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# A STUDY OF THE SURFACE AREAS OF PARTICULATE MICROCRYSTALLINE SILICA AND SILICA SAND

R. N. Leamson, Josephus Thomas, Jr., and H. P. Ehrlinger III

## ABSTRACT

Studies of surface area by the Brunauer, Emmett, and Teller method (BET method) as a function of particle size for ground silica sand and for particulate microcrystalline ("amorphous") silica emphasize the physical differences in these two compositionally similar substances. The silica sand possesses only external surface, the area of which increases with decreasing particle size in a predictable relationship based on a model of smooth, uniform, and nonporous spheres. The model incorporates an experimentally determined roughness factor. Sieve and sub-sieve size particles of microcrystalline silica, however, are aggregates of tiny crystallites, many of them less than  $0.1 \mu$  in diameter. These aggregates are porous and quite permeable to nitrogen, the adsorbate gas. Because of the high permeability, the measured surface area changes surprisingly little with particle size from  $100 \mu$  down to  $10 \mu$ . As the particle diameter decreases below  $10 \mu$ , the surface area increases.

Ultrasonic treatment of microcrystalline silica slurries or suspensions is beneficial in breaking down aggregates. In comparing the sedimentation behavior of samples subjected to ultrasonic vibration with that of others not treated, it was found that the ultrasonically treated ones gave a higher yield of colloidal particles in the decantate. The dried residue from the decantate had a surface area of  $16 \text{ m}^2/\text{g}$ .

Data also are presented comparing BET surface area and the surface area obtained by air permeametry methods. The inadequacy of the latter for use with porous particles is clearly shown.

## INTRODUCTION

Silica is the most abundant mineral in the earth's crust. It occurs in nature in varying degrees of purity and in a number of forms, such as quartz, tridymite, chalcedony, opal, flint, chert (in nodules or massive beds), agate, diatomite, and tripoli.

Silica has a variety of applications in industry. In the finely divided form, it is used as a filler in paints, hard rubber goods, gypsum plasters, plastics, soaps, floor tile preparations, and in buffing formulations. When used as a filler material, particle size and surface area are physical characteristics of prime importance. Silica of extremely small particle size and high surface area (over 100 m<sup>2</sup>/g) can be produced synthetically from the reaction of certain silicon compounds (e.g. silicon tetrachloride) with water. Surface area is a function of particle size if the particles are nonporous.

In Illinois, finely divided silica is produced commercially by grinding either silica sand or microcrystalline silica. The latter occurs in deposits in extreme southern Illinois and is often called "amorphous" silica, or sometimes tripoli. Lamar (1953) has described these deposits and has provided some physical characterization.

Sand grains differ markedly from microcrystalline silica particles of comparable size. The sand grains are discrete with essentially no porosity, and considerable grinding is necessary to reduce the material to a "flour" that is fine enough for certain filler applications. On the other hand, visually definable particles of microcrystalline silica are almost always aggregates of extremely small crystals, many of which cannot be resolved with a light microscope (less than 0.2  $\mu$ ). The more friable particles are easily broken down to a flour by gently rubbing them between the fingers; this property gives rise to the term "soft" silica. There is a certain amount of porosity associated with aggregates, depending on the size and arrangement of the component crystallites.

This study was initiated to obtain basic information concerning the surface areas of these particulate silicas. The study is a part of a continuing program aimed at more fully characterizing the chemical and physical properties of the state's natural resources to help provide a firm foundation for possible new commercial applications.

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## SILICA SOURCES

The St. Peter Sandstone, one of the source materials for the ground silica studies reported here, is composed of a homogeneous sand characterized by its

purity and roundness of grains. This well known formation has been a major commercial source of high quality glass sand for many years; it has been excellently characterized by Lamar (1927) and by Willman and Payne (1942).

The microcrystalline silica deposits of southern Illinois, which make up the other source material, are, in contrast, far from homogeneous. Although the chemical composition may be fairly uniform throughout a given volume of the substance, the degree of friability may vary widely throughout this same volume. In view of Lamar's (1953) description and partial characterization of these deposits, only a brief review seems necessary here, which is supplemented by the authors' observations.

