

# FINAL TECHNICAL REPORT<sup>1</sup>

## *Project Title*

Linking Deposit Morphology and Clogging in Subsurface Remediation

## *Funding Agency*

U.S. Department of Energy  
Subsurface Biogeochemical Research Program  
Exploratory Grant, \$150,000, 2011-2013  
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## **1. Executive Summary**

Groundwater is a crucial resource for water supply, especially in arid and semiarid areas of the United States west of the 100<sup>th</sup> meridian. Accordingly, remediation of contaminated groundwater is an important application of science and technology, particularly for the U.S. Department of Energy (DOE), which oversees a number of groundwater remediation sites from Cold War era mining. Groundwater remediation is complex, because it depends on identifying, locating, and treating contaminants in the subsurface, where remediation reactions depend on interacting geological, hydrological, geochemical, and microbiological factors. Within this context, *permeability* is a fundamental concept, because it controls the rates and pathways of groundwater flow. Colloid science is intimately related to permeability, because when colloids are present (particles with equivalent diameters between 1 nanometer and 10 micrometers), changes in hydrological or geochemical conditions can trigger a detrimental reduction in permeability called *clogging*. Accordingly, clogging is a major concern in groundwater remediation. Several lines of evidence suggest that clogging by colloids depends on (1) colloid deposition, and (2) deposit morphology, that is, the structure of colloid deposits, which can be quantified as a fractal dimension. This report describes research, performed under a 2-year, exploratory grant from the DOE's Subsurface Biogeochemical Research (SBR) program. This research employed a novel

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<sup>1</sup> This report contains no patentable material or protected data.

laboratory technique to simultaneously measure flow, colloid deposition, deposit morphology, and permeability in a flow cell, and also collected field samples from wells at the DOE's Old Rifle remediation site. Field results indicate that suspended solids at the Old Rifle site have fractal structures. Laboratory results indicate that clogging is associated with colloid deposits with smaller fractal dimensions, in accordance with previous studies on initially clean granular media. Preliminary modeling has identified the deposit radius of gyration as a candidate variable to account for clogging as a function of (1) colloid accumulation and (2) deposit morphology.

## 2. Technical Summary

### 2.1. Goals, Objectives, and Accomplishments

The goals of this project were as follows:

- (1) Develop a novel technique to measure the fractal dimension of colloid deposits.
- (2) Study the relationship between deposit fractal dimension and clogging.
- (3) Develop a new modeling approach to quantify results.

Goal 1 has been accomplished with a novel application of static light scattering in refractive index matched (RIM) porous media. Goal 2 has been accomplished through a suite of filtration experiments in which a constant concentration of suspended colloids was pumped into a column of RIM porous media over a range of hydrological (*i.e.*, fluid velocity) and geochemical (*i.e.*, ionic strength) conditions. Results indicate that clogging is associated with colloid deposits with smaller fractal dimensions. Goal 3 remains the subject of ongoing work, but preliminary modeling has identified the deposit radius of gyration as a candidate variable to account for clogging as a function of colloid accumulation and deposit morphology.

### 2.2. Summary of Project Activities

This research investigated the hypotheses that colloid deposit fractal dimension could serve as a unifying variable that captures the related effects of hydrological and geochemical conditions on clogging. The approach was to extend previous work, supported by a Program Development Grant from Lawrence Berkeley National Laboratory, that developed a novel apparatus to measure fractal dimension using static light scattering (SLS) in refractive index matched (RIM) porous media. The porous media was granular Nafion, a nontoxic fluorinated ionomer rendered essentially transparent in a solution of 42% isopropanol and 58% deionized water. The suspended colloids were carboxylate-modified polystyrene microspheres with a diameter of approximately 100 nm, which were destabilized by the addition of  $MgCl_2$ . This combination of fluid, colloids, and salt resulted in a critical coagulation concentration<sup>2</sup> in the range of 1-2 mM.

Along the way, several technical problems were identified and solved. For example, it was observed that Nafion swells in the working fluid, and that the degree of swelling depends on the ionic strength, such that porosity also depends on ionic strength. Accordingly porosity was measured at various ionic strengths by displacing the working fluid from above with a measured volume of vegetable oil. Additionally, a technique for real time measurement of specific deposit was developed using static light scattering data.

