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*PRACTICAL PROBLEMS IN PARTICLE
SIZE AND SURFACE
AREA MEASUREMENTS*

A. A. WINER AND I. F. WRIGHT

MINERAL PROCESSING DIVISION

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3) Institute of Engineering Research, University of California, is investigating the mixing of powders and the parameters that can be related to sinterability.

Unless the methods give meaningful data, materials cannot be wisely selected; nor can their properties be fully utilized. Various methods for fine powder characterization were chosen and several problems were encountered.

Particle counting and size measurement

In recent years, many studies of old and new methods of particle characterization have been made (1, 2, 3). The complexity of sizing has been recognized; particle shape, density, area, irregularity, agglomeration and friability are factors which must be considered. In some cases, a single parameter such as particle size distribution or surface area may be sufficient to define a powder for control purposes. In other cases, characterization by a single parameter may be inadequate and completely misleading.

Photo-sedimentation, one of the common methods for particle sizing, has been used for many years. However, Kaye and Treasure (4) only recently noted that convection currents due to surface cooling caused by evaporation of the liquid disturb the suspension, changing the concentration and particle

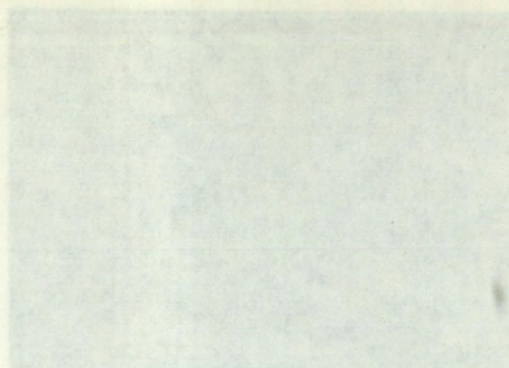


Figure 1: EEL Photo-sedimentation sedimentometer.

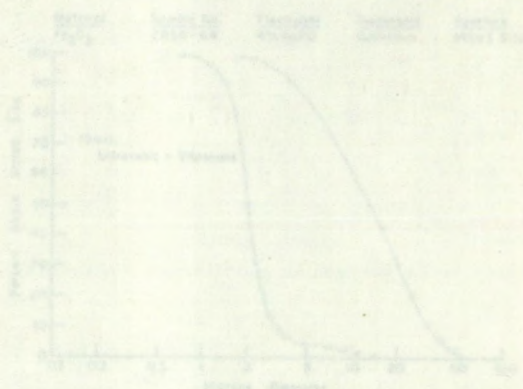


Figure 2: The effect of particle dispersion on the apparent size distribution.

Practical Problems in Particle Size and Surface Area Measurements

by A. A. Winer

I. F. Wright

Introduction

Modern manufacturing techniques require an understanding of the physico-chemical properties and behaviour of the materials used, in order to maximize production and obtain precise quality control. Classic methods for characterizing materials are now being critically examined for their utility in modern technology. The current efforts of well known organizations, listed below, are indicative of the importance attached to the necessity of completely characterizing powders for modern technology:

1) Warren Springs Laboratory is studying

Abstract

Different techniques for particle size measurement employ different physical principles, and therefore may well show different results. Some methods used in practice are compared and discussed.

Variations in the test results may also be due to material characteristics, such as porosity, surface activity and the tendency of some finely divided powders to agglomerate. These may require additional analytical techniques, such as surface area measurement by gas adsorption. A relatively simple and rapid surface area technique is discussed.

the factors affecting the cohesive behaviour of powders, and the blending of powders and particles.

2) Welwyn Hall Research Association is

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investigating methods for particle size analysis, flow properties, compaction and classification of powders.

3) Institute of Engineering Research, University of California, is investigating the mixing of powders and the parameters that can be related to sinterability.

Unless the methods give meaningful data, materials cannot be wisely selected, nor can their properties be fully utilized. Various methods for fine powder characterization were chosen and several problems were encountered.

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Photo-sedimentation, one of the common methods for particle sizing, has been used for many years. However, Kaye and Treasure (4) only recently noted that convection currents due to surface cooling caused by evaporation of the liquid disturb the suspension, changing the concentration and impairing the accuracy. They suggested a cover to overcome this difficulty. We suggest that hexanediol can be used to decrease evaporation by forming a monomolecular layer on the surface of the liquid. This compound has been used to inhibit evaporation of reservoir water. Figure 1 shows an EEL Photo-Extinction Sedimentometer made by Evans Electroselenium Limited of England, which is based on the light scattering principle.