The deposits range from very loose and crumbly (friable) silica through a firmer stone to chert. A gradual grading of the soft substance to a very firm stone is found in many instances. The grading is primarily horizontal, and the very firm silica often has the appearance of a highly fractured, bedded chert.

In certain areas, in addition to the very firm silica, nodules of chert may be found, which do not grade into their matrix, although they often show evidence of weathering. These nodules fit the classical descriptions (Fron del, 1962), being generally flattened, often knobby or warty, and having a white "rind" or patina. Those nodules that fracture cleanly and conchoidally usually have a fresh, firm fracture surface and a very thin patina (fig. 1A). Other nodules more often fracture along planes, have cracks (sometimes completely or partly filled) along the fracture surface, and usually appear quite weathered. These have a thicker patina (fig. 1B).

Each nodule is surrounded by a layer of very fine white material. This layer is usually about  $\frac{1}{2}$ -inch thick and is somewhat moist and plastic. It dries to a soft lump that crumbles to a powder under light pressure. It consists of a mixture of kaolinite, mica, and very fine silica. No grains larger than 200 mesh ( $74 \mu$ ) were obtained when dried pieces were gently crushed by hand.

The character of these silica deposits varies greatly with respect to the degree of firmness of the various components and, to some extent, to the mineralogical composition. During commercial processing, clay seams and occasionally the more massive chert are removed by hand before rough crushing, but, in gen-



Fig. 1 - Chert nodules present in microcrystalline silica deposits. A. Fractured nodule showing fresh, firm surface and thin patina. Approximately actual size. B. Fractured nodule with thicker patina and weathered appearance. Approximately actual size.

eral, most of the fine silica produced from these deposits is a ground composite of the silica just as it comes from the mine. It was, therefore, also of interest in this study to determine whether differences in hardness or friability of the crude material were reflected in surface-area values of ground samples.

## METHODS OF INVESTIGATION

### Sample Preparation

With regard to sample preparation, this study is divided essentially into three major parts: (1) the study of commercially packaged materials as received, (2) the study of microcrystalline silica collected in the field, (3) the study of the colloidal microcrystalline fraction recovered from the beneficiation of coarser aggregates by ultrasonic treatment of water suspensions.

The commercial silica is sold in various grades, which are determined primarily by the particle size distribution. Surface-area measurements were made on a series of these samples as received. However, because of the heterogeneity of the microcrystalline silica deposits (previously discussed), much of the work on this substance was conducted with samples obtained directly from the deposits. Considerable care was taken to obtain specimens that were homogeneous in hardness, texture, color, etc. Data on these various material types were obtained primarily from the seven mine samples described below, which will be referred to hereafter by number:

- (1) A very dense, gray chert in the form of distinct nodules (fig. 1A) (found in two mines only).
- (2) A white silica of intermediate hardness (somewhat friable), which is the principal matrix material for the nodules described in sample 1.
- (3) A very hard white silica stone, nearly chert-like, but not occurring in nodules.
- (4) A medium hard white silica stone similar to sample 2 but from another mine.
- (5) Powdered silica easily crumbled from the mine walls (same mine as sample 4).
- (6) A very soft uniform powder, composed of fine silica and clay, found immediately adjacent to and surrounding the nodules in sample 1.
- (7) A heterogeneous mixture of material resulting from recent blasting near the ceiling of one of the mines.

These seven samples were further characterized by X-ray diffraction. Samples 3, 4, and 5 produced diffraction patterns showing only quartz. The pattern for sample 1 showed quartz and a small quantity of calcite. Tracings for sam-

ples 2, 6, and 7 showed quartz with some kaolinite. Sample 6, besides quartz, contained an appreciable quantity of kaolinite and a small amount of mica.

