

Contents

Preface *xiii*

Section 1 Chemical Looping Process Concepts *1*

1	The Moving Bed Fuel Reactor Process	3
	<i>Andrew Tong, Mandar V. Kathe, Dawei Wang, and Liang-Shih Fan</i>	
1.1	Introduction	3
1.2	Modes of Moving Bed Fuel Reactor Operation	4
1.2.1	Counter-Current Moving Bed Fuel Reactor:	5
1.2.2	Co-current Moving Bed Fuel Reactor	8
1.3	Chemical Looping Reactor System Design Considerations for Moving Bed Fuel Reactors	10
1.3.1	Mass Balance and Solids Circulation Rate	10
1.3.2	Heat Management	11
1.3.3	Sizing of Reactors	12
1.3.4	Sizing of the Air Reactor	13
1.3.5	Gas Sealing	13
1.3.6	Solids Circulation Control	14
1.3.7	Process Pressure Balance	17
1.4	Counter-Current Moving Bed Fuel Reactor Applications in Chemical Looping Processes	18
1.4.1	Counter-Current Moving Bed Fuel Reactor Modeling	18
1.4.2	Syngas Chemical Looping Process	20
1.4.3	Coal Direct Chemical Looping Process Development	23
1.5	Co-current Moving Bed Fuel Reactor Applications in Chemical Looping Processes	27
1.5.1	Coal to Syngas Chemical Looping Process	27
1.5.2	Methane to Syngas Chemical Looping Process	29
1.5.3	CO ₂ Utilization Potential	31
1.5.4	MTS Modularization Strategy	32
1.6	Concluding Remarks	36
	References	37

2	Single and Double Loop Reacting Systems	41
	<i>Justin Weber</i>	
2.1	Introduction	41
2.2	Reactor Types	43
2.2.1	Fluid Beds	45
2.2.2	Spouted Beds	45
2.2.3	Risers	46
2.3	Gas Sealing and Solids Control	47
2.4	Single Loop Reactors	48
2.5	Double (or More) Loop Reactors	48
2.6	Solid Fuel Reactors	50
2.6.1	Volatiles	50
2.6.2	Carbon Leakage	51
2.6.3	Ash Separation	52
2.7	Pressurized Reactors	52
2.8	Solid Circulation Rate	53
2.9	Lessons Learned	55
2.9.1	Solids and Pressure Balance Control	55
2.9.2	Solids in Reactor Exhaust	56
2.9.3	Condensation in Exhaust	56
2.9.4	Self-Fluidization	57
2.9.5	Cyclones	57
2.10	Summary	58
	Acknowledgements	58
	References	58
3	Chemical Looping Processes Using Packed Bed Reactors	61
	<i>Vincenzo Spallina, Fausto Gallucci, and Martin van Sint Annaland</i>	
3.1	Introduction	61
3.2	Oxygen Carriers for Packed Bed Reactor	63
3.3	Chemical Looping Combustion	65
3.4	Chemical Looping Reforming	73
3.5	Other Chemical Looping Processes	78
3.5.1	Chemical Looping for H ₂ Production	78
3.5.2	Cu–Ca Process for Sorption Enhanced Reforming	84
3.6	Conclusions	86
	Nomenclature	87
	References	88
4	Chemical Looping with Oxygen Uncoupling (CLOU) Processes	93
	<i>Kevin J. Whitty, JoAnn S. Lighty, and Tobias Mattisson</i>	
4.1	Introduction	93
4.2	Fundamentals of the CLOU Process	95
4.2.1	CLOU Oxygen Carriers	97
4.2.2	CLOU Oxygen Carrier Oxidation	98
4.2.3	CLOU Oxygen Carrier Reduction (“Uncoupling”)	99

4.3	CLOU Reactor Design	100
4.3.1	Fuel Flow and Overall Balances	101
4.3.2	Energy Considerations	102
4.3.3	Air Reactor Design	103
4.3.4	Fuel Reactor Design	106
4.3.5	Loop Seal Design	107
4.3.6	Sulfur	109
4.4	Status of CLOU Technology Development	110
4.4.1	Laboratory-Scale CLOU Testing	110
4.4.2	Development-Scale and Pilot-Scale Systems	111
4.5	Future Development of CLOU Technology	118
	References	119
5	Pressurized Chemical Looping Combustion for Solid Fuel	123
	<i>Liangyong Chen, Zhen Fan, Rui Xiao, and Kunlei Liu</i>	
5.1	Introduction	123
5.2	Coal-Based Pressurized Chemical Looping Combustion Combined Cycle	124
5.2.1	Concept	124
5.2.2	Process of the Direct Coal-Fueled PCLC Developed by UK-CAER	125
5.2.3	Process of the Direct Coal-Fueled PCLC at SEU, China	127
5.3	Fundamentals and Experiments of Pressurized Chemical Looping Combustion	128
5.3.1	Transient Oxidation of Magnetite to Hematite in PCLC	128
5.3.2	The Solid Behaviors in the Solid-Fueled PCLC (Fuel Reactor Side)	129
5.3.2.1	Materials	129
5.3.2.2	Experiment Setup	130
5.3.2.3	In situ Gasification	133
5.3.2.4	Combustion Efficiency	136
5.4	Direct Coal-Fueled PCLC Demonstration in Laboratory Scale	139
5.4.1	100 kW _{th} PCLC Facility at SEU, China	139
5.4.2	50 kW _{th} PCLC Unit at UK-CAER	142
5.5	Tech-economic Analysis	143
5.5.1	Technical Performance Evaluation on the Direct Coal-Fueled PCLC-CC	143
5.5.1.1	Combined Cycle	145
5.5.1.2	PCLC Unit	145
5.5.1.3	Physical Properties	145
5.5.1.4	Case Study	146
5.5.1.5	Optimization of Plant Configuration	148
5.5.2	Performance of the UK-CAER's PCLC-CC Plant	148
5.6	Technical Gaps and Challenges	155
	References	157

