FRACTAL CHARACTERISTICS OF COLLOID DEPOSITION

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ABSTRACT

It is widely accepted that colloids play an important role in the contaminant migration process at present. However, the colloid deposition structure on rock surfaces has scarcely been studied. In this paper, preliminary results for a fractal characterization for colloid deposition in saturated fractures are presented, which consider the pH value, ionic strength, and flow rate of the solution. Under different chemical conditions, deposition behavior obviously changed, and fractal analysis appears to be an effective tool to capture the evolution and general behavior of depositions. Scanning Electron Microscopy (SEM) is used to observe the colloidal growth on granite surfaces and to acquire the visual image on a detailed level. The images are analyzed for their mass fractal dimensions. The influence on colloid fractal deposition is discussed.

Keyword: Colloid Deposition, Fractal, Fracture Medium, DLVO Theory, Heterogeneity, Adsorption Isotherm, Zeta Potential, Contaminant Migration

1   INTRODUCTION

The mobility of hydrophobic contaminants, metals, and radio nuclides through porous media may be enhanced by colloidal materials (for example, clays, silicates, iron oxides, bacteria, viruses, and humic acids) (McGraw, 1996). Therefore, it is necessary to understand the mechanisms that include colloid generation, stability, mobility and deposition.

Filtration effects, which lead to colloid retention, can be thought to eliminate colloids from the aqueous phase and include both physical and chemical interactions and mechanical processes. Colloids deposited on the surface of media are the typical filtration process. In some theoretical models, colloid matrix migration is considered as filtration. The shortage of knowledge about filtration effects causes most transport models to deal with this effect by introducing an empirical factor (Smith & Degueldre, 1993).

Deposition phenomenon is where colloidal particles are retained only if attractive forces dominate when the colloidal particles collide with solid surfaces, with the exception of a gravity sink. The deposition process is divided into two steps: transport and attachment. The transport process is dominated by the advection diffusion equation. Because of the interaction of various influencing factors, such as flow rate, geochemical condition, and colloidal size distribution, the precise description of colloid transport in the subsurface is difficult to achieve at present. The attachment is controlled by the chemical characteristics of colloid particles and rock interfaces as well as the solution chemistry. However, a theoretical model about this complex process has not been developed.

The quantification of the interaction between rock and colloid is fundamental to determining colloid retention. The evaluation of the surface area available for colloid retention is a critical parameter. Considering the high heterogeneity exhibited on granite surfaces because of the presence of different minerals and the pore distributions or roughness, almost no experimental measurements exist, and most of the available data are based on theoretical models (Swanton, 1995).

Deposition phenomena are related to the fractal process, and many such models have been developed to simulate this process (Russ, 1994). Fractal geometry has been used to quantitatively describe gas adsorption onto irregular surfaces (Pfeifer, Avnir, & Farin, 1983). Fractal dimensions can quantify the deposition structure and describe some subjective properties.

As mentioned above, the retention factor is given by batch experiments or theoretical estimations. However, these approaches consider all the filtration effects at once and cannot explain colloidal deposition characteristics on the surface in detail. This paper uses a fractal approach to quantitatively describe the characteristics of colloid deposition.

2 EXPERIMENTAL SECTION

2.1 Experimental Materials

2.1.1 Colloid Material

Fluorescent polystyrene particles with carboxylate functional groups (manufactured by Invitrogen Corporation) were used as model colloids in the following experiments. The particles have a diameter of 1μm are spherical and mono-dispersed.

2.1.2 Fractured Media

Two different granite planes (5mm in height, 40mm in length, and 30mm in width) were used to simulate the granite fracture. The two pieces were packed in the polystyrene container with a 1mm aperture.

2.1.3 Solution Chemistry

NaCl salts (analytical reagent grade) were used to control ionic strength (0, 10^{-3}M). The electrolyte was made by the ionic exchange water. The standard colloid solution was diluted to 20ppm by the electrolyte above. The pH values of solution were 5.67 and 5.75 at 23.6ºC and 29.1ºC respectively when the ionic strength was 0 and 10^{-3}M. The zeta potentials of fluorescent polystyrene particles were -43.2mV and -27.7mV when the ionic strength was 0 and 10^{-3}M, respectively.