An electronic particle size analyzer of the single aperture type, the Coulter Counter, operates as follows. The particles in suspension pass through a sensing zone, changing the resistivity by displacing the liquid volumetrically. Counting and size analysis are done rapidly. Various aperture sizes are used for measuring a complete size distribution. A newer model of the Coulter Counter contains a series of apertures that permit the recording of particle size distribution data during a single pass. If agglomerates are present, the instrument will "see" them as single particles.

The dispersion of particles has an effect on the apparent size distribution. To examine this factor, one sample of a fine iron oxide powder was dispersed in an electrolyte and a duplicate sample was similarly dispersed and then subjected to 15 minutes of ultrasonic vibration. The particle size distribution

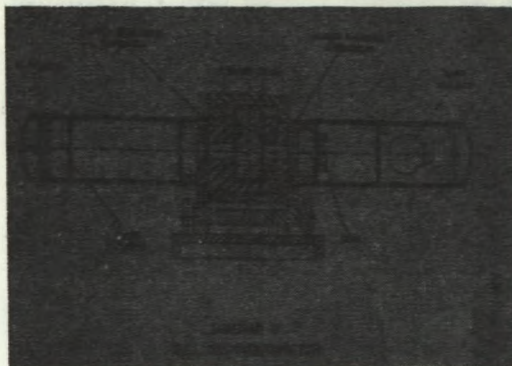


Figure 1: EEL Photo-extinction sedimentometer.

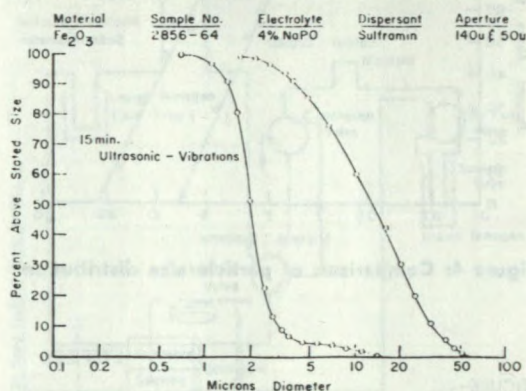


Figure 2: The effect of particle dispersion on the apparent size distribution.

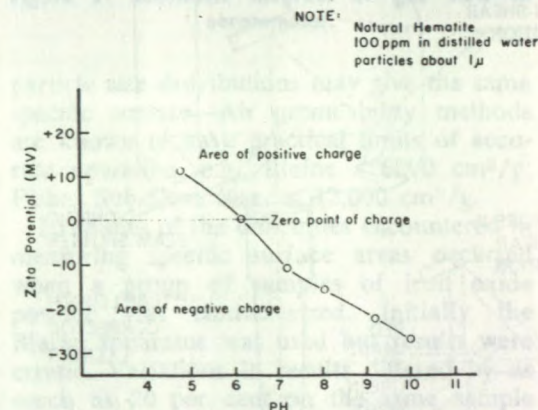


Figure 3: Zeta potential of natural hematite.

of each sample was determined with the Coulter Counter. As illustrated in Figure 2, the ultrasonic bath was very effective in dispersing agglomerates.

The degree of particle dispersion can be indicated by the zeta potential of the suspension. A graph of zeta potential obtained with the Zeta Meter, using natural hematite dispersed in distilled water, is shown in Figure 3.

Most particles of colloidal size are negatively charged, the size of the total charge being proportional to the degree of dispersion. Maximum agglomeration occurs at zero point of charge, where Van der Waal's forces predominate.

Suspensions of very fine dispersed powders are difficult to examine microscopically because of Brownian motion. Thermal drying

of the suspension causes agglomerates to form. Freeze-drying overcomes this difficulty; the dispersed particles are fixed by quick freezing the water, and the ice then sublimates under vacuum, preventing agglomeration. Particle size, shape and distribution can then be determined with an optical or electron microscope.

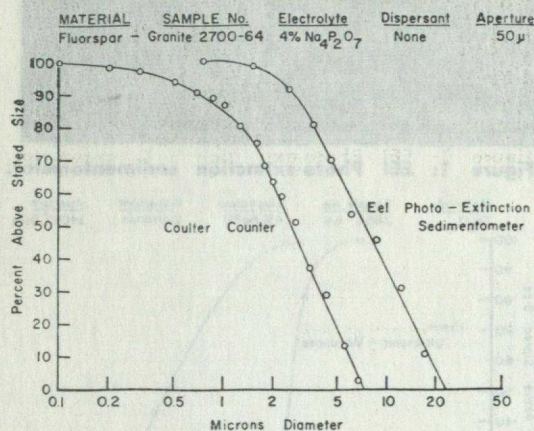


Figure 4: Comparison of particle size distribution.

