Final Technical Report

Federal Agency and Organization: DOE EERE – Geothermal Technologies Program

Recipient Organization: Cornell University
DUNS Number: 872612445
Recipient Address: Cornell University, Olin Hall Rm. 230, Ithaca, NY, 14583

Award Number: DE-EE0006764
Project Title: A reactive tracer method for predicting EGS reservoir geometry and thermal lifetime: development and field validation
Project Period: 09/30/2014 to 3/31/2021
Principal Investigator: Jefferson Tester
Professor of Sustainable Energy Systems
Cornell University

Date of Report Submission: 14 December 2020 (original submission) / February 2022 (revised submission)

Project Partners:
Matthew Becker (no cost-sharing)
AltaRock staff (no cost-sharing)
Peter Rose (no cost-sharing)

DOE Project Team: DOE Contracting Officer – Laura Merrick
DOE Project Officer – William Vandermeer
Project Monitor – Alexandra Prisjatschew

NB - Added Disclaimer language and acknowledgement on next page

Jefferson W. Tester
Signature ______________________

Date__15 February 2022_____________

Authors of the final report

Adam J. Hawkins and Jefferson W. Tester
DOE disclaimer

Acknowledgements

The information, data, or work presented herein was funded in part by the Office of Energy Efficiency and Renewable Energy (EERE), U.S. Department of Energy, Geothermal Technologies Office, under Award Number DE-EE0006764. We also appreciate contributions provided by members of Cornell's geothermal research group. Initial development and testing of the C-dot tracers used in field testing by Emmanuel Giannelis, Lawrence Cathles, Laura Sinclair, and X. Zhou. Other important contributions included assistance with theoretical modeling by Don Fox and Don Koch; laboratory experiments to characterize tracer kinetics by Jay T. Bender, Robbie D. Grooms, Colette J. Schissel, and Gloria Xiang Gu; and assistance with the field work at the Altona site from Koenraad Beckers, Maciej Lukawski, Ivan Beentjes, George Schnaars, and more. In addition, the authors are grateful for the contributions to our project provided by a number of external collaborators. These include Matthew Becker at the California State University, Long Beach, Ground Penetrating Radar work by George Tsoflias at the University of Kansas, Roland Horne and Rita Okoroafor at Stanford University, and more. Special thanks to the William H. Miner Agricultural Research Institute in Chazy, New York. Periodic discussions with representatives of the U.S. DOE Geothermal Technology Office also provided helpful guidance during the course of the project.

ABSTRACT

The project summarized here (DOE Award No. DE-EE0006764) was intended to develop a methodology for predicting advective heat transfer in fracture-dominated crystalline rock. Our goal was to determine if a combination of inert and reactive tracers could adequately constrain the effective heat transfer surface area between an injection-production well pair. Our approach consisted of: 1. developing a novel computational framework; 2. Performing heat and tracer experiments at meso-scale; and 3. Comparing predictions of advective heat transfer to the "true" thermal breakthrough measured at the Altona site. Below is a summary of project activities/findings, a summary of project tasks, and a conclusion.

PROJECT ACTIVITIES AND FINDINGS

The novel computational framework consisted of a hybrid finite element/boundary element method for simulating fluid flow, heat transfer, and tracer transport in a discrete rock fracture. This simulator allowed for rapid calculation of heat and mass transfer without sacrificing accuracy. Once the field tests were performed at the meso-scale Altona field laboratory, the novel simulator was used to predict thermal breakthrough using a combination of Principal Component Analysis (PCA) and a Genetic Algorithm (GA). The inverse problem was solved by minimizing an objective function that evaluated the L-squared norm between measured and simulated tracer/pressure measurements.

At the end of the project, several novel insights were gained. The most important insight is that effective heat transfer surface area can be determined by two main methods. The simpler method is to measure inert tracer breakthrough curves and frictional pressure loss between an injector and producer. The theoretical development of this simple method is described in Hawkins et al. (2020) and is demonstrated for a commercial-scale site (Fenton Hill) in Tester et al. (2021).

The second method consists of adsorbing tracer tests combined with inert tracer tests. As discussed in Hawkins et al. (2018) and Wu et al. (2021b) the adsorbing tracer approach enabled adequate forecasting of thermal breakthrough. Additional insights include: 1. Heterogeneous kinetics resulting in >100x increase in reactivity (Hawkins et al., 2021); 2. Rate-limited adsorption preventing retardation of cations relative to anions (Hawkins et al., 2018); 3. The importance of treating hydrodynamic dispersion physically rather than as an empirical fitting parameter (Hawkins et al., 2020); and 4. The mean fracture aperture does not dictate thermal breakthrough, but does influence the system's hydraulic performance (Hawkins et al., 2017b).

