# Contents

Preface xiii

# Section 1 Chemical Looping Process Concepts 1

- 1 The Moving Bed Fuel Reactor Process 3
  - Andrew Tong, Mandar V. Kathe, Dawei Wang, and Liang-Shih Fan

|v

- 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<sub>2</sub> Utilization Potential *31*
- 1.5.4 MTS Modularization Strategy 32
- 1.6 Concluding Remarks 36 References 37

vi

Contents	
2	Single and Double Loop Reacting Systems 41 Justin Weber
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
	Vincenzo Spallina, Fausto Gallucci, and Martin van Sint Annaland
3.1	Introduction 61

- Oxygen Carriers for Packed Bed Reactor 63 3.2
- 3.3 Chemical Looping Combustion 65
- 3.4 Chemical Looping Reforming 73
- 3.5 Other Chemical Looping Processes 78
- Chemical Looping for H<sub>2</sub> Production 78 3.5.1
- 3.5.2 Cu–Ca Process for Sorption Enhanced Reforming 84
- 3.6 Conclusions 86 Nomenclature 87 References 88

#### Chemical Looping with Oxygen Uncoupling (CLOU) 4 **Processes** 93

Kevin J. Whitty, JoAnn S. Lighty, and Tobias Mattisson

- 4.1 Introduction 93
- 4.2 Fundamentals of the CLOU Process 95
- 4.2.1CLOU Oxygen Carriers 97
- 4.2.2 CLOU Oxygen Carrier Oxidation 98
- CLOU Oxygen Carrier Reduction ("Uncoupling") 4.2.3 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 Liangyong Chen, Zhen Fan, Rui Xiao, and Kunlei Liu

