

NOTE

Specific surface: determination and relevance

J.C. Santamarina, K.A. Klein, Y.H. Wang, and E. Prencke

Abstract: Specific surface captures the combined effects of particle size and slenderness in a measurement that is independent and complementary to grain-size distribution. There are various methods to measure specific surface, including gas adsorption in dry conditions and selective molecular absorption in aqueous suspensions. The measurement procedure can have an important effect on measured values, yet such sensitivity is informative in itself. The amount of surface in a soil mass determines the balance between surface-related forces and gravimetric–skeletal forces acting on a soil particle, affects fabric formation, supports rich energy coupling mechanisms, governs conduction, and controls sorption and retardation during chemical diffusion.

Key words: specific surface, surface area, methylene blue, gas adsorption, fabric, Atterberg limits, grain-size distribution.

Résumé : La surface spécifique comprend des effets combinés de la grosseur des particules et de leur minceur dans une mesure qui est indépendante et complémentaire à la distribution granulométrique. Il existe diverses méthodes pour mesurer la surface spécifique, incluant l'adsorption de gaz dans des conditions sèches et l'adsorption moléculaire sélective dans des suspensions aqueuses. La procédure de mesure peut avoir une influence importante sur les valeurs mesurées; néanmoins, une telle sensibilité fournit en elle-même une certaine information. La quantité de surface dans une massif de sol détermine la balance entre les forces reliées aux surfaces et les forces de gravité prises par le squelette, forces qui agissent sur une particule de sol, affectent la formation de la fabrique, supportent les mécanismes d'énergie de couplage, gouvernent la conduction, et contrôlent la sorption et le retard durant la diffusion chimique.

Mots clés : surface spécifique, aire de surface, bleu méthylène, adsorption de gaz, fabrique, limites d'Atterberg, distribution granulométrique.

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Introduction

The forces governing the behavior of coarse-grained soils are different from those affecting fine-grained soils. Coarse-grained soils are significantly impacted by self-weight and skeletal forces, and the importance of electrical and capillary forces increases as particle size decreases or specific surface S_s increases. The specific surface of a particle is the ratio of its surface area A_s to its mass M . The relevance of specific surface to soil behavior can be inferred by comparing the magnitude of electrical interparticle forces F_{elec} to the weight W of a particle:

$$[1] \quad \frac{F_{elec}}{W} = \frac{A_s(R_{ddl} - Att)}{Mg} = S_s \frac{(R_{ddl} - Att)}{g}$$

where g is acceleration (in m/s^2); and R_{ddl} and Att are the repulsion and attraction electrical forces acting between two particles, respectively (in N/m^2). In the case of unsaturated soils, the ratio between the weight of a particle and the interparticle capillary force F_{cap} is relevant (Cho and Santamarina 2001):

$$[2] \quad \frac{F_{cap}}{W} = \frac{A_s \left(\frac{\xi S_s}{w} \right)}{Mg} = S_s^2 \left(\frac{\xi}{wg} \right)$$

where ξ is a proportionality constant, and w is the gravimetric moisture content. Equations [1] and [2] show that as specific surface increases, the importance of electrical and capillary contact-level forces increases. Parametric evalua-

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tions with eqs. [1] and [2] suggest a simple guideline to separate soil behavior: physical processes that govern soil behavior change when the specific surface of the soil exceeds $\sim 1 \text{ m}^2/\text{g}$ (Santamarina et al. 2001). Soils with higher specific surface experience sedimentation and fabric formation controlled by environmental factors (e.g., pH and ionic concentration in the pore fluid), shrinkage and stiffening in unsaturated conditions, and mechanical–chemical coupling.

Even small amounts of fines can have a considerable effect on the behavior of coarse soils. Fines fill pore spaces between larger particles, control the permeability of the soil, determine whether a given loading condition is drained or undrained, and increase the elastic and degradation threshold strain of soils. Furthermore, a relatively small percentage of fines can form stabilizing buttresses at contacts that provide significant strength and stiffness to the soil (e.g., loess). The Unified Soil Classification System recognizes these observations, clearly separates fines from coarse soils, captures the importance of fines in coarse soils, and even addresses whether those fines are of high or low plasticity, that is, high or low specific surface.

Theoretical relationships for the specific surface of various particle geometries are summarized in Table 1. These relations show that specific surface is controlled by the smallest dimension of the particle. There is a double effect of particle size on specific surface: as the particle size decreases, S_s increases not only due to the inverse relationship between specific surface and size, but also because the shape of small particles tends towards platy and rod-like geometries. Table 2 summarizes typical particle characteristics and specific surface values for common clay minerals. Therefore, specific surface measurements provide independent and complementary information to grain-size distribution, which is particularly important for high specific surface minerals.

The objectives of this paper are (i) to present the underlying physical phenomena and implementation methodologies for two specific surface measurement techniques, (ii) to investigate the advantages and disadvantages of these techniques, and (iii) to further explore the implications of specific surface as a relevant soil parameter for geotechnical and mineral engineering purposes.

