible to predict the properties of coal/water dispersions on the basis of a more limited characterization of each coal.

Despite the proprietary aspects of current practice in slurry formulation, we venture to

hope that sufficient detailed information on the behavior of a wide variety of coals in water dispersion will become available to enlarge our knowledge not only of coal/water systems but of concentrated dispersions in general.

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