Preliminary work with these field samples showed that the very small crystals or aggregates (less than  $1\ \mu$ ) tended to cling strongly to the larger particles, resulting in poor separation either by sieving or by air elutriation. Under such circumstances, little value could be placed on the measured surface areas of the larger size fractions because of the unknown microcrystalline content (less than  $1\ \mu$ ). In order to get cleaner separation and to be assured that the larger particle fractions were truly coherent aggregates, ultrasonics was used to dislodge the small loose particles from the larger aggregates. Samples were broken down in a jaw crusher and, where necessary, pulverized further with mortar and pestle. The crushed samples (about 100 g) were stirred with 500 ml of distilled water for about 1 hour, and then agitated ultrasonically (Autosonic Model Pa-2001, Powertron Ultrasonics Corp., Long Island, New York) for 3 minutes with hand stirring. The slurries were diluted to about 1  $\ell$  and centrifuged for 5 minutes, leaving particles smaller than about  $1\ \mu$  in the supernatant. The supernatant liquid was separated from the residue, which was then diluted to 500 ml, and the process was repeated twice. The supernatants were combined and evaporated to dryness, as were the residues.

The dried particles from the supernatant represented the less than  $1\ \mu$  fraction of crystals or aggregates of crystals. The dried residues, which were made up of crystals or aggregates of crystals greater than  $1\ \mu$  in size, were sieved, and all that passed a 200-mesh screen (greater than  $74\ \mu$ ) were subjected to further separation by air elutriation (Roller Particle Size Analyzer, Aminco, Silver Spring, Maryland). The smallest size fraction separated by air elutriation for the study was 1 to  $5\ \mu$ .

The clay minerals and mica, where present, were concentrated in the supernatant after the centrifuge step. These components may have constituted as much as half of the sample in the less than  $1\ \mu$  fraction of sample 6.

An additional series of microcrystalline samples was prepared for study to determine whether the quantity of the colloid fraction (less than  $2\ \mu$ ) increased after ultrasonic treatment, or to what extent the surface area of the colloid fraction changed, or possibly both. For this part of the study, one of the commercial powders was used in which 92 percent of the particles were less than  $40\ \mu$  in diameter and 29 percent were less than  $5\ \mu$ . Six portions of 10.000 g each of this sample were weighed out. Each of three of the samples was added to about 0.5  $\ell$  of water. The suspension was thoroughly mixed, poured into a 1  $\ell$  graduated cylinder, diluted to 1000 ml, stirred, and allowed to stand without further agitation. One sample was decanted after 1 day, another after 2 days, and the third after 5 days. Both the decantate and the residue were evaporated to dryness and weighed, and the surface area was determined for each. The remaining three samples were each mixed with about 200 ml of water, and the suspensions thus formed were treated for 1 minute with a Bronwill Biosonik II generator (Bronwill Scientific, Rochester, New York) operating at half-power. These were then diluted and allowed to settle as before, except that the last sample settled for 7 days rather than 5. Again, the dried fractions were weighed and their surface areas measured.

#### Surface-Area Determination

Surface areas were determined by the classical gas adsorption method of Brunauer, Emmett, and Teller (1938) - BET method - with nitrogen as the adsorbate

at liquid nitrogen temperature (about 77° K). A dynamic system, similar to that described by Nelsen and Eggertsen (1958), was used to obtain the adsorption-desorption data.

Surface-area values obtained by the BET method are often used as standards for evaluating other methods. Where considerable porosity is present, it is the only method that gives total internal and external surface area.

Air permeametry, a simpler and common method for determining surface area, is based on the resistance that a packed bed of the substance offers to a flow of air. It seems appropriate here to emphasize that permeametry, in view of its common industrial usage, provides realistic comparative surface-area values for nonporous powders, but for particles with appreciable internal surface or porosity, or for compacted powders of very small particle size, the method yields low values when compared with data from the BET method. Consequently, the disparity between results from the two methods usually increases with increasing surface area. An example of the discrepancy between the methods is shown in a study on whiting limestone by Bessey and Soul (1954). Similar comparative data for selected silica samples are given later in the paper.

## RESULTS AND DISCUSSION

Uniform nonporous spheres of a substance have a specific surface area ( $S_w$ ) that follows the simple relationship,  $S_w = \frac{6}{\rho d}$ , where  $\rho$  is the absolute density of the substance in g/cc,  $d$  is the diameter of the spheres in microns, and  $S_w$  is in square meters per gram. It is readily seen from this relationship that for a given weight of substance, decreasing the particle diameter to one-tenth its original value will increase the surface area tenfold. Particles, of course, are not always smooth spheres, and surface roughness brings about higher values than those calculated when such an assumption is made.

