CUTTING-EDGE TECHNOLOGY

KARINE BALLERAT-BUSSEROLLES YING WU JOHN J. CARROLL





Cutting-Edge Technology for Carbon Capture, Utilization, and Storage Scrivener Publishing 100 Cummings Center, Suite 541J Beverly, MA 01915-6106

Advances in Solar Cell Materials and Storage

Series Editors: Nurdan Demirci Sankir and Mehmet Sankir

Scope: Because the use of solar energy as a primary source of energy will exponentially increase for the foreseeable future, this new series on Advances in Solar Cell Materials and Storage will focus on new and novel solar cell materials and their application for storage. The scope of this series deals with the solution-based manufacturing methods, nanomaterials, organic solar cells, flexible solar cells, batteries and supercapacitors for solar energy storage, and solar cells for space.

Submission to the series: Please submit book proposals to Nurdan Sankir at dnurdan@yahoo.com

Publishers at Scrivener Martin Scrivener (martin@scrivenerpublishing.com) Phillip Carmical (pcarmical@scrivenerpublishing.com)

Cutting-Edge Technology for Carbon Capture, Utilization, and Storage

Karine Ballerat-Busserolles, Ying (Alice) Wu and John J. Carroll





This edition first published 2018 by John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA and Scrivener Publishing LLC, 100 Cummings Center, Suite 541J, Beverly, MA 01915, USA © 2018 Scrivener Publishing LLC

For more information about Scrivener publications please visit www.scrivenerpublishing.com.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, except as permitted by law. Advice on how to obtain permission to reuse material from this title is available at http://www.wiley.com/go/permissions.

Wiley Global Headquarters

111 River Street, Hoboken, NJ 07030, USA

For details of our global editorial offices, customer services, and more information about Wiley products visit us at www.wiley.com.

Limit of Liability/Disclaimer of Warranty

While the publisher and authors have used their best efforts in preparing this work, they make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives, written sales materials, or promotional statements for this work. The fact that an organization, website, or product is referred to in this work as a citation and/or potential source of further information does not mean that the publisher and authors endorse the information or services the organization, website, or product may provide or recommendations it may make. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for your situation. You should consult with a specialist where appropriate. Neither the publisher nor authors shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages. Further, readers should be aware that websites listed in this work may have changed or disappeared between when this work was written and when it is read.

Library of Congress Cataloging-in-Publication Data

ISBN 978-1-119-36348-4

Cover image: Tree tops, Schlegelfotos | Dreamstime.com . ${\rm CO}_2$, Ollaweila | Dreamstime.com Cover design by Kris Hackerott

Set in size of 11pt and Minion Pro by Exeter Premedia Services Private Ltd., Chennai, India

Printed in the USA

10 9 8 7 6 5 4 3 2 1

Contents

Pre	eface			XV
Int	rodu	ction		xvii
Pa	Part I: Carbon Capture and Storage			1
1	Car	bon Ca	pture Storage Monitoring ("CCSM")	3
	E.D	. Rode,	L.A. Schaerer, Stephen A. Marinello and	
	<i>G. v</i>	. Hante	elmann	
	1.1	Introd	luction	4
	1.2	State of	of the Art Practice	5
	1.3	Marm	ot's CCSM Technology	6
	1.4	Princi	ples of Information Analysis	10
	1.5	Opera	ting Method	12
	1.6	Instru	mentation and Set up	14
		Abbre	viations	16
		Refere	ences	16
2	Key	Techno	ologies of Carbon Dioxide Flooding	
	and	Storag	e in China	19
	Had	Mingq	iang and Hu Yongle	
	2.1	Backg	round	20
	2.2	Key Te 2.2.1	echnologies of Carbon dioxide Flooding and Storage CO ₂ Miscible Flooding Theory in Continental	21
		222	Sedimentary Reservoirs	21
		2.2.2	and Salt Water Layers	22
		2.2.3	Reservoir Engineering Technology of CO ₂ Flooding and Storage	22
		2.2.4	High Efficiency Technology of Injection and Production for CO_2 Flooding	23

