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FOSSIL ENERGY QUARTERLY REPORT

January 1, 1990 - March 31, 1990

D. Birlingmair, W. Buttermore, T. Chmielewski, and J. Pollard

**Ames Laboratory
Iowa State University
Ames, Iowa 50011-3020**

Date Transmitted: April, 1990

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Pittsburgh, Pennsylvania**

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Prepared for: Pittsburgh Energy Technology Center
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ABSTRACT

During the second quarter of work on this new project, critical review of the literature continued. Several new references related to gravity separation were identified and evaluated. A synopsis was assembled to summarize techniques developed by various researchers for the float/sink separation of ultrafine coal. In the reviewed literature, it was commonly concluded that substantial improvements in washability results for ultrafine coals can be obtained only through the application of dynamic (centrifugal) procedures, and through the use of dispersing aids such as ultrasound and surfactants. These results suggest the presence of physicochemical phenomena, typical of colloidal systems.

In theoretical studies this quarter, the effects of Brownian motion on fine particle sedimentation have been identified and theoretically quantitated. The interaction between Brownian and gravitational forces was calculated, and a model was prepared to permit estimation of critical particle size in float/sink separations.

In laboratory studies this quarter, aliquots of Upper Freeport coal were prepared and subjected to laboratory float/sink separations to investigate the relative effectiveness of static and centrifugal techniques for fine and ultrafine coal. This series will verify results of earlier work and provide a basis for comparing the effects which may result from further modifications to the separation techniques resulting from insights gained in the basic phenomena governing float/sink processes.

STUDY OF FINE AND ULTRAFINE PARTICLES FOR COAL CLEANING
D. Birlingmair, W. Buttermore, T. Chmielewski, and J. Pollard

OBJECTIVE

The primary objective of this research is to identify improved means for predicting the cleanability of fine and ultrafine coal. The study will investigate the phenomena which govern laboratory techniques used to separate coal ground to fine and ultrafine sizes for the determination of washability characteristics. This investigation seeks to identify and quantify factors other than gravity which affect separation, establish limitations of density-based separation, and develop techniques which will provide more accurate and consistent prediction of cleanability.

PROGRESS

LITERATURE REVIEW

During this quarter, several new references related to techniques of gravity separation were identified and reviewed. Also, a synopsis was assembled to summarize techniques developed by various researchers for the float/sink separation of ultrafine coal.

Synopsis of Sink/Float Techniques.

Theoretically, it is expected that yield/ash and yield/sulfur relationships should be improved (i.e., lower ash or sulfur contents at constant yield) in washability tests when coal is crushed to finer sizes, since mineral impurities are more completely liberated from combustible material. However, the observed results do not confirm those assumptions. According to experimental data presented by numerous authors, essential improvements in float/sink washability results are only possible by the application of dynamic, centrifugal procedures, as well as by solid phase pretreatment such as thermal drying or utilization of surfactants, to reduce interparticle attractive forces. The evident improvement in yield/ash and yield/sulfur relationships as a result of the pretreatment procedure is widely reported in the literature (1-13). A summary of techniques and experimental procedures for float/sink separations of fine and ultrafine coals is presented in Table 1. The reported results suggest the presence of physicochemical phenomena, typical in fine particle-particle interactions and resulting from forces specific to colloidal systems.

Table 1. Development of techniques for float/sink separations of fine and ultrafine coal.

