

Reactive Transport in Natural and Engineered Systems

85 *Reviews in Mineralogy and Geochemistry*

85

TABLE OF CONTENTS

1	Reactive Transport at the Crossroads	
		<i>Carl I. Steefel</i>
INTRODUCTION		1
HISTORICAL DEVELOPMENT		1
MATHEMATICAL FORMULATION		2
NUMERICAL FORMULATION		4
Reaction terms		4
Coupling of reaction and transport terms		5
REACTIVE TRANSPORT ADVANCES		7
Pore scale and continuum models		7
Contaminant transport		8
Ion exchange and transport		8
Surface complexation and transport		10
The laboratory–field rate discrepancy		11
Incorporating isotope fractionation		12
Electrostatic effects on reactive transport		16
Nernst–Planck equation		16
Transport in the EDL		18
Multiphase reactive systems		20
Chemical–mechanical		20
Watersheds and beyond		20
CONCLUSIONS		21
ACKNOWLEDGMENTS		21
REFERENCES		21

2 Multiscale Approaches in Reactive Transport Modeling

Sergi Molins, Peter Knabner

INTRODUCTION	27
SINGLE-SCALE DESCRIPTION OF REACTIVE TRANSPORT.....	28
Separate fluid and solid continua: Pore-scale equations.....	29
Single porous continuum: Darcy-scale equations	29
Multiscale aspects of process coupling	30
UPSCALING AND EFFECTIVE MODELS	31
Upscaling interfacial reactions	33
Upscaling interfacial reactions with evolving geometries.....	34
COMBINING SCALE REPRESENTATIONS	35
Hybrid multiscale models.....	35
Darcy–Brinkman–Stokes approach.....	36
MULTI-RATE AND MULTI-CONTINUA MODELS.....	37
Multi-rate models	38
Multi-continua models	39
Multiple interacting continua	40
MULTISCALE MODEL APPLICATIONS.....	40
Granular porous media	40
Fractured media.....	43
Surface–subsurface hydrologic coupling.....	44
SUMMARY AND CONCLUSIONS.....	45
ACKNOWLEDGMENTS.....	47
REFERENCES	47

3 Modeling Reactive Transport Processes in Fractures

Hang Deng, Nicolas Spycher

INTRODUCTION	49
FRACTURE ALTERATION DRIVEN BY GEOCHEMICAL REACTIONS	51
Fracture opening due to mineral dissolution	51
The alteration of rock matrix bordering the fracture.....	54
Fracture closing due to mineral precipitation.....	55
CONCEPTUAL AND NUMERICAL MODELS.....	56
Generic formulation of the governing equations.....	57
1D modeling of near-fracture rock matrix alteration	59
2D modeling of cross-aperture processes.....	60
2D modeling of processes in the fracture plane	62
3D pore-scale modeling of geochemical fracture alteration.....	64
CONTROLS ON DISSOLUTION-DRIVEN	
REACTIVE TRANSPORT PROCESSES IN FRACTURES.....	65
The impact of flow and reaction rates	65
The impact of mineralogy	66
CONCLUDING REMARKS.....	68
ACKNOWLEDGMENTS.....	70
REFERENCES	70

4 Reactive Transport Modeling of Coupled Processes in Nanoporous Media

Christophe Tournassat, Carl I. Steefel

INTRODUCTION	75
NANOPOROUS MEDIA: SMALL PORES, LARGE SURFACES AND MEMBRANE PROPERTIES	77
Surface and microstructural properties of nanoporous materials	77
Ion distribution in the vicinity of charged surfaces	79
Semi-permeable properties	82
NON-COUPLED AND COUPLED TRANSPORT PROCESSES	82
Transport equations in traditional reactive transport modeling	82
Coupled transport processes and thermodynamics of irreversible processes	83
POISSON–BOLTZMANN EQUATION AND ION CONCENTRATION DISTRIBUTION CALCULATIONS IN REACTIVE TRANSPORT CODES	85
The mean electrostatic potential model	85
Dual continuum representation of the pore space	87
Influence of ionic strength on the dual continuum model predictions	89
COUPLED TRANSPORT PROCESSES IN REACTIVE TRANSPORT CODES— THE ISOTHERMAL NO-FLOW CONDITION	91
Nernst–Planck equation in the isothermal, no-flow, and no external electric field condition	91
Nernst–Planck equation in the isothermal and no-flow condition in the presence of an external electric field	94
BEYOND DIFFUSION, COUPLINGS WITH ADVECTIVE FLOW	97
Advective displacement method and reactive transport calculations	97
Osmotic membrane efficiency	99
Nernst–Planck equation in the isothermal, no external electric field, no current condition, and in the presence of advective flow	100
From dual continuum to multi-continuum	101
CONCLUSIONS	102
ACKNOWLEDGEMENTS	102
REFERENCES	102

