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Reactive surface of glass particles under aqueous corrosion

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Abstract

Glass dissolution rates are normalized to the glass surface area in contact with solution, and experiments are very often carried out using crushed and sieved materials whose size is narrowed between an upper and a lower value. Surface area of such particles could be determined by gas adsorption or geometric considerations. Although crushed particles cannot be assimilated with simple geometric shapes, rates normalized with—spheres of the same size—geometric surface area are underestimated but are close to those found for polished monoliths. Overestimation of the reactive surface when using gas adsorption measurements is discussed.

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1. Introduction

With the choice of geological repository for nuclear waste glasses, many countries are driven to study aqueous dissolution of glass to assess long-term behavior of glass canisters. Many experimental protocols meant to study glass dissolution mechanisms and kinetics involve particles. Two main methods are currently used to measure their surface area: gas adsorption with application of the BET model¹ or geometrical measurement—assuming glass particles as smooth and non-porous spheres.

Surface areas measured by gas adoption (S_{BET}) are systematically higher than geometric surface areas (S_{geo}) by a factor of 1.6 to 4.5^{2,3}. This gap raise a persisting debate in the community about the best way to evaluate the “reactive surface” of glass particles, defined here as the relevant glass/water interfacial area.

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The quantification of this surface is important for the description and the modeling of interfacial processes such as glass dissolution. This surface area has also a direct influence on the normalized alteration rates measured during leaching tests (commonly expressed in $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$). Previous studies²⁻⁵ concluded that alteration rates normalized to S_{geo} are closer—than those normalized to S_{BET} —to those measured on polished monoliths. However, crushed glass particles are not spherical and their surface irregularities are not taken into account in S_{geo} calculation. Improving the methodology for reactive surface measurement and understanding the difference between S_{BET} and S_{geo} is the objective of this experimental study.

2. Materials and methods

2.1. Glass samples

Two glasses (Table 1) were used in the present study: the international nuclear reference glass (ISG glass) and Type S SiLibeads[®] glass beads (Sigmund Lindner) whose geometry is mastered and produced from soda lime glass by a thermal rounding process. ISG glass powders were obtained by successive crushing and sieving steps. Rectangular monoliths of these two glasses were cut and polished using SiC abrasive papers before a final polishing involving diamond suspensions of 6 μm , 3 μm and 1 μm .

Table 1. International Simple Glass (ISG) and Type S glass compositions expressed in oxide weight percent.

ISG glass	SiO ₂	B ₂ O ₃	Na ₂ O	Al ₂ O ₃	CaO	ZrO ₂
Oxide wt%	56.2±1.5	17.3±0.9	12.2±0.7	6.1±0.8	5.0±0.6	3.3±0.5
Type S glass	SiO ₂	Na ₂ O	CaO	MgO	Al ₂ O ₃	
Oxide wt%	72.5±0.9	13.0±0.8	9.1±0.3	4.2±0.1	0.6±0.2	

2.2. Solid analyses

Surface area measurements. S_{BET} was measured by Kr adsorption on sample surface (Micromeritics ASAP 2020). The estimation of the amount of gas needed to form a monolayer on the solid surface was estimated by the BET model¹. S_{geo} was calculated assuming a spherical geometry for smooth non-porous glass particles with normally distributed sizes: $S_{\text{geo}} = 3/(\rho\cdot R)$ where ρ is the glass density and R the average radius of the particles. S_{geo} of monoliths was determined using a digital caliper (their surface area is far too low to perform S_{BET} measurements).

Atomic Force Microscopy (AFM). A Multimode 8 and Nanoscope V controller (Veeco, Santa Barbara, CA) was used in Tapping Mode (free amplitude ≈ 1 V with RTE SP antimony (n) doped silicium tips, $K = 40$ N·nm⁻¹, $f_0 = 300$ kHz, Bruker) or PeakForce Mode (force ≈ 100 pN with a SNL silicon tip on Nitride lever, $K = 0.35$ N·nm⁻¹, Bruker). Measured topography data were processed by NanoScope Analysis software v1.40 to calculate the difference ΔS between the analyzed region's three dimensional surface area and its two-dimensional, footprint area.