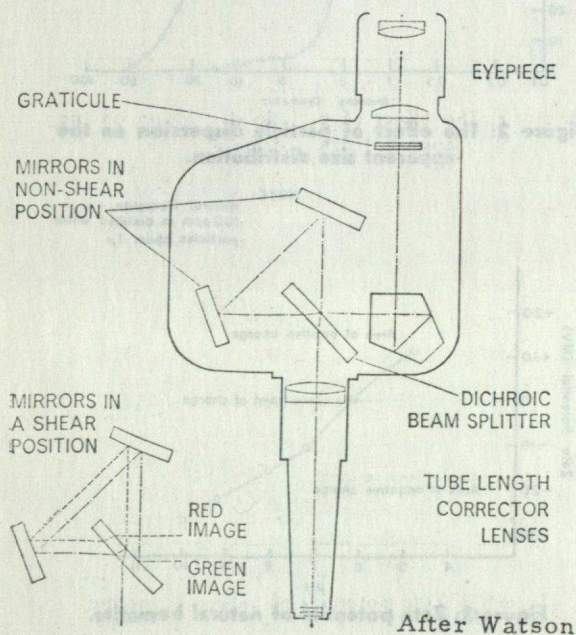
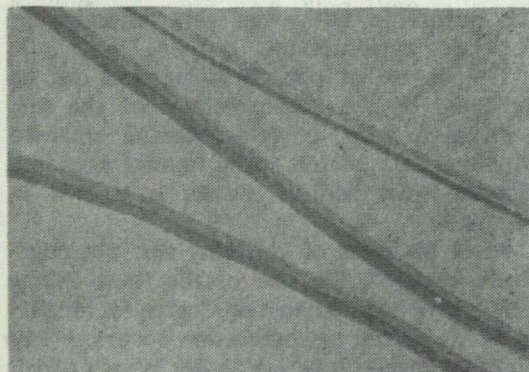


Figure 5: Schematic diagram of an image splitting device.

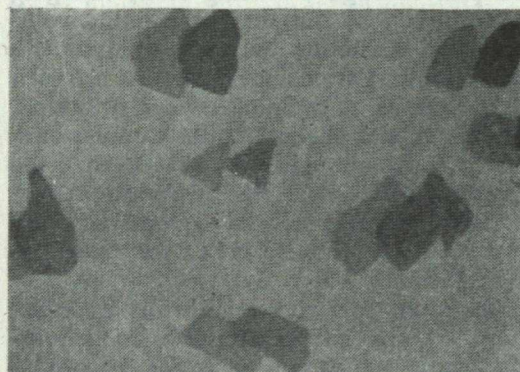


A photomicrograph of skin wool, approximate magnification $\times 60$. The bottom fibre is exactly sheared, but small areas of overlap show variations of diameter.

A comparison of particle-size distribution curves of a ground sample of fluorspar-bearing granite, obtained with the EEL Sedimentometer and the Coulter Counter, is shown in Figure 4. The curve obtained with the photo-sedimentometer indicates a coarser particle size distribution, suggesting agglomerates in the suspension. A visual estimate of the particle size distribution was made on a duplicate sample by an experienced mineralogist using a microscope, and was compared to nominally similar particle size ranges obtained from Figure 4. The comparison is shown in Table 1.

The results obtained with the Sedimentometer appear to compare more closely with those of the visual estimate, which is accepted as the control. The Coulter Counter, surprisingly, does not appear to have included larger, apparently non-agglomerated particles which were seen with the microscope. The reason is not known, but the possibility of sampling error is always present. Adding to the confusion, substantial errors have recently been found (5) in the use of the microscope for particle size measurement. An error of 10 to 40 per cent may occur when small particles are measured, because tangential light striking the particle at other than its midpoint causes imaginary edges to be viewed.

Image splitting devices have recently become available for particle size measurement with the microscope (6). They make the procedure much simpler and less fatiguing, with consequent gain in accuracy. The two images of the particle are moved from a blanked out position (black) to a position where they are just touching one another (exactly sheared). The distance is read on a micrometer scale or readout device. An adapter which can be used as a "Go or No Go" gauge may be added to the split image device (7). Particles within the limits of the range setting oscillate and touch each other in a particular manner. A schematic diagram of an image splitting device is shown in



Particles of coarse emery powder magnified approximately 60 times. The exactly sheared component images of two particles can be clearly seen.

Figure 6: Microscopic view of sheared images.

Figure 5 and sheared images of particles are shown in Figure 6.