Finally, a novel carbon-based nanoparticle was found to behave in an inert/conservative fashion at the Altona field site (Hawkins et al., 2017a, 2020) and at the EGS Collab site (Wu et all., 2021a). This C-Dot nanoparticle is environmentally-benign and easily detected via fluorescence spectroscopy. The methodology of creating these specific C-Dots is described in Sinclair et al. (2020).

PROJECT TASKS

Budget period 1

Budget period 1 largely focused on developing the computational framework (numerical simulator and machine learning algorithm) necessary to interpret field test results in future budget periods. The numerical simulator is a hybrid boundary element/finite element method for discrete rock fracture with non-uniform fracture aperture. The machine learning algorithm solves an inverse problem for non-uniform aperture using a combination of Principal Component Analysis (PCA) and a Genetic Algorithm (GA). The objective function of the inverse search is the L-squared norm between measured and simulated tracer breakthrough curves and the frictional pressure loss measured between injector-producer well pairs.

Budget period 1 consisted of three tasks. Task 1 is titled "Tracer-based fracture geometry inversion" and consisted of applying the inversion routine to synthetic reservoir data. These results are discussed in Fox (2016). Task 2 is titled "Application of inversion method to previously collected tracer data" and the results are discussed in Hawkins et al. (2020). Task 3 is titled "Simulate transient reservoir temperatures from a suite of models" and results for this task are also discussed in Hawkins et al. (2020).

All four milestones listed under Budget period 1 were reached. These included: 1. Applying the inversion method to a known, synthetic fracture aperture distribution; 2. Successful inversion of suite of reservoir models; 3. Correct solution for aperture distribution identified; and 4. Generation of reservoir performance probability graph for Altona.

Budget period 2

The bulk of the field experiments performed as part of this project were completed in Budget period 2. The main tasks included selecting appropriate tracers in advance of the field testing program, recording thermal breakthrough between an injector-producer well pair, and performing inert and reactive tracer tests.

Budget period 2 consisted of three tasks. Task 1 is titled "Selection of appropriate tracer suite and test parameters." In this task, Phenyl Acetate was identified as an ideal thermally-degrading tracer to be used at the Altona site. In addition, adsorbing tracers were used (cesium) and nanoparticle tracers were also used (carbon-dots). In task 2, titled "Field testing at Altona," the heat exchange experiment and tracer experiments were performed at the Altona field site. This consisted of injecting heated fluids (74 °C) continuously for six days. The initial temperature of the production well fluids was about 11 °C and rose to about 30 °C by the end of the six-day test. During the six-day test, four tracer tests were performed using a combination of nanoparticles, cesium, iodide, and phenyl acetate.

The thermally-degrading tracer test results are described in Hawkins et al. (2017a) and in Hawkins et al. (2021). The adsorbing tracer tests are discussed in Hawkins et al. (2018) and in Wu et al. (2021). The nanoparticle field tests are described in Hawkins et al. (2017a, 2020) and Sinclair et al. (2020) describes laboratory-measurements of their behavior in laboratory packed-bed column tests.

All five milestones listed under Budget period 2 were reached. These included: 1. Selection reactive tracers (cesium and phenyl acetate); 2. Thermal breakthrough was recorded at the production well; 3. inert, thermally-degrading, and adsorbing tracer tests were completed at the Altona site; 4. Laboratory analysis of sample concentrations; and 5. Identification of reservoir models that best represent the reservoir structure at Altona.

Budget period 3

Prior to the onset of this project the initial plan in Budget period 3 was to perform an upscaled version of the Altona field tests in a commercial-scale geothermal system. Similarly, the associated computational methods used in interpreting the Altona results were going to be applied to the results of the commercial-scale field tests. The original tasks included: 1. Development of a preliminary set of models for the commercial-scale site and identify appropriate thermally reactive tracer candidates; 2. Collect tracer data from the selected site; 3. Interpret tracer test results; and 4. Give recommendations to the reservoir operators.