5 Mixing and Reactive Fronts in the Subsurface

Massimo Rolle, Tanguy Le Borgne

INTRODUCTION	111
Scales of mixing in porous media	112
MIXING AND MIXING-CONTROLLED REACTIONS	115
Dispersion in porous media	115
Mechanisms of mixing and mixing enhancement	116
Quantification of mixing	121
Mixing dynamics and reactive processes	126
EXAMPLES OF MIXING AND REACTIONS AT DIFFERENT SCALES	129
Micromodel experiments	129

Intermediate laboratory scale experiments	131
Field-scale investigation	133
CONCLUSIONS AND OUTLOOK	135
REFERENCES	137

6

Multiphase Multicomponent Reactive Transport and Flow Modeling

Irina Sin, Jérôme Corvisier

INTRODUCTION	143
GOVERNING PROCESSES	144
Capillary pressure and wettability	145
Relative permeability	148
Diffusion	151
General formulations of multiphase flow	151
Geochemical reactions.....	154
EOS and pressure correction	159
Density.....	159
Feedback on fluid and matrix properties	160
MATHEMATICAL AND NUMERICAL APPROACHES	
OF MMF&RT MODELING.....	161
Multiphase multicomponent flow (MMF) approaches.....	162
Coupling MMF&RT.....	165
Discussions.....	168
APPLICATIONS.....	169
Phase equilibrium and solubility	169
Gas chromatography.....	174
Gas chromatography and density-driven flow	176
DISCUSSIONS AND PERSPECTIVES	182
SUMMARY	184
REFERENCES	185

7

Reactive Transport in Evolving Porous Media

Nicolas Seigneur, K. Ulrich Mayer, Carl I. Steefel

INTRODUCTION	197
CONTINUUM SCALE GOVERNING EQUATIONS	
AND EVOLVING PARAMETERS	200
Governing equations.....	200
GOVERNING PARAMETERS AND INTERDEPENDENCIES	202
EVOLUTION OF POROUS MEDIA AT THE PORE SCALE	203
Porous media structure at the pore scale—Effective porosity and connectivity	203
Evolution of flow and transport parameters at the pore scale.....	204
Evolution of reactivity at the pore scale	204
EFFECT OF MINERAL DISSOLUTION AND PRECIPITATION	
ON POROUS MEDIA	205
Mineral dissolution.....	205

Mineral precipitation	208
INTEGRATED ASSESSMENT OF THE IMPACT OF MINERAL REACTIONS ON POROUS MEDIA	209
RELATIONSHIPS FOR MODELING EVOLUTION OF CONTINUUM-SCALE PARAMETERS	211
Evolution of porosity	211
Tortuosity and diffusivity as a function of porosity.....	211
Permeability as a function of porosity.....	214
Evolving reactivity	217
CASE STUDIES OF REACTIVE TRANSPORT IN EVOLVING POROUS MEDIA	220
Effects of coupled dissolution–precipitation reactions on permeability and flow pattern	220
Effects of dissolution on pore connectivity and diffusivity	222
Evolving reactivity	224
CHALLENGES OF AND OPPORTUNITIES FOR REACTIVE TRANSPORT MODELING IN EVOLVING POROUS MEDIA	227
State of the science for modeling reactive transport in evolving porous media	227
Extreme cases: Complete clogging and solid structure collapse.....	227
Unsaturated flow relationships	228
Numerical approaches for coupling of flow and reactive transport.....	228
Towards an integrated model for evolving porous media.....	228
Opportunities related to imaging techniques, pore scale modeling and upscaling....	229
CONCLUSIONS.....	229
ACKNOWLEDGMENTS.....	230
REFERENCES	231

8 Stable Isotope Fractionation by Transport and Transformation

Jennifer L. Druhan, Matthew J. Winnick, Martin Thullner

INTRODUCTION	239
Basic fractionation in a closed system.....	240
FRACTIONATION IN OPEN SYSTEMS: THE INFLUENCE OF TRANSPORT	242
Rayleigh distillation	243
Example: Equilibrium and kinetic effects	243
Mixing	245
Example: Mixing of multiple flow paths during sampling.....	247
FRACTIONATION BY MINERAL GROWTH: SOLUTIONS AND SOLIDS	250
FRACTIONATION BY MICROBIAL POPULATIONS: THE MANY STEPS OF METABOLISM.....	253
Enzymatic reactions: A comment on catalysis	256
Mass transfer and bioavailability.....	257
SUMMARY AND FUTURE OPPORTUNITIES	259
ACKNOWLEDGMENTS.....	260
REFERENCES	260

