

3D Study of Gas Hydrate Formation and Dissociation in Porous Media and DEM Modeling of Granular Materials

A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Zaher Asem Jarrar
December 2020

Copyright © 2020 by Zaher Asem Jarrar
All rights reserved.

DEDICATION

To my parents, Asem and Sahab, for their endless love and support, because of them, I am who I am today.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisor Prof. Khalid Alshibli, the Department of Civil and Environmental Engineering, the University of Tennessee- Knoxville (UTK). Prof. Alshibli has always been a source of motivation, enthusiasm, and immense knowledge. His guidance and insights provided me with continual support that inspired this final product. I would also like to thank Prof. Angel Palomino, Prof. Claudia Rawn, and Prof. Riyadh Al-Raoush, for serving on my dissertation committee.

This dissertation was made possible by funding from NPRP grant # NPRP8-594-2-244 from the Qatar national research fund (a member of Qatar Foundation); the Institute for a Secure and Sustainable Environment (ISSE), University of Tennessee-Knoxville, USA; and the US National Science Foundation (NSF) under Grant No. CMMI-1362510. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of funding agencies.

I would like to acknowledge Dr. Mark Rivers for his helpful guidance at the Advanced Photon Source (APS), Argonne National Laboratory (ANL). This dissertation used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. I acknowledge the support of GeoSoilEnviroCARS (Sector 13), which is supported by the National Science Foundation - Earth Sciences (EAR-1634415), and the Department of Energy, Geosciences (DE-FG02-94ER14466).

I would like to acknowledge the help of Dr. Wadi Imseeh for his help and support acquiring data during APS visits, and Jamal Hannun for his help with some of the image processing. I would also like to thank my research colleague at UTK Amirsalar Moslehy and Prof. Alshibli's group research undergraduates for their help and support during the span of my graduate school.

ABSTRACT

Natural methane gas hydrates availability and ongoing rise in demand for energy, motivated researchers to consider gas hydrates as a potential energy source. Production of methane from hydrate-bearing sediments requires hydrate dissociation for releasing mobile methane gas in sediments prior to gas production operations. Fines may migrate through or clog the pore space of sandy sediments depending on the geometry and topology of the pore space. This dissertation employs unique in situ experiments and techniques to gain a comprehensive understanding of the associated physical processes (such as fines migration, clogging and gas driven fracture) and validation of hydrate dissociation models' assumptions. 3D synchrotron micro-computed tomography (SMT) was used to acquire 3D direct visualizations of fines clogging, hydrate formation, hydrate dissociation, and gas driven fracture in porous media that help evaluating optimal conditions for the various gas production strategies. A new high-pressure low temperature flow cell was developed to monitor in-situ hydrate formation and dissociation. Pink beam SMT scanning was used to monitor hydrate formation in a specimen composed of silica sand, water, and Xe gas. Direct measurements of hydrate volume and hydrate surface area suggest that even with a combination of hydrate pore habit formed within the 3D porous media, estimation of hydrate surface area as a linear relation with (hydrate volume)^{2/3} is best for hydrate saturation less than a threshold value depending on the dissociation method and driving force. Furthermore, a new simple and physically-realistic regression model was developed to estimate tortuosity of porous media (saturated and unsaturated) based on geometric tortuosity measurements from 130 3D images of natural unconsolidated sand systems.

The particulate nature of granular materials makes it essential to study the behavior of these distinct particles to gain a fundamental knowledge of the bulk material behavior and characteristics. Fracture of sand particles greatly influences the constitutive relationships and deformation characteristics of natural granular materials. Discrete Element Method (DEM) is a numerical technique that has been widely used to model discontinuous materials. High resolution 3D SMT images along with DEM modelling techniques are used in this dissertation to simulate multiscale in-situ experiments reproducing the actual shape of sand particles. Sand particles are modeled as agglomerates of rigid blocks or sub-spheres to study the evolution and distribution of particle fracture, and particle fracture mechanisms. Results suggest that normalizing calculated stresses with I_{sph} yields better estimates of sand particles tensile strength. Ignoring morphology by modeling sand particles as idealized spheres fails to simulate the fracture behavior of silica sand. The proposed bonded block model (BBM) approach presented in this dissertation was proven to successfully predict load-displacement behavior, fractured particles, fracture pattern, and breakage energy by direct comparison with SMT images. Contact loading conditions, number of contact points, and particle geometry interaction have significant effects on fracture pattern of

particles. Energy dissipating through slippage was found to range between 25% to 35% of the total work input by the external load, and thus should be considered when estimating breakage energy.

TABLE OF CONTENTS

Chapter One General Introduction	1
Motivational Background	2
Dissertation Objectives.....	3
Literature Review	4
Gas Production from Methane Hydrate	4
Hydrate Formation and Dissociation Experimental Studies	6
Hydrate Dissociation Kinetics	7
DEM modeling of Particle Fracture	8
Dissertation Outline	9
References	10
Chapter Two 3D Synchrotron Computed Tomography Study on the Influence of Fines on Gas Driven Fracture in Sandy Sediments	17
Introduction	18
Experimental Setup and Methodology.....	19
3D Synchrotron Micro-Computed Tomography (SMT)	20
Image Analysis	20
Segmentation of the Images	20
Fines Segmentation	21
Local Measurements	21
Representative Elementary Volume (REV).....	21
Local Porosity	22
Local Fines Concentration	22
Tracking of Displacement and Rotation of Sand Particles.....	23
Conclusions.....	23
Acknowledgments	24
References	25
Appendix A: Figures	29
Chapter Three 3D Measurements of Hydrate Surface Area during Hydrate formation and Dissociation in Porous Media using Dynamic 3D Imaging	48
Introduction	50
Materials and Experimental Setup.....	52
3D synchrotron micro-computed tomography (SMT).....	53
Results	54
Image Analysis	54
Initial Hydrate Distribution and Pore Habit	54
Hydrate Formation Experiment.....	55
Hydrate volume and surface area.....	56
Hydrate specific area and dissociation rate	57
Conclusions.....	58
Acknowledgments	59
References	60
Appendix A: Tables	67

Appendix B: Figures	68
Chapter Four New Model for Estimating Geometric Tortuosity of Saturated and Unsaturated Porous Media using 3D Synchrotron Micro-Computed Tomography Imaging	90
Introduction	91
Materials and Methodology	94
3D Synchrotron Micro-computed Tomography (SMT)	94
Materials and Experimental Method	95
Results and Discussion	95
Sand Particles Segmentation.....	95
Wetting and Non-wetting Phases Segmentation.....	96
Particle Morphology and Gradation	96
Tortuosity Measurements	96
Conclusions.....	98
Acknowledgments	98
References	100
Appendix A: Tables	106
Appendix B: Figures	109
Chapter Five Discrete element study of morphology effects on fracture of single sand particles.....	116
Introduction	117
Morphology	118
Discrete element modelling	119
Overview.....	119
Calibration.....	119
Simulations and Stress Calculation	119
Results	120
Conclusions.....	120
Acknowledgments	121
References	122
Appendix A: Tables	126
Appendix B: Figures	127
Chapter Six 3D Evaluation of Sand Particle Fracture using Discrete Element Method and Synchrotron Micro-computed Tomography Images	134
Introduction	135
Experimental Work.....	136
Image Analysis	137
Modeling Approach	137
Model Calibration	139
Fracture of Three-Particle Sand Specimens	141
Breakage Energy.....	142
Conclusions.....	143
Acknowledgments	144
References	145

Appendix A: Tables	150
Appendix B: Figures	152
Chapter Seven Conclusions and Recommendations.....	160
Summary of Major Conclusions.....	161
Recommendations for Future Work.....	162
Vita.....	164

LIST OF TABLES

Table 3-1. Porosity and initial hydrate saturation values for the four sections of the depressurization and thermal stimulation experiments.	67
Table 3-2. Results of multivariable linear regression of dissociation rate for the thermal stimulation experiment.	67
Table 4-1. Summary of the physical properties of the 130 porous media systems used to determine geometric tortuosity.	107
Table 4-2. Results of the nonlinear regression model for geometric tortuosity.	108
Table 5-1. DEM model parameters.	126
Table 6-1. Summary of DEM Model Parameters.	150
Table 6-2. Comparison between experimental and DEM results of the cube and single sand particle experiments.	150
Table 6-3. Comparison between experimental and DEM results of the three-sand particle experiments.	151
Table 6-4. Summary of breakage energy results for the three-particle experiments	151

LIST OF FIGURES

Figure 1-1. Summary of dissertation objectives.	5
Figure 2-1. Experimental setup at Beamline 13D, Advanced Photon Source, Argonne National Laboratory.	29
Figure 2-2. Image post-processing steps: (a) filtered image acquired at energy level higher than Iodine edge (33.269 keV); (b) gas phase binarized image; (c) filtered image acquired at lower energy level than Iodine edge (33.069 keV); (d) solids phase binarized image; (e) three-phase segmented image; (f) labeled sand particles for the 2% kaolinite specimen acquired at the second state of the test (i.e., 0.4 ml was drained out of the sample while injecting CO ₂ at a constant pressure of 27.6 kPa (4 psi), sand is white, brine is grey and gas is black.	30
Figure 2-3. Intensity histogram of a sample image for the initial state when the system was saturated with brine and 4% kaolinite specimen.	31
Figure 2-4. Greyscale image of the third state of the 6% kaolinite specimen where a total of 1.0 ml of brine solution was drained out of the saturated specimen while injecting CO ₂ at a constant pressure of 27.6 kPa. High fines concentration displayed as bright voxels.	32
Figure 2-5. Porosity variation over different cubical volumes of 6% kaolinite specimen.	33
Figure 2-6. Variation of porosity in x-z direction in the initial state and the final state of 0% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700.	34
Figure 2-7. Variation of porosity in x-z direction in the initial state and the final state of 2% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700.	35
Figure 2-8. Variation of porosity in x-z direction in the initial state and the final state of 4% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700.	36
Figure 2-9. Variation of porosity in x-z direction in the initial state and the final state of 6% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700.	37
Figure 2-10. Variation of porosity in y-z direction in the initial state and the final state of 6% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700.	38

Figure 2-11. Porosity histograms for initial state of (a) 0% kaolinite; (b) 2% kaolinite; (c) 4% kaolinite;(d) 6% kaolinite and final state of (e) 0% kaolinite; (f) 2% kaolinite; (g) 4% kaolinite; (h) 6% kaolinite specimens.....	39
Figure 2-12. Variation of fines concentration in x-z direction in the initial state and the final state of 2% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700.	40
Figure 2-13. Variation of fines concentration in x-z direction in the initial state and the final state of 4% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700	41
Figure 2-14. Variation of fines concentration in x-z direction in the initial state and the final state of 6% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700.	42
Figure 2-15. Variation of fines concentration in y-z direction in the initial state and the final state of 6% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700.	43
Figure 2-16. Fine concentration histograms for initial state of (a) 2% kaolinite; (b) 4% kaolinite;(c) 6% kaolinite and final state of (d) 2% kaolinite; (e) 4% kaolinite; (f) 6% kaolinite specimens.....	44
Figure 2-17. Particle displacement for the final state of 6% kaolinite specimen at (a) x-z slice 300; (b) x-z slice 500; (c) x-z slice 700; (d) y-z slice 300; (e) y-z slice 500; (f) y-z slice 700.	45
Figure 2-18. Variation of displacement of particles at the final state of 6% kaolinite specimen for a section near fracture.....	46
Figure 2-19. Particle rotation for the final state of 6% kaolinite specimen at: (a) x-z slice 300; (b) x-z slice 500; (c) x-z slice 700; (d) y-z slice 300; (e) y-z slice 500; (f) y-z slice 700.	47
Figure 3-1. (a) Schematic of the high-pressure low-temperature flow cell; (b) flow cell on stage without thermal insulation; and (c) experimental setup at Beamline 13D of the Advanced Photon Source, Argonne National Laboratory.	68
Figure 3-2. Grain size distribution of ASTM 20-30 sand.	69
Figure 3-3. (a) Hydrate phase boundary and experimental pressure-temperature measurements; and (b) change of temperature, pressure and hydrate equilibrium pressure during hydrate dissociation in the thermal stimulation experiment.....	70
Figure 3-4. Example SMT-P slice images show hydrate formation with time.....	71
Figure 3-5. Hydrate phase segmentation (a) filtered image; (b) hydrate voxels selected; and (c) image histogram.....	72

Figure 3-6. Volume rendering images of hydrate during dissociation for a vertical section of the specimen for the depressurization experiment from beginning of the test to $t = 22.5$ min, time-lapse between images is 45 seconds.....	73
Figure 3-7. Volume rendering images of hydrate during dissociation for a vertical section of the specimen for the depressurization experiment from $t = 22.5$ min to $t = 37.5$ min, time-lapse between images is 45 seconds.....	74
Figure 3-8. Volume rendering images of hydrate during dissociation for a vertical section of the specimen for the thermal stimulation experiment from beginning of the test to $t = 22.5$ min, time-lapse between images is 45 seconds.....	75
Figure 3-9. Specimen scanned region and divided vertical sections (specimen inner diameter is 9.2 mm).	76
Figure 3-10. Schematic of different hydrate pore habit: (a) surface coating; (b) cementing; (c) pore filling; and (d) load bearing.....	77
Figure 3-11. Initial hydrate pore habit distribution highlighted in volume rendering images for the depressurization experiment for: (a) Section 1; (b) Section 2; (c) Section 3; and (d) Section 4 of the specimen.	78
Figure 3-12. Volume rendering image for section 1 of the thermal stimulation experiment showing the pore-filling pore habit.....	79
Figure 3-13. Hydrate volume changes with time.....	80
Figure 3-14. Hydrate specific area changes with hydrate saturation with volume rendering snapshots at selected hydrate saturation showing the evolution of hydrate pore-habit: (a) surface coating pore-habit; (b) hydrate start to fill space between surrounding wall and sand particles; (c) cementing pore-habit; and (d) pore filling pore-habit.....	81
Figure 3-15. Variation of $(\text{hydrate volume})^{2/3}$ versus: (a) combined interfacial area measurements; (b) total hydrate interfacial area; (c) hydrate-sand interfacial area; and (d) hydrate-gas interfacial area along with initial best fit lines and 95% prediction bands for the depressurization experiment.	82
Figure 3-16. Variation of (a) combined interfacial area measurements; (b) total hydrate interfacial area; (c) hydrate-sand interfacial area; and (d) hydrate-gas interfacial area with hydrate volume along with best quadratic fit and 95% prediction bands for the depressurization experiment.	83
Figure 3-17. Change of measured dissociation rate with predicted dissociation rate according to Equation 3-1 with time for the depressurization experiment.	84
Figure 3-18. Variation of $(\text{hydrate volume})^{2/3}$ versus: (a) combined interfacial area measurements; (b) total hydrate interfacial area; (c) hydrate-sand interfacial area; and (d) hydrate-gas interfacial area along with initial best fit lines and 95% prediction bands for the thermal stimulation experiment.	85
Figure 3-19. Variation of (a) combined interfacial area measurements; (b) total hydrate interfacial area; (c) hydrate-sand interfacial area; and (d) hydrate-gas interfacial area with hydrate volume along with best cubic fit and 95% prediction bands for the thermal stimulation experiment.....	86
Figure 3-20. Change of (a) hydrate specific area; and (b) hydrate dissociation rate with time during dissociation for the depressurization experiment.....	87

Figure 3-21. Change of hydrate surface area with (hydrate volume) ^{2/3} during hydrate dissociation for the four vertical sections of the specimen for the depressurization experiment along with volume rendering images at selected points.	88
Figure 3-22. Change of measured and predicted hydrate dissociation rate with hydrate saturation along with the linear regression model for the thermal stimulation experiment.	89
Figure 4-1. Histograms of (a) porosity; (b) median grain diameter; (c) roundness index; (d) sphericity index; (e) uniformity coefficient; and (f) coefficient of curvature of the 130 systems reported in this study.	109
Figure 4-2. Image processing steps for on a zoomed view of an XY slice of one of the systems: (a) raw image; (b) filtered image; (c) binarized sand image; (d) binarized sand separated image; (e) sand labeled image; (f) binarized non wetting phase image; (g) three-phase segmented image, gas is black, water is gray, and sand is white; and (h) histogram of the filtered image.	110
Figure 4-3. Sample 2D cross-section and volume rendering snapshots for selected labeled images from (a) Group 1; (b) group 5; (c) Group 8; (d) Group 118; (e) Group 21; and (f) Group 130.	111
Figure 4-4. Change of relative tortuosity with degree of saturation for the 130 systems.	112
Figure 4-5. Measured geometric tortuosity from SMT images versus predicted geometric tortuosity estimated from Equation 4-12.	113
Figure 4-6. Comparison of the predicted saturated geometric tortuosity using the model in Equation 4-12 with analytical and theoretical models from the literature.	114
Figure 4-7. Comparison of the predicted relative tortuosity using the model in Equation 4-11 with the model proposed by (Ghanbarian et al. 2013).	115
Figure 5-1. Agglomerate generation procedure: (a) Mother sphere; (b) the STL file positioned within the mother sphere.	127
Figure 5-2. Experimental and DEM force-displacement curves for calibration of the DEM model.	128
Figure 5-3. Visualization of fracture of the calibrated particle: (a) SMT image for the particle before loading; (b) SMT image for the fractured particle; (c) DEM agglomerate before loading; (d) DEM fractured agglomerate.	129
Figure 5-4. (a) Sphericity; and (b) roundness histograms for the simulated agglomerates.	130
Figure 5-5. Tensile strength of DEM agglomerates calculated from Equation 5-3 vs. (a) I_{sph} ; and (b) I_R	131
Figure 5-6. Tensile strength of DEM agglomerates calculated from Equation 5-4 vs. (a) I_{sph} ; and (b) I_R	132
Figure 5-7. Histogram distribution of tensile strength of DEM agglomerates calculated from (a) Equation 5-3; and (b) Equation 5-4.	133
Figure 6-1. Linear parallel contact model between two polyhedral blocks.	152

Figure 6-2. SMT images and DEM model of (a) silica cube; and (b) ASTM 20-30 Ottawa sand particle; and force displacement curves for (c) silica cube; and (d) ASTM 20-30 Ottawa sand particle.....	153
Figure 6-3. Influence of varying (a) parallel bond normal and shear strength; (b) ratio between bond normal and shear stiffness; (c) bond effective modulus; (d) friction coefficient; (e) bond radius multiplier; and (f) stiffness of the contacts between the loading plate and the blocks on the behavior of BBM simulations of 1D compression tests on the silica cubes.	154
Figure 6-4. Flow chart of model calibration procedure.....	155
Figure 6-5. Variation of peak load from 1D compression DEM simulations with different rigid block sizes.....	156
Figure 6-6. SMT and DEM images and comparison of force versus compressive displacement for 3 three-particle 1D compression experiments, actual shape DEM model, and equivalent spheres DEM model. BSM results are from Cil and Alshibli (2015). Surrounding walls were hidden in the images of DEM models for a better visualization.	157
Figure 6-7. Number of rigid blocks in contact and loading distances obtained from real shape agglomerates models for (a) Test 1; (b) Test 2; and (c) Test 3.	158
Figure 6-8. Cumulative change in fracture surface area versus net work of load (energy dissipated by slip subtracted from total input energy) for the three-particle tests.....	159

CHAPTER ONE

GENERAL INTRODUCTION

Motivational Background

The availability of methane hydrates and the expected increase in energy demand encouraged researchers to consider methane production from methane hydrates as a potential energy source. It is estimated that more than 95% of methane hydrates occur in marine environments where the conditions of high pressure and low temperature are satisfied. The production of methane from hydrate-bearing sediments requires hydrate dissociation to free the methane gas in sediments prior to gas production operation. During gas production from unconsolidated sediments, it is anticipated that emergent phenomena such as fluid expansion and migration of fine particles take place. Fines migration and accumulation in narrow pore-throats may lead to clogging which in turn to the development of gas-driven fracture.

During methane production from sandy sediments, fines may migrate through the pore space and clog narrow constrictions of the pore space (i.e., pore-throats). The extent of fines migration and clogging depend on factors such as fines concentration, gas flow rate and geometry and topology of the pore scale (i.e., pore size distribution, throat size distribution and the ratio of the size of the pore throat to the size of the fine particle). The clogged pore throats create local zones that are under extremely high pressure generate fractures. Gas hydrate dissociation can also be affected by heat and mass transfer properties of porous media. Heat and mass of porous media can vary depending on permeability, relative permeability, and tortuosity.

Despite extensive research on hydrate dissociation and in-situ hydrate production, there is a knowledge gap of fines effects on gas production from sandy sediments, especially at the pore-scale. Key questions such as what are the most relevant parameters determining conditions for gas-driven fracturing and what will be the role of fine migration, clogging and gas-driven fractures in transport of methane gas in unconsolidated sediments during depressurization have not been answered adequately. Moreover, most classical hydrate dissociation models assume hydrates to be a constant number of equal-sized spheres dissociating at a constant rate. However, studies reporting change of hydrate surface area during dissociation are limited.

3D synchrotron micro-computed tomography (SMT) is used in this dissertation to better understand the mechanisms of gas production from hydrate bearing sediments. Unique in situ experiments that involve monitoring gas hydrate formation and dissociation were used to gain a comprehensive understanding of the associated physical processes (such as fines migration, clogging and gas driven fracture) and validation of hydrate dissociation models' assumptions.

Granular materials are composed of discrete solid particles with ranges of particle size and morphology. The response of granular materials to applied stresses is highly complex and influenced by many internal and external factors, including material state (density), applied stress, material fabric and the physical properties of individual particles (size and morphology). Fracture of sand particles has been investigated by many researchers and it plays a significant role in determining the

plastic bulk volume changes of granular materials under different loading conditions. Particle fracture phenomenon and force transmission mechanisms in natural granular assemblies such as sands have not been fully understood due to the lack of micro-scale experimental measurements.

Discrete Element Modeling (DEM) is an excellent tool that has been used by researchers to better understand the influence of particle fracture on the behavior of granular materials. DEM permits acquiring micromechanical information such as particle motion and inter-particle contact forces. The majority of DEM work fail to capture the actual shape of sand particles due to the difficulty in generating complex shapes. Particle shape and morphology have been shown experimentally and computationally to play a significant role in determining the macroscopic properties of granular materials. This dissertation will employ high resolution 3D SMT images to simulate multiscale in-situ experiments reproducing the actual shape of sand particles. DEM simulations will work as a virtual laboratory to study the effects of particle-level morphology on force and stress transmission in granular materials.

Dissertation Objectives

The dissertation discusses two distinct topics; and therefore, the objectives are listed for each topic separately. Figure 1-1 presents a summary of the dissertation objectives. The objective of the first part of the dissertation is to provide fundamental understanding of underlying coupled processes of fines migration, clogging, gas-driven fracturing to evaluate optimal conditions for the various production strategies. SMT is used to obtain 3D direct visualizations of fines clogging, hydrate formation, hydrate dissociation, and gas driven fracture in porous media. This facilitates the selection of the most efficient production technology adequate for the local geological/geographic conditions. Detailed objectives are as follows:

- Direct visualizations of fines, fines clogging, and gas driven fracture using monochromatic synchrotron micro-computed tomography (SMT-M) imaging during multiphase flow experiments on brine saturated uniform silica sand mixed with kaolinite at different percentages by weight.
- Investigate the validity of hydrate sphericity assumptions used in classical hydrate dissociation models. Dynamic SMT scanning using pink beam (SMT-P) will be used to measure the evolution of hydrate surface area during hydrate dissociation.
- Utilize SMT-P imaging to investigate the change of tortuosity of porous media with water saturation and develop a simple formula that relates the geometric tortuosity to global porosity and saturation.

This second part of the dissertation employs high resolution 3D SMT-M along with DEM modelling techniques to simulate multiscale in-situ experiments reproducing the actual shape of sand particles. Measurements obtained from DEM models can help advance the understanding of the relationship between particles interaction

at the micro-scale and the response of granular materials at the macro-scale. Detailed objectives are as follows:

- Derive a model to predict the tensile strength of single sand particles taking in consideration their morphology (sphericity and roundness) using results of DEM simulations of unconfined 1D compression tests for more than 100 particles with various sizes and shapes.
- Study the evolution and distribution of particle fracture, particle fracture mechanisms, and deformation characteristics of sand modelled as agglomerates (rigid blocks and sub-spheres). Each simulated particle matches the actual 3D shape of sand particles that were acquired from SMT-M images.

Literature Review

This dissertation is structured into five Chapters that have been published in peer-reviewed journals, or in the process of being submitted for possible publication. Each Chapter begins with an “Introduction” Section that presents a thorough literature review about the corresponding subject matter. The following sub-sections give a top-level summary of the thorough literature that was reviewed for the five chapters.

Disclaimer: Portions of this literature review will be repeated in subsequent chapters.

Gas Production from Methane Hydrate

Methane gas hydrates are crystalline inclusion compounds formed from methane (CH_4) and water, and are found at low temperature and high pressure conditions in marine continental margin and permafrost sediments. Methane hydrate is considered to be a potential energy source, with worldwide reserves on the order of 500-10,000 Gt of carbon (Milkov 2004; Ruppel and Pohlman 2008). Methane production from hydrate-bearing sediments requires hydrate dissociation for releasing mobile methane gas in sediments prior to gas production operation. Therefore, gas production from hydrate bearing sediments can be divided into two processes: hydrate dissociation and release of free methane gas (hydrate dissociation); and production of mobile pore fluids including free methane gas by dropdown of the well pressure (gas production).

There are currently four main techniques to investigate hydrate dissociation; they are: thermal stimulation, depressurization, chemical injection and CH_4 - CO_2 replacement (Chong et al. 2016; Merey et al. 2018; Xu and Li 2015).

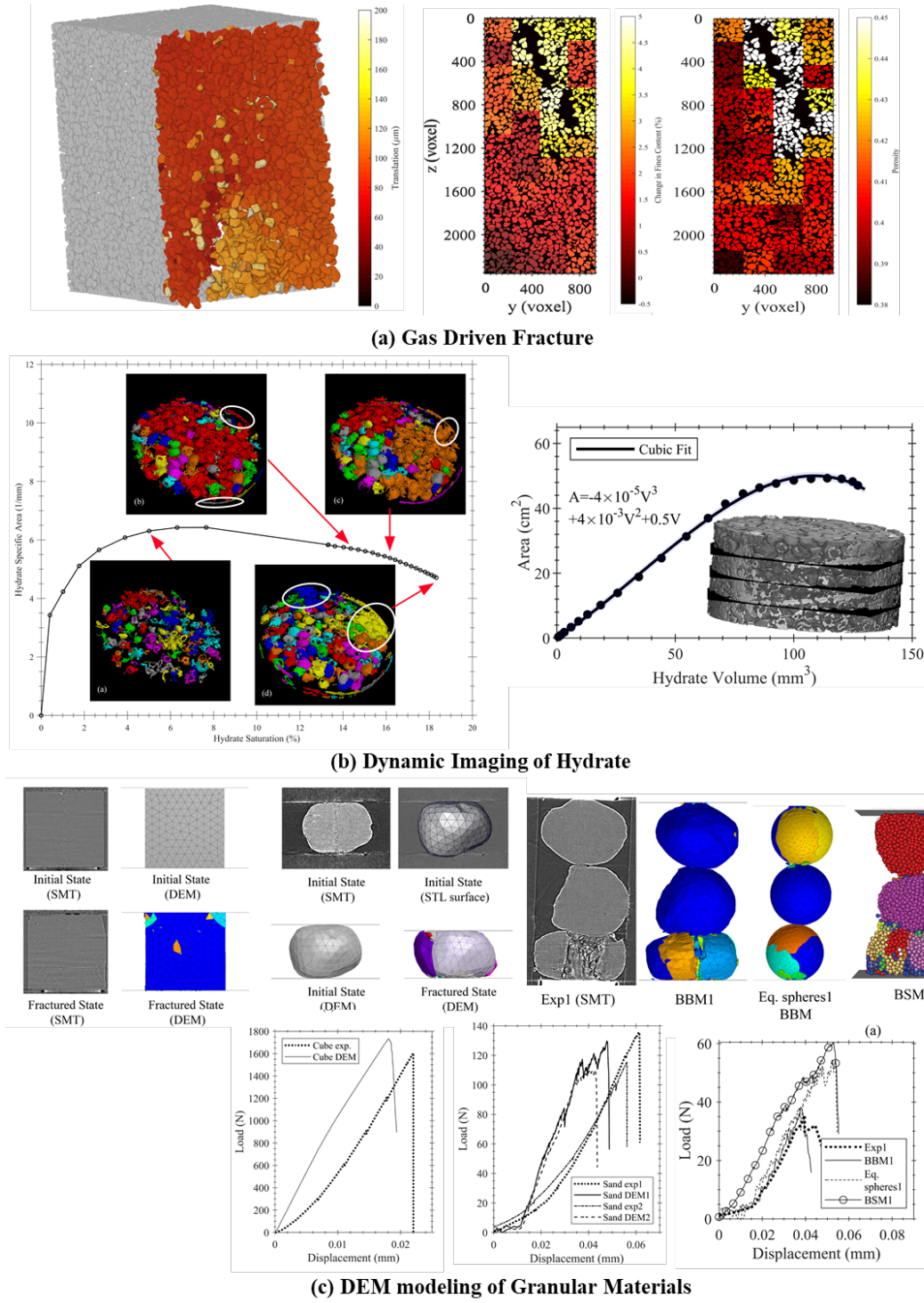


Figure 1-1. Summary of dissertation objectives.

Thermal stimulation and depressurization are applied by altering local pressure and temperature conditions of gas hydrate reservoirs, resulting in hydrate destabilization and dissociation to water and gas (Chen et al. 2018; Konno et al. 2017; Konno et al. 2010; Minagawa et al. 2015). Chemical injection technique involves introducing a chemical to shift hydrate equilibrium curve for hydrates to dissociate at in-situ conditions (Daraboina et al. 2013; Moridis et al. 2013), while CH₄-CO₂ replacement requires injecting CO₂ gas in hydrate reservoirs to replace CH₄ molecules in hydrate cages (Hyodo et al. 2014; Liu et al. 2016). Among the four techniques, depressurization is considered the most economically feasible technique (Collett et al. 2015; Huang et al. 2016). A better understanding of the kinetics of hydrate dissociation and the accompanying phenomena's is essential to accurately predict gas production potential from natural hydrate reservoirs. Emergent phenomena include fluid expansion, migration of fine particles, fines clogging resulting from the migration and accumulation of fine particles at pore throats, and gas-driven fracture generation.

It is known that the preferential path of gas invasion for clay-rich sediments usually takes place through conduit opening or fracturing (Choi et al. 2011; Jain and Juanes 2009; Wiseall et al. 2015). However, Jung et al. (2012) showed that in multiphase systems, flow of CO₂ through saturated sandy sediments with small amount of fines fraction (i.e. ~4%), fractures could develop due to fines clogging. The extent of fines migration and clogging depend on factors such as fines concentration, gas flow rate and geometry and topology of the pore scale (i.e., pore size distribution, throat size distribution and the ratio of the size of the pore throat to the size of the fine particle). As the capillary pressure at a clogged pore throat increases, it creates local zones that are under extremely high gas pressure caused by hydrate dissociation.

Hydrate Formation and Dissociation Experimental Studies

Due to the difficulty of obtaining pressurized core samples of natural hydrates, researchers attempted alternative approaches to study gas hydrate. These attempts include using effective media models based on assumed hydrate habits in the pore space (Attias et al. 2020; Ghosh et al. 2010; Qian et al. 2017); laboratory specimens with hydrates formed by ice seeding (Chen et al. 2010; Zylyftari et al. 2014) or unsaturated/percolating gas phase (Chen and Espinoza 2018a; Kneafsey et al. 2007); and analogue hydrate formers such as tetrahydrofuran clathrate hydrate (THF) (Kumar et al. 2016; Lee et al. 2007; Mahabadi et al. 2016). Each approach has its own limitation, but the gathered data provide insightful information on the effect of hydrate formation and dissociation on the physical properties of sediments including hydraulic conductivity, strength, and stiffness. Additionally, several studies have reported that hydrate formation history has a profound effect on the physical properties of hydrate bearing sediments (Ebinuma et al. 2005; Waite et al. 2009). In the last three decades, x-ray Computed Tomography (CT) has emerged as a powerful non-destructive 3D scanning technique to visualize the internal structure of materials. Industrial micro-

focus CT scanners have been used to study properties of laboratory-prepared hydrates where it is challenging to separate different phases and monitor gas-solid-liquid contact properties (Han et al. 2018; Lei et al. 2019; Seol and Kneafsey 2009). Chen and Espinoza (2018a) studied hydrate formation process and the change in pore habit using three different experiments: CH₄ hydrate formation on water droplets, Xenon (Xe) hydrate formation in water and gas (without sand), and Xe hydrate formation in a porous media. Chen and Espinoza (2018b) used micro-focus x-ray radiography to study Xe hydrate dissociation kinetics. The apparatus does not have a temperature control feature, and thus temperature was maintained at room temperature. Chen and Espinoza (2018b) first measured the initial hydrate volume and surface area before dissociation based on a full reconstructed 3D image and showed that hydrate surface area can be approximated as a linear function of (hydrate volume)^{2/3}. They observed two conditions where the relationship between the hydrate dissociation rate and (hydrate volume)^{2/3} deviates from linearity. First, at a hydrate saturation higher than a certain threshold (35%-45%). Hydrate dissociation rate oscillates around a constant value for hydrate saturation higher than the threshold. Second, dissociation of patchy hydrates in large pores stays constant initially and is significantly slower than hydrate dissociation in small pores. (Wu et al. 2020) investigated the cementation failure behavior and localized shear deformation during consolidated drained triaxial tests of Xe hydrates using micro-focus x-ray tomography. In the plasticity region of the stress-strain curve, they observed that hydrates begin to shed from the periphery of the cemented structure. They also reported that the hydrate-cemented cluster structure was completely damaged and crushed into small pieces in the yielding region of the stress-strain curve. Hydrate pore-habit refers to how hydrates are distributed within the pores of the host sediments which can fundamentally alter the physical properties of hydrate-bearing sediments, including, shear strength and stiffness (Waite et al. 2009). In the literature, hydrate pore-habits are mainly divided into four types: surface coating, cementing, pore filling, and load-bearing. Surface coating hydrates form as films on the surface of host sediment particles while cementing hydrates form at the meniscus between host sediment particles. Pore filling hydrates start to form at the surface of host sediment particles and grow outward, filling the pore space. Load bearing hydrates form at high hydrate saturation where they can carry some of the load applied to the host sediments.

Hydrate Dissociation Kinetics

A better understanding of the kinetics of hydrate dissociation is essential to accurately predict gas production potential from natural hydrate reservoirs. Many theoretical (Oyama et al. 2009; Windmeier and Oellrich 2013), analytical (Hong et al. 2003; Selim and Sloan 1989), and numerical (Gamwo and Liu 2010; Jamaluddin et al. 1989) dissociation kinetic models were developed by researchers since the 1980s to simulate hydrate dissociation process. Kim et al. (1987) proposed what is considered as the most classical hydrate dissociation model until this date (Yin et al. 2016). They studied Methane hydrate dissociation

using a semi-batch stirred tank reactor, and proposed the hydrate dissociation rate to be:

$$-\frac{dn_H}{dt} = k_d A_S (f_e - f) \quad 1-1$$

where $-\frac{dn_H}{dt}$ is the molar hydrate dissociation rate (mol.s^{-1}), k_d is the hydrate dissociation rate constant ($\text{mol.m}^{-2}.\text{Pa}^{-1}.\text{s}^{-1}$), A_S is the surface area of hydrate (m^2), f_e is the fugacity of gas at hydrate equilibrium pressure and temperature conditions (Pa), and f is the fugacity of gas in the bulk gas phase (Pa). The hydrate dissociation rate constant can be described by an Arrhenius-type equation as:

$$k_d = k_d^0 e^{-\frac{\Delta E}{RT}} \quad 1-2$$

Where k_d^0 is the intrinsic dissociation rate constant ($\text{mol.m}^{-2}.\text{Pa}^{-1}.\text{s}^{-1}$), ΔE is the activation energy (J.mol^{-1}), R is the universal gas constant ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$), and T is the absolute temperature (K) (Clarke and Bishnoi 2001; Kim et al. 1987). Although the intrinsic dissociation rate constant is independent of pressure, temperature, and hydrate surface area, different studies reported different values of k_d^0 by orders of magnitude for batch reactors (Clarke and Bishnoi 2001; Kim et al. 1987) and porous media (Kneafsey et al. 2007; Moridis et al. 2005). This may be attributed to the fact that none of these studies measured the surface area of hydrates. They instead estimated the surface area based on hydrate particle size by either assuming they all have the same initial diameter (Kim et al. 1987), or by measuring hydrate particles sizes using particle size analyzer (Clarke and Bishnoi 2001), or estimated the surface area as a linear combination of (hydrate saturation)^{2/3} (Moridis et al. 2005). These estimates were based on the assumptions that hydrates are fixed number of spheres dissociating at a uniform rate, meaning that the surface area of hydrates can be estimated as a linear function of (hydrate volume)^{2/3}. Several studies reported observing secondary hydrate dissociation during hydrate formation (Chen and Espinoza 2018a; Ning et al. 2013). The reduction of permeability during hydrate formation and the exothermic nature of hydrate formation process, which results in a release of heat energy as hydrate form, can trigger hydrate dissociation in localized regions (Ning et al. 2013)

DEM modeling of Particle Fracture

Fracture of sand particles plays a significant role in determining the plastic bulk volume changes of granular materials under different loading conditions. Particle breakage has been investigated using experimental, analytical, and numerical approaches at different scales ranging from a single particle to laboratory size specimens (Altuhafi and Coop 2011; Bolton et al. 2008; Cavarretta et al. 2017; McDowell et al. 1996; Nakata et al. 1999; Zhao et al. 2015). Discrete Element Modeling (DEM) has been widely used to better understand the influence of particle fracture on the behavior of granular materials. In the scope of DEM, particle fracture can be modeled using two common approaches. The first approach

replaces a larger sphere with a group of smaller spheres with different diameters when a pre-defined fracture criterion is met (Lobo-Guerrero and Vallejo 2005; Lobo-Guerrero et al. 2006; McDowell and de Bono 2015). This approach requires selection of a breakage criterion governed by a measured or assumed characteristic particle tensile stress. The second approach simulates a sand particle as an agglomerate of small spheres bonded together using an appropriate contact model. Examples of contact models include simple contact bond model (McDowell and Harireche 2002; Robertson and Bolton 2001), parallel bond model (BPM) (Bobet et al. 2009; Hanley et al. 2011; Potyondy and Cundall 2004; Tomac and Gutierrez 2017), and flat-joint contact bond model (FJM) (Potyondy 2012; Potyondy 2015; Wu and Xu 2016). To better capture the actual particle morphology and microstructure of sand particles, which have been shown experimentally and computationally to play a significant role in determining the macroscopic properties of granular materials (Alshibli and Cil 2018; Andrade et al. 2012; Cho et al. 2006; Ma et al. 2017), spheres in the second approach can be replaced with bonded polyhedral blocks (Galindo-Torres et al. 2012; Gao 2013; Nicksiar and Martin 2014). The bonded block model (BBM) has been widely used in recent years to investigate fracture and fragmentation process in rock (Mohammadnejad et al. 2018; Turichshev and Hadjigeorgiou 2017).

Dissertation Outline

The dissertation consists of seven chapters: Chapter 1 is a general introduction. Chapter 2 presents a 3D synchrotron computed tomography study on the influence of fines on gas driven fractures in sandy sediments. Chapter 3 presents a study about 3D measurements of hydrate surface area during hydrate formation and dissociation in porous media using dynamic 3D imaging. Chapter 4 presents a new model for estimating geometric tortuosity of saturated and unsaturated porous media using 3D synchrotron micro-computed tomography imaging. Chapter 5 presents a discrete element study of morphology and size effects on fracture of single sand particles. Chapter 6 presents three-dimensional evaluation of sand particle fracture using discrete element method and synchrotron micro-computed tomography images. Chapter 7 highlights the major conclusions from this dissertation and suggests recommendations for future research.

References

- Alshibli, K. A., and Cil, M. B. (2018). "Influence of Particle Morphology on the Friction and Dilatancy of Sand." *Journal of Geotechnical and Geoenvironmental Engineering*, 144(3), 04017118.
- Altuhafi, F., and Coop, M. R. (2011). "Changes to particle characteristics associated with the compression of sands." *Géotechnique*, 61(6), 459.
- Andrade, J. E., Lim, K.-W., Avila, C. F., and Vlahinić, I. (2012). "Granular element method for computational particle mechanics." *Computer Methods in Applied Mechanics and Engineering*, 241-244, 262-274.
- Attias, E., Amalokwu, K., Watts, M., Falcon-Suarez, I. H., North, L., Hu, G. W., Best, A. I., Weitemeyer, K., and Minshull, T. A. (2020). "Gas hydrate quantification at a pockmark offshore Norway from joint effective medium modelling of resistivity and seismic velocity." *Marine and Petroleum Geology*, 113, 104151.
- Bobet, A., Fakhimi, A., Johnson, S., Morris, J., Tonon, F., and Yeung, M. R. (2009). "Numerical Models in Discontinuous Media: Review of Advances for Rock Mechanics Applications." *Journal of Geotechnical and Geoenvironmental Engineering*, 135(11), 1547-1561.
- Bolton, M., Nakata, Y., and Cheng, Y. (2008). "Micro-and macro-mechanical behaviour of DEM crushable materials." *Géotechnique*, 58(6), 471-480.
- Cavarretta, I., O'Sullivan, C., and Coop, M. R. (2017). "The relevance of roundness to the crushing strength of granular materials." *Géotechnique*, 67(4), 301-312.
- Chen, L., Feng, Y., Kogawa, T., Okajima, J., Komiya, A., and Maruyama, S. (2018). "Construction and simulation of reservoir scale layered model for production and utilization of methane hydrate: The case of Nankai Trough Japan." *Energy*, 143, 128-140.
- Chen, P.-C., Huang, W.-L., and Stern, L. A. (2010). "Methane Hydrate Synthesis from Ice: Influence of Pressurization and Ethanol on Optimizing Formation Rates and Hydrate Yield." *Energy & Fuels*, 24(4), 2390-2403.
- Chen, X., and Espinoza, D. N. (2018a). "Ostwald ripening changes the pore habit and spatial variability of clathrate hydrate." *Fuel*, 214, 614-622.
- Chen, X., and Espinoza, D. N. (2018b). "Surface area controls gas hydrate dissociation kinetics in porous media." *Fuel*, 234, 358-363.
- Cho, G.-C., Dodds, J., and Santamarina, J. C. (2006). "Particle Shape Effects on Packing Density, Stiffness, and Strength: Natural and Crushed Sands." *Journal of Geotechnical and Geoenvironmental Engineering*, 132(5), 591-602.
- Choi, J. H., Seol, Y., Boswell, R., and Juanes, R. (2011). "X-ray computed-tomography imaging of gas migration in water-saturated sediments: From capillary invasion to conduit opening." *Geophysical Research Letters*, 38(17).
- Chong, Z. R., Yang, S. H. B., Babu, P., Linga, P., and Li, X.-S. (2016). "Review of natural gas hydrates as an energy resource: Prospects and challenges." *Applied Energy*, 162, 1633-1652.

- Clarke, M., and Bishnoi, P. R. (2001). "Determination of the activation energy and intrinsic rate constant of methane gas hydrate decomposition." *The Canadian Journal of Chemical Engineering*, 79(1), 143-147.
- Collett, T., Bahk, J.-J., Baker, R., Boswell, R., Divins, D., Frye, M., Goldberg, D., Husebø, J., Koh, C., Malone, M., Morell, M., Myers, G., Shipp, C., and Torres, M. (2015). "Methane Hydrates in Nature—Current Knowledge and Challenges." *Journal of Chemical & Engineering Data*, 60(2), 319-329.
- Daraboina, N., Malmos, C., and von Solms, N. (2013). "Synergistic kinetic inhibition of natural gas hydrate formation." *Fuel*, 108, 749-757.
- Ebinuma, T., Kamata, Y., Minagawa, H., Ohmura, R., Nagao, J., and Narita, H. "Mechanical properties of sandy sediment containing methane hydrate." Tapir forlag, Trondheim (Norway).
- Galindo-Torres, S. A., Pedroso, D. M., Williams, D. J., and Li, L. (2012). "Breaking processes in three-dimensional bonded granular materials with general shapes." *Computer Physics Communications*, 183(2), 266-277.
- Gamwo, I. K., and Liu, Y. (2010). "Mathematical Modeling and Numerical Simulation of Methane Production in a Hydrate Reservoir." *Industrial & Engineering Chemistry Research*, 49(11), 5231-5245.
- Gao, F. (2013). "Simulation of failure mechanisms around underground coal mine openings using discrete element modelling."
- Ghosh, R., Sain, K., and Ojha, M. (2010). "Effective medium modeling of gas hydrate-filled fractures using the sonic log in the Krishna-Godavari basin, offshore eastern India." *Journal of Geophysical Research: Solid Earth*, 115(B6).
- Han, G., Kwon, T. H., Lee, J. Y., and Kneafsey, T. J. (2018). "Depressurization-induced fines migration in sediments containing methane hydrate: X-ray computed tomography imaging experiments." *Journal of Geophysical Research: Solid Earth*, 123(4), 2539-2558.
- Hanley, K. J., O'Sullivan, C., Oliveira, J. C., Cronin, K., and Byrne, E. P. (2011). "Application of Taguchi methods to DEM calibration of bonded agglomerates." *Powder technology*, 210(3), 230-240.
- Hong, H., Pooladi-Darvish, M., and Bishnoi, P. R. (2003). "Analytical Modelling of Gas Production From Hydrates in Porous Media." *PETSOC-03-11-05*, 42(11), 45-56.
- Huang, Y.-J., Wu, C.-Y., and Hsieh, B.-Z. (2016). "Effect of Fluid Saturation on Gas Recovery from Class-3 Hydrate Accumulations Using Depressurization: A Case Study of the Yuan-an Ridge Site in Southwestern Offshore Taiwan." *Energy Procedia*, 97, 310-317.
- Hyodo, M., Li, Y., Yoneda, J., Nakata, Y., Yoshimoto, N., Kajiya, S., Nishimura, A., and Song, Y. (2014). "A comparative analysis of the mechanical behavior of carbon dioxide and methane hydrate-bearing sediments." *American Mineralogist*, 99(1), 178-183.
- Jain, A. K., and Juanes, R. (2009). "Preferential Mode of gas invasion in sediments: Grain-scale mechanistic model of coupled multiphase fluid flow

- and sediment mechanics." *Journal of Geophysical Research: Solid Earth*, 114(B8).
- Jamaluddin, A. K. M., Kalogerakis, N., and Bishnoi, P. R. (1989). "Modelling of decomposition of a synthetic core of methane gas hydrate by coupling intrinsic kinetics with heat transfer rates." *The Canadian Journal of Chemical Engineering*, 67(6), 948-954.
- Jung, J. W., Jang, J., Santamarina, J. C., Tsouris, C., Phelps, T. J., and Rawn, C. J. (2012). "Gas Production from Hydrate-Bearing Sediments: The Role of Fine Particles." *Energy & Fuels*, 26(1), 480-487.
- Kim, H. C., Bishnoi, P. R., Heidemann, R. A., and Rizvi, S. S. H. (1987). "Kinetics of methane hydrate decomposition." *Chemical Engineering Science*, 42(7), 1645-1653.
- Kneafsey, T. J., Tomutsa, L., Moridis, G. J., Seol, Y., Freifeld, B. M., Taylor, C. E., and Gupta, A. (2007). "Methane hydrate formation and dissociation in a partially saturated core-scale sand sample." *Journal of Petroleum Science and Engineering*, 56(1), 108-126.
- Konno, Y., Fujii, T., Sato, A., Akamine, K., Naiki, M., Masuda, Y., Yamamoto, K., and Nagao, J. (2017). "Key Findings of the World's First Offshore Methane Hydrate Production Test off the Coast of Japan: Toward Future Commercial Production." *Energy & Fuels*, 31(3), 2607-2616.
- Konno, Y., Masuda, Y., Hariguchi, Y., Kurihara, M., and Ouchi, H. (2010). "Key Factors for Depressurization-Induced Gas Production from Oceanic Methane Hydrates." *Energy & Fuels*, 24(3), 1736-1744.
- Kumar, A., Daraboina, N., Kumar, R., and Linga, P. (2016). "Experimental Investigation To Elucidate Why Tetrahydrofuran Rapidly Promotes Methane Hydrate Formation Kinetics: Applicable to Energy Storage." *The Journal of Physical Chemistry C*, 120(51), 29062-29068.
- Lee, J. Y., Yun, T. S., Santamarina, J. C., and Ruppel, C. (2007). "Observations related to tetrahydrofuran and methane hydrates for laboratory studies of hydrate-bearing sediments." *Geochemistry, Geophysics, Geosystems*, 8(6).
- Lei, L., Liu, Z., Seol, Y., Boswell, R., and Dai, S. (2019). "An investigation of hydrate formation in unsaturated sediments using X-ray computed tomography." *Journal of Geophysical Research: Solid Earth*.
- Liu, W., Luo, T., Li, Y., Song, Y., Zhu, Y., Liu, Y., Zhao, J., Wu, Z., and Xu, X. (2016). "Experimental study on the mechanical properties of sediments containing CH₄ and CO₂ hydrate mixtures." *Journal of Natural Gas Science and Engineering*, 32, 20-27.
- Lobo-Guerrero, S., and Vallejo, L. E. (2005). "Analysis of crushing of granular material under isotropic and biaxial stress conditions." *Soils and foundations*, 45(4), 79-87.
- Lobo-Guerrero, S., Vallejo, L. E., and Vesga, L. F. (2006). "Visualization of crushing evolution in granular materials under compression using DEM." *International Journal of Geomechanics*, 6(3), 195-200.