Unfortunately, a combination of insufficient funds, geographic limitations imposed by the DOE, and insufficient time prevented the project team from reaching thee five milestones we specified at the beginning of the project. As a result, the project team focused instead on thoroughly investigating several fascinating findings that resulted from the Altona field testing program. These included: 1. Heterogeneous kinetics of phenyl acetate hydrolysis (Hawkins et al., 2021); 2. Rate-limiting kinetics of the adsorbing tracer cesium (Hawkins et al., 2018); and 3. Demonstration of the necessity for joint pressure-tracer inversion (Hawkins et al., 2020).

CONCLUSION

A combination of meso-scale field tests, computational methods, and laboratory experiments demonstrated that tracer tests enable adequate forecasting of thermal breakthrough in fracture-dominated geothermal systems. From the perspective of commercial-scale geothermal systems, perhaps the most impactful finding is that our novel, simple methodology that consists of an inert tracer test and measurements of frictional pressure loss allows for adequate constraints on effective heat transfer surface area. In addition, the data set collected at the Altona site represents a detailed data set consisting of temperature measurements and tracer test results. These data are now publically available via the Geothermal Data Repository (GDR) and will allow for future methods for predicting thermal breakthrough to be evaluated. Other important data sets collected during this project include Ground

Penetrating Radar (GPR), Fiber-optic Distributed Temperature Sensing (FO-DTS), and LIDAR-measurements of the surface topography of the Altona site.

REFERENCES

Fox, D. B., Koch, D. L., and Tester, J. W. (2015), The effect of spatial aperture variations on the thermal performance of discretely fractured geothermal reservoirs. *Geothermal Energy,* 3(1), 1-29. doi:10.1186/s40517-015-0039-z.

Fox, D. B., Koch, D. L., and Tester, J. W. (2016), An analytical thermo-hydraulic model for discretely fractured geothermal reservoirs*.* *Water Resources Research*, 52, 1-26. doi:10.1002/2016WR018666.

Fox, D. B. (2016), *Thermal Hydraulic Modeling of Discretely Fractured Geothermal Reservoirs* (Doctor of Philosophy), Cornell University.

Hawkins, A. J. (2017), *Reactive Tracers for Characterizing Fractured Geothermal Reservoirs* (Doctor of Philosophy), Cornell University.

Hawkins, A. J., Fox, D. B., Becker, M. W., and Tester, J. W. (2017a), Measurement and simulation of heat exchange in fractured bedrock using inert and thermally degrading tracers. *Water Resources Research*, 53, 1210-1230. doi: 10.1002/2016WR019617.

Hawkins, A. J., Becker, M. W., and Tsoflias, G. P. (2017b), Evaluation of inert tracers in a bedrock fracture using ground penetrating radar and thermal sensors. *Geothermics*, 67, 86-94.

Hawkins, A. J., Becker, M. W., & Tester, J. W. (2018), Inert and adsorptive tracer tests for field measurement of flow-wetted surface area. *Water Resources Research,* 54, 5341-5358. https://doi.org/10.1029/2017WR021910.

Hawkins, A. J., Fox, D. B., Koch, D. L., Becker, M. W., and Tester, J. W. (2020), Predictive inverse model for advective heat transfer in a short-circuited fracture: Dimensional analysis, machine learning, and field demonstration. *Water Resources Research*, 56, e2020WR027065. https://doi.org/10.1029/2020WR027065.

Hawkins, A. J., Bender, J. T., Grooms, R. D., Schissel, C. J., and Tester, J. W. (2021), Temperature-responsive smart tracers for field-measurement of inter-well thermal evolution: Heterogeneous kinetics and field demonstration. *Geothermics*, 92, 102046. https://doi.org/10.1016/j.geothermics.2021.102046.

Sinclair, L. et al. (2020), Optimization of fluorescence and surface adsorption of citric acid/ethanolamine carbon nanoparticles for subsurface tracers. *Carbon*, 169, 395-402.

Tester, J. W., Beckers, K. F., Hawkins, A. J., and Lukawski, M. Z. (2021), The evolving role of geothermal energy for decarbonizing the United States. *Energy & Environmental Science*, 14, 6211-6241. https://doi.org/10.1039/D1EE02309H.

Wu, H., et al. (2021a), Characterization of flow and transport in a fracture network at the EGS Collab field experiment through stochastic modeling of tracer recovery. *Journal of Hydrology*, 593, 125888. https://doi.org/10.1016/j.jhydrol.2020.125888.