2.2 Column Experiment

Transport experiments were performed in the granite column. Before the experiments, a colloid solution was placed in the supersonic device for 20 minutes to eliminate the aggregation. A peristaltic pump was used to pump the solution upwards into the column, and the effluents were collected by the fractional collector (Figure 1). During the experiment, a magnetic stirrer was used to protect colloid particle aggregations. The temperature was kept at 24ºC, and the flow rate was controlled at 30ml/h. Colloidal concentration of the samples was determined by fluorescent spectrophotometer (RF-5300PC Shimadzu Corporation).
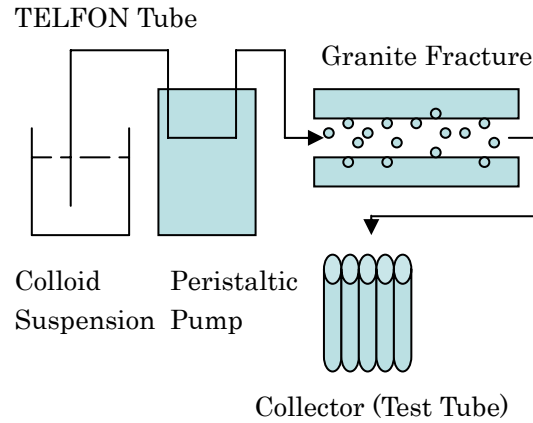
Figure 1. Experimental Column Equipment

2.3 Surface Measurement

When each experiment was completed, the granite samples were taken out to observe colloidal deposition by SEM-EDX. Because granite does not have a carbon component, SEM-EDX was adjusted to a specific resolution to acquire the carbon distribution with regards to the colloidal distribution as well as the mineral composition information.

3 FRACTAL DIMENSIONAL MEASUREMENT

3.1 Methods of Measuring Fractal Dimension

Fractal objects generally have a noninteger dimension less than the corresponding Euclidean (topological) dimension. Fractal dimension does not necessarily imply any potential mechanism of deposition generation, and it represents an attempt to estimate a spatial property of particle deposition (Smith, Lange, & Marks, 1996).

Various definitions for fractal dimension exist, such as similarity dimension, Hausdorff dimension, box dimension,and Minkowski dimension, but they can acquire the similar information from the same fractal object. The most straightforward method is box dimension. It can be determined by counting the number (N) of "boxes" covering a spatial pattern, as a function of box size (l). Then, the formulation below will be obtained:

$$N(l) = (\frac{L}{l})^D \qquad \text{Eq. (1)}$$

where L refers to the size of the entire spatial domain under consideration and D is box dimension.

Scale-dependent dimension is an inherent property of natural fractal structure. Perfect self-similarity only exists in the mathematic formulation or computer code. This is a fact that fractals in natural objects only represent the limit layer structure. In other words, they cannot be magnified infinitely. Thus, the minimum structure must be determined for a natural fractal.

SEM-EDX can accurately reflect the surface element distribution on a granite surface. Carbon distribution can be determined by adopting a minimum measure to represent the colloid distribution. In this work, all images were 512 by 384, representing 522μm by 392μm. In other words, a pixel represented a colloid particle. Colloid particles were made to equal gray level 0, while the background surface was made to equal gray level 255.