AUTHOR AND APPLIED PARAMETERS	CONCLUSIONS
Porter, J.B. (1) Faugner, B. (2)	The acceleration of separation using centrifugal techniques when compared to static techniques was observed.
Hall, P.E. (3) 500 by 50 μm	No separation was observed by normal gravitational forces for particles below 50 μm .
Palowitch, E.R., and Nasiatka, T.M. (4) minus 1180 μm minus 75 μm 1500 rpm 20 min. centrifugation	<ol style="list-style-type: none"> 1. Static procedure cannot be used as a reference float/sink method for colloidal sized coal particles. 2. Particle size and amount of ultrafine coal are limiting parameters in centrifugal techniques. 3. Gravity separation of colloidal particles is not possible using static techniques.
Jones, R.K. and Smitham, J.B. (5) minus 53 and 16 μm solid/liquid = 4% 7000 rpm 30 min. centrifugation	Poorer yield/ash relationships for finer size fractions was observed.
Smit, F.J. and Bhasin, A.K. (6) solid/liquid = 8% 1550 - 1600 rpm 45 min. centrifugation	Better yield/ash relationships were observed for 1.4 than for 1.3 specific gravity. At 1.3 specific gravity, recovery tended to be lower and became less reproducible as the particle size decreases.
Hohman, D.G. (7) minus 1180, 150, 75, and 44 μm solid/liquid = 5% 1500 rpm 30 min. centrifugation	Increasing differences in yield/ash relationships were observed between static and centrifugal techniques as the top size of the coal decreased. The centrifugal technique appeared to be necessary to obtain washability curves for minus 150 μm or finer coal.
Simons, F.J., and Keller, D.V. Jr. (8) ultrafine size particles 1.3 specific gravity	The optimum separation was observed using the following parameters: 15 lb/ton Aerosol OT-100 (dispersing agent) 0.1 min. conditioning

AUTHOR AND APPLIED PARAMETERS	CONCLUSIONS
surfactant ultrasonic treatment moisture control solid/liquid = 5% 5000 rpm	2 min. ultrasonic treatment zero moisture content
Cavallaro, J.A., and Killmeyer, R.P. (9,10) minus 230, 150, 44, and 16 μm techniques. Poorer yield/ash results were solid/liquid = 5% Aerosol OT-100, 15 lb/ton zero moisture conditioning, 0.1 min. sonication, 120 s	The optimized procedure resulted in consistently better yield/ash relationships as the particle size decreased when compared to previous techniques. Poorer yield/ash results were observed for minus 15 μm particles, particularly at 1.3 specific gravity.
Dumm, T.F., and Hogg, R. (11) may require very long separation time (hours) minus 10 μm 2000 rpm for 1.3 specific gravity, 15 min. for 1.4 to 2.0 Aerosol OT-100, 2%	Micron sized particle of near-gravity material in a high speed centrifuge. Three hours required specific gravity.
Dumm, T.F., and Hogg, R. (12) for separation of very fine, near-gravity 90% minus 75 μm solid/liquid = 1% Aerosol OT-100, 2%	Centrifugation time of up to 20 h was required particles, particularly the 1.3 and 1.6 specific gravity fractions. Solid concentration should be below 1% to avoid aggregation.
Glesser D., and Hervol, J. (13) size fractions below 75 μm . Pretreatment of 1200 rpm for 20 min. 150 by 75 μm and minus 75 μm	Centrifugal techniques should be used for all slurry with sonication and non-aqueous dispersant was suggested.
Kalb, G.W., (14) minus 75 μm 3000 rpm for 20 min. surfactant sonication fines.	Under the conditions used, no separation of minus 20 μm material was observed. The effectiveness of separation was a function of the amount of ultrafine material in the sample. A staged milling technique was used to avoid excessive

Palowitch and Nasiatka (4) stated that when the ultrafine fractions are not removed from the sample being float/sink tested it is anticipated that there will be a difference between the results evaluated by static and centrifugal procedures. Therefore, the static procedure cannot be used as a reference when colloidal size particles are present. The amount of ultrafine material present in the sample limits the effectiveness of both static and centrifugal techniques regardless of the top size. Therefore, the ability to separate gravimetrically a specific minus 75 μm (200 U.S. sieve) sample has no correlation to the potential of separation of other minus 75 μm samples.