Leaching tests and solution analysis. Glass initial dissolution rates (r_0) were determined by static leaching tests at 90°C. The leaching solution consisted of a KOH solution giving a pH_{90°C} of 10 ± 0.1 , continuously stirred and always sufficiently diluted ($[\text{Si}] < 3$ mg·L⁻¹). Dissolved silica concentrations—used for r_0 calculations—were determined photometrically (Merck Spectroquant[®] Silicate Test, Cary[®] 50 Scan UV-Vis spectrophotometer) with a method analogous to ASTM D859-10.

3. Results and discussion

3.1. S_{BET} vs S_{geo}

For ISG crushed glass particles, the $S_{\text{BET}}/S_{\text{geo}}$ ratio is 2.6 ± 0.2 (Table 2), showing the difference between a smooth, non-porous sphere and a glass particle with a complex shape and presenting surface features accessible to gas atoms. For Type S beads—highly spherical sample (sphericity values of 0.92 to 0.97⁶)—this ratio is reduced to 1.7 ± 0.4 (Table 2), but still higher than 1. This indicates that glass surface present defects accessible to gas atoms, increasing S_{BET} . The difference between S_{BET} and S_{geo} can thus be explained by the existence of a “shape factor” F_s ,

(i.e. the difference between a sphere and the real shape of the particle) and a “roughness factor” F_r due to the sample surface features.

Table 2. Values of S_{BET} and S_{geo} for ISG and Type S glass particles as a function of particle size.

Glass	Size fraction (μm)	S_{BET} ($\text{cm}^2 \cdot \text{g}^{-1}$)	S_{geo} ($\text{cm}^2 \cdot \text{g}^{-1}$)	$S_{\text{BET}}/S_{\text{geo}}$
ISG	20-40	2065	800	2.6
ISG	40-63	1120	466	2.4
ISG	63-125	630	255	2.5
ISG	125-250	345	128	2.7
Type S SiLibeads [®]	90-150	270	200	1.4
Type S SiLibeads [®]	150-250	155	120	1.3
Type S SiLibeads [®]	250-500	125	64	2.0
Type S SiLibeads [®]	500-750	75	38	2.0
Type S SiLibeads [®]	750-1000	51	27	1.9

3.2. Characterization of samples roughness measurable by AFM

For polished monoliths, ΔS (the surface increase due to roughness) is close to 1% (Fig. 1.a). For Type S glass beads (Fig. 1.b), roughness measurements are similar within the same particle size but vary from one granulometry to another. ΔS of Type S glass beads does not exceed 10%—note that the higher ΔS is, the higher is the $S_{\text{BET}}/S_{\text{geo}}$ ratio. AFM analyses are much more difficult to be performed for ISG glass crushed particles (Fig. 1.c) because of the step heights (e.g. conchoidal fractures): the only areas on which a measurement is possible are those located near the upper surface and oriented in parallel to the scanning plane. In such areas, ΔS doesn't exceed 30%. For both types of samples—and despite the non-representativeness of ISG glass particle analyses— ΔS values cannot explain the entire gap between S_{BET} and S_{geo} . This difference could then be explained by the fact that the cross section of a Kr atom (20 \AA^2) is smaller than the AFM tip (10-20 nm). These two “probes” do not have the same size, so they do not address the same defects size scale: surface features taken into account for S_{BET} are predominantly smaller than those achievable for AFM.