Wu, H., Fu, P., Hawkins, A. J., Tang, H., and Morris, J. P. (2021b), Predicting thermal performance of an Enhanced Geothermal System from tracer tests in a data assimilation framework. *Water Resources Research*, 57, e2021WR030987. https://doi.org/10.1029/2021WR030987.

APPENDIX A: PROJECT OUTPUT

All project output produced by the project is referenced below and is followed by the abstracts of each peer-reviewed publication. In addition, we have uploaded pdf versions of each peer-reviewed publication to the GTO's Geothermal Data Repository (GDR).

Peer-reviewed Publications:

1. Fox, D. B., Koch, D. L., and Tester, J. W. (2015), The effect of spatial aperture variations on the thermal performance of discretely fractured geothermal reservoirs. *Geothermal Energy,* 3(1), 1-29. doi:10.1186/s40517-015-0039-z.
2. Fox, D. B., Koch, D. L., and Tester, J. W. (2016), An analytical thermo-hydraulic model for discretely fractured geothermal reservoirs. *Water Resources Research*, 52, 1-26. doi:10.1002/2016WR018666.
3. Hawkins, A. J., Fox, D. B., Becker, M. W., and Tester, J. W. (2017a), Measurement and simulation of heat exchange in fractured bedrock using inert and thermally degrading tracers. *Water Resources Research*, 53, 1210-1230. doi: 10.1002/2016WR019617.
4. Hawkins, A. J., Becker, M. W., and Tsoflias, G. P. (2017b), Evaluation of inert tracers in a bedrock fracture using ground penetrating radar and thermal sensors. *Geothermics*, 67, 86-94.
5. Hawkins, A. J., Becker, M. W., & Tester, J. W. (2018), Inert and adsorptive tracer tests for field measurement of flow-wetted surface area. *Water Resources Research,* 54, 5341-5358. https://doi.org/10.1029/2017WR021910.
6. Sinclair, L. et al. (2020), Optimization of fluorescence and surface adsorption of citric acid/ethanolamine carbon nanoparticles for subsurface tracers. *Carbon*, 169, 395-402.
7. Hawkins, A. J., Fox, D. B., Koch, D. L., Becker, M. W., and Tester, J. W. (2020), Predictive inverse model for advective heat transfer in a short-circuited fracture: Dimensional analysis, machine learning, and field demonstration. *Water Resources Research*, 56, e2020WR027065. https://doi.org/10.1029/2020WR027065.
8. Hawkins, A. J., Bender, J. T., Grooms, R. D., Schissel, C. J., and Tester, J. W. (2021), Temperature-responsive smart tracers for field-measurement of inter-well thermal evolution: Heterogeneous kinetics and field demonstration. *Geothermics*, 92, 102046. https://doi.org/10.1016/j.geothermics.2021.102046.
9. Tester, J. W., Beckers, K. F., Hawkins, A. J., and Lukawski, M. Z. (2021), The evolving role of geothermal energy for decarbonizing the United States. *Energy & Environmental Science*, 14, 6211-6241. https://doi.org/10.1039/D1EE02309H.
10. Wu, H., et al. (2021a), Characterization of flow and transport in a fracture network at the EGS Collab field experiment through stochastic modeling of tracer recovery. *Journal of Hydrology*, 593, 125888. https://doi.org/10.1016/j.jhydrol.2020.125888.
11. Wu, H., Fu, P., Hawkins, A. J., Tang, H., and Morris, J. P. (2021b), Predicting thermal performance of an Enhanced Geothermal System from tracer tests in a data assimilation framework. *Water Resources Research*, 57, e2021WR030987. https://doi.org/10.1029/2021WR030987.

Conference Proceedings

1. Fox, D. B., Koch, D. L., and Tester, J. W. (2014), Modeling discretely fractured geothermal reservoirs: A focus on thermal recovery, fracture intersections, and fracture roughness. *Proceedings in* Geothermal Resources Council 38th Annual Meeting.
2. Hawkins, A. J., Fox, D., Zhao, R., Tester, J., Cathles, L., Koch, D., and Becker, M. (2015), Predicting thermal breakthrough from tracer tests: Simulations and observations in a low-temperature field laboratory. *Proceedings in* 40th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA, January 26-28, 2015.
3. Hawkins, A. J., Fox, D., Becker, M., and Tester, J. (2016), Meso-scale field testing of reactive tracers in a model geothermal reservoir. *Proceedings in* 41st Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA, February 22-24, 2016.
4. Christensen, J. N., Hawkins, A., Brown, S. T., Sonnenthal, E., Sturchio, N., and DePaolo, D. J. (2017), The use of ^{222}Rn to constrain fracture characteristics: Experiments conducted at the meso-scale model geothermal reservoir site at Altona, New York. *Proceedings in* 42nd

Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA, February 13-15, 2017.