Surface area measurement

The relationship between particle size and outer surface area can be appreciated by envisaging the sedimenting method of particle size measurement as a liquid permeability technique, i.e., a liquid flowing through a porous bed. Particle size results can usually be converted to surface area by simple calculation. Results obtained with the Fisher Sub-Seive Sizer, for example, can be reported as average particle size or as surface area. Thornton (9) has shown that outer surface areas of particles can be calculated from Coulter Counter results.

Accuracy of results obtained by permeability methods can be increased and at times may approach those by gas adsorption; if variables such as gas flow are considered. Holdsworth (8), in his discussion of permeability methods, has calculated factors for Knudsen, Maxwell, Poiseuille and slip flows, which can be used in permeability calculations. Permeability methods are also discussed in an ASTM publication (10), by Connor (11) and by Washington (12).

Finely divided powders cannot always be characterized by single parameter methods, such as air permeability or gas adsorption. If agglomeration of particles occurs, the Coulter Counter, which measures the particle volume by a change of resistivity due to liquid displaced, or air permeability methods, which measure the outer specific surface of the particles, will give surface area results that are smaller than those by gas adsorption which measures the inner surface (capillaries, pores, etc.) also and is little affected by agglomeration of particles. The permeability methods are relatively simple and, fortunately, the gas adsorption technique has been greatly simplified (13) (14).

An instrument manufactured by Perkin-Elmer, based on gas chromatography is used in measuring total surface area. Cylinders containing mixtures of nitrogen and helium are used.

The amount of nitrogen adsorbed or desorbed is detected by the change in thermal conductivity of the gas mixture. The change is indicated by a recorder and digital read-out. Modification of the instrument using quick-disconnect valves permits various points on the adsorption curve to be determined quickly. The flow of gas and its detection is shown schematically in Figure 7. Further simplification of this instrument is intended.

Experience has indicated that there are a number of problems in measuring the specific surface of very finely divided powders. Erratic results can be obtained with different permeability methods and even with the same method, especially with a powder whose surface is highly active. Different

TABLE 1

Comparison of Particle Size Distribution Data

Range	Visual Estimate %	EEL Sedimentometer %	Coulter Counter %
+ 25	25	5	0
- 25 + 10	35	33	0
- 10 + 5	35	27	20
- 5	5	35	80

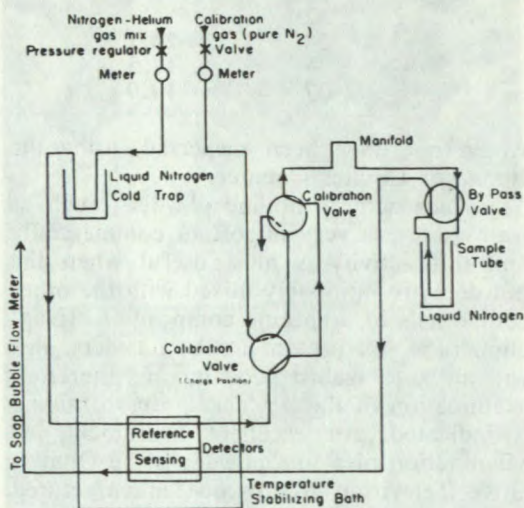


Figure 7: Schematic diagram of gas flow in sorptometer.

particle size distributions may give the same specific surface. Air permeability methods are known to have practical limits of accurate operation, e.g., Blaine ≤ 6000 cm²/g; Fisher Sub-Sieve Sizer $\leq 12,000$ cm²/g.

Examples of the difficulties encountered in measuring specific surface areas occurred when a group of samples of iron oxide powder was characterized. Initially the Blaine apparatus was used but results were erratic. Variations in results differed by as much as 20 per cent on the same sample with the same skilled operator. The Coulter Counter and gas adsorption techniques were used to further characterize these samples. Table 2 summarizes the results obtained. The Blaine and Coulter Counter results are reported in different units, but should be proportional to one another. The calculations, for surface area/density in column 3, were made according to Thornton (9). If the density of the powders had been known, the specific surface could have been calculated.

There are no significant correlations between the surface areas determined by the Blaine and Coulter Counter, as shown in Table 2. Use of either the Coulter Counter or the Blaine apparatus alone would therefore have resulted in misleading conclusions. The results of gas adsorption by the Sorptometer show that the powders have different total surface areas, and therefore the surface activity would be expected to vary. This

TABLE 2

Summary Results of Surface Area Determinations by Selected Methods

Sample No.	Blaine seconds	Coulter Counter Surface area/density m^2/cm^3	Sorptometer Gas adsorption m^2/g
29	18.1	7.69	10.2
30	27.2	6.78	9.2
31	36.6	6.20	7.7
35	21.2	2.75	6.33
33	—	4.24	5.18
38	—	6.80	4.27
32	—	4.71	3.57
34	26.1	4.31	3.42
36	17.5	5.0	1.87
37	10.0	5.41	1.43

would not have been suspected, using the Blaine or Coulter Counter.