Specific surface: measurement techniques

There are various techniques to measure the specific surface of solids. Gas adsorption (i.e., the condensation of molecules on the mineral surface) determines surface area from the relationship between applied pressure and volume of gas forced into the specimen (water vapor is included in this group). Another technique is the absorption of molecules from solution onto a solid surface, in particular, dyes such as methylene blue. Additionally, specific surface values can be inferred from known thermodynamic properties (e.g., heat of immersion of a powder in a liquid), the rate of dissolution of soluble materials, microscopy, and the diffusiveness of X-ray diffraction patterns. Details of these measurement techniques can be found in Adamson (1990). Gas adsorption and methylene blue absorption techniques are described in detail, including the basic theories that support these two methodologies and the implementation procedures.

Gas adsorption measurements

The Brunauer, Emmett, and Teller (BET) gas adsorption theory is the foundation for the measurement of surface area in high specific surface materials (Brunauer et al. 1938). Brunauer et al. (1938) derived an isotherm for the adsorption of multimolecular layers of gas on a solid adsorbent similar to Langmuir's derivation for a unimolecular layer. The BET equations represent the general shape of actual experimental isotherms, and from these isotherms the volume of gas required to form a unimolecular layer of gas on adsorbents can be computed. Surface area is determined using the following relationship:

$$[3] \quad \frac{P}{V_{\text{ads}}(P_0 - P)} = \frac{1}{V_m c} + \frac{c - 1}{V_m c} \frac{P}{P_0}$$

where P is the applied pressure, P_0 is the saturation pressure (it is near atmospheric pressure for nitrogen at 75 K), V_{ads} is the volume of gas adsorbed at P/P_0 , V_m is the volume of adsorbate for one monolayer of surface coverage, and c is related to the heat of adsorption in the first and subsequent adsorbed layers. Plots of $P/[V_{\text{ads}}(P_0 - P)]$ versus P/P_0 yield a straight line, from which the slope and intercept can be used to determine V_m and c . The surface area A_s of the specimen is

$$[4] \quad A_s = \frac{V_m}{V_{\text{molecule}}} A_{\text{molecule}}$$

where V_{molecule} is the volume of the adsorbate molecule, and A_{molecule} is the cross-sectional area of the adsorbate molecule.

Procedure

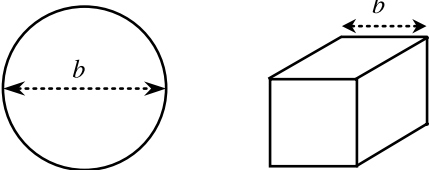
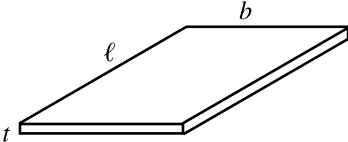
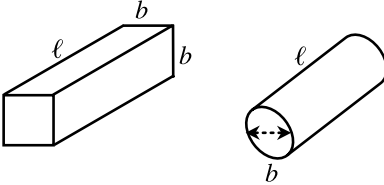
Measurements in this study were conducted using a Quantachrome NOVA 1200 Gas Sorption Analyzer. Nitrogen gas was selected as the adsorbate. Gas adsorption data were analyzed by a data-reduction program provided by the manufacturer, which is based on multipoint BET gas adsorption theory.

The gas adsorption procedure was verified using two pore glass bead specimens with known specific surfaces. The manufacturer's (Corning Corp., Pittsburgh, P.A.) values were 38.3 and 153 m^2/g , respectively. The corresponding specific surface values measured in this study were 39.6 and 163 m^2/g . Figure 1 presents the BET plots.

Methylene blue absorption measurements

Methylene blue (MB) dye has been used to determine the surface area of clay minerals for several decades. The chemical formula is $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$, with a corresponding molecular weight of 319.87 g/mol. Methylene blue in aqueous solution is a cationic dye, $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}^+$, which absorbs to negatively charged clay surfaces (Hang and Brindley 1970; Chen et al. 1999). Hence, the specific surface of particles can be determined by the amount of absorbed methylene blue. The surface area covered by one methylene blue molecule is typically assumed to be 130 \AA^2 ($1 \text{ \AA} = 0.1 \text{ nm}$). It is important to highlight that the technique is done in water suspensions, thus expansive minerals can expose all available surface area.

Table 1. Specific surface and particle geometry: the smallest dimension controls the specific surface.

Geometry	Equations $S_s = \frac{A_s}{M}$	Examples
Sphere or cube:		<p>Amorphous clay minerals Allophane, hollow spherules $b = 50 \text{ \AA}$, $G_s = 2.65$ $S_s = 453 \text{ m}^2/\text{g}$</p> <p>(Extreme case: $b = 9.6 \text{ \AA}$, then $S_s = 2358 \text{ m}^2/\text{g}$)</p>
Thin plate:	 <p>$\ell \gg t$ and $b \gg t$</p>	<p>Sheet structure clay minerals Montmorillonite (extreme case: fully swollen) $t = 9.6 \text{ \AA}$, $G_s = 2.65$ $S_s = 786 \text{ m}^2/\text{g}$</p>
Prism and rod:	 <p>$\ell \gg b$</p>	<p>Chain structure clay minerals Palygorskite, thread $b = 100 \text{ \AA}$, $G_s = 2.65$ $S_s = 151 \text{ m}^2/\text{g}$</p>

Note: G_s , specific gravity of the particle mineral; (S_s platy particle dimensions $b \times b \times t$)/(S_s cube $b \times b \times b$) = $(\beta + 2)/3$, where $\beta = b/t$; ρ_w , mass density of water (1 g/cm^3).