- Ma, G., Zhou, W., Regueiro, R. A., Wang, Q., and Chang, X. (2017). "Modeling the fragmentation of rock grains using computed tomography and combined FDEM." *Powder Technology*, 308, 388-397.
- Mahabadi, N., Zheng, X., and Jang, J. (2016). "The effect of hydrate saturation on water retention curves in hydrate-bearing sediments." *Geophysical Research Letters*, 43(9), 4279-4287.
- McDowell, G., Bolton, M., and Robertson, D. (1996). "The fractal crushing of granular materials." *Journal of the Mechanics and Physics of Solids*, 44(12), 2079-2101.
- McDowell, G., and Harireche, O. (2002). "Discrete element modelling of soil particle fracture." *Géotechnique*, 52(2), 131-135.
- McDowell, G. R., and de Bono, J. P. (2015). "On the micro mechanics of one-dimensional normal compression." *Géotechnique*, 63(11), 895-908.
- Merey, S., Al-Raoush, R. I., Jung, J., and Alshibli, K. A. (2018). "Comprehensive literature review on CH₄-CO₂ replacement in microscale porous media." *Journal of Petroleum Science and Engineering*, 171, 48-62.
- Milkov, A. V. (2004). "Global estimates of hydrate-bound gas in marine sediments: how much is really out there?" *Earth-Science Reviews*, 66(3), 183-197.
- Minagawa, H., Ito, T., Kimura, S., Kaneko, H., Noda, S., and Narita, H. "Depressurization and electrical heating of hydrate sediment for gas production." *Proc., Proceedings of the International Offshore and Polar Engineering Conference*, 82-88.
- Mohammadnejad, M., Liu, H., Chan, A., Dehkhoda, S., and Fukuda, D. (2018). "An overview on advances in computational fracture mechanics of rock." *Geosystem Engineering*, 1-24.
- Moridis, G. J., Collett, T. S., Boswell, R., Hancock, S., Rutqvist, J., Santamarina, C., Kneafsey, T., Reagan, M. T., Pooladi-Darvish, M., Kowalsky, M., Sloan, E. D., and Coh, C. (2013). "Gas Hydrates as a Potential Energy Source: State of Knowledge and Challenges." *Advanced Biofuels and Bioproducts*, J. W. Lee, ed., Springer New York, New York, NY, 977-1033.
- Moridis, G. J., Seol, Y., and Kneafsey, T. J. (2005). "Studies of reaction kinetics of methane hydrate dissociation in porous media."
- Nakata, A., Hyde, M., Hyodo, H., and Murata (1999). "A probabilistic approach to sand particle crushing in the triaxial test." *Géotechnique*, 49(5), 567-583.
- Nicksiar, M., and Martin, C. D. (2014). "Factors Affecting Crack Initiation in Low Porosity Crystalline Rocks." *Rock Mechanics and Rock Engineering*, 47(4), 1165-1181.
- Ning, F., Wu, N., Yu, Y., Zhang, K., Jiang, G., Zhang, L., Sun, J., and Zheng, M. (2013). "Invasion of drilling mud into gas-hydrate-bearing sediments. Part II: Effects of geophysical properties of sediments." *Geophysical Journal International*, 193(3), 1385-1398.

- Oyama, H., Konno, Y., Masuda, Y., and Narita, H. (2009). "Dependence of Depressurization-Induced Dissociation of Methane Hydrate Bearing Laboratory Cores on Heat Transfer." *Energy & Fuels*, 23(10), 4995-5002.
- Potyondy, D. O. (2012). "A Flat-Jointed Bonded-Particle Material For Hard Rock." *46th U.S. Rock Mechanics/Geomechanics Symposium*, American Rock Mechanics Association, Chicago, Illinois, 10.
- Potyondy, D. O. (2015). "The bonded-particle model as a tool for rock mechanics research and application: current trends and future directions." *Geosystem Engineering*, 18(1), 1-28.
- Potyondy, D. O., and Cundall, P. (2004). "A bonded-particle model for rock." *International journal of rock mechanics and mining sciences*, 41(8), 1329-1364.
- Qian, J., Wang, X., Collett, T. S., Dong, D., Guo, Y., Su, P., and Liang, J. (2017). "Gas hydrate accumulation and saturations estimated from effective medium theory in the eastern Pearl River Mouth Basin, South China Sea." *Interpretation*, 5(3), SM33-SM48.
- Robertson, D., and Bolton, M. D. (2001). "DEM simulations of crushable grains and soils." *4th International Conference on Micromechanics of Granular Media Powders and Grains* Sendai, Japan, 623-626.
- Ruppel, C. D., and Pohlman, J. W. (2008). "Climate change and global carbon cycle: Perspectives and opportunities." *Fire in the Ice: NETL Methane Hydrate Newsletter*, 8(1), 5-8.
- Selim, M. S., and Sloan, E. D. (1989). "Heat and mass transfer during the dissociation of hydrates in porous media." *AIChE Journal*, 35(6), 1049-1052.
- Seol, Y., and Kneafsey, T. J. (2009). "X-ray computed-tomography observations of water flow through anisotropic methane hydrate-bearing sand." *Journal of Petroleum Science and Engineering*, 66(3-4), 121-132.
- Tomac, I., and Gutierrez, M. (2017). "Coupled hydro-thermo-mechanical modeling of hydraulic fracturing in quasi-brittle rocks using BPM-DEM." *Journal of Rock Mechanics and Geotechnical Engineering*, 9(1), 92-104.
- Turichshev, A., and Hadjigeorgiou, J. (2017). "Development of Synthetic Rock Mass Bonded Block Models to Simulate the Behaviour of Intact Veined Rock." *Geotechnical and Geological Engineering*, 35(1), 313-335.
- Waite, W. F., Santamarina, J. C., Cortes, D. D., Dugan, B., Espinoza, D. N., Germaine, J., Jang, J., Jung, J. W., Kneafsey, T. J., Shin, H., Soga, K., Winters, W. J., and Yun, T. S. (2009). "Physical properties of hydrate-bearing sediments." *Reviews of Geophysics*, 47(4).
- Windmeier, C., and Oellrich, L. R. (2013). "Theoretical Study of Gas Hydrate Decomposition Kinetics—Model Development." *The Journal of Physical Chemistry A*, 117(40), 10151-10161.
- Wiseall, A., Cuss, R., Graham, C., and Harrington, J. (2015). "The visualization of flow paths in experimental studies of clay-rich materials." *Mineralogical Magazine*, 79(6), 1335-1342.

- Wu, P., Li, Y., Liu, W., Sun, X., Kong, X., and Song, Y. (2020). "Cementation Failure Behavior of Consolidated Gas Hydrate-Bearing Sand." *Journal of Geophysical Research: Solid Earth*, 125(1), e2019JB018623.
- Wu, S., and Xu, X. (2016). "A Study of Three Intrinsic Problems of the Classic Discrete Element Method Using Flat-Joint Model." *Rock Mechanics and Rock Engineering*, 49(5), 1813-1830.
- Xu, C.-G., and Li, X.-S. (2015). "Research progress on methane production from natural gas hydrates." *RSC Advances*, 5(67), 54672-54699.
- Yin, Z., Chong, Z. R., Tan, H. K., and Linga, P. (2016). "Review of gas hydrate dissociation kinetic models for energy recovery." *Journal of Natural Gas Science and Engineering*, 35, 1362-1387.
- Zhao, B., Wang, J., Coop, M., Viggiani, G., and Jiang, M. (2015). "An investigation of single sand particle fracture using X-ray micro-tomography." *Géotechnique*, 65(8), 625-641.
- Zylyftari, G., Ahuja, A., and Morris, J. F. (2014). "Nucleation of cyclopentane hydrate by ice studied by morphology and rheology." *Chemical Engineering Science*, 116, 497-507.

CHAPTER TWO
3D SYNCHROTRON COMPUTED TOMOGRAPHY STUDY ON THE
INFLUENCE OF FINES ON GAS DRIVEN FRACTURE IN SANDY
SEDIMENTS

A version of this chapter is published as Jarrar Z. A., Al-Raoush R. I., Hannun J. A., Alshibli K. A., & Jung J. (2020). 3D Synchrotron Computed Tomography Study on the Influence of Fines on Gas Driven Fractures in Sandy Sediments. *Geomechanics for Energy and the Environment*, 23, 100105. <https://doi.org/10.1016/j.gete.2018.11.001>

My contribution to this paper is performing majority of the experimental tests, data analysis, and preparing the original draft and all figures.

Abstract: Production of methane from hydrate-bearing sediments requires hydrate dissociation for releasing mobile methane gas in sediments prior to gas production operations. Fines may migrate through or clog the pore space of sandy sediments depending on the geometry and topology of the pore space. Multiphase flow experiments were conducted on brine saturated uniform silica sand mixed with kaolinite at different percentages by weight with similar preparation procedure. Fines were segmented by selecting voxels with high computed tomography (CT) numbers in the brine phase of the images. Representative element volume (REV) procedure was used to study local porosity and local fines concentration of specimens. A cubical REV with a side length of 850 μm was selected. For low fines content (less than 6%), gas percolated through the specimens with no major particle displacement or porosity change. For 6% kaolinite specimen, fractures were initiated, and propagated by densifying surrounding sediments. Local fines concentration study showed that fines migrated through the pores for specimens with fines content less than 6%. For the 6% kaolinite specimen, fines concentrated near fractures due to clogging. Clogging induced an increase in the capillary pressure at the pore throats and caused the capillary pressure to overcome the effective stress between sand particle, and fractures to be initiated. Sand particles experienced up to 200 μm displacement and 15° rotation due to gas driven fracture in the 6% kaolinite specimen.

Keywords: Gas production, hydrate bearing sediments, gas driven fracture, 3D synchrotron micro-computed tomography, fines clogging

Introduction

The availability of methane hydrates and the expected increase in energy demand encouraged researchers to consider methane production from methane hydrates as a potential energy source. It is estimated that more than 95% of methane hydrates occur in marine environments where the conditions of high pressure and low temperature are satisfied (Max et al. 2013). The production of methane from hydrate-bearing sediments requires hydrate dissociation to free the methane gas in sediments prior to gas production operation. Multiphase flow is defined as simultaneous flow of two or more fluids with different states (i.e. gas or liquid). Methane hydrate sediments typically exist in form of unconsolidated sediments. During gas production from unconsolidated sediments, it is anticipated that

emergent phenomena such as fluid expansion and migration of fine particles take place. Fines migration and accumulation in narrow pore-throats may lead to clogging which in turn to the development of gas-driven fracture.

It is known that the preferential path of gas invasion for clay-rich sediments usually takes place through conduit opening or fracturing (Choi et al. 2011; Wiseall et al. 2015). However, in sand-dominant permeable sediments with a small fraction of fines, fluid flow caused by depressurization causes migration of fine particles, resulting in clogging of pore throats in flow paths. Fines migration and clogging in single-phase and multi-phase flow have been investigated using two-dimensional (2D) microfluidic pore models, three-dimensional (3D) porous sediments models, and numerical simulations (Agbangla et al. 2012; Holtzman and Juanes 2010; Imdakm and Sahimi 1991; Jang and Santamarina 2014; Jung et al. 2017; Wan and Wilson 1994). During methane production from sandy sediments, fines may migrate through the pore space and clog narrow constrictions of the pore space (i.e., pore-throats). The extent of fines migration and clogging depend on factors such as fines concentration, gas flow rate and geometry and topology of the pore scale (i.e., pore size distribution, throat size distribution and the ratio of the size of the pore throat to the size of the fine particle). The clogged pore throats create local zones that are under extremely high pressure generate fractures. Jung et. al. (Jung et al. 2012) showed that in multiphase systems, flow of CO₂ through saturated sandy sediments with small amount of fines fraction (i.e. ~4%), fracture(s) could develop due to fines clogging.

Despite extensive research on hydrate dissociation and in-situ hydrate production, there is a knowledge gap that needs to be resolved to develop technical and economically viable methane production strategies from gas hydrate reservoirs. Therefore, to better understand the mechanisms of gas production from hydrate bearing sediments, a comprehensive understanding of the associated physical processes such as fines migration, clogging and gas driven fracture is needed.

In this paper, direct visualizations of fines, fines clogging, and gas driven fracture were monitored using 3D synchrotron micro-computed tomography (SMT) imaging. Multiphase flow experiments were conducted on brine saturated uniform fraction of F75 Ottawa silica sand mixed with kaolinite at different percentages by weight. Moreover, evolution of local fines concentration, local porosity, and translation of sand particles and their variation with gas driven fracture were investigated for the specimens with different fines content using REV procedure.

Experimental Setup and Methodology

A size fraction of F75 Ottawa silica sand with grain size between US sieve #60 (0.250 mm) and sieve #70 (0.210 mm) was used in this study. The sand was obtained from the US Silica Company and has a specific gravity of solids, G_s , of 2.65, a maximum void ratio, e_{max} , of 0.78 and a minimum void ratio, e_{min} , of 0.50. Dixie Clay Kaolin (Vanderbilt Minerals Company, TN, USA) was used to represent the fines. It has a mean particle size of 0.6 μ m and a G_s of 2.62. Dry sand was first mixed with kaolinite powder at different kaolinite fraction by weight. The specimens

were prepared to be in loose packing state since gas hydrates in marine environment are deposited in loose sediments (Hyodo et al. 2014). The porosity of specimens was targeted to be around 40%. Then, the sand-kaolinite mixture was deposited into a 9.52 mm (3/8 in.) diameter acrylic cylindrical cell that was partially filled with distilled water. The cell has two ports; an upper port that was connected to a DigiFlow pressure-volume actuator (flow pump); and a bottom port that was connected to a pressure regulator connected to a CO₂ gas source.

3D Synchrotron Micro-Computed Tomography (SMT)

X-ray computed tomography (CT) is a powerful non-destructive imaging technique in which an x-ray beam impinges a rotating object where the passing attenuated x-ray is recorded by a detector (Figure 2-1). The collected attenuation data are then processed to reconstruct 3D volume of the object. An enhancement to the conventional X-ray CT is the use of a synchrotron radiation source that has the advantages of tunable energy levels, higher resolution and less noise of the images (Alshibli et al. 2014).

In this study, the SMT scans were acquired at Beamline 13D, Advanced Photon Source (APS), Argonne National Laboratory (ANL), Illinois, USA. Shows the experimental setup. Potassium Iodide (KI) was added to the water to serve as a doping agent when analyzing the images to enhance the contrast of the brine phase and hence facilitate its segmentation in the images. At each state of the experiments, two different scans at two energy levels were acquired. The first energy level was acquired below the edge of iodine (33.069 keV) while the second one was acquired above it (33.269 keV). The resolution of the acquired images is approximately 3.9 μm /pixel. Four systems containing different kaolinite content (i.e., 0%, 2%, 4%, and 6%) were prepared, imaged and analyzed at different states. The first state is defined as the initial state of the specimen where the system is saturated with brine and a prescribed percentage of fines. The second state is established after pumping out 0.4 ml of brine solution out of the saturated specimen while injecting CO₂ at a constant pressure of 27.6 kPa (4 psi). At the third state, another 0.6 ml of brine was drained out and the scan was acquired. At the fourth state, CO₂ pressure was increased to 41.4 kPa (6 psi) and the scan was acquired without pumping out more water.

Image Analysis

Segmentation of the Images

SMT images were processed, enhanced and segmented using Avizo 9.4 software (FEI 2017). First, anisotropic diffusion filter was applied on the greyscale images to reduce noise and enhance contrast of edges. Then, user-defined values of image intensity ranges were used in the interactive thresholding module to segment (binarize) the images (i.e., voxels of values zeros and ones). Images acquired at the energy level below Iodine edge (i.e., 33.069 keV) were used to identify the sand and voids whereas gas was identified from the other phases using

the images acquired at the higher energy level (i.e., 33.269 keV). Arithmetic operations were then performed on the segmented images to yield one segmented image that contains all the phases where voxels of each phase were assigned a distinct value (i.e., sand particles have a voxel value of two, brine has a voxel value of one, and gas has a voxel value of zero). Sand particles in contact were separated using Avizo Separate Objects module, which removes small areas of contact between particles. Finally, to track the displacement and rotation of individual sand particles, each sand particle was labeled with a unique identification number using Labeling module in Avizo. Figure 2-2 presents the steps of the image segmentation that was performed on the images acquired at the second state of the test for the 2% kaolinite specimen.

Fines Segmentation

Separation of fines from other phases was a challenging task due to their small sizes and since they are mixed with the water phase. One way to infer zones with high concentration of fines is by considering zones in the water phase with a higher density (higher CT number). Figure 2-3 shows the image intensity histogram of the initial state of 4% kaolinite specimen. The highlighted region in the histogram include voxels of sand particles and fines. After selecting the voxels within this region, voxels of sand particles were excluded based on the three-phase segmented image. After that, the detected regions with high concentration of fines were highlighted in the filtered image and appear as bright white spots. Figure 2-4 shows the greyscale image of third state scan for the 6% kaolinite specimen with regions of high fines concentration displayed as bright voxels. Both clogging and gas driven fracture are detected in Figure 2-4. Clogging of the pore space due to fines is observed near the boundary of the CO₂ brine interface.

Local Measurements

Representative Elementary Volume (REV)

REV of an image is defined as the smallest sub-volume that represents the sample where the property of interest is constant regardless of the size of the sample. The size of the REV is selected to be large enough to smooth out fluctuations and small enough to eliminate macroscopic changes of the property of interest (Bear 2013). Researchers used different methods to determine REV of various properties of granular materials such as porosity, interfacial area, saturation, volumetric strain, and shear strain (Al-Raoush 2012; Al-Raoush 2014; Amirrahmat et al. 2018). In this study, REV was computed for porosity by calculating porosity within cubical regions of different sizes of the image of the 6% kaolinite initial state specimens. Figure 2-5 shows the variation of porosity over different sizes of the image of 6% kaolinite specimen where a cube with side length of 850 μm is considered the minimum REV of the system and therefore was selected for this study. 3D images were divided into multiple REV and variation of local porosity and fines concentration were examined.

Local Porosity

The REV was used to compare porosity variations due to CO₂ injection in the systems by comparing porosity values of images at the fourth state to those of the first state of the experiments. Figure 2-6 to Figure 2-10 shows the variation of porosity for several 2D slices of the initial and final states of the tested specimens. For 0%, 2%, and 4% kaolinite specimens (Figure 2-6 to Figure 2-8), initial local porosity ranged from 30% to 45% and did not vary considerably for the final state of the specimens. This indicates that CO₂ percolated through pore space without changing the porosity of sediments or generating fractures. On the other hand, when the percentage of fines increased to 6% kaolinite specimen, a change of porosity was observed due to the development of fractures at different locations as can be observed in Figure 2-9 and Figure 2-10. The development of fractures significantly changed the distribution of porosity of the system. High porosity was observed in zones where fractures took place whereas low porosity was observed in zones around fractures. As fractures propagate, sediments surrounding fractures densifies. Figure 2-11 shows porosity distribution histograms for the initial and final states of the tested specimens. For 0% kaolinite, 2% kaolinite, and 4% kaolinite specimens, porosity histogram distributions are almost identical whereas the histogram of the 6% kaolinite specimen tends to be more right-skewed for the final state compared to the initial state (Figure 2-11(d) and Figure 2-11(h)). This skewness is caused by the densification of sediments as fractures are generated.

Local Fines Concentration

Fines concentration of each REV was calculated as the volume ratio of fines to sand contained in that REV. Figure 2-12 to Figure 2-15 show the variation of fines concentration for several 2D slices for the initial and final states of 2% kaolinite, 4% kaolinite, and 6% kaolinite specimens. Fines concentrations obtained from image analysis of the initial states are consistent with fines concentration obtained from weight measurements during specimens' preparation. This observation helps to develop confidence in the selected intensity range used in segmentation of fines. Although a homogenous distribution of fines was targeted during specimens' preparation, a slight local heterogeneity of fines distribution within each specimen is observed from Figure 2-12 to Figure 2-15. For 2% kaolinite and 4% kaolinite specimens (Figure 2-12 and Figure 2-13), fines concentration decreases from initial to final states, which indicates that fines migrated through the pores without clogging. Figure 2-14 and Figure 2-15 display variation of fines concentration for several 2D slices for the initial and final states of 6% kaolinite specimen in x-z and y-z directions, respectively. In contrast to 2% kaolinite and 4% kaolinite specimens, local fines concentration increased in the 6% kaolinite in REV's near the fracture boundaries due to fines clogging. Clogging induced an increase in the capillary pressure at the sediments pore throats which caused the capillary pressure to overcome the effective stress between sand particle and fractures were initiated. Figure 2-16 shows fines concentration distribution histograms for the initial and final states of the tested specimens. Histograms of the final state of 2% kaolinite

and 4% kaolinite specimens tend to be more right-skewed compared to the initial state (Figure 2-16(d) and Figure 2-16(e)). This is a manifestation of fines migration phenomenon which causes a reduction in fines concentration. On the other hand, final state histogram of the 6% kaolinite specimen (Figure 2-16(f)) tends to be left-skewed compared to the initial state. This is due to fines clogging which lead to an increase in fines concentration and generation of gas driven fractures.

Tracking of Displacement and Rotation of Sand Particles

A code developed by Al-Raoush (2007) and modified by Druckrey et al. (2016) was used to conduct further quantitative analysis to obtain several physical properties of labeled sand particles including volume, surface area, centroid, and lengths and orientation of particles' longest, shortest, and intermediate axes. In the labeled image (Figure 2-2(f)), each particle has a distinct label identifying it from other particles. This label may not be necessarily the identical for same particle in a labeled image of a different loading state. Therefore, a Matlab code was used to track labeled particles from one state to another. The code loops through all labeled particles in the first image and isolates a searching sub-volume surrounding each particle. The searching sub-volume was made large enough to account for particles displacement. Then, each particle is matched by searching for a label in the second image that has the same physical properties within the searching sub-volume. Finally, the two labels are given the same identification number. More description of the code can be found in Druckrey and Alshibli (2014). Finally, particle displacement was calculated as the change of centroid location from one image to another whereas the rotation of a particle was calculated based on the change of the orientation of the particle's longest axis.

Figure 2-17 shows variation of particle displacement for several 2D slices for the final states of 6% kaolinite specimen in x-z and y-z directions. Referring to Figure 2-17, particles near fractures can experience a displacement as high as 200 μm , while a homogeneous distribution of displacements is observed for particles far away from fractures. This can also be observed from the 3D volume rendering of the variation of displacement shown in Figure 2-18. Moreover, Figure 2-18 presents variation of particle rotation for several 2D slices for the final states of 6% kaolinite specimen in x-z and y-z directions. Rotation of particles ranged from 0 to 15°, where particles near fractures experience the highest rotation. Particles in zones away from fractures did not experience major rotations.

Conclusions

Multiphase flow experiments were conducted on uniform Ottawa silica sand initially saturated with brine and mixed with fines (i.e., kaolinite) at different percentages by weight (0%, 2%, 4% and 6%) at different injection rates of CO₂. CT was used to obtain non-destructive 3D images of these systems. Image processing algorithms were used to segment and identify different phases in the images and perform quantitative analysis. Fines were segmented by selecting voxels with high CT numbers in the brine phase of the images. Fines concentration values obtained

from image analysis are consistent with those obtained using weight measurements during specimens' preparation. Gas invaded the 0%, 2% and 4% kaolinite specimens by "percolation", while it invaded the 6% specimen by "fracturing" or "conduit opening". This threshold value of 6% between percolation and fracturing may not be necessarily the same for other systems with different fines size, sand size and porosity. A cubical representative element with an edge size of 850 μm was found to be sufficient for local porosity and fines concentration investigation. For specimens with fines concentration less than 6%, gas percolated through the pores without any major porosity change or fracturing. For 6% kaolinite specimen, gas driven fractures propagated by densifying surrounding sediments. fines concentration decreases from initial to final states for the 2% and 4% kaolinite specimens. This indicates that fines migrated through the pores without clogging. For 6% kaolinite specimen, fines concentration increased near fractures' boundaries due to fines clogging. Clogging induced an increase in the capillary pressure at the pore throats and caused the capillary pressure to overcome the effective stress between sand particle, and fractures to be initiated. Particles near fractures experienced the highest displacement and rotations in the 6% kaolinite specimen. Due to gas driven fracture, particles experienced up to 200 μm displacement and 15° rotation.

Acknowledgments

This research was made possible by the National Priorities Research Program (NPRP) grant # NPRP8-594-2-244 from Qatar National Research Fund (a member of Qatar Foundation). The findings achieved herein are solely the responsibility of the authors. The SMT images were collected using the X-ray Operations and Research Beamline Station 13-BMD at Argonne Photon Source (APS), Argonne National Laboratory. The authors thank Dr. Mark Rivers of APS for help in performing the SMT scans. They also acknowledge the support of GeoSoilEnviroCARS (Sector 13), which is supported by the National Science Foundation, Earth Sciences (EAR-1128799), and the US Department of Energy (DOE), Geosciences (DE-FG02-94ER14466). Use of the Advanced Photon Source, an Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory, was supported by DOE under contract no. DE-AC02-06CH11357.

References

- Agbangla, G. C., Climent, É., and Bacchin, P. (2012). "Experimental investigation of pore clogging by microparticles: Evidence for a critical flux density of particle yielding arches and deposits." *Separation and purification technology*, 101, 42-48.
- Al-Raoush, R. (2007). "Microstructure characterization of granular materials." *Physica A: Statistical mechanics and its Applications*, 377(2), 545-558.
- Al-Raoush, R. (2012). "Change in microstructure parameters of porous media over representative elementary volume for porosity." *Particulate Science and Technology*, 30(1), 1-16.
- Al-Raoush, R. I. (2014). "Experimental investigation of the influence of grain geometry on residual NAPL using synchrotron microtomography." *Journal of contaminant hydrology*, 159, 1-10.
- Alshibli, K. A., Druckrey, A. M., Al-Raoush, R. I., Weiskittel, T., and Lavrik, N. V. (2014). "Quantifying morphology of sands using 3D imaging." *Journal of Materials in Civil Engineering*, 27(10), 04014275.
- Amirrahmat, S., Alshibli, K. A., Jarrar, M. F., Zhang, B., and Regueiro, R. A. (2018). "Equivalent continuum strain calculations based on 3D particle kinematic measurements of sand." *International Journal for Numerical and Analytical Methods in Geomechanics*.
- Bear, J. (2013). *Dynamics of fluids in porous media*, Courier Corporation.
- Choi, J. H., Seol, Y., Boswell, R., and Juanes, R. (2011). "X-ray computed-tomography imaging of gas migration in water-saturated sediments: From capillary invasion to conduit opening." *Geophysical Research Letters*, 38(17).
- Druckrey, A. M., and Alshibli, K. A. "3D behavior of sand particles using X-ray synchrotron micro-tomography." *Proc., Geo-Congress 2014: Geo-characterization and Modeling for Sustainability*, 2814-2821.
- Druckrey, A. M., Alshibli, K. A., and Al-Raoush, R. I. (2016). "3D characterization of sand particle-to-particle contact and morphology." *Computers and Geotechnics*, 74, 26-35.
- FEI. 2017. Avizo, version 9.5FEI, Hillsboro, OR.
- Holtzman, R., and Juanes, R. (2010). "Crossover from fingering to fracturing in deformable disordered media." *Physical Review E*, 82(4), 046305.
- Hyodo, M., Li, Y., Yoneda, J., Nakata, Y., Yoshimoto, N., and Nishimura, A. (2014). "Effects of dissociation on the shear strength and deformation behavior of methane hydrate-bearing sediments." *Marine and petroleum geology*, 51, 52-62.
- Imdakh, A., and Sahimi, M. (1991). "Computer simulation of particle transport processes in flow through porous media." *Chemical engineering science*, 46(8), 1977-1993.
- Jang, J., and Santamarina, J. C. (2014). "Evolution of gas saturation and relative permeability during gas production from hydrate-bearing sediments: Gas invasion vs. gas nucleation." *Journal of Geophysical Research: Solid Earth*, 119(1), 116-126.

- Jung, J., Cao, S. C., Shin, Y.-H., Al-Raoush, R. I., Alshibli, K., and Choi, J.-W. (2017). "A microfluidic pore model to study the migration of fine particles in single-phase and multi-phase flows in porous media." *Microsystem Technologies*, 1-10.
- Jung, J. W., Jang, J., Santamarina, J. C., Tsouris, C., Phelps, T. J., and Rawn, C. J. (2012). "Gas Production from Hydrate-Bearing Sediments: The Role of Fine Particles." *Energy & Fuels*, 26(1), 480-487.
- Max, M. D., Johnson, A. H., and Dillon, W. P. (2013). *Natural Gas Hydrate-Arctic Ocean Deepwater Resource Potential*, Springer.
- Wan, J., and Wilson, J. L. (1994). "Colloid transport in unsaturated porous media." *Water Resources Research*, 30(4), 857-864.
- Wiseall, A., Cuss, R., Graham, C., and Harrington, J. (2015). "The visualization of flow paths in experimental studies of clay-rich materials." *Mineralogical Magazine*, 79(6), 1335-1342.

Appendix

Appendix A: Figures

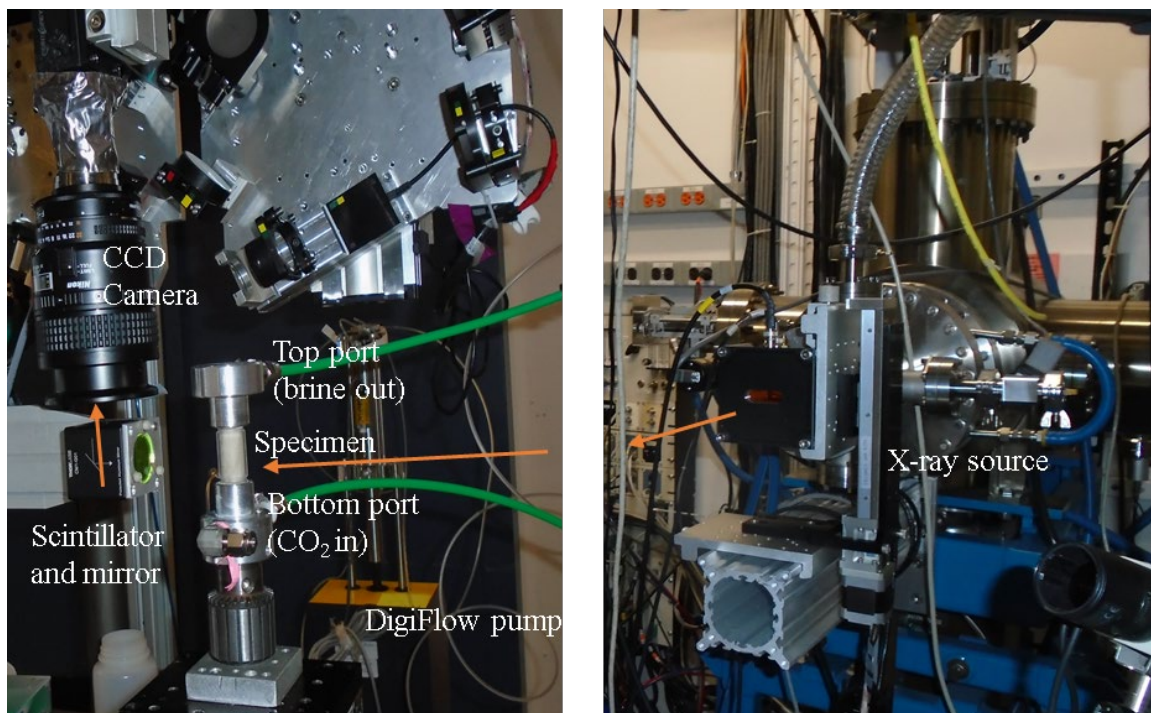


Figure 2-1. Experimental setup at Beamline 13D, Advanced Photon Source, Argonne National Laboratory.

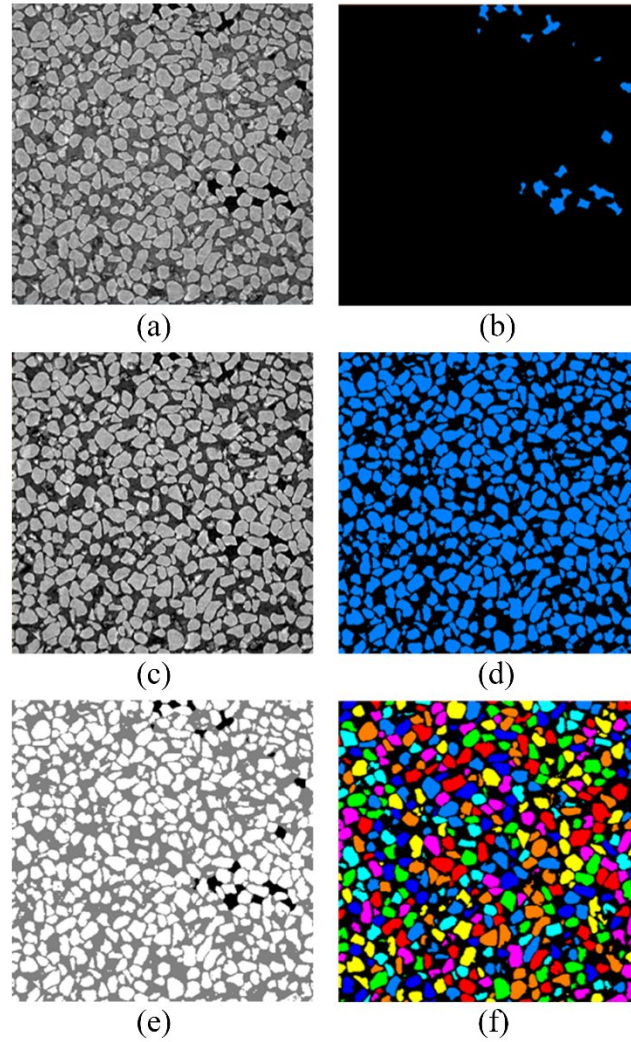


Figure 2-2. Image post-processing steps: (a) filtered image acquired at energy level higher than Iodine edge (33.269 keV); (b) gas phase binarized image; (c) filtered image acquired at lower energy level than Iodine edge (33.069 keV); (d) solids phase binarized image; (e) three-phase segmented image; (f) labeled sand particles for the 2% kaolinite specimen acquired at the second state of the test (i.e., 0.4 ml was drained out of the sample while injecting CO₂ at a constant pressure of 27.6 kPa (4 psi), sand is white, brine is grey and gas is black.

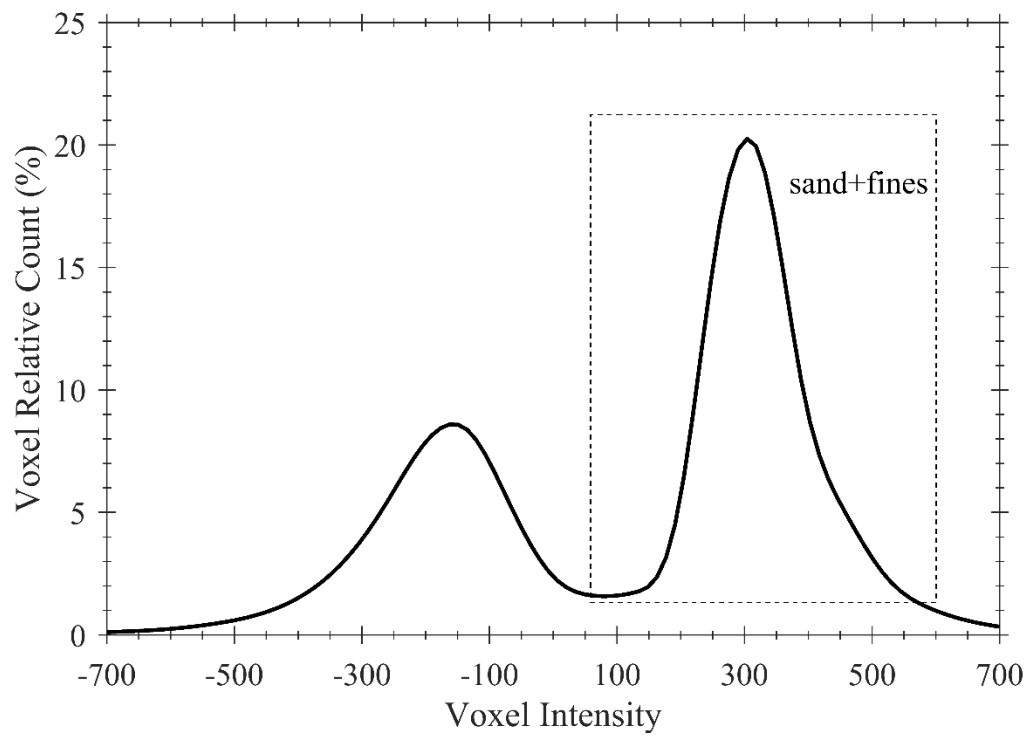


Figure 2-3. Intensity histogram of a sample image for the initial state when the system was saturated with brine and 4% kaolinite specimen.

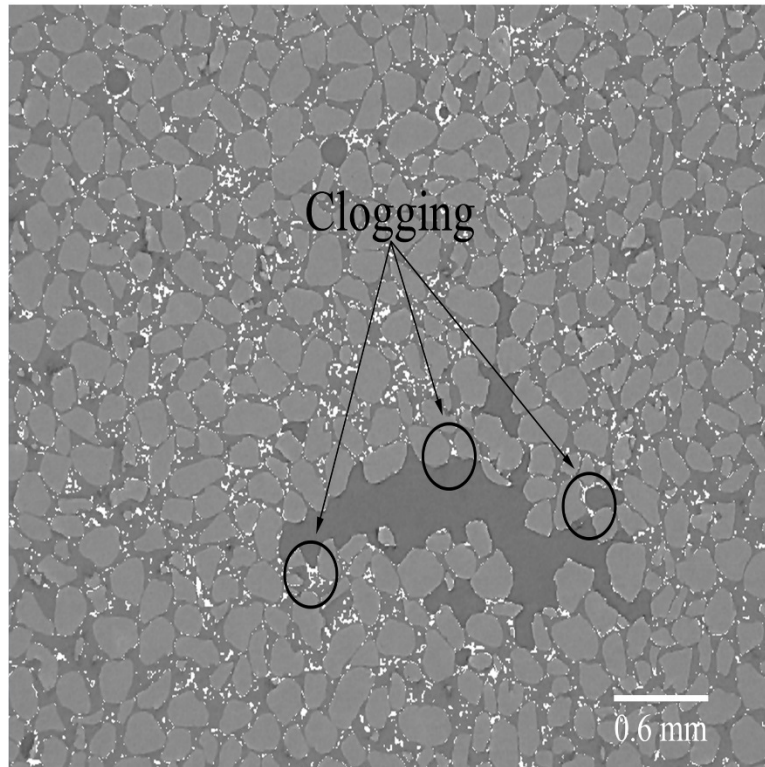


Figure 2-4. Greyscale image of the third state of the 6% kaolinite specimen where a total of 1.0 ml of brine solution was drained out of the saturated specimen while injecting CO₂ at a constant pressure of 27.6 kPa. High fines concentration displayed as bright voxels.

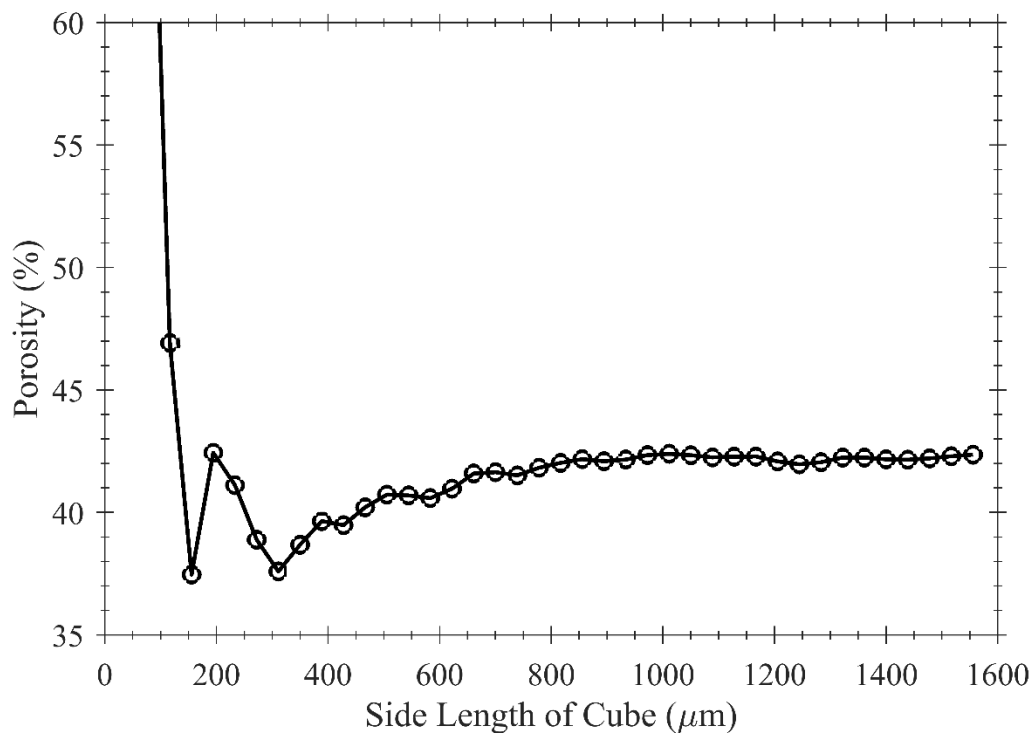


Figure 2-5. Porosity variation over different cubical volumes of 6% kaolinite specimen.

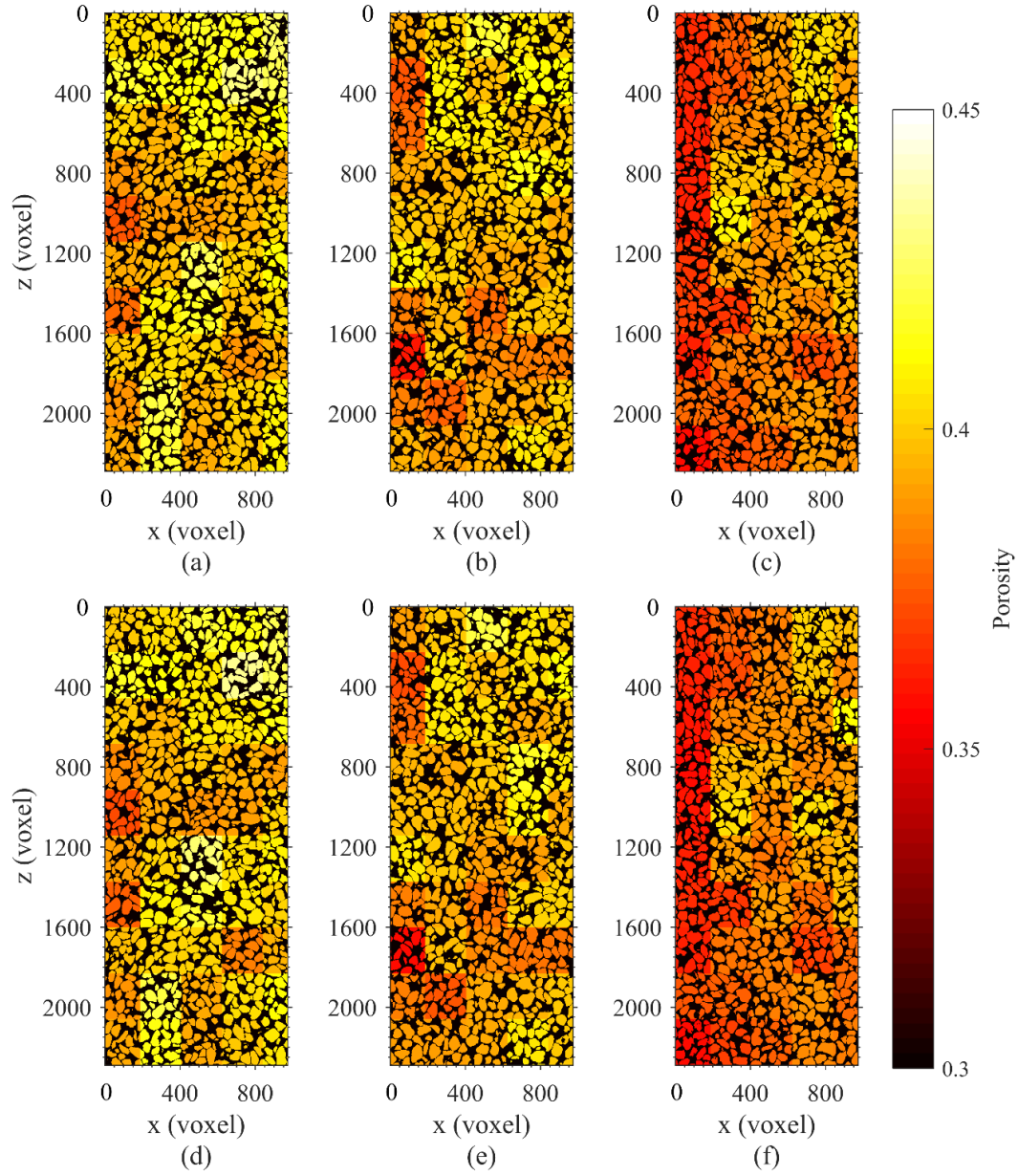


Figure 2-6. Variation of porosity in x-z direction in the initial state and the final state of 0% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700.

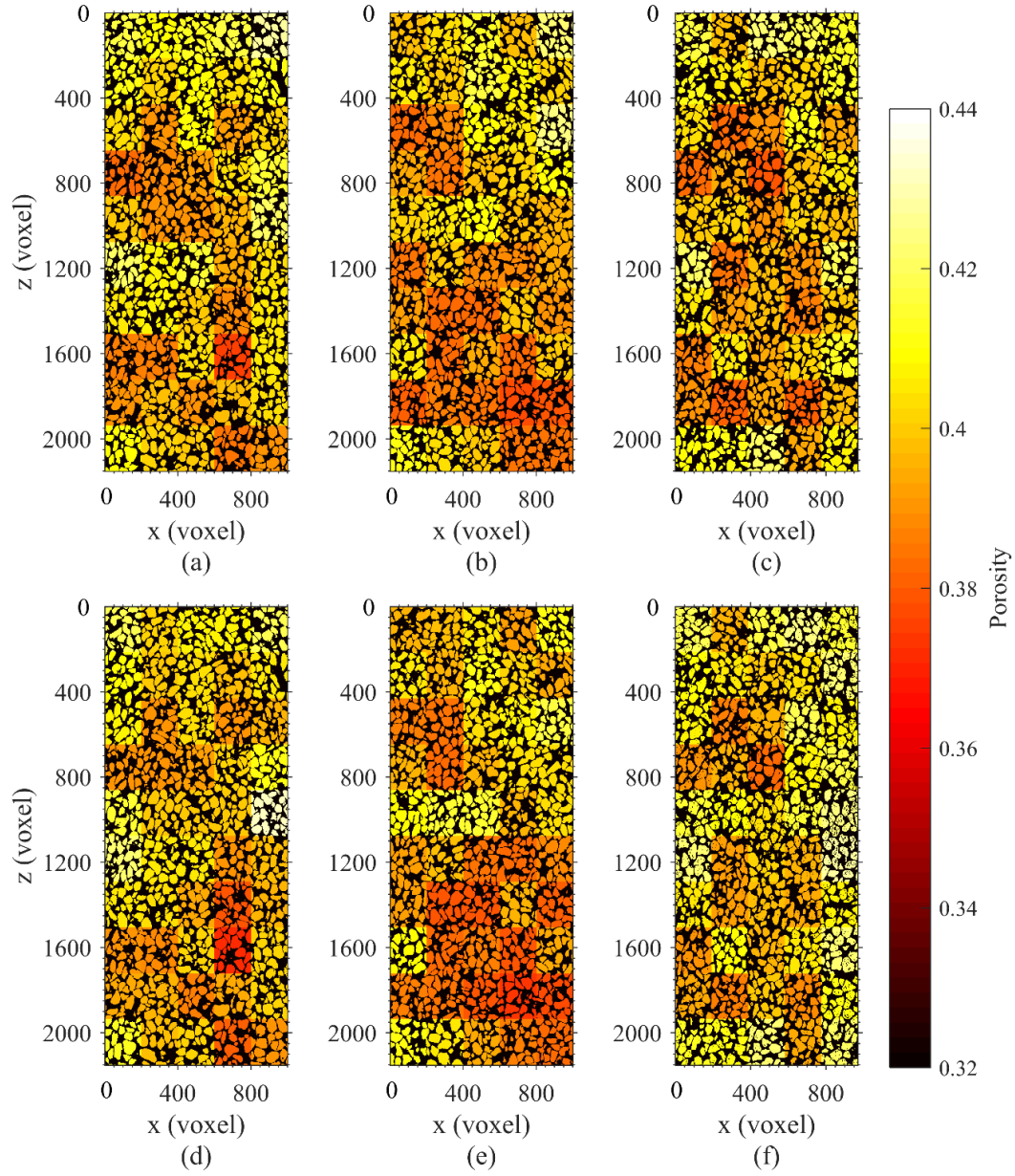


Figure 2-7. Variation of porosity in x-z direction in the initial state and the final state of 2% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700.