Surface activity of fine powders, such as iron oxides, is very important commercially and this activity is most useful when the powders are intimately mixed with the other compounds in a specific composition. If agglomerates are present in the powders, this will mitigate against good mixing, therefore examination of the powders prior to mixing is indicated. An excellent instrument for examination of a fine powder is the Quantitative Television Microscope manufactured by Metals Research Ltd., Cambridge, England. The image of a powder is projected on a TV screen, and any agglomerates can be easily seen. The occupied surface area and particle size of the powder and other useful information can be obtained from this instrument. Figure 8 shows a front view of the instrument, and Figures 9 and 10 respectively, show on the TV screen a relatively well dispersed powder and an agglomerate present in the powder.

A scanning electron microscope has been built by Cambridge Instruments Ltd., Cambridge, England. Surface details not normally visible by other means can be viewed with this instrument at high magnification and good resolution. An image of the sample surface is formed by secondary emission of electrons and transmitted to a camera and TV screen. Metallizing of non-conducting surfaces is required.

Scanning electron micrographs of spray-dried, natural iron oxide, are shown at various magnifications in Figure 11. The depth of focus and resolution possible with this instrument can easily be appreciated.

The results of surface area comparisons for lead zirconate-titanate (PZT) samples by various techniques are shown in Table 3.

The results for Samples MR3 and C show surprisingly good agreement since two distinctly different physical principles are involved in the measurements, i.e., light scattering and gas adsorption. The specific surface area is very low for Sample C; probably the particles are very coarse and

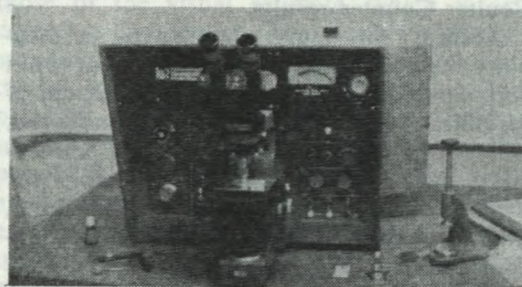


Figure 8: Quantitative television microscope.

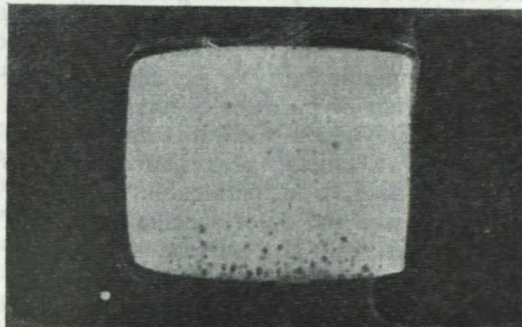


Figure 9: A well dispersed sample of synthetic iron oxide.



Figure 10: An agglomerate present in the synthetic iron oxide.

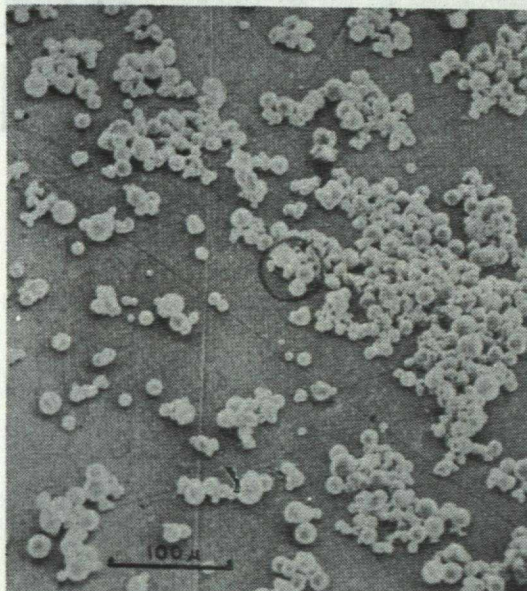
have little inner surface. The Innes method has a lower limit of operation of approximately $1 \text{ m}^2/\text{g}$, and therefore agreement with the other two methods is good.