Procedure

Methylene blue chloride powder (Fisher Scientific, Pittsburgh, P.A.) was used in this study. Two different procedures were implemented to measure specific surface.

Method 1: European standard (spot test)

The step-by-step procedure is given as follows (Kandhal and Parker 1998): (i) prepare the methylene blue solution by mixing 1.0 g of dry powder with 200 mL of deionized water; (ii) prepare the soil suspension by mixing 10 g of oven-dry soil with 30 mL of deionized water; (iii) add the methylene blue solution to the soil suspension in 0.5 mL increments; (iv) for each addition of MB, mix the soil suspension for 1 min, remove a small drop of the suspension, and place it on Fisher brand filter paper P5; (v) if the unabsorbed methylene

blue forms a permanent light blue halo around the soil aggregate spot, the “end point” has been reached (i.e., the MB has replaced cations in the double layer and coated all the mineral surfaces); and (vi) determine the specific surface from the amount of MB required to reach the end point. The relationship between specific surface and MB used is

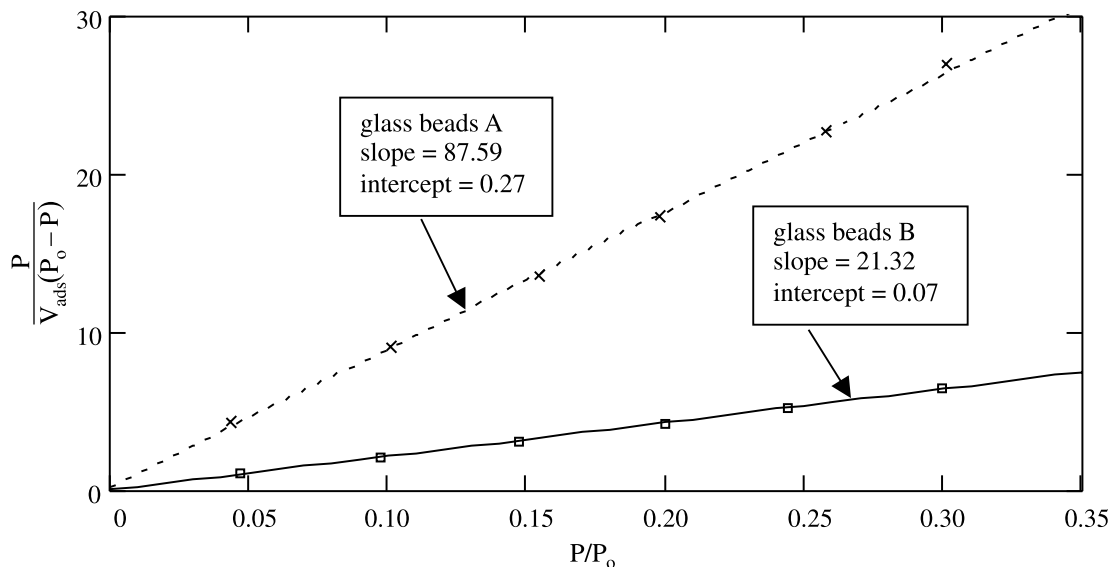
$$[5] \quad S_s = \frac{1}{319.87} \frac{1}{200} (0.5N) A_v A_{MB} \frac{1}{10}$$

where N is the number of MB increments added to the soil suspension solution, A_v is Avogadro’s number ($6.02 \times 10^{23}/\text{mol}$), and A_{MB} is the area covered by one MB molecule (typically assumed to be 130 \AA^2).

Table 2. Properties of selected clay minerals (data compiled from Yong and Warkentin 1975; Zelazny and Calhoun 1977; Mitchell 1993).

	Montmorillonite	Illite	Kaolinite	Attapulgite
Length L_p (nm)	1–500	100–2000	300–3000	4000–5000
Aspect ratio	100	10	3–10	400–1000
S_s (m ² /g)	400–800	80–100	10–20	140–170
LL (%)	100–950	60–120	30–110	160–230
PL (%)	50–100	35–60	25–40	100–140
Activity	0.9–7.0	0.5–1.0	0.3–0.5	0.5–1.2

Fig. 1. Multipoint BET data for two specimens of controlled micropore glass beads (Quantachrome NOVA 1200 Gas Sorption Analyzer). Note that the linear relationship is only valid for $P/P_0 < \sim 0.3$.