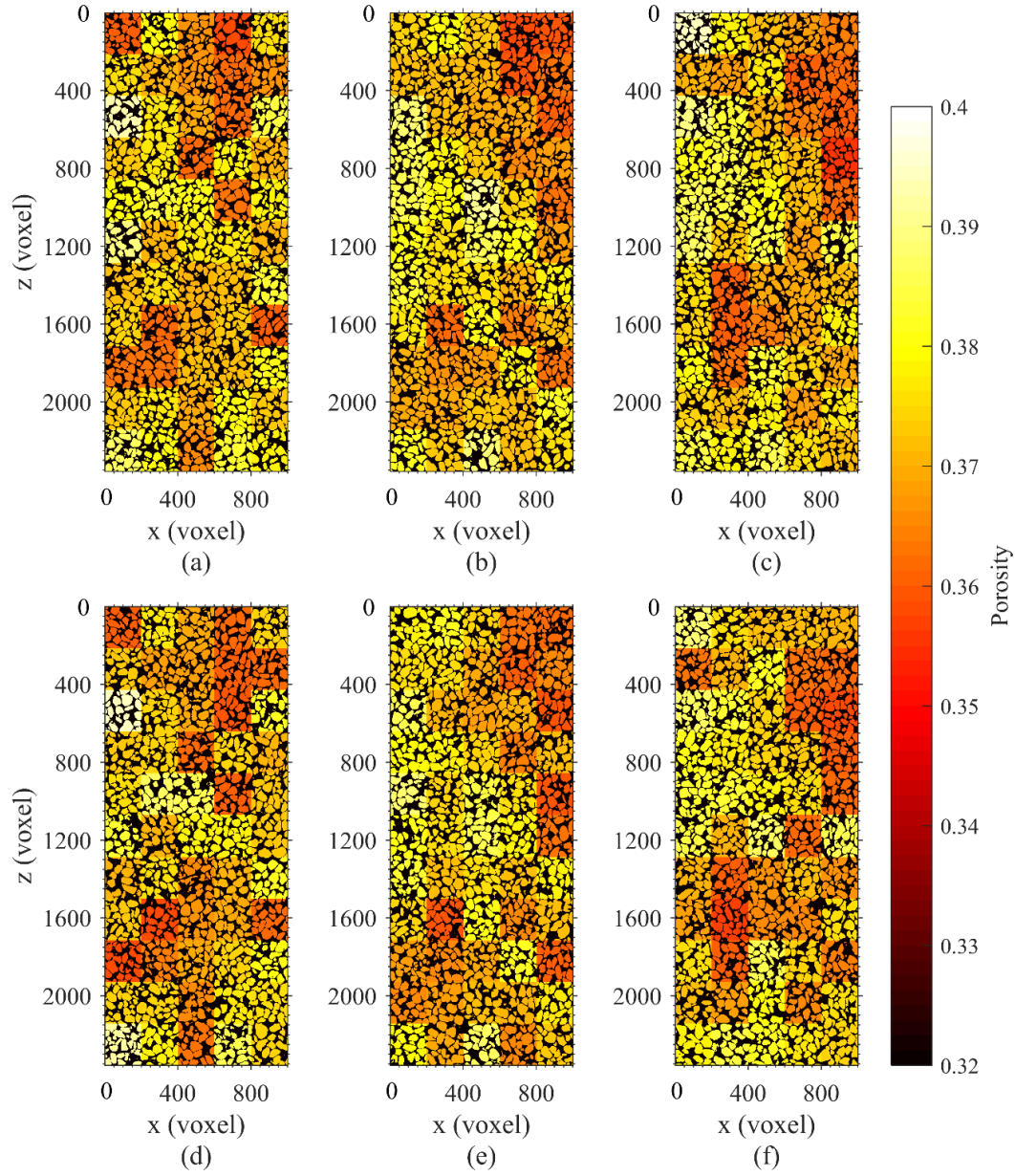


Figure 2-8. Variation of porosity in x-z direction in the initial state and the final state of 4% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700.

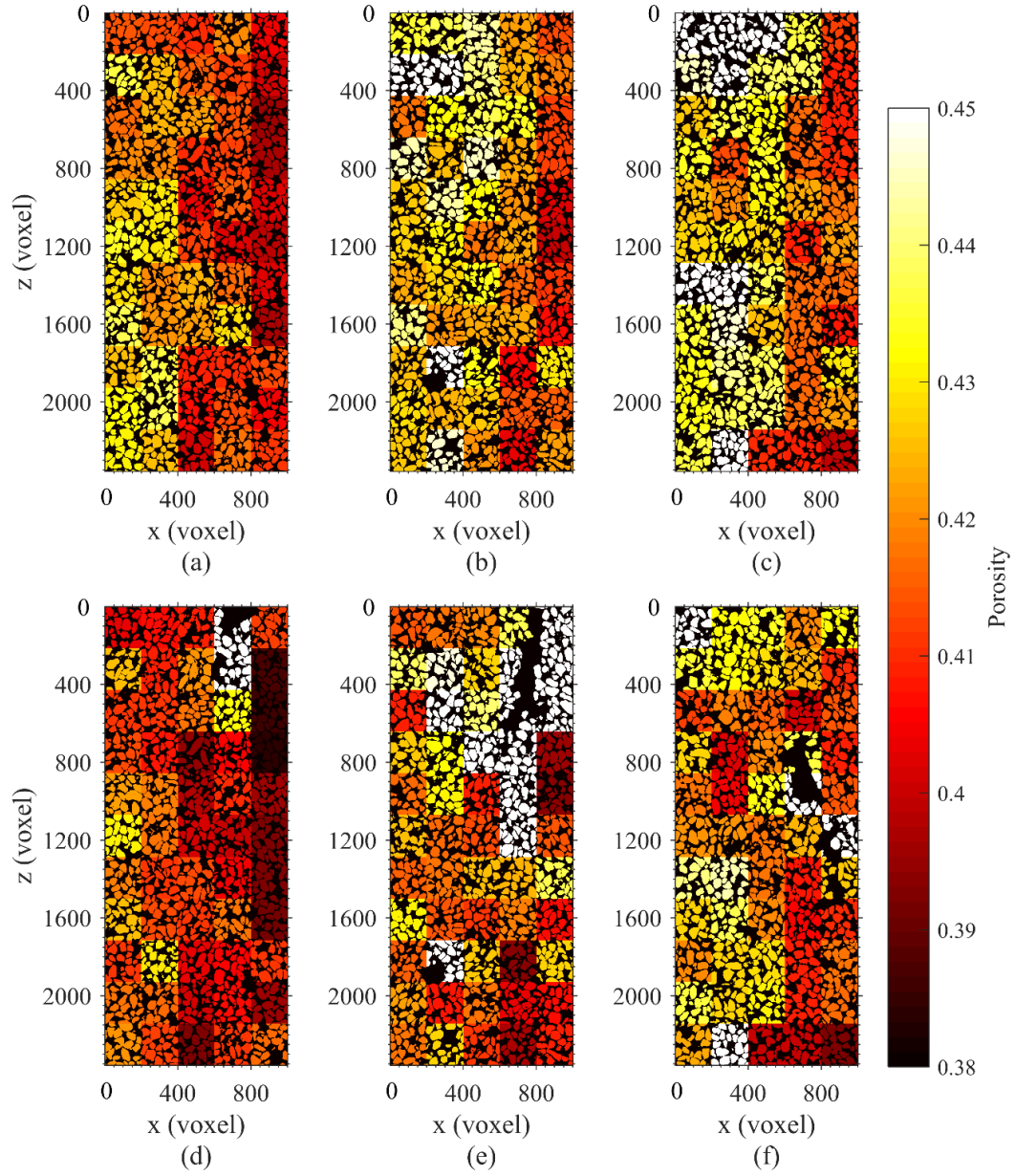


Figure 2-9. Variation of porosity in x-z direction in the initial state and the final state of 6% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700.

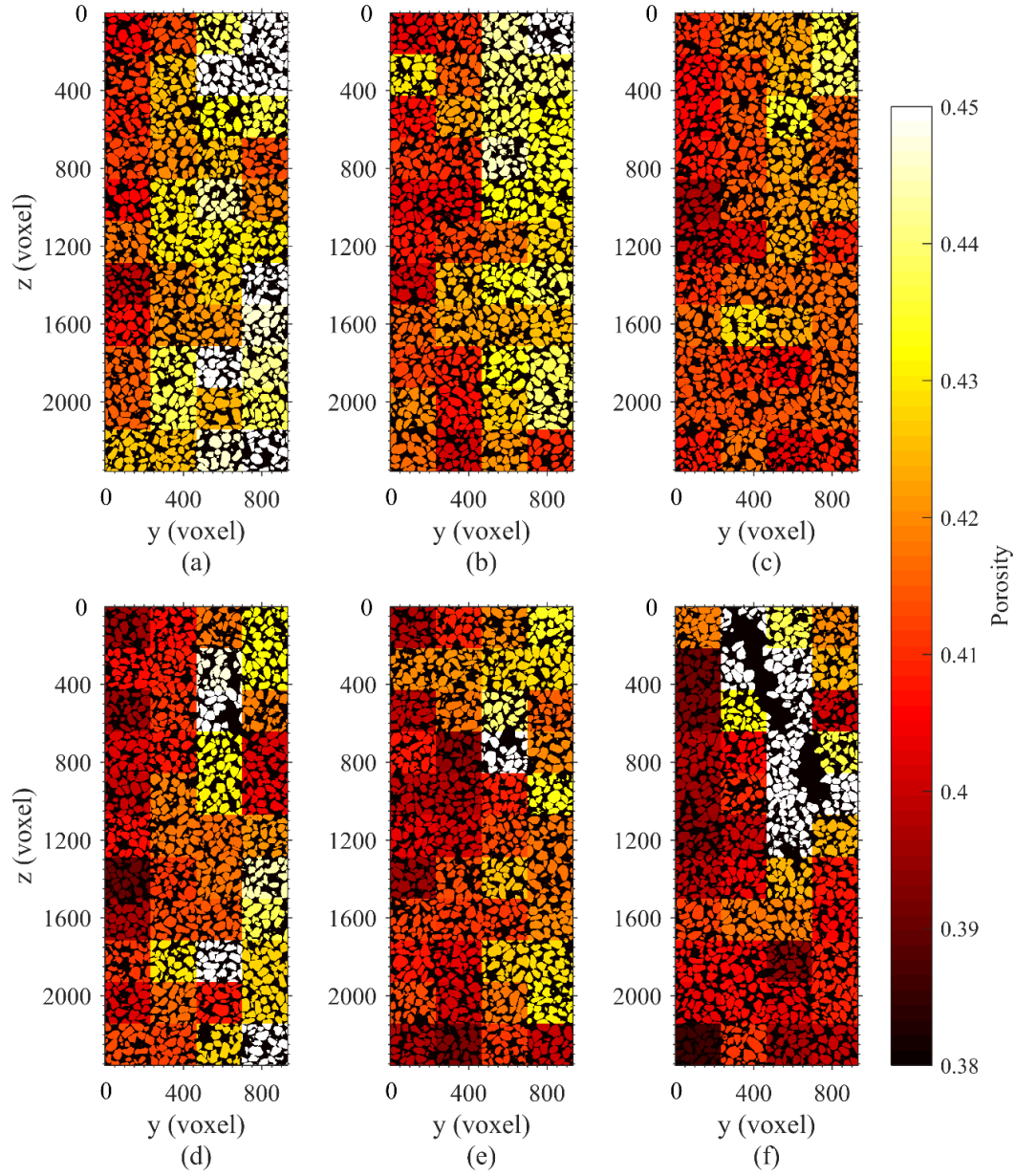


Figure 2-10. Variation of porosity in y-z direction in the initial state and the final state of 6% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700.

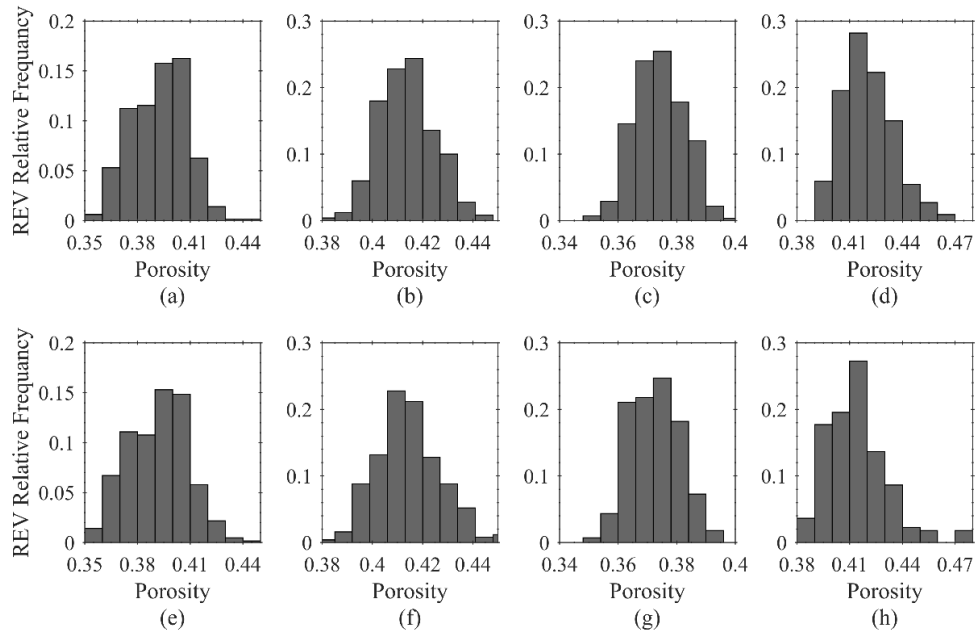


Figure 2-11. Porosity histograms for initial state of (a) 0% kaolinite; (b) 2% kaolinite; (c) 4% kaolinite; (d) 6% kaolinite and final state of (e) 0% kaolinite; (f) 2% kaolinite; (g) 4% kaolinite; (h) 6% kaolinite specimens.

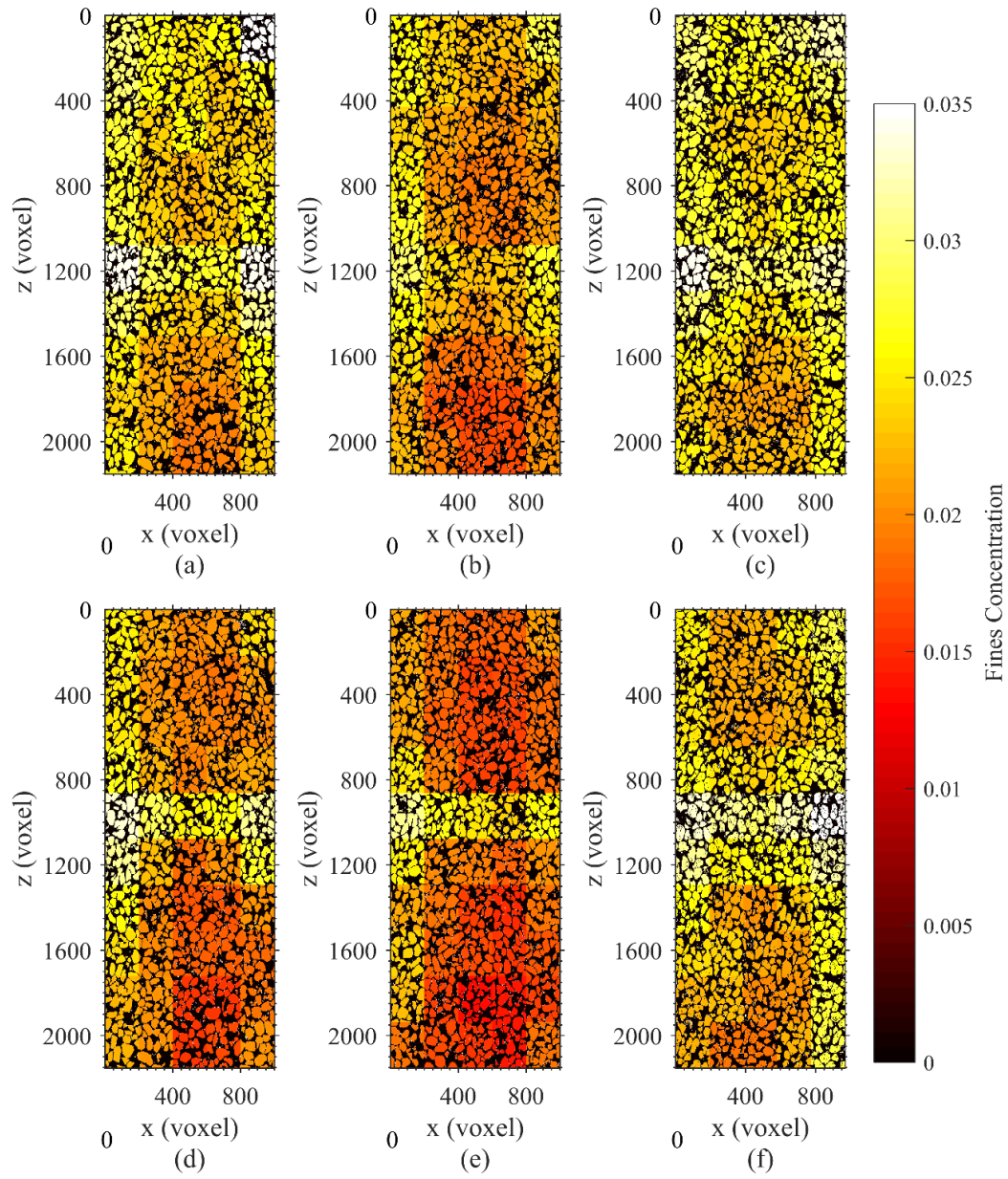


Figure 2-12. Variation of fines concentration in x-z direction in the initial state and the final state of 2% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700.

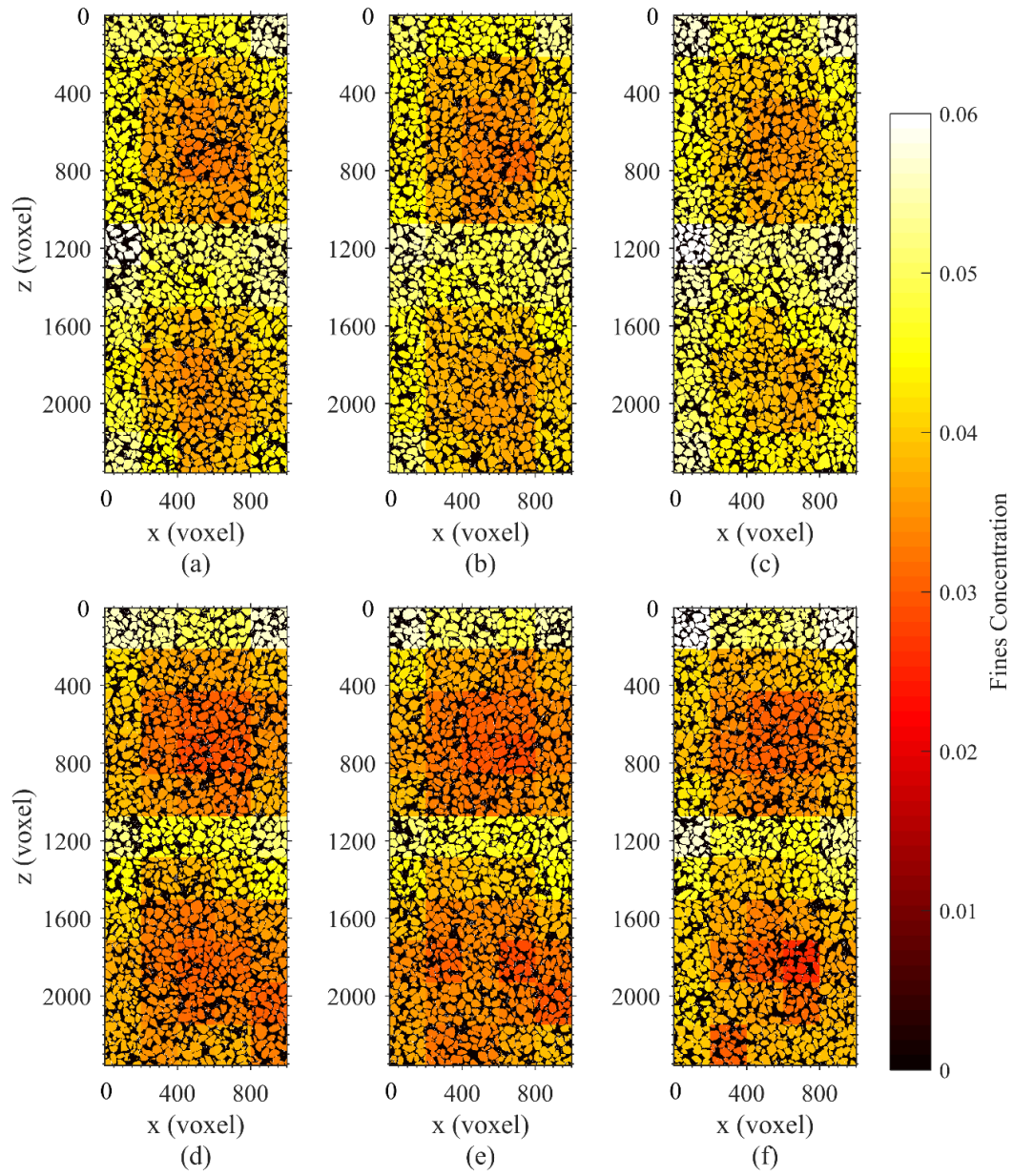


Figure 2-13. Variation of fines concentration in x-z direction in the initial state and the final state of 4% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700

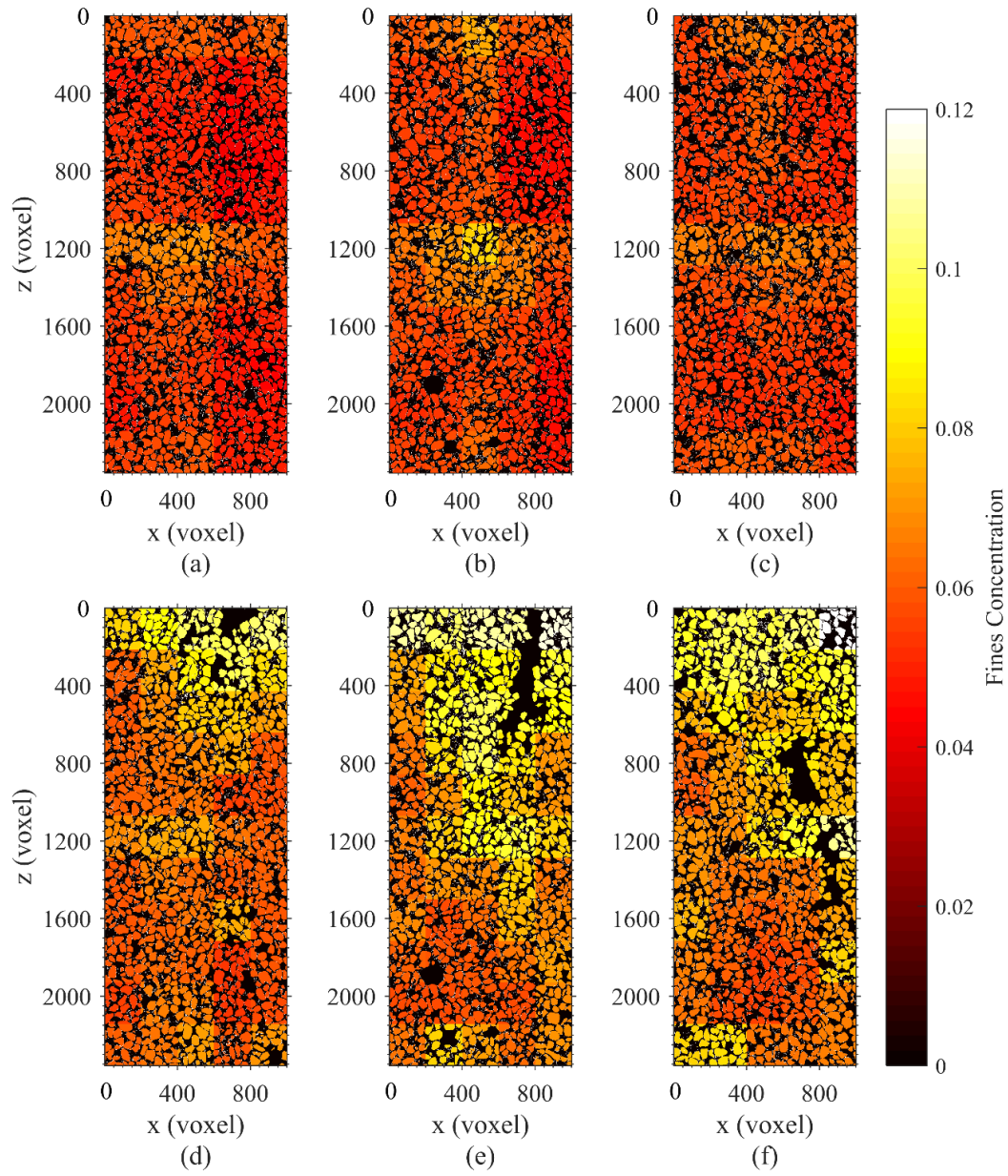


Figure 2-14. Variation of fines concentration in x-z direction in the initial state and the final state of 6% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700.

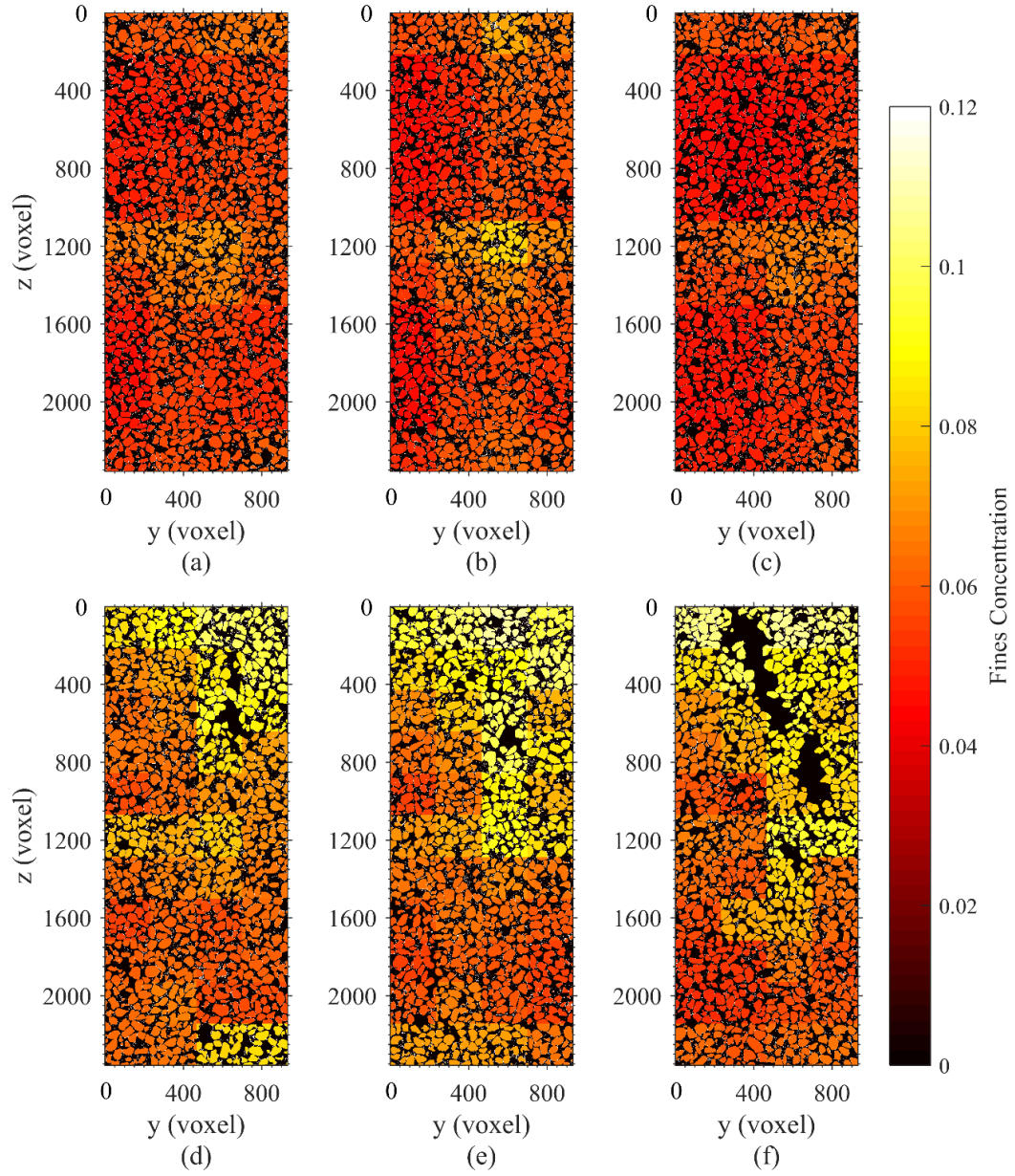


Figure 2-15. Variation of fines concentration in y-z direction in the initial state and the final state of 6% kaolinite specimen at: (a) initial state, slice 300; (b) initial state, slice 500; (c) initial state, slice 700; (d) final state, slice 300; (e) final state, slice 500; (f) final state, slice 700.

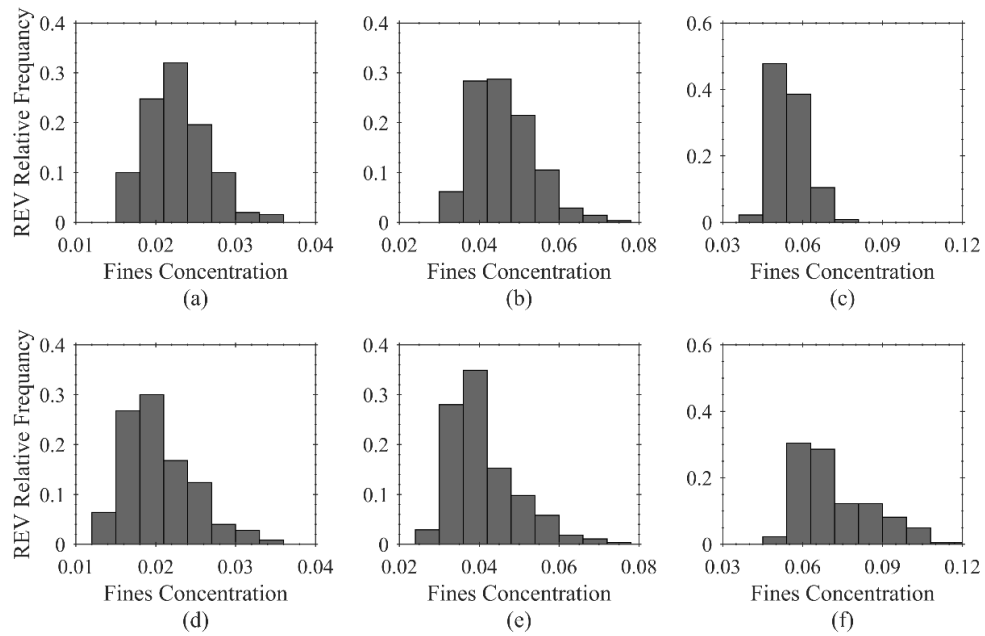


Figure 2-16. Fine concentration histograms for initial state of (a) 2% kaolinite; (b) 4% kaolinite; (c) 6% kaolinite and final state of (d) 2% kaolinite; (e) 4% kaolinite; (f) 6% kaolinite specimens.

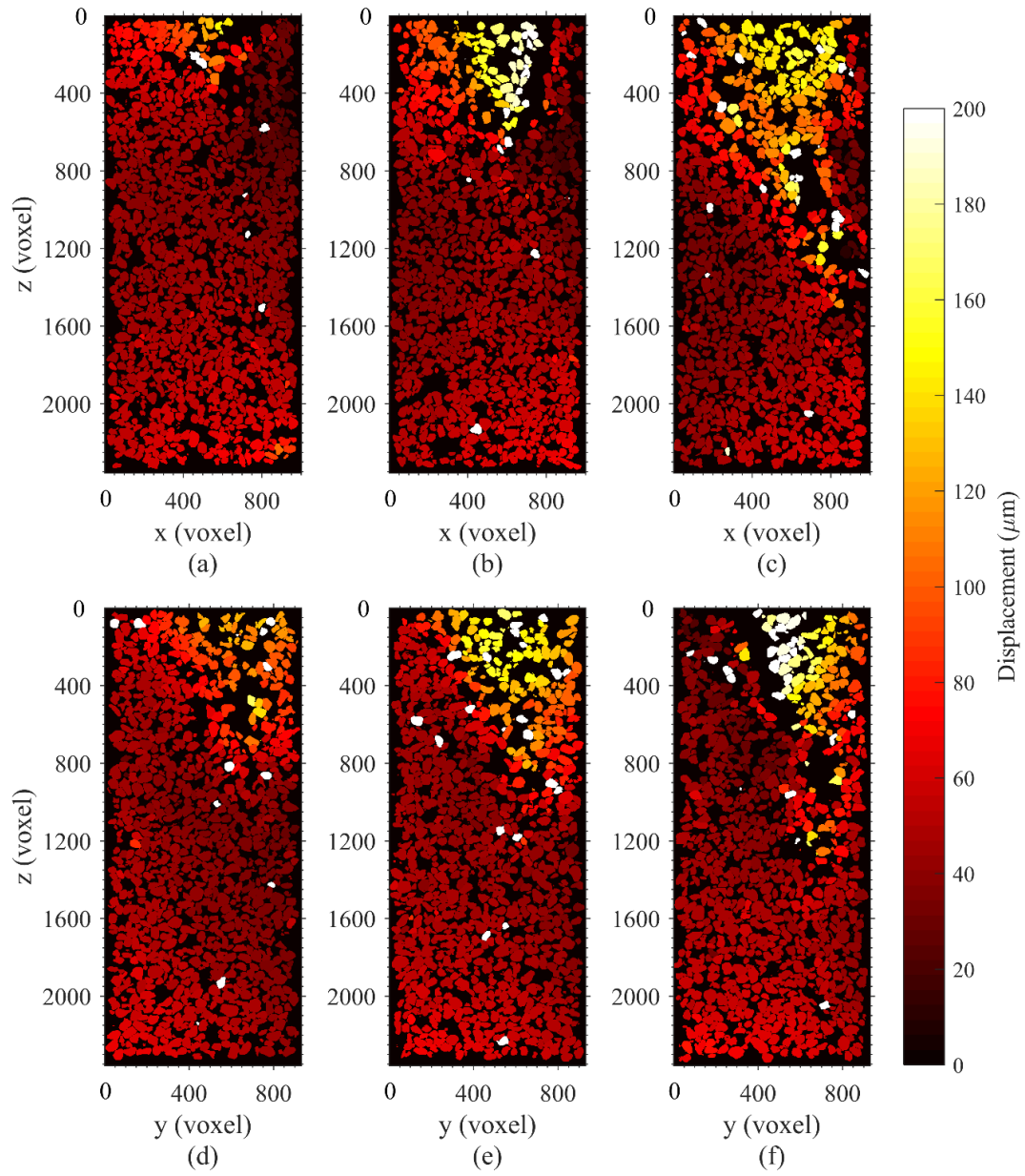


Figure 2-17. Particle displacement for the final state of 6% kaolinite specimen at (a) x-z slice 300; (b) x-z slice 500; (c) x-z slice 700; (d) y-z slice 300; (e) y-z slice 500; (f) y-z slice 700.

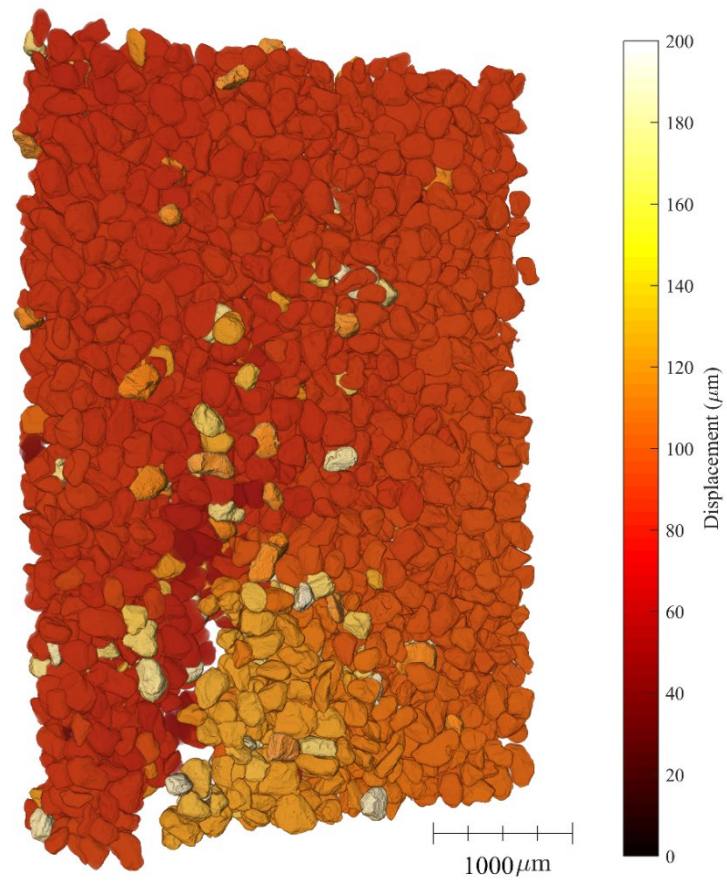


Figure 2-18. Variation of displacement of particles at the final state of 6% kaolinite specimen for a section near fracture.

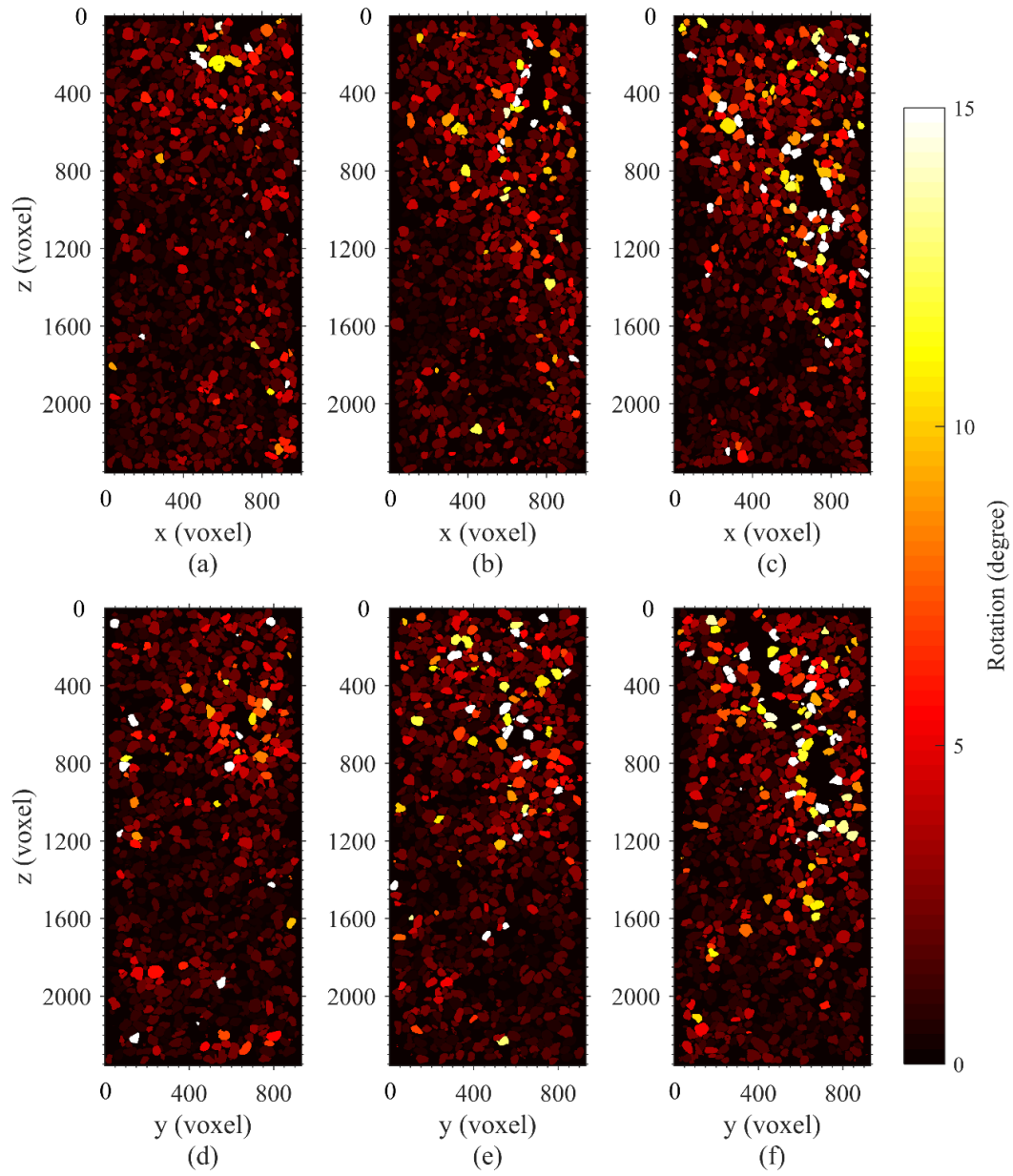


Figure 2-19. Particle rotation for the final state of 6% kaolinite specimen at: (a) x-z slice 300; (b) x-z slice 500; (c) x-z slice 700; (d) y-z slice 300; (e) y-z slice 500; (f) y-z slice 700.

CHAPTER THREE

**3D MEASUREMENTS OF HYDRATE SURFACE AREA DURING
HYDRATE FORMATION AND DISSOCIATION IN POROUS MEDIA
USING DYNAMIC 3D IMAGING**

A version of this chapter is published as Jarrar Z. A., Alshibli K. A., Al-Raoush R. I., & Jung J. (2020). 3D Measurements of Hydrate Surface Area during Hydrate Dissociation in Porous Media using Dynamic 3D Imaging. *Fuel*, 265, 116978. <https://doi.org/10.1016/j.fuel.2019.116978>

My contribution to this paper is performing majority of the experimental tests, data analysis, and preparing the original draft and all figures.

The hydrate formation part was published as Alshibli K. A., & Jarrar Z. A., (2020). 4D Dynamic Synchrotron Micro Computed Tomography (SMT) Imaging of Gas-Water Interface at High Pressure and Low Temperature. *Geotechnical Testing Journal*. <https://doi.org/10.1520/GTJ20190332>

My contribution to this paper is performing some of the experimental tests, data analysis of hydrate formation part, preparing the figures of the hydrate formation part, and writing the hydrate formation results discussion part.

Abstract: A better understanding of the kinetics of hydrate dissociation is essential to reliably predict gas production potential from natural hydrate reservoirs. Most hydrate dissociation models assume hydrates to be a constant number of equal-sized spheres dissociating at a constant rate. This paper uses dynamic 3D synchrotron micro-computed tomography (SMT) imaging to study hydrate surface area evolution during Xenon hydrate dissociation. Hydrates are formed inside a high-pressure low-temperature cell filled with partially saturated ASTM 20-30 Ottawa sand. Hydrate dissociation is initiated through depressurization in the first experiment and through thermal stimulation in the second experiment. During dissociation, continuous full 3D SMT images were acquired where each scan took 45 seconds to complete. A combination of cementing, pore-filling, and surface coating pore-habits were observed for the depressurization experiment and pore-filling for the thermal stimulation experiment. Hydrate specific area increased initially with increasing hydrate saturation and began to decrease after a threshold, which is an evidence of Ostwald Ripening. For hydrate saturation less than 10%, the predominant pore-habit was surface coating. Cementing pore-habit was observed at 15% hydrate saturation, and pore-filling hydrate pore-habit was observed with further increase in hydrate saturation. Surface coating hydrates dissociate faster than hydrates with pore-filling pore habit due to the higher specific area which allows for more surface for hydrates to dissociate it. Direct measurements of hydrate volume and hydrate surface area suggest that even with a combination of hydrate pore habit formed within the 3D porous media, estimation of hydrate surface area as a linear relation with (hydrate volume)^{2/3} is best for hydrate saturation less than a threshold value depending on the dissociation

method and driving force. $(\text{hydrate volume})^2$ and $(\text{hydrate volume})^3$ were found to better estimate hydrate interfacial area in comparison to $(\text{hydrate volume})^{2/3}$ for the depressurization experiment and thermal stimulation experiment, respectively.

Keywords: Gas hydrates, computed tomography, 3D imaging, dissociation rate, hydrate pore habit

Introduction

Natural methane gas hydrates availability and ongoing rise in demand for energy, motivated researchers to consider gas hydrates as a potential energy source. Gas hydrates refer to ice-like structures formed under certain pressure and temperature conditions where gas (guest molecules) is trapped within a crystal structure of water (host molecules) by van der Waals forces (Bonnetfoy et al. 2005). Different gas hydrate structures form depending on the molecular diameter of the guest molecules; primarily classified as structure I and structure II (Sloan 2003; Ye and Liu 2012). More than 95% of natural hydrates occur in marine environment where elevated pressure and low temperature conditions are satisfied (Max et al. 2013; Sloan Jr and Koh 2007), and approximately 99% of these hydrates are Methane (CH_4) hydrates (Kvenvolden 1995; Merey et al. 2018). Methane gas production from hydrate-bearing sediments requires hydrate dissociation in order to release Methane gas into sediments prior to gas production operations. Hydrate dissociation is a kinetic endothermic process that requires heat to break the bonds between guest and host molecules to produce water and gas. There are currently four main techniques to investigate hydrate dissociation; they are: thermal stimulation, depressurization, chemical injection and CH_4 - CO_2 replacement (Chong et al. 2016; Merey et al. 2018; Xu and Li 2015).

Thermal stimulation and depressurization are applied by altering local pressure and temperature conditions of gas hydrate reservoirs, resulting in hydrate destabilization and dissociation to water and gas (Chen et al. 2018; Konno et al. 2017; Konno et al. 2010; Minagawa et al. 2015). Chemical injection technique involves introducing a chemical to shift hydrate equilibrium curve for hydrates to dissociate at in-situ conditions (Daraboina et al. 2013; Moridis et al. 2013), while CH_4 - CO_2 replacement requires injecting CO_2 gas in hydrate reservoirs to replace CH_4 molecules in hydrate cages (Hyodo et al. 2014; Liu et al. 2016). Among the four techniques, depressurization is considered the most economically feasible technique (Collett et al. 2015; Huang et al. 2016).

A better understanding of the kinetics of hydrate dissociation is essential to accurately predict gas production potential from natural hydrate reservoirs. Many theoretical (Oyama et al. 2009; Windmeier and Oellrich 2013), analytical (Hong et al. 2003; Selim and Sloan 1989), and numerical (Gamwo and Liu 2010; Jamaluddin et al. 1989) dissociation kinetic models were developed by researchers since the 1980s to simulate hydrate dissociation process. Kim et al. (1987) proposed what is considered as the most classical hydrate dissociation model until this date (Yin et al. 2016). They studied Methane hydrate dissociation

using a semi-batch stirred tank reactor, and proposed the hydrate dissociation rate to be:

$$-\frac{dn_H}{dt} = k_d A_S (f_e - f) \quad 3-1$$

where $-\frac{dn_H}{dt}$ is the molar hydrate dissociation rate (mol.s⁻¹), k_d is the hydrate dissociation rate constant (mol.m⁻².Pa⁻¹.s⁻¹), A_S is the surface area of hydrate (m²), f_e is the fugacity of gas at hydrate equilibrium pressure and temperature conditions (Pa), and f is the fugacity of gas in the bulk gas phase (Pa). The hydrate dissociation rate constant can be described by an Arrhenius-type equation as:

$$k_d = k_d^0 e^{-\frac{\Delta E}{RT}} \quad 3-2$$

Where k_d^0 is the intrinsic dissociation rate constant (mol.m⁻².Pa⁻¹.s⁻¹), ΔE is the activation energy (J.mol⁻¹), R is the universal gas constant (8.314 J.mol⁻¹.K⁻¹), and T is the absolute temperature (K) (Clarke and Bishnoi 2001; Kim et al. 1987). Although the intrinsic dissociation rate constant is independent of pressure, temperature, and hydrate surface area, different studies reported different values of k_d^0 by orders of magnitude for batch reactors (Clarke and Bishnoi 2001; Kim et al. 1987) and porous media (Kneafsey et al. 2007; Moridis et al. 2005). This may be attributed to the fact that none of these studies measured the surface area of hydrates. They instead estimated the surface area based on hydrate particle size by either assuming they all have the same initial diameter (Kim et al. 1987), or by measuring hydrate particles sizes using particle size analyzer (Clarke and Bishnoi 2001), or estimated the surface area as a linear combination of (hydrate saturation)^{2/3} (Moridis et al. 2005). These estimates were based on the assumptions that hydrates are fixed number of spheres dissociating at a uniform rate, meaning that the surface area of hydrates can be estimated as a linear function of (hydrate volume)^{2/3}.

Recently, Chen and Espinoza (2018) used microfocus x-ray radiography to study Xenon hydrate dissociation kinetics by first measuring the initial hydrate volume and surface area before dissociation based on a full reconstructed 3D image. They showed that hydrate surface area can be approximated as a linear function of (hydrate volume)^{2/3}. Then, they started hydrate dissociation by depressurization while capturing a total of 126 2D X-ray radiographs at a resolution of 49.79 µm /pixel and a time-resolution of 1 radiograph/second during the 40-minute dissociation experiment. Volume of hydrate was estimated based on assuming a linear relation between the change in hydrate volume and the change in x-ray numbers in the radiographs. The changes of those estimated volumes with time were used to calculate hydrate dissociation rates and reported a linear relationship between hydrate dissociation rate and (hydrate volume)^{2/3}.

This paper revisits the work of Chen and Espinoza (2018); however, it uses in-situ high-speed 3D tomography to study kinetics of Xenon hydrates dissociation and to directly measure volumes and surface areas of hydrates during dissociation. Hydrates were formed inside a special high-pressure low-temperature cell filled

with partially saturated ASTM 20-30 Ottawa silica sand. Hydrate dissociation was triggered through depressurization and continuous full 3D SMT images were acquired during the dissociation. Direct measurements of hydrate volume and hydrate surface area were obtained from the images to test the validity hydrate surface area estimation commonly used in hydrate dissociation models. Additionally, effects of hydrate pore-habit and specific surface on hydrate dissociation rate were investigated.

Materials and Experimental Setup

In this study, Methane gas was substituted by Xenon gas; an analog to Methane gas in previous studies, due to its high X-ray attenuation coefficients compared to Methane, which enhances phase contrast between hydrate and other phases in the reconstructed images (Chen and Espinoza 2018; Jin et al. 2008; Sell et al. 2016). Both gases form structure I clathrate hydrates with similar solubility and diffusivity properties (Chaouachi et al. 2015; Yang et al. 2016). Xenon hydrate has much lower equilibrium pressure compared to Methane hydrate. For example, the equilibrium pressure for Methane hydrate is 7.1 MPa at 10° C whereas it is 0.4 MPa for Xenon hydrate at the same temperature (Ewing and Ionescu 1974; Kim et al. 1987).

The chamber of the flow cell used in this study was machined using polyether ether ketone (PEEK) material, a strong material that has excellent x-ray attenuation. The cylindrical cell has a height of 70.2 mm and an inner diameter of 9.7 mm, and is capable of sustaining an internal pressure of 150 MPa (Figure 3-1a). A cooling coil connected to a commercial cooling unit and is attached to the base plate of the cell. A circulated refrigerant gas is used to cool the cell, and a thermocouple housed in the top end plate is used to control the temperature inside the cell (Figure 3-1a). An acrylic chamber and foam thermal insulation is used to isolate the cell and preserve the temperature within the cell (Figure 3-1a). The bottom port is connected to a pressure regulator connected to Xenon gas source.

