

DETERMINATION OF SURFACE AREAS OF MINERAL POWDERS BY ADSORPTION CALORIMETRY¹

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Abstract—Adsorption calorimetry was used to develop a method for determining the surface area of low-surface-area materials ($<1 \text{ m}^2/\text{g}$), which required no pretreatment of the surface, such as outgassing at elevated temperatures. The method involved flowing heptane through a small amount of sample (0.15 to 1.0 g) in the flow cell of a commercial microcalorimeter. When thermal equilibrium was reached at the powder-heptane interface, pure heptane was replaced with a heptane carrier-solution containing 0.6 volume % n-butanol (n-BuOH) as the preferential adsorbate. The integral enthalpy of preferential saturation adsorption, ΔH_{sat} , of n-BuOH on the surface was found to be a function of the BET surface area of the sample. An empirical relationship between ΔH_{sat} and BET surface area was determined over a surface area range of about three orders of magnitude (0.095 to $81 \text{ m}^2/\text{g}$) by performing adsorption experiments on five α -alumina standard reference powders. The technique was applied to the determination of surface areas of untreated rock and mineral powders.

Key Words—Adsorption calorimetry, α -Alumina, n-Butanol, Fracture-filling minerals, Surface area.

INTRODUCTION

A knowledge of the surface area of powdered materials is required in many industrial and scientific applications. In the field of radioactive waste management, for example, the ability of rocks and minerals to act as barriers to the migration of radioactive species from a radioactive waste disposal vault must be determined (Grutter *et al.*, 1986; Sargent and Vandergraaf, 1988). Powdered mineral and rock samples are commonly used to quantify the interactions between aqueous radioactive species and constituents of the geological barrier. A knowledge of the surface areas of the powdered samples is required to distinguish between surface area effects and mineralogical effects when comparing the sorptive capacity of different barrier constituents.

Several methods are commonly used to determine the surface area of powders, including the BET method (Brunauer *et al.*, 1938) and methods using preferential adsorption or adduct formation with polar molecules, such as glycerol (Madsen, 1977), ethylene glycol (Dyal and Hendricks, 1950), or methylene blue (Pham and Brindley, 1970). Adsorption calorimetry (ADCAL) has been suggested for routine surface area determination (Saluja *et al.*, 1987). The method proposed by these authors assumes proportionality between surface area and the enthalpy of integral saturation adsorption, ΔH_{sat} , of n-butanol (n-BuOH) ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CHOH}$) from a n-heptane ($\text{CH}_3(\text{CH}_2)_5\text{CH}_3$) carrier solution. A proportionality constant, k_{SA} , determined from a standard reference material of known BET surface area, is used

to calculate surface areas of powders of similar composition. The main advantages of this technique over more widely used procedures are that measurements can be conducted at room temperature and on $<0.4 \text{ g}$ of sample material (Saluja *et al.*, 1987).

The present paper examines the extension of the ADCAL technique to include mineral powders (1) which have not been previously treated by outgassing at elevated temperatures and (2) which have surface area $<1 \text{ m}^2/\text{g}$. No single proportionality factor was found to be applicable over the range of surface area studied, particularly over the range 0.095 to $0.78 \text{ m}^2/\text{g}$. An empirical calibration curve was therefore generated and applied to the determination of surface areas of several minerals and rock powders pertinent to geological formations proposed for radioactive waste disposal.

EXPERIMENTAL

Standard reference materials

Three standard reference α -alumina powders were obtained from the National Bureau of Standards (NBS), Washington, D.C. The powders had certified BET surface areas of 0.095, 0.283, and $0.78 \text{ m}^2/\text{g}$ (NBS catalog numbers 8007, 8006, and 8008, respectively). Two additional reference aluminas having quoted BET surface areas of 14.1 ± 0.6 and $81.0 \pm 6.2 \text{ m}^2/\text{g}$ were obtained from Duke Scientific of Palo Alto, California, through Mono Research Laboratories of Brampton, Ontario (Mono catalog numbers 387 and 388, respectively).

The reference aluminas were determined by X-ray powder diffraction (XRD) to be primarily α - Al_2O_3 . The XRD patterns of the three samples having the lower surface area indicated the possible presence of sodium

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Table 1. Particle size distribution of α -alumina samples.

