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# Reactive surface of glass particles under aqueous corrosion

Maxime Fournier[a],[*], Michaël Odorico[b], Elodie Nicoleau[a], Aurélien Ull[a], Pierre Frugier[a], Stéphane Gin[a]

*[a]CEA, DEN, DTCD, SECM, F-30207 Bagnols sur Cèze, France*
*[b]ICSM-UMR5257 CEA/CNRS/UM2/ENSCM, Site de Marcoule, BP17171, F-30207 Bagnols sur Cèze, France*

**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 model[1] 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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* Corresponding author. Tel.: +33 466797710.
  *E-mail address:* maxime.fournier@cea.fr

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 $g \cdot m^{-2} \cdot d^{-1}$). Previous studies[2-5] 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 | $SiO_2$ | $B_2O_3$ | $Na_2O$ | $Al_2O_3$ | 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 | $SiO_2$ | $Na_2O$ | CaO | MgO | $Al_2O_3$ | |
| 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 model[1]. $S_{geo}$ was calculated assuming a spherical geometry for smooth non-porous glass particles with normally distributed sizes: $S_{geo} = 3/(\rho \cdot R)$ where $\rho$ 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 RTESP 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 $\Delta S$ 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 $10 \pm 0.1$, continuously stirred and always sufficiently diluted ([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 $S_{BET}/S_{geo}$ ratio is $2.6 \pm 0.2$ (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 0.97[6])—this ratio is reduced to $1.7 \pm 0.4$ (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" $F_s$