		2.2.5 CO, Long-Dista	nce Pipeline Transportation and	
		Supercritical Inj	ection Technology	23
		2.2.6 Fluid Treatment	and Circulating Gas Injection	
		Technology of C	CO, Flooding	24
		2.2.7 Reservoir Moni	toring and Dynamic Analysis and	
		Evaluation Tech	nology of CO. Flooding	24
	2.3	Existing Problems and	Technical Development Direction	25
		2.3.1 The Vital Comn	unal Troubles & Challenges	25
		2.3.2 Further Orienta	tion of Technology Development	25
3	Maj	ping CCUS Technologi	cal Trajectories	
	and	Business Models: The C	case of CO ₂ -Dissolved	27
	<i>X</i> . C	aliègue, A. Laude and I	N. Béfort	
	3.1	Introduction		27
	3.2	CCS and Roadmaps: Fr	om Expectations to Reality	29
	3.3	CCS Project Portfolio:	Between Diversity and Replication	30
		3.3.1 Demonstration	Process: Between Diversity and	
		Replication		30
		3.3.2 Diversity of the	Current Project Portfolio	32
	3.4	Going Beyond EOR: O	ther Business Models for Storage?	36
		3.4.1 The EOR Legacy		36
		3.4.2 From EOR to a	CCS Wide-Scale Deployment	37
	3.5	Coupling CCS and Geo	thermal Energy: Lessons from	
		the CO ₂ -DISSOLVED I	Project Study	39
		3.5.1 CO_2 -DISSOLVE	D Concept	39
		3.5.2 Techno-Econon	ic Analysis of CO ₂ -DISSOLVED	41
		3.5.3 Business Model	s and the Replication/Diversity	
		Dilemma		42
	3.6	Conclusion		42
		Acknowledgements		43
		References		43
4	Fea	ibility of Ex-Situ Dissol	ution for Carbon Dioxide	
	Seq	iestration		47
	Yur	Leonenko		
	4.1	Introduction		47
	4.2	Methods to Accelerate	Dissolution	50
		4.2.1 In-situ		50
		4.2.2 Ex-situ		52
	4.3	Discussion and Conclu	sions	56
		Acknowledgments		57
		References		57

Contraction	
CONTENTS	V11

Part II: EOR			59
5	CO, Gas Injection as an EOR Technique – Phase Behavior		
	Con	siderations	61
	Henrik Sørensen and Jawad Azeem Shaikh		
	5.1	Introduction	61
	5.2	Features of CO ₂	62
	5.3	Miscible CO ₂ Drive	63
	5.4	Immiscible CO, Drives and Density Effects	68
	5.5	Asphaltene Precipitation Caused by Gas Injection	72
	5.6	Gas Revaporization as EOR Technique	75
	5.7	Conclusions	76
		List of Symbols	76
		References	77
		Appendix A Reservoir Fluid Compositions	
		and Key Property Data	78
_	04		
6	Stuc	ly on Storage Mechanisms in CO ₂ Flooding	0.2
	for	Water-Flooded Abandoned Reservoirs	83
	Rui	Wang, Chengyuan Lv, Yongqiang Tang, Shuxia Zhao,	
	Zen	gmin Lun and Maolei Cui	
	6.1	Introduction	83
	6.2	CO ₂ Solubility in Coexistence of Crude Oil and Brine	85
	6.3	Mineral Dissolution Effect	88
	6.4	Relative Permeability Hysteresis	90
	6.5	Effect of CO_2 Storage Mechanisms on CO_2 Flooding	92
	6.6	Conclusions	93
		References	93
7	The	Investigation on the Key Hydrocarbons of Crude	
,	Oil	Swelling via Supercritical CO	95
	Hai	shui Han Shi Li Yinglong Chen Ke Thang Hongwei Yu	20
	and	Zamin Ii	
	<i>unu</i> 7 1	Letter duction	06
	7.1	Hudrogenhan Selection	90
	7.2	Even aview and Spectron	97
	1.3	Experiment Section	97 07
		7.3.1 Principle	9/
		7.3.2 Apparatus and Samples	99 100
		7.3.5 Experimental Scheme Design	100
		/.3.4 Procedures	100
	1.4	Kesuits and Discussion	101