5. Hawkins, A. J., Fox, D., Becker, M., and Tester, J. (2017c), An inverse model for predicting reservoir structure and thermal lifetime using inert and adsorbing tracers. *Proceedings in* 42nd Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA, February 13-15, 2017.
6. Gu, X, Hawkins, A. J., and Tester, J. W. (2018), Temperature-dependent kinetics of phenyl acetate hydrolysis. *Proceedings in* 43rd Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA, February 12-14, 2018.
7. Hawkins, A., Becker, M., and Tester, J. (2018b), A summary of tracer and thermal tests conducted at the Altona Field Laboratory. *Proceedings in* GRC Transactions, Vol. 42.
8. Bender, J. T., Hawkins, A. J., Grooms, R. D., Schissel, C. J., and Tester, J. W. (2020), Heterogeneous hydrolysis of a thermally degrading tracer. *Proceedings in* 45th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA, February 10-12, 2020.

Graduate Degrees (e.g., Ph. D., M. S., M. Eng.)

1. Zhao, Y. (2015), *The Use of Nanoparticles to Assess Subsurface Flow Heterogeneity* (Doctor of Philosophy), Cornell University.
2. Fox, D. B. (2016), *Thermal Hydraulic Modeling of Discretely Fractured Geothermal Reservoirs*. (Doctor of Philosophy), Cornell University.
3. Zhou, X. (2016), *Kinetics of Phenyl Acetate Tracer for Geothermal System*. (Master of Engineering), Cornell University.
4. Hawkins, A. J. (2017), *Reactive Tracer for Characterizing Fractured Geothermal Reservoirs.* (Doctor of Philosophy), Cornell University.
5. Gu, X. (2018), *Hydrolysis Kinetics of Phenyl Acetate as a Reactive Tracer under Heterogeneous Conditions*. (Master of Science), Cornell University.

Media Reports:

1. https://research.cornell.edu/news-features/beneath-our-feet-geothermal-energy
2. https://www.cheme.cornell.edu/news/smith-school-seniors-take-home-top-honors-aiche-meeting

Networks/Collaborations Fostered (If Applicable):

1. Lawrence Berkeley National Laboratory (LBNL)
    a. Shaun Brown
    b. John Christensen
    c. Eric Sonnenthal
2. Stanford University, Energy Resources Engineering
    a. Prof. Roland N. Horne
    b. Rita Okoroafor
3. Reykjavik Energy
    a. Bjarni Kristjansson
    b. Edda Aradottir
    c. Ingvi Gunnarsson
4. Colorado State University, Fort Collins
    a. Prof. William Sanford
5. Tohoku University

a. Prof. Anna Suzuki

Awards, Prizes, and Recognition (If Applicable):

1. TomKat Center Postdoctoral Fellowship (2016)
    a. Awardee: Adam J. Hawkins
    b. Awarded by: TomKat Center for Sustainable Energy, Stanford University
2. Excellence in Research (2017)
    a. Awardee: Adam J. Hawkins
    b. Awarded by: Earth and Atmospheric Sciences, Cornell University
3. Editor's Choice Award (2018)
    a. Awardee: Adam J. Hawkins and co-authors
    b. Awarded by: Water Resources Research
    c. Awarded for:
        i. Hawkins, A. J., Becker, M. W., and Tester, J. W. (2018), Inert and adsorptive tracer tests for field measurement of flow-wetted surface area. *Water Resources Research*, *54*, 5341-5358. https://doi.org/10.1029/2017WR021910.
4. Undergraduate Student Poster in "Catalysis & Reaction Engineering V" – Third Place (2019)
    a. Awardee: Jay T. Bender
        i. Co-authors: Adam Hawkins; Colette Schissel, Robert Grooms, and Jefferson W. Tester
    b. Awarded by: American Institute of Chemical Engineers (AIChE)
    c. Awarded for: "Homogeneous Hydrolysis of a Thermally-degrading Tracer"
    d. Media: https://www.cheme.cornell.edu/news/smith-school-seniors-take-home-top-honors-aiche-meeting
5. Best E-Poster (2020)
    a. Awardee: Rita Okoroafor
        i. Co-authors: Adam J. Hawkins, Roland N. Horne
        ii. Awarded by: Geothermal Resources Council Annual Meeting
        iii. Awarded for: "Geomechanical considerations in modeling heat extraction from Enhanced Geothermal Systems"