9

Microbial Controls on the Biogeochemical Dynamics in the Subsurface

Martin Thullner, Pierre Regnier

INTRODUCTION	265
TRADITIONAL APPROACHES FOR SIMULATING BIOGEOCHEMICAL PROCESSES IN THE SUBSURFACE	266
Reaction networks for biogeochemistry	266
Kinetics of geomicrobial reactions	267
THERMODYNAMICALLY INFORMED MODELS	271
Incorporating bioenergetics in models of microbial dynamics	271
Energetics of catabolic reactions	271
Bioenergetic theory: the F_T term	273
Quantifying growth yields	275
Energetics of anabolism and maintenance	276
Carbon Use Efficiency as an alternative to Y_s	278
INTEGRATION OF MICROBIAL SEQUENCING DATA IN GEOMICROBIAL MODELS	278
CONSIDERING THE ECOLOGICAL BEHAVIOR OF MICROORGANISMS	280
Microbe–microbe interactions	281
Interactions between microbes and their physical environment	282
CONSIDERING STABLE ISOTOPE SIGNATURES	284
Stable isotopes as tracers of matter fluxes into biomass	285
Stable isotopes as indicators of degradation pathways	286
SCALE EFFECTS	287
CONCLUSIONS	290
ACKNOWLEDGMENTS	291
REFERENCES	291

10

Understanding and Predicting Vadose Zone Processes

*Bhavna Arora, Dipankar Dwivedi, Boris Faybishenko,
Raghavendra B. Jana, Haruko M. Wainwright*

INTRODUCTION	303
FIELD CONDITIONS, OBSERVATIONS AND TECHNIQUES	305
Conceptualization	306
In situ measurements in the vadose zone	306
In situ measurements in the saturated zone	309
Remote sensing and geophysical observations	309
GEOCHEMICAL MODELING OF SUBSURFACE SYSTEMS	310
Conceptualization	311
Description of the hydrological system	311
Description of the geochemical system	312
Model domain and discretization	312
Initial and boundary conditions	313
SOIL MOISTURE STUDIES	314

Soil moisture measurements.....	314
Soil moisture modeling	315
Scaling of soil moisture.....	315
Remarks.....	317
APPLICATION OF GEOCHEMICAL MODELING	
TO VADOSE ZONE STUDIES.....	318
Identifying critical interfaces through zonation	318
Identifying critical time periods through wavelet and entropy approaches.....	318
Case studies	319
CURRENT MODEL LIMITATIONS AND FUTURE OPPORTUNITIES	321
Model validation.....	321
Uncertainty quantification	321
Development of benchmarks	322
Future opportunities	322
SUMMARY	323
ACKNOWLEDGMENTS.....	323
REFERENCES	323

11 Abiotic and Biotic Controls on Soil Organo–Mineral Interactions: Developing Model Structures to Analyze Why Soil Organic Matter Persists

*Dipankar Dwivedi, Jinyun Tang, Nicholas Bouskill,
Katerina Georgiou, Stephany S. Chacon, William J. Riley*

INTRODUCTION	329
THE EMERGENT PICTURE OF SOIL ORGANIC MATTER STABILITY	330
Microbial and plant processes	331
Organo–mineral interactions	332
EMERGING TECHNOLOGIES	332
Microbial traits that affect SOM stability.....	333
MODELING SOM DYNAMICS	334
Traditional modeling approaches	334
Transitional modeling approaches.....	335
Next-generation process representation approaches	335
CURRENT USE OF REACTIVE TRANSPORT MODELING	
OF SOM DYNAMICS	337
Variably saturated flow.....	339
Reactive transport equations.....	340
Biological reaction rates	340
Mineral reactions	341
Sorption reactions.....	341
SUMMARY	342
ACKNOWLEDGMENT.....	343
REFERENCES	343

12 Reactive Transport Processes that Drive Chemical Weathering: From Making Space for Water to Dismantling Continents

Kate Maher, Alexis Navarre-Sitchler

INTRODUCTION	349
OVERVIEW OF TRANSFERS WITHIN THE WEATHERING ZONE	350
CONTROLS ON THE MIGRATION OF WEATHERING FRONTS	356
Chronosequences as a bridge between the laboratory and the field	356
Evaluating the assumptions of isotopic proxies for weathering using RTM approaches	359
The effect of heterogeneity on reaction fronts and overall chemical weathering rates	360
CONTROLS ON WEATHERING FRONTS ALONG HILLSLOPES	363
CATCHMENT-SCALE RTM MODELS.....	365
FRONTIERS IN WEATHERING MODELS	369
The role of RTM models in the short-term carbon cycle	369
The role of weathering models in water quality	371
Models of global weathering	372
CONCLUSIONS.....	372
ACKNOWLEDGMENTS.....	373
REFERENCES	373