0.095 m ² /g ¹ Alumina		0.283 m ² /g Alumina		0.78 m ² /g Alumina		14.1 m ² /g Alumina		81 m ² /g Alumina	
Diameter (μ m)	%	Diameter (μ m)	%	Diameter (μ m)	%	Diameter (μ m)	%	Diameter (μ m)	%
<20	15	<11	13	<5	13	<11	56	<10	34
20–40	25	11–21	14	5–10	40	11–21	32	10–20	35
40–60	13	21–32	49	11–15	40	21–32	8	20–30	17
60–80	26	32–43	21	15–20	7	>32	3	30–40	3
80–100	14	>43	2					40–50	6
>100	8							>50	4

¹ Surface area.

oxide. The material having the largest surface area consisted of ~60% α -alumina and ~40% δ -alumina. The remaining reference material was free from any detectable impurity. The trace amounts of sodium in the aluminas should have no effect on experimentally determined surface areas as the oxide sorption sites for n-butanol bonding are expected to be similar. Particle size distributions were determined by image analysis using scanning electron microscopy (SEM); the results are shown in Table 1. Independent BET surface area measurements for the standard reference materials were obtained from Particle Data Laboratories, Elmhurst, Illinois. These values are listed in Table 2 together with those provided by the suppliers.

The reference alumina powders were used to determine the relationship between BET surface area and ΔH_{sat} of n-BuOH from a heptane-carrier solution.

Mineral and rock powders

The most probable path for aqueous radioactive wastes to take from an engineered disposal vault to the surface is through water-bearing fractures. Therefore, it is essential that the interactions of dissolved contaminants with those minerals commonly found lining the fractures be assessed. The ADCAL procedure was applied to powdered minerals representative of fracture-filling minerals found in granitic rock (Kamineni and Dugal, 1982; Kamineni *et al.*, 1986). The mineral powders were characterized by XRD, X-ray fluorescence, and other standard analytical techniques to determine their composition and purity. In addition to the frac-

ture-filling minerals, the surface areas of powdered samples of granite, gabbro, and basalt were also determined. The source of each mineral and rock sample is given in Table 3, along with the particle size fraction as determined by wet sieving.

Method

Details of the apparatus and the experimental method used were reported by Saluja *et al.* (1987). The published procedure was modified by placing the peristaltic pump downstream of the flow cell to reduce bubble formation and thus improve baseline stability. Typical flow rates ranged from 0.12 to 0.14 ml/min. The amount of sample required to produce a measurable response ranged from 0.15 to 1.0 g.

Determination of the optimum n-butanol concentration

The ΔH_{sat} is dependent on the initial concentration of n-BuOH used as the probe adsorbate. Groszek (1966)

Table 3. Size fraction of minerals and rocks.

Geological material	Source	Size fraction (μ m)
Basalt	Sentinel Gap, Washington	106–180
Gabbro	Rouyn-Noranda, Quebec	106–180
Granite	Lac du Bonnet, Manitoba	106–180
Calcite ¹	Synthetic	<45
Chlorite ²	Yancey County, North Carolina	106–180
Epidote ²	Calumet, Colorado	106–180
Goethite ²	Biwabik, Minnesota	106–180
Gypsum ³	Synthetic	106–180
Illite-muscovite	Cigar Lake, Saskatchewan	75–180
Kaolinite (KGa-1)	Source Clays Repository, The Clay Minerals Society	<45
Hematite ¹	Synthetic	<45
Muscovite ²	Unknown	106–180
Quartz ²	Arkansas	106–180

¹ Fisher Scientific, Winnipeg, Manitoba.

² Ward's Natural Science Establishment, Rochester, New York.

³ Prepared from plaster of paris at Atomic Energy of Canada Limited, Pinawa, Manitoba.

Table 2. Quoted and measured BET surface areas of alumina standard reference materials.