ASTM 20-30 Ottawa sand was used in this study. It is a natural silica sand with a grain size between US sieve #20 (0.841 mm) and sieve #30 (0.595 mm) and specific gravity of solids of 2.65, mined and marketed by US Silica Company. The grain size distribution of ASTM 20-30 is shown in Figure 3-2. This size distribution was selected to (1) reasonably balance the resolution of images and number of sand particles in the field of view and (2) be consistent with previous and other studies of Xe hydrate (Chen and Espinoza 2018; Chen et al. 2018; Jarrar et al. 2020). The sand was partially saturated with a 4% by weight KI-brine solution (initial KI saturation = 52%) to enhance contrast in SMT images. Two steel meshes with 0.420 mm opening size were installed near the top and bottom ports to prevent sand migration. A plastic spacer and a stainless steel spring were placed on the top of the upper steel mesh to provide surcharge pressure at the top of the specimen. Xenon gas was then injected through the bottom port of the cell to displace water to reduce the initial degree of saturation.

3D synchrotron micro-computed tomography (SMT)

X-ray computed tomography (CT) is a powerful non-destructive imaging technique in which the x-ray beam of a CT scanner impinges a rotating object and the collected attenuation data are used to reconstruct a 3D volume image of the object. 3D SMT is an enhancement to industrial CT with the utilization of a monochromatic x-ray beam, which eliminates beam-hardening artifacts and enables tuning photon energy (Al-Raoush 2012; Al-Raoush 2014; Alshibli and Reed 2012; Kinney and Nichols 1992; Wildenschild et al. 2013). In previous studies, both CT (Kneafsey and Moridis 2014; Lei et al. 2019) and SMT (Chaouachi et al. 2015; Jarrar et al. 2018; Yang et al. 2016) imaging were used to study gas hydrate dissociation and emergent phenomena in sandy sediments. However, the use of a monochromator in SMT greatly reduces the flux and increases data acquisition time, since it only transmits about 0.1% of the beam (Rivers 2016). Alternatively, a grazing incidence mirror and an x-ray absorbing foil can be used instead of the monochromator to eliminate high and low energy x-ray photons. This improvement is known as pink beam synchrotron micro-computed tomography (PSMT), and can yield an x-ray flux three orders of magnitude higher than the monochromatic beam (Rivers 2016). Therefore, the use of PSMT reduces data acquisition time significantly and makes an ideal option for in-situ monitoring of dynamic studies (Andrew et al. 2015; Godinho et al. 2016).

In this study, PSMT images were acquired at Beamline 13D of the Advanced Photon Source (APS), Argonne National Laboratory (ANL), IL, USA. The experimental setup in beamline 13D at APS is shown in Figure 3-1b. Two dissociation experiments were performed in this study; one with hydrates dissociating by depressurization and one with hydrates dissociating by thermal stimulation. For the depressurization experiment, the cell was cooled to $10 \pm 1^\circ \text{C}$ temperature and Xenon gas was injected at an initial pressure of 1.9 MPa to initiate hydrate formation. After one hour of hydrate formation, hydrate dissociation was triggered through depressurization by closing the inlet valve from the gas source and releasing Xenon gas to the atmosphere. After all hydrates were dissociated, Xenon gas was injected again at an initial pressure of 1.9 MPa to form hydrates for the thermal stimulation experiment. After three hours of hydrate formation at a temperature of 14°C , the temperature was increased so the pressure-temperature conditions are below Xenon hydrate equilibrium conditions. Figure 3-3a depicts hydrate phase boundary and experimental pressure-temperature measurements, while Figure 3-3b depicts the change of temperature, pressure, and equilibrium pressure during hydrate dissociation for the thermal stimulation experiment. Xenon hydrate equilibrium conditions were interpolated from the results of Ewing and Ionescu (1974) and Ohgaki et al. (2000).

During formation and dissociation, continuous full 3D PSMT images were acquired. Images were collected in pink beam mode with 1 mm Aluminum absorber and 1.5 milli-radian mirror angle and an exposure time of 8 ms. Each scan took approximately 45 seconds to complete (12 seconds collection time and the remaining time is for saving raw data to a file server), and a total of 60 scans

were acquired. Each raw image had a size of 1920 pixel × 1920 pixel × 880 pixel, with a resolution of approximately 5.4 μm/voxel. All scans were acquired near the bottom third of the specimen and did not cover the full height.

Results

Image Analysis

Raw images were pre-processed and reconstructed to 3D 16-bit integer volumes using the multi-threading software package “tomoRecon” (Rivers 2012). Reconstructed 3D volumes were processed and segmented using Avizo 9.7 software (FEI 2018). Median filter was used to reduce the contrast and soften the edges of the grayscale images by setting the pixel value to the median of the neighboring pixels (FEI 2018). Figure 3-4 shows samples of filtered SMT-P images at selected times during Xe hydrate formation. The SMT-P images showed more ring artifacts compared to SMT-M images caused by defects in the mirror which locally change the spectrum in the beam. Then, user-defined values of image intensity range were input to the interactive thresholding module in Avizo to isolate the hydrate phase voxels (Figure 3-5b). All voxels with a CT number of 750 or higher were assigned to the hydrate phase. This threshold was selected based on the image histogram (Figure 3-5c) and was checked visually for appropriateness. The same threshold was used to estimate the volume of the initial bright voxels that are not in the hydrate phase in the initial image (before hydrate formation). The reported values of hydrate volume excluded the initial bright voxels by subtracting their total volume ($\sim 0.2 \text{ mm}^3$) from the hydrate volume measurements. Figure 3-6 and Figure 3-7 display volume rendering images of the hydrate phase during dissociation for a vertical cross-section of the specimen for the depressurization experiment with a time-lapse of 45 seconds, while Figure 3-8 presents the volume rendering images during hydrate dissociation for the thermal stimulation experiment.

Initial Hydrate Distribution and Pore Habit

The specimen was divided into four equal vertical sections (Figure 3-9), with initial porosity of the host sediments ranging from 0.410 (Section 3) to 0.428 (Section 4). Hydrate pore-habit refers to where hydrates are distributed within the pores of the host sediments, which can cause fundamental changes to the physical properties of hydrate-bearing sediments such as permeability, shear strength, and stiffness (Mahabadi et al. 2019; Waite et al. 2009). There are mainly four common hydrate pore-habits that are discussed in the literature: surface coating, cementing, pore filling, and load bearing. Surface coating hydrates form as films on the surface of host sediment particles and are usually associated with excess gas condition. Cementing hydrates form at contacts between host sediment particles while pore filling hydrates form at the surface of host sediment particles and grow outward filling the pore space. Finally, load bearing refers to hydrates at high hydrate saturation where they can carry some of the load applied to the host sediments. A

schematic of the different hydrate pore habit is depicted in Figure 3-10. Initial hydrate saturation for the depressurization experiment ranged from 9.9% (Section 4) to 28.3% (Section 2). Hydrates were distributed heterogeneously with multiple pore-habits, which is in agreement with observations from natural hydrate (Tréhu et al. 2004; Xiao et al. 2017) and laboratory studies (Chen et al. 2018; Kneafsey et al. 2011). A combination of cementing, pore-filling, and surface coating pore-habits were observed in Sections 1 and 2 (Figure 3-11a and b), while the pore-habit in Sections 3 and 4 were predominantly surface coating (Figure 3-11 c and d). For the thermal stimulation experiment, the initial hydrate saturation was significantly higher than the depressurization experiment ranging from 73.2% for Section 4 and 87.1% for Section 1. The predominant pore-habit for all four sections was pore filling (Figure 3-12). Table 3-1 lists porosity and initial hydrate saturation values for the four sections of the depressurization and thermal stimulation experiments.

Hydrate Formation Experiment

Figure 3-13 shows the variation of hydrate volume with time during Xe hydrate formation, where each point represents measurements from a full 3D reconstructed image. Around minute 12 of hydrate formation, secondary hydrate dissociation was observed. Similar observations were reported by other studies where secondary hydrate dissociation exist during hydrate formation (Chen and Espinoza 2018; Ning et al. 2013). This phenomenon can be explained by the change of heat and mass transfer properties of host sediments during hydrate formation. The reduction of permeability during hydrate formation and the exothermic nature of hydrate formation process, which results in a release of heat energy as hydrate form, can trigger hydrate dissociation in localized regions (Ning et al. 2013). shows the variation of hydrate specific area with hydrate saturation during Xe hydrate formation along with volume rendering snapshots of a vertical section of the specimen at selected hydrate saturation. Initially, specific area of hydrate increases with increasing hydrate saturation up to a threshold (10% hydrate saturation), after which specific area begins to decrease with increasing hydrate saturation. This is an evidence of Ostwald Ripening, which refers to the phenomenon where larger crystals consume smaller ones to minimize free surface energy (Zhang 2008).

For hydrate saturation less than 10% in this study, the predominant pore-habit is surface coating, where hydrates are encapsulated on the surface of the host sand particles (Figure 3-14a). At 13% hydrate saturation, hydrates start to form in the space between the surrounding wall and sand particles (highlighted regions of Figure 3-14b). As hydrate saturation increases to 15%, wedge-shaped hydrates are observed to form in the narrow space between sand particles, forming a cementing hydrate pore-habit (highlighted regions of Figure 3-14c). As hydrate saturation increases, hydrates continue to grow outward from cementing and surface coating, changing their pore-habit to pore-filling hydrates growing freely in the surrounding pore space (highlighted regions of Figure 3-14d).

Hydrate volume and surface area

According to hydrate sphericity assumptions proposed by Kim et al. (1987), the change of hydrate surface area with $(\text{hydrate volume})^{2/3}$ should be linear during dissociation. Figure 3-15 shows scatter plots of total hydrate interfacial area (total surface area), hydrate-sand interfacial area, and hydrate-gas interfacial area with $(\text{hydrate volume})^{2/3}$ measured from the 3D PSMT images of the depressurization experiment. Hydrate-gas interfacial area represents the total surface area of the hydrate phase in contact with the gas phase. Similarly, hydrate-sand interfacial area represents the total surface area of the hydrate phase in contact with the sand phase, while the total interfacial area is the sum of hydrate-gas interfacial area and hydrate-sand interfacial area and is a measure of the total surface area of the hydrate phase. The reported interfacial area measurements do not account for the micro-pores within hydrate structures which cannot be detected at the resolution of this study. These micro-pores have been observed by 3D SMT imaging (Chaouachi et al. 2017) and field-emission scanning electron microscopy (Kuhns et al. 2000) with sizes ranging from sub-micron to few microns. That said, the reported interfacial areas can be overestimates of the actual areas. Referring to Figure 3-15, good linear fits can be observed for low hydrate volumes up to a certain threshold, after which, interfacial area deviate from linearity. This threshold corresponds to 7%, 6%, and 8% hydrate saturation for total interfacial area (Figure 3-15b), hydrate-gas interfacial area (Figure 3-15c), and hydrate-sand interfacial area (Figure 3-15d), respectively. Coefficients of determination (R^2) and root mean square errors (RMSE) values for the three models are also presented in Figure 3-15. R^2 values ranged from 0.16 (hydrate-sand interfacial area) to 0.35 (hydrate-gas interfacial area), while RMSE values ranged from 2.23 (hydrate-gas interfacial area) to 6.28 (total interfacial area). Therefore, hydrate surface area can be estimated to be linear with $(\text{hydrate volume})^{2/3}$ during hydrate dissociation in porous media for hydrate saturation less than a certain threshold (8% in this study), based on direct observations and measurements from 3D PSMT images.

Additionally, best fit polynomials between hydrate volume and interfacial areas were investigated. Figure 3-16 presents scatter plots of total hydrate interfacial area, hydrate-sand interfacial area, and hydrate-gas interfacial area with hydrate volume, along with the best quadratic fit models for the depressurization experiment. As shown in Figure 3-16, quadratic fit models provide excellent prediction of interfacial area with R^2 values higher than 0.98. Therefore, it is suggested that $(\text{hydrate volume})^2$ can give better estimation of hydrate surface area than $(\text{hydrate volume})^{2/3}$ based on results obtained from this study. Figure 3-17 compares hydrate dissociation rates measured experimentally from PSMT images with predicted dissociation rates calculated from Equation 3-1 with time for the depressurization experiment. Hydrate surface area are estimated once to be linear with $v^{2/3}$ (circles in Figure 3-17) and once according to the polynomial fits provided in Figure 3-16 (squares in Figure 3-17). Estimating hydrate surface area according to the polynomials reported in this study improved the prediction of

hydrate dissociation rates (RMSE=0.44) compared to estimating hydrate surface area to be linear with $v^{2/3}$ (RMSE=0.79).

Figure 3-18 shows scatter plots of total hydrate interfacial area, hydrate-sand interfacial area, and hydrate-gas interfacial area with (hydrate volume)^{2/3} measured from the 3D PSMT images for the thermal stimulation experiment. Figure 3-18 also presents R^2 and RMSE values for the three linear models. Similar to the depressurization experiment, good linear fits can be observed for hydrate volumes smaller than a certain threshold, after which, interfacial area begins to deviate from linearity. This threshold corresponds to 28% hydrate saturation for total interfacial area (Figure 3-18b) and hydrate gas interfacial area (Figure 3-18c), and 12% hydrate saturation for hydrate-sand interfacial area (Figure 3-18d). Total interfacial area and hydrate-gas interfacial area showed better overall linearity with (hydrate volume)^{2/3} in the thermal stimulation experiment compared to the depressurization experiment with significantly higher R^2 values. Additionally, best fit polynomials between hydrate volume and interfacial areas were investigated. Figure 3-19 presents scatter plots of total hydrate interfacial area, hydrate-sand interfacial area, and hydrate-gas interfacial area with hydrate volume, along with the best cubic fit models, which were found to best estimate interfacial area with hydrate volume. These cubic fit models provide excellent prediction of interfacial area with R^2 values higher than 0.98.

Hydrate specific area and dissociation rate

Figure 3-20a displays the change in hydrate specific area with time during dissociation for Sections 1 through 4. For Sections 1 and 2, hydrate specific area decreased with time, which indicates that hydrates with higher specific area dissociate first resulting in a reduction of the total specific area of that section (Figure 3-20a). Therefore, hydrates with surface coating pore habit are expected to dissociate faster than hydrates with pore-filling pore habits. This also can be observed in the volume rendering images depicted in Figure 3-21a-e that shows surface coating hydrates dissociated before pore filling hydrates. For Sections 3 and 4, hydrates are predominantly surface coating (Figure 3-11c and e) and therefore have higher specific area compared to Sections 1 and 2 (Figure 3-20a). During dissociation, specific area of Sections 3 and 4 fluctuated around a constant value with no obvious trend (Figure 3-20a) since most hydrates in these sections have the same pore habit (surface coating). Figure 3-20b depicts the change in hydrate dissociation rate with time during hydrate dissociation for Sections 1 and 2, and Sections 3 and 4. Hydrate dissociation rates were measured experimentally by dividing the change in the measured hydrate volume by the scan time (45 seconds) between consecutive 3D PSMT images. Higher dissociation rates are observed for Sections 3 and 4 in comparison with Sections 1 and 2, which is attributed to the higher specific area in Sections 3 and 4 which means they have more surface to dissociate at (Figure 3-20a).

During the depressurization experiment, the temperature and pressure were kept constant, and therefore, hydrate equilibrium pressure also remained constant

throughout the test. However, during hydrate dissociation by thermal stimulation, pressure, temperature, and therefore, hydrate equilibrium pressure were changing during the test (see Figure 3-3). In this study, multiple linear regression analysis was conducted to propose a simple model that relates hydrate dissociation rate with hydrate saturation (S), absolute temperature (T), pressure (P), and the hydrate equilibrium pressure (P_e). The least-square method was used to estimate regression coefficients that minimize the vertical deviation from each data point to the regression line. The p-value is used to assess the significance of each regression coefficient. A low p-value means that the null hypothesis that the coefficient is equal to zero can be rejected. In other words, a predictor with a low p-value is considered significant to the model, because changing the value of its coefficient changes the response of the model. The estimated regression coefficients for each predictor in the model, along with their corresponding p-value are listed in Table 3-2. The prediction model had an R^2 value of 0.94 and an RMSE value of 0.88. The change of measured and predicted hydrate dissociation rate with hydrate saturation along with the linear regression model for the thermal stimulation experiment are depicted in Figure 3-22. It can be observed from Figure 3-22 that the hydrate dissociation rate remains almost constant at the start of the dissociation process. This constant dissociation rate can be attributed to the exposure of the micro-pores within hydrates, which compensates for the loss in hydrate surface area during dissociation.

Conclusions

This paper employed dynamic 3D PSMT imaging in studying hydrate surface area evolution during Xenon hydrate dissociation. Hydrates were formed inside a high-pressure low-temperature flow cell filled with partially saturated ASTM 20-30 Ottawa silica sand and two hydrate dissociation experiments were conducted. The cell was cooled to 10° C temperature in the first experiment and to 14° C in the second experiment. Xenon gas was injected at an initial pressure of 1.9 MPa for both experiments. Hydrate dissociation was triggered through depressurization in the first experiment by closing the inlet valve from the gas source and releasing Xenon gas to the atmosphere and by thermal stimulation in the second experiment. During dissociation, continuous full 3D tomography images were acquired where each scan took 45 seconds to complete. A combination of cementing, pore-filling, and surface coating initial pore-habits were observed for the depressurization experiment, while pore-filling pore habit was predominant in the thermal stimulation experiment. Initially, specific area of hydrate increased with increasing hydrate saturation up to 10% hydrate saturation. As hydrate saturation exceeded 10%, specific area began to decrease, which is an evidence of Ostwald Ripening. The predominant pore-habit was surface coating for hydrate saturation less than 10%. At 13% hydrate saturation, hydrates started to form in the space between the surrounding wall and sand particles. Cementing pore-habit was observed at 15% hydrate saturation, and pore-filling hydrate pore-habit was observed with further increase in hydrate saturation. Surface coating hydrates dissociate faster than

hydrates with pore-filling pore habit. This is explained by the higher specific area in the surface coating hydrates, which allows for more surface for hydrates to dissociate it. Results suggest that with a combination of hydrate pore habit formed within the 3D porous media, estimation of hydrate surface area as a linear relationship with (hydrate volume)^{2/3} is best for hydrate saturation less than a specific threshold value. The value of this threshold varies depending on the dissociation method and the driving dissociation force and was found to be 7% for the depressurization experiment and 28% for the thermal stimulation experiment. (hydrate volume)² was found to better estimate hydrate interfacial area compared to (hydrate volume)^{2/3} in the depressurization experiment, while (hydrate volume)³ provided better estimates of the interfacial area for the thermal stimulation experiment. Findings of this study along with dynamic SMT imaging technique can be used to improve hydrate dissociation models and predictability of gas production from natural hydrate reservoirs. Finally, multiple linear regression analysis was conducted to predict hydrate dissociation rate variation using hydrate saturation, temperature pressure, and hydrate equilibrium pressure as predictors. The model provided good estimates of dissociation rate with an R² value of 0.94 and an RMSE value of 0.88.

Acknowledgments

This publication was made possible by partial funding from NPRP grant # NPRP8-594-2-244 from the Qatar national research fund (a member of Qatar Foundation) and the Institute for a Secure and Sustainable Environment (ISSE), University of Tennessee-Knoxville, USA. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of funding agencies. The authors would like to thank Mr. Wadi Imseeh for his help during scanning and Mr. Jamal Hannun for his help in interfacial area analysis. This paper used resources of the Advanced Photon Source (APS), a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory (ANL) under Contract No. DE-AC02-06CH11357. The PSMT images presented in this paper were collected using the x-ray Operations and Research Beamline Station 13-BMD at Argonne Photon Source (APS), ANL. We thank Dr. Mark Rivers of APS for help in performing the SMT scans. We also acknowledge the support of GeoSoilEnviroCARS (Sector 13), which is supported by the National Science Foundation, Earth Sciences (EAR-1128799), and the DOE, Geosciences (DE-FG02-94ER14466). The authors would also like to thank the anonymous reviewers who contributed with comments and suggestions to improve this paper.

References

- Al-Raoush, R. (2012). "Change in Microstructure Parameters of Porous Media Over Representative Elementary Volume for Porosity." *Particulate Science and Technology*, 30(1), 1-16.
- Al-Raoush, R. I. (2014). "Experimental investigation of the influence of grain geometry on residual NAPL using synchrotron microtomography." *Journal of Contaminant Hydrology*, 159, 1-10.
- Alshibli, K. A., and Reed, A. H. (2012). *Advances in computed tomography for geomaterials: GeoX 2010*, John Wiley & Sons.
- Andrew, M., Menke, H., Blunt, M. J., and Bijeljic, B. (2015). "The Imaging of Dynamic Multiphase Fluid Flow Using Synchrotron-Based X-ray Microtomography at Reservoir Conditions." *Transport in Porous Media*, 110(1), 1-24.
- Bonnefoy, O., Gruy, F., and Herri, J. M. (2005). "Van der Waals interactions in systems involving gas hydrates." *Fluid Phase Equilibria*, 231(2), 176-187.
- Chaouachi, M., Falenty, A., Sell, K., Enzmann, F., Kersten, M., Haberthür, D., and Kuhs, W. F. (2015). "Microstructural evolution of gas hydrates in sedimentary matrices observed with synchrotron X-ray computed tomographic microscopy." *Geochemistry, Geophysics, Geosystems*, 16(6), 1711-1722.
- Chaouachi, M., Neher, S. H., Falenty, A., and Kuhs, W. F. (2017). "Time Resolved Coarsening of Clathrate Crystals: The Case of Gas Hydrates." *Crystal Growth & Design*, 17(5), 2458-2472.
- Chen, L., Feng, Y., Kogawa, T., Okajima, J., Komiya, A., and Maruyama, S. (2018). "Construction and simulation of reservoir scale layered model for production and utilization of methane hydrate: The case of Nankai Trough Japan." *Energy*, 143, 128-140.
- Chen, X., and Espinoza, D. N. (2018). "Ostwald ripening changes the pore habit and spatial variability of clathrate hydrate." *Fuel*, 214, 614-622.
- Chen, X., and Espinoza, D. N. (2018). "Surface area controls gas hydrate dissociation kinetics in porous media." *Fuel*, 234, 358-363.
- Chen, X., Verma, R., Espinoza, D. N., and Prodanović, M. (2018). "Pore-Scale Determination of Gas Relative Permeability in Hydrate-Bearing Sediments Using X-Ray Computed Micro-Tomography and Lattice Boltzmann Method." *Water Resources Research*, 54(1), 600-608.
- Chong, Z. R., Yang, S. H. B., Babu, P., Linga, P., and Li, X.-S. (2016). "Review of natural gas hydrates as an energy resource: Prospects and challenges." *Applied Energy*, 162, 1633-1652.
- Clarke, M., and Bishnoi, P. R. (2001). "Determination of the activation energy and intrinsic rate constant of methane gas hydrate decomposition." *The Canadian Journal of Chemical Engineering*, 79(1), 143-147.
- Collett, T., Bahk, J.-J., Baker, R., Boswell, R., Divins, D., Frye, M., Goldberg, D., Husebø, J., Koh, C., Malone, M., Morell, M., Myers, G., Shipp, C., and Torres, M. (2015). "Methane Hydrates in Nature—Current Knowledge and Challenges." *Journal of Chemical & Engineering Data*, 60(2), 319-329.

- Daraboina, N., Malmos, C., and von Solms, N. (2013). "Synergistic kinetic inhibition of natural gas hydrate formation." *Fuel*, 108, 749-757.
- Ewing, G. J., and Ionescu, L. G. (1974). "Dissociation pressure and other thermodynamic properties of xenon-water clathrate." *Journal of Chemical and Engineering Data*, 19(4), 367-369.
- FEI. 2018. Avizo, version 9.7FEI, Hillsboro, OR.
- Gamwo, I. K., and Liu, Y. (2010). "Mathematical Modeling and Numerical Simulation of Methane Production in a Hydrate Reservoir." *Industrial & Engineering Chemistry Research*, 49(11), 5231-5245.
- Godinho, J. R. A., Gerke, K. M., Stack, A. G., and Lee, P. D. (2016). "The dynamic nature of crystal growth in pores." *Scientific Reports*, 6, 33086.
- Hong, H., Pooladi-Darvish, M., and Bishnoi, P. R. (2003). "Analytical Modelling of Gas Production From Hydrates in Porous Media." *PETSOC-03-11-05*, 42(11), 45-56.
- Huang, Y.-J., Wu, C.-Y., and Hsieh, B.-Z. (2016). "Effect of Fluid Saturation on Gas Recovery from Class-3 Hydrate Accumulations Using Depressurization: A Case Study of the Yuan-an Ridge Site in Southwestern Offshore Taiwan." *Energy Procedia*, 97, 310-317.
- Hyodo, M., Li, Y., Yoneda, J., Nakata, Y., Yoshimoto, N., Kajiyama, S., Nishimura, A., and Song, Y. (2014). "A comparative analysis of the mechanical behavior of carbon dioxide and methane hydrate-bearing sediments." *American Mineralogist*, 99(1), 178-183.
- Jamaluddin, A. K. M., Kalogerakis, N., and Bishnoi, P. R. (1989). "Modelling of decomposition of a synthetic core of methane gas hydrate by coupling intrinsic kinetics with heat transfer rates." *The Canadian Journal of Chemical Engineering*, 67(6), 948-954.
- Jarrar, Z. A., Al-Raoush, R. I., Hannun, J. A., Alshibli, K. A., and Jung, J. (2018). "3D synchrotron computed tomography study on the influence of fines on gas driven fractures in Sandy Sediments." *Geomechanics for Energy and the Environment*, 100105.
- Jarrar, Z. A., Alshibli, K. A., Al-Raoush, R. I., and Jung, J. (2020). "3D measurements of hydrate surface area during hydrate dissociation in porous media using dynamic 3D imaging." *Fuel*, 265, 116978.
- Jin, Y., Nagao, J., Hayashi, J., Shimada, W., Ebinuma, T., and Narita, H. (2008). "Observation of Xe Hydrate Growth at Gas-Ice Interface by Microfocus X-ray Computed Tomography." *The Journal of Physical Chemistry C*, 112(44), 17253-17256.
- Kim, H. C., Bishnoi, P. R., Heidemann, R. A., and Rizvi, S. S. H. (1987). "Kinetics of methane hydrate decomposition." *Chemical Engineering Science*, 42(7), 1645-1653.
- Kinney, J. H., and Nichols, M. C. (1992). "X-Ray Tomographic Microscopy (XTM) Using Synchrotron Radiation." *Annual Review of Materials Science*, 22(1), 121-152.

- Kneafsey, T. J., and Moridis, G. J. (2014). "X-Ray computed tomography examination and comparison of gas hydrate dissociation in NGHP-01 expedition (India) and Mount Elbert (Alaska) sediment cores: Experimental observations and numerical modeling." *Marine and Petroleum Geology*, 58, 526-539.
- Kneafsey, T. J., Seol, Y., Gupta, A., and Tomutsa, L. (2011). "Permeability of Laboratory-Formed Methane-Hydrate-Bearing Sand: Measurements and Observations Using X-Ray Computed Tomography." *SPE-139525-PA*, 16(01), 78-94.
- Kneafsey, T. J., Tomutsa, L., Moridis, G. J., Seol, Y., Freifeld, B. M., Taylor, C. E., and Gupta, A. (2007). "Methane hydrate formation and dissociation in a partially saturated core-scale sand sample." *Journal of Petroleum Science and Engineering*, 56(1), 108-126.
- Konno, Y., Fujii, T., Sato, A., Akamine, K., Naiki, M., Masuda, Y., Yamamoto, K., and Nagao, J. (2017). "Key Findings of the World's First Offshore Methane Hydrate Production Test off the Coast of Japan: Toward Future Commercial Production." *Energy & Fuels*, 31(3), 2607-2616.
- Konno, Y., Masuda, Y., Hariguchi, Y., Kurihara, M., and Ouchi, H. (2010). "Key Factors for Depressurization-Induced Gas Production from Oceanic Methane Hydrates." *Energy & Fuels*, 24(3), 1736-1744.
- Kuhs, W. F., Klapproth, A., Gotthardt, F., Techmer, K., and Heinrichs, T. (2000). "The formation of meso- and macroporous gas hydrates." *Geophysical Research Letters*, 27(18), 2929-2932.
- Kvenvolden, K. A. (1995). "A review of the geochemistry of methane in natural gas hydrate." *Organic Geochemistry*, 23(11), 997-1008.
- Lei, L., Seol, Y., Choi, J.-H., and Kneafsey, T. J. (2019). "Pore habit of methane hydrate and its evolution in sediment matrix – Laboratory visualization with phase-contrast micro-CT." *Marine and Petroleum Geology*, 104, 451-467.
- Liu, W., Luo, T., Li, Y., Song, Y., Zhu, Y., Liu, Y., Zhao, J., Wu, Z., and Xu, X. (2016). "Experimental study on the mechanical properties of sediments containing CH₄ and CO₂ hydrate mixtures." *Journal of Natural Gas Science and Engineering*, 32, 20-27.
- Mahabadi, N., Dai, S., Seol, Y., and Jang, J. (2019). "Impact of hydrate saturation on water permeability in hydrate-bearing sediments." *Journal of Petroleum Science and Engineering*, 174, 696-703.
- Max, M. D., Johnson, A. H., and Dillon, W. P. (2013). *Natural Gas Hydrate-Arctic Ocean Deepwater Resource Potential*, Springer.
- Merey, S., Al-Raoush, R. I., Jung, J., and Alshibli, K. A. (2018). "Comprehensive literature review on CH₄-CO₂ replacement in microscale porous media." *Journal of Petroleum Science and Engineering*, 171, 48-62.
- Minagawa, H., Ito, T., Kimura, S., Kaneko, H., Noda, S., and Narita, H. "Depressurization and electrical heating of hydrate sediment for gas production." *Proc., Proceedings of the International Offshore and Polar Engineering Conference*, 82-88.

- Moridis, G. J., Collett, T. S., Boswell, R., Hancock, S., Rutqvist, J., Santamarina, C., Kneafsey, T., Reagan, M. T., Pooladi-Darvish, M., Kowalsky, M., Sloan, E. D., and Coh, C. (2013). "Gas Hydrates as a Potential Energy Source: State of Knowledge and Challenges." *Advanced Biofuels and Bioproducts*, J. W. Lee, ed., Springer New York, New York, NY, 977-1033.
- Moridis, G. J., Seol, Y., and Kneafsey, T. J. (2005). "Studies of reaction kinetics of methane hydrate dissociation in porous media."
- Ning, F., Wu, N., Yu, Y., Zhang, K., Jiang, G., Zhang, L., Sun, J., and Zheng, M. (2013). "Invasion of drilling mud into gas-hydrate-bearing sediments. Part II: Effects of geophysical properties of sediments." *Geophysical Journal International*, 193(3), 1385-1398.
- Ohgaki, K., Sugahara, T., Suzuki, M., and Jindai, H. (2000). "Phase behavior of xenon hydrate system." *Fluid Phase Equilibria*, 175(1), 1-6.
- Oyama, H., Konno, Y., Masuda, Y., and Narita, H. (2009). "Dependence of Depressurization-Induced Dissociation of Methane Hydrate Bearing Laboratory Cores on Heat Transfer." *Energy & Fuels*, 23(10), 4995-5002.
- Rivers, M. L. "tomoRecon: High-speed tomography reconstruction on workstations using multi-threading." *Proc., Developments in X-Ray Tomography VIII*, International Society for Optics and Photonics, 85060U.
- Rivers, M. L. (2016). *High-speed tomography using pink beam at GeoSoilEnviroCARS*, SPIE.
- Selim, M. S., and Sloan, E. D. (1989). "Heat and mass transfer during the dissociation of hydrates in porous media." *AIChE Journal*, 35(6), 1049-1052.
- Sell, K., Saenger, E. H., Falenty, A., Chaouachi, M., Haberthür, D., Enzmann, F., Kuhs, W. F., and Kersten, M. (2016). "On the path to the digital rock physics of gas hydrate-bearing sediments—processing of in situ synchrotron-tomography data." *Solid Earth*, 7(4), 1243-1258.
- Sloan, E. D. J. (2003). *Fundamental Principles and Application of Natural Gas Hydrates*, 426, 353-363.
- Sloan Jr, E. D., and Koh, C. A. (2007). *Clathrate hydrates of natural gases*, CRC press.
- Tréhu, A. M., Long, P. E., Torres, M. E., Bohrmann, G., Rack, F. R., Collett, T. S., Goldberg, D. S., Milkov, A. V., Riedel, M., Schultheiss, P., Bangs, N. L., Barr, S. R., Borowski, W. S., Claypool, G. E., Delwiche, M. E., Dickens, G. R., Gracia, E., Guerin, G., Holland, M., Johnson, J. E., Lee, Y. J., Liu, C. S., Su, X., Teichert, B., Tomaru, H., Vanneste, M., Watanabe, M., and Weinberger, J. L. (2004). "Three-dimensional distribution of gas hydrate beneath southern Hydrate Ridge: constraints from ODP Leg 204." *Earth and Planetary Science Letters*, 222(3), 845-862.
- Waite, W. F., Santamarina, J. C., Cortes, D. D., Dugan, B., Espinoza, D. N., Germaine, J., Jang, J., Jung, J. W., Kneafsey, T. J., Shin, H., Soga, K., Winters, W. J., and Yun, T. S. (2009). "Physical properties of hydrate-bearing sediments." *Reviews of Geophysics*, 47(4).

- Wildenschild, D., Rivers, M. L., Porter, M. L., Iltis, G. C., Armstrong, R. T., and Davit, Y. (2013). "Using Synchrotron-Based X-Ray Microtomography and Functional Contrast Agents in Environmental Applications." *Soil–Water–Root Processes: Advances in Tomography and Imaging*, S. H. Anderson, and J. W. Hopmans, eds., The Soil Science Society of America, Inc., Madison, WI, 1-22.
- Windmeier, C., and Oellrich, L. R. (2013). "Theoretical Study of Gas Hydrate Decomposition Kinetics—Model Development." *The Journal of Physical Chemistry A*, 117(40), 10151-10161.
- Xiao, K., Zou, C., Lu, Z., and Deng, J. (2017). "Gas hydrate saturations estimated from pore-and fracture-filling gas hydrate reservoirs in the Qilian Mountain permafrost, China." *Scientific Reports*, 7(1), 16258.
- Xu, C.-G., and Li, X.-S. (2015). "Research progress on methane production from natural gas hydrates." *RSC Advances*, 5(67), 54672-54699.
- Yang, L., Falenty, A., Chaouachi, M., Haberthür, D., and Kuhs, W. F. (2016). "Synchrotron X-ray computed microtomography study on gas hydrate decomposition in a sedimentary matrix." *Geochemistry, Geophysics, Geosystems*, 17(9), 3717-3732.
- Yang, L., Falenty, A., Chaouachi, M., Haberthür, D., and Kuhs, W. F. (2016). "Synchrotron X-ray computed microtomography study on gas hydrate decomposition in a sedimentary matrix." *Geochemistry, Geophysics, Geosystems*, 17(9), 3717-3732.
- Ye, Y., and Liu, C. (2012). *Natural Gas Hydrates: Experimental Techniques and Their Applications*, Springer Science & Business Media.
- Yin, Z., Chong, Z. R., Tan, H. K., and Linga, P. (2016). "Review of gas hydrate dissociation kinetic models for energy recovery." *Journal of Natural Gas Science and Engineering*, 35, 1362-1387.
- Zhang, Y. (2008). *Geochemical kinetics*, Princeton University Press.

Appendices

Appendix A: Tables

Table 3-1. Porosity and initial hydrate saturation values for the four sections of the depressurization and thermal stimulation experiments.

Section	Porosity	Initial hydrate degree of saturation, S (%)	
		Depressurization	Thermal stimulation
1	0.418	26.6	87.1
2	0.424	28.3	85.3
3	0.411	23.9	79.9
4	0.428	9.9	73.2

Table 3-2. Results of multivariable linear regression of dissociation rate for the thermal stimulation experiment.

Parameter	Coefficient Estimate	p-value
T	-457.4	0.05
P	5520.2	<0.01
$P_e - P$	5007.8	<0.01
S^3	-9.5×10^{-5}	<0.01
Statistical Constant	127803.2	N/A

Appendix B: Figures

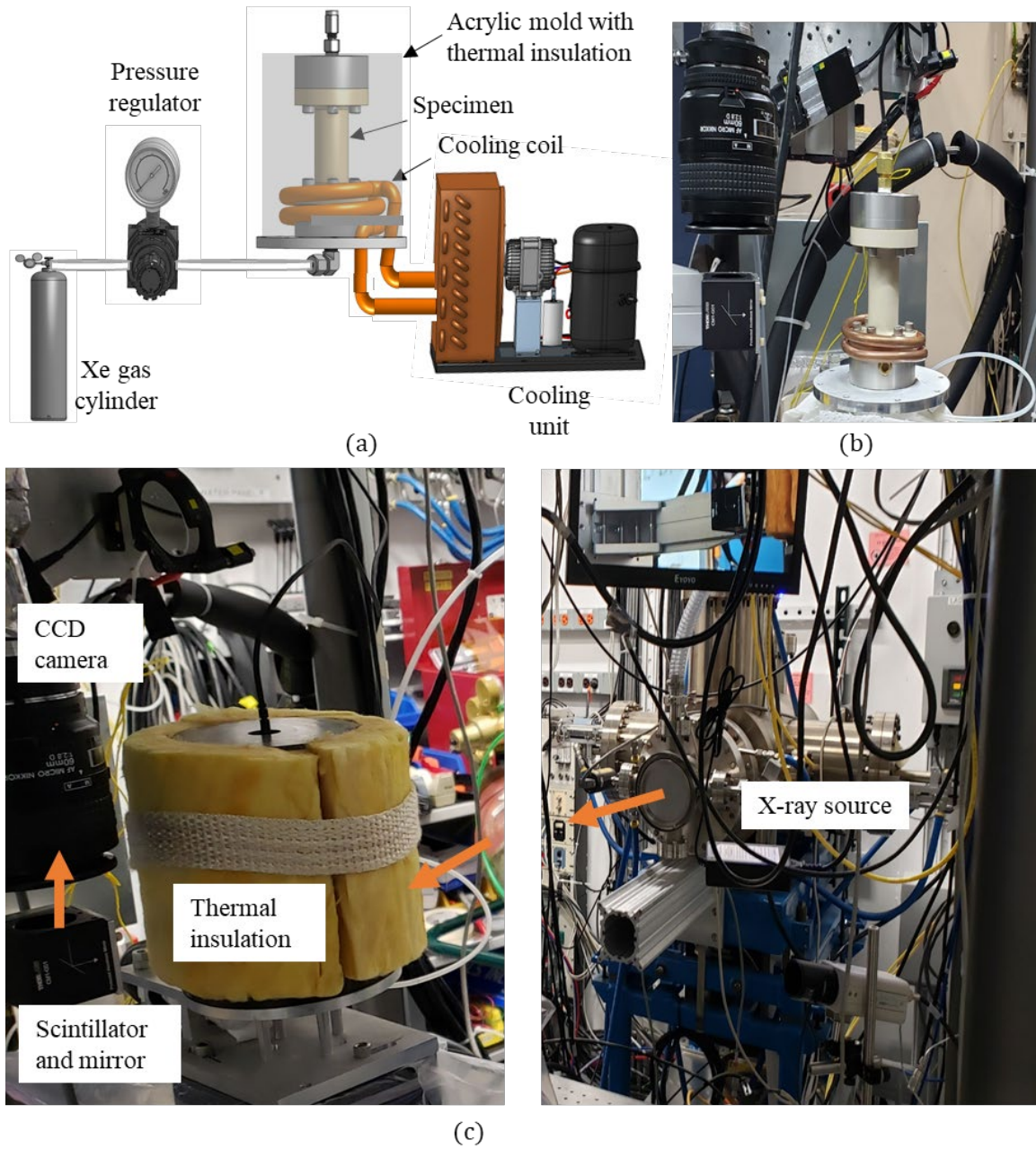


Figure 3-1. (a) Schematic of the high-pressure low-temperature flow cell; (b) flow cell on stage without thermal insulation; and (c) experimental setup at Beamline 13D of the Advanced Photon Source, Argonne National Laboratory.

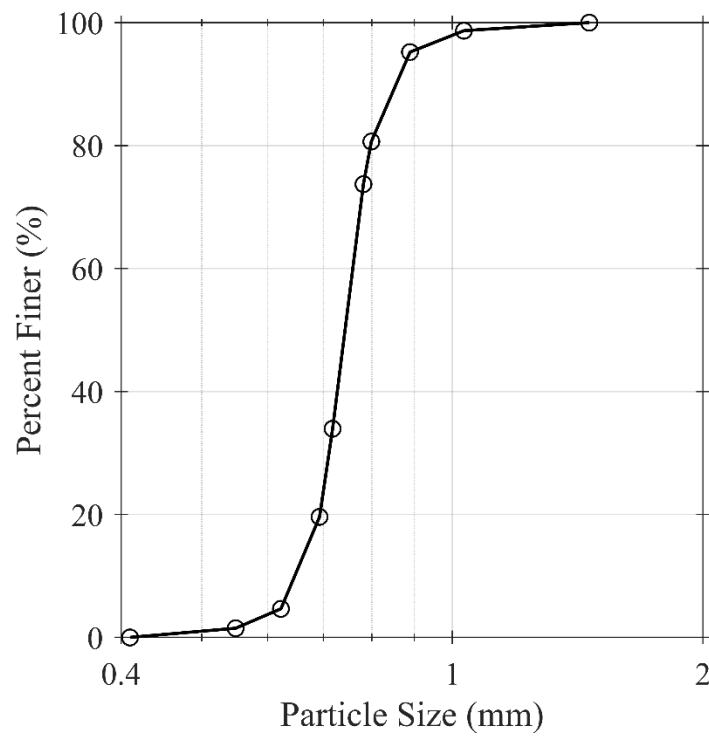


Figure 3-2. Grain size distribution of ASTM 20-30 sand.

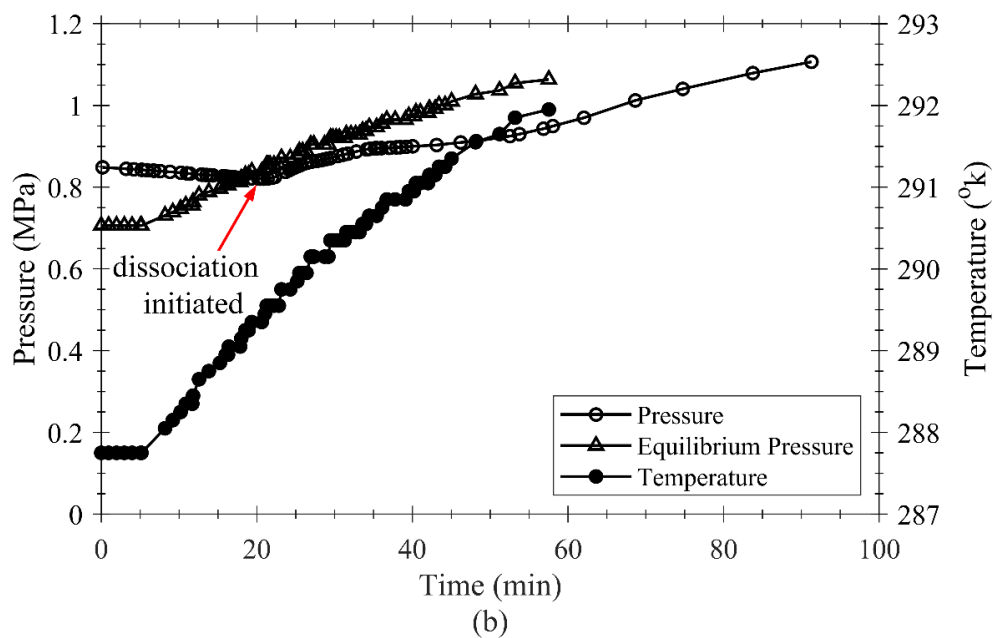
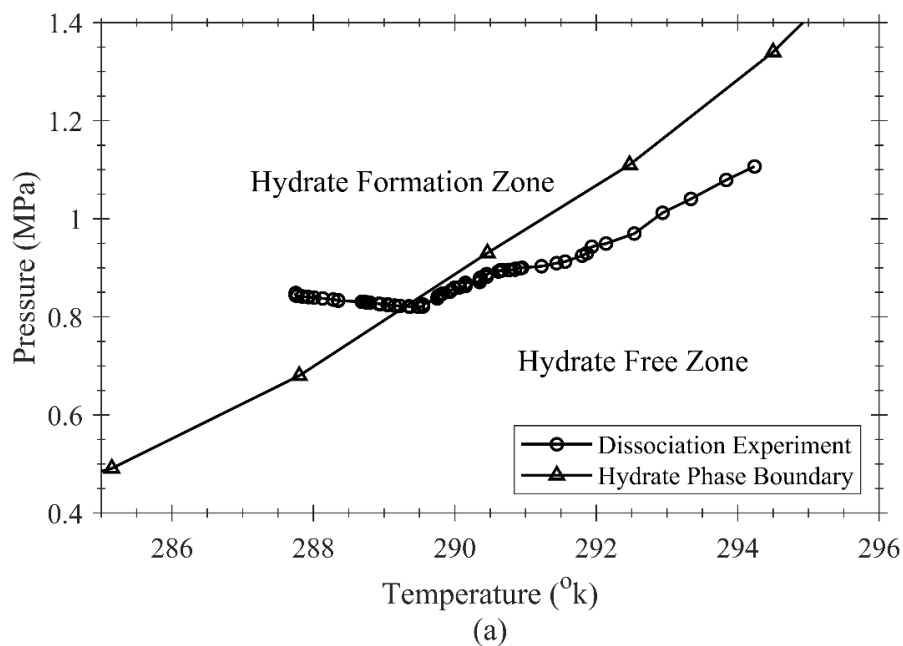


Figure 3-3. (a) Hydrate phase boundary and experimental pressure-temperature measurements; and (b) change of temperature, pressure and hydrate equilibrium pressure during hydrate dissociation in the thermal stimulation experiment.

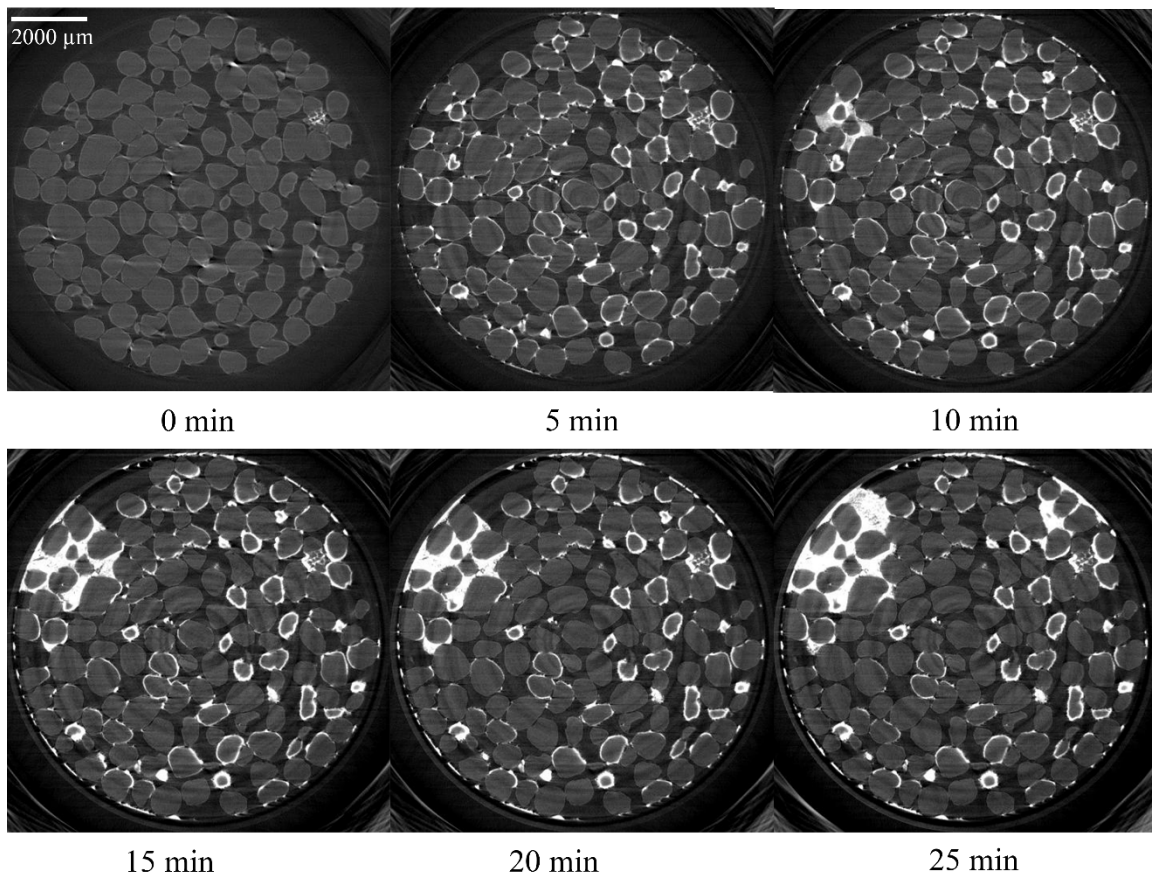


Figure 3-4. Example SMT-P slice images show hydrate formation with time.

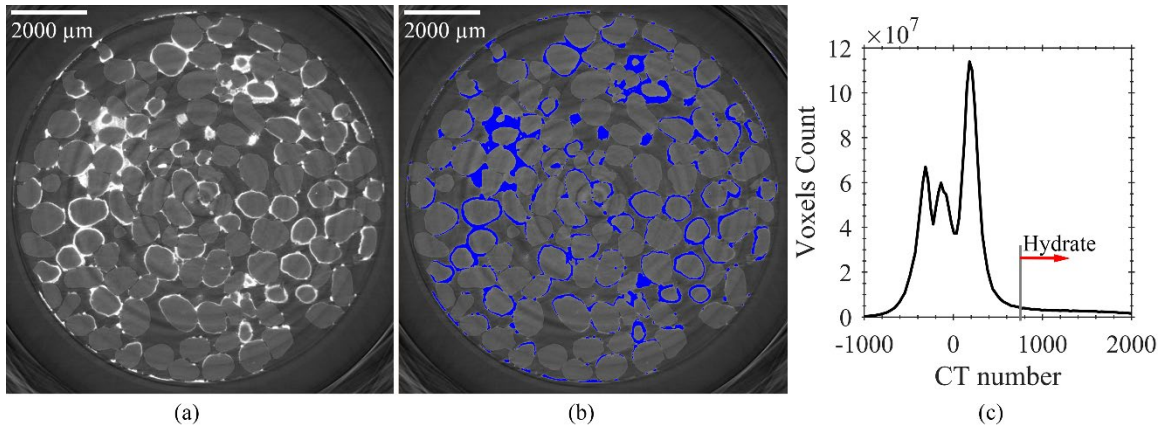


Figure 3-5. Hydrate phase segmentation (a) filtered image; (b) hydrate voxels selected; and (c) image histogram.