APPENDIX B: JOURNAL PUBLICATION ABSTRACTS

1. Fox et al. (2015):

Fox, D. B., Koch, D. L., and Tester, J. W. (2015), The effect of spatial aperture variations on the thermal performance of discretely fractured geothermal reservoirs. *Geothermal Energy,* 3(1), 1-29. doi:10.1186/s40517-015-0039-z.

Abstract: The effect of spatial aperture variations on the thermal performance of discretely fractured geothermal reservoirs was investigated using finite element method solutions to the convective heat transfer in the fracture coupled with a boundary integral description of conductive heat transfer in the rock. The dipolar flow was generated by a source of fluid volume at an injection well and a sink at a production well within a circular fracture. The statistics of the thermal performance of an ensemble of fracture realizations was evaluated. Fractures with self-affine aperture fields where long range correlations dominant over short range correlations were generated. The results showed that spatial aperture variations most frequently lead to diminished thermal performance by creating flow channeling that reduces the heat transfer area. Enhanced thermal performance occurred in the less common cases when the aperture was small in the region between the wellbores, causing fluid flow to sweep out greater areas of the fracture and extract heat from a larger area. The standard deviation of the apertures had the largest influence on the thermal performance, while the spatial correlation of the aperture played a secondary role. Larger values of the standard deviation led to more adverse thermal performance. For the range of standard deviations investigated, the fraction of fractures exhibiting enhanced thermal performance compared to the base case of no aperture variations ranged from 34 to 49 %. The degradation of thermal performance due to aperture variations was largest when the well bore spacing was a larger fraction of the fracture diameter. Reservoirs consisting of two non-intersecting fractures connected to the same injection and production wells were also modeled. The uneven split of the flow between the reservoirs in this case caused a further deterioration of thermal performance compared with the single fracture reservoirs. However, flow control was able to overcome nearly all of the additional loss of thermal performance for the multi-fracture reservoir.

2. Fox et al. (2016):

Fox, D. B., Koch, D. L., and Tester, J. W. (2016), An analytical thermo-hydraulic model for discretely fractured geothermal reservoirs*. Water Resources Research*, 52, 1-26. doi:10.1002/2016WR018666.

Abstract: In discretely fractured reservoirs such as those found in Enhanced/Engineered Geothermal Systems (EGS), knowledge of the fracture network is important in understanding the thermal hydraulics, i.e., how the fluid flows and the resulting temporal evolution of the subsurface temperature. The purpose of this study was to develop an analytical model of the fluid flow and heat transport in a discretely fractured network

that can be used for a wide range of modeling applications and serve as an alternative analysis tool to more computationally intensive numerical codes. Given the connectivity and structure of a fracture network, the flow in the system was solved using a linear system of algebraic equations for the pressure at the nodes of the network. With the flow determined, the temperature in the fracture was solved by coupling convective heat transport in the fracture with one-dimensional heat conduction perpendicular to the fracture, employing the Green's function derived solution for a single discrete fracture. The predicted temperatures along the fracture surfaces from the analytical solution were compared to numerical simulations using the TOUGH2 reservoir code. Through two case studies, we showed the capabilities of the analytical model and explored the effect of uncertainty in the fracture apertures and network structure

on thermal performance. While both sources of uncertainty independently produce large variations in production temperature, uncertainty in the network structure, whenever present, had a predominant influence on thermal performance.

3. Hawkins et al. (2017a):

Hawkins, A. J., Fox, D. B., Becker, M. W., and Tester, J. W. (2017a), Measurement and simulation of heat exchange in fractured bedrock using inert and thermally degrading tracers. *Water Resources Research*, 53, 1210-1230. doi: 10.1002/2016WR019617.