Milled Canadian chrysotile asbestos samples were characterized by air permeability (Blaine-Dyckerhoff) and gas adsorption techniques. The Blaine-Dyckerhoff instrument is essentially a mechanized Blaine,

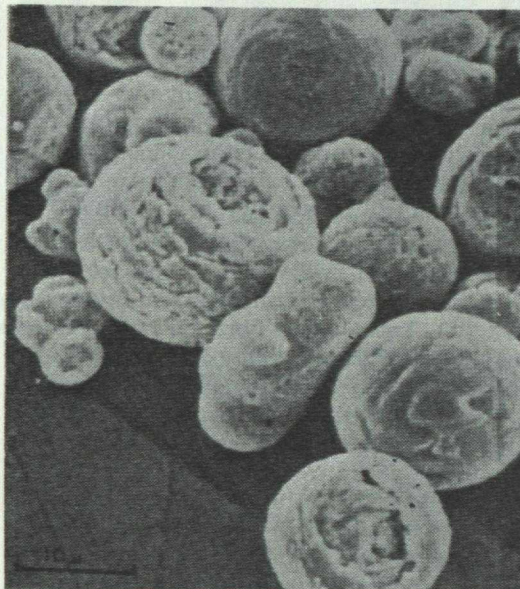
TABLE 3
Surface Area Comparisons of PZT Samples*

Sample	EEL Sedimentometer m ² /g	Gas Adsorption (Chromatographic) m ² /g	Gas Adsorption (Innes Method) m ² /g
PZT-MR3	15.3	—	16.2
PZT-C	1.58	1.5	1

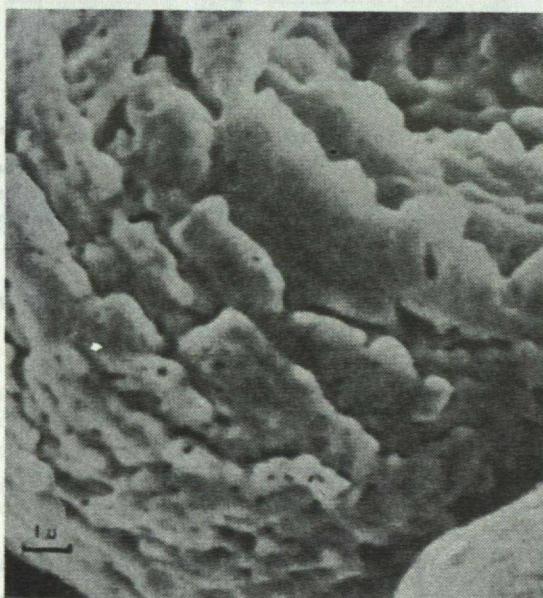
*Average of at least 3 tests.



(a) ×20



(b) ×200



(c) ×800



(d) ×4000

Figure 11: Surface views of spray-dried natural iron oxide at various high magnifications by electron scanning microscope (courtesy Pulp and Paper Research Institute).

using a cell with a capacity of 50g. The clock is started and stopped automatically by electrical contacts in the falling liquid column at the rear of the instrument. Figure 12 shows a front and rear view of the instrument.

A summary of results is shown in Table 4 and in graphical form in Figure 13. The gas

adsorption technique resulted in much higher surface areas, as expected. Chrysotile is a fibrous, hydrated magnesium silicate (magnesium analogue of kaolin), with capillaries, pore space and an active surface. Air permeability techniques are used in the asbestos industry to determine the degree of separation of fibres (fiberization), but the limita-

tion of the characterization must be recognized.

Surface areas of milled, well opened fibres from Quebec and California were compared by air permeability and gas adsorption techniques. The results are shown in Table 5.

Air permeability results by the two methods are in relatively good agreement. The difference in results is probably due to the packing techniques of the two cells. Interestingly, the California sample has a lower outer surface area than the Quebec fibre. The gas adsorption method resulted in very high specific surface area values for both samples of fibre, but in this case the total surface area of the California sample is more than twice that of the Quebec sample.

Because the California fibre had an extraordinary high surface area, by gas adsorption, compared to the Quebec fibre, scanning electron micrographs were taken (Figures 14 and 15). The Quebec fibre appears cylindrical; the California fibre seems nearly flat and approximately double the width. The particle shape of the two types of fibre and the relation between shape and surface area will be investigated further.

Total specific surface area measurements may also be used to determine reaction rates. Because of the complexity of reactions that can take place, a simple physico-chemical mechanism is usually assumed, i.e., that one factor controls the reaction rate. The rapid chromatographic technique for surface area determinations has been used at the Mines Branch as a measure of the reaction rate.