Method 2: titration

Precision can be improved by means of accurate analytical techniques to determine the amount of absorbed MB. In this case, a spectrophotometer is used. The value of specific surface is derived from the point of complete cation replacement determined on the titration curve. This point should correspond to the end point in the spot test (Hang and Brindley 1970; note that some additional MB may still absorb after this point). The step-by-step procedure is given as follows: (i) mix 2.0 g of oven-dry specimen with 200 mL of deionized water; (ii) add the MB solution to the soil suspension (the concentration is the same as that used in the spot method); (iii) continually mix the suspension for about 2 h, then let it sit overnight to reach absorption equilibrium and allow particle settlement; (iv) carefully remove 5 mL of the fluid, place it in a test tube, and centrifuge it; (v) measure the remnant concentration of MB in the fluid (in this study, a Beckman DU-64 spectrophotometer, wavelength = 6650 Å, was used); (vi) add more MB solution and repeat the previous steps (for convenience, a set of suspensions can be prepared in advance); and (vii) plot the amount of MB added versus the amount of absorbed MB and identify the point of complete cation replacement (see typical data in Fig. 2). The specific surface is computed from the amount of absorbed MB at the optimum point:

$$[6] \quad S_s = \frac{m_{MB}}{319.87} A_v A_{MB} \frac{1}{m_s}$$

where m_{MB} is the mass of the absorbed MB at the point of complete cation replacement, and m_s is the mass of the soil specimen.

Measurement issues

Various measurement difficulties and biases associated with gas adsorption and methylene blue absorption techniques are explored in this section using selected minerals, and the values are summarized in Table 3.

Gas adsorption

The specific surface measured by gas adsorption is biased by the molecular size of the adsorbate relative to the size of small pores and crevices (pore throats smaller than the adsorbent) and when the topography is fractal. It is important to highlight that the measurement is performed on a dry specimen. Thus, the molecules of the selected gas cannot cover the interlayer surface in expansive layer-silicates (e.g., montmorillonite), which remain tightly bound under dry conditions, rendering low values of specific surface. Results for different mono-ionic montmorillonites presented in Table 3 show that although the N_2 adsorbate can penetrate the interlayer in Al^{3+}

Fig. 2. The determination of the point of complete replacement of cations from the titration curve (data correspond to the Fuller's earth specimen).

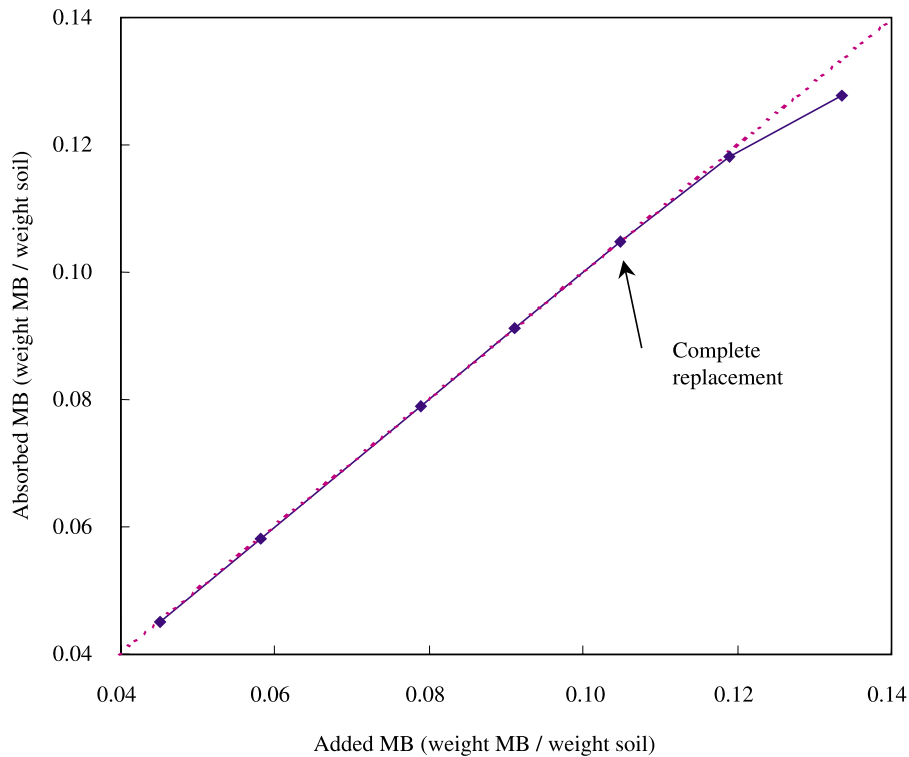


Table 3. Comparison between N₂ adsorption and MB absorption techniques (the presence of swelling minerals should be suspected when the MB measurements are significantly higher than the gas adsorption measurements).

Soil type	S_s (m ² /g)		References
	MB absorption ^a	N ₂ adsorption	
Na-montmorillonite	700 ^b	31	Chen et al. 1999
Al-montmorillonite	509 ^b	37	Chen et al. 1999
Fe-montmorillonite	410 ^b	47	Chen et al. 1999
Georgia Fuller's earth (fines; Oil Dry Corporation of America)	256 ^b	88 ^c	This study
Mexico City clay (without sieving)	230 ^b	40 ^c	This study
Oswego illite	78 ^b	68	Hang and Brindley 1970
Florida kaolinite	35 ^b	33	Hang and Brindley 1970
Delaminated kaolinite	8.6 ^b	5.5	Hang and Brindley 1970
Kaolinite	28 ^d	30	Aringhieri et al. 1992
Georgia kaolin (RP-2; Wilkinson Kaolin Associates)	33 ^b ; (29, 34, 35) ^e	22 ^c	This study

^aAssumed area covered by one molecule = 130 Å².