Table 1 shows surface-area values, both calculated and experimental, for various sieve and sub-sieve fractions (the latter isolated by air elutriation) of silica

TABLE 1 - EXPERIMENTAL AND CALCULATED VALUES FOR THE SURFACE AREA OF GROUND NONPOROUS SILICA SAND

Experimental		Calculated	
Particle diameter range ( $\mu$ )	Surface area ( $m^2/g$ )	Particle diameter ( $\mu$ )	Surface area ( $m^2/g$ )
74 - 105	0.10	90	.025
20 - 30	0.29	25	.091
15 - 20	0.36	17.5	.129
5 - 10	1.01	7.5	.302
1 - 5	3.78	3	.755
		2	1.13
		1	2.26
		0.1	22.6

flour from ground St. Peter sand. The calculated values were obtained by using a silica density of 2.65 and a particle diameter equal to the mean of the particle size range shown for each of the experimental values. To obtain the 1 to 5  $\mu$  fraction shown, the less than 1  $\mu$  fraction was removed from the decantate after centrifugation of a suspension of the 0 to 5  $\mu$  fraction separated by air elutriation.

It is seen from table 1 that the measured surface area (BET) is approximately 3 to 4 times that calculated for a given particle size. This factor represents the surface roughness (plus the nonuniformity) and can be used to predict rather closely the specific surface area of ground silica sand if the particle size range is known and deviations from the mean are not extreme.

Experimental values were not obtained with sieve fractions larger than those shown in table 1 because the precision of the method, with the apparatus in use, decreases as the surface area decreases below about 0.1  $m^2/g$ .

In the case of the microcrystalline silica, curves for surface area, as a function of particle size, are markedly different from those of the sand when the particles are larger than about 15  $\mu$ . Figure 2 graphically summarizes the results from numerous determinations on various sieve and sub-sieve fractions of the field

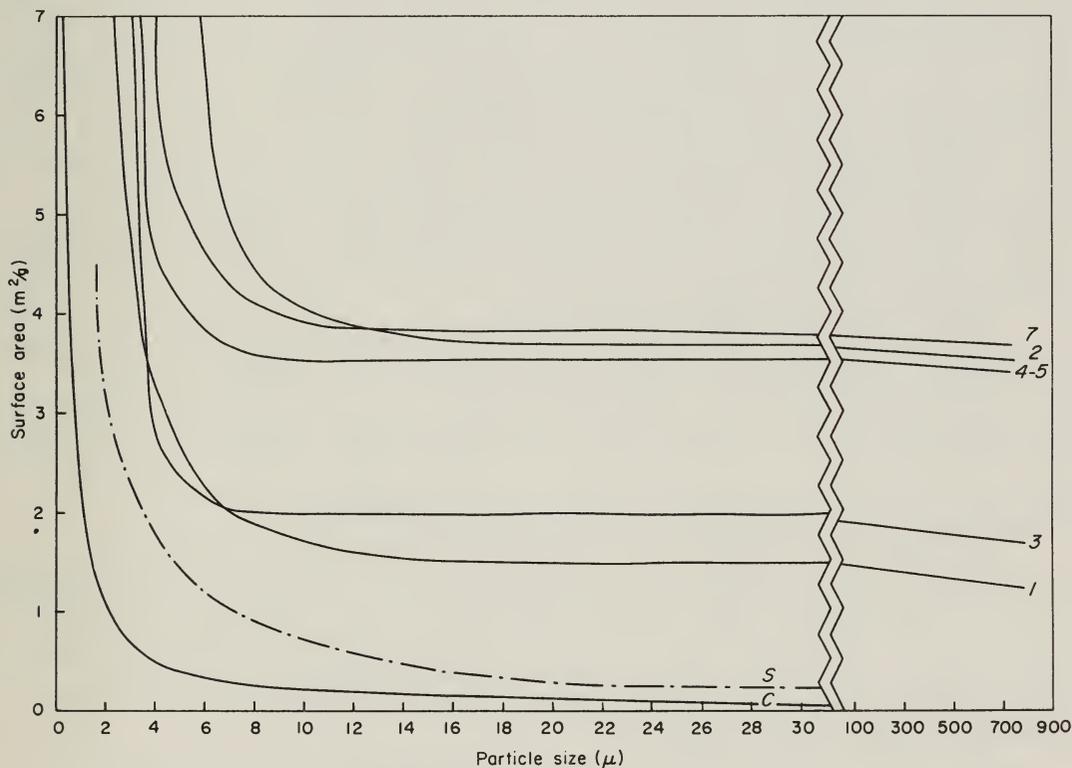


Fig. 2 - Surface area (BET method) versus particle size for microcrystalline silica and for silica sand. (Numbers on the curves correspond to field sample numbers. S=experimental curve for ground silica sand; C=calculated curve for smooth, nonporous silica spheres.)