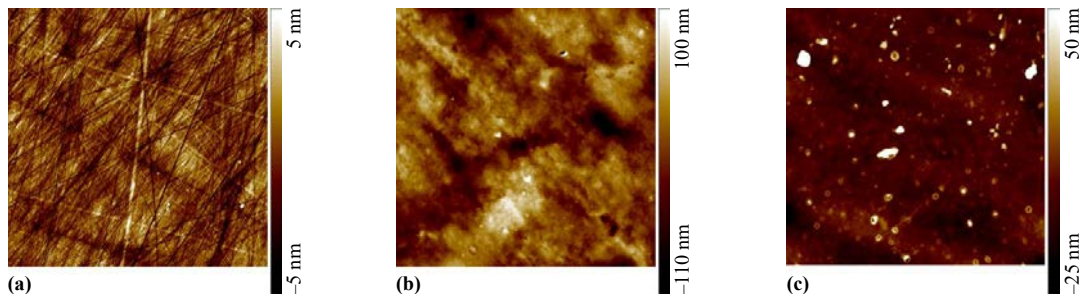


Fig. 1. $10 \mu\text{m} \times 10 \mu\text{m}$ AFM images of (a) ISG glass polished monolith ($\Delta S = 1.0\%$); (b) 500-750 μm Type S glass bead ($\Delta S = 4.6\%$); (c) 63-125 μm ISG glass crushed particle ($\Delta S = 1.1\%$).

3.3. Initial dissolution rate measurements

For ISG glass particles, r_0 measurements (Fig. 2.a) were conducted 5 times on the same 63-125 μm particle batch (relative standard deviation $\text{RSD} = 2.6 \cdot 10^{-2}$), on 5 monoliths ($\text{RSD} = 4.5 \cdot 10^{-2}$), and twice on the three other particle sizes ($\text{RSD} = 8.5 \cdot 10^{-2}$). RSD is lower for tests conducted on the same particle batch (good repeatability of measurements) and is multiplied by ≈ 3 when various glass particle sizes are used. For Type S glass (Fig. 2.b), the measurements were performed twice for each bead size ($\text{RSD} = 13.7 \cdot 10^{-2}$) and on 3 monoliths ($\text{RSD} = 7.4 \cdot 10^{-2}$).

Measurements performed on ISG glass and normalized to S_{geo} are closer to those obtained with monoliths but do not overlap (Fig. 2.a). This overlap is clearly visible for Type S glass beads because of their spherical shape (Fig. 2.b). Fig. 2 indicates that for ISG crushed particles: $F_s = 1.3$, $F_r = 1.9$ and for Type S glass beads: $F_s \approx 1$, $F_r = 1.7$. These results show that surface features accessible to gas atoms—predominantly contributing to S_{BET} —have little effect on the glass dissolution rate, presumably because they are too small to contribute for a significant time to the ingress of water.

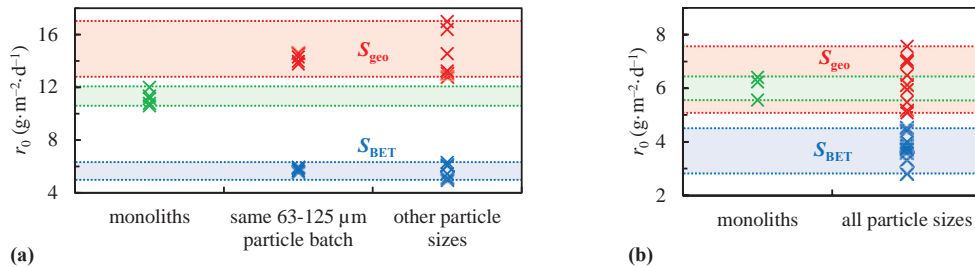


Fig. 2. Comparison of r_0 measurements on (a) ISG glass and (b) Type S glass. r_0 measured on glass particles are normalized to S_{geo} or S_{BET} .

4. Conclusions

The accurate measurement of the external surface of fragmented and non-porous materials—with complex morphologies and roughness—is difficult and the uncertainty of r_0 measurements can reach $\pm 25\%$. Both reasons partly explain why the debate around glass reactive surface is lasting for so long. In order to be compared to the dissolution rate measured on polished monoliths, the rate measured on glass crushed particles ($S_{\text{BET}}/S_{\text{geo}} \approx 2.5$) and normalized to S_{geo} should be divided by 1.3 while the rate normalized to S_{BET} should be multiplied by 1.9.

Both particles shape and their surface state contribute to the difference between S_{BET} and S_{geo} . This difference is mainly explained by surface features accessible to gas atoms. Their nature and the way they interact with water are unknown. It can also be concluded that S_{BET} should be used with caution for glass/water reactive interfacial area measurement.

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