^bTitration method.

^cMaterials were tested as received. Prior to gas adsorption measurements, the specimens were degassed for approximately 3 h at temperatures between 100°C and 150°C (low temperatures are required for these specimens to prevent mineral alteration).

^dSpot test.

^eSpot tests done by different operators.

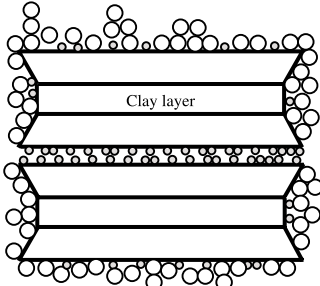
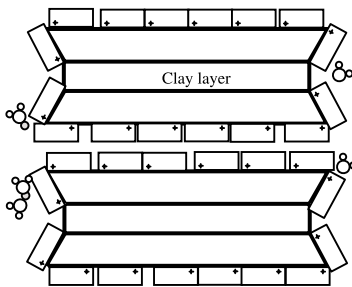
and Fe³⁺ montmorillonites more than in Na⁺ montmorillonite, the measured specific surface remains significantly lower than the surface exposed in wet conditions.

The dry condition is attained by heating and degassing the specimen. The temperature imposed may chemically alter some minerals. For example, degassing ochre for 1 h at 300°C following the standard procedure causes the dehydroxylation of ochre (FeOOH) to hematite (Fe₂O₃) and causes a reduction in specific surface (Klein 1999). Bentonite suffers a similar fate (Zerwer and Santamarina 1994).

Methylene blue absorption

The methylene blue molecule has a rectangular shape with dimensions of approximately 17 Å × 7.6 Å × 3.25 Å. This molecule may attach to the mineral surface in various orientations, so the area covered by one methylene blue molecule may vary: (i) if the molecule lies on its largest face on the surface under study, the covered area is about 130 Å² per molecule (Hang and Brindley 1970; Aringhieri et al. 1992; Chen et al. 1999); (ii) if the molecule is tilted (65–70°) with respect to the surface under study, the covered area is about

Table 4. Schematic representation of gas adsorption (dry) and methylene blue (wet) techniques.

Measurement technique	Schematic representations of interactions between adsorbate and adsorbent at the molecular scale	Sorption characteristics	Area of adsorbate
Gas adsorption		<ul style="list-style-type: none"> • Particle remains neutral with adsorbed counterions • Neutral N₂ attach by van der Waal's forces (physisorption) • Multilayer adsorption can take place • BET Theory • Only the external surface is reached • Limited amount of N₂ can move into interlayer vacancies 	~16.2 Å ²
MB absorption		<ul style="list-style-type: none"> • Counterions are exchanged by methylene blue molecules • Ionic Coulombian attraction develops between MB and the mineral surface (chemisorption) • Primarily monolayer absorption 	~130 Å ²

Note: The case of a swelling clay is described for completeness. Particles are not to scale relative to molecules and ions.

○ Cations ○ N₂ ○ Water □ MB

66 Å² per molecule (Hähner et al. 1996; study on muscovite mica surfaces); and (iii) if the longest axis is oriented perpendicular to the surface, the covered area is about 24.7 Å² per molecule (Borkovec et al. 1993).

The uncertainty in the assumption of the covered area can affect the estimation of specific surface by more than 100%. The most common assumption is that the molecule lies flat on the mineral surface on its largest face; in this case, the area covered by one methylene blue molecule is about 130 Å². Results in this study using kaolin confirm this value.

The amount of absorption increases with surface area and surface charge density, which is affected by pH and ionic concentration. Furthermore, absorption involves ion replacement, which depends greatly on the valence, size, and relative concentration of ions (Mitchell 1993). Test results show that MB cations replace Na⁺ more easily than Fe³⁺ and Al³⁺, therefore MB yields higher specific surface values for Na-montmorillonite compared with Fe-montmorillonite and Al-montmorillonite (see Table 3) (Hang and Brindley 1970; Chen et al. 1999). Similarly, excess salts in the solution not only alter the effective surface charge density, but also compete with methylene blue to be absorbed onto the surface. The dissolution of CaCO₃ and clay particles may influence the accuracy of measurements (Aringhieri et al. 1992). Furthermore, the accuracy of this method is limited by the size of adsorbates.

Test results in Table 3 show that the spot test can produce results similar to those obtained by titration. Operator-related errors in judging the end point may cause ±10% error.

Comparison

The two techniques to measure specific surface described previously involve the sorption of an adsorbate. The methylene blue technique involves high bonding energy (ionic Coulombian attraction – chemisorption) and it is generally limited to a monolayer. In the gas absorption method, gas molecules are attracted to the surface by van der Waals forces (physisorption), and multiple layers may form. Multilayer adsorption is considered in the BET theory used to analyze the experimental results.

The MB absorption method renders higher values of specific surface in swelling clays, as interlayer surfaces can be reached by exchangeable ions after hydration (montmorillonite, Fuller's earth, and Mexico City clay; Table 3). However, for nonswelling clay minerals such as kaolinite, there is no significant difference in specific surface determined with either dry or wet measurement procedures. A schematic, comparative representation of the two methods is presented in Table 4.