Abstract: Multicomponent groundwater tracer tests were conducted in a well-characterized field site in Altona, NY using inert carbon-cored nanoparticles and a thermally degrading phenolic compound. Experiments were conducted in a mesoscale reservoir consisting of a single subhorizontal bedding plane fracture located 7.6 m below ground surface contained between two wells separated by 14.1 m. The reservoir rock, initially at 11.78C, was heated using 748C water. During the heating process, a series of tracer tests using thermally degrading tracers were used to characterize the progressive in situ heating of the fracture. Fiber-Optic Distributed Temperature Sensing (FODTS) was used to measure temperature rise orthogonal to the fracture surface at 10 locations. Recovery of the thermally degrading tracer's product was increased as the reservoir was progressively heated indicating that the advancement of the thermal front was proportional to the mass fraction of the thermally degrading tracer recovered. Both GPR imaging and FODTS measurements reveal that flow was reduced to a narrow channel which directly connected the two wells and led to rapid thermal breakthrough. Computational modeling of inert tracer and heat transport in a two-dimensional discrete fracture demonstrate that subsurface characterization using inert tracers alone could not uniquely characterize the Altona field site. However, the inclusion of a thermally degrading tracer may permit accurate subsurface temperature monitoring. At the Altona field site, however, fluid-rock interactions appear to have increased reaction rates relative to laboratory-based measurements made in the absence of rock surfaces.

4. Hawkins et al. (2017b):

Hawkins, A. J., Becker, M. W., and Tsoflias, G. P. (2017b), Evaluation of inert tracers in a bedrock fracture using ground penetrating radar and thermal sensors. *Geothermics*, 67, 86-94.

Abstract: The spatial distribution of fracture/matrix heat exchange was measured while hot water was circulated through a single bedding plane fracture in shallow bedrock. The field site is interpreted here as a simple model for a geothermal reservoir. Thermal breakthrough was recorded at the production well and Fiber-Optic Distributed Temperature Sensing (DTS) monitored temperature in the rock matrix. Conservative tracer tests revealed that the reservoir fluid volume in two separate experiments were nearly identical. Thermal breakthrough measurements, however, revealed that reservoir fluid volume did not correlate to thermal performance because the two experiments encountered different effective areas of heat transfer along the fracture. Ground Penetrating Radar imaging of subsurface tracer transport and DTS corroborate these findings.

5. Hawkins et al. (2018):

Hawkins, A. J., Becker, M. W., & Tester, J. W. (2018), Inert and adsorptive tracer tests for field measurement of flow-wetted surface area. *Water Resources Research,* 54, 5341-5358. https://doi.org/10.1029/2017WR021910.

Abstract: Field tests in a discrete rock fracture validated a combined inert/adsorbing tracer test method to estimate the contact area between fluids circulating through a fracture and the bulk rock matrix (i.e., flow-wetted surface area, A). Tracer tests and heat injections occurred at a mesoscale well field in Altona, NY.

A subhorizontal bedding plane fracture 7.6 m below ground surface connects two wells separated by 14.1 m. Recovery of the adsorbing tracer cesium was roughly 72% less than the inert tracer iodide. Using an advection-dispersion-reaction model in one-dimension, the adsorbing/inert tracer method identified substantial flow channelization. These results are consistent with Ground Penetrating Radar (GPR) and thermal sensors. All characterization methods suggest circulating fluids were concentrated in a narrow, 1–2 m wide channel directly connecting the injection and production well. The inert/adsorbing tracer method identified two flow channels with areas of 28 and 80 m2. A one-dimensional heat transport model predicted production well temperature rises 20.58C in 6 days, whereas measured temperature rise was 17.68C. For comparison, two-dimensional heat transport through a fracture of uniform aperture (i.e., homogeneous permeability) predicted roughly 670 days until production well temperature would rise 17.68C. This suggests that the use of a fracture of uniform aperture to predict heat transport may drastically over predict the thermal performance of a geothermal system. In the context of commercial geothermal reservoirs, the results of this study suggest that combined inert/adsorbing tracer tests could predict production well thermal drawdown, leading to improved reservoir monitoring and management.

<u>6. Sinclair et al. (2020):</u>

Sinclair, L. et al. (2020), Optimization of fluorescence and surface adsorption of citric acid/ethanolamine carbon nanoparticles for subsurface tracers. *Carbon*, 169, 395-402.