		7.4.1 Results and Data Processing	101
		7.4.2 Volume Swelling Influenced by the Hydrocarbon	
		Property	103
		7.4.3 A New Parameter of Molar Density	
		for Evaluating Hydrocarbon Volume Swelling	104
		7.4.4 Advantageous Hydrocarbons	105
	7.5	Conclusions	109
		Acknowledgments	109
		Nomenclature	109
		References	110
8	Por	e-Scale Mechanisms of Enhanced Oil Recovery by CO	
	Inje	ection in Low-Permeability Heterogeneous Reservoir	113
	Ze-1	min Ji, Shi Li and Xing-longChen	
	8.1	Introduction	114
	8.2	Experimental Device and Samples	114
	8.3	Experimental Procedure	115
		8.3.1 Experimental Results	117
	8.4	Quantitative Analysis of Oil Recovery in	
		Different Scale Pores	118
	8.5	Conclusions	120
		Acknowledgments	120
		References	120
Pa	rt III	: Data – Experimental and Correlation	123
9	Exp	perimental Measurement of CO, Solubility in a 1 mol/kgw	r
	CaC	Cl, Solution at Temperature from 323.15 to 423.15 K and	
	Pres	ssure up to 20 MPa	125
	<i>M</i> . <i>I</i>	Poulain, H. Messabeb, F. Contamine, P. Cézac, J.P. Serin,	
	J.C.	Dupin and H. Martinez	
	9.1	Introduction	125
	9.2	Literature Review	126
	9.3	Experimental Section	127
		9.3.1 Chemicals	127
		9.3.2 Apparatus	128
		9.3.3 Operating Procedure	128
		9.3.4 Analysis	129
	9.4	Results and Discussion	130
	9.5	Conclusion	130
		Acknowledgments	132
		References	132

10	Dete	rmination of Dry-Ice Formation during the	
	Dep	ressurization of a CO ₂ Re-Injection System	135
	J.A.	Feliu, M. Manzulli and M.A. Alós	
	10.1	Introduction	136
	10.2	Thermodynamics	137
	10.3	Case Study	139
		10.3.1 System Description	139
		10.3.2 Objectives	141
		10.3.3 Scenarios	141
		10.3.4 Simulation Runs Conclusions	145
	10.4	Conclusions	146
11	Phas	e Equilibrium Properties Aspects of CO ₂ and	
	Acid	Gases Transportation	147
	<i>A. C</i>	hapoy and C. Coquelet	
	11.1	Introduction	148
		11.1.1 State of the Art and Phase Diagrams	150
	11.2	Experimental Work and Description of	
		Experimental Setup	151
	11.3	Models and Correlation Useful for the Determination	
		of Equilibrium Properties	157
	11.4	Presentation of Some Results	159
	11.5	Conclusion	165
		Acknowledgments	166
		References	166
12	Ther	modynamic Aspects for Acid Gas Removal	
	fron	n Natural Gas	169
	Tian	yuan Wang, Elise El Ahmar and Christophe Coquelet	
	12.1	Introduction	169
	12.2	Thermodynamic Models	171
	12.3	Results and Discussion	173
		12.3.1 Hydrocarbons and Mercaptans Solubilities	
		in Aqueous Alkanolamine Solution	173
		12.3.2 Acid Gases (CO_2/H_2S) Solubilities in Aqueous	
		Alkanolamine Solution	174
		12.3.3 Multi-component Systems Containing CO_2 -H ₂ S-	
		Alkanolamine-Water-Methane-Mercaptan	177
	12.4	Conclusion and Perspectives	178
		Acknowledgements	179
		Reterences	179