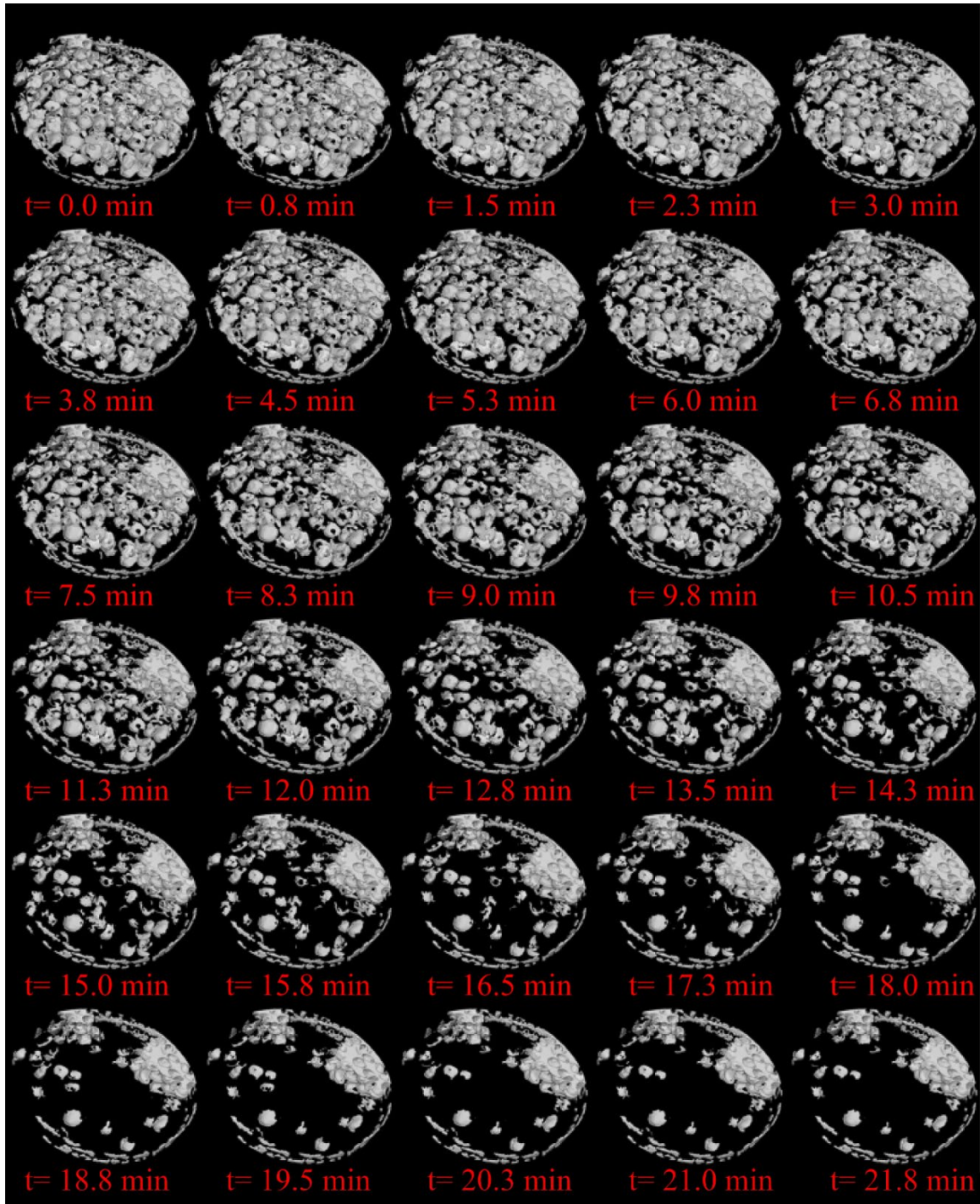


Figure 3-6. Volume rendering images of hydrate during dissociation for a vertical section of the specimen for the depressurization experiment from beginning of the test to $t = 22.5$ min, time-lapse between images is 45 seconds.

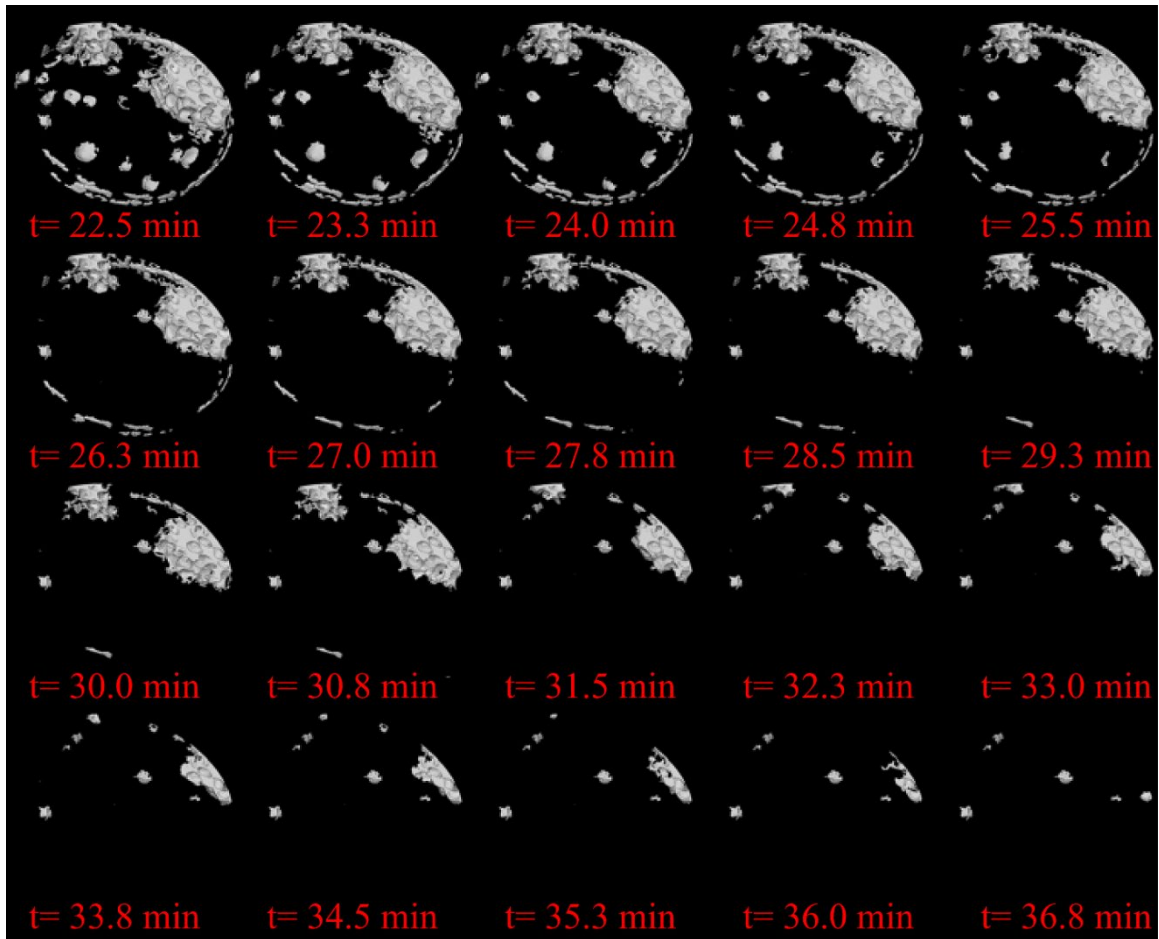


Figure 3-7. Volume rendering images of hydrate during dissociation for a vertical section of the specimen for the depressurization experiment from $t= 22.5$ min to $t= 37.5$ min, time-lapse between images is 45 seconds.

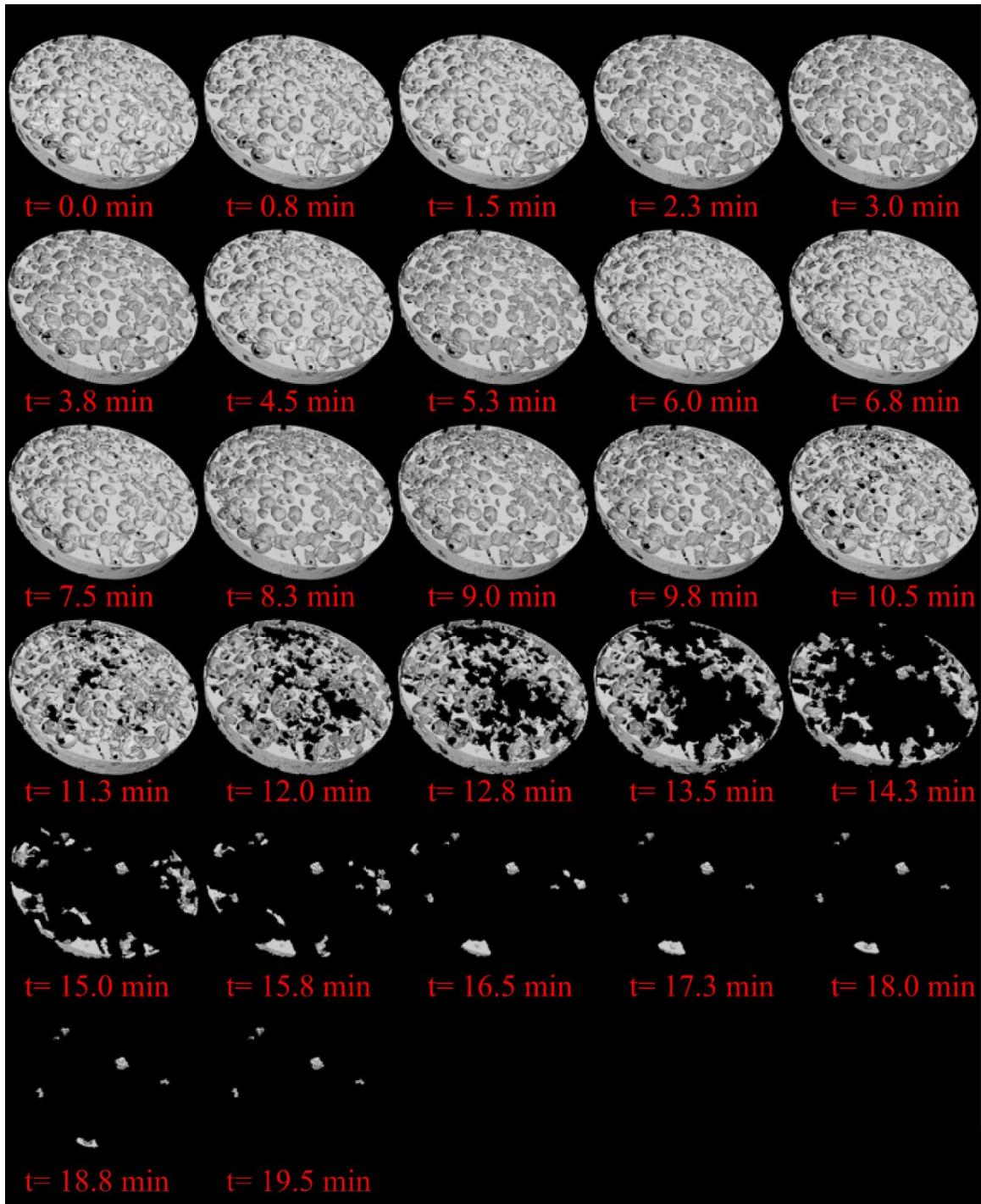


Figure 3-8. Volume rendering images of hydrate during dissociation for a vertical section of the specimen for the thermal stimulation experiment from beginning of the test to $t = 22.5$ min, time-lapse between images is 45 seconds.

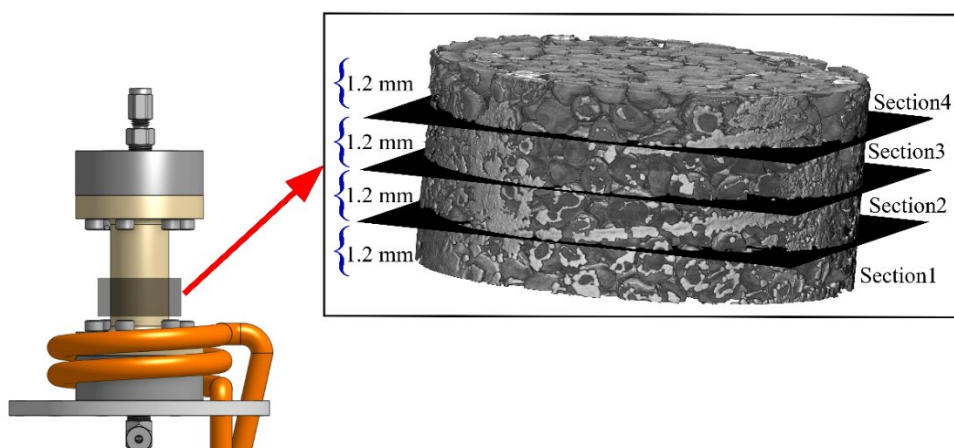


Figure 3-9. Specimen scanned region and divided vertical sections (specimen inner diameter is 9.2 mm).

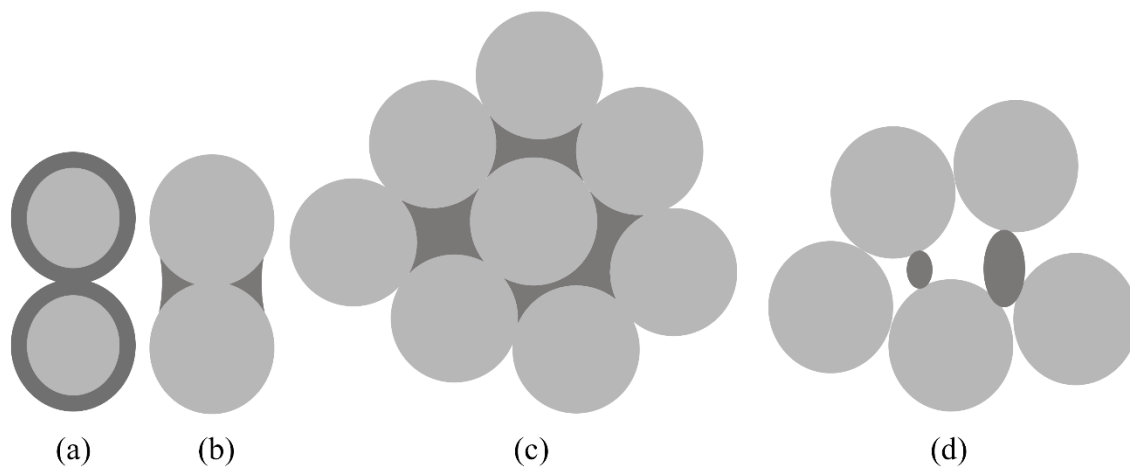


Figure 3-10. Schematic of different hydrate pore habit: (a) surface coating; (b) cementing; (c) pore filling; and (d) load bearing.

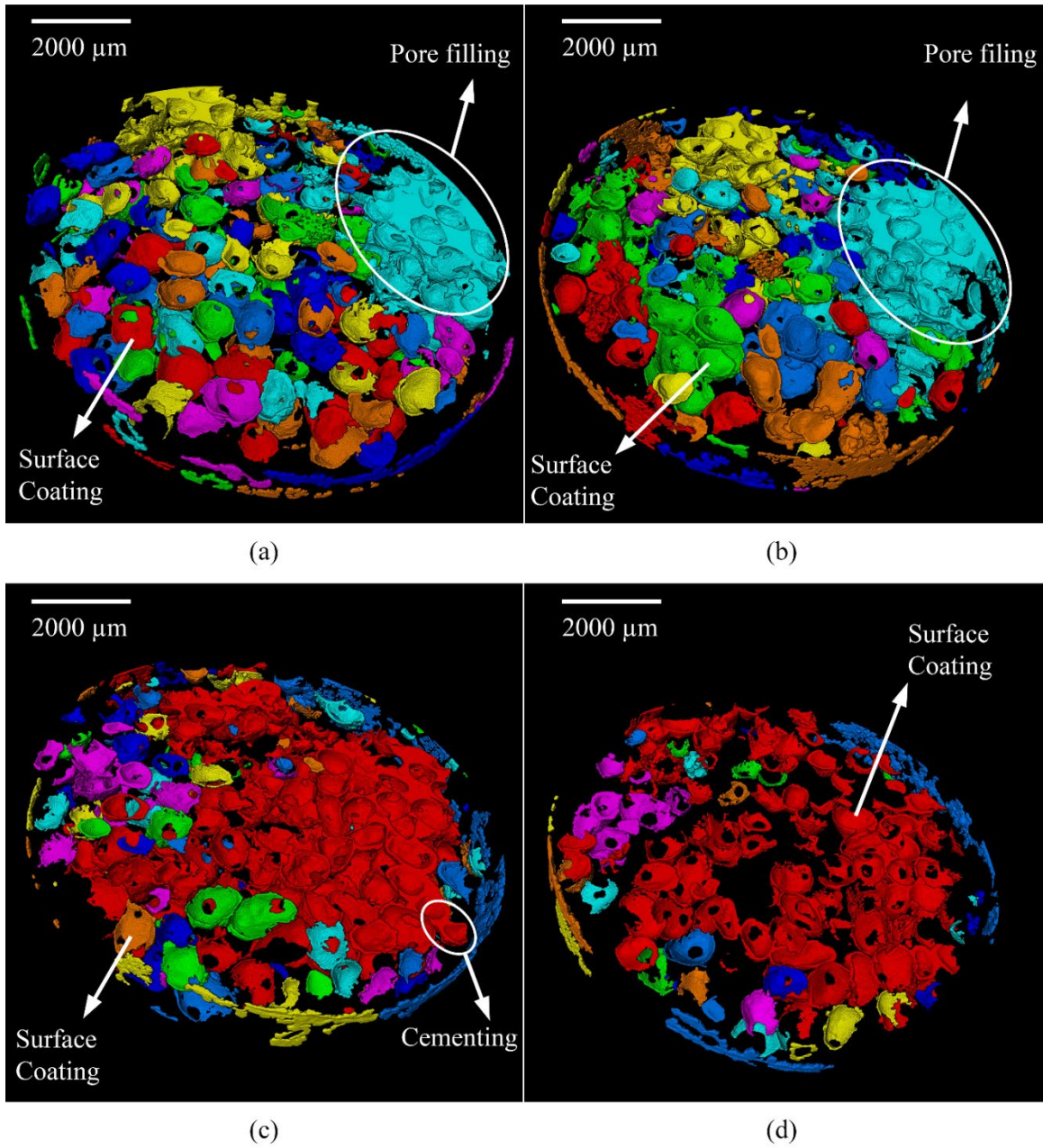


Figure 3-11. Initial hydrate pore habit distribution highlighted in volume rendering images for the depressurization experiment for: (a) Section 1; (b) Section 2; (c) Section 3; and (d) Section 4 of the specimen.

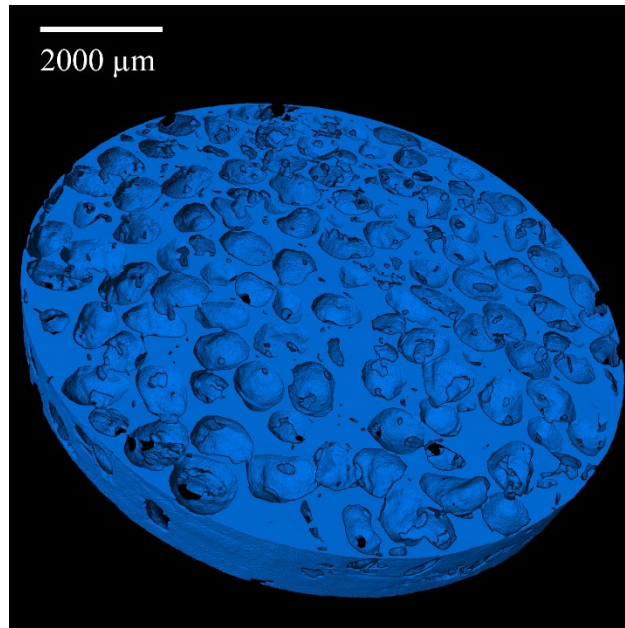


Figure 3-12. Volume rendering image for section 1 of the thermal stimulation experiment showing the pore-filling pore habit.

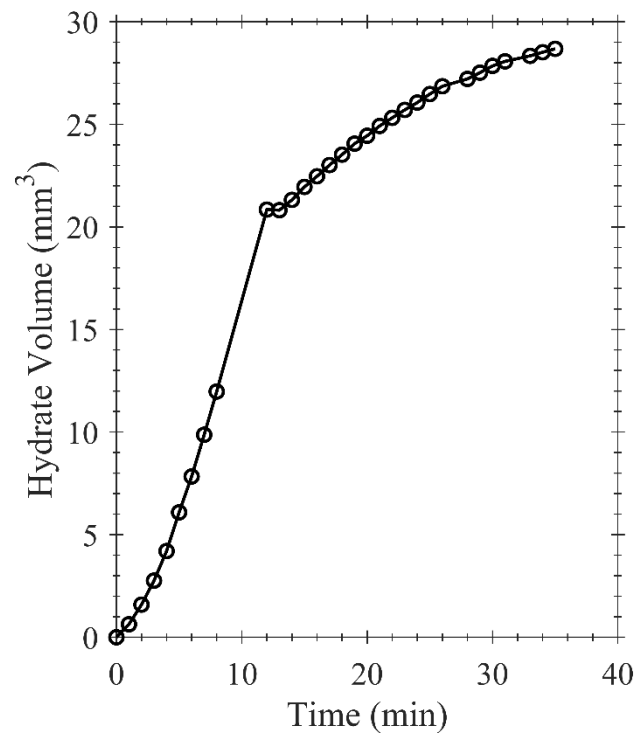


Figure 3-13. Hydrate volume changes with time.

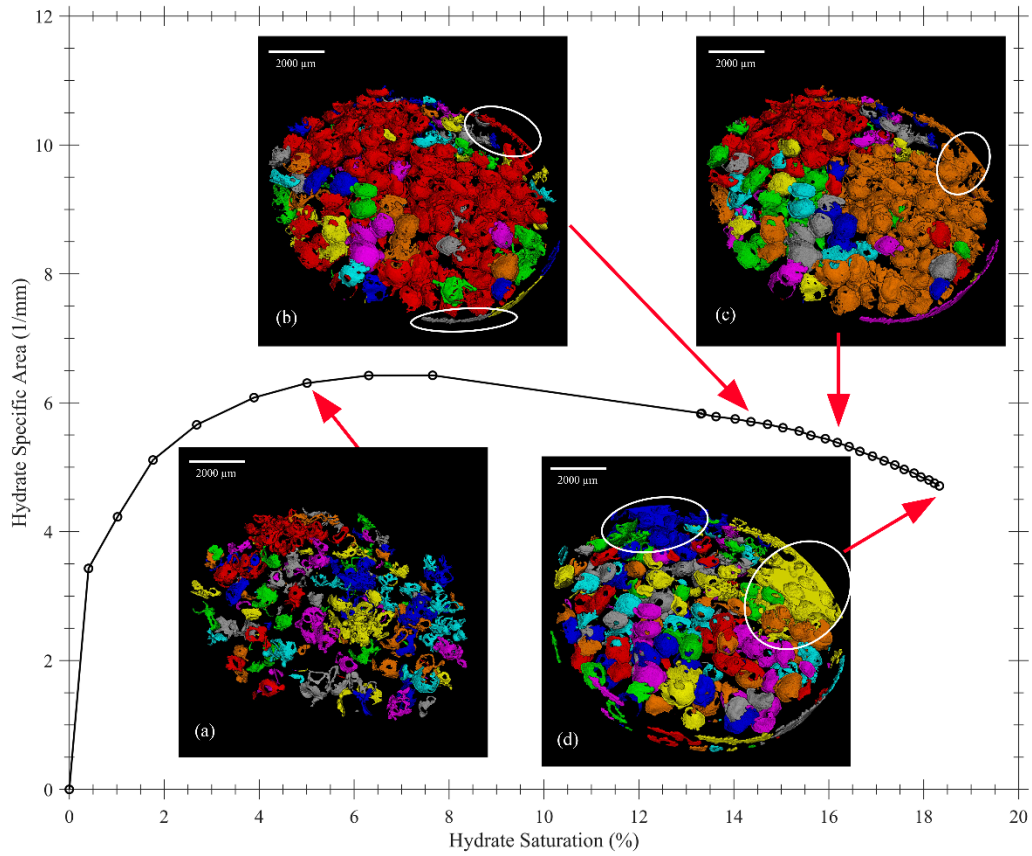


Figure 3-14. Hydrate specific area changes with hydrate saturation with volume rendering snapshots at selected hydrate saturation showing the evolution of hydrate pore-habit: (a) surface coating pore-habit; (b) hydrate start to fill space between surrounding wall and sand particles; (c) cementing pore-habit; and (d) pore filling pore-habit

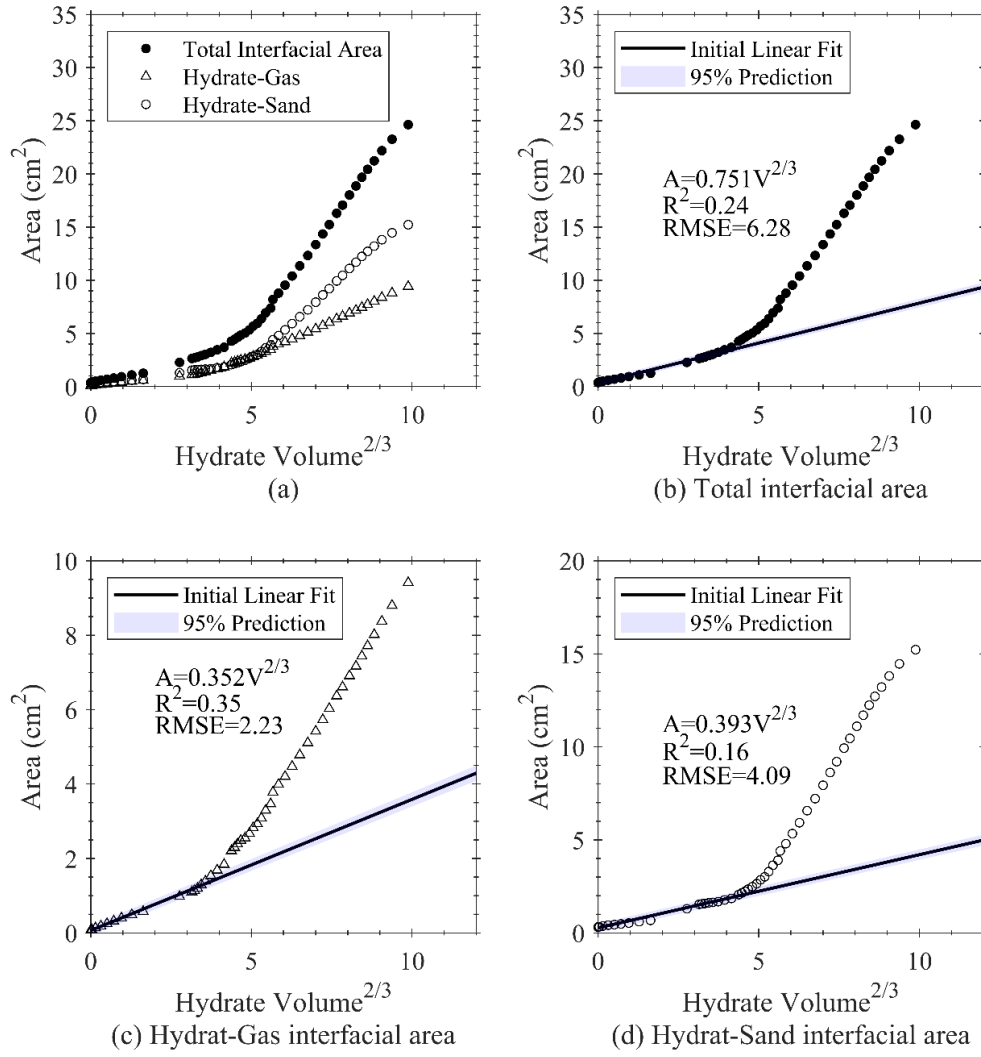


Figure 3-15. Variation of $(\text{hydrate volume})^{2/3}$ versus: (a) combined interfacial area measurements; (b) total hydrate interfacial area; (c) hydrate-sand interfacial area; and (d) hydrate-gas interfacial area along with initial best fit lines and 95% prediction bands for the depressurization experiment.

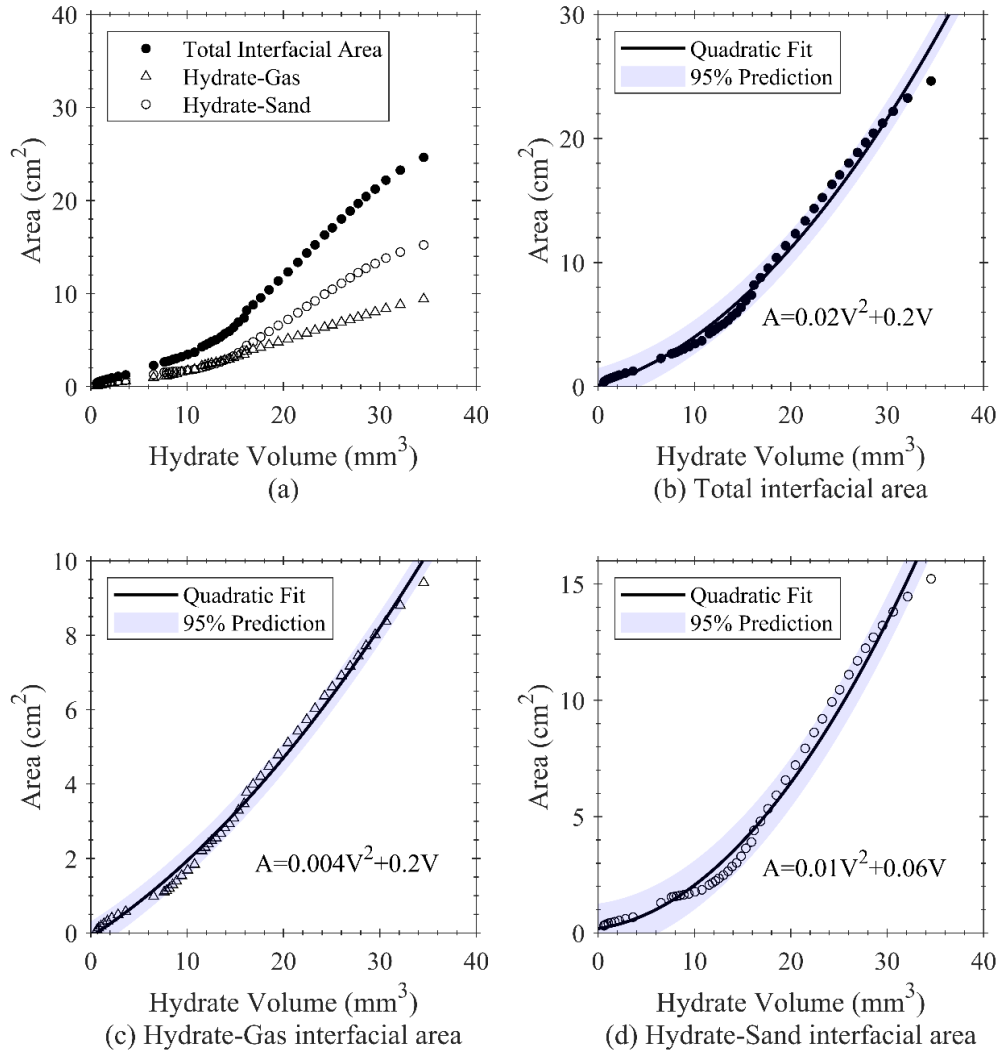


Figure 3-16. Variation of (a) combined interfacial area measurements; (b) total hydrate interfacial area; (c) hydrate-sand interfacial area; and (d) hydrate-gas interfacial area with hydrate volume along with best quadratic fit and 95% prediction bands for the depressurization experiment.

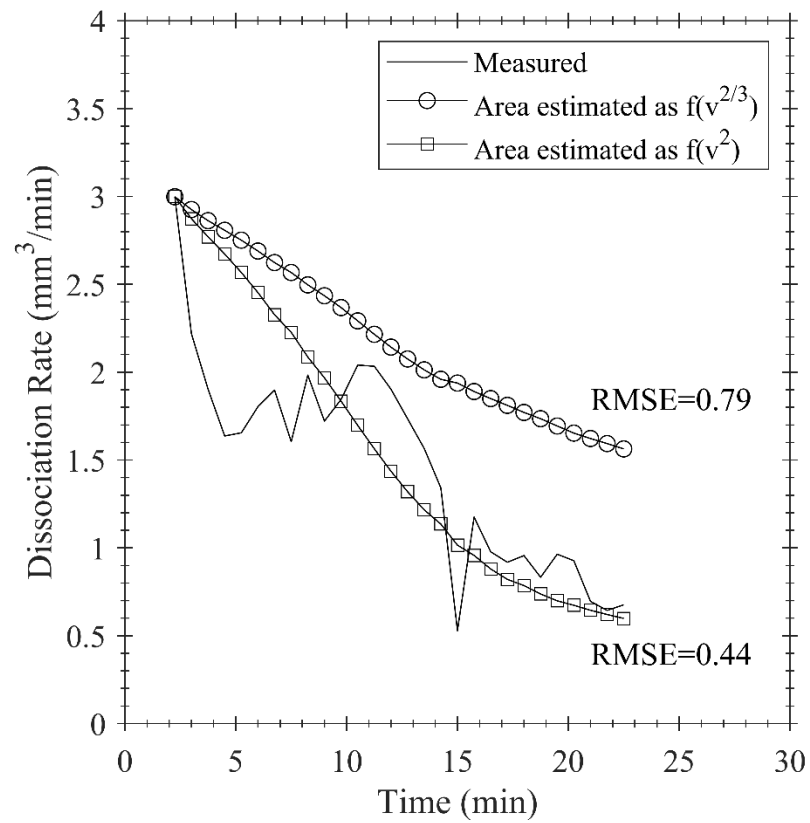


Figure 3-17. Change of measured dissociation rate with predicted dissociation rate according to Equation 3-1 with time for the depressurization experiment.

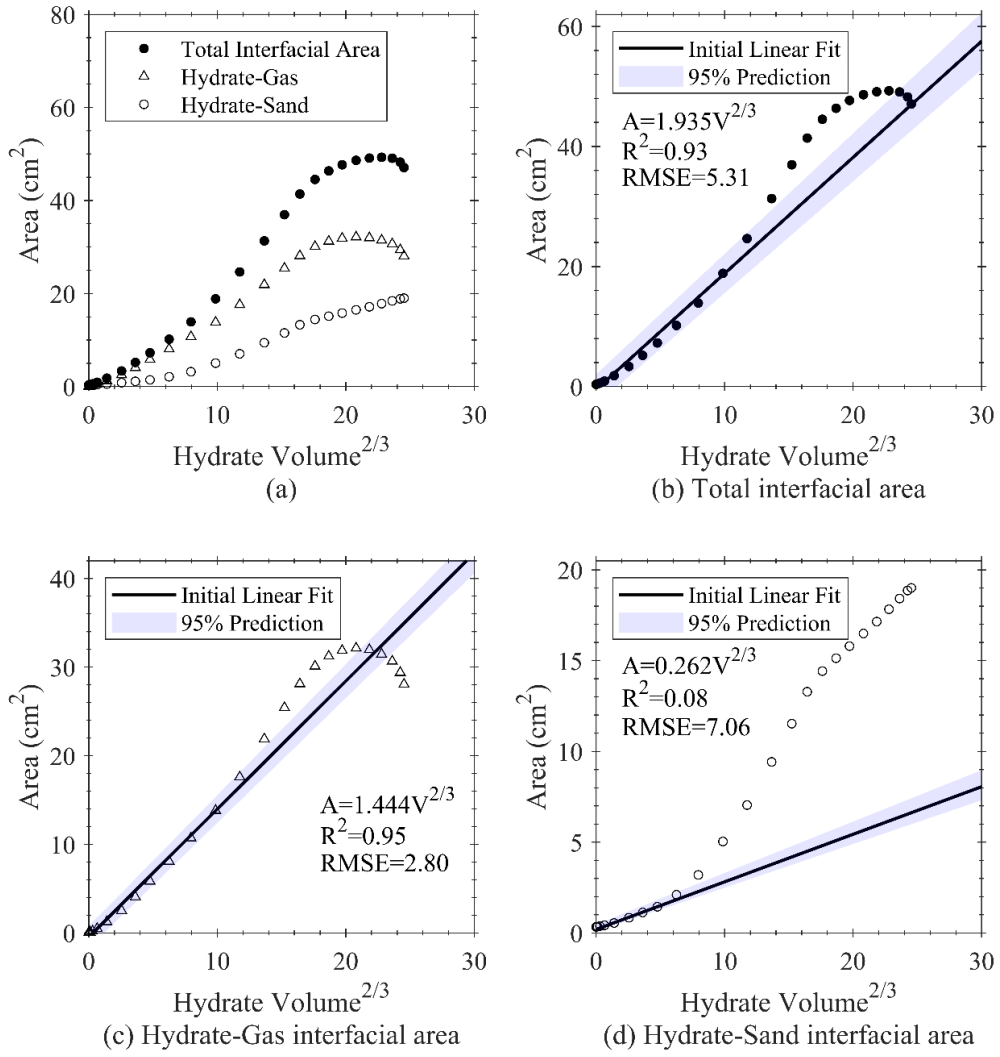


Figure 3-18. Variation of (hydrate volume)^{2/3} versus: (a) combined interfacial area measurements; (b) total hydrate interfacial area; (c) hydrate-sand interfacial area; and (d) hydrate-gas interfacial area along with initial best fit lines and 95% prediction bands for the thermal stimulation experiment.

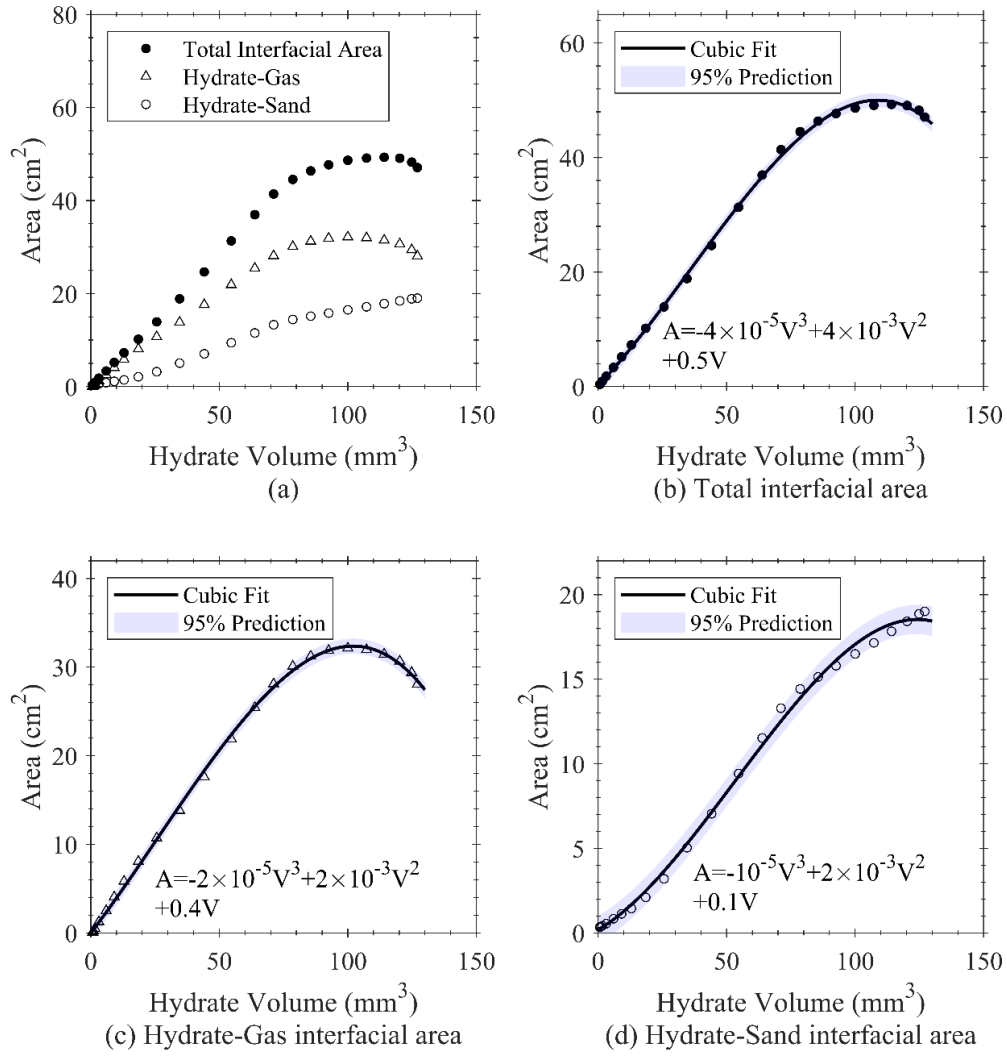


Figure 3-19. Variation of (a) combined interfacial area measurements; (b) total hydrate interfacial area; (c) hydrate-sand interfacial area; and (d) hydrate-gas interfacial area with hydrate volume along with best cubic fit and 95% prediction bands for the thermal stimulation experiment.

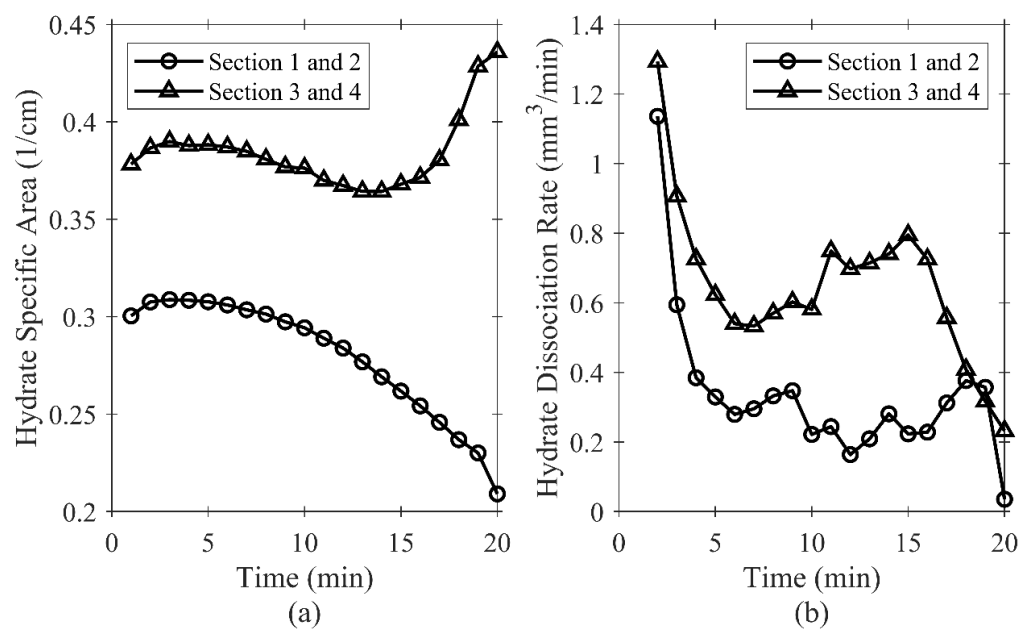


Figure 3-20. Change of (a) hydrate specific area; and (b) hydrate dissociation rate with time during dissociation for the depressurization experiment.

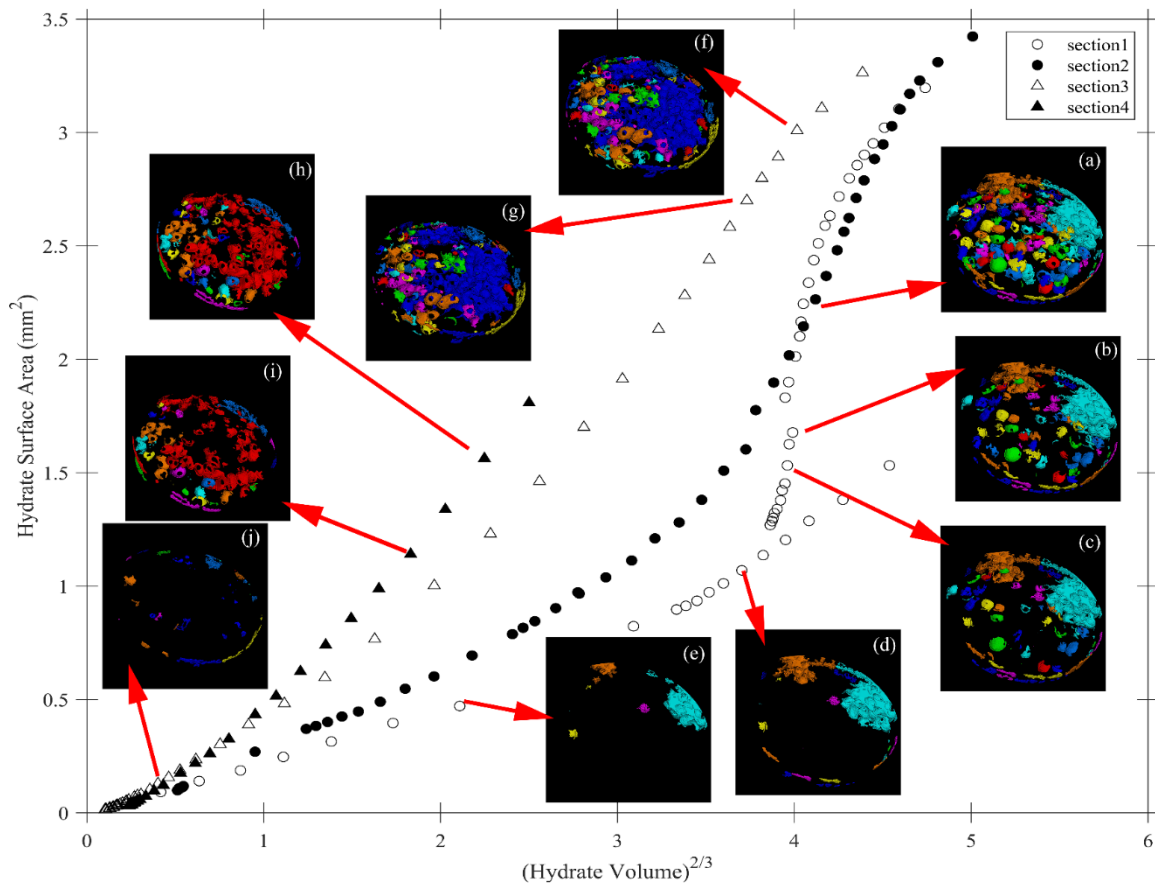


Figure 3-21. Change of hydrate surface area with (hydrate volume) $^{2/3}$ during hydrate dissociation for the four vertical sections of the specimen for the depressurization experiment along with volume rendering images at selected points.

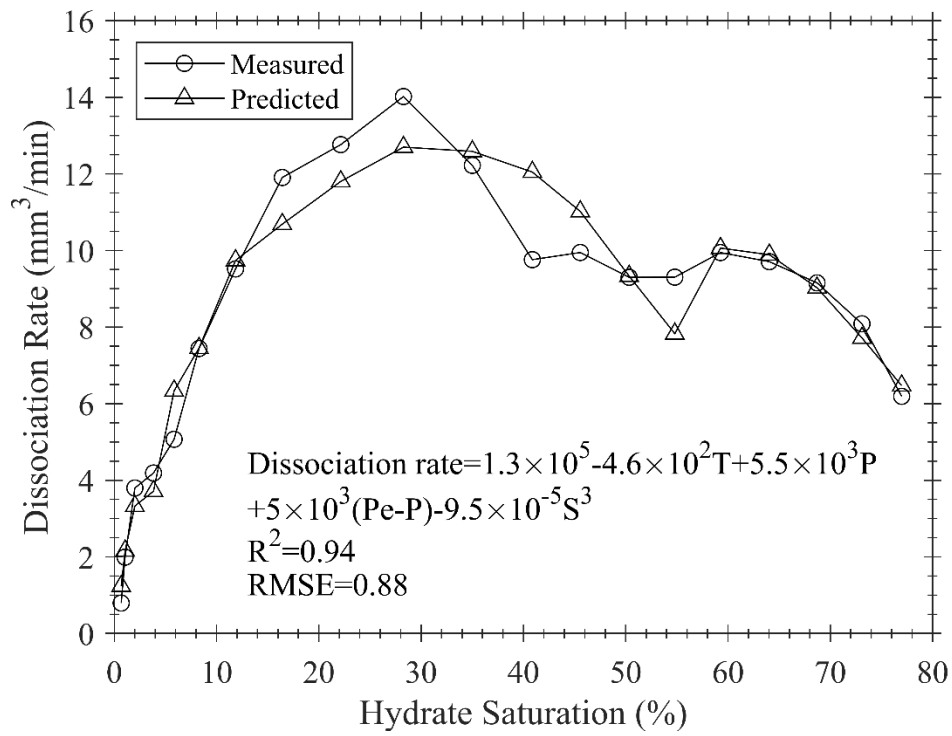


Figure 3-22. Change of measured and predicted hydrate dissociation rate with hydrate saturation along with the linear regression model for the thermal stimulation experiment.

CHAPTER FOUR

**NEW MODEL FOR ESTIMATING GEOMETRIC TORTUOSITY OF
SATURATED AND UNSATURATED POROUS MEDIA USING 3D
SYNCHROTRON MICRO-COMPUTED TOMOGRAPHY IMAGING**

A version of this chapter is currently in preparation to be submitted to a peer-reviewed journal as Jarrar Z., Al-Raoush R., Alshibli K., Hannun J., New Model for Estimating Geometric Tortuosity of Saturated and Unsaturated Porous Media using Synchrotron Micro-Computed Tomography Imaging.