Kalb (14) suggested that when minus 20 μm (500 U.S. sieve) particles are present in the coal slurry, they cannot be separated even though surfactant, sonication, and 20 minutes of centrifugation at 3000 rpm are employed in the float/sink procedure. Therefore, overmilling of the sample preceding the washability tests is expected to be disadvantageous in the preparation of raw coal samples.

The majority of the reference material on centrifugal float/sink techniques (1-13) compares results to static procedures, emphasizes the reduced time period involved, and limits the sample description to top size only. The major advantage of centrifugal techniques is the ability to separate more of the colloidal size particles which cannot be separated with static techniques. According to earlier literature (15), static float/sink tests were not conducted on the minus 75 μm (200 U.S. sieve) material as the coal particles were too small to respond to the test. All minus 75 μm coal was considered to float at a specific gravity of 1.35. Introduction of a dynamic (centrifugal) procedure made separation of minus 200 U.S. sieve particles both possible and effective.

Dumm and Hogg (11,12), investigating the size/specific gravity distribution of ultrafine coal and the distribution of sulfur and ash with respect to particle size, concluded that conventional washability techniques can be extended to include minus 75 μm size particles. However, certain precautions have to be undertaken. Centrifugation time should be considerable (up to 20 hours at 1000 rpm) for very small near-gravity particles to separate, particularly the 1.3 and 1.6 specific gravity fractions. Care also must be taken to ensure that ultrafine particles are well dispersed in the heavy liquid and that they remain dispersed during separation. The authors suggest the solids content in suspension should be kept as low as possible (preferably less than 1% solid to liquid by weight) to reduce the probability of particle collision and, consequently, to reduce aggregation (agglomeration).

THEORETICAL WORK

During this quarter of effort, the effects of Brownian motion on fine particle sedimentation have been identified and theoretically quantitated. The interaction of Brownian forces and gravitational force is considered, and a model prepared which permits estimation of critical particle size in float sink separations.

Brownian forces result from random jostling (collision) of particles by the molecules of the suspending fluid due to thermal agitation and fluctuate on a very short time scale. This allows one to take a time average and replace the forces by a diffusion constant $D = kT/R_w$, where k is the Boltzmann constant, T is absolute temperature, and R_w is a resistance coefficient relating to a particle's motion (translational or rotational) in response to the net force acting on it. The resistance coefficient increases as the particle becomes larger, that is, D decreases. Therefore, large particles are less affected by Brownian forces than small ones.

Estimation of Critical Particle Size in Float/Sink Separations.

Provided that no convection currents or other physical forces play a part, the motion of colloidal particles (including coal and ash-forming mineral particles) will arise from one of two sources: a random motion resulting from collisions of particles with molecules of the suspending medium (Brownian movements) and a vertical motion resulting from the force of gravity. If the forces caused by the kinetic bombardment of the molecules of the suspending medium equal or exceed the force of gravity acting on the particles, the effect of the latter will be balanced or overbalanced and the particles will not settle. It is apparent, therefore, that there exists a critical size for particles with a given difference in density than the suspending liquid. Particles larger than this size will settle and those of smaller size will remain suspended.

The critical size of a settling particle will be that size for which a balance exists between the Brownian forces resulting from the kinetic energy of the molecules of the suspending medium and the forces of gravitation. The critical diameter of a spherical particle will be such that the Brownian movement for a given period of time is just equal to the gravitational fall for the same period of time.

The mean displacement $(\Delta^2)^{1/2}$ of a particle in t seconds due to Brownian motion can be calculated from Einstein's equation:

$$(\Delta^2)^{1/2} = (2RTt/3N\pi\eta d)^{1/2} = (2kTt/3\pi\eta d)^{1/2} \quad (\text{Eq. 1})$$

where: R - is the gas constant

k - the Boltzmann constant, equals 1.38×10^{-23} J/molecule °K
since $k = R/N$

N - Avogadro's number

η - viscosity of liquid (for aqueous suspension, 1 cp)