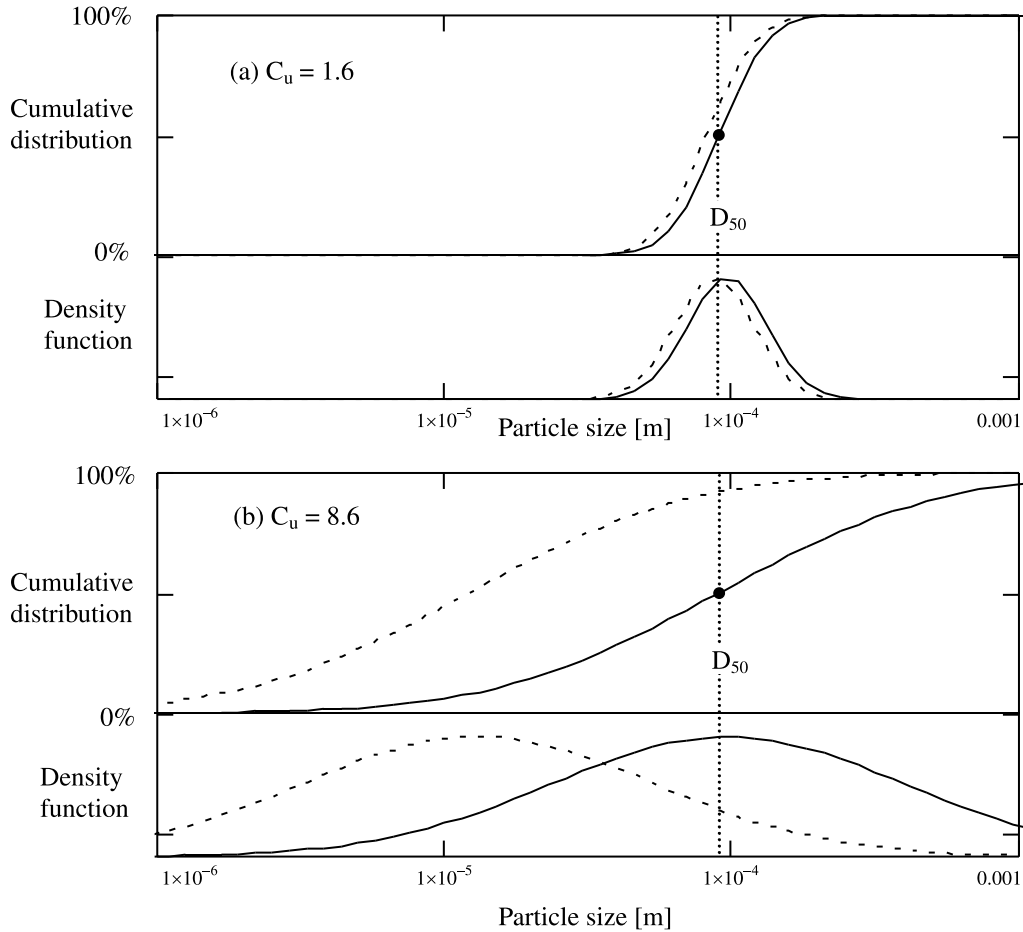
Discussion: relevance and applications

The macroscale engineering behavior of fine-grained minerals is strongly affected by the size and the shape of particles. These two geometric characteristics also determine the specific surface.

Grain-size distribution

Equations in Table 1 highlight the relationship between specific surface and the size of a grain. The specific surface

Fig. 3. Cumulative grain-size (solid line) and specific surface (broken line) distributions and corresponding density functions for three soils with the same D_{50} but different coefficients of uniformity C_u . The prevailing contribution of small particles to specific surface increases with increasing C_u .



of a soil made of spherical or cubical particles, with a cumulative grain-size distribution represented by a straight line in the standard semilogarithmic plot, is

$$[7] \quad S_s = \frac{3(C_u + 7)}{4\rho_w G_s D_{50}}$$

where C_u is the coefficient of uniformity, ρ_w is the mass density of water, G_s is the specific gravity of the minerals, and D_{50} is the particle diameter corresponding to 50% passing. The straight-line distribution assumption enforces the coefficient of curvature to be $C_c = C_u^{-0.2}$. Figure 3 presents the contribution to the total mass and to the total surface of a soil by the different grain-size fractions (both cumulative and density distributions are shown for three soils with the same D_{50}). These results highlight the importance of C_u on specific surface for the same mean particle size: as the coefficient of uniformity increases, a wider range of particle sizes is present and the contribution of the smaller particles to the total surface of the soil increases.