My contribution to this paper is performing some of the experimental tests, some of the image processing, all tortuosity results analyses, and preparing the original draft and majority of figures.

Abstract: Tortuosity has a significant impact on the transport and flow characteristics of porous media, which plays a major role in many applications such as enhanced oil recovery, contaminant transport in aquifers, and fuel cells. Most analytical and theoretical models for determining tortuosity have been developed for ideal systems with assumptions that might not be representative of natural porous media. In this paper, full 3D tomography images of 130 natural unconsolidated porous media systems with a range of porosity, saturation, grain size distribution, and morphology were acquired using 3D monochromatic and pink-beam synchrotron micro-computed tomography imaging. Geometric tortuosity was directly measured from the 3D images, and multivariate nonlinear regression analysis was used to develop a simple model for tortuosity of saturated and unsaturated natural unconsolidated porous media. Wetting phase saturation was found to provide a good estimate of relative tortuosity with an R^2 value of 0.94, even with the variation of porosity in the porous media systems. I_{sph} and Cu had insignificant effects on the estimated value of tortuosity, and therefore, were excluded from the regression model. The proposed regression model was assessed by comparisons with theoretical and analytical models available in the literature and was found to give better estimates of geometric tortuosity with an R^2 value of 0.9 and RMSE value of 0.117.

Keywords: Synchrotron computed tomography, tortuosity, unsaturated porous media

Introduction

Fluid transport in porous media can be found in a wide range of applications, including enhanced oil recovery, contaminant transport in aquifers, geological storage of Carbon Dioxide, fuel cells, and batteries. Tortuosity of transport paths in the pore space has a profound impact on the transport and flow characteristics of porous media. Pore space tortuosity affects electrical conductivity (Garrouh et al. 2001; Weerts et al. 2001), permeability (Duda et al. 2011; Vervoort and Cattle 2003), diffusion (Gao et al. 2014; Grathwohl 2012), thermal conductivity (Qin et al. 2019; Xu et al. 2018), fluid entrapment (Androutsopoulos and Salmas 2000; Salmas and Androutsopoulos 2001), and acoustics properties (Li and Payandeh 2016; Zielinski 2012) of porous media. Due to these diverse applications, tortuosity has been categorized in the literature into four main classes: geometric, diffusive,

hydraulic, and electric. Geometric tortuosity, τ , is defined as the ratio of the average length of the geometrical paths through the porous medium to the straight line length across the medium (Clennell 1997). Diffusive tortuosity, τ_d , is defined as the square of the ratio of the average length of a chemical's diffusive pathway to the straight line length (Epstein 1989). Clennell (1997) defined hydraulic tortuosity τ_h , as the square of the ratio of the flux-weighted average path length for hydraulic flow to the straight-line length. Electric tortuosity, τ_e , is defined as the square of the ratio of the average path length for electrical flow to the straight line length (Wong 1999). More information about different types of tortuosity are referred to in the critical review conducted by Ghanbarian et al. (2013a).

Many theoretical, analytical, and experimental approaches have been proposed in the literature to model tortuosity in porous media. The focus of this study will be on the geometric tortuosity. Lanfrey et al. (2010) developed a theoretical tortuosity model for fixed-bed randomly packed with identical particles as:

$$\tau = 1.23 \times \frac{(1 - \phi)^{4/3}}{I_R^2 \phi} \quad 4-1$$

where ϕ is the porosity, I_R is the roundness factor for one particle and is defined as:

$$I_R = \frac{\sqrt[3]{36\pi V_p^2}}{S_p} \quad 4-2$$

where V_p is the volume of particle and S_p is its surface area. By definition, $S_p = 1$ for spheres and is < 1 for non-spherical particles. Pisani (2011) derived a simple expression of tortuosity as a function of porosity by numerical simulation of diffusion process in porous media made of spherical particles as:

$$\tau = 1 + 0.64(1 - \phi) \quad 4-3$$

Yu and Li (2004) developed a simple-geometry tortuosity model for a 2D porous medium composed of square particles:

$$\tau = \frac{1}{2} \left[1 + \frac{1}{2} \sqrt{1 - \phi} + \frac{\sqrt{(\sqrt{1 - \phi} - 1)^2 + \frac{1 - \phi}{4}}}{1 - \sqrt{1 - \phi}} \right] \quad 4-4$$

Ahmadi et al. (2011) used a volume averaging approach to express tortuosity of mono-sized spherical arrays as:

$$\tau = \sqrt{\frac{2\phi}{3 \left[1 - 1.209(1 - \phi)^{\frac{2}{3}} \right]}} + \frac{1}{3} \quad 4-5$$

Furthermore, Li and Yu (2011) proposed a recursive model for the tortuosity of the flow path in Sierpinski carpet:

$$\tau = \left(\frac{19}{18}\right)^{\frac{\ln(\phi)}{\ln(\frac{8}{9})}} \quad 4-6$$

The Sierpinski carpet used a pore fractal model that consists of different-size particles but with the same pore size. All models presented earlier were derived for fully saturated or dry porous systems. However, previous analytical and theoretical models determine tortuosity for ideal systems with underlying assumptions that might not be representative of natural porous material. Ghanbarian et al. (2013) developed a geometric tortuosity model applicable for saturated and unsaturated porous media based on percolation theory and finite-size scaling approach:

$$\tau = \left[\frac{\theta - \theta_t + \left(\frac{C}{L_s}\right)^{\frac{1}{\nu}}}{1 - \theta_t} \right]^{v - \nu D_x} \quad 4-7$$

where ν is a scaling component which equals $\frac{4}{3}$ in 2D and 0.88 in 3D, D_x is the fractal dimensionality, C is a numerical factor, L_s is the system size, θ is the water content, and θ_t is the critical water content for percolation, which is the minimum water content required for the existence of a system-spanning cluster of interconnected waterfilled pores. (Ghanbarian et al. 2013) also defined the relative tortuosity (τ_r) as the ratio of geometrical tortuosity in an unsaturated medium to the geometrical tortuosity of the same medium at full saturation (τ_s):

$$\tau_r = \frac{\tau}{\tau_s} = \left[\frac{\theta - \theta_t + \left(\frac{C}{L_s}\right)^{\frac{1}{\nu}}}{\phi - \theta_t + \left(\frac{C}{L_s}\right)^{\frac{1}{\nu}}} \right]^{v - \nu D_x} \quad 4-8$$

Experimentally, tortuosity has been measured indirectly by conducting fluid diffusion experiments (Corrochano et al. 2015; Soukup et al. 2015) and electrical conductivity measurements (Coleman and Vassilicos 2008; Morin et al. 2010). For example, Iversen and Jørgensen (1993) determined tracer diffusion coefficients of sulfate and methane in different types of sediments including sandy sediments and fine-grained silt and clay, and used it to estimate tortuosity as:

$$\tau = \sqrt{1 + 2(1 - \phi)} \quad 4-9$$

Comiti and Renaud (1989) proposed the following equation to estimate tortuosity based on permeability measurements for PVC platy particles and glass spheres as:

$$\tau = 1 - p \ln(\phi) \quad 4-10$$

where p is a fitting parameter which depends on the shape of particles and was reported by Mauret and Renaud (1997) to be 0.49 for the case of spheres beds.

While these experimental methods provide a fair estimate of tortuosity, they fail to relate the estimated tortuosity to the geometry and topology of the pore space. Recent advances in nondestructive imaging techniques such as x-ray computed tomography (CT) motivated researchers to investigate the complex pore structure of porous media. Several algorithms were reported in the literature to measure the geometric tortuosity using 3D volume images. These algorithms include medial axis (Al-Raoush and Madhoun 2017; Takahashi et al. 2009), Dijkstra algorithm (Pardo-Alonso et al. 2014), random walk simulation (Promentilla et al. 2016), chessboard distance algorithm (FEI 2018), and thin-line skeleton (Rotger et al. 2003). Available commercial software use different algorithms for measuring tortuosity from 3D tomography images. For example, the medial axis algorithm is used in 3DMA software (Jung et al. 2014; Takahashi et al. 2015) and 3DMA-Rock software (Naveed et al. 2013; Neethirajan et al. 2008), while the chessboard distance algorithm is used in Avizo software (FEI 2018). Naveed et al. (2013) used 3DMA-Rock software to estimate tortuosity of 10 sand specimens with different shapes and mean particle diameters and reported that geometric tortuosity can be estimated as:

$$\tau = 0.19d_{50} + 1.45 \quad 4-11$$

where d_{50} is the mean particle diameter in mm. However, the model described in Equation 4-9 did not consider the effects of porosity on tortuosity values and was developed based on a limited number of statistical points (10 data points).

The objective of this study is to develop a simple and physically-realistic regression model that estimates tortuosity of porous media (saturated and unsaturated). Geometric tortuosity measurements for 130 3D images of natural unconsolidated sand systems obtained using in-situ 3D Synchrotron microcomputed tomography (SMT) images are used to develop the regression model.

Materials and Methodology

3D Synchrotron Micro-computed Tomography (SMT)

3D synchrotron micro-computed tomography (SMT) is an enhancement to industrial CT where a synchrotron radiation source is used to produce a high-intensity x-ray beam. Typical SMT imaging utilizes a monochromator (SMT-M) to produce a monochromatic x-ray beam with tunable energy allowing for element-specific imaging and reducing beam hardening artifacts (Kinney and Nichols 1992). However, the use of a monochromator reduces the flux significantly, transmitting only 0.1% of the beam energy, which increases data acquisition time and makes it unsuitable for monitoring dynamic processes (Rivers 2016). An alternative is the use of pink beam technique (SMT-P) where the monochromator is replaced with a grazing mirror and x-ray absorbing foil. SMT-P can yield an x-ray flux three orders of magnitude higher than SMT-M, reducing the data acquisition time to few seconds and makes a favorable option for in-situ monitoring of dynamic processes (Jarrar et al. 2020; Rivers 2016). In this study, both SMT-M and SMT-P techniques were used to acquire 3D images of unsaturated,

unconsolidated sand systems at different degrees of saturation. All scans were acquired at Beamline 13D of the Advanced Photon Source (APS), Argonne National Laboratory (ANL), IL, USA.

Materials and Experimental Method

The sand used in this study is silica sand obtained from two suppliers: US Silica (Katy, TX) and Agsco (Wheeling, IL) Companies. All experiments used a 6.35 mm (1/4 in.) inner diameter by 38.1 mm (1.5 in.) height Aluminum cylindrical cell with two ports: an upper port connected to a DigiFlow pressure-volume actuator (flow pump); and a bottom port connected to a pressure regulator connected to a CO₂ gas source. Sand was deposited into the partially filled with water cell to achieve an initial fully saturated state. During testing, water (wetting phase) was pumped out of the cell at a flow rate of 0.01 ml per minute while injecting CO₂ (non-wetting phase) at a constant pressure of 3 psi. Full 3D tomography scans were acquired continuously using SMT-P (83 systems) and SMT-M (47 systems) and reconstructed into 3D volume images. A total of 130 systems of unsaturated, unconsolidated sediments with wide ranges of degree of saturation (S), porosity, roundness (I_R), sphericity (I_{sph}), median grain diameter (D_{50}), and grain size distribution were reported in this study.

Table 4-1 presents a summary of the physical properties of the 130 porous media systems. The degree of saturation ranged from 13.5% to 100%; porosity ranged from 0.3 to 0.5; and D_{50} ranged from 370 μm to 960 μm . Moreover, histograms of porosity, D_{50} , I_R , I_{sph} , Cu , and Cc of the 130 systems are depicted in Figure 4-1. The 3D images had three different sizes: 1920×1920×1200 voxels with a spatial resolution of 4.29 $\mu\text{m}/\text{voxel}$ (83 images), 550×550×520 voxels with a spatial resolution of 11.22 $\mu\text{m}/\text{voxel}$ (13 images), and 400×400×400 voxels with a spatial resolution of 11.22 $\mu\text{m}/\text{voxel}$ (34 images).

Results and Discussion

Sand Particles Segmentation

PerGeos software (FEI 2019) was used to analyze 3D images including image enhancement and segmentation. Figure 4-2 summarized image processing steps for on a zoomed view of an XY slice of one of the systems. First, a combination of anisotropic diffusion and median filters were used to reduce noise in the grayscale SMT images and enhance their contrast. The anisotropic diffusion filter compares the value of each voxel with its six neighboring voxels, and diffuse the voxel if the difference is smaller than the diffusion stop threshold value. The resulting image is a smoothed grayscale image with sharp particle edges (Figure 4-2b). The next step is to segment the filtered image to separate sand particles from the surrounding wetting and non-wetting phases (Figure 4-2c). Filtered images were binarized using the interactive thresholding module in which user-defined values of image intensity ranges were input to binarize the images. The thresholding range was selected based on intensity histograms of the images and was verified

visually for accuracy before proceeding with the segmentation. Then, the Separate Objects module in PerGeos software was used to separate sand particles, and each particle was assigned a unique numerical label (Figure 4-2d and e). The Separate Objects module is a combination of watershed, distance transform, and numerical reconstruction algorithms that accurately remove small areas of contact between particles. Sample 2D cross-section and volume rendering snapshots for selected labeled images where each labeled particle consists of connected voxels occupying a cubical point in 3D space are depicted in Figure 4-3. Labeled sand images were then used to calculate the porosity as the ratio between the volume of voids and the total volume of each system. The volume of each particle was calculated as the summation of all voxels within the particle.

Wetting and Non-wetting Phases Segmentation

Similar to sand particles segmentation, the filtered images were used to segment the non-wetting phase using the interactive thresholding module. The thresholding range was selected based on the images histograms and was checked visually for accuracy. Finally, arithmetic operations were performed on the binarized sand and non-wetting phase images to yield one segmented image with all three phases of solids, wetting, and non-wetting with each phase having a distinct value (i.e., solid particles have a value of 3, wetting phase has a value of 2, and non-wetting phase has a value of 1) (Figure 4-2g). The three-phase segmented images were used to calculate the degree of saturation as the ratio between the volume of the wetting phase and the total volume of voids (wetting phase+ non-wetting phase) of all systems.

Particle Morphology and Gradation

Two morphology indices were adopted to quantify the morphology of sand particles: roundness (I_R), and sphericity (I_{sph}) indices. Alshibli et al. (2015) proposed a definition of I_{sph} based 3D SMT images as:

$$I_{sph} = \frac{V_p}{V_s} \quad 4-12$$

where V_s is the volume of a sphere with a diameter equal to the shortest length that passes through the centroid of the particle. In this study, the definition proposed by Lanfrey et al. (2010) (Equation 4-2) is used to calculate I_R , while the definition proposed by Alshibli et al. (2015) (Equation 4-12) is used to calculate I_{sph} .

Uniformity coefficient ($Cu = \frac{D_{60}}{D_{10}}$), and coefficient of curvature ($Cc = \frac{D_{30}^2}{D_{10}D_{60}}$) are used to describe the grain size distribution of the sand systems where D_{10} , D_{30} , and D_{60} are the diameters corresponding to 10%, 30%, and 60% finer in the particle-size distribution, respectively.

Tortuosity Measurements

Binarized images, where the wetting phase voxels have values of 1 and the non-wetting phase and sand voxels have values of 0, are then used to obtain the

geometric tortuosity using the tortuosity module in PerGeos software. The module calculates the tortuosity of a path formed by the centroids on each plane along the z-axis of the binarized 3D image by computing the path length through the centroids divided by the number of planes along the z-axis (FEI 2018). Figure 4-4 presents the change of relative tortuosity with water saturation for the 130 sand systems along with the best power fit (depicted as solid line in Figure 4-4), which is found to be:

$$\tau_r = S^{-0.435} \quad 4-13$$

The power function of water saturation (Equation 4-13) provides a good estimate of the relative tortuosity (R^2 value of 0.94) even with the variation of porosity in the sand systems. It should be emphasized again that this is applicable only for the porosity range of the natural unconsolidated porous media systems investigated here. Furthermore, the minimum allowable value of τ_r according to Equation 4-13 is 1.0 and is reached when S is equal to 1.0, which is in agreement with the definition of τ_r .

Multivariate nonlinear regression was used to propose a model that estimates geometric tortuosity of saturated and unsaturated porous media using S , ϕ , D_{50} , I_{sph} , I_R , C_u , C_c as possible predictors. Regression coefficients were determined based on the least square fit which minimizes the sum of the squares of the residuals. The p-value was used to assess the significance of each regression coefficient. A coefficient with a low p-value means that the null hypothesis that the coefficient is equal to zero can be rejected. Only variables with a p-value less than 0.05 are kept in the model. The regression yielded the following model:

$$\tau = \phi^{-0.350} S^{-0.435} C_c^{0.538} I_R^{-0.480} \quad 4-14$$

with a root mean squared error (RMSE) of 0.117 and an R^2 value of 0.90. Effects of I_{sph} and C_u were found to be insignificant based on their p-value and were excluded from the regression model. Table 4-2 lists the nonlinear regression coefficients along with their standard errors and corresponding p-values and Figure 4-5 displays the measured geometric tortuosity obtained from SMT images versus the predicted geometric tortuosity estimated from Equation 4-14 along with 1:1 line. I_{sph} and C_u were excluded from the regression model because the corresponding p-value of these two predictors was larger than the 0.05 threshold. In other words, changing the power coefficient of the two predictors did not change the response of the model, and therefore, their effects were insignificant.

Figure 4-6 compares the predicted saturated geometric tortuosity calculated using the model proposed in Equation 4-14 with analytical, theoretical, and empirical models obtained from the literature. Referring to Figure 4-6, Mauret and Renaud (1997) and Ghanbarian et al. (2013) models underestimate the geometric tortuosity values while Iversen and Jørgensen (1993) and Lanfrey et al. (2010) models overestimate tortuosity for the porosity range reported in this study. It should be noted that for Ghanbarian et al. (2013) model, θ_t was approximated to be 0.1ϕ (Hunt 2004), and finite-size effect was neglected. Yu and Li (2004) model overlaps with the statistical fit model (Equation 4-14) at porosity value of 0.45; but

began to diverge and overestimate the tortuosity as porosity decreased. Li and Yu (2011) model shows good agreement with the statistical fit model defined by Equation 4-14, but starts to diverge for porosity values less than ~ 0.3 . Figure 4-7 presents a comparison of the predicted relative geometric tortuosity using the statistical fit model in Equation 4-13 with the model proposed by Ghanbarian et al. (2013) that was derived based on percolation theory (θ_t was approximated to be 0.1ϕ and finite-size effect was neglected). It can be seen from Figure 4-7 that the model generated based on percolation theory is in good agreement with the statistical fit model from Equation 4-13, with an R^2 value of 0.77. The model starts to slightly diverge at degrees of saturation lower than ~ 0.25 .

Conclusions

Multivariate nonlinear regression fitting was used to propose a geometric tortuosity model for saturated and unsaturated porous media based on in-situ 3D images of unconsolidated sand systems. Full 3D tomography images of 130 natural sand systems with a range of porosity, saturation, grain size distribution, and morphology were acquired using SMT-M and dynamic SMT-P imaging techniques. The degree of saturation of the sand systems ranged from 13.5% to 100%, while the porosity ranged from 0.30 to 0.50. All images were segmented and analyzed, and the geometric tortuosity of each system was determined using PerGeos commercial software.

Even with the variation of porosity in the sand systems, the relative tortuosity can be estimated as a power function of saturation only with an R^2 value of 0.94. This is only true for the porosity range investigated in this study (0.30 to 0.50). Multivariate nonlinear regression was used to propose a model that estimates geometric tortuosity of saturated and unsaturated porous media with S , ϕ , D_{50} , I_{sph} , I_R , C_u , C_c as possible predictors. Effects of I_{sph} and C_u were found to be insignificant based on their p-value and were excluded from the regression model. The proposed model provided a good estimate of geometric tortuosity with an R^2 value of 0.90 and RMSE value of 0.117. The proposed model yields better estimates of saturated geometric tortuosity compared to the analytical and theoretical models found in the literature, which can be attributed to the fact that these models were developed for ideal systems with assumptions that might not be representative of natural porous media.

Acknowledgments

This publication was made possible by partial funding from NPRP grant # NPRP8-594-2-244 from the Qatar national research fund (a member of Qatar Foundation) and the Institute for a Secure and Sustainable Environment (ISSE), University of Tennessee-Knoxville, USA. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of funding agencies. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of

Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. We acknowledge the support of GeoSoilEnviroCARS (Sector 13), which is supported by the National Science Foundation - Earth Sciences (EAR-1634415), and the Department of Energy, Geosciences (DE-FG02-94ER14466). We thank Dr. Mark Rivers of APS for his help in performing the SMT scans. The authors also thank Dr. Wadi Imseeh for his help with scanning.

References

- Ahmadi, M. M., Mohammadi, S., and Hayati, A. N. (2011). "Analytical derivation of tortuosity and permeability of monosized spheres: A volume averaging approach." *Physical Review E*, 83(2), 026312.
- Al-Raoush, R. I., and Madhoun, I. T. (2017). "TORT3D: A MATLAB code to compute geometric tortuosity from 3D images of unconsolidated porous media." *Powder Technology*, 320, 99-107.
- Alshibli, K. A., Druckrey, A. M., Al-Raoush, R. I., Weiskittel, T., and Lavrik Nickolay, V. (2015). "Quantifying Morphology of Sands Using 3D Imaging." *Journal of Materials in Civil Engineering*, 27(10), 04014275.
- Androustopoulos, G. P., and Salmas, C. E. (2000). "Tomography of Macro-Meso-Pore Structure Based On Mercury Porosimetry Hysteresis." *Chemical Engineering Communications*, 181(1), 137-177.
- Clennell, M. B. (1997). "Tortuosity: a guide through the maze." *Geological Society, London, Special Publications*, 122(1), 299.
- Coleman, S. W., and Vassilicos, J. C. (2008). "Transport Properties of Saturated and Unsaturated Porous Fractal Materials." *Physical Review Letters*, 100(3), 035504.
- Comiti, J., and Renaud, M. (1989). "A new model for determining mean structure parameters of fixed beds from pressure drop measurements: application to beds packed with parallelepipedal particles." *Chemical Engineering Science*, 44(7), 1539-1545.
- Corrochano, B. R., Melrose, J. R., Bentley, A. C., Fryer, P. J., and Bakalis, S. (2015). "A new methodology to estimate the steady-state permeability of roast and ground coffee in packed beds." *Journal of Food Engineering*, 150, 106-116.
- Duda, A., Koza, Z., and Matyka, M. (2011). "Hydraulic tortuosity in arbitrary porous media flow." *Physical Review E*, 84(3), 036319.
- Epstein, N. (1989). "On tortuosity and the tortuosity factor in flow and diffusion through porous media." *Chemical Engineering Science*, 44(3), 777-779.
- FEI. 2018. Avizo, version 9.7FEI, Hillsboro, OR.
- FEI. 2019. PerGeos, version 2019FEI, Hillsboro, OR.
- Gao, X., Diniz da Costa, J. C., and Bhatia, S. K. (2014). "Understanding the diffusional tortuosity of porous materials: An effective medium theory perspective." *Chemical Engineering Science*, 110, 55-71.
- Garrouch, A. A., Ali, L., and Qasem, F. (2001). "Using Diffusion and Electrical Measurements to Assess Tortuosity of Porous Media." *Industrial & Engineering Chemistry Research*, 40(20), 4363-4369.
- Ghanbarian, B., Hunt, A. G., Ewing, R. P., and Sahimi, M. (2013a). "Tortuosity in Porous Media: A Critical Review." *Soil Science Society of America Journal*, 77(5), 1461-1477.
- Ghanbarian, B., Hunt, A. G., Sahimi, M., Ewing, R. P., and Skinner, T. E. (2013b). "Percolation Theory Generates a Physically Based Description of Tortuosity in Saturated and Unsaturated Porous Media." *Soil Science Society of America Journal*, 77(6), 1920-1929.

- Grathwohl, P. (2012). *Diffusion in natural porous media: contaminant transport, sorption/desorption and dissolution kinetics*, Springer Science & Business Media.
- Hunt, A. G. (2004). "Continuum percolation theory for water retention and hydraulic conductivity of fractal soils: estimation of the critical volume fraction for percolation." *Advances in Water Resources*, 27(2), 175-183.
- Iversen, N., and Jørgensen, B. B. (1993). "Diffusion coefficients of sulfate and methane in marine sediments: Influence of porosity." *Geochimica et Cosmochimica Acta*, 57(3), 571-578.
- Jarrar, Z. A., Alshibli, K. A., Al-Raoush, R. I., and Jung, J. (2020). "3D measurements of hydrate surface area during hydrate dissociation in porous media using dynamic 3D imaging." *Fuel*, 265, 116978.
- Jung, J., Hamachi, M., Obara, Y., Tanikura, I., and Watanabe, S. (2014). "Analysis of Damage in Specimen Under Cyclic Uniaxial Loading Test by X-Ray CT Method." *ISRM International Symposium - 8th Asian Rock Mechanics Symposium*, International Society for Rock Mechanics and Rock Engineering, Sapporo, Japan, 7.
- Kinney, J. H., and Nichols, M. C. (1992). "X-ray tomographic microscopy (XTM) using synchrotron radiation." *Annual review of materials science*, 22(1), 121-152.
- Lanfrey, P. Y., Kuzeljevic, Z. V., and Dudukovic, M. P. (2010). "Tortuosity model for fixed beds randomly packed with identical particles." *Chemical Engineering Science*, 65(5), 1891-1896.
- Li, A., and Payandeh, S. "An overview of path tortuosity measures for tracking and monitoring." *Proc., 2016 IEEE 7th Annual Information Technology, Electronics and Mobile Communication Conference (IEMCON)*, 1-6.
- Li, J.-H., and Yu, B.-M. (2011). "Tortuosity of Flow Paths through a Sierpinski Carpet." *Chinese Physics Letters*, 28(3), 034701.
- Mauret, E., and Renaud, M. (1997). "Transport phenomena in multi-particle systems—I. Limits of applicability of capillary model in high voidage beds-application to fixed beds of fibers and fluidized beds of spheres." *Chemical Engineering Science*, 52(11), 1807-1817.
- Morin, R. H., LeBlanc, D. R., and Troutman, B. M. (2010). "The Influence of Topology on Hydraulic Conductivity in a Sand-and-Gravel Aquifer." *Groundwater*, 48(2), 181-190.
- Naveed, M., Hamamoto, S., Kawamoto, K., Sakaki, T., Takahashi, M., Komatsu, T., Moldrup, P., Lamandé, M., Wildenschild, D., Prodanovic, M., and de Jonge, L. W. (2013). "Correlating Gas Transport Parameters and X-Ray Computed Tomography Measurements in Porous Media." *Soil Science*, 178(2).
- Neethirajan, S., Jayas, D. S., White, N. D. G., and Zhang, H. (2008). "Investigation of 3D geometry of bulk wheat and pea pores using X-ray computed tomography images." *Computers and Electronics in Agriculture*, 63(2), 104-111.

- Pardo-Alonso, S., Vicente, J., Solórzano, E., Rodriguez-Perez, M. Á., and Lehmhus, D. (2014). "Geometrical Tortuosity 3D Calculations in Infiltrated Aluminium Cellular Materials." *Procedia Materials Science*, 4, 145-150.
- Pisani, L. (2011). "Simple Expression for the Tortuosity of Porous Media." *Transport in Porous Media*, 88(2), 193-203.
- Promentilla, M. A. B., Cortez, S. M., Papel, R. A. D. C., Tablada, B. M., and Sugiyama, T. (2016). "Evaluation of microstructure and transport properties of deteriorated cementitious materials from their X-ray computed tomography (CT) images." *Materials*, 9(5), 388.
- Qin, X., Cai, J., Xu, P., Dai, S., and Gan, Q. (2019). "A fractal model of effective thermal conductivity for porous media with various liquid saturation." *International Journal of Heat and Mass Transfer*, 128, 1149-1156.
- Rivers, M. L. (2016). *High-speed tomography using pink beam at GeoSoilEnviroCARS*, SPIE.
- Rotger, D., Rosales, M., Garcia, J., Pujol, O., Mauri, J., and Radeva, P. "ActiveVessel: a new multimedia workstation for intravascular ultrasound and angiography fusion." *Proc., Computers in Cardiology, 2003*, 65-68.
- Salmas, C. E., and Androutsopoulos, G. P. (2001). "A Novel Pore Structure Tortuosity Concept Based on Nitrogen Sorption Hysteresis Data." *Industrial & Engineering Chemistry Research*, 40(2), 721-730.
- Soukup, K., Hejtmánek, V., Čapek, P., Stanczyk, K., and Šolcová, O. (2015). "Modeling of contaminant migration through porous media after underground coal gasification in shallow coal seam." *Fuel Processing Technology*, 140, 188-197.
- Takahashi, H., Seida, Y., and Yui, M. (2009). "3D X-ray CT and diffusion measurements to assess tortuosity and constrictivity in a sedimentary rock." *Diffus Fundam*, 11, 1-11.
- Takahashi, M., Takada, N., Sato, M., and Lin, W. (2015). "Three Dimensional Pore Geometry and Fluid Flow of Kimachi Sandstone Under Different Stress Condition: Suggestion to Conservation of Tuffaceous World Cultural Heritage." *Proc., Engineering Geology for Society and Territory - Volume 8*, Springer International Publishing, 135-138.
- Vervoort, R. W., and Cattle, S. R. (2003). "Linking hydraulic conductivity and tortuosity parameters to pore space geometry and pore-size distribution." *Journal of Hydrology*, 272(1), 36-49.
- Weerts, A. H., Kandhai, D., Bouten, W., and Sloot, P. M. A. (2001). "Tortuosity of an Unsaturated Sandy Soil Estimated using Gas Diffusion and Bulk Soil Electrical Conductivity." *Soil Science Society of America Journal*, 65(6), 1577-1584.
- Wong, P.-Z. (1999). "4. Conductivity, Permeability, and Electrokinetics." *Experimental Methods in the Physical Sciences*, P.-z. Wong, ed., Academic Press, 119-159.
- Xu, W., Jia, M., and Gong, Z. (2018). "Thermal conductivity and tortuosity of porous composites considering percolation of porous network: From

- spherical to polyhedral pores." *Composites Science and Technology*, 167, 134-140.
- Yu, B.-M., and Li, J.-H. (2004). "A Geometry Model for Tortuosity of Flow Path in Porous Media." *Chinese Physics Letters*, 21(8), 1569-1571.
- Zielinski, T. G. "Inverse identification and microscopic estimation of parameters for models of sound absorption in porous ceramics." 95-108

Appendices

Appendix A: Tables

Table 4-1. Summary of the physical properties of the 130 porous media systems used to determine geometric tortuosity.

Group	ϕ (%)	D_{50} (μm)	I_R	I_{sph}	C_u	C_c	S (%)	# of systems	Image Size (voxels)	Image Resolution ($\mu\text{m}/\text{voxel}$)
1	45.8	525	0.77	1.76	1.51	1.08	72.0-100	4	1920×1920×1200	4.92
2	47.2	426	0.78	1.72	1.33	1.02	83.3-100	6		
3	46.6	421	0.78	1.70	1.31	1.03	83.1-100	5		
4	43.8	431	0.76	1.63	1.40	1.08	71.4-100	8		
5	50.4	368	0.76	1.48	1.39	1.06	67-100	9		
6	44.3	368	0.78	1.55	1.30	1.01	71.3-100	9		
7	45.6	392	0.70	1.31	1.57	1.12	59.4-100	12		
8	39.9	411	0.76	1.59	2.05	1.02	43.5-100	10		
9	39.5	443	0.76	1.58	2.36	1.10	34.7-100	10		
10	39.3	412	0.75	1.57	2.20	1.09	42.0-100	10		
11	35.0	626	0.86	1.71	2.76	1.03	74.7-100	4	400×400×400	11.22
12	34.0	602	0.87	1.70	2.66	1.00	39.8-100	6		
13	34.7	608	0.87	1.73	2.66	1.02	31.0-100	15		
14	35.2	596	0.88	1.72	1.46	1.11	13.5-100	9		
15	33.3	796	0.91	1.72	1.17	0.97	100	1	550×550×520	
16	35.6	511	0.87	1.64	1.26	0.98	100	1		
17	37.2	516	0.69	1.22	1.65	0.98	100	1		
18	33.2	539	0.87	1.58	1.37	0.98	100	1		
19	30.4	572	0.85	1.50	1.54	0.99	100	1		
20	36.5	652	0.89	1.58	1.23	0.99	100	1		
21	47.5	959	0.74	1.82	1.36	0.97	100	1		
22	48.3	618	0.69	1.29	1.60	0.90	100	1		
23	48.9	690	0.55	0.93	2.10	1.02	100	1		
24	45.8	673	0.71	1.35	1.82	0.90	100	1		
25	48.2	722	0.67	1.24	1.91	1.01	100	1		
26	43.5	776	0.74	1.54	1.39	0.96	100	1		
27	39.6	712	0.82	1.56	1.31	0.99	100	1		

Table 4-2. Results of the nonlinear regression model for geometric tortuosity.

Model: $\tau = \phi^{\beta_1} S^{\beta_2} C^{\beta_3} I_R^{\beta_4}$			
Coefficient	Estimate	Standard Error	p-value
β_1	-0.350	0.0140	<0.01
β_2	-0.435	0.0148	<0.01
β_3	0.538	0.1253	<0.01
β_4	-0.480	0.0531	<0.01

Appendix B: Figures

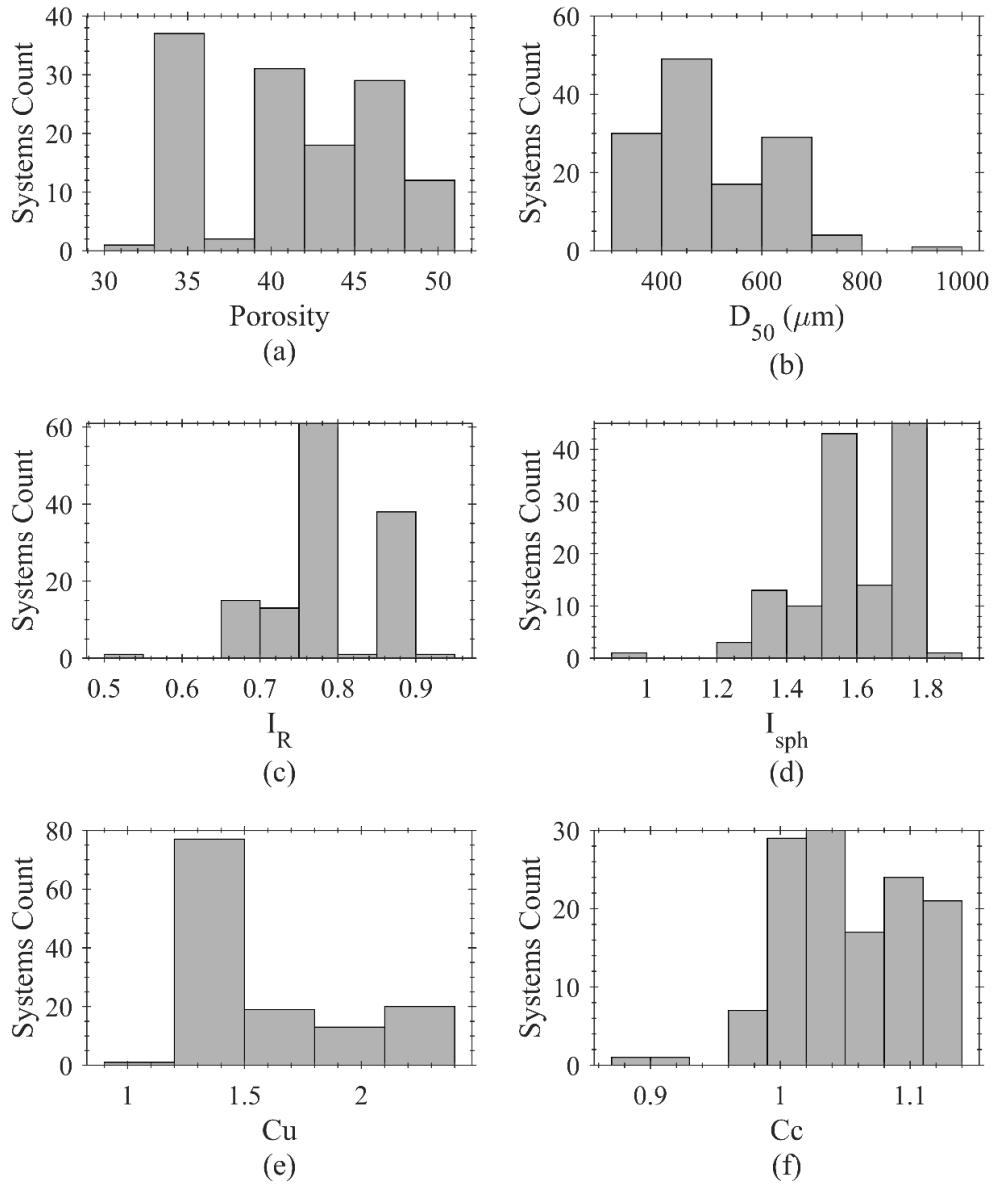


Figure 4-1. Histograms of (a) porosity; (b) median grain diameter; (c) roundness index; (d) sphericity index; (e) uniformity coefficient; and (f) coefficient of curvature of the 130 systems reported in this study.

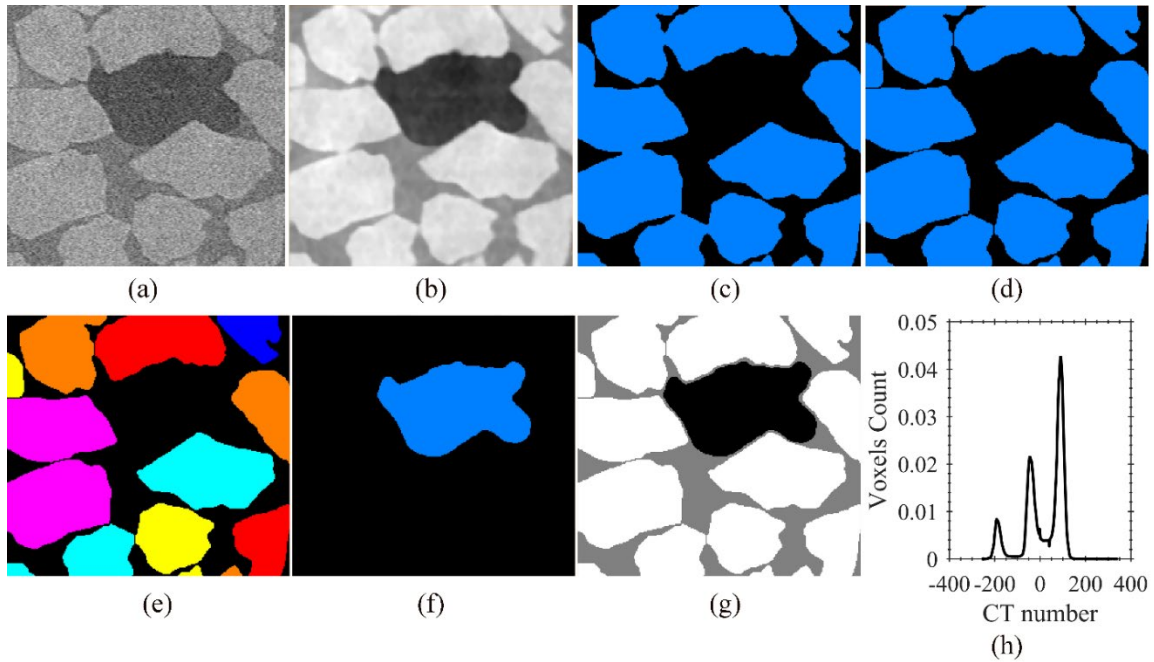


Figure 4-2. Image processing steps for on a zoomed view of an XY slice of one of the systems: (a) raw image; (b) filtered image; (c) binarized sand image; (d) binarized sand separated image; (e) sand labeled image; (f) binarized non wetting phase image; (g) three-phase segmented image, gas is black, water is gray, and sand is white; and (h) histogram of the filtered image.

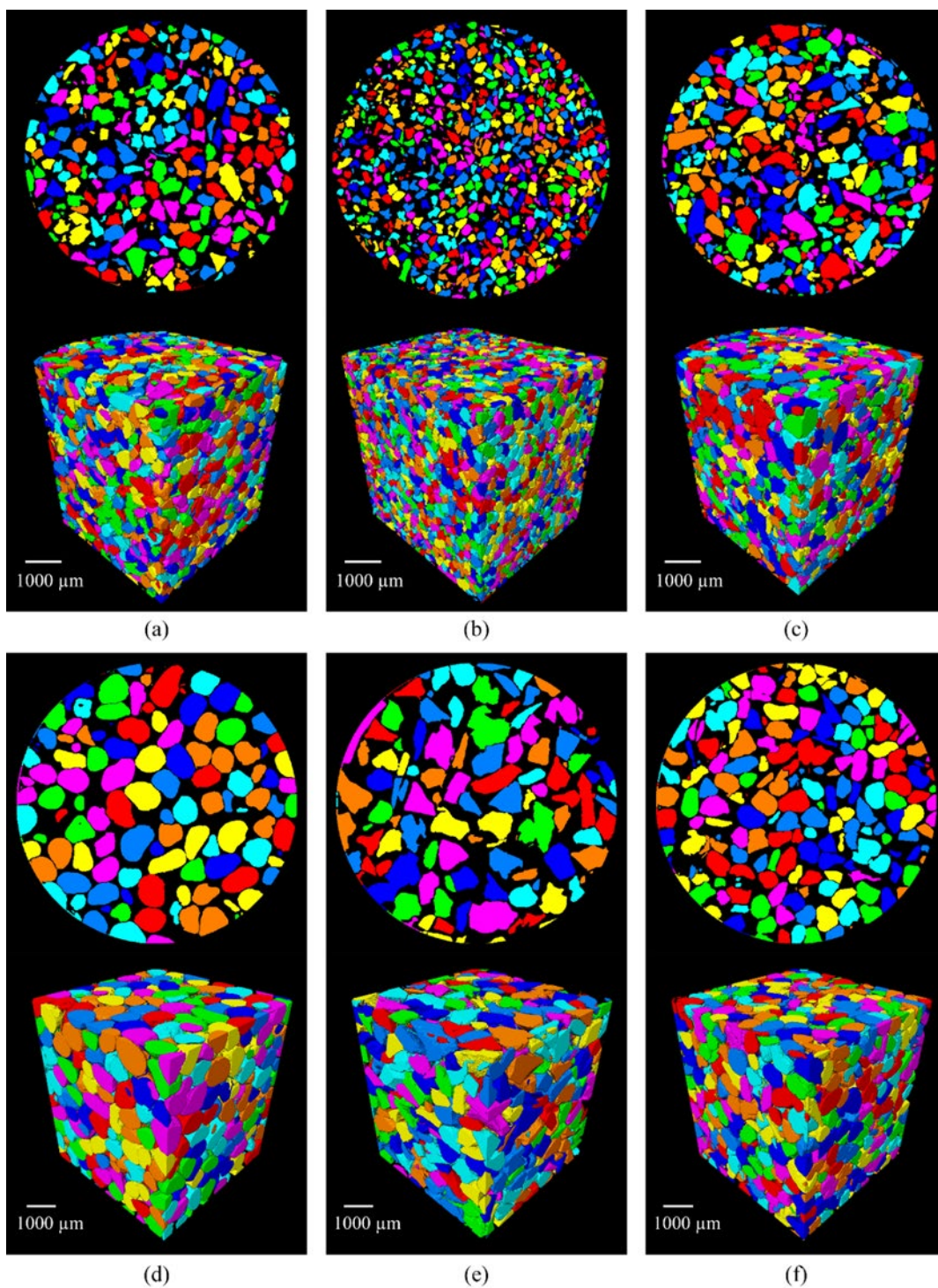


Figure 4-3. Sample 2D cross-section and volume rendering snapshots for selected labeled images from (a) Group 1; (b) group 5; (c) Group 8; (d) Group 118; (e) Group 21; and (f) Group 130.

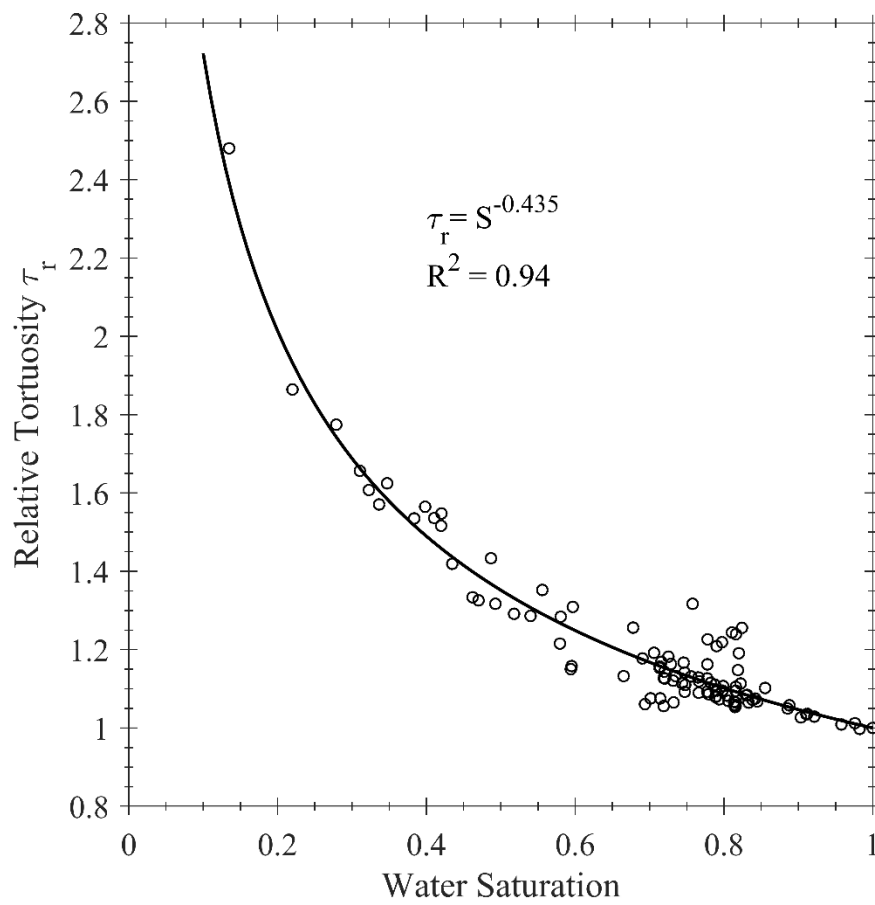


Figure 4-4. Change of relative tortuosity with degree of saturation for the 130 systems.

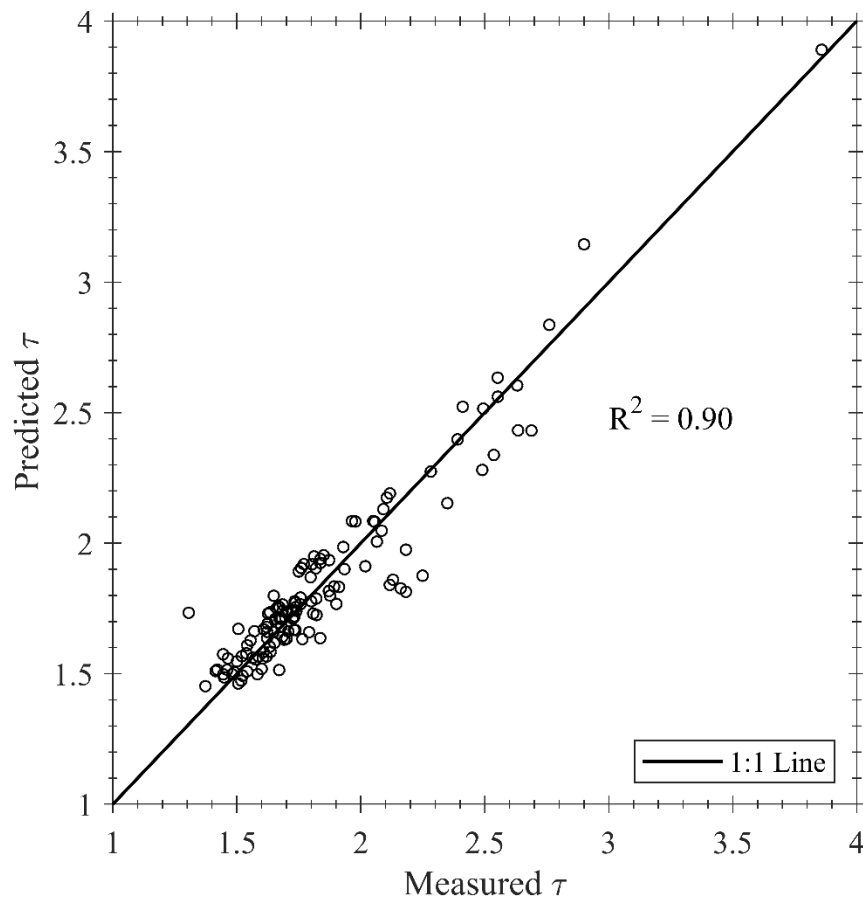


Figure 4-5. Measured geometric tortuosity from SMT images versus predicted geometric tortuosity estimated from Equation 4-12.