Abstract: The tunable fluorescence and biocompatibility of fluorescent carbon nanoparticles (FCNs) makes them appealing tracers in geothermal, environmental, and clinical applications. Here, we address FCNs synthesized from reaction and pyrolysis of citric acid and ethanolamine. We examine the fluorescence and the adsorption of these FCNs as critical parameters that influence their use in applications. FCN fluorescence was observed to develop during pyrolysis and measured at pyrolysis temperatures ranging from 190 to 250°C. Transmission electron microscopy shows that the FCN average diameter of approximately 13 nm is unaffected by pyrolysis temperature. However, pyrolysis temperature strongly affects fluorescence, which peaks at 210°C. The surface hydrophobicity of the FCNs increases with pyrolysis temperature as measured by retention on reverse phase chromatography. Together, these results suggest that particle surface functionalities provide both fluorescence and hydrophilicity, and that these surface functionalities are destroyed with excessive pyrolysis. To examine their surface adsorption, quartz crystal microbalance measurements demonstrate that pyrolysis temperature increases FCN adsorption on mineral surfaces. Surfaces with greater hydrophobicity show greater FCN adsorption. Adsorption is unaffected by the presence of mono- or divalent ions in solution. This suggests adsorption by hydrophobic interaction for the Fe2O3, SiO2, and AlSiO surfaces studied.

<u>7. Hawkins et al. (2020):</u>

Hawkins, A. J., Fox, D. B., Koch, D. L., Becker, M. W., and Tester, J. W. (2020), Predictive inverse model for advective heat transfer in a short-circuited fracture: Dimensional analysis, machine learning, and field demonstration. *Water Resources Research*, 56, e2020WR027065. https://doi.org/10.1029/2020WR027065.

Abstract: Identifying fluid flow maldistribution in planar geometries is a well-established problem in subsurface science/engineering. Of particular importance to the thermal performance of enhanced (or "engineered") geothermal systems is identifying the existence of nonuniform (i.e., heterogeneous) permeability and subsequently predicting advective heat transfer. Here, machine learning via a genetic algorithm (GA) identifies the spatial distribution of an unknown permeability field in a two-dimensional Hele-Shaw geometry (i.e., parallel plates). The inverse problem is solved by minimizing the L2 norm between simulated residence time distribution (RTD) and measurements of an inert tracer breakthrough curve (BTC) (C-Dot nanoparticle). Principal component analysis (PCA) of spatially correlated permeability fields enabled reduction of the parameter space by more than a factor of 10 and restricted the

inverse search to reservoir-scale permeability variations. Thermal experiments and tracer tests conducted at the mesoscale Altona Field Laboratory (AFL) demonstrate that the method accurately predicts the effects of extreme flow channeling on heat transfer in a single bedding-plane rock fracture. However, this is only true when the permeability distributions provide adequate matches to both tracer RTD and frictional pressure loss. Without good agreement to frictional pressure loss, it is still possible to match a simulated RTD to measurements, but subsequent predictions of heat transfer are grossly inaccurate. The results of this study suggest that it is possible to anticipate the thermal effects of flow maldistribution, but only if both simulated RTDs and frictional pressure loss between fluid inlets and outlets are in good agreement with measurements.

8. Hawkins et al. (2021):

Hawkins, A. J., Bender, J. T., Grooms, R. D., Schissel, C. J., and Tester, J. W. (2021), Temperature-responsive smart tracers for field-measurement of inter-well thermal evolution: Heterogeneous kinetics and field demonstration. *Geothermics*, 92, 102046. https://doi.org/10.1016/j.geothermics.2021.102046.

Abstract: Temperature-responsive smart tracers (i.e., "thermally-degrading" or "thermo-sensitive") enable advanced warning of "premature thermal breakthrough" and may therefore improve reservoir management and reduce financial risk. Successful calculation of inter-well fluid temperatures requires that temperature-dependent kinetics are known, which typically result from homogeneous batch reactor experiments. However, recent meso-scale field experiments at the Altona Field Laboratory involving fluid flow in a discretely-fractured reservoir suggest that silica-fluid interfaces may accelerate hydrolysis kinetics. Here, the Arrhenius parameters of phenyl acetate hydrolysis are investigated under heterogeneous reaction conditions in packed-bed column experiments. The breakthrough curve of the reaction product is compared to an inert reference tracer (carbon-cored nanoparticles). Temperatures experienced during field testing ranging from 10 to 40 °C were studied using a phosphate buffer solution to maintain a near-neutral pH, as found in the reservoir. The empirically-determined pre-exponential factor and activation energy values are subsequently used in a first-order kinetic model to improve calculations of effective reservoir temperatures for these meso-scale field tests. The results suggest that hydrolysis reactions can directly monitor reservoir temperatures, but only if the influence of solid-fluid interactions are carefully accounted for.