13	Spee	ed of Sound Measurements for a CO ₂ Rich Mixture	181	
	P. Ahmadi and A. Chapoy			
	13.1	Experimental Section	182	
		13.1.1 Material	182	
		13.1.2 Experimental Setup	182	
	13.2	Results and Discussion	183	
	13.3	Conclusion	184	
		References	185	
14	Mut	ual Solubility of Water and Natural Gas with Different		
	CO_2	Content	187	
	H.M	I. Tu, P. Guo, J.F. Du, Shao-fei Wang, Ya-ling Zhang,		
	Yan	-kui Jiao and Zhou-hua Wang		
	14.1	Introduction	188	
	14.2	Experimental	190	
		14.2.1 Materials	190	
		14.2.2 Experimental Apparatus	190	
		14.2.3 Experimental Procedures	192	
	14.3	Thermodynamic Model	193	
		14.3.1 The Cubic-Plus-Association Equation of State	193	
		14.3.2 Parameterization of the Model	195	
	14.4	Results and Discussion	196	
		14.4.1 Phase Behavior of CO_2 -Water	196	
		14.4.2 The Mutual Solubility of Water-Natural Gas	198	
	14.5	Conclusion	207	
		Acknowledgement	211	
		References	211	
15	Effe	ct of SO ₂ Traces on Metal Mobilization in CCS	215	
	A. M	lartínez-Torrents, S. Meca, F. Clarens, M. Gonzalez-Riu		
	and	M. Rovira		
	15.1	Introduction	215	
	15.2	Experimental	216	
		15.2.1 Sample Preparation	216	
		15.2.1.1 Sandstone	216	
		15.2.1.2 Brine	217	
		15.2.2 Experimental Set-up	217	
		15.2.3 Experimental Methodology	217	
	15.3	Results and Discussion	219	
		15.3.1 Major Components	219	

	15.3.2 Trace Metals	222
	15.3.2.1 Strontium	224
	15.3.2.2 Manganese	225
	15.3.2.3 Copper	226
	15.3.2.4 Zinc	226
	15.3.2.5 Vanadium	227
	15.3.2.6 Lead	227
	15.3.3 Metal Mobilization	228
	15.4 Conclusions	230
	Acknowledgements	231
	References	232
16	Experiments and Modeling for CO ₂ Capture Processes	
	Understanding	235
	Yohann Coulier, William Ravisy, J-M. Andanson,	
	Jean-Yves Coxam and Karine Ballerat-Busserolles	
	16.1 Introduction	236
	16.2 Chemicals and Materials	240
	16.3 Vapor-Liquid Equilibria	241
	16.3.1 Experimental VLE of Pure Amine	241
	16.3.2 Experimental VLE of {Amine – H_2O } System	243
	16.3.3 Modeling VLE	243
	16.4 Speciation at Equilibrium	245
	16.4.1 Equilibrium Measurements 1H and 13C NMR	246
	16.4.2 Modeling of Species Concentration	249
	Acknowledgment	252
	References	252
Par	t IV: Molecular Simulation	255
17	Kinetic Monte Carlo Molecular Simulation of Chemical	
	Reaction Equilibria	257
	Braden D. Kelly and William R. Smith	
	References	261
18	Molecular Simulation Study on the Diffusion Mechanism	
	of Fluid in Nanopores of Illite in Shale Gas Reservoir	263
	P. Guo, M.H. Zhang and H.M. Tu	
	18.1 Introduction	264
	18.2 Models and Simulation Details	265
	18.2.1 Models and Simulation Parameters	265
	18.2.2 Data Processing and Computing Methods	266

	18.3 Results and Discussion	268
	18.3.1 Variation Law of Self Diffusion Coefficient	268
	18.3.2 Density Distribution	270
	18.3.3 Radial Distribution Function	271
	18.4 Conclusions	273
	Acknowledgements	274
	References	275
19	Molecular Simulation of Reactive Absorption of CO ₂	
	in Aqueous Alkanolamine Solutions	277
	Weikai Qi and William R. Smith	
	References	279
Pa	rt V: Processes	281
20	CO ₂ Capture from Natural Gas in LNG Production.	
	Comparison of Low-Temperature Purification Processes	
	and Conventional Amine Scrubbing	283
	Laura A. Pellegrini, Giorgia De Guido, Gabriele Lodi	
	and Saeid Mokhatab	
	20.1 Introduction	284
	20.2 Description of Process Solutions	286
	20.2.1 The Ryan-Holmes Process	288
	20.2.2 The Dual Pressure Low-Temperature	
	Distillation Process	290
	20.2.3 The Chemical Absorption Process	292
	20.3 Methods	295
	20.4 Results and Discussion	298
	20.5 Conclusions	303
	Nomenclature	304
	Abbreviations	304
	Symbols	305
	Subscripts	305
	Superscripts	306
	Greek Symbols	306
	References	306
21	CO ₂ Capture Using Deep Eutectic Solvent and Amine (MEA)	
	Solution	309
	Mohammed-Ridha Mahi, Ilham Mokbel, Latifa Négadi	
	and Jacques Jose	
	21.1 Experimental Section	309