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<sup>2</sup> That is, the ionic strength above which colloid aggregation is observed.

Laboratory results confirmed the fractal geometry of colloid deposits within Nafion, showed a consistent pattern of declining fractal dimension with increasing colloid accumulation, and indicated that clogging is associated with deposits having smaller fractal dimensions. These results are consistent with expectations for colloid deposition in initially clean granular media.

In parallel, field samples were collected from the Old Rifle field site in Western Colorado, with assistance from site manager Kenneth Williams. Samples were extracted, packed, shipped to Denver, and analyzed in our SLS apparatus operating in batch mode. Results indicate that the suspended solids did indeed have fractal structures, and it was observed that the well having suffered the most clogging had both the highest concentration of suspended solids and the lowest fractal dimension of the samples analyzed.

This grant provided tuition, fees, salary, and travel support for graduate student Eric Roth, who was selected in a competitive process in Summer 2011. This student performed the lion's share of the research reported here and made six conference presentations: the Subsurface Biogeochemical Research program's PI meeting in 2012 and 2013, the American Chemical Society's Colloid and Surface Science Symposium in 2012 and 2013, and the American Geophysical Union's Fall Meeting in 2012 and 2013.

### 2.3. Products Developed

The background, methods, results and conclusions summarized in this Final Technical Report<sup>3</sup> are covered in full detail in the master thesis of graduate student Eric Roth.<sup>4</sup> This thesis includes the preliminary results presented in six conference presentations,<sup>5</sup> and will form the basis for two refereed publications that are currently in preparation (see §4 Appendix).

This grant also supported two related projects whose goals were translational. First, this grant supported an invited review article in *Reviews of Geophysics*, published by the American Geophysical Union (AGU), which summarized the dynamics of permeability in geologic settings, with particular application to enhanced geothermal energy (EGR).<sup>6</sup> Second, this grant supported a chapter in the book *Clogging Issues Associated with Managed Aquifer Recharge Methods*, published by the International Association of Hydrogeologists (IAH), that explained how hydrologic and geochemical factors impact clogging in managed aquifer recharge.<sup>7</sup>

## 3. Budget Summary

Total spending was approximately \$1000 below the total budget of \$150,000. The only significant difference between budgeted amounts and actual spending was in Section G-6, whose budget included \$15,000 of user fees for the Colorado Advanced Photonics Laboratory, but this facility stopped collecting user fees before the beginning of the grant period. Accordingly, with permission from DOE/SBR Program Officer David Lesmes, these funds were reallocated to salary for PI David Mays and graduate student Eric Roth (and associated fringe benefits) and to travel.

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<sup>3</sup> Uploaded to DOE's E-Link as DOE-CU-Denver-0006962-1.

<sup>4</sup> Uploaded to DOE's E-Link as DOE-CU-Denver-0006962-2.

<sup>5</sup> Uploaded to DOE's E-Link as DOE-CU-Denver-0006962-5 through DOE-CU-Denver-0006962-10.

<sup>6</sup> Uploaded to DOE's E-Link as DOE-CU-Denver-0006962-3.

<sup>7</sup> Uploaded to DOE's E-Link as DOE-CU-Denver-0006962-4 and DOE-CU-Denver-0006962-11.

Section	Category	Budgeted Amount	Actual Spending
A	Senior Personnel	\$12,684	\$20,173
B	Other Personnel	\$34,000	\$40,481
C	Fringe Benefits	\$4,019	\$5,079
E	Travel	\$9,514	\$16,010
G-1	Materials and Supplies	\$10,626	\$8,800
G-2	Publication Costs	\$600	\$0
G-6	Other	\$32,742	\$10,439
I	Indirect Costs	\$45,815	\$47,988
	<b>Totals →</b>	<b>\$150,000</b>	<b>\$148,970</b>

#### 4. Appendix: Products Developed

This section lists Scientific and Technical Information (STI) under award DE-SC0006962. Except as noted, each of these will be made available through the DOE Energy Link (E-Link).