samples. Sample 6 is not included because of its high clay content. The numbers on the curves correspond to the field sample numbers. For purposes of comparison, the experimental curve (labeled S) for ground silica sand is included, as is the calculated curve (labeled C) for smooth, nonporous silica spheres. The figure is broken to show the details for particles less than  $35 \mu$  in size and, at the same time, to show the extent of change occurring in surface area for much larger particles. The experimental curve for ground silica sand and the calculated curve for silica spheres are not extended as they would be essentially together on the horizontal axis at the ordinate scale used.

The most significant aspect of the data illustrated for the microcrystalline silica is that for a given sample, there is very little difference in the measured surface area for the largest fraction studied (20 mesh, or about  $840 \mu$ ) and for the sub-sieve size particles down to about  $10 \mu$ . This reflects the porous nature of the particle aggregates and their permeability to the adsorbate gas ( $N_2$ ). The samples that are most friable yield slightly higher surface areas than the more tightly compacted chert and chert-like samples (1 and 3), as might be expected. The surface-area values of  $3.5$  to  $4.0 \text{ m}^2/\text{g}$  for the more friable aggregates would indicate that the average crystallite size in the aggregate is less than  $2 \mu$ , although, in reality, a very broad range of crystallite size is represented in the aggregate, perhaps from about  $200 \mu$  to well below  $0.1 \mu$ . The lower surface-area value for the chert and chert-like samples in comparable sieve size fractions is not necessarily a result of larger average-size crystallites, of which the particle aggregate is constituted. In all probability, differences in crystallite size distribution within a given sample and varying degrees of compactness of the crystallites contribute largely to the differences in surface area. Compactness and close fit between crystals would, of course, reduce the total internal surface available for the adsorbate. The more gradual curve for sample 1 (chert) when compared with that for sample 3 would indicate that occluded pores may also contribute to a lower measurable surface area in the more compact stone.

With such little change in surface area over a wide range of particle size, oil adsorption characteristics of the microcrystalline silica should not vary appreciably for particle aggregates in the size range of  $10$  to  $1000 \mu$ . This, of course, would not be the case for ground silica sand where a continual decrease in surface area accompanies increasing particle size. Oil adsorption with the latter should increase with decreasing particle size. Oil adsorption studies are now in progress at the Geological Survey and will be published at a later date.

The fact that the larger sieve fractions (20 to 100 mesh, or about  $150$  to  $800 \mu$ ), excluding the chert, retain a relatively high ( $3.5 \text{ m}^2/\text{g}$ ) surface area suggests that the microcrystalline silica should be an excellent inert substrate for a column-packing material in gas chromatography applications. Particulate aggregates for this application must retain some strength and hold together during several handling steps. For this reason, the medium hard silica (sample 4, for example) should be superior to the more friable samples.

The surface area of ground silica sand approaches that of the particulate microcrystalline silica only in the very fine fractions (less than  $2 \mu$ ). The difficulty in reducing nonporous particles to this size and smaller by grinding is well recognized. Much less mechanical energy is required to disintegrate the more friable microcrystalline silica aggregates to particles of this size.

