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Glass dissolution rate measurement and calculation revisited

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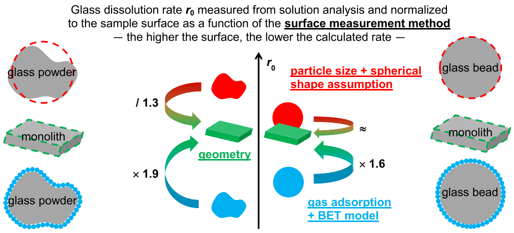
HIGHLIGHTS

- Initial dissolution rates r_0 measured on glass particles or monoliths are compared.
- Repeatability of r_0 measurements and samples preparation procedure is quantified.
- Assimilating powders to spheres is the best way to estimate their reactive surface.
- r_0 (monolith) $=$ 0.8 $\times$ r_0 (powder, normalization to spherical geometric surface area).
- r_0 (monolith) $=$ 1.9 $\times$ r_0 (powder, normalization to BET surface area).

GRAPHICAL ABSTRACT



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ABSTRACT

Aqueous dissolution rate measurements of nuclear glasses are a key step in the long-term behavior study of such waste forms. These rates are routinely normalized to the glass surface area in contact with solution, and experiments are very often carried out using crushed materials. Various methods have been implemented to determine the surface area of such glass powders, leading to differing values, with the notion of the reactive surface area of crushed glass remaining vague. In this study, around forty initial dissolution rate measurements were conducted following static and flow rate (SPFT, MCFT) measurement protocols at 90 °C, pH 10. The international reference glass (ISG), in the forms of powders with different particle sizes and polished monoliths, and soda-lime glass beads were examined. Although crushed glass grains clearly cannot be assimilated with spheres, it is when using the samples geometric surface (S_{geo}) that the rates measured on powders are closest to those found for monoliths. Overestimation of the reactive surface when using the BET model (S_{BET}) may be due to small physical features at the atomic scale—contributing to BET surface area but not to AFM surface area. Such features are very small compared with the thickness of water ingress in glass (a few hundred nanometers) and should not be considered in rate calculations. With a S_{BET}/S_{geo} ratio of 2.5 ± 0.2 for ISG powders, it is shown here that rates measured on powders and normalized to S_{geo} should be divided by 1.3 and rates normalized to S_{BET} should be multiplied by 1.9 in order to be compared with rates measured on a monolith. The use of glass beads indicates that the geometric surface gives a good estimation of glass reactive surface if sample geometry can be precisely described. Although data clearly shows the repeatability of measurements, results must be given with a high uncertainty of approximately ±25%.

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1. Introduction

The vitrification of high level waste from spent fuel reprocessing and the choice of the geological disposal force many countries (France, Japan, United Kingdom, etc.) to study the long term behavior of borosilicate glass waste form [1,2]. Under disposal conditions, the main cause of glass degradation is aqueous dissolution. To assess the environmental impact and ensure the safety of the geological disposal, glass alteration studies are essential. Radionuclide release depends primarily on the glass dissolution rate, which is directly related to the glass surface in contact with water.

Many tests have been standardized to identify waste glass dissolution parameters and mechanisms [3]. These tests—under static or flow rate conditions—simulate a wide variety of experimental conditions and use glass monoliths or powders obtained by crushing. The design of these tests routinely involves the glass surface in contact with the leachant volume as a dimensioning parameter. In addition to experiments, the study of glass long-term behavior uses modeling to access the very long time scales [4,5]. The quality of predictions of geochemical models is particularly dependent on “reactive” surface data to efficiently describe interfacial mechanisms such as dissolution. The “reactive” surface is defined here as the glass-water interfacial area. There is currently no consensus on how to determine this surface area; indeed, such difficulties can be partially explained by the fact that geometric and specific surface areas are rarely equal for physical—e.g. porosity—or chemical—e.g. surface sites reactivity—reasons.

For decades, experimenters determined glass waste form dissolution rates by using powders (e.g. Refs. [6–16]). There are two common ways to estimate glass reactive surface: physisorption of gaseous molecules or geometric considerations. Calculations based on gas molecule physisorption require an estimate of the gas cross sectional area and of the amount of gas necessary to form a monolayer on the powdered sample. The specific surface area is then evaluated by the application of Brunauer-Emmett-Teller (BET) equations [17] to nitrogen or krypton adsorption data.