##### *Current Report*

###### DOE-CU-Denver-0006962-1

Mays, D.C. (2013), Linking deposit morphology and clogging in subsurface remediation, Final Technical Report, Subsurface Biogeochemical Research Program, U.S. Department of Energy, Washington, DC.

##### *Academic Thesis*

###### DOE-CU-Denver-0006962-2

Roth, E.J. (2013), Linking colloid deposit morphology and clogging: Insights by measurement of deposit fractal dimension, M.S. thesis, Department of Civil Engineering, University of Colorado Denver, Denver, CO.

##### *Refereed Publications*

###### DOE-CU-Denver-0006962-3

Manga, M., I. Beresnev, E.E. Brodsky, J.E. Elkhoury, D. Elsworth, S. Ingebritsen, D.C. Mays, and C.-Y. Wang (2012), Changes in permeability by transient stresses: Field observations, experiments, and mechanisms, *Reviews of Geophysics*, 50, RG2004, doi:10.1029/2011RG000382.

###### DOE-CU-Denver-0006962-4

Mays, D.C. (2013), Clogging in managed aquifer recharge: Flow, geochemistry, and clay colloids, in Martin, R., ed., *Clogging Issues Associated with Managed Aquifer Recharge Methods*, International Association of Hydrogeologists (IAH) Commission on Managing Aquifer Recharge, Australia, 14-24.

(IN PREPARATION)

Roth, E.J., M.E. Mont-Eton, B. Gilbert, T.C. Lei, and D.C. Mays, Measurement of colloidal phenomena during flow through refractive index matched porous media, in preparation for *Review of Scientific Instruments*.

(IN PREPARATION)

Roth, E.J., M.E. Mont-Eton, T.C. Lei, B. Gilbert, and D.C. Mays, Colloid deposit morphology and clogging in porous media: Fundamental insights through investigation of deposit fractal dimension, in preparation for *Environmental Science and Technology*.

*Conference Presentations*

DOE-CU-Denver-0006962-5

Mays, D.C., E.J. Roth, T.C. Lei, J.B. Ajo-Franklin and B. Gilbert (2012), Colloids, deposits, and clogging in groundwater remediation, Subsurface Biogeochemical Research Program, Principal Investigator Meeting, Washington, DC, April 30-May 2, 2012.

DOE-CU-Denver-0006962-6

Roth, E.J. and D.C. Mays (2012), Linking colloid deposit morphology and clogging via fractal dimension, 86<sup>th</sup> Colloid and Surface Science Symposium, American Chemical Society, Baltimore, Maryland, June 10-13, 2012.

DOE-CU-Denver-0006962-7

Roth, E.J., M.E. Mont-Eton and D.C. Mays (2012) Linking colloid deposit morphology and clogging in porous media, H43E-1407, Fall Meeting, American Geophysical Union, San Francisco, California, December 3-7, 2012.

DOE-CU-Denver-0006962-8

Roth, E.J., J. Ajo-Franklin, T.C. Lei, B. Gilbert, and D.C. Mays (2013), Colloid deposit morphology and permeability of porous media, Terrestrial Ecosystem Science/Subsurface Biogeochemical Research, Joint Investigators Meeting, Potomac, MD, May 14-15, 2013.

DOE-CU-Denver-0006962-9

Roth, E.J. and D.C. Mays (2013), Clogging by colloid deposits: Fluid velocity, ionic strength, and fractal dimension, 87<sup>th</sup> Colloid and Surface Science Symposium, American Chemical Society, Riverside, California, June 23-26, 2013.

DOE-CU-Denver-0006962-10

Roth, E.J. and D.C. Mays (2013), Colloid deposit morphology and clogging in aquifers, reservoirs, filters, and reactors: New insights through categorization with fractal dimension, H13B-1327, Fall Meeting, American Geophysical Union, San Francisco, California, December 9-13, 2013.

DOE-CU-Denver-0006962-11

Mays, D.C. (2013), Clogging in managed aquifer recharge: Hydrodynamics and geochemistry, H11F-1216, Fall Meeting, American Geophysical Union, San Francisco, California, December 9-13, 2013.