d - particle diameter, m

Assuming that a run-of-mine coal sample consists of three specific gravity (ρ_s) fractions; organic coal ($\rho_s = 1.35$), quartz ($\rho_s = 2.6$), and pyrite ($\rho_s = 5.0$), we estimated the critical particle diameter of each fraction suspended in a liquid of specific gravity, $\rho_l = 1.3$, and of viscosity, $\eta = 1$ cp. The relation between static sedimentation distance and particle size for coal, quartz, and pyrite were calculated from the Stokes equation:

$$v = d^2(\rho_s - \rho_l)g/18\eta \quad (\text{Eq. 2})$$

where: v - velocity of sedimentation

d - particle diameter

ρ_s , ρ_l - densities of solid and liquid, respectively

g - gravitational constant

η - viscosity of liquid

Values were calculated for sedimentation times of 1, 10^2 , and 10^4 seconds and plotted in Figure 1. The relation between mean displacement and particle size was calculated for Brownian motion according to Einstein (Eq. 1), assuming the same periods of time, and is also presented in Figure 1. The point of intersection of two lines for a given time indicates the critical value of particle radii for float/sink separation.

For example, consider a float/sink separation in which the sedimentation of near-gravity ($\rho_s - \rho_l = 0.05$) coal particles, quartz ($\rho_s - \rho_l = 1.3$) and pyrite ($\rho_s - \rho_l = 3.7$) takes place simultaneously. To determine the critical particle diameter for coal at 100 s sedimentation time, follow the sedimentation line labeled "t = 100 s, $\rho_s - \rho_l = 0.05$ (coal)" to the intersection with the Brownian motion line labeled "t = 100 s." A critical particle radius of 50 μm is found. This is equivalent to a particle diameter of 100 μm (approximately 150 U.S. sieve). At this size, Brownian movement and movement resulting from the forces of gravity are equal. The critical particle diameters are evaluated in the same manner for quartz and pyrite particles. After the same period of time (100 s), the critical particle diameters for quartz and pyrite are found to be 26 μm and 17 μm , respectively. Laboratory experiments will be designed to verify the critical particle sizes predicted by this relationship.

Fig. 1. Estimation of critical particle diameter of fine and ultrafine coal, quartz, and pyrite when the sedimentation of solids is affected by Brownian motion. Specific gravity and viscosity of the liquid are assumed to be 1.3 and 1 cp respectively.

LABORATORY WORK

During this quarter, aliquots of Upper Freeport coal were prepared for use in studying the relative effectiveness of static and centrifugal float/sink separation techniques for fine and ultrafine coal. The series of float/sink separations included in this report were undertaken to verify results of earlier work and to provide a basis for comparing the effects which may result from modifications to the separation techniques resulting from control of factors which affect dispersion, agglomeration, attraction or repulsion of particles, and physical entrapment.

Sample Preparation

The original 1500 pound sample was riffled into 25-pound aliquots and stored under argon pressure. For this series of experiments, one aliquot was split into 8 portions and individual portions were ground to top sizes of 1180, 150, 75, and 45 μm (16, 100, 200, and 325 U.S. sieve). Initial grinding utilized a Straub model 4E grinding mill. After initial grinding, material of the desired size was separated using ASTM screens and an ATM Sonic Sifter and the oversize was recrushed in a Holmes 501XL pulverizer and Janke & Kunkel K. G. analytical mill until 95 % passed the desired sieve size. After each sample was ground and sized it was purged with argon and sealed in a glass jar until use. Before a sample was used, it was dried at 107°C until the weight of the sample was constant.

Float/sink Separation Procedures

In contrast to the usual technique of sieving coarse coal into several size fractions prior to float/sink separations, the difficulties encountered in sieving ultrafine coal makes size separations impractical. Therefore, specific gravity separations were performed on the entire sample, and the top size is the only limiting parameter specified.