Section 2 Oxygen Carriers 159

- 6 Regenerable, Economically Affordable Fe_2O_3 -Based Oxygen Carrier for Chemical Looping Combustion 161**
Hanjing Tian, Ranjani Siriwardane, Esmail R. Monazam, and Ronald W. Breault
- 6.1 Introduction 161
 - 6.2 Primary Oxide Selection 162
 - 6.3 Supported Single Oxides 166
 - 6.4 Natural Oxide Ores 170
 - 6.5 Supported Binary Oxides System 173
 - 6.5.1 Thermodynamic Analysis of $\text{CuO-Fe}_2\text{O}_3$ Phases 173
 - 6.5.2 Decomposition–Oxidation Cycle of Chemical Looping Oxygen Uncoupling 174
 - 6.5.3 Coal Chemical Looping Combustion 174
 - 6.5.4 Chemical Looping Combustion with Methane as Fuel 177
 - 6.5.5 Bulk Phase and Oxidation State Analysis of Mixed $\text{CuO-Fe}_2\text{O}_3$ System 180
 - 6.5.6 Synergetic Reactivity–Structure of $\text{CuO-Fe}_2\text{O}_3$ Oxygen Carriers 182
 - 6.6 Kinetic Networks of Fe_2O_3 -based Oxygen Carriers 185
 - 6.7 50-kW_{th} Methane/Air Chemical Looping Combustion Tests 191
- References 195
- 7 Oxygen Carriers for Chemical-Looping with Oxygen Uncoupling (CLOU) 199**
Tobias Mattisson and Kevin J. Whitty
- 7.1 Introduction 199
 - 7.2 Thermodynamics of CLOU 202
 - 7.2.1 Equilibrium Partial Pressure of O_2 202
 - 7.2.2 Thermal Considerations 207
 - 7.3 Overview of Experimental Investigations of CLOU Materials 208
 - 7.3.1 Copper Oxide 209
 - 7.3.2 Combined and Mixed Oxides 210
 - 7.3.3 Naturally Occurring Oxygen Carriers 216
 - 7.4 Kinetics of Oxidation and Reduction of Oxygen Carriers in CLOU 217
 - 7.5 Conclusions 219
- Acknowledgment 219
 References 220
- 8 Mixed Metal Oxide-Based Oxygen Carriers for Chemical Looping Applications 229**
Fanxing Li, Nathan Galinsky, and Arya Shafieharhood
- 8.1 Overview 229
 - 8.2 Mixed Oxides for Chemical Looping with Oxygen Uncoupling (CLOU) 232

8.3	Mixed Oxides for iG-CLC	235
8.4	Mixed Oxides for Chemical Looping Reforming (CLR)	241
8.4.1	Chemical Looping Reforming	241
8.4.2	Monometallic Redox Catalysts for CLR	242
8.5	Redox Catalyst Improvement Strategies	244
8.6	Mixed Oxides for Other Selective Oxidation Applications	247
8.6.1	Oxidative Coupling of Methane	248
8.6.2	Oxidative Dehydrogenation (ODH) of Ethane	249
8.7	Toward Rationalizing the Design of Mixed Metal Oxides	250
8.8	Future Directions	251
	References	252
9	Oxygen Carrier Structure and Attrition	263
	<i>Nathan Galinsky, Samuel Bayham, Esmail Monazam, and Ronald W. Breault</i>	
9.1	Introduction	263
9.2	Oxygen Carrier Structure	264
9.2.1	Unsupported Oxygen Carriers	264
9.2.1.1	Surface	264
9.2.1.2	Structure	266
9.2.1.3	Gas Pores and Diffusion	269
9.2.1.4	Ilmenite	270
9.2.2	Supported Oxygen Carriers	271
9.2.2.1	Copper Oxides	271
9.2.2.2	Iron Oxides	272
9.3	Attrition	275
9.3.1	Sources of Attrition	276
9.3.2	Solids Properties Relevant to Attrition	278
9.3.2.1	Hardness	279
9.3.2.2	Fracture Toughness	281
9.3.3	Mechanistic Modeling of Attrition	283
9.3.3.1	Attrition due to Wear (Abrasion)	283
9.3.3.2	Impact Attrition	285
9.4	Attrition Modeling	285
9.4.1	Unsteady-State Models	286
9.4.2	Steady-State Models	287
9.4.3	System Modeling	288
9.5	Experimental Testing	289
9.5.1	Nanoindentation	289
9.5.2	Fluidized Beds	291
9.5.3	Impact Testing	292
9.5.4	Jet Cup	293
	References	295