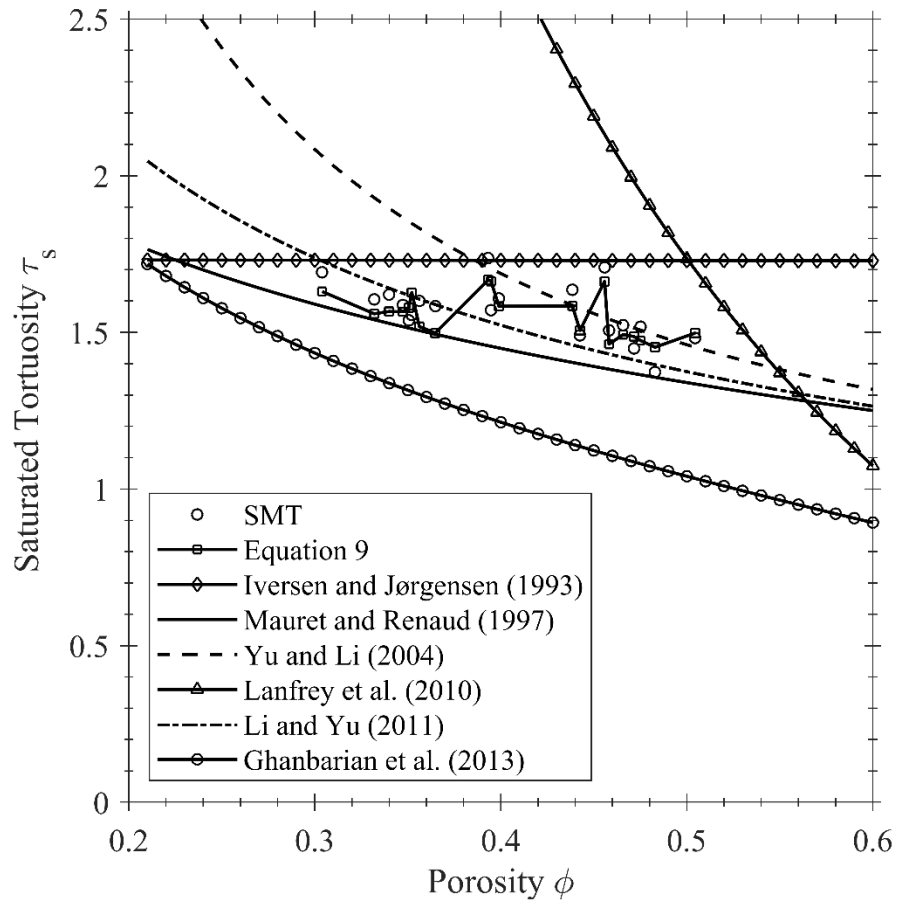


Figure 4-6. Comparison of the predicted saturated geometric tortuosity using the model in Equation 4-12 with analytical and theoretical models from the literature.

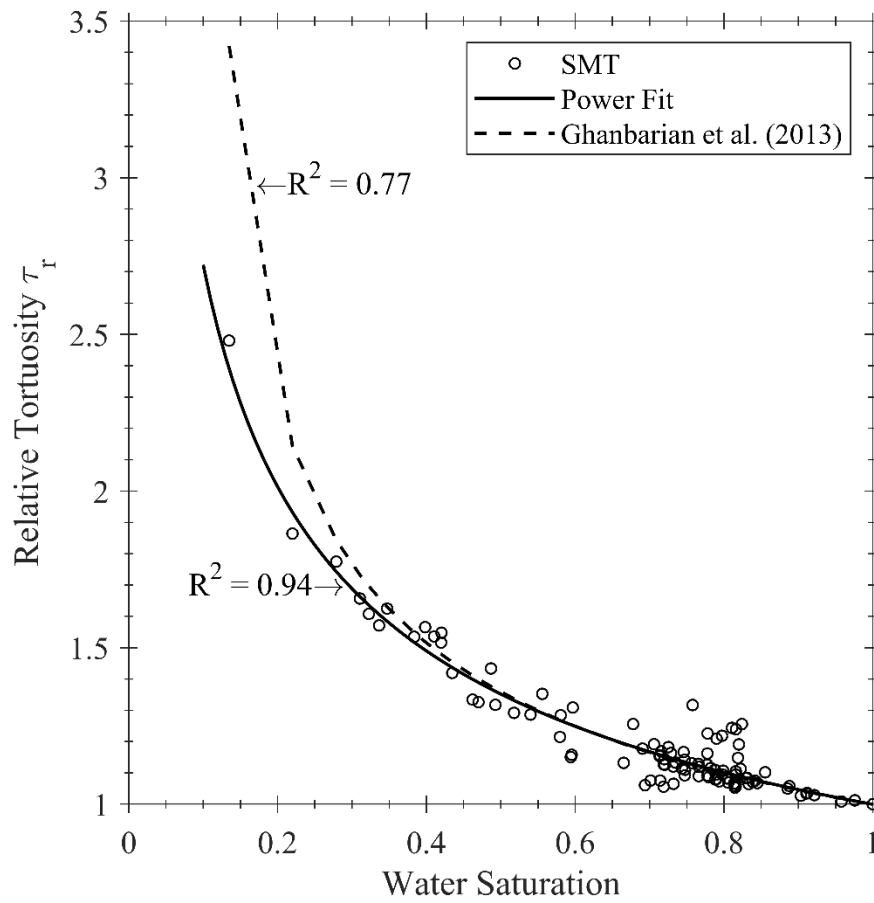


Figure 4-7. Comparison of the predicted relative tortuosity using the model in Equation 4-11 with the model proposed by (Ghanbarian et al. 2013).

CHAPTER FIVE
DISCRETE ELEMENT STUDY OF MORPHOLOGY EFFECTS ON
FRACTURE OF SINGLE SAND PARTICLES

A version of this chapter was submitted as a conference paper as Jarrar Z. A. & Alshibli K. A. (2018). Discrete Element Study of Morphology and Size Effects on Fracture of Single Sand Particles. *4th quadrennial international symposium organized under the auspices of Technical Committee 105 (Geo-Mechanics from Micro to Macro)*, Atlanta, GA, 10-13 September, 2018. (in press)

My contribution to this paper is developing all DEM simulations, analysis of DEM results, and preparing the original draft and all figures.

Abstract: The particulate nature of granular materials makes it essential to study the behavior of these distinct particles to gain a fundamental knowledge of the bulk material behavior and characteristics. Fracture of sand particles greatly influences the constitutive relationships and deformation characteristics of natural granular materials. Discrete Element Method (DEM) is a numerical method that has been widely used to model discontinuous materials. Although particles in DEM are typically modeled as rigid incompressible spheres, several approaches have been proposed in the literature to model fracture of sand particles. This paper presents the results of DEM simulations of unconfined 1D compression tests for 100 particles with various sizes and shapes. Single sand particles were modelled as agglomerates of spheres that are bonded together at their contacts using the linear parallel bond model. The agglomerates match the actual 3D shape of sand particles that were acquired from high resolution 3D Synchrotron Microcomputed Tomography (SMT) images. Effects of morphology (sphericity and roundness) on tensile strength are investigated based on calculated values of the model proposed by Hiramatsu and Oka (1966). Tensile strength values tend to increase as sphericity of agglomerates increases, while no specific trend is observed with variation of roundness. A modification of Hiramatsu and Oka (1966) model is proposed by normalizing stress with respect to sphericity index. The mean tensile strength of all agglomerates calculated from the proposed model is within 5% of the parallel bond strength used in DEM simulations

Keywords: Computed tomography, fracture of silica sand, bonded agglomerates, PFC3D

Introduction

The particulate nature of granular materials makes it essential to study the behavior of these discrete particles to gain a fundamental knowledge of the bulk material behavior and characteristics. Granular material behavior and fracture under loading have been extensively researched at the particle scale both experimentally and numerically (Cavarretta and O'sullivan 2012; Cil and Alshibli 2012; McDowell and Bolton 1998; Nakata 2005; Zhang et al. 2016; Zhao et al. 2015). Moreover, morphology of particles has a significant effect on the engineering properties of granular materials. Morphology is generally expressed in terms of surface texture (roughness), sphericity, and roundness.

Discrete Element Modeling (DEM) is a numerical method that gained a wide acceptance in modeling discontinuous materials. DEM algorithm was originally proposed by Cundall and Strack (1979) for geo-mechanics applications. The crushable behavior of particles using DEM can be represented using two common approaches. The first approach replaces a particle with a group of particles with different diameters when a fracture criterion is met under a predefined algorithm (Lobo-Guerrero et al. 2006; McDowell and de Bono 2013). The challenge in this approach lays in the definition of the state of stress at which crushing of particles will occur. In the second approach, particles are modeled as agglomerates consisting of a number of subspheres bonded together (Cil and Alshibli 2015; Hanley et al. 2011; McDowell and Harireche 2002; Moreno et al. 2003). This approach requires a high computational power if a full-size specimen is to be simulated. In this paper, results of DEM simulations of unconfined 1D compression tests for 100 particles with various sizes and shapes are presented. Single sand particles were modelled as agglomerates of spheres that are bonded together at their contacts using the linear parallel bond model. The agglomerates match the actual 3D shape of sand particles that were acquired from high resolution 3D Synchrotron Microcomputed Tomography (SMT) images. Effects of morphology (sphericity and roundness) on calculated values of tensile strength approximation are studied.

Morphology

This Alshibli et al. (2014) presented a study of the morphology of sand particles using high resolution 3D Synchrotron Microcomputed Tomography (SMT) images. In SMT imaging, high intensity beams are passed through a specimen that was positioned between a synchrotron radiation source and a detector. High resolution 3D images are obtained by scanning the specimens at different rotation stages. Moreover, they introduced two indices to quantify sphericity and roundness based those SMT images. The sphericity index (I_{sph}) was defined as:

$$I_{sph} = \frac{V_p}{V_s} \quad 5-1$$

where V_p is the volume of the particle; and V_s is the volume of the sphere with a diameter equal to the shortest diameter of the particle that passes through its center of mass. I_{sph} is equal to 1.0 as in the case of a spherical particle and in most cases has a value larger than 1.0. Moreover, the roundness index (I_R) was defined as:

$$I_R = \frac{A_p}{4\pi \left(\frac{d_L + d_I + d_S}{6} \right)^2} \quad 5-2$$

where A_p is the 3D surface area of the particle; d_L , d_I , and d_S are the longest, intermediate, and shortest diameter of the particle that passes through its center of mass, respectively. The denominator in Equation 5-2 represents the surface area of a sphere that has a diameter equals to the average of d_L , d_I , and d_S . These indices were adopted to quantify morphology of sand particles in this paper.

Discrete element modelling

Overview

DEM simulations were performed using the three dimensional particle flow code PFC3D V5.0 (Itasca Consulting Group 2014). Single sand particles were modelled as agglomerates of spheres that are bonded together at their contacts using the linear parallel bond model that can transmit both force and moment between the contacted spheres (Potyondy and Cundall 2004). Spheres with uniform size distribution were randomly generated within a spherical region, forming a “mother sphere” using the material modelling support in PFC (FistPkg) (Itasca Consulting Group 2014). The porosity of the mother sphere was chosen to be 0.35, which was shown by Potyondy and Cundall (2004) to produce a dense assembly. The ratio between the maximum and minimum radii of the sub-spheres was selected to be 1.2, and the minimum radius was 50 μm . The system was driven to a static equilibrium using the boundary-contraction procedure adapted from McDowell et al. (2006), which was implemented in the PFC material modelling support. Surface of sand particles were imported as STereoLithography (STL) file format, then positioned within the mother sphere and trimmed by removing spheres that are located within the mother sphere but outside the surface of the sand particle (Figure 5-1). This results in an agglomerate that matches the actual 3D shape of the sand particle.

Calibration

The experimental force-displacement curve obtained from a single particle crushing experiment of an ASTM 20-30 Ottawa sand particle was used to calibrate the micro properties of the linear parallel bond model. The experimental setup was the same as the one used by Druckrey and Alshibli (2016), where the sand particle is positioned between two loading plates and the top plate moves downward at a constant displacement rate. The two loading plates were modeled as two rigid walls, and the displacement rate of the top wall was selected to be slow enough to ensure a quasi-static loading condition. The surface of the calibrated particle was imported to the model, and the loading plates were positioned as per the SMT image. Figure 5-2 shows both the experimental and DEM force displacement curves, and Figure 5-3 presents fractured of the calibrated particle obtained from both SMT images (experimentally) and DEM model (agglomerate). Moreover, the micro parameters used in the DEM are summarized in Table 1.

Simulations and Stress Calculation

Single particle crushing simulations were conducted on 100 agglomerates with different shapes and sizes. The agglomerates represent the surfaces of actual 3D particles shapes acquired from SMT images. Sphericity and roundness histograms for the agglomerates are presented in Figure 5-4. All particles fractured under a major tensile splitting breaking the particle into multiple fragments. Hiramatsu and Oka (1966) provided theoretical solutions for the stress state within an elastic spherical body loaded diametrically. They also proposed that the tensile strength within a sphere (σ) can be approximated as:

$$\sigma = 0.9 \frac{F}{d_f^2}$$

5-3

where F is the load at failure and d_f is the distance between loading plates at failure. Although Equation 5-3 does not account for the shape of the body, it has been widely used as a rapid formula to approximate tensile strength within rock or sand (Hiramatsu and Oka 1966; Segall et al. 2007).

Results

Figure 5-5 shows a scatter plot of tensile strength of the DEM agglomerates that were calculate based on Equation 5-3 with I_{sph} (Figure 5-5a) and I_R (Figure 5-5b). For spherical agglomerates ($I_{sph} = I_R = 1$), values of tensile strength calculated from Equation 5-3 closely match the model input parameter for parallel bond strength of 230 MPa. Tensile strength values tend to increase as sphericity of agglomerates increases, while no specific trend is observed with variation of the roundness index. For agglomerates modeled in this study, the calculated tensile strength is expected to be around the parallel bond strength (230 MPa) regardless of agglomerate morphology. The variation observed in Figure 5-6 is because Equation 5-3 was derived for a spherical elastic body and does not account for morphology. Therefore, a new model for estimating the tensile strength of agglomerates is proposed by normalizing Equation 5-3 with respect to I_{sph} . Modified tensile strength (σ^*) can therefore be calculated as:

$$\sigma^* = 0.9 \frac{F}{I_{sph} d_f^2}$$

5-4

Figure 5-6 shows a scatter plot of tensile strength of the DEM agglomerates calculate based on Equation 5-4 with I_{sph} (Figure 5-5a) and I_R (Figure 5-5b). The scatter shown in Figure 5-6 closely match the parallel bond strength used in the model. Histograms of tensile strength distribution of DEM agglomerates calculated from Equation 5-3 and Equation 5-4 are shown in Figure 5-7. The mean value of tensile strength calculated from Equation 5-3 and Equation 5-4 are 313.3 MPa and 219.7 MPa, respectively. The mean tensile strength of all agglomerates calculated from Equation 5-3 differs from the parallel bond strength used in the model by 36%, while the mean of tensile strengths calculated from Equation 5-4 is within 5% of the parallel bond strength.

Conclusions

Results of DEM simulations of unconfined 1D compression tests for 100 particles with various shapes were presented in this study. Single sand particles were modelled as agglomerates of spheres that are bonded together at their contacts using the linear parallel bond model. The agglomerates match the actual 3D shape of sand particles that were acquired from high resolution 3D Synchrotron Microcomputed Tomography images. Tensile strength approximation of agglomerates were calculated using Hiramatsu and Oka (1966) model (Equation 5-3). For spherical agglomerates ($I_{sph} = I_R = 1$), values of tensile strength calculated from Equation 5-3 closely match the model input parameter for parallel bond strength. Tensile strength values tend to increase as sphericity of

agglomerates increases, while no specific trend is observed with variation of the roundness index. A modification of Equation 5-3 is proposed by normalizing stress calculated from Equation 5-3 with I_{sph} (Equation 5-4). The mean tensile strength of all agglomerates calculated from Equation 5-3 differs by 36% of the parallel bond strength used in the model, while the mean of tensile strengths calculated from Equation 5-4 is within 5% of the parallel bond strength.

Acknowledgments

The authors would like to thank Itasca Consulting Group for providing PFC3D license as part of the Itasca Educational Partnership academic program. The authors would also like to thank Dr. David Potyondy for his suggestions and valuable comments. This material is partially funded by the US National Science Foundation (NSF) under Grant No. CMMI-1362510. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the NSF.

References

- Alshibli, K. A., Druckrey, A. M., Al-Raoush, R. I., Weiskittel, T., and Lavrik, N. V. (2014). "Quantifying morphology of sands using 3D imaging." *Journal of Materials in Civil Engineering*, 27(10), 04014275.
- Cavarretta, I., and O'sullivan, C. (2012). "The mechanics of rigid irregular particles subject to uniaxial compression." *Geotechnique*, 62(8), 681-692.
- Cil, M., and Alshibli, K. (2012). "3D assessment of fracture of sand particles using discrete element method." *Géotechnique Lett*, 2(July–September), 161-166.
- Cil, M. B., and Alshibli, K. A. (2015). "Modeling the influence of particle morphology on the fracture behavior of silica sand using a 3D discrete element method." *Comptes Rendus Mécanique*, 343(2), 133-142.
- Cundall, P. A., and Strack, O. D. (1979). "A discrete numerical model for granular assemblies." *Geotechnique*, 29(1), 47-65.
- Hanley, K. J., O'Sullivan, C., Oliveira, J. C., Cronin, K., and Byrne, E. P. (2011). "Application of Taguchi methods to DEM calibration of bonded agglomerates." *Powder technology*, 210(3), 230-240.
- Hiramatsu, Y., and Oka, Y. "Determination of the tensile strength of rock by a compression test of an irregular test piece." *Proc., International Journal of Rock Mechanics and Mining Sciences & Geomechanics Abstracts*, Elsevier, 89-90.
- Itasca Consulting Group, I. 2014. Particle Flow Code, version 5.0, Minneapolis: Itasca.
- Lobo-Guerrero, S., Vallejo, L. E., and Vesga, L. F. (2006). "Visualization of crushing evolution in granular materials under compression using DEM." *International Journal of Geomechanics*, 6(3), 195-200.
- McDowell, G., and Bolton, M. (1998). "On the micromechanics of crushable aggregates." *Géotechnique*, 48(5), 667-679.
- McDowell, G., and Harireche, O. (2002). "Discrete element modelling of soil particle fracture." *GEOTECHNIQUE-LONDON*, 52(2), 131-136.
- McDowell, G., Harireche, O., Konietzky, H., Brown, S., and Thom, N. (2006). "Discrete element modelling of geogrid-reinforced aggregates." *Proceedings of the Institution of Civil Engineers-Geotechnical Engineering*, 159(1), 35-48.
- McDowell, G. R., and de Bono, J. P. (2013). "On the micro mechanics of one-dimensional normal compression." *Géotechnique*, 63(11), 895.
- Moreno, R., Ghadiri, M., and Antony, S. (2003). "Effect of the impact angle on the breakage of agglomerates: a numerical study using DEM." *Powder Technology*, 130(1), 132-137.
- Nakata, Y. "Macro and micro mechanical behaviour of crushable soil under compression." *Proc., Geomechanics: Testing, Modeling, and Simulation*, ASCE, 585-599.
- Potyondy, D., and Cundall, P. (2004). "A bonded-particle model for rock." *International journal of rock mechanics and mining sciences*, 41(8), 1329-1364.

- Segall, A. E., Scheetz, B. E., Shelleman, D. L., Hellmann, J. R., and Luscher, W. G. (2007). "A critical review of the diametral compression method for determining the tensile strength of spherical aggregates." *Journal of Testing and Evaluation*, 35(6), 1-6.
- Zhang, Y., Buscarera, G., and Einav, I. (2016). "Grain size dependence of yielding in granular soils interpreted using fracture mechanics, breakage mechanics and Weibull statistics." *Géotechnique*, 66(2), 149-160.
- Zhao, B., Wang, J., Coop, M., Viggiani, G., and Jiang, M. (2015). "An investigation of single sand particle fracture using X-ray micro-tomography." *Géotechnique*, 65(8), 625-641.

Appendices

Appendix A: Tables

Table 5-1. DEM model parameters.

Parameter	Value
Parallel bond group:	
Effective modulus (GPa)	70
Normal to shear stiffness ratio	2.0
Radius multiplier	1.0
Normal strength (MPa)	230
Shear strength (MPa)	230
Linear group:	
Effective modulus (GPa)	70
Normal to shear stiffness ratio	2.0
Friction	0.5

Appendix B: Figures

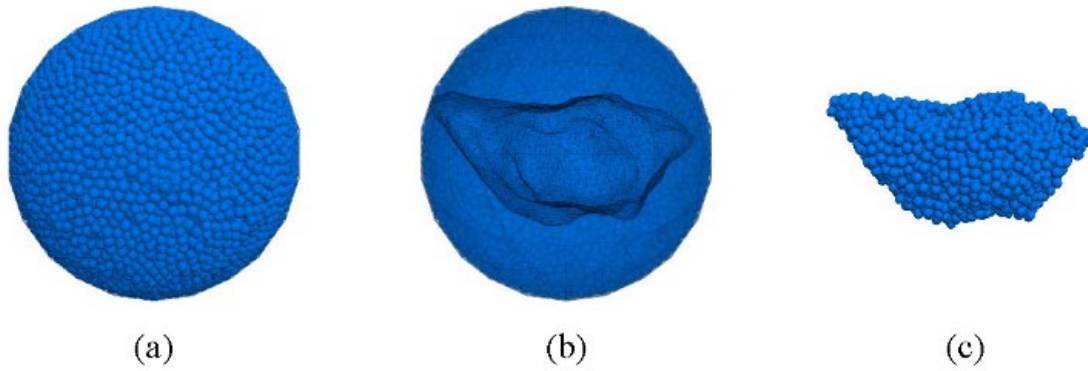


Figure 5-1. Agglomerate generation procedure: (a) Mother sphere; (b) the STL file positioned within the mother sphere.

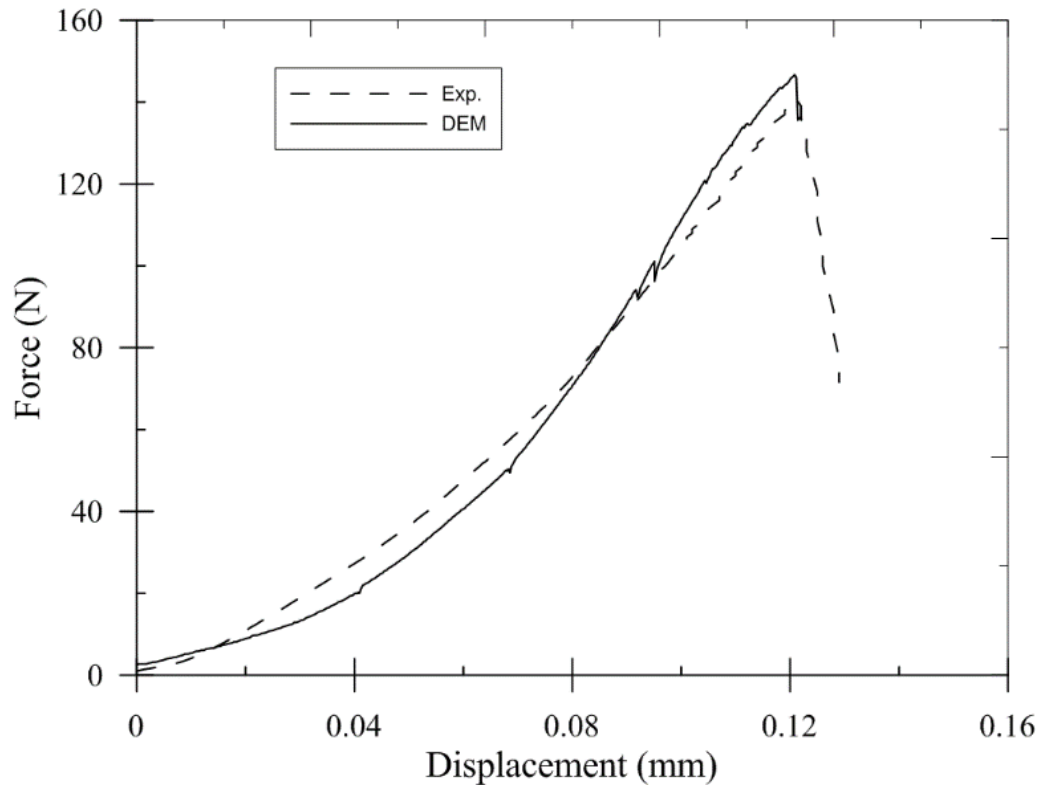


Figure 5-2. Experimental and DEM force-displacement curves for calibration of the DEM model.

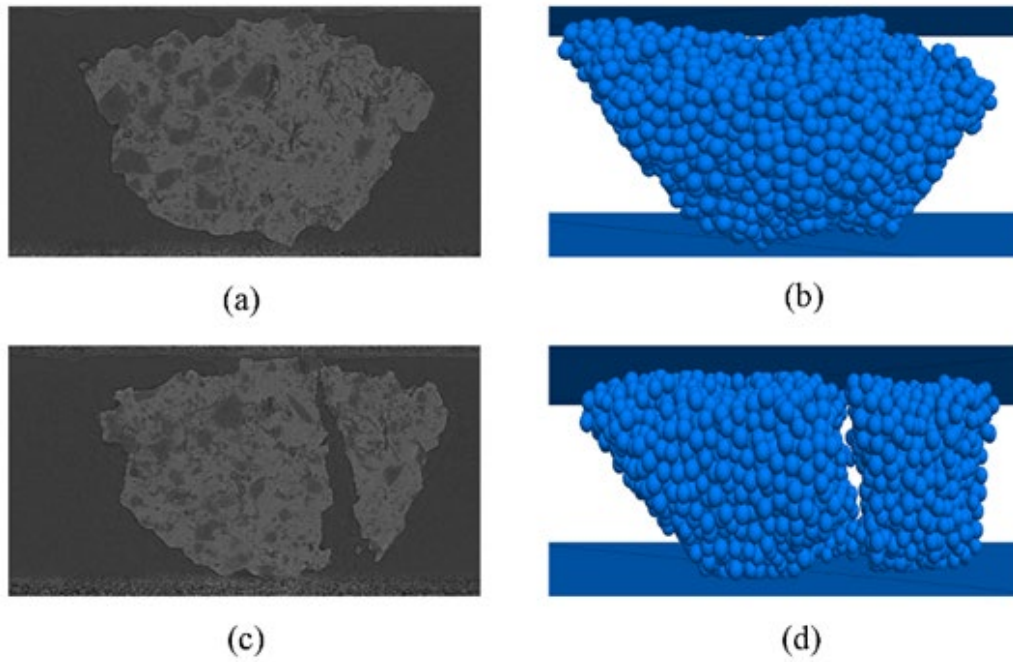


Figure 5-3. Visualization of fracture of the calibrated particle: (a) SMT image for the particle before loading; (b) SMT image for the fractured particle; (c) DEM agglomerate before loading; (d) DEM fractured agglomerate.

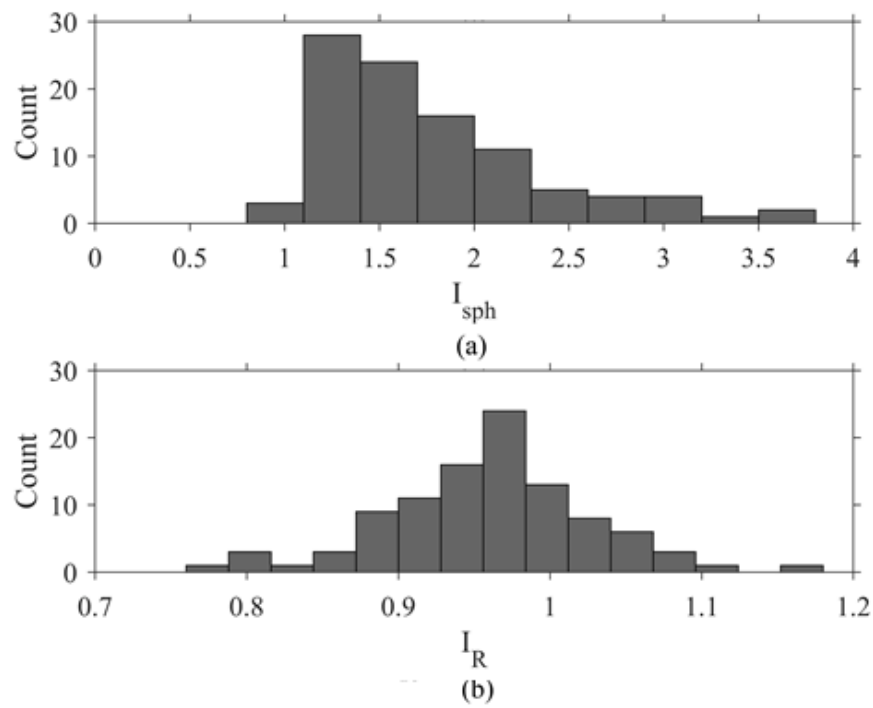


Figure 5-4. (a) Sphericity; and (b) roundness histograms for the simulated agglomerates.

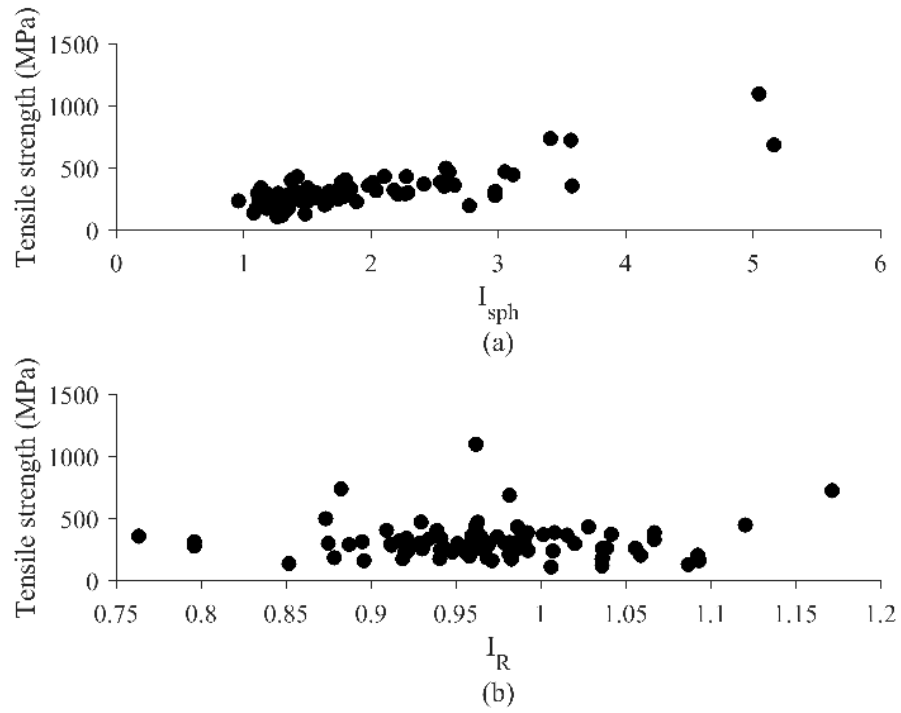


Figure 5-5. Tensile strength of DEM agglomerates calculated from Equation 5-3
vs. (a) I_{sph} ; and (b) I_R

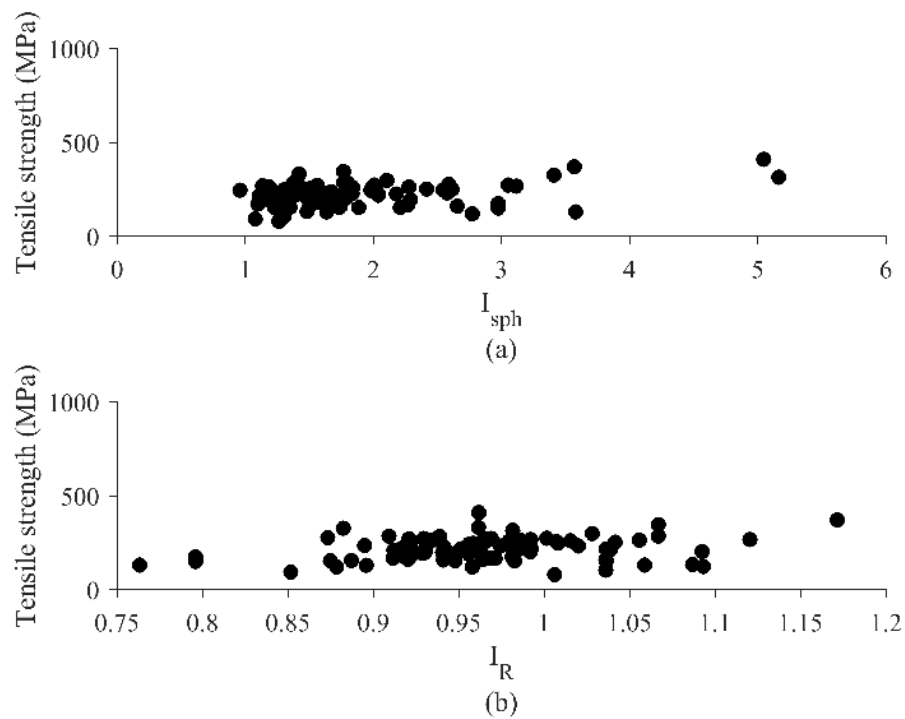


Figure 5-6. Tensile strength of DEM agglomerates calculated from Equation 5-4
vs. (a) I_{sph} ; and (b) I_R

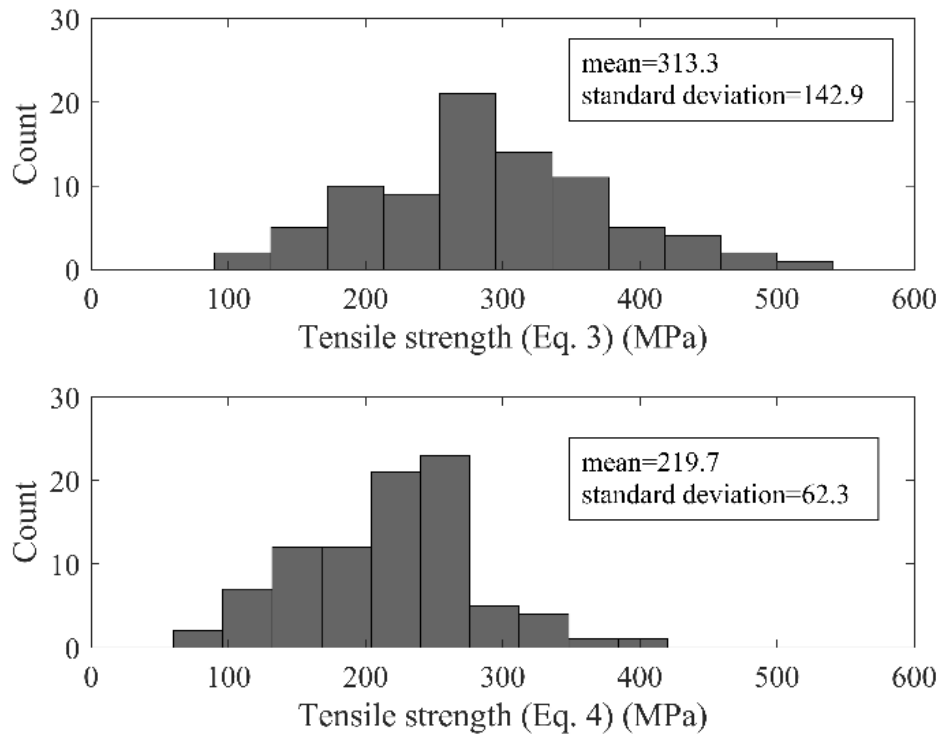


Figure 5-7. Histogram distribution of tensile strength of DEM agglomerates calculated from (a) Equation 5-3; and (b) Equation 5-4.

CHAPTER SIX

**3D EVALUATION OF SAND PARTICLE FRACTURE USING
DISCRETE ELEMENT METHOD AND SYNCHROTRON MICRO-
COMPUTED TOMOGRAPHY IMAGES**

A version of this chapter is published as Jarrar Z. A., Alshibli K. A., & Al-Raoush R. I., (2020). Three-Dimensional Evaluation of Sand Particle Fracture using Discrete Element Method and Synchrotron Micro-computed Tomography Images. *Journal of Geotechnical and Geoenvironmental Engineering*, 146, 06020007. [https://doi.org/10.1061/\(ASCE\)GT.1943-5606.0002281](https://doi.org/10.1061/(ASCE)GT.1943-5606.0002281)

My contribution to this paper is developing all DEM simulations, analysis of DEM results, and preparing the original draft and all figures.

Abstract: Recent research showed that fracture of sand particles plays a significant role in determining the plastic bulk volumetric changes of granular materials under different loading conditions. One of the major tools used to better understand the influence of particle fracture on the behavior of granular materials is Discrete Element Modeling (DEM). This paper employs the Bonded block model (BBM) to simulate the fracture behavior of sand. Each sand particle is modeled as an agglomerate of rigid blocks bonded at their contacts using the linear-parallel contact model that was developed by Potyondy and Cundall (2004), which can transmit both moment and force. DEM simulated particles closely matched the actual 3D shape of sand particles acquired using high resolution 3D Synchrotron Microcomputed Tomography (SMT). Results from unconfined 1D compression of a single synthetic silica cube were used to calibrate the model parameters. Particle fracture was investigated for specimens composed of three sand particles that were loaded under confined 1D compression. Breakage energy measured from DEM models were found to match well with those measured experimentally. The paper focuses on studying the effects of contact loading condition and particle interaction on fracture mode of particles using BBM that can closely capture 3D shape of real sand particles.

Keywords: Computed tomography, fracture of silica sand, bonded blocks model, PFC3D

Introduction

The fracture of sand particles plays a significant role in determining the plastic bulk volume changes of granular materials under different loading conditions. Particle breakage has been investigated using experimental, analytical, and numerical approaches at different scales ranging from a single particle to laboratory size specimens (Altuhafi and Coop 2011; Bolton et al. 2008; Cavarretta et al. 2017; McDowell et al. 1996; Nakata et al. 1999; Zhao et al. 2015). Discrete Element Modeling (DEM) has been widely used to better understand the influence of particle fracture on the behavior of granular materials. In the scope of DEM, particle fracture can be modeled using two common approaches. The first approach replaces a larger sphere with a group of smaller spheres with different diameters when a pre-defined fracture criterion is met (Lobo-Guerrero and Vallejo 2005;

Lobo-Guerrero et al. 2006; McDowell and de Bono 2015). This approach requires selection of a breakage criterion governed by a measured or assumed characteristic particle tensile stress. The second approach simulates a sand particle as an agglomerate of small spheres bonded together using an appropriate contact model. Examples of contact models include simple contact bond model (McDowell and Harireche 2002; Robertson and Bolton 2001), parallel bond model (BPM) (Bobet et al. 2009; Hanley et al. 2011; Potyondy and Cundall 2004; Tomac and Gutierrez 2017), and flat-joint contact bond model (FJM) (Potyondy 2012; Potyondy 2015; Wu and Xu 2016). To better capture the actual particle morphology and microstructure of sand particles, which have been shown experimentally and computationally to play a significant role in determining the macroscopic properties of granular materials (Alshibli and Cil 2018; Andrade et al. 2012; Cho et al. 2006; Ma et al. 2017), spheres in the second approach can be replaced with bonded polyhedral blocks (Galindo-Torres et al. 2012; Gao 2013; Nicksiar and Martin 2014). The bonded block model (BBM) has been widely used in recent years to investigate fracture and fragmentation process in rock (Mohammadnejad et al. 2018; Turichshev and Hadjigeorgiou 2017).

In this paper, BBM approach is used to investigate the fracture behavior of sand. Rigid blocks are used to generate zero-porosity agglomerates for a better representation of the actual morphology and microstructure of sand particles. The rigid blocks are bonded together at their contacts using the linear-parallel bond model that can transmit both moment and force (Potyondy and Cundall 2004). Each simulated particle matches the actual 3D shape of sand particles acquired from high resolution 3D Synchrotron Microcomputed Tomography (SMT). Model parameters for the current study were calibrated based on experimental data that were acquired from unconfined compression experiments conducted on synthetic silica cubes. The model was used to compare load-displacement and fracture behavior of sand obtained from 1D compression tests conducted on single sand particles and specimens composed of three sand particles.

Experimental Work

Unconfined 1D compression experiments were conducted on three 1 mm synthetic single crystal silica cubes (manufactured by MaTeck Company, Germany) and two particles of ASTM 20-30 Ottawa sand that were loaded separately. ASTM 20-30 is a natural silica sand that has rounded particles and a grain size between US sieve #20 (0.841 mm) and #30 (0.595 mm). In these experiments, each sand particle or cube was placed between two loading plates and the top plate moved downward at a constant displacement rate of 0.1 mm/minute ($1.7 \times 10^{-3} \text{ s}^{-1}$ global strain rate). The SMT scans were acquired at beamline 13D, Advanced Photon Source (APS), Argonne National Laboratory (ANL), Illinois, USA. Each sand particle or cube was scanned twice: initially before applying load and after fracture was observed. The acquired images have a spatial resolution of $1.98 \text{ } \mu\text{m}/\text{voxel}$. More information about the experimental setup can be found in Druckrey and Alshibli (2016). Additionally, three 1D compression experiments were conducted on sand columns

consisting of three particles. Sand particles were deposited into an acrylic cylindrical mold that has an inner diameter of 1 mm and were compressed at a constant displacement rate of 0.2 mm/minute ($7.2 \times 10^{-4} \text{ s}^{-1}$ global strain rate). All experiments presented in this study were performed under a strain rate less than 0.01/s which is within quasi-static loading condition for dry sand (Song et al. 2009). Multiple in situ SMT images were acquired at an energy level of 23 keV to produce images with a spatial resolution of $4.95 \text{ } \mu\text{m}/\text{voxel}$. Each sand column was scanned multiple times including the initial state before loading, during loading, and a final scan after the onset of fracture. More information about this setup can be found in Cil and Alshibli (2012).

Image Analysis

Acquired SMT scans were processed, enhanced and segmented using Avizo 9.7 software (FEI 2018). First, anisotropic diffusion filter was applied to the grayscale images to reduce noise and enhance edges contrast (FEI 2018). Then, filtered images were subtracted from unfiltered images to verify that filtering did not affect the spatial position of particles' edges. Filtered images were then binarized using interactive thresholding module where user-defined values of image intensity ranges were input to binarize the images. Sand voxels were assigned a value of 1 and air voxels were assigned a value of 0. Particles were then separated using the Separate Objects module in Avizo software, and each particle was assigned a distinct numerical label. The Separate Objects module is a combination of watershed, distance transform, and numerical reconstruction algorithms that accurately remove small area of contact between particles (FEI 2018). More details about segmentation procedure can be found in Druckrey et al. (2016). High resolution 3D surfaces were constructed using the marching cube algorithm (Lorensen and Cline 1987) that produces a triangular approximation of the interface by computing iso-surfaces from discrete data.

Modeling Approach

DEM simulations were conducted using the particle flow code PFC3D 6.0 (Itasca 2018), which can model polyhedral objects with triangular facets (rigid blocks). In PFC3D, the full inertia tensor of rigid blocks is used to update the rotational equations of motion. The overlap state of rigid blocks is determined using the Gilbert–Johnson–Keerthi (GJK) algorithm (Gilbert et al. 1988) which adopts the concept of the Minkowski difference to efficiently detect the overlap status of convex shapes (Itasca 2018). A set of rigid blocks can be constructed to fill a volume or set of volumes with a specified minimum and maximum edge length. To simulate a sand particle, rigid blocks were constructed by meshing the 3D surfaces extracted from SMT images. The fracture behavior of the sand was introduced by cementing the rigid blocks together at their contacts using the linear-parallel bond model that can transmit both moment and force (Potyondy and Cundall 2004). This results in a crushable agglomerate of rigid blocks that closely matches the shape of an actual sand particle.

In the linear-parallel bond model, two interfaces work in parallel: a linear elastic frictional interface and a finite-size linear elastic bonded interface that carries force and moment (Itasca 2018). Slip is introduced in the linear elastic interface by imposing a Coulomb limit on the shear force. Since the two interfaces work in parallel, the existence of parallel bond does not prevent slip. In PFC3D, the following parameters are used to define a parallel bond: parallel bond normal strength (σ^n), parallel bond shear strength (τ), parallel bond normal stiffness ($\bar{k}^n$), parallel bond shear stiffness ($\bar{k}^s$), contact normal stiffness (k^n), contact shear stiffness (k^s), parallel bond radius multiplier (λ), and inter-particle friction coefficient (μ). The bond can be pictured as a cylindrical cementing glue composed of a set of elastic springs distributed over a circular cross-section on the contact plane with a beam length ($\bar{L}$) approaching zero (Figure 6-1) (Potyondy and Cundall 2004). The bond breaks when tensile or shear stress exceeds the specified strength parameters. The size of the bond is controlled through λ by:

$$\bar{R} = \lambda R^* \quad 6-1$$

where $\bar{R}$ is the bond radius, R^* is the equivalent radius of a circle with an area equal to the contact area. The contact area is calculated as the overlapped volume between the blocks in contact divided by the penetration depth. The penetration depth is the minimum distance that the blocks in contact must be displaced along the contact normal to no longer penetrate (Itasca 2018). In this study, parallel bond effective modulus ($\bar{E}$) is used to set the value of $\bar{k}^n$ as:

$$\bar{k}^n = \frac{\bar{E}}{(R_1 + R_2)} \quad 6-2$$

where R_1 and R_2 are the radii of the minimal enclosing spheres of the blocks in contact (Figure 6-1).

Results from unconfined 1D compression tests on 1 mm synthetic silica cubes composed of a single silica crystal were used to calibrate the linear-parallel model parameters. The cube was selected due to its simple geometry which eliminates the effects particle shape and morphology at contacts. 6600 rigid blocks with a maximum edge length of 100 μm were constructed within a $(1000 \mu\text{m})^3$ cubical volume to simulate the silica cube (Figure 6-2a). The system was then cycled under gravity to ensure that the rigid blocks are in contact with the bottom loading plate and were permitted to reach equilibrium. Loading plates were modeled as rigid walls, and the loading rate was selected slow enough to ensure a quasi-static loading condition in which no change in force-displacement behavior was detected with further reduction of loading plate speed. The corresponding loading rate was found to be 0.035 m/sec.

The influence of varying the model parameters on the force-displacement behavior are presented in Figure 6-3. Changing the bond strength affects the peak load without changing the stiffness (Figure 6-3a). Alternatively, increasing the ratio between normal and shear stiffness (κ) decreases the overall stiffness and increases the peak load (Figure 6-3b). Changing the bond effective modulus changes the stiffness without changing the peak load (Figure 6-3c). Increasing the

friction coefficient and radius multiplier results in increasing the stiffness and peak load as can be seen from Figure 6-3d and Figure 6-3e.

Model Calibration

Since the DEM parameters have combined effects, calibration of the model requires conducting multiple simulations to closely match the force-displacement behavior observed in the experiments. A total of seventeen simulations were performed to identify the appropriate calibration parameters listed in Table 6-1. First, the stiffness of the contacts between the loading plate and the blocks (k) was selected by matching the stiffness measured from unconfined 1D compression on a single-block cube with the stiffness measured experimentally. Figure 6-3f displays the variation of the model results with different values of contact stiffness. The initial ductile experimental response was not matched because it is mainly attributed to deformation of micro-asperities and elastic deformation at contacts (Antonyuk et al. 2005; Cavarretta et al. 2017), which are not accounted for in the rigid blocks DEM model. Consequently, the cube used in the parametric study simulations presented earlier was used to obtain the calibrated values of the remaining parameters. Parallel bond effective modulus was chosen to be 70 GPa based on the silica cube effective modulus value reported by the manufacturer (MaTeck 2019). Parallel bond normal and shear strength were assumed equal to allow normal and shear bond failure. A flow chart of the calibration procedure is depicted in Figure 6-4. Fragmentation at corners and edges of the cube after peak load were observed in both SMT images and DEM model Figure 6-2a presents images obtained from SMT and DEM simulations, where fragmentation at corners and edges after peak load were observed in both SMT images and DEM model. Figure 6-2c shows the force versus compressive displacement curves for the experiment and the model. Table 6-2 presents the difference in stiffness, peak load, and displacement at peak load measured from the experiments and simulations. Peak load obtained numerically is within 2.2% of that measured experimentally. The difference in the displacement at peak load is 10.9%, while the difference in the average stiffness is 0.8%.

After identifying the model parameters, simulations of unconfined 1D compression test on two ASTM 20-30 Ottawa sand particles were conducted using the same model parameters. The SMT images representing 3D surface of the sand particle were imported to PFC3D, and rigid blocks were constructed within that surface, similar to the procedure followed when modeling the cube. Similar to the cube results, the peak load predicted by the DEM model is very close to the experimental measurement (4.4% difference) (Table 6-2). However, the model did not show good prediction of the average stiffness and displacement at peak load. The stiffness obtained from the DEM model was 85% higher than the stiffness measured experimentally. The reduction in stiffness is attributed to effects of surface roughness and asperity interaction. Otsubo et al. (2015) used bender elements to study the effects of surface roughness on the stiffness on borosilicate ballotini spheres and reported that surface roughness caused a reduction in small-

strain stiffness at low confining pressure. This effect diminishes as confining pressure increases. The surface roughness effects are not captured in the current DEM model; therefore, the model failed to predict the stiffness of unconfined 1D compression test on single sand particles.

Additionally, three 1D confined compression experiments of columns of three ASTM 20-30 Ottawa sand particles were simulated. A higher number of particles and contact points and the introduced mold confinement increases the possibilities of fractured particles. In order to model these experiments, each rigid block that was in contact with another block from a different sand particle was assigned a linear model. Surrounding acrylic mold was modeled as a frictionless rigid wall positioned to match the SMT images. A linear model with the same properties as the linear group mentioned in Table 6-1 was assigned to these contacts. The sensitivity of the model to the number of rigid blocks used to simulate particles was investigated first by generating different surfaces with different number of faces (triangles on the surface). A higher number of faces yields a better representation of sand surface morphology. Each surface was then imported to PFC3D and 1D compression simulations were conducted. Figure 6-5 presents the variation of peak load from the DEM simulations with different rigid blocks sizes which shows that the peak load tends to approach a constant value when block edge length is less than 60 μm . Thus, block edge length (element size) was selected to be 60 μm (8% of sand particle length) to run subsequent DEM simulations.

Although the model did not predict the stiffness from unconfined 1D compression test on single sand particle well (in terms of stiffness and displacement at peak load), the model did a better job in predicting the behavior of 1D confined compression of three sand particle columns experiments. Similarly, Cil and Alshibli (2014) reported that calibrating the linear-parallel model parameters based on unconfined 1D compression test of a single sand particle underestimates the stress-strain behavior of laboratory-size specimens, where sand particles are modeled using agglomerates of bonded sub-spheres (BSM). This is attributed to effects of surface roughness and asperity interaction. Otsubo and O'Sullivan (2018) conducted experimental and numerical assessment on the effects of surface roughness on small-strain stiffness and reported that at low confining pressure, the overall response of soil samples is governed by asperity interaction. Moreover, they reported that the sensitivity of small-strain stiffness to surface roughness decreases with higher confining pressure. In this study, the introduced confinement in the three sand particle columns experiments minimized the effects of surface roughness on the stiffness and overall behavior and were predicted well in the DEM model. This highlights the advantage of selecting the silica cube geometry in calibrating the model instead of the actual sand particle to eliminate the effects of surface roughness and improve the model prediction with higher confinement.