Conclusions

Characterization of fine powders is not always simple. The method must be chosen to give meaningful answers, and in many cases

more than one technique is necessary. Fortunately, progress is being made, as evidenced by the new instrumentation that is

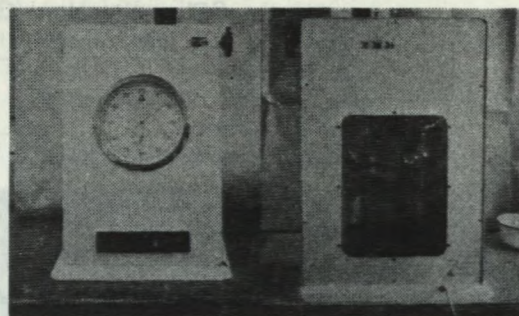


Figure 12: Blaine-Dyckerhoff instrument.

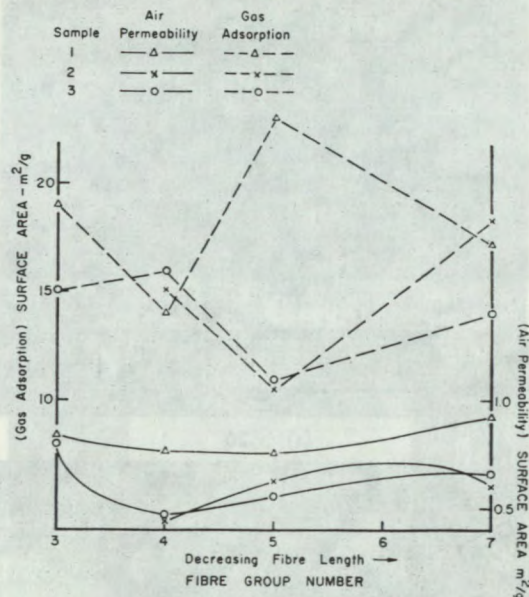


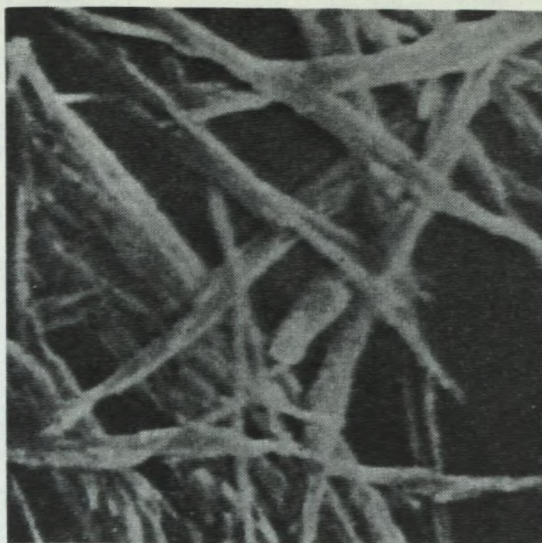
Figure 13: Surface area comparisons of chrysotile asbestos fibres. Fibre length vs. gas adsorption (sorptionmeter). Fiber length vs. air permeability (Blaine-Dyckerhoff).

TABLE 4
Surface Area Comparisons of Chrysotile Asbestos

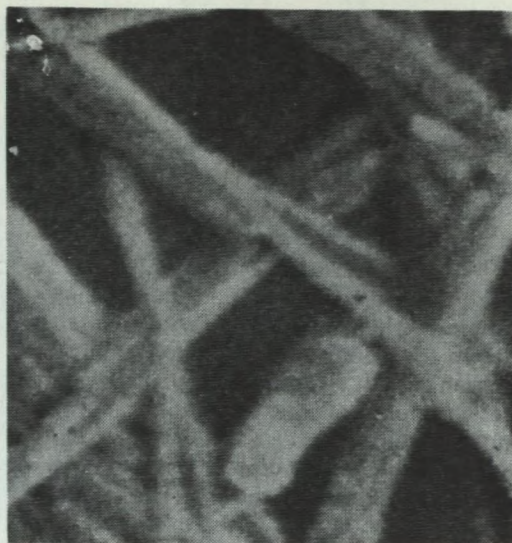
Sample No.	Air Permeability (Blaine-Dyckerhoff) m ² /g				Gas Adsorption (Sorptionmeter) m ² /g			
	Group No. 3	Group No. 4	Group No. 5	Group No. 7	Group No. 3	Group No. 4	Group No. 5	Group No. 7
1	0.84	0.76	0.75	0.92	19	14	23	17.2
2	—	0.44	0.62	0.60	—	15.1	10.5	18.3
3	0.80	0.47	0.56	0.66	15	16	11	14

TABLE 5
Surface Area Comparisons Milled, Well Opened Fibre from Quebec and California

Sample	Air Permeability		Gas Adsorption (Sorptionmeter) m ² /g
	Fisher Sub-Sieve Sizer m ² /g	Lea and Nurse m ² /g	
Quebec	3.21	2.73	23.5
California	2.65	2.28	53.2