Section 3 Commercial Design Studies of CLC Systems 303

- 10 Computational Fluid Dynamics Modeling and Simulations of Fluidized Beds for Chemical Looping Combustion 305**
Subhodeep Banerjee and Ramesh K. Agarwal
 - 10.1 Introduction 305
 - 10.2 Reactor-Level Simulations of CLC Using CFD 308
 - 10.3 Governing Equations 310
 - 10.4 Eulerian–Lagrangian Simulation of a Spouted Fluidized Bed in a CLC Fuel Reactor with Chemical Reactions 313
 - 10.5 Spouted Fluidized Bed Simulation Results 316
 - 10.6 Eulerian–Lagrangian Simulation of a Binary Particle Bed in a Carbon Stripper 319
 - 10.7 Binary Particle Bed Simulation Results 324
 - 10.8 Summary and Conclusions 328
 - References 328
- 11 Calcium- and Iron-Based Chemical Looping Combustion Processes 333**
Robert W. Stevens Jr., Dale L. Keairns, Richard A. Newby, and Mark C. Woods
 - 11.1 Introduction 333
 - 11.2 CLC Plant Design, Modeling, and Cost Estimation Bases 334
 - 11.2.1 Design Basis 334
 - 11.2.2 Cost Estimation Basis 335
 - 11.2.3 Reactor Modeling Basis 336
 - 11.3 Chemical Looping Combustion Reference Plant Descriptions 337
 - 11.3.1 General CLC Power Plant Configuration 338
 - 11.3.2 Reference Plant Stream Conditions 341
 - 11.4 Chemical Looping Combustion Reference Plant Performance 342
 - 11.5 Chemical Looping Combustion Reference Plant Cost 352
 - 11.6 Chemical Looping Combustion Reference Plant Performance and Cost Sensitivities 360
 - 11.6.1 Reactor Temperature Sensitivity 362
 - 11.6.2 Reactor Velocity Sensitivity 365
 - 11.6.3 Carbon Gasification Efficiency Sensitivity 367
 - 11.6.4 Reducer Oxygen Carrier Conversion Sensitivity 368
 - 11.6.5 COE Sensitivity to Oxygen Carrier Makeup Rate and Price 370
 - 11.6.6 COE Sensitivity to Char–Oxygen Carrier Separator Cost 371
 - 11.7 Summary and Conclusions 372
 - References 375
- 12 Simulations for Scale-Up of Chemical Looping with Oxygen Uncoupling (CLOU) Systems 377**
JoAnn S. Lighty, Zachary T. Reinking, and Matthew A. Hamilton
 - 12.1 Introduction 377
 - 12.2 Process Modeling 377
 - 12.2.1 Background 377
 - 12.2.2 Aspen Plus Modeling 378
 - 12.2.3 Other Approaches to Material and Energy Balance Determinations 383

12.2.4	Autothermal Operation	385
12.2.5	Using Process Modeling for Steam Production Estimates	385
12.2.6	Summary	386
12.3	Computational Fluid Dynamic Simulations	387
12.3.1	Background	387
12.3.2	Summary of the Literature	388
12.3.3	Conclusions	394
	References	394

Section 4 Other Chemical Looping Processes 397

13	Calcium Looping Carbon Capture Process	399
	<i>Yiang-Chen Chou, Wan-Hsia Liu, and Heng-Wen Hsu</i>	
13.1	Introduction	399
13.1.1	Fundamental Principles of Calcium Looping Process	399
13.1.2	Thermodynamics and Reaction Equilibrium of CaO and CaCO ₃	402
13.2	Current Status of Calcium Looping Process	404
13.2.1	Kilowatt-Scale Calcium Looping Facility	404
13.2.2	Megawatt-Scale Calcium Looping Plant	410
13.3	Strategies for Enhancing Sorbent Recyclability and Activity	415
13.3.1	Synthesis of CaO Sorbent from Inorganic or Organometallic Precursors	417
13.3.2	Incorporation of Dopant or Inert Stabilizer with Calcium-Based Sorbents	418
13.3.3	Sorbent Reactivation Through Additional Processing	423
	References	428
14	Chemical Looping of Low-Cost MgO-Based Sorbents for CO₂ Capture in IGCC	435
	<i>Hamid Arastoopour and Javad Abbasian</i>	
14.1	Introduction	435
14.2	MgO-Based Sorbent	438
14.3	Reaction Model for Carbon Capture and Regeneration	443
14.4	CFD Simulations of the Regenerative Carbon Dioxide Capture Process	447
14.4.1	Two-dimensional Simulation of the Regenerator and the Carbonator in the CFB Loop	447
14.4.2	Three-dimensional Simulation of Carbon Capture and Regeneration in the Absorber and Regenerator Reactors	450
14.5	Preliminary Economic Assessment	452
	Acknowledgment	457
	References	457