Fracture of Three-Particle Sand Specimens

To demonstrate the need to capture the actual morphology of sand particles, the three-particle 1D compression experiments were modeled twice, once with agglomerates representing the actual shape of particles and once with equivalent spherical agglomerates. An equivalent sphere is defined here as a sphere that has the same volume as the particle. SMT and DEM images along with force-displacement curves measured experimentally and based on DEM models are depicted in Figure 6-6. For the first test (Figure 6-6a), the bottom particle was the first one to fracture both experimentally and in BBM. This observation is supported by the model proposed by Hiramatsu and Oka (1966) for the maximum tensile stress within a sphere loaded diametrically (σ):

$$\sigma = 0.9 \frac{F}{d_f^2} \quad 6-3$$

where F is the load at failure and d_f is the distance between loading plates at failure. If we define loading distance (d^*) as the average vertical distance between the upper and lower contacts (either particle-to-particle or particle-to-plate), equation 6-3 can be used to explain why the bottom particle was the first one to fracture, since it has the smallest loading distance among the three particles (Figure 6-7a), thus the highest maximum tensile stress. Extensive fragmentation is observed from SMT images to take place in the middle region of the bottom particle, between the upper contact area (with the middle particle) and the lower contact area (with the loading plate). A similar pattern is observed in BBM where fragments are shown in different colors. Moreover, the load versus compressive displacement behavior measured experimentally matches that obtained from real-shape agglomerate very closely (Figure 6-6a). The difference in peak load was 8.2% and the difference in displacement at peak load was 4.3% (Table 6-3). On the other hand, the DEM model using equivalent spheres exhibited a higher peak load than the experiment and very different fracture patterns. Figure 6-6a also presents an image of a DEM simulation using BSM reported by Cil and Alshibli (2015). Figure 6-6a manifests how rigid blocks agglomerates better match the shape, fracture pattern, and fragmentation of sand particles when compared to agglomerates composed of a large number of sub-spheres. Additionally, rigid blocks better match the surface contact between the agglomerates and loading plate, which was shown by Cil and Alshibli (2015) to greatly affect the load corresponding to failure.

For the second test (Figure 6-6b), the top particle was the first particle to fracture experimentally with multiple major cracks between the upper and lower contact areas. In BBM, the top particle was also observed to fracture with a similar fracture pattern. The peak load in BBM was within 1.5% difference of that in the experiment. It can be observed from Figure 6-7b that the top particle has the lowest number of total contact points. The low number of contact points resulted in a higher concentration of stresses, which caused the particle to fracture even though it has the highest diametric loading distance among the three particles. Similar to test1,

equivalent spheres had a higher peak load compared to the real-shape agglomerates and experimental measurements. The top particle was the first to fracture in the equivalent spherical agglomerates, but the fracture pattern in the model could not be compared with the experimental one due to the different morphology. On the other hand, BSM predicted a higher peak load and displacement, and the first particle to fracture was the middle particle, which deviates from the experimental observations and BBM results.

For the third test, it was revealed from SMT images that the middle particle penetrated the surrounding acrylic mold wall (red circle in Figure 6-6c). This introduced fixity to that particle made it susceptible to higher stresses causing it to fracture first. This experimental flaw was not observed in the other two experiments. The fixity was introduced in the DEM models by constraining the blocks in the regions that are shown to penetrate the surrounding wall in SMT images. The first particle to fracture was the middle one in both experiment and BBM, the bottom one in BSM, and the top one in the equivalent spherical BBM. Both BSM and equivalent spherical BBM underestimated the peak load and the displacement at peak load. However, BBM predicted peak load well with a difference of only 4.5% of the experiment. Moreover, the displacement at peak measured from BBM was within 16.2% of the displacement obtained from the experiment.

Breakage Energy

Breakage energy refers to the energy dissipation caused by the creation of new surfaces during fracture. Breakage energy can be calculated as the ratio of the incremental input energy to the incremental change in surface area obtained from in situ SMT images (Landis et al. 2003; Zhao et al. 2015). The change in surface area of particles and fragments was measured directly from SMT images, while input energy is usually assumed to be equal to the work calculated from the force-displacement curve. However, the input energy dissipates not only through breakage, but also through other mechanisms such as friction and slip between particles and loading plates. DEM is a useful tool that can be used to track and monitor energy dissipation through such mechanisms, which cannot be measured experimentally (Afshar et al. 2017; Wang et al. 2012). In this study, breakage energy was calculated for the three-particle DEM models and compared with the ones measured experimentally. To get an accurate estimation of the breakage energy, slip dissipation was subtracted from the work done by the load, the same approach was also followed by (Afshar et al. 2017). Energy dissipating through slippage was found to range between 25% to 35% of the total work done by the external load. This is significantly lower than the 70% reported by Afshar et al. (2017) for 1D compression of an assembly of agglomerates made of spheres. In the DEM models, change in surface area due to fracturing was measured by tracking the broken bonds between the rigid blocks. When a bond breaks, the connected rigid blocks are separated and new surfaces are generated.

Figure 6-8 shows the change of the net work of load with the cumulative change in fracture surface area for the three-particle tests measured experimentally and using DEM. In Figure 6-8, the energy dissipated due to slip was obtained from the BBM and was then subtracted from the total input energy for both experiments and BBM to find the net work of load. Values of breakage energy were calculated as the slope of each curve in Figure 6-8 and were reported in Table 6-4. Experimental breakage energy ranged from 90.3 N/m to 605.6 N/m. Breakage energies measured from BBM match well with breakage energies measured experimentally (within 15% difference). Table 6-4 presents the total number block contacts with another block from a different sand particle for each test. For the first and second test, the energy required to initiate fracture in sand particles increases as the number of contact points increases. Therefore, more energy is required to fragment particles with higher number of contact points. Hence, under the same conditions of input energy (or compressive stress), particles with lower number of contacts are expected to fracture easier. The relatively higher value of breakage energy for the third test, however, is mainly attributed to the experimental flaw mentioned earlier where the middle particle penetrated the surrounding acrylic mold which was modeled as fixity in BBM. Therefore, a major part of the input energy was dissipated through this process.

Conclusions

The BBM approach was used to investigate the fracture behavior of sand. Each sand particle was modeled as an agglomerate of rigid blocks bonded together at their contacts using the linear-parallel contact model. This approach provides improvement in capturing the actual shape of sand particles by utilizing high resolution imaging techniques such as SMT. Agglomerates micro models were calibrated based on results from unconfined 1D compression of a single silica cube. The selection of silica cube in calibrating the model in lieu of the actual sand particle eliminates the effects of surface roughness and improves the model prediction with a higher confinement. The results demonstrated how ignoring morphology by modeling sand particles as idealized spheres fail to simulate the fracture behavior of silica sand. Investigation of particle fracture in the three-particle sand specimens revealed that contact loading condition, number of contact points, and particle geometry interaction have significant effects on fracture pattern of particles. An increase in number of contacts increases the required stress to fracture a particle. For particles with similar number of contact points, first particles to fracture are those with the smallest loading distance. Energy dissipating through slippage was found to range between 25% to 35% of the total work input by the external load, and thus should be considered when estimating breakage energy. Breakage energy measured from the DEM models matched well with the breakage energy measured based on SMT images. Breakage energy results suggest that more fragmentation is expected for an assembly of particles with a smaller number of contact points under the same state of compressive stress. Finally, the BBM approach was proven to successfully predict load-displacement behavior,

fractured particles, fracture pattern, and energy released due to crack initiation by direct comparison with SMT images.

Acknowledgments

This material is partially funded by the US National Science Foundation (NSF) under Grant No. CMMI-1362510. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the NSF. The authors would like to thank Dr. Mehmet Cil for conducting sand-columns experiments, and Dr. Andrew Druckrey for conducting cube fracture experiments. The SMT images were collected using the X-ray Operations and Research Beamline Station 13-BMD at Argonne Photon Source (APS), Argonne National Laboratory. The authors thank Dr. Mark Rivers of APS for help in performing the SMT scans. They also acknowledge the support of GeoSoilEnviroCARS (Sector 13), which is supported by the National Science Foundation, Earth Sciences (EAR-1128799), and the US Department of Energy (DOE), Geosciences (DE-FG02-94ER14466). Use of the Advanced Photon Source, an Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory, was supported by DOE under contract no. DE-AC02-06CH11357. The authors would also like to thank the anonymous reviewers who contributed with comments and suggestions to improve this paper.

References

- Afshar, T., Disfani, M. M., Arulrajah, A., Narsilio, G. A., and Emam, S. (2017). "Impact of particle shape on breakage of recycled construction and demolition aggregates." *Powder Technology*, 308, 1-12.
- Alshibli, K. A., and Cil, M. B. (2018). "Influence of Particle Morphology on the Friction and Dilatancy of Sand." *Journal of Geotechnical and Geoenvironmental Engineering*, 144(3), 04017118.
- Altuhafi, F., and Coop, M. R. (2011). "Changes to particle characteristics associated with the compression of sands." *Géotechnique*, 61(6), 459.
- Andrade, J. E., Lim, K.-W., Avila, C. F., and Vlahinić, I. (2012). "Granular element method for computational particle mechanics." *Computer Methods in Applied Mechanics and Engineering*, 241-244, 262-274.
- Antonyuk, S., Tomas, J., Heinrich, S., and Mörl, L. (2005). "Breakage behaviour of spherical granulates by compression." *Chemical Engineering Science*, 60(14), 4031-4044.
- Bobet, A., Fakhimi, A., Johnson, S., Morris, J., Tonon, F., and Yeung, M. R. (2009). "Numerical Models in Discontinuous Media: Review of Advances for Rock Mechanics Applications." *Journal of Geotechnical and Geoenvironmental Engineering*, 135(11), 1547-1561.
- Bolton, M., Nakata, Y., and Cheng, Y. (2008). "Micro-and macro-mechanical behaviour of DEM crushable materials." *Géotechnique*, 58(6), 471-480.
- Cavarretta, I., O'Sullivan, C., and Coop, M. R. (2017). "The relevance of roundness to the crushing strength of granular materials." *Géotechnique*, 67(4), 301-312.
- Cho, G.-C., Dodds, J., and Santamarina, J. C. (2006). "Particle Shape Effects on Packing Density, Stiffness, and Strength: Natural and Crushed Sands." *Journal of Geotechnical and Geoenvironmental Engineering*, 132(5), 591-602.
- Cil, M., and Alshibli, K. (2012). "3D assessment of fracture of sand particles using discrete element method." *Géotechnique Letters*, 2(3), 161-166.
- Cil, M. B., and Alshibli, K. A. (2014). "3D evolution of sand fracture under 1D compression." *Géotechnique*, 64(5), 351.
- Cil, M. B., and Alshibli, K. A. (2015). "Modeling the influence of particle morphology on the fracture behavior of silica sand using a 3D discrete element method." *Comptes Rendus Mécanique*, 343(2), 133-142.
- Druckrey, A. M., and Alshibli, K. A. (2016). "3D finite element modeling of sand particle fracture based on in situ X-Ray synchrotron imaging." *International Journal for Numerical and Analytical Methods in Geomechanics*, 40(1), 105-116.
- Druckrey, A. M., Alshibli, K. A., and Al-Raoush, R. I. (2016). "3D characterization of sand particle-to-particle contact and morphology." *Computers and Geotechnics*, 74, 26-35.
- FEI. 2018. Avizo, version 9.7FEI, Hillsboro, OR.

- Galindo-Torres, S. A., Pedroso, D. M., Williams, D. J., and Li, L. (2012). "Breaking processes in three-dimensional bonded granular materials with general shapes." *Computer Physics Communications*, 183(2), 266-277.
- Gao, F. (2013). "Simulation of failure mechanisms around underground coal mine openings using discrete element modelling."
- Gilbert, E. G., Johnson, D. W., and Keerthi, S. S. (1988). "A fast procedure for computing the distance between complex objects in three-dimensional space." *IEEE Journal on Robotics and Automation*, 4(2), 193-203.
- Hanley, K. J., O'Sullivan, C., Oliveira, J. C., Cronin, K., and Byrne, E. P. (2011). "Application of Taguchi methods to DEM calibration of bonded agglomerates." *Powder technology*, 210(3), 230-240.
- Hiramatsu, Y., and Oka, Y. (1966). "Determination of the tensile strength of rock by a compression test of an irregular test piece." *International Journal of Rock Mechanics and Mining Sciences & Geomechanics Abstracts*, 3(2), 89-90.
- Landis, E. N., Nagy, E. N., and Keane, D. T. (2003). "Microstructure and fracture in three dimensions." *Engineering Fracture Mechanics*, 70(7), 911-925.
- Lobo-Guerrero, S., and Vallejo, L. E. (2005). "Analysis of crushing of granular material under isotropic and biaxial stress conditions." *Soils and foundations*, 45(4), 79-87.
- Lobo-Guerrero, S., Vallejo, L. E., and Vesga, L. F. (2006). "Visualization of crushing evolution in granular materials under compression using DEM." *International Journal of Geomechanics*, 6(3), 195-200.
- Lorensen, W. E., and Cline, H. E. (1987). "Marching cubes: A high resolution 3D surface construction algorithm." *Proceedings of the 14th annual conference on Computer graphics and interactive techniques*, ACM, 163-169.
- Ma, G., Zhou, W., Regueiro, R. A., Wang, Q., and Chang, X. (2017). "Modeling the fragmentation of rock grains using computed tomography and combined FDEM." *Powder Technology*, 308, 388-397.
- MaTeck (2019). "Fused Silica UV-VIS Grade (SiO₂)."
<<https://mateck.com/info/fused-silica-uv-vis-grade-sio2.html>>.
(01/10/2019, 2019).
- McDowell, G., Bolton, M., and Robertson, D. (1996). "The fractal crushing of granular materials." *Journal of the Mechanics and Physics of Solids*, 44(12), 2079-2101.
- McDowell, G., and Harireche, O. (2002). "Discrete element modelling of soil particle fracture." *Géotechnique*, 52(2), 131-135.
- McDowell, G. R., and de Bono, J. P. (2015). "On the micro mechanics of one-dimensional normal compression." *Géotechnique*, 63(11), 895-908.
- Mohammadnejad, M., Liu, H., Chan, A., Dehkhoda, S., and Fukuda, D. (2018). "An overview on advances in computational fracture mechanics of rock." *Geosystem Engineering*, 1-24.

- Nakata, A., Hyde, M., Hyodo, H., and Murata (1999). "A probabilistic approach to sand particle crushing in the triaxial test." *Géotechnique*, 49(5), 567-583.
- Nicksiar, M., and Martin, C. D. (2014). "Factors Affecting Crack Initiation in Low Porosity Crystalline Rocks." *Rock Mechanics and Rock Engineering*, 47(4), 1165-1181.
- Otsubo, M., and O'Sullivan, C. (2018). "Experimental and DEM assessment of the stress-dependency of surface roughness effects on shear modulus." *Soils and Foundations*, 58(3), 602-614.
- Otsubo, M., O'Sullivan, C., Sim, W., and Ibraim, E. (2015). "Quantitative assessment of the influence of surface roughness on soil stiffness."
- Potyondy, D. O. (2012). "A Flat-Jointed Bonded-Particle Material For Hard Rock." *46th U.S. Rock Mechanics/Geomechanics Symposium*, American Rock Mechanics Association, Chicago, Illinois, 10.
- Potyondy, D. O. (2015). "The bonded-particle model as a tool for rock mechanics research and application: current trends and future directions." *Geosystem Engineering*, 18(1), 1-28.
- Potyondy, D. O., and Cundall, P. (2004). "A bonded-particle model for rock." *International journal of rock mechanics and mining sciences*, 41(8), 1329-1364.
- Robertson, D., and Bolton, M. D. (2001). "DEM simulations of crushable grains and soils." *4th International Conference on Micromechanics of Granular Media Powders and Grains* Sendai, Japan, 623-626.
- Song, B., Chen, W., and Luk, V. (2009). "Impact compressive response of dry sand." *Mechanics of Materials*, 41(6), 777-785.
- Tomac, I., and Gutierrez, M. (2017). "Coupled hydro-thermo-mechanical modeling of hydraulic fracturing in quasi-brittle rocks using BPM-DEM." *Journal of Rock Mechanics and Geotechnical Engineering*, 9(1), 92-104.
- Turichshev, A., and Hadjigeorgiou, J. (2017). "Development of Synthetic Rock Mass Bonded Block Models to Simulate the Behaviour of Intact Veined Rock." *Geotechnical and Geological Engineering*, 35(1), 313-335.
- Wang, M. H., Yang, R. Y., and Yu, A. B. (2012). "DEM investigation of energy distribution and particle breakage in tumbling ball mills." *Powder Technology*, 223, 83-91.
- Wu, S., and Xu, X. (2016). "A Study of Three Intrinsic Problems of the Classic Discrete Element Method Using Flat-Joint Model." *Rock Mechanics and Rock Engineering*, 49(5), 1813-1830.
- Zhao, B., Wang, J., Coop, M., Viggiani, G., and Jiang, M. (2015). "An investigation of single sand particle fracture using X-ray micro-tomography." *Géotechnique*, 65(8), 625-641.

Appendices

Appendix A: Tables

Table 6-1. Summary of DEM Model Parameters.

Parameter	Value
Parallel bond group	
Effective modulus (GPa)	70
Normal to shear stiffness ratio	2
Radius multiplier	1
Normal strength (MPa)	290
Shear strength (MPa)	290
Linear group	
Effective modulus (GPa)	70
Normal to shear stiffness ratio	2
Friction	0.5

Table 6-2. Comparison between experimental and DEM results of the cube and single sand particle experiments.

	Cube exp.	Cube BBM	Difference (%)	Single sand particle exp.	Single sand particle BBM	Difference (%)
Peak load (N)	1605.1	1640.3	2.2	135.7	129.8	4.4
Displacement at peak load (mm)	0.0220	0.0196	10.9	0.0612	0.0477	22.1
Average stiffness (N/mm)	86334	87043	0.8	1623*	4403*	171.2*
				3122**	5763**	84.6**

*Displacement range 0.015 to 0.03 mm

**Displacement range 0.03 to 0.04 mm

Table 6-3. Comparison between experimental and DEM results of the three-sand particle experiments.

Test	Peak load (N)	Difference (%)	Displacement at peak load (mm)	Difference (%)
Test1 Exp.	35.4	8.2	0.0396	4.3
Test1 BBM	38.3		0.0379	
Test2 Exp.	34.2	1.5	0.0541	15.9
Test2 BBM	33.7		0.0455	
Test3 Exp.	57.9	4.5	0.104	16.2
Test3 BBM	60.5		0.0872	

Table 6-4. Summary of breakage energy results for the three-particle experiments

Test	Breakage Energy (N/m)		Difference (%)	Total Number BBM contacts of blocks from different sand particles
	Exp.	BBM		
Test 1	90.3	80.2	11.2	117
Test 2	205.1	187.4	8.7	169
Test 3	605.6	514.6	15.0	120

Appendix B: Figures

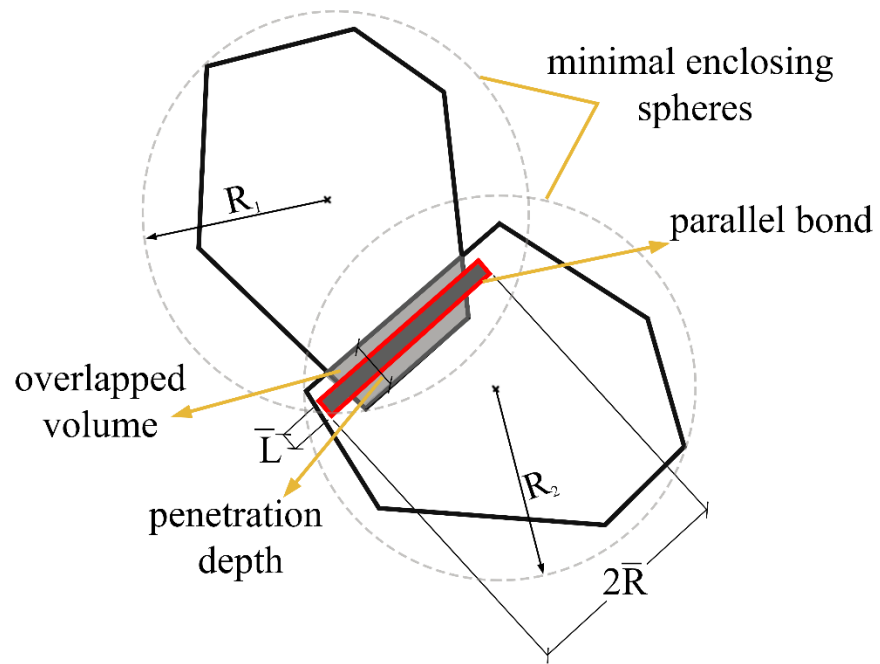


Figure 6-1. Linear parallel contact model between two polyhedral blocks.

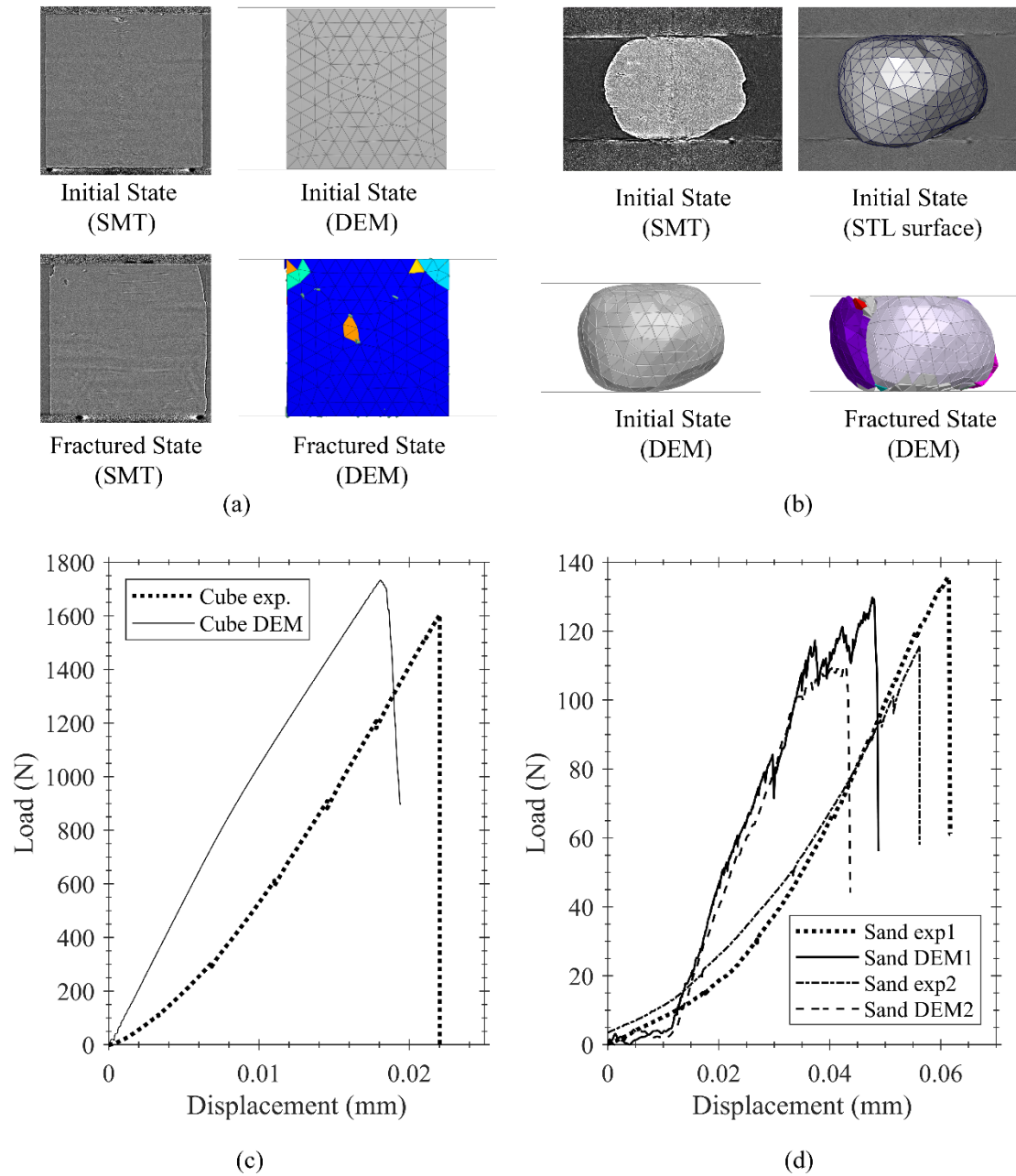


Figure 6-2. SMT images and DEM model of (a) silica cube; and (b) ASTM 20-30 Ottawa sand particle; and force displacement curves for (c) silica cube; and (d) ASTM 20-30 Ottawa sand particle.

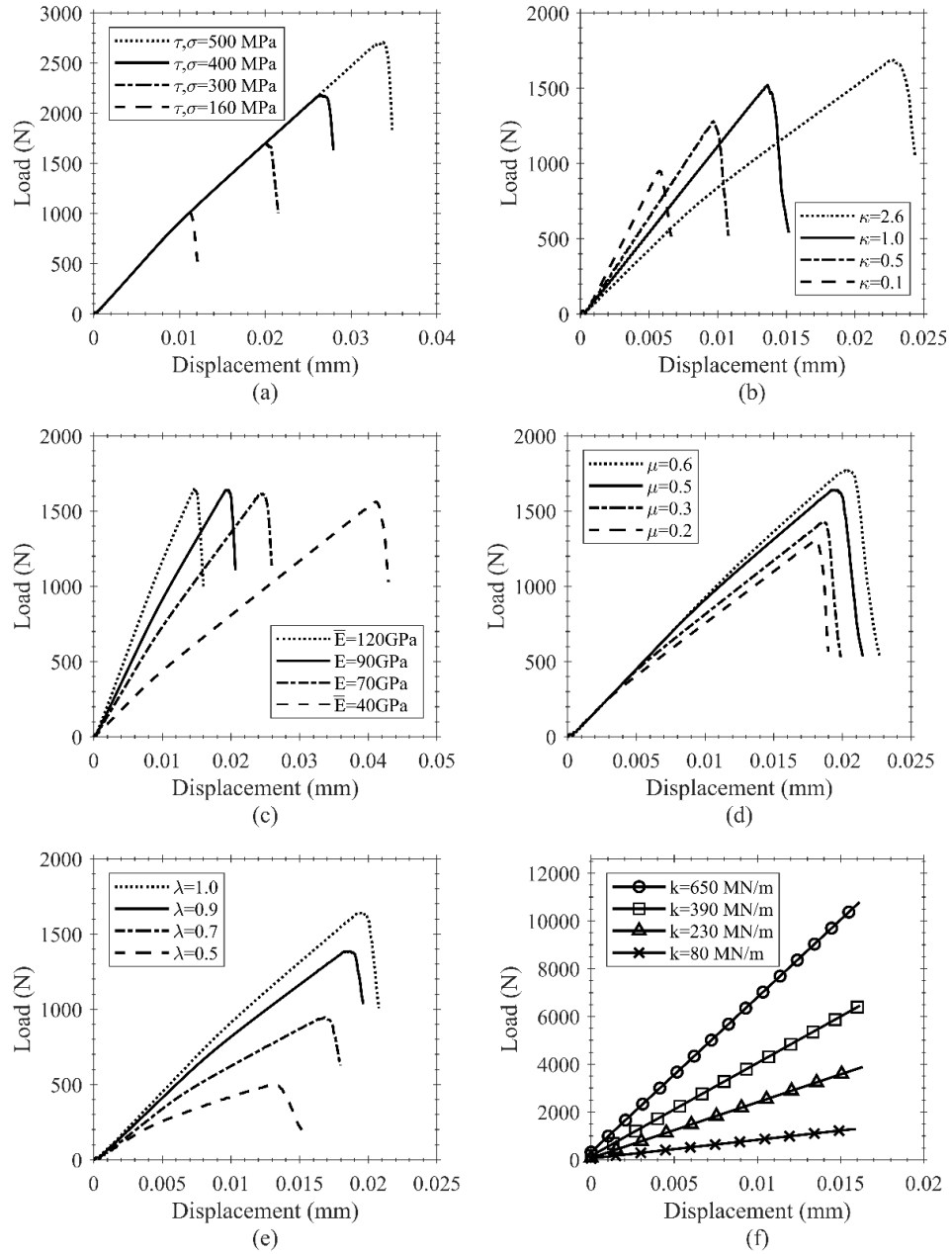


Figure 6-3. Influence of varying (a) parallel bond normal and shear strength; (b) ratio between bond normal and shear stiffness; (c) bond effective modulus; (d) friction coefficient; (e) bond radius multiplier; and (f) stiffness of the contacts between the loading plate and the blocks on the behavior of BBM simulations of 1D compression tests on the silica cubes.

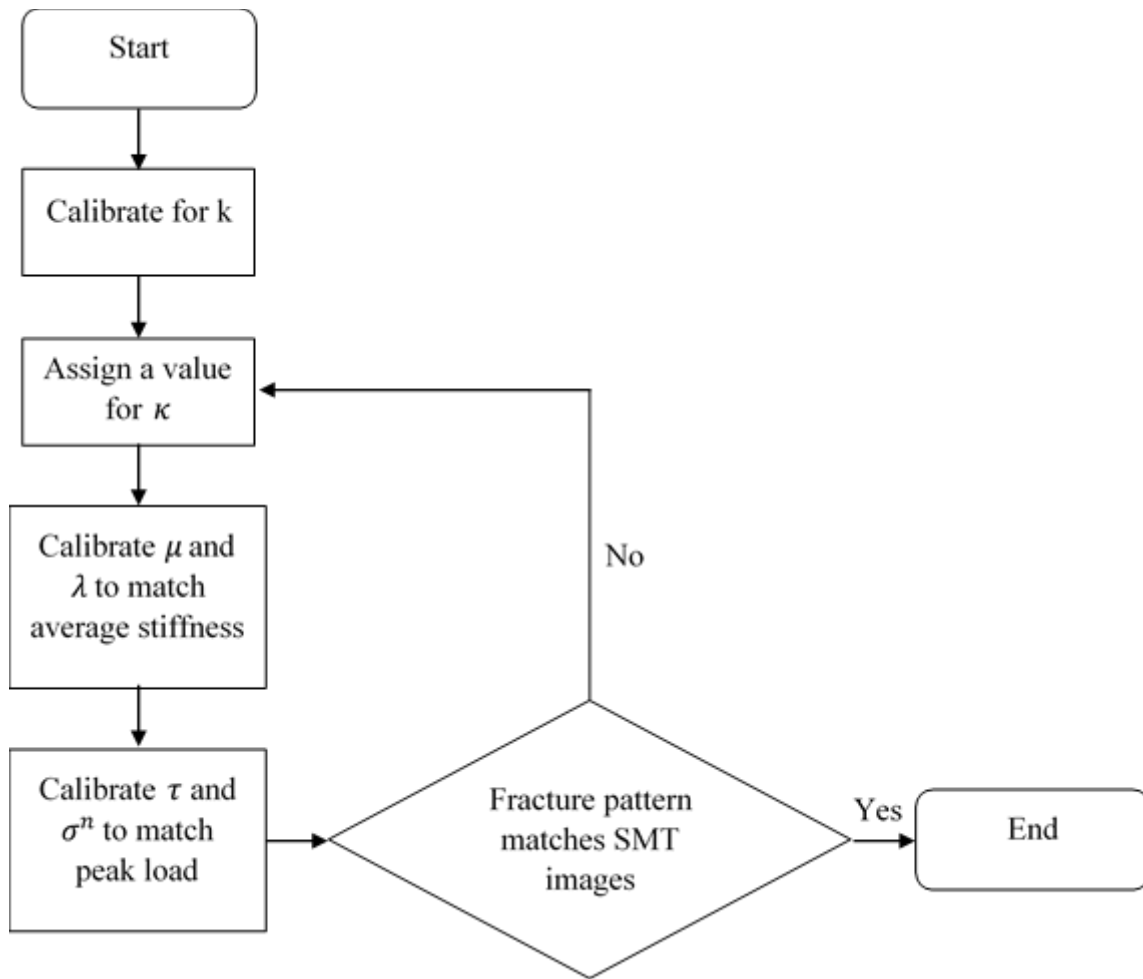


Figure 6-4. Flow chart of model calibration procedure.

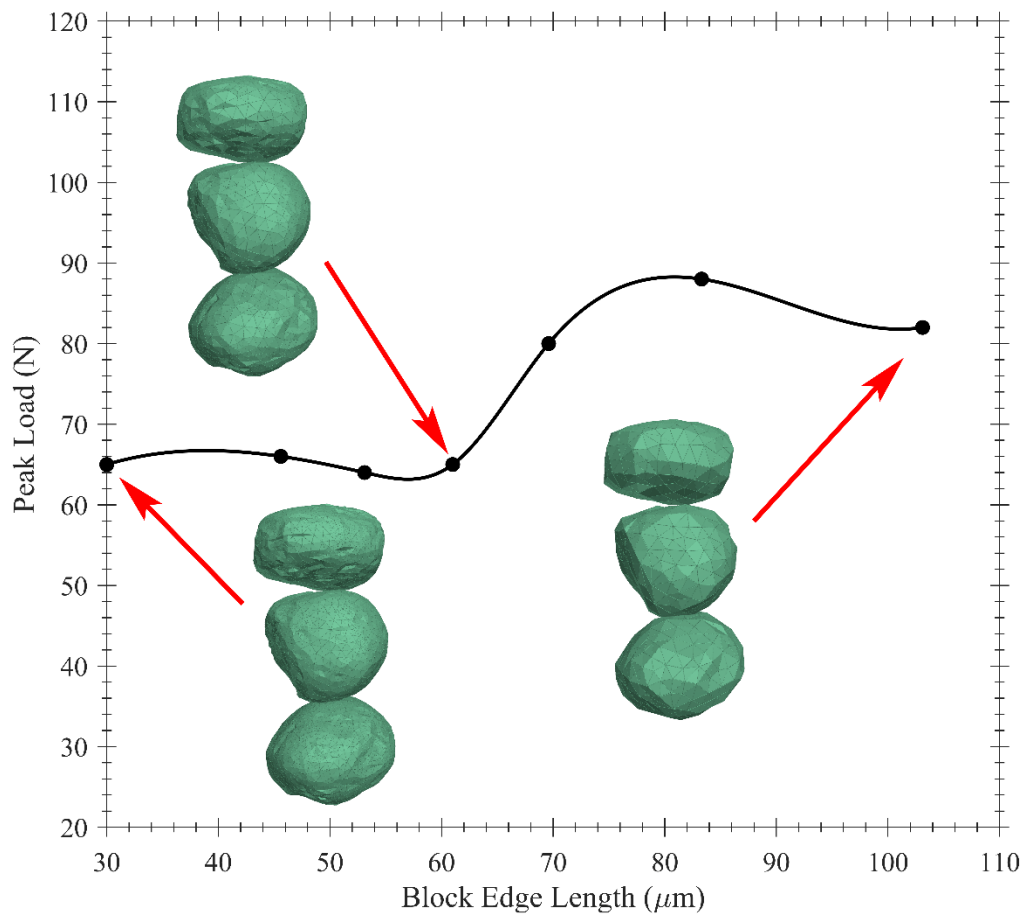


Figure 6-5. Variation of peak load from 1D compression DEM simulations with different rigid block sizes.

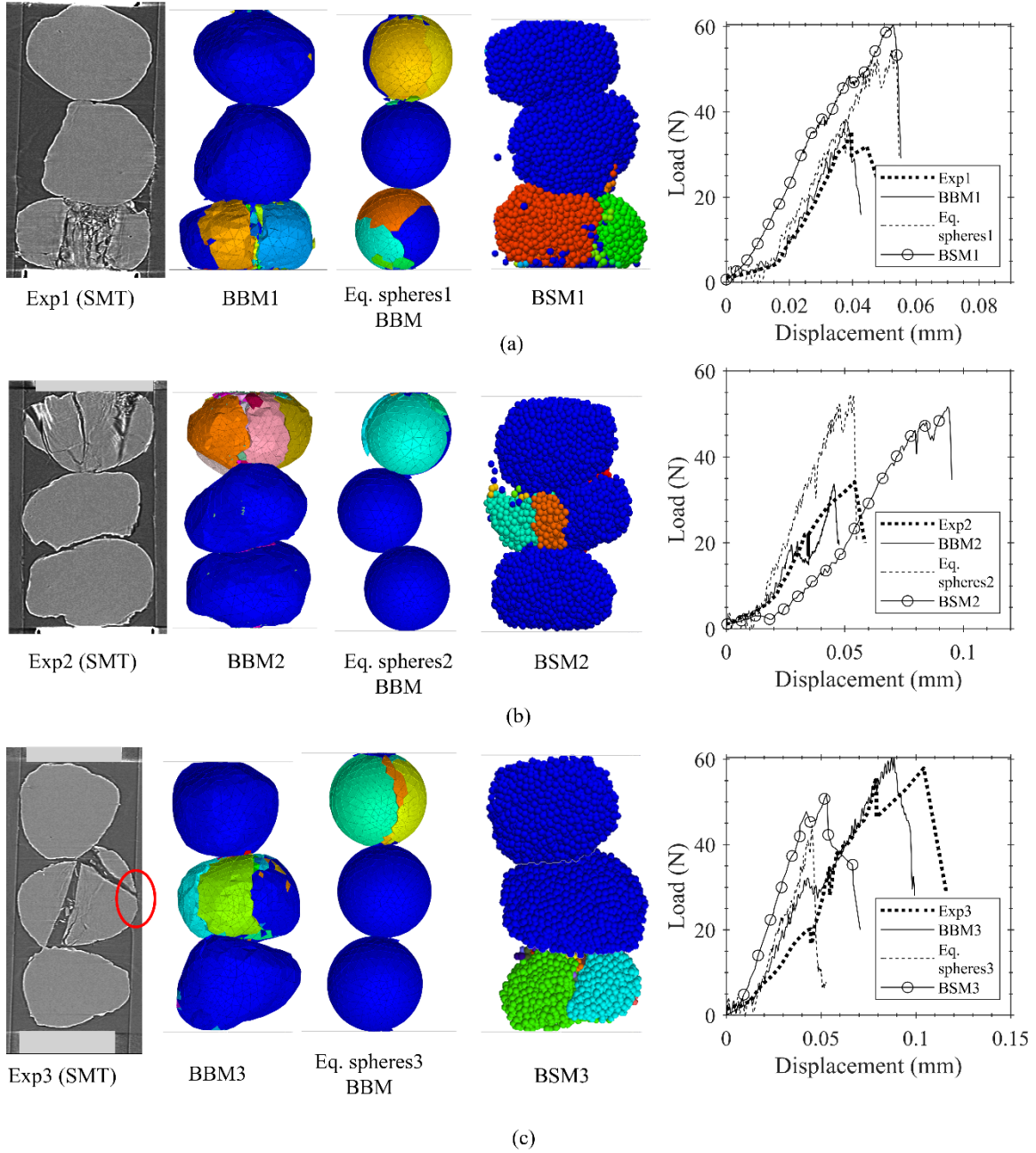


Figure 6-6. SMT and DEM images and comparison of force versus compressive displacement for 3 three-particle 1D compression experiments, actual shape DEM model, and equivalent spheres DEM model. BSM results are from Cil and Alshibli (2015). Surrounding walls were hidden in the images of DEM models for a better visualization.

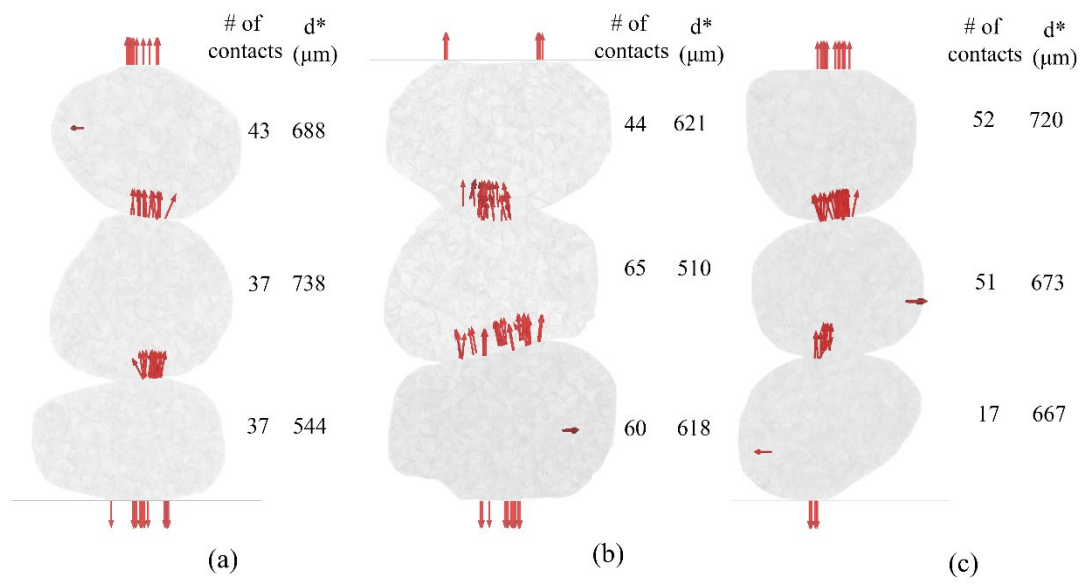


Figure 6-7. Number of rigid blocks in contact and loading distances obtained from real shape agglomerates models for (a) Test 1; (b) Test 2; and (c) Test 3.

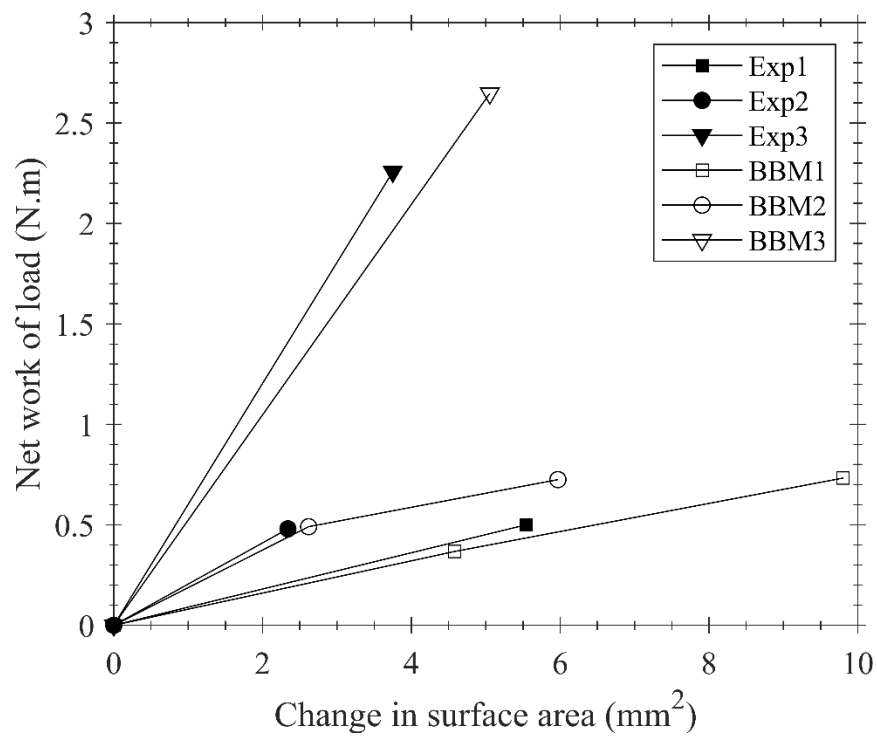


Figure 6-8. Cumulative change in fracture surface area versus net work of load (energy dissipated by slip subtracted from total input energy) for the three-particle tests.

CHAPTER SEVEN

CONCLUSIONS AND RECOMMENDATIONS

Summary of Major Conclusions

This dissertation investigated fundamental underlying coupled processes during gas production from hydrate bearing sediments. SMT was used to obtain 3D direct visualizations of fines clogging, hydrate formation, hydrate dissociation, and gas driven fracture in porous media. Additionally, this dissertation employed high resolution 3D SMT-M along with DEM modeling techniques to simulate multiscale in-situ experiments reproducing the actual shape of sand particles. The following is a summary of the major findings of the dissertation:

1. Gas invaded the 0%, 2% and 4% kaolinite specimens by “percolation”, while it invaded the 6% specimen by “fracturing” or “conduit opening”. For specimens with fines concentration less than 6%, gas percolated through the pores without any major porosity change or fracturing. For 6% kaolinite specimen, gas driven fractures propagated by densifying surrounding sediments. Fines migrated through the pores without clogging for the 2% and 4% kaolinite specimens. For 6% kaolinite specimen, fines concentration increased near fractures’ boundaries due to fines clogging. Clogging induced an increase in the capillary pressure at the pore throats and caused the capillary pressure to overcome the effective stress between sand particles, and fractures to be initiated.
2. A combination of cementing, pore-filling, and surface coating initial pore-habits were observed for the hydrate depressurization experiment, while pore-filling pore habit was predominant in the hydrate thermal stimulation experiment. As hydrate saturation exceeded 10%, specific area began to decrease, which is an evidence of Ostwald Ripening. Surface coating hydrates dissociate faster than hydrates with pore-filling pore habit. This is explained by the higher specific area in the surface coating hydrates, which allows for more surface for hydrates to dissociate it.
3. Results suggest that with a combination of hydrate pore habit formed within the 3D porous media, estimation of hydrate surface area as a linear relationship with $(\text{hydrate volume})^{2/3}$ is best for hydrate saturation less than a specific threshold value. The value of this threshold varies depending on the dissociation method and the driving dissociation force and was found to be 7% for the depressurization experiment and 28% for the thermal stimulation experiment.
4. $(\text{hydrate volume})^2$ was found to better estimate hydrate interfacial area compared to $(\text{hydrate volume})^{2/3}$ in the depressurization experiment, while $(\text{hydrate volume})^3$ provided better estimates of the interfacial area for the thermal stimulation experiment.
5. Multivariate nonlinear regression fitting was used to propose a geometric tortuosity model for saturated and unsaturated porous media based on in-situ 3D images of 130 unconsolidated sand systems. Even with the variation of porosity in the sand systems, the relative tortuosity can be estimated as a power function of saturation only, with an R^2 value of 0.94. Effects of I_{sph} and C_u were found to be insignificant based on their p-value. The proposed

model provided a good estimate of geometric tortuosity with an R^2 value of 0.90 and RMSE value of 0.117. The proposed model yields better estimates of saturated geometric tortuosity compared to the analytical and theoretical models found in the literature.

6. Normalizing calculated stresses with I_{sph} was found to yield better estimates of sand particles tensile strength. This finding was based on the results of DEM simulations of unconfined 1D compression tests for 100 particles with various shapes and sizes.
7. The bonded block model (BBM) approach was proven to successfully predict load-displacement behavior, fractured particles, fracture pattern, and energy released due to crack initiation by direct comparison with SMT images. Contact loading conditions, number of contact points, and particle geometry interaction have significant effects on fracture pattern of particles. An increase in number of contacts increases the required stress to fracture a particle. For particles with a similar number of contact points, first particles to fracture are those with the smallest loading distance. Energy dissipating through slippage was found to range between 25% to 35% of the total work input by the external load, and thus should be considered when estimating breakage energy. Breakage energy results suggest that more fragmentation is expected for an assembly of particles with a smaller number of contact points under the same state of compressive stress.

Recommendations for Future Work

Based on the findings reported in this dissertation, the following recommendations are suggested for future work:

1. Gas driven fracturing is a complex process that involves multiphase flow, capillary forces acting at the fracture interface, and friction forces between particles. The complexity of the multiphase flow process and the wide range of fracture patterns makes gas driven fracture poorly understood fundamentally. The process of gas driven fracture nucleation and propagation from the perspective of capillary pressure can be studied in future research. Capillary pressure can be calculated pore by pore by utilizing SMT imaging technique and measuring curvature of the three-phase interfaces. Additional multiphase flow experiments with different sand particles morphology, porosity, fines content, and fines type are needed to develop a physics-based model that predicts the conditions where gas driven fracture might occur.
2. Gas hydrate dissociation can be affected by heat and mass transfer properties of porous media. Heat and mass of porous media can vary depending on permeability, relative permeability, and tortuosity. Dynamic SMT images obtained in this dissertation can be used in future work to generate 3D pore structures (pore network models) and compare the results with other hydrate pore-habit based models used in the literature. The extracted 3D pore network models can be used to investigate the evolution of relative permeability with

hydrate saturation using Lattice Boltzmann method, in addition to the evolution of tortuosity of porous media during hydrate formation and dissociation.

3. The influence of fines on hydrate formation and dissociation rate is another interesting topic that can be investigated further. This can be done by conducting experiments similar to the ones presented in Chapter 3, but with sand-fines mixtures instead of clean sand. An accurate physical description is important to assess the productivity potential of hydrate bearing sediments reservoirs.
4. Upscaling modeling can be used in future work to validate the proposed hydrate dissociation models provided in this dissertation with data from field-scale hydrate production operations.
5. The BBM model was proven to be effective in capturing the fracture behavior and breakage energy for unconfined 1D compression of single and three-particle sand specimens. Future work should focus on testing the capability of the proposed approach in capturing fracture behavior of sand in larger-scale specimens with different loading conditions. The loading conditions can include conventional triaxial compression, direct shear test, dynamic and high-strain impact loading conditions.

VITA

Zaher Jarrar, a graduate research and teaching assistant in the Department of Civil and Environmental Engineering at the University of Tennessee, Knoxville, studied Civil Engineering at Birzeit University, Palestinian Authorities from August 2007 to May 2012. He graduated with distinction and was honored by the dean in the graduation ceremony in 2012. After he graduated from Birzeit University, he worked as a teaching assistant there for one year. Away from academic life, Jarrar was hired by Consolidated Contractors International Company (CCC) in 2013. He was sent to Saudi Arabia to be part of the 20 billion dollar Riyadh Metro Project. In August 2015, Jarrar traveled to the United States to pursue his studies after he got a graduate assistantship from the University of Tennessee. He received his Master of Science degree from the Department of Civil and Environmental Engineering at the University of Tennessee, Knoxville, in 2018. His current research focuses on understanding underlying physical processes of the emergent phenomena during gas production from hydrate-bearing sediments. Mr. Jarrar's research also employs Discrete Element modelling (DEM) as a tool to simulate force transmission and fracture in granular assemblies under loading.