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Accessibilities of reactive minerals in consolidated sedimentary rock: An imaging study of three sandstones

Catherine A. Peters *

Department of Civil & Environmental Engineering, Princeton University, Princeton, NJ 08544, United States

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ABSTRACT

Widespread implementation of geological storage of CO_2 requires an understanding of dissolution reactions with formation minerals. This will be aided by reactive transport modeling, which relies on accurate estimates of the accessible surface areas of reactive minerals in consolidated sedimentary rocks. For three Viking sandstones (Alberta sedimentary basin, Canada), we have employed backscattered electron microscopy and energy dispersive X-ray spectroscopy to examine mineral content and to statistically characterize mineral contact with pore space. Porosities range from 20% in a lightly-cemented sandstone with grains on the order of 100 μm, to 8% in a highly-cemented shaly sandstone with a mix of primary pore space and fractures, to 7% in a lightly-cemented conglomerate sandstone with grain sizes between 500 μm and 1 mm. In all three specimens, kaolinite is the primary authigenic clay mineral cementing quartz grains. It accounts for only 5% to 31% of mineral content, but 65% to 86% of pore-mineral contact boundaries. The sandstone specimen has 6% minerals in the "reactive" category, which in this study includes minerals other than kaolinite and quartz, such as K-feldspar, apatite and pyrite. For this specimen, only one third of the reactive minerals are accessible to pore fluids due to clay-mineral grain coatings. For the shaly sandstone, only one fifth of its 5% reactive minerals are accessible to pore fluids due to regions of cementation of fine detrital matrix. Thus, if a mineral volume fraction is used in reactive transport modeling as a proportional measure of accessible surface area in consolidated sandstones, the reaction rates are likely to be overestimated by three to five times. The conglomerate sandstone has only 1% of its mineral matter in this category, and these are often found as inclusions rather than grains.

1. Introduction

Under the high pressure conditions that are expected in geological storage of carbon dioxide (Bruant et al., 2002), the solubility of CO_2 in aquifer brines is on the order of 1 $\text{mol}\cdot\text{kg}^{-1}$ (Bachu and Adams, 2003; Duan and Sun, 2003; Portier and Rochelle, 2005). This is substantial in comparison to the 10^{-5} $\text{mol}\cdot\text{kg}^{-1}$ typically found in surface waters. The resulting carbonic acid in deep aquifers will produce acidic solutions, which will dissolve feldspars, zeolites and other aluminosilicates, and precipitate clay minerals and carbonates (Baines and Worden, 2004; Pearce et al., 2004; Giammar et al., 2005). These reactions are important because they will affect the fate of injected CO_2, the pH buffering of acidified brines, and the porosity and permeability of receptor formations and cap rocks.

Reactive transport modeling for geological CO_2 injection into sedimentary formations is uniquely challenging because reaction and flow processes occur in sedimentary rocks (Gaus et al., 2005; Knauss et al., 2005; White et al., 2005; Lagneau et al., 2005; Li et al., 2006; Xu et al., 2007; Andre et al., 2007; Gherardi et al., 2007). Such media is often highly consolidated due to diagenesis that has produced kaolinite and other authigenic clay minerals from acidic alteration of aluminosilicates such as feldspars (Emery et al., 1990; Lanson et al., 2002; Worden and Morad, 2003). These clay minerals accumulate in pore spaces and on grain surfaces because of their small size, contributing to the cementation of sedimentary clastic media and reducing the connection between pore fluids and reactive minerals. This complicates the process of predicting reactions with these minerals. Excellent discussions of the challenges of reactive transport modeling in consolidated media have been presented in the literature (Steefel and Lichtner, 1998; Berkowitz, 2002; Kang et al., 2003), often in the context of nuclear waste disposal and radionuclide migration (Glassley et al., 2002; Spycher et al., 2003; MacQuarrie and Mayer, 2005). Similar issues are important not only for reactive transport modeling but also for reaction path models (Gunter et al., 1993, 2000; Zerai et al., 2006).