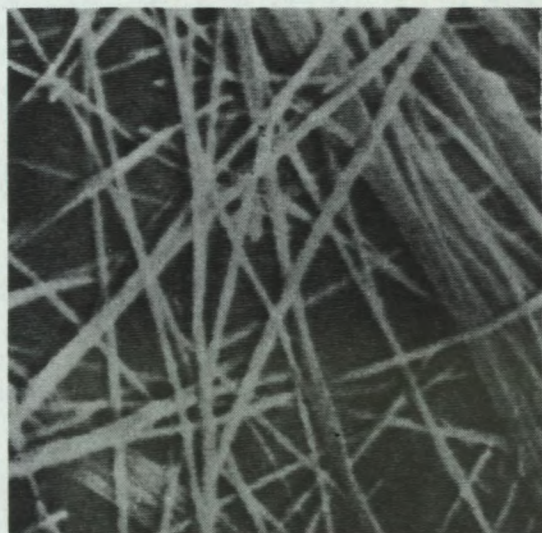


(a) $\times 30,000$

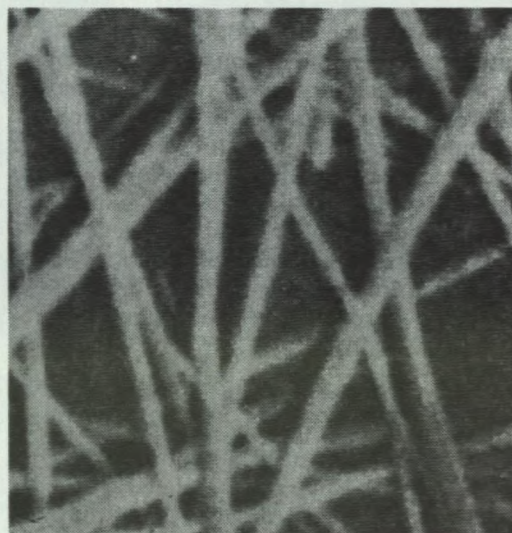


(b) $\times 60,000$

Figure 14: Scanning electron micrographs of California milled, well opened asbestos fibre (courtesy Pulp and Paper Research Institute).



(a) $\times 30,000$



(b) $\times 60,000$

Figure 15: Scanning electron micrographs of a Quebec milled, well opened asbestos fibre (courtesy Pulp and Paper Research Institute).

continually becoming available. The increasing scientific scrutiny of the principles and methods for characterizing finely powdered particles indicates that this progress will continue.

Acknowledgments

The authors acknowledge with thanks data supplied by various staff members from the Mines Branch.

References

1. Analytical Methods Committee, "Classification of Methods For Determining Particle-Size: A Review", 88, March (1963).
2. S. Zhewin, "Chemical Instrumentation", Chem. Ed. 40, 6 (1963).
3. H. Fishmeister *et al.*, "A Comparative Study of Methods For Particle-Size Analysis in the Sub-Sieve Range", Powder Metallurgy, 7 (1961).
4. B. H. Kaye and C. R. G. Treasure, "Thermal Stability of Sedimenting Suspensions Used to Measure Particle-Size Distribution". Materials and Research Standards, (Nov. 1965).
5. "Staff Evaluation of Microscopic Sphere Measurement", Mineral Processing, Dec. (1965).
6. J. Dyson, "Precise Measurement of Small Objects", A. E. I. Eng. 1, 1, (1961).
7. J. Dyson and P. J. W. Noble, "An Image Splitting Microscope Used as a 'Go or Not Go' Gauge", J. Royal Micros. S., 81, (Dec. 1962).
8. S. D. Holdsworth, "Characterization of Porous Materials", Chemical & Process Engineering, (April 1963).
9. M. J. Thornton, "The Application of the Coulter Counter to Problems in the Size Analysis of Insoluble Drugs", J. Pharmacy, 15 (No. 11) (Nov. 1963).
10. ASTM, "Symposium on Particle Size Measurement", ASTM Special Technical Publication No. 234, (1958).
11. P. Connor, "Surface Area Measurements", The Industrial Chemist, (May 1961).
12. R. A. Washington, "Construction and Calibration of an Apparatus For the Measurement of Surface Areas of Powdered Samples", Geological Survey, Paper 64-49, Department of Mines and Technical Surveys, Ottawa, (1965).
13. H. W. Dalschner and F. H. Stross, "An Efficient Dynamic Method for Surface Area Determinations", Anal. Chem., 34 9, (1962).
14. Louis Bini and R. L. Dioch, Jr., "Modification of the Innes Equation For Determining Surface Areas of Low Area Solids", Anal. Chem., 31, (8) (Aug. 1959).