Slenderness

Expressions in Table 1 show that specific surface is determined by the smallest particle dimension, therefore specific surface captures information about the slenderness of parti-

cles (see the note to Table 1). Equation [7] can be extended to platy particles (dimensions $b \times b \times t$, where b is the length and width of the particle and t is the particle thickness), assuming that particles in the given specimen have similar slenderness $\beta = b/t$:

$$[8] \quad S_s = \frac{(C_u + 7)}{4\rho_w G_s D_{50}} (\beta + 2)$$

This equation permits computing the mean slenderness from the measured specific surface and grain-size distribution. For the fine-grained Georgian kaolin documented in Table 3 ($C_u = 9$, $D_{50} = 360$ nm, $S_s = 32$ m²/g), the computed slenderness is $\beta \approx 6$. Particle slenderness increases the potential for anisotropic behavior, promotes strain localization and shear banding, and controls residual strength due to the alignment of platy particles at large strains (Skempton 1985). Results from reversible direct shear tests show that the residual friction angles for montmorillonite, illite, and kaolinite are 5°, 10°, and 15°, respectively. This trend is inversely related to the specific surface and the slenderness of these soils.

Internal porosity

Specific surface measurements using nitrogen gas adsorption for fine- and coarse-grained Fuller’s earth specimens

vary by less than 10%, even though the mean grain size of the coarse-grained specimen ($D_{50} = 2.2 \times 10^{-3}$ m) is approximately 30 times larger than that of the fine-grained specimen ($D_{50} = 7 \times 10^{-5}$ m). This result confirms the presence of an extensive, intercommunicated porous network within the particles in both cases, and confirms that the internal porosity controls the measured specific surface. A similar situation may be found in other natural soil formations that render aggregations and conglomerations.

Atterberg limits

Atterberg limits are the most relevant index properties used for the identification, classification, and description of fine-grained particles and the prediction of fine-grained soil behavior. The limits are measured in terms of water content; for an adsorbed water layer of thickness h , the corresponding water content for platy particles is

$$[9] \quad w = hS_s\rho_w$$

where ρ_w is the density of water. Indeed, the liquid limit (LL) and plastic limit (PL) reflect the specific surface of the soil, the thickness of the diffuse double layer, and the fabric that tends to form under the prevailing pore fluid conditions (Mitchell 1993; Muhunthan 1991). The dependence of LL, PL, plasticity index (PI), and activity on S_s is suggested in the data summarized in Table 2. Farrar and Coleman (1967) developed a relationship between LL and S_s (based on 19 British clays with liquid limits ranging from 28 to 121); in terms of specific surface,

$$[10] \quad S_s = 1.8LL - 34$$

where the units for LL and S_s are percent and m^2/g , respectively.

Conduction and diffusion

Darcy's law prescribes a linear relationship between the seepage velocity v and the gradient i , $v = ki$, where k is the hydraulic conductivity. In the ideal case of flow through a cylindrical tube, the seepage velocity v is given by the Hagen-Poiseuille equation. This model is generalized to porous media as the Kozeny-Carman equation (Perloff and Baron 1976). The Kozeny-Carman equation can be expressed in terms of specific surface to highlight the importance of viscous drag along grain walls:

$$[11] \quad k = \frac{1}{S_s^2} \frac{\theta\gamma_w}{\eta\rho_s^2} \frac{e^3}{1+e}$$

where θ is the shape and tortuosity factor, γ_w is the unit weight of water, ρ_s is the density of the material that makes up the grain, η is the fluid viscosity, and e is the void ratio of the soil. The empirical Hazen equation, $k \propto D_{10}^2$, highlights the dominant contribution of the finer components of the soil which determine specific surface. It follows from the results presented in Fig. 3 that no given size, such as D_{10} in this case, can be unequivocally used to characterize specific surface. An alternative semiempirical equation can be obtained by combining eqs. [7] and [11], resulting in $k \propto (D_{50}^2 \text{ and } C_u^{-2})$.

Other conduction and diffusion phenomena are strongly affected by specific surface. For example, the electrical conductivity of a fine-grained soil saturated with a low ionic

concentration fluid is determined by surface conduction and specific surface. Because the penetration depth of electromagnetic waves decreases with increasing conductivity of the medium, ground penetrating radar (GPR) is often useless in clayey soils, even if the pore fluid has a very low ionic concentration. In the case of diffusion, the sorption of species on particle surfaces causes retardation, and the effective diffusion coefficient is inversely proportional to the specific surface of the soil.

Finally, rich energy coupling phenomena develop in high specific surface soils because of surface-level phenomena. These include electro-osmosis, electro-seismicity, and chemo-osmosis (Mitchell 1993).

Other applications

Results presented earlier in the paper suggest the potential use of specific surface in various geotechnical engineering applications and in the characterization of mineral resources. A few examples are as follows: (i) assessing the extent of internal and interconnected microporosity; (ii) characterizing the average slenderness of fine particles; (iii) computing the charge density on particle surfaces ρ_s (C/m^2), knowing the specific surface S_s (m^2/g) and the cation exchange capacity (CEC; C/g) ($\rho_s \approx CEC/S_s$); (iv) identifying the extent of fines coating coarse particles; in petroleum production, fines coating coarser particles may detach when the pore fluid is changed ("water shock"), migrate, and clog pore throats, thereby causing a dramatic decrease in permeability ("formation damage"); and (v) quality control and process monitoring, including natural and industrial situations such as the evolution of residual soils, cement hydration, pyrometamorphosis of minerals (e.g., ochre, bentonite), and the effectiveness of mineral separation processes; the methylene blue technique is systematically used in mineral processing, such as in the kaolin industry.