Rate laws used in such models are usually obtained from laboratory measurements using crushed mineral samples, and the reported rates are normalized by BET-measured surface areas. The resulting rates are used in the field by multiplying by the mineral surface area in the matrix of interest. Thus, what is needed for field application is a "BET-consistent mineral-fluid interfacial surface area" (Kieffer et al., 1999).

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* Tel.: +1 609 258 5645; fax: +1 609 258 2799.
E-mail address: cap@princeton.edu.

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There has been substantial discussion about the uncertainties associated with measuring and assigning surface areas to minerals, and much of this discussion has centered on the discrepancies between surface areas measured by BET gas adsorption and those deduced from geometric considerations of grain dimensions (Brantley et al., 1999; Brantley and Mellott, 2000; Lüttge, 2005). Surface roughness has been used to account for angularity, internal surface area, and intragrain porosity that is not captured in a geometric representation of a grain (Hodson et al., 1997; White and Brantley, 2003). Uncertainty also exists due to the differences in reactivities of surfaces for a given mineral. Some of the issues that have been raised are the importance of edge surface areas for microporous minerals such as smectites (Metz et al., 2005), non-etch pit surfaces in quartz grains (Gautier et al., 2001), and fresh as opposed to weathered surfaces in feldspars (Anbeek, 1992). Collectively, such studies have pointed to the challenge in quantifying reactive mineral surface areas, even for the ground, impurity-free materials used in the laboratory.

For consolidated media, there is the added complexity of quantifying surface areas for mineralogically heterogeneous materials that are partially cemented. The common approach is for surface area to be calculated from a geometrical calculation of spherical grains with mean grain diameter. The surface area is apportioned according to volume fractions of different minerals, as determined by X-ray diffraction. Often a roughness factor is used, and for clay minerals, surface areas are increased by one or two orders of magnitude to account for their small particle sizes and microporous structure. Lastly, there is often a reduction to account for the variety of reasons that effective surface areas of reactive minerals in consolidated media are much smaller than those estimated by spherical geometry and roughness. Zerai et al. (2006) and Xu et al. (2007) scaled surface areas by 10^{-2} to account for mineral grain coatings, obscuring of minerals, and preferential fluid flow. Gaus et al. (2005) scaled surface areas by 10^{-3} to account for the difference between total and reactive surface areas.

These order-of-magnitude adjustments highlight the mismatch between the high precision of reaction rate constants determined in the laboratory and the broad strokes of guesstimation in applying rate laws in reactive transport modeling for consolidated media. It is uniformly true that modelers acknowledge the large degree of speculation and approximation in parameters related to surface areas. This issue has been addressed in the literature, such as by Kieffer et al. (1999), Jové Colón et al. (2004), Brosse et al. (2005), and Noiriel et al. (2008), all of whom inferred surface areas from dissolution rates in column experiments, by Emmanuel and Berkowitz (2005) who simulated mineral precipitation in a porous medium to examine spatial patterns of porosity changes, and by Fischer and Gaupp (2004) who examined changes in rock surface areas down to the nanometer scale. Given the timely importance of understanding CO_2-rock interactions in geological storage, there is a need to quantify accessible surface areas in sandstones found in sedimentary basins.

In this study, we have taken a different approach to examine the question of accessibilities of reactive minerals in consolidated sedimentary rocks. Through a combination of Backscattered Electron (BSE) microscopy and Energy Dispersive X-ray (EDX) analysis of thin sections, we used image analysis methods to quantify the accessibility of minerals to formation fluids in typical sedimentary sandstones. The main goal is to determine the extent to which mineral accessibility is well represented by measures of mineral abundance, such as volume fraction. This provides insight on how uncertain are the estimates of surface areas that are often used in reactive transport and reaction path models in the context of deep sedimentary formations.