21.2	Results and Discussion	310
	21.2.1 Validation of the Experimental Method	310
	21.2.2 Solubility of CO ₂ in the Solvent DES/MEA	311
	21.2.3 Solubility of CO_2^2 – Comparison Between	
	DES + MEA and DES Solvent	313
	21.2.4 Solubility of CO_2 – Comparison Between	
	$(DES + MEA)$ and $(H_2O + MEA)$ Solvent	313
21.5	Conclusion	315
	References	315
22 The 1	Impact of Thermodynamic Model Accuracy on Sizing	
and	Operating CCS Purification and Compression Units	317
S. La	isala, R. Privat and JN. Jaubert	
22.1	Introduction	318
22.2	Thermodynamic Systems in CCUS Technologies	319
	22.2.1 Compositional Characteristics of CO_2	
	Captured Flows	319
	22.2.2 Post-Combustion	320
	22.2.3 Oxy-Fuel Combustion	321
	22.2.4 Pre-Combustion	324
22.3	Operating Conditions of Purification and	
	Compression Units	329
22.4	Quality Specifications of CO ₂ Capture Flows	332
22.5	Cubic Equations of State for CCUS Fluids	334
22.6	Influence of EoS Accuracy on Purification and	
	Compression Processes	340
22.7	Purification by Liquefaction	340
22.8	Purification by Stripping	347
22.9	Compression	351
22.10) Conclusions	354
	Nomenclature and Acronyms	355
	References	357
Index		361

Preface

With the ratification of the Paris Agreement, we are now committing ourselves to achieving a temperature target of below 2°C, which represents a significant mitigation challenge. Going below 1.5 °C increases immensely this mitigation challenge. CCS has been identified as a key mitigation technology option and the IPCC 5th Assessment report showed that the least cost mitigation portfolio needs to include CCS. Unfortunately CCS has not been deployed as quickly as expected: the current global CO₂ capture and storage capacity is only 40 million tons per year, which is a tiny fraction of the 36 billion tons per year of CO₂ emitted around the globe. Nevertheless, important demonstration projects are emerging such as Boundary Dam & Quest projects in Canada and Petranova project in Texas. In Norway, three projects have also been preselected for a demonstrator to be launched in 2022.

The application of CCS to industrial sectors other than power (e.g., steel, cement, refining) is expected to deliver half of the global emissions reduction from CCS by 2050. In the near future, these industrial applications will open up, especially in Europe; there will be new opportunities and avenues for CCS that can accelerate its deployment. For these process industries, no possible alternatives for CO₂ mitigation exist that could be new energies for fossil fuels.

In North America, Enhanced Oil Recovery (EOR) is the main application considered as it allows CO_2 valorization. EOR contributes also to GHG mitigation as 40 to 50 % of the injected CO_2 remains stored. At the end of the oil production, it is also possible to continue CO_2 injection to store it in the depleted reservoirs. CO_2 -EOR has been used for over 40 years, particularly in West Texas and New Mexico.

In Europe and China CO_2 EOR will also be considered but it has to be deployed, and storage in deep saline aquifers might also play an important role when a CCS business model exists, which needs to have legislation more operative, a real incentive to finance the first CCS demonstrators, and finally a CO₂ price higher than 50 \notin /t and not at 5 \notin /t as today.

 $\rm CO_2$ Utilization may also be considered for specific applications but it will not play an important role.

