An experimental study of the reactive surface area of the Fontainebleau sandstone as a function of porosity, permeability, and fluid flow velocity

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Over the past several decades, there have been a large number of experimental studies of mineral dissolution and precipitation rates (see White and Brantley, 1995; Oelkers 1996). As a result of these studies, it is now possible to compute the dissolution and, in some cases, the precipitation rates per unit surface area of most major rock forming minerals as a function of temperature, pH, solution composition, and the chemical affinity of the mineral hydrolysis reaction. Application of these advances to the accurate prediction of the rate and extent of reactive transport in natural systems is currently hindered by a poor understanding of the physical properties of rocks, most specifically, the reactive surface area of minerals in natural systems. The goal of this research is to bridge this knowledge gap by measuring the reactive surface area of a simple sandstone as a function of its permeability, porosity, and fluid flow velocity.

Materials and experimental methods

All experiments were performed using cores of Fontainebleau sandstone. This Oligocene sandstone, found in the Ile de France region, is ideally suited for this study because its composition is ~100% quartz, has a well sorted grain size of 250 µm, and has a porosity variation from 2 to 30% and a permeability ranging from 0.1 to 10,000 mD without any noticeable grain size modification. Consequently, the effect of porosity, permeability, and bulk flow velocity on reactive surface area can be studied individually from other parameters (see Bourbie and Zinszner, 1985)

The reactive surface areas of Fontainebleau sandstones cores, 4.5 cm in length and 2.2 cm in diameter, were measured in a single pass plug flow reactor, equipped with a pressure transducer to allow for *in situ* permeability measurement during the experiments. This reactor permits experiments to be performed at constant temperatures up to 150°C and at bulk flow velocities ranging from 1 to 14,000 m/yr. The core is held in a flexible jacket at a ~6 bar confining pressure to prevent fluid from passing around the core during the experiments. A 0.1 m ionic strength reactive fluid with a pH of 10.4 at 80°C comprised of demineralized/degassed H_2O, and reagent grade NaCl and NaOH was passed through the core at constant rate until a constant steady-state outlet silica concentration and permeability is obtained. Experimental results indicate that steady-state is reached in one week or less for each sample. The fluid pressure is kept at a constant 1 bar at the outlet, but it varies with bulk flow velocity and permeability at the inlet. The reactive surface area is obtained by comparing the steady state outlet silica concentration obtained from these experiments to normalized quartz dissolution rates at the same solution composition and temperature using traditional mixed flow reactors.

Preliminary results and discussion

Preliminary results on the effect of fluid velocity on the measured reactive surface area for a sandstone core with a 8.9% porosity and a permeability ranging from 7–93 mD are illustrated in Fig. 1. The results shown in this figure were generated using BET normalized specific quartz dissolution rates computed using equations and parameters reported by Dove (1994). Measurement of the specific dissolution rate of Fontainebleau quartz in the same reactive solutions used for the core experiments is currently in progress, and will be used to refine these results. It can be seen in Fig. 1 that the measured reactive surface area of the Fontainebleau sandstone increases from 54 to 117 cm^{-1} with increasing bulk fluid velocity from 28 to 1383 m/yr. A possible explanation for this increase in reactive surface area

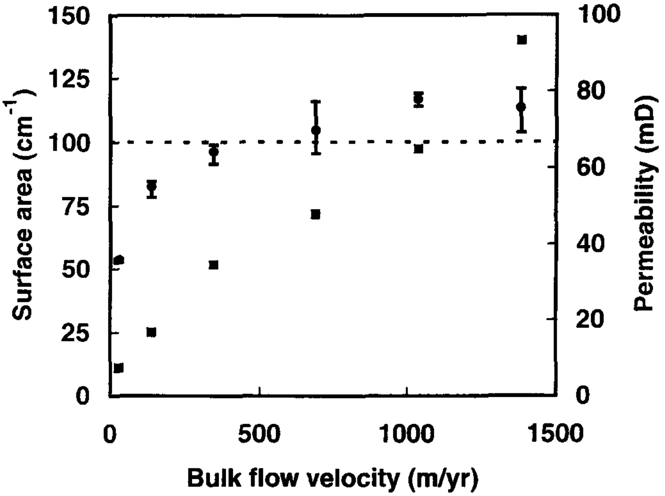

FIG. 1. Variation with bulk fluid velocity of measured reactive surface area and permeability of a Fontainebleau sandstone core with a porosity of 8.9%. The filled circles and squares correspond to measured reactive surface areas and permeabilities, respectively, whereas the dashed line represents a geometrically computed surface area of 100.3 cm^{-1} generated from a model described by Canals and Meunier (1995) – see text.

is that the fluid pressure at the inlet increases with increasing bulk flow velocity, from 1.25 to 4.5 bars. An increased inlet fluid pressure may open additional pathways for fluid flow, thus exposing additional quartz surfaces to the reacting fluid. This possibility is supported by the *in situ* permeability measurements which exhibit a 9 fold increase with increasing bulk flow velocity in these experiments.

Measured reactive surface areas can be compared to those obtained from various theoretical models. Assuming the sandstone consisted of ideal spheres with a diameter of 250 μm, a geometrically estimated surface area of 177 cm^{-1} is obtained. The intergrown sphere model of Canals and Meunier (1995) yields an interfacial surface area of 100.3 cm^{-1}. The semi-empirical Kozeny-Carman (Carman, 1937) equation given by

$$k = \frac{\phi^3}{5s^2(1-\phi^2)} \qquad (1)$$

where k stands for the permeability, s refers to the interfacial mineral surface area, and ϕ designates the porosity suggests a interfacial surface area that *decreases* from 1400 to 400 cm^{-1} with increasing bulk flow velocity flow from 28 to 1383 m/yr. This comparison indicates that the geometric models yield surface areas that are within a factor of 2 of the measured reactive surface area. The best representation is that of the intergrown sphere model, which yields a surface area close to the average of the measured values. In contrast, the Konezy-Carman equation provides a relatively poor estimate of the reactive surface area. One possible origin for this latter discrepancy is that the fluid may not be passing through all of the pores in the rock; if the measured reactive surface areas are used to represent s in Eqn. (1), an effective rock porosity increasing from 1.5 to 3.6% with increasing bulk flow velocity is obtained.

The reactive surface areas of sandstones with a large range of permeability and porosity are being determined. Preliminary results indicate that the reactive surface areas, in general, increases with increasing permeability and increasing porosity. The degree to various theoretical and empirical equations can quantitatively describe measured reactive surface areas will be discussed.

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