4.   RESULTS AND DISCUSSION

4.1. Breakthrough Curve

Preliminary experimental results are represented as the breakthrough curve in Figure 2. It indicates that colloidal particles have no obvious retention effect although some particles were deposited on the granite fracture.
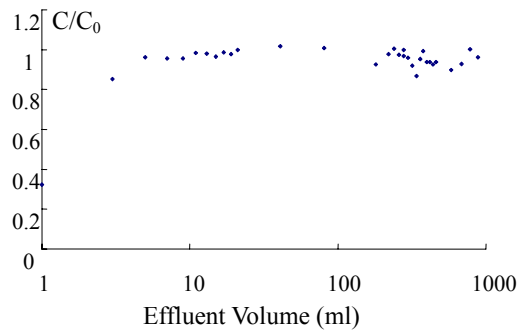

Figure 2. Experimental Breakthrough Curve

4.2. Fractal Morphology

The fractal dimensions determined from a 2-D digitized image of the colloid deposition surface are an objective measure of the spatial complexity. The process of colloid deposition can be captured from statistical aspects using fractal morphology although it cannot give any explanation to the essential properties of evolution process.

4.2.1   Fractal Dimension

Fractal dimensions can quantify the coverage of colloid particles on the granite surface. Some dimension values are given in Figure 3. The linear fitting results undoubtedly indicated the fractal nature of deposition phenomenon. Compared to SEM images, fractal dimensions increase with the surface irregularity. On a region of smooth surface, colloidal deposition behavior has a random trend, and the fractal dimensional value almost becomes 1. In contrast, this value approximates 2 in the rough region. In other words, this dimension can represent the surface irregularity index. The prediction can be made that colloid deposition will sharply increase in natural fracture systems.
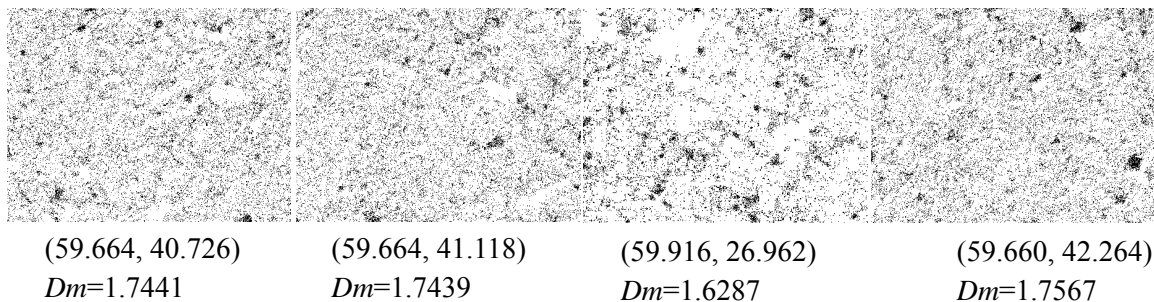

| (59.664, 40.726) | (59.664, 41.118) | (59.916, 26.962) | (59.660, 42.264) |
| Dm=1.7441 | Dm=1.7439 | Dm=1.6287 | Dm=1.7567 |

Figure 3. Colloid distribution in Granite Surfaces, Dm is box dimension. (*X, Y*) is position information

4.2.2   Explanation for Dimension Difference

The reason for the change of dimension values is related to surface charged heterogeneity. The surface charge distribution due to the surface heterogeneity is not uniform and leads to a "favorable site" or "unfavorable site" of colloid deposition.

Heterogeneous charge distribution can be described at both macroscopic and microscopic levels. Microscopic heterogeneity can be explained as the imperfections in the arrangement of ions within the crystal lattice, while macroscopic heterogeneities are the result of differences in surface charge properties of adjacent crystal faces and the presence of bulk or surface-bound chemical impurities (Russ & Russ, 1987). Because of the heterogeneity of surface charge, colloid particles are not adsorbed uniformly at the granite surface. This results in the change of fractal dimensions.

5   CONCLUSION

The observation of SEM-EDX images indicated that colloid particles of $1\mu m$ diameter should be dominated by advection transport because the micro-pore structure is not found in the granite surface. It is believed that colloid deposition on granite surfaces shows the property of fractal geometry. The most promising approach is to build the links between this geometry and surface structure. This link will improve the understanding of the filtration effect. The experimental data is not enough to provide an explanation about some phenomenon including the ionic strength and flow rate influence. This will be completed in future experiments. In addition, colloid deposition behavior on the rough surface will be the focus of future work. It will be necessary to understand the filtration effect.

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