Material	BET surface area (m ² /g)	
	Quoted ¹	Measured ²
α -Al ₂ O ₃	0.095	0.13 ± 0.04
α -Al ₂ O ₃	0.283	0.24 ± 0.01
α -Al ₂ O ₃	0.780	0.67 ± 0.04
Alumina	14.1 ± 0.6	13.1 ± 1.0
Alumina	81.0 ± 6.2	83.8 ± 2.0

¹ By supplier.

² Particle Data Laboratories, Elmhurst, Illinois.

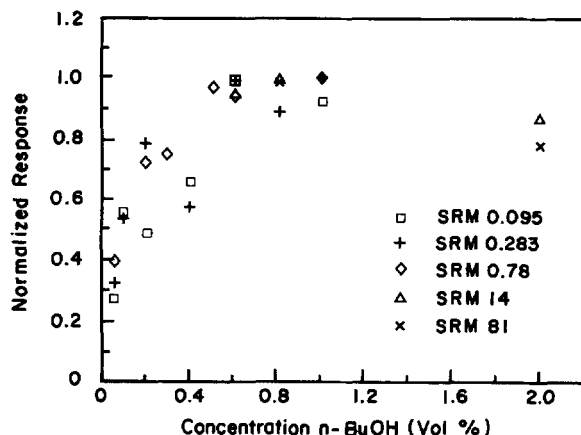


Figure 1. Normalized ΔH_{sat} for adsorption on reference alumina samples as a function of n-butanol concentration.

and Saluja *et al.* (1987) determined the optimum n-BuOH concentration by passing increasingly concentrated n-BuOH solutions (from 0.01 to 0.2 volume %) over a single sample of the reference powder until no further heat production was observed. In the present study, several measurements were made on fresh portions of each reference alumina powder, equilibrated with flowing heptane, to determine the optimum n-BuOH concentration, while ensuring that the measured response was free from complications due to the residual adsorbate.

The range of concentrations examined was 0.05 to 2.0 volume %. The results are shown in Figure 1, in which the response (in J/m²) has been normalized to the largest value measured for each reference alumina.

A concentration of 0.6 volume % n-BuOH in heptane was required to produce the maximum ΔH_{sat} over the range of surface area studied here. Concentrations >0.6 volume % of n-BuOH have less reproducible results if used with the lowest surface area aluminas, but did not significantly increase ΔH_{sat} on the higher surface area reference materials. Therefore, 0.6 volume % of n-BuOH in heptane was used as the standard in

Table 4. Coefficient of saturation sorption (k_{SA}) values and integral heat of saturation adsorption per unit weight (ΔH_{uw}) values determined for reference alumina samples.

Reference alumina	BET surface area (m ² /g)	k_{SA} (m ² /J)		ΔH_{uw} (J/g)
α -Al ₂ O ₃	0.095	28		3.4×10^{-3}
α -Al ₂ O ₃	0.283	21	21.5 ¹	1.35×10^{-2}
α -Al ₂ O ₃	0.78	14		5.57×10^{-2}
α -Al ₂ O ₃	14.1	7.4	7.6 ¹	1.91
α - + δ -Al ₂ O ₃	81	6.1		13.3

¹ Outgassed 20 hr at 105°C, 760 mm Hg vacuum.

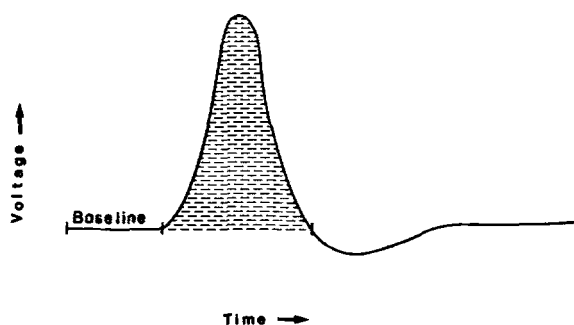


Figure 2. Delineation of adsorption peak area used in calculations.

determining surface areas of the powdered mineral and rock samples.