- 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<sub>th</sub> PCLC Facility at SEU, China 139
- 5.4.2 50 kW<sub>th</sub> 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 <sub>2</sub> O <sub>3</sub> -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 CuO– $Fe_2O_3$ 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 CuO–Fe <sub>2</sub> O <sub>3</sub>
	System 180
6.5.6	Synergetic Reactivity–Structure of CuO–Fe <sub>2</sub> O <sub>3</sub> Oxygen Carriers 182
6.6	Kinetic Networks of $Fe_2O_3$ -based Oxygen Carriers 185
6.7	50-kW <sub>th</sub> 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	Tobias Mattisson and Kevin J. Whitty Introduction 199
7.1 7.2	Tobias Mattisson and Kevin J. Whitty Introduction 199 Thermodynamics of CLOU 202
7.1 7.2 7.2.1	Tobias Mattisson and Kevin J. WhittyIntroduction199Thermodynamics of CLOU202Equilibrium Partial Pressure of $O_2$ 202
7.1 7.2 7.2.1 7.2.2	Tobias Mattisson and Kevin J. WhittyIntroduction 199Thermodynamics of CLOU 202Equilibrium Partial Pressure of $O_2$ 202Thermal Considerations 207
7.1 7.2 7.2.1 7.2.2 7.3	Tobias Mattisson and Kevin J. WhittyIntroduction 199Thermodynamics of CLOU 202Equilibrium Partial Pressure of $O_2$ 202Thermal Considerations 207Overview of Experimental Investigations of CLOU Materials 208
7.1 7.2 7.2.1 7.2.2 7.3 7.3.1	Tobias Mattisson and Kevin J. WhittyIntroduction 199Thermodynamics of CLOU 202Equilibrium Partial Pressure of $O_2$ 202Thermal Considerations 207Overview of Experimental Investigations of CLOU Materials 208Copper Oxide 209
7.1 7.2 7.2.1 7.2.2 7.3 7.3.1 7.3.2	Tobias Mattisson and Kevin J. WhittyIntroduction 199Thermodynamics of CLOU 202Equilibrium Partial Pressure of $O_2$ 202Thermal Considerations 207Overview of Experimental Investigations of CLOU Materials 208Copper Oxide 209Combined and Mixed Oxides 210
7.1 7.2 7.2.1 7.2.2 7.3 7.3.1 7.3.2 7.3.3	Tobias Mattisson and Kevin J. WhittyIntroduction 199Thermodynamics of CLOU 202Equilibrium Partial Pressure of $O_2$ 202Thermal Considerations 207Overview of Experimental Investigations of CLOU Materials 208Copper Oxide 209Combined and Mixed Oxides 210Naturally Occurring Oxygen Carriers 216
7.1 7.2 7.2.1 7.2.2 7.3 7.3.1 7.3.2 7.3.3 7.4	Tobias Mattisson and Kevin J. WhittyIntroduction199Thermodynamics of CLOU202Equilibrium Partial Pressure of $O_2$ 202Thermal Considerations207Overview of Experimental Investigations of CLOU Materials208Copper Oxide209Combined and Mixed Oxides210Naturally Occurring Oxygen Carriers216Kinetics of Oxidation and Reduction of Oxygen Carriers in
7.1 7.2 7.2.1 7.2.2 7.3 7.3.1 7.3.2 7.3.3 7.4	Tobias Mattisson and Kevin J. WhittyIntroduction 199Thermodynamics of CLOU 202Equilibrium Partial Pressure of $O_2$ 202Thermal Considerations 207Overview of Experimental Investigations of CLOU Materials 208Copper Oxide 209Combined and Mixed Oxides 210Naturally Occurring Oxygen Carriers 216Kinetics of Oxidation and Reduction of Oxygen Carriers inCLOU 217
<ul> <li>7.1</li> <li>7.2</li> <li>7.2.1</li> <li>7.2.2</li> <li>7.3</li> <li>7.3.1</li> <li>7.3.2</li> <li>7.3.3</li> <li>7.4</li> <li>7.5</li> </ul>	Tobias Mattisson and Kevin J. WhittyIntroduction 199Thermodynamics of CLOU 202Equilibrium Partial Pressure of $O_2$ 202Thermal Considerations 207Overview of Experimental Investigations of CLOU Materials 208Copper Oxide 209Combined and Mixed Oxides 210Naturally Occurring Oxygen Carriers 216Kinetics of Oxidation and Reduction of Oxygen Carriers inCLOU 217Conclusions 219
7.1 7.2 7.2.1 7.2.2 7.3 7.3.1 7.3.2 7.3.3 7.4 7.5	Tobias Mattisson and Kevin J. WhittyIntroduction 199Thermodynamics of CLOU 202Equilibrium Partial Pressure of $O_2$ 202Thermal Considerations 207Overview of Experimental Investigations of CLOU Materials 208Copper Oxide 209Combined and Mixed Oxides 210Naturally Occurring Oxygen Carriers 216Kinetics of Oxidation and Reduction of Oxygen Carriers inCLOU 217Conclusions 219Acknowledgment 219