Because crystallites less than  $2 \mu$  in size constitute a large portion of the microcrystalline silica aggregates, size fractionation by sedimentation was conducted to concentrate the colloidal fraction (less than  $2 \mu$ ). The surface area of

TABLE 2 - SEPARATION OF THE COLLOID FRACTION OF MICROCRYSTALLINE SILICA AND DETERMINATION OF ITS SURFACE AREA, WITH AND WITHOUT ULTRASONIC DISPERSION

Without ultrasonic treatment			With ultrasonic treatment		
Settling time (days)	Weight of dried decantate (percentage of original sample)	Surface area (m <sup>2</sup> /g)	Settling time (days)	Weight of dried decantate (percentage of original sample)	Surface area (m <sup>2</sup> /g)
1	8.0	8.4	1	9.2	11.0
2	4.6	9.9	2	7.3	12.7
5	1.4	12.5	7	4.8	16.5

the fraction was determined, and tests were made to see if a greater proportion of this fraction could be separated from the whole by ultrasonic dispersion. This finer fraction, with a relatively higher surface area, might possibly be used to advantage in some special applications. The commercial sample used in this study represented a broad range of particle size distribution and had a surface area of 4.7 m<sup>2</sup>/g, as received. Data are shown in table 2.

No clay minerals could be detected by X-ray diffraction in the decantate silica from ultrasonic treatment and 7-day settling when a thin film, prepared by allowing some of the suspension to dry on a glass slide, was examined.

After ultrasonic dispersion, a greater percentage of colloidal silica remains in the decantate for comparable settling periods, and the surface area of the decantate fraction is greater than that of the original sample by a factor of 3 to 4. Thus, the ultrasonic treatment is beneficial in breaking down the aggregates in a water suspension. Longer ultrasonic treatment might result in an even greater percentage recovery of the finer fraction than that shown in table 2.

The commercial composites that were studied gave surface-area values that ranged from about 3.2 to 6.3 m<sup>2</sup>/g; for comparison, a commercial cream tripoli and a rose tripoli, both from Missouri, gave values of 4.92 and 1.86 m<sup>2</sup>/g, respectively.

It was pointed out earlier that permeametry methods can produce reliable results in surface-area determinations with nonporous powders of rather low (less than 1 m<sup>2</sup>/g) surface area. When internal porosity is present, when very finely divided particles of greater surface area (more than 1 m<sup>2</sup>/g) are tested, or when channeling or aggregation occurs in the packed beds used in permeametry, the method gives lower results than does the more accurate BET method.

This is clearly shown in figure 3, which depicts the surface areas of seven commercial samples of microcrystalline silica determined by the BET method and compared with the surface areas obtained by permeametry measurements. BET values range from about 3.2 m<sup>2</sup>/g to 6.3 m<sup>2</sup>/g. The values from permeametry for the same samples range from 0.75 m<sup>2</sup>/g to 1.5 m<sup>2</sup>/g. If the methods agreed perfectly, the points would fall on the dashed line or on a continuation of it. The BET surface areas are so much greater, however, that the points lie considerably above the dashed line. Although, in general, an increase in BET surface area accompanies an increase in surface area by permeametry for the various samples, as shown by the solid line, the points are badly scattered and the agreement is poor. Three of the samples, for example, showed little difference in surface