By assuming particles have a certain geometry (glass grains are usually treated as spheres, or more rarely as cubes [18]), the geometric surface area can be calculated as a function of particle size. Assuming a spherical geometry for smooth non-porous glass grains with normally distributed sizes, the geometric surface area of a particle is calculated using Eq. (1) [19] where S_{geo} is the glass surface ($m^2\ kg^{-1}$), ρ the glass density ($kg\ m^{-3}$) and R the average radius of the particles (m). Note that the estimation of the average radius R requires an—often implicit—assumption on the distribution of the radius of the grains, their surface area or volume. The arithmetic mean $(R_{min} + R_{max})/2$ is the most commonly used; the quadratic mean or other estimators may also be encountered [20].

$$S_{geo} = \frac{3}{\rho \cdot R} \tag{1}$$

Surface measured by the BET method systematically gives higher values than geometric measurements, that lead to a debate in the community about the surface that should be used as the glass “reactive” surface. The S_{BET}/S_{geo} ratio is interpreted to be representative of the irregular shapes and surface roughness of glass particles [21–26]. In the case of glass powders, the extent of S_{BET} can also indicate the presence of finer-grained particles produced by glass crushing and adherent to glass grains of the required size fraction [21,22]. These fine particles develop a large specific surface. Pierce et al. gave S_{BET}/S_{geo} values between 1.6 and 4.5 [21,22,27].

Glass dissolution rate—always announced relatively to the glass surface—is then calculated by mass balance from Eq. (2) [28] where r is the dissolution rate ($g\ m^{-2}\ d^{-1}$), m_i the amount of tracer i leached during the time Δt, m_{i0} the amount of tracer i in the pristine glass and S the so-called glass reactive surface. An iterative version of Eqs. (1) and (2) is used to take into account the evolution of the surface due to the loss of material from the glass over time. These calculations are of primary importance because the maximum release limit of radionuclides is conditioned by the release of glass constituents that are known to be alteration tracers (e.g. for borosilicate waste glass, boron or lithium if present at >1 wt.% [29]). Tracers are not retained in secondary amorphous or crystalline phases formed during glass alteration.

$$r = \frac{m_i}{S \cdot \Delta t \cdot m_{i0}} \tag{2}$$

One wonders what glass surface determination method gives a “true” value for glass dissolution rate, i.e. what is the glass reactive surface area with respect to its dissolution. It is generally considered that the rate calculated from the geometric surface area of monoliths—with at least the two larger sides that are optical-grade polished—is a practical reference. Experiments conducted with SON68 glass (inactive surrogate of French R7T7 nuclear glass) as powders and monoliths in a single-pass flow-through system with the same flow-to-surface area ratio [30] show that the dissolution rate values obtained for powders, with normalization to their geometric surface area, coincide with those obtained for monoliths. In comparison, the rates normalized to BET surface area are slower and generally outside the 2σ experimental uncertainty. The same conclusions were drawn by Inagaki et al. [31] (on the International Simple Glass) and by Pierce et al. [21,22] (on various American low-activity waste glasses) in comparisons of their own experimental data with the literature. Although the experimental evidence cannot be doubted, these results are surprising because glass grains are obviously not spherical and their surface irregularities are not taken into account when calculating the geometric surface area from Eq. (1). Furthermore, it is noted that cases also exist—though they are more rare—where rate calculations normalized to the BET surface area are comparable to rates measured on monoliths [32].

Such questions also exist to determine the reactive surface of natural glasses [33] or crystals [34]. The use of the geometric surface is advised by Wolf-Boenisch et al. [33] (on natural glasses) and Gautier et al. [35] (on quartz grains) because it is considered to be more representative of the reactive surface of such materials. However, Jeschke and Dreybrodt [36] indicate that the dissolution rate of a mineral is related to its morphology: the geometric surface may be used only when the rate constant of the reaction (depending on the reactive surface) is small compared to the mass transport constant D/ε, where D is the diffusion coefficient in the thickness ε of the alteration layer.

In this paper, initial dissolution rates measured on glass particles and monoliths were compared. The initial dissolution rate was chosen because it is the most favorable glass alteration regime for precise rate measurements. Rates determined on particle samples were normalized to geometric or specific surface areas measured by gas adsorption. The aim of the authors is to give quantitative elements for the comparison of results achieved by the international teams working on the subject, according to their experimental protocols. This paper also considers the uncertainties related to alteration rates measurements. Finally this study gives the opportunity to answer questions related to the relevance of crushing and washing protocols and to the repeatability of rate measurements.