The study was conducted for three different sandstones, allowing comparisons to be drawn related to structural and mineral features. The samples are from the Viking formation in the Alberta sedimentary basin in Canada. For each sandstone sample, thirty to fifty BSE images were generated. An image segmentation algorithm was developed to broadly categorize mineral types. Segmented images were used to statistically relate pore-to-mineral contact to sandstone characteristics such as spatial distribution of clay minerals and structural nature of pore space. This is an extension of a preliminary study presented in Peters et al. (2006).

2. Sedimentary rock samples and sample preparation

The sedimentary rock samples used in this work are clastic sandstones from the Alberta sedimentary basin in western Canada. The sedimentary succession in this basin, and associated lithology and hydrostratigraphy, are described by Bachu et al. (1994). Core samples come from the Viking formation, taken at depths ranging from 500 to 2000 m. This formation is an example of one that would be suitable for geological storage of CO_2 (Bachu and Adams, 2003). Viking sandstones have porosities ranging from 1% to 30% and permeabilities ranging from 0.01 to 1000 mD (Foscolos et al., 1982; Reinson and Foscolos, 1986).

The cores used in this work are from abandoned gas wells. The samples' reference numbers (with short names in parentheses) are 11-27-023-03w4 (3w4), 10-19-056-10w4 (10w4), and 06-32-059-14w5 (14w5). The samples are qualitatively described as sandstone, shaly sandstone, and conglomerate sandstone, respectively. The sample 14w5 may be better labelled as a breccia sandstone due to the large number of angular grains. Specimen preparation, done by FPC Geologic Labs (Dallas, Texas), included sectioning, impregnating with epoxy resin, adhering to rectangular glass slides, and polishing. At Princeton, the VCR IBS/TM250 Ion Beam Sputterer was used to add 25 nm of conductive carbon coating to each slide.

3. Backscattered electron microscopy and image acquisition

The thin sections were imaged using a high-resolution field-emission Scanning Electron Microscope (SEM), the FEI/Philips XL30 FEG-SEM at Princeton's Imaging and Analysis Center, using a beam intensity of 20 kV and a working distance of 15 mm. This SEM is equipped for EDX analysis using the Princeton Gamma-Tech IMIX PTS EDX system.

The SEM was used in backscatter mode to produce BSE maps. In scanning electron microscopy, the amount of electron backscattering is proportional to mean atomic number. BSE images of thin sections of geological samples reveal variations in mineral matter, and allow relative identification of minerals (Dilks and Graham, 1985; Tovey and Krinsley, 1991). The EDX system was used for single-point analysis for identification of specific mineral phases.

For each of the three specimens, two types of BSE images were obtained: a set of larger-scale images to provide information on pore space and a set of smaller-scale images for mineral analysis. For each specimen there were at least five (sandstone and shaly sandstone), and as many as fourteen (conglomerate sandstone) larger-scale images ranging from 21× to 25× magnification with a pixel resolution of 3 to 4 µm. Each image covered 16 mm^2, so the total pore space analysis for each specimen covered at least 80 mm^2. The resolution needed for mineralogical analysis is greater than that needed for porosity analysis. The images used for this purpose had magnification 100× and resolution of 1.8 µm, and the image size was merely 1270 µm by 830 µm. The needed high magnification led to significant variability across images. This was overcome by examining a large number of images. For each specimen, a total of 30 images were analyzed at this magnification, so a substantial total area of 32 mm^2 was analyzed. For all the images, the locations were assigned by randomly locating sites on a rectangular region covering nearly the entire thin section, an area of 2 cm × 3.5 cm.

The image files generated by the FEI microscope software were converted to TIFF images. The pixels in the original image file are rectangular, so the conversion to TIFF (with square pixels) produces images that are compressed by 10% in the vertical direction. We opted not to use an interpolation algorithm to restore the images to the correct aspect ratio, due to the error that would have been introduced. The calculations of percentages of mineral categories and pore