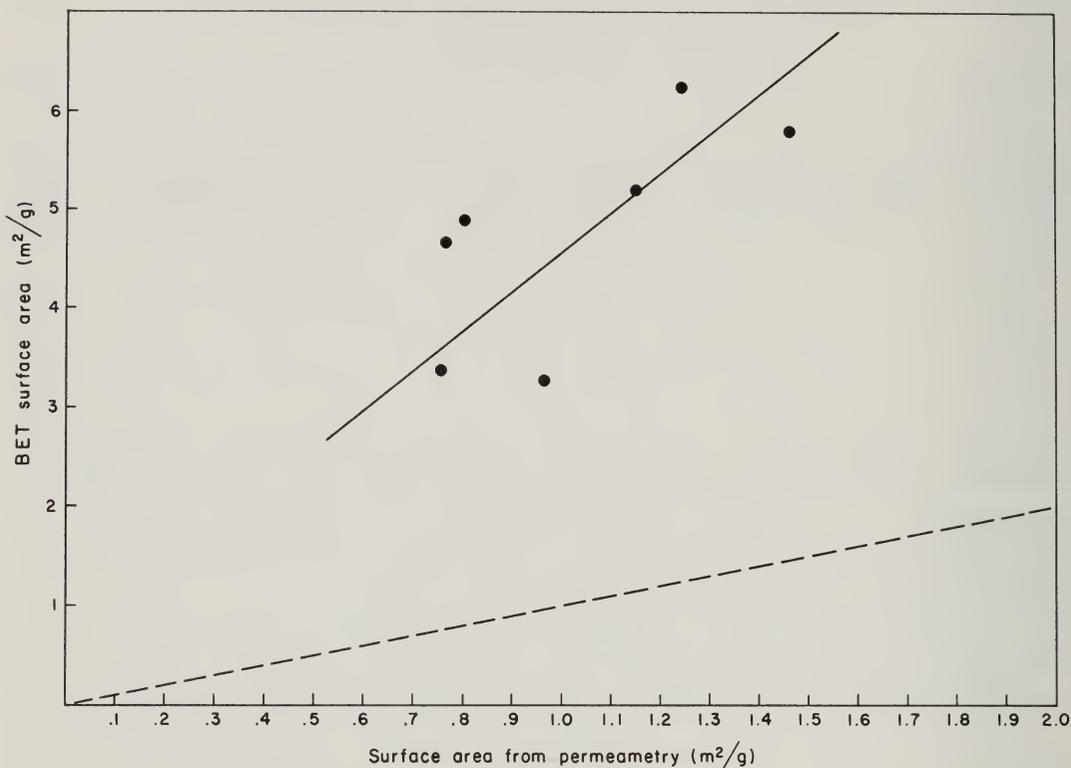


Fig. 3 - Surface area (BET method) versus surface area by permeametry for commercial microcrystalline silica samples. (Dashed line would indicate perfect agreement between the two methods.)

area by permeametry ( $0.75 \text{ m}^2/\text{g}$  to  $0.80 \text{ m}^2/\text{g}$ ), but ranged from  $3.4$  to  $4.9 \text{ m}^2/\text{g}$  by the BET method. In addition, the sample with the lowest surface area ( $3.2 \text{ m}^2/\text{g}$ ) by the BET method actually gave a higher surface area ( $0.96 \text{ m}^2/\text{g}$ ) than three of the other samples by permeametry.

The problems involving the surface area of porous aggregates are well recognized (Orr and Dallavalle, 1959). There is no consistent way to relate gas permeability data with gas adsorption data when the sample is porous. For whiting, Bessey and Soul (1954) found that the ratio of values for the adsorption method to those of the permeametry method was 1.6 with an uncertainty of  $\pm 12$  percent. The results shown in the present study with microcrystalline silica give a ratio of 4.8 with an uncertainty of  $\pm 30$  percent. For nonporous silica sand, a ratio of 1.2 to 1.3 is estimated from rather meager data. Thus, it is obvious that the discrepancy between the two methods increases as materials in question become more porous.

#### SUMMARY

Surface-area studies of ground silica sand (silica flour) and of microcrystalline ("amorphous") silica by the BET method show the following:

- (1) The surface area of ground silica sand is all external. It increases predictably with decreasing particle size when a surface roughness factor is used.
  - (2) Sieve and sub-sieve size particles (below  $1\ \mu$  in many cases) of microcrystalline silica are, for the most part, porous aggregates of very small crystallites, many less than  $0.2\ \mu$  in diameter. The aggregates are highly permeable to gases, such as nitrogen, which is the common adsorbate gas used in the BET method. As a result, the surface area of a given weight of particles  $1000\ \mu$  in diameter differs very little from that of the same weight of particles  $10\ \mu$  in diameter. Surface area increases more rapidly as the particle diameter decreases below about  $10\ \mu$ .
  - (3) Ultrasonic energy is useful in breaking down the microcrystalline aggregates in water slurries or suspension. With such treatment, followed by sedimentation, the percentage of the colloidal fraction (less than  $2\ \mu$ ) that can be isolated is increased. The latter had a surface area of  $16\ \text{m}^2/\text{g}$ , which (reflecting the very small particle size) is 3 to 4 times that of most commercial composites of this type.
  - (4) Surface-area values obtained by the BET method are often used as standards for evaluating other methods. Permeametry methods are commonly used in industry for determining surface area, as the apparatus is simpler to use. The shortcomings of the permeametry method with the porous materials, however, are well recognized and are re-emphasized here in a comparison of data obtained by the two methods on silica.
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