13 Watershed Reactive Transport

Li Li

WATERSHEDS AS HYDRO-BIOGEOCHEMICAL REACTORS.....	381
FUNDAMENTALS OF WATERSHED HYDROLOGY.....	383
Water balance	383
Modeling watershed hydrological processes	386
An example of hydrological processes in the Shale Hills catchment.....	388
FUNDAMENTALS OF SOIL BIOGEOCHEMISTRY	389
Biogeochemical reactions.....	389
Chemical weathering	394
WATERSHED REACTIVE TRANSPORT MODELLING	395
A brief history of reactive transport modeling	395
Examples of hydrological and biogeochemical coupling	397
How do extreme hydrological events influence water chemistry?	399
RESEARCH FRONTIERS	400
Drivers of chemical weathering in natural systems.....	400
Watershed response to hydrological changes: Concentration discharge relationships.....	402
Reaction rates at the watershed scale: linking travel time, age, and reactions	404
CONCLUSIONS AND LOOKING FORWARD.....	405
ACKNOWLEDGMENT	406
REFERENCES	406

14

RTM for Waste Repositories

Olivier Bildstein, Francis Claret, Pierre Frugier

INTRODUCTION	419
A need for numerical simulations.....	419
A need to consider coupled processes.....	421
REACTIVE TRANSPORT MODELING.....	422
Governing equations.....	422
The critical need for thermodynamic databases.....	423
Modeling materials and reactive interfaces.....	424
MATERIALS IN PHYSICAL CONTACT WITH AIR.....	424
Corrosion of carbon steel components in oxic conditions.....	426
Oxic transient: impact on claystone.....	427
Atmospheric concrete carbonation.....	427
THE IRON–CLAY INTERFACE.....	429
First modeling studies at the scale of the disposal cell.....	429
First modeling attempts to fit batch experiment results.....	430
A decade of RTM evolution of simulations at the scale of the disposal cell.....	430
A recent return to modeling experimental results.....	433
THE CLAY CONCRETE INTERFACE.....	433
A brief materials mineralogy overview and associated chemical gradient at the materials interface.....	433
Reactive transport modeling of laboratory and in situ scale experiments.....	435
Reactive transport modeling of the long-term evolution of clay–concrete interfaces.....	438
OTHER INTERFACES WITHOUT EXTENSIVE RTM STUDIES.....	442
The glass–(iron)–clay interface.....	442
The glass–concrete–(clay) interface.....	444
The iron–concrete interface in anoxic conditions.....	445
GENERAL CONCLUSION AND PERSPECTIVES.....	445
REFERENCES.....	447

15

Acid Water–Rock–Cement Interaction and Multicomponent Reactive Transport Modeling

Jordi Cama, Josep M. Soler, Carles Ayora

INTRODUCTION	459
Geological storage of CO ₂	460
Acid mine drainage treatment.....	461
Outline.....	461
LABORATORY EXPERIMENTS AND FULL SCALE SYSTEM.....	462
Laboratory-scale experiments.....	462
Full scale system.....	464
MULTICOMPONENT REACTIVE TRANSPORT MODELING (MCRTM).....	464
Brief description of MCRTM.....	464
Numerical discretization.....	466
Parameterization.....	467

MCRTM IN CO ₂ -RICH WATERS.....	474
Column experiments: reservoir and cap rocks	474
Column experiments: reservoir/cap rocks and Portland cement	477
Percolation experiments: reservoir and cap rocks	478
MCRTM: limitations and alternative approaches.....	481
MCRTM IN AMD-WATERS.....	482
Interaction between AMD and Portland cement/sedimentary rock	482
Interaction between AMD and limestone	485
Interaction between AMD and DAS: column experiments	486
Interaction between AMD and DAS: field-scale passive remediation treatment	488
CONCLUSIONS AND REMARKS ON FUTURE WORK	491
Conclusions	491
Remarks on future work	492
ACKNOWLEDGMENTS.....	493
REFERENCES	493

16 Industrial Deployment of Reactive Transport Simulation: An Application to Uranium *In situ* Recovery

Vincent Lagneau, Olivier Regnault, Michaël Descostes

INTRODUCTION	499
IN SITU RECOVERY	500
SIMULATION OF IN SITU RECOVERY OPERATIONS	502
Reactive transport model for the KATCO Mine.....	502
SIMULATION TO MINIMIZE ENVIRONMENTAL IMPACT	513
Geochemical mechanisms involved in post acidic ISR mining.....	515
Main geochemical mechanisms involved in environmental impact assessment	519
LESSONS LEARNT FOR INDUSTRIALIZATION.....	525
ACKNOWLEDGMENT.....	525
REFERENCES	525

RiMG Series

HISTORY OF RiMG	529
HOW TO PUBLISH IN RiMG.....	529