The links between Atterberg limits and permeability with specific surface, and causal associations inferred from published correlations, suggest that various engineering properties must be correlated to specific surface, such as the compression coefficient C_c and the coefficient of consolidation c_v .

Conclusions

The specific surface of a soil is a valuable and distinct index property for the characterization of fine-grained soils and particulate minerals. The following conclusions follow from this study:

- (1) The value of specific surface permits inferring the mean slenderness of particles (knowing the grain-size distribution), the extent of particle coating by smaller particles or the extent of interconnected internal particle porosity (knowing the particle diameter), and the surface charge density (knowing the cation exchange capacity).
- (2) In some cases, the determination of the specific surface of a soil can be used as an expeditious measurement in lieu of more cumbersome techniques, such as the determination of a grain size using the hydrometer test (which presumes spherical particles). Thus, the determination of specific surface is a convenient measurement for monitoring industrial processing of minerals.

(3) Specific surface is particularly relevant in the interpretation of a soil response that is significantly affected by surface processes, such as liquid limit, hydraulic and electrical conduction, and chemical diffusion.

(4) In general, the $S_s \approx 1 \text{ m}^2/\text{g}$ boundary suggests a drastic change in the physical–chemical phenomena that take place within a soil. When the specific surface of the soil exceeds $S_s \approx 1 \text{ m}^2/\text{g}$, surface-related forces may control the soil response, alter fabric formation, cause shrinkage in unsaturated conditions, change the small strain stiffness, modify the threshold strain, affect strength, alter internal conduction and diffusion processes, and promote rich energy coupling mechanisms.

(5) The size of the adsorbate and the characteristics of the surface affect the values measured with both gas adsorption (dry) and methylene blue absorption (wet). If swelling minerals are present, measurement methods that use dry specimens underpredict the specific surface of the soil, thus measurement techniques that use aqueous suspensions should be implemented.

(6) The methylene blue spot test is a simple and reliable technique for the determination of the specific surface of soils, including swelling clays. It can be readily implemented in the laboratory.

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References

- Adamson, A.W. 1990. *Physical chemistry of surfaces*. 5th ed. John Wiley & Sons, New York.
- Aringhieri, R., Pardini, G., Gispert, M., and Solé, A. 1992. Testing a simple methylene blue method for surface area estimation in soils. *Agrochimica*, **36**(3): 224–232.
- Borkovec, M., Wu, Q., Degovics, G., Lagner, P., and Sticher, H. 1993. Surface area and size distributions of soil particles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **73**: 65–76.
- Brunauer, S., Emmett, P.H., and Teller, E. 1938. Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, **60**: 309–319.
- Chen, G., Pan, J., Han, B., and Yan, H. 1999. Adsorption of methylene blue on montmorillonite. *Journal of Dispersion Science and Technology*, **20**(4): 1179–1187.
- Cho, G.C., and Santamarina, J.C. 2001. Unsaturated particulate materials — particle level studies. *Journal of Geotechnical and Geoenvironmental Engineering, ASCE*, **127**(1): 84–96.
- Farrar, D.M., and Coleman, J.D. 1967. The correlation of surface area with other properties of nineteen British clays. *Journal of Soil Science*, **18**(1): 118–124.
- Hähner, G., Marti, A., Spencer, N.D., and Caseri, W.R. 1996. Orientation and electronic structure of methylene blue on mica: a near edge X-ray adsorption fine structure spectroscopy study. *Journal of Chemical Physics*, **104**(19): 7749–7757.
- Hang, P.T., and Brindley, G.W. 1970. Methylene blue absorption by clay minerals: determination of surface areas and cation exchange capacities (clay-organic studies XVIII). *Clays and Clay Minerals*, **18**: 203–212.
- Kandhal, P.S., and Parker, F. 1998. Aggregate tests related to asphalt concrete performance in pavements. National Cooperative Highway Research Program NCHRP Report 405.
- Klein, K. 1999. Electromagnetic properties of high specific surface minerals. Ph.D. thesis, Department of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Ga.
- Mitchell, J.K. 1993. *Fundamentals of soil behavior*. 2nd ed. John Wiley & Sons, New York.
- Muhunthan, B. 1991. Liquid limit and surface area of clays. *Géotechnique*, **41**: 135–138.
- Perloff, W.H., and Baron, W. 1976. *Soil mechanics*. John Wiley & Sons, New York.
- Santamarina, J.C., Klein, K.A., and Fam, M.A. 2001. *Soils and waves*. John Wiley & Sons, New York.
- Skempton, A.W. 1985. Residual strength of clays in landslides, folded strata and the laboratory. *Géotechnique*, **35**: 3–18.
- Yong, R.N., and Warkentin, B.P. 1975. *Soil properties and behavior*. Elsevier Scientific Publishing Company, New York.
- Zelazny, L.W., and Calhoun, F.G. 1977. Palygorskite (attapulgite), sepiolite, talc, pyrophyllite, and zeolites. *In Minerals in soil environment*. Edited by J.B. Dixon and S.B. Weed. Soil Science Society of America, Madison, Wis., pp. 435–470.
- Zerwer, A., and Santamarina, J.C. 1994. Double layers in pyromorphosed bentonite: index properties and complex permittivity. *Applied Clay Science*, **9**: 283–291.