Static method. Separatory flasks were fabricated by removing the bottom of an Erlenmeyer flask and joining it neck-to-neck to another Erlenmeyer flask. The flask was filled with 4000 ml of heavy liquid (Certigrav) at a specific gravity of 1.300 and maintained at an accuracy of 0.0005 by means of a spindle hydrometer at ambient temperature. Approximately 170 g of coal was introduced and stirred into the heavy medium. After standing for up to 12 hours, separation was considered complete when the center of the fluid was translucent. The float material was then decanted and the float and sink fractions were filtered and dried at a temperature of 80-85°C. The 1.300 sink fraction was separated at a specific gravity of 1.400. Subsequently, the 1.400 sink fraction was separated at a specific gravity of 1.600. Each specific gravity fraction was then weighed and analyzed for ash and total sulfur content as well as for heating value.

Dynamic method. Dynamic float/sink separations were performed using an International Model K centrifuge. Hourglass shaped centrifuge jars containing 400 ml of Certigrav and 40 g of coal were centrifuged at 1600 rpm for 20 minutes and allowed to coast to a stop without braking. Float and sink fractions were separated, dried, and analyzed using the same procedures as for static separations.

Methods of Analysis

Analysis of minus 170 U.S. sieve size particles was performed using a Leeds & Northrup Model 0771-1 particle size analyzer and the coarser particles were analyzed using standard ASTM sieves. Ash content analyses were performed using the procedure according to ASTM D 3174 82. The total sulfur content of each specific gravity fraction was determined using Fisher Model 475 total sulfur analyzer according to prescribed procedures. Heating values were determined separately for each specific gravity fraction, using adiabatic procedures conforming to ASTM-D2015. A Parr Model 1241 oxygen bomb calorimeter equipped with a Parr Model 1710 calorimeter controller, providing a completely automated experimental procedure, was used.

Results and Discussion

Float/sink separation of Upper Freeport coal crushed to minus 1180 μm using static and centrifugal techniques, presented in Figure 2, resulted in similar relationships between weight yield, mineral content, sulfur content, and heating value recovery. However, the weight yield was significantly greater for centrifugal separations than for static separations at all specific gravities.

The results of specific gravity separations of coal ground to top sizes of 150 and 75 μm show progressively greater deviations when static and centrifugal separations were performed (Figures 3 and 4).

In Figure 5, comparisons of static float/sink separations with the samples crushed to different top sizes are shown. The cumulative ash exhibits the greatest disparity resulting from particle size differences, particularly at low specific gravities of separation. Comparisons of the same samples, separated centrifugally, respond more closely to the expected results as shown in Figure 6. However, the cumulative ash content curves in figure 6 indicate a lower ash content for the minus 200 U.S. sieve sample than for the finer minus 325 U.S sieve sample. Whether this result is due to misplaced particles of fine-size material or due to variability in ash content among aliquots of the same sample is not yet clear. A more complete evaluation of these effects is currently underway. Results for the Upper Freeport coal will be presented when the series of tests is complete.

Fig. 2. Results of static and centrifugal washability tests on Upper Freeport coal crushed to minus 16 mesh.

Fig. 3. Results of static and centrifugal washability tests on Upper Freeport coal crushed to minus 100 mesh.

Fig. 4. Results of static and centrifugal washability tests on Upper Freeport coal crushed to minus 200 mesh.

Fig. 5. Comparative results of static washability tests on Upper Freeport coal crushed to minus 16, 100, and 200 mesh.

Fig. 6. Comparative results of dynamic (Centrifugal) washability tests on Upper Freeport coal crushed to minus 16, 100, 200, and 325 mesh.

FUTURE WORK

In the next reporting period, theoretical studies will continue with an evaluation of colloidal properties of ultrafine solids as they relate to sink/float separation. Laboratory tests will continue with investigations of float/sink separations of minus 45 μm (325 U.S. sieve) coal using the most promising techniques given in the literature and other variations appropriate. In addition, a more hydrophobic coal (Illinois No. 6) will be evaluated.

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