RESULTS AND DISCUSSION

Adsorption thermograms

Adsorption thermograms for mineral and rock powders in the lower surface area range (0.095 to 0.78 m²/g) typically showed an "overshoot" of the initial baseline as the system returned to equilibrium (Figure 2). The reason for this "overshoot" is not clear, but it may have involved a reverse phenomenon of desorption and replacement of n-BuOH with heptane. In a relative sense, the overshoot does not pose a problem, because the criteria for peak delineation, and thus calculation of the change in enthalpy, was consistent for all experiments. The curve was delineated by extrapolating the initial baseline until it intercepted the opposite side of the peak (Figure 2). The voltage-time curve was then integrated to determine the change in enthalpy produced by n-BuOH adsorption on each sample powder.

Determination of specific surface area

Earlier studies (Groszek, 1966; Steinberg, 1981; Saluja *et al.*, 1987), determined that a proportionality factor, k_{SA} , could be calculated, which was applicable as a surface calibration factor for a given class of adsorbents. Groszek (1966) and Steinberg (1981) reported a k_{SA} value for nonporous oxide powders of 11.5 m²/J. Saluja *et al.* (1987) determined a value of 9.7 m²/J using a SiO₂ standard reference powder and kaolinite KGa-1 with the same adsorbate and carrier solution. Their data suggest that a common proportionality constant can be applied to a wide range of aluminosilicate minerals having surface areas >10 m²/g.

If a discrete value for k_{SA} exists for a given class of adsorbates and mineral powders, the specific surface area (A) can be determined from

$$A \text{ (m}^2\text{/g)} = k_{SA} \text{ (m}^2\text{/J)} \Delta H_{sat} \text{ (J/g)} / w \text{ (g)}, \quad (1)$$

where w is the weight of mineral powder used and ΔH_{sat} is determined from the electrical calibration (Saluja *et al.*, 1987). The present study shows, however, that a

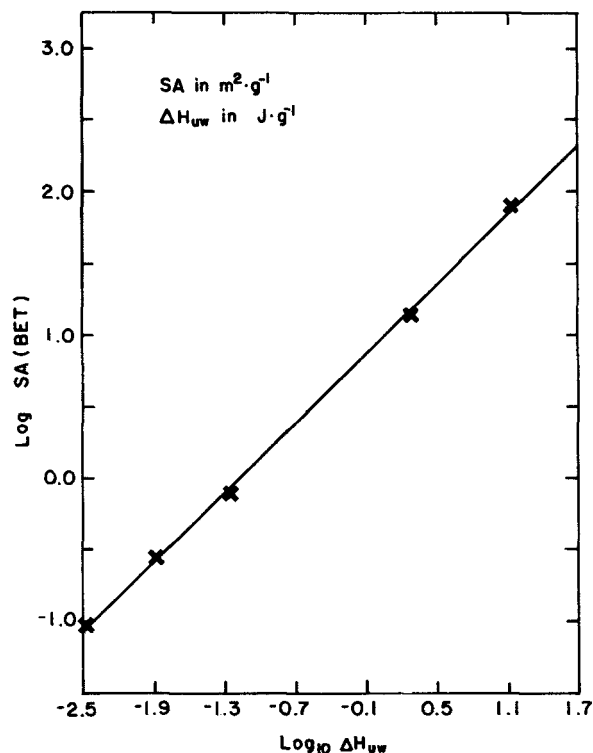


Figure 3. Log ΔH_{uw} vs. log BET surface area for reference alumina samples.

simple, discrete value for k_{SA} cannot be used for untreated alumina powders over the surface area range 0.095 to 81 m²/g. The dependence of k_{SA} on surface area was examined by calculating a proportionality value from Eq. (1) for each of the reference alumina samples. The calculated values (Table 4) are not constant over the entire surface area range used in this study. The ΔH_{sat} was not directly proportional to the increase in the BET surface area. The heat of adsorption per mole of n-BuOH should have remained constant for a given class of powder surfaces; however, sorption site distributions, such as number and types of sorption sites, may not have varied linearly over the three orders of magnitude surface area range studied. For example, steric effects due to the larger ($> 1.5 \times$) size of n-BuOH molecules relative to N₂ or Kr gas adsorbates may have inhibited their ability to reach all sorption sites, in particular, those kinetically hindered and, thus, only partially accessible, during the course of a 10–20-min experiment. The distribution of sorption sites on the powder surfaces having < 1 m²/g surface area may have had a larger fraction of unavailable, or only partially accessible, sorption sites, compared with the fraction on the powder surfaces with surface area > 1 m²/g.