7.1 7.2 7.2.1 7.2.2 7.3 7.3.1 7.3.2 7.3.3 7.4 7.5	Tobias Mattisson and Kevin J. WhittyIntroduction 199Thermodynamics of CLOU 202Equilibrium Partial Pressure of $O_2$ 202Thermal Considerations 207Overview of Experimental Investigations of CLOU Materials 208Copper Oxide 209Combined and Mixed Oxides 210Naturally Occurring Oxygen Carriers 216Kinetics of Oxidation and Reduction of Oxygen Carriers inCLOU 217Conclusions 219Acknowledgment 219References 220
7.1 7.2 7.2.1 7.2.2 7.3 7.3.1 7.3.2 7.3.3 7.4 7.5	Tobias Mattisson and Kevin J. WhittyIntroduction199Thermodynamics of CLOU202Equilibrium Partial Pressure of $O_2$ 202Thermal Considerations207Overview of Experimental Investigations of CLOU Materials208Copper Oxide209Combined and Mixed Oxides210Naturally Occurring Oxygen Carriers216Kinetics of Oxidation and Reduction of Oxygen Carriers inCLOU217Conclusions219Acknowledgment219References220
<ul> <li>7.1</li> <li>7.2</li> <li>7.2.1</li> <li>7.2.2</li> <li>7.3</li> <li>7.3.1</li> <li>7.3.2</li> <li>7.3.3</li> <li>7.4</li> <li>7.5</li> <li>8</li> </ul>	Tobias Mattisson and Kevin J. WhittyIntroduction 199Thermodynamics of CLOU 202Equilibrium Partial Pressure of O2 202Thermal Considerations 207Overview of Experimental Investigations of CLOU Materials 208Copper Oxide 209Combined and Mixed Oxides 210Naturally Occurring Oxygen Carriers 216Kinetics of Oxidation and Reduction of Oxygen Carriers inCLOU 217Conclusions 219Acknowledgment 219References 220Mixed Metal Oxide-Based Oxygen Carriers for Chemical
<ul> <li>7.1</li> <li>7.2</li> <li>7.2.1</li> <li>7.2.2</li> <li>7.3</li> <li>7.3.1</li> <li>7.3.2</li> <li>7.3.3</li> <li>7.4</li> <li>7.5</li> <li>8</li> </ul>	Tobias Mattisson and Kevin J. WhittyIntroduction 199Thermodynamics of CLOU 202Equilibrium Partial Pressure of O2 202Thermal Considerations 207Overview of Experimental Investigations of CLOU Materials 208Copper Oxide 209Combined and Mixed Oxides 210Naturally Occurring Oxygen Carriers 216Kinetics of Oxidation and Reduction of Oxygen Carriers inCLOU 217Conclusions 219Acknowledgment 219References 220Mixed Metal Oxide-Based Oxygen Carriers for ChemicalLooping Applications 229
<ul> <li>7.1</li> <li>7.2</li> <li>7.2.1</li> <li>7.2.2</li> <li>7.3</li> <li>7.3.1</li> <li>7.3.2</li> <li>7.3.3</li> <li>7.4</li> <li>7.5</li> <li>8</li> </ul>	<td< th=""></td<>
<ul> <li>7.1</li> <li>7.2</li> <li>7.2.1</li> <li>7.2.2</li> <li>7.3</li> <li>7.3.1</li> <li>7.3.2</li> <li>7.3.3</li> <li>7.4</li> <li>7.5</li> <li>8</li> <li>8.1</li> </ul>	Tobias Mattisson and Kevin J. Whitty         Introduction 199         Thermodynamics of CLOU 202         Equilibrium Partial Pressure of O2 202         Thermal Considerations 207         Overview of Experimental Investigations of CLOU Materials 208         Copper Oxide 209         Combined and Mixed Oxides 210         Naturally Occurring Oxygen Carriers 216         Kinetics of Oxidation and Reduction of Oxygen Carriers in         CLOU 217         Conclusions 219         Acknowledgment 219         References 220         Mixed Metal Oxide-Based Oxygen Carriers for Chemical         Looping Applications 229         Fanxing Li, Nathan Galinsky, and Arya Shafieharhood         Overview 229
<ul> <li>7.1</li> <li>7.2</li> <li>7.2.1</li> <li>7.2.2</li> <li>7.3</li> <li>7.3.1</li> <li>7.3.2</li> <li>7.3.3</li> <li>7.4</li> <li>7.5</li> <li>8</li> <li>8.1</li> <li>8.2</li> </ul>	<td< th=""></td<>

#### Contents ix

- 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

Nathan Galinsky, Samuel Bayham, Esmail Monazam, and Ronald W. Breault

- 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

**x** Contents

# 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 Baneriee and Ramesh K. Aaarwal
- 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
	Yiang-Chen Chou, Wan-Hsia Liu, and Heng-We	en Hsu

- 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<sub>3</sub> 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

# 14Chemical Looping of Low-Cost MgO-Based Sorbents for CO2Capture in IGCC435

Hamid Arastoopour and Javad Abbasian

- 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

Index 461