The relationship between the ΔH_{sat} evolved per unit weight (g) of material, abbreviated ΔH_{uw} , vs. the quoted BET specific surface areas of these materials is shown

Table 5. Adsorption calorimetry (ADCAL) and BET specific surface areas for rock types and fracture-filling minerals.

Material	Specific surface area (m ² /g)	
	ADCAL	BET ¹
Basalt	1.4	0.58 ± 0.09
Gabbro	0.55	0.30 ± 0.02
Granite	0.32	0.21 ± 0.06
Calcite	1.2	0.69 ± 0.13
Chlorite	2.6	2.38 ± 0.07
Epidote	0.38	0.21 ± 0.05
Goethite	1.3	1.35 ± 0.01
Gypsum	2.4	1.44 ± 0.16, ² 19.6 ± 1.9 ³
Illite-muscovite	16.3	12.2
Kaolinite (KGa-1)	10.5	8.38 ± 0.19, ⁴ 7.9 ± 0.9, ⁴ 10.1 ⁵
Hematite	14.7	11.8 ± 0.7
Muscovite	6.4	5.2 ± 0.6
Quartz	0.06	0.10 ± 0.05

¹ Determined by N₂ at Particle Data Laboratories, Elmhurst, Illinois.

² Degassed at room temperature.

³ Degassed at 120°C for 5 hr.

⁴ Duplicate samples.

⁵ Value from van Olphen and Fripiat (1979).

in Table 4 and Figure 3. The ΔH_{uw} of each fracture-filling mineral and rock type was experimentally determined. For the three orders of magnitude difference in surface area for five of the reference aluminas, the ΔH_{uw} ranged from 3.4 to 1.33×10^4 mJ/g. The calibration curve, produced empirically from the measurements on the reference aluminas, was used to estimate surface areas of unknown samples assuming similar sorption reactions of n-BuOH with the reference aluminas and unknown rocks and minerals. The surface areas of unknowns were calculated from the simplified equation

$$\log A = a \log \Delta H_{uw} + b, \quad (2)$$

where a and b are constants having the values of 0.812 and 0.956, respectively. The error associated with the calculation is $\pm 10\%$. The calculated ADCAL surface area values are compared with their BET specific surface areas in Table 5. In general, the specific surface areas determined by the modified ADCAL method are in fair agreement with the specific surface areas determined by the BET method.

The kaolinite used in this study (KGa-1) has a reported BET surface area of 10.1 m²/g (van Olphen and Fripiat, 1979). A value of 10.5 m²/g was determined by the ADCAL method described here. For two samples of this clay submitted to Particle Data Laboratories for BET analysis on separate occasions, the specific surface areas were reported as 7.9 ± 0.9 and 8.4 ± 0.2 m²/g. The data in Table 2 show that the BET specific surface areas determined by Particle Data Laboratories for the reference aluminas were lower than the values quoted by the suppliers for the range 0.283

to 14.0 m²/g. Specific surface area determinations by this particular commercial laboratory may give systematically lower values, which may, in part, account for the differences observed in this study. In addition, different adsorbates are known to gain accessibility to different sorption sites (van Olphen and Fripiat, 1979). The n-BuOH and the nitrogen may, in fact, have measured slightly different surfaces in some samples, which could have been a major factor in the observed differences in measured specific surface area.

SUMMARY AND CONCLUSIONS

The use of sorption microcalorimetry as a tool for the measurement of surface area over a three-orders-of-magnitude range has been refined. The current experiments show that for alumina powders the number of sorption sites available to the probe adsorbate is not linearly proportional to the increase in the surface area, particularly for surface areas <1 m²/g. An empirical relationship between BET surface area and the change in saturation adsorption enthalpy per unit weight, ΔH_{uw} , was determined for five standard reference alumina powders (Figure 3). Eq. (2) was derived from this relationship and used to estimate the surface areas of a variety of untreated rock and mineral powder types. The work has demonstrated that the ADCAL method can be used for reliable surface area determinations of untreated mineral powders including those with surface areas <1 m²/g.

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