A lot of research efforts have still to be made to develop the affordable technologies allowing generalization of CO_2 capture facilities throughout the world. Amine processes have been used since 1920 in order to decarbonize natural gas but progress has to be made in reducing CO_2 capture cost, which represents 85% of the CCS final cost.

This book contains the papers presented during the CETCCUS conference which was hosted by ICCF in Clermont-Ferrand from 25th to 27th September 2017. This conference was dedicated to CO_2 Capture Utilization and Storage technologies.

We hope that it will enable as many people as possible to have a better understanding of the mechanisms involved as well as the technological and economic challenges still to be taken up to deploy CCUS technologies around the globe.

> **Paul Broutin** CO₂ Capture Manager IFP Energies nouvelles Solaize, France

Introduction

A conference with the name Cutting Edge Technology for Carbon Capture, Utilization, and Storage (CETCCUS) was held in Clermont-Ferrand, France, in September 2017. The conference attract both academic, industry, and government representatives to discuss the latest technology related to carbon capture, utilization, and storage (CCUS).

Presenters came from France, Spain, Switzerland, Italy, Denmark, the United Kingdom, Canada and China with co-authors from several other countries, showing the worldwide interest in this topic. This book is a collection of the papers presented at the conference.

The tone for the meeting was set by our keynote speaker M. Paul Broutin and his comments are briefly summarized in the preface to this volume.

Many excellent papers were presented that included new relevant experimental data, models for the data, molecular simulations, new processes for removing carbon dioxide from gas streams, and discussion of enhanced oil recovery (EOR), which is still the main method for utilization of CO_2 . This book is a collection of the papers from the conference. We believe these papers shows the quality of the research in this field.

We were pleased to have had several students present at the conference. And we would like to note Ms. Marie Poulain (Chapter 9) who was awarded the ProSim Prize for Best Student Paper.

Finally, we would like to thank our sponsors: Axelera, Gas Liquids Engineering. ProSim, Swagelok, Club CO₂, Société française de physique, Société Chimique de France, The National Center for Scientific Research, Université Clermont Auvergne, Clermont-Ferrand Chemistry Institute, Auvergne Rhône Alpes Region, and The City of Clermont-Ferrand.

> **K.B., J.J.C., & Y.W.** September 2017

Part I CARBON CAPTURE AND STORAGE

Carbon Capture Storage Monitoring ("CCSM")

E.D. Rode^{1,*}, L.A. Schaerer¹, Stephen A. Marinello¹ and G. v. Hantelmann²

¹Marmot Passive Monitoring Technologies SA, Morges, Switzerland ²Ronnenberg, Germany

Abstract

It is a matter of fact that the manmade emission of CO_2 is contributing to global warming. In the public discussion, the CO_2 emission seems to be attributed mostly to energy generation – this is only partially true because the emissions from other industrial activities make significant contributions too.

In the light of current knowledge and technical developments the only way to reduce those emissions is to separate CO_2 and store it underground. There is no other solution – and this solution is technically possible. At least in Europe public awareness is considering CO_2 storage as a "Final Waste Material Deposit" similar to a deposit of "Nuclear Waste".

The main technical concern for such an underground storage is that no adequate monitoring method is available to permanently monitor the fluid behavior in the underground storage.

Therefore the public awareness is afraid of unexpected and uncalculated HAZARDS which may cause severe damage in the storage environment.

This paper describes a method to control the storage environment and the dynamic behavior of the fluids in storage. This method uses the omnipresent seismic background noise as a tool for monitoring the underground storage, regarded as a Technical Dynamic System.

The proposed method is based on the buildup of a "Forensic Event Space" calculating the near future of the system. The method can be used as a HAZARD assessment system for storage operations.

Keywords: permanent monitoring, Forensic Event Space

^{*}Corresponding author: paul.rode@passive-monitoring.com

Karine Ballerat-Busserolles, Ying Wu, and John J. Carroll (eds.) Cutting-Edge Technology for Carbon Capture, Utilization, and Storage, (3–18) © 2018 Scrivener Publishing LLC

1.1 Introduction

One of the key problems of our industrialized civilization and social economic systems is the destabilization of the biosphere by manmade emissions, which can no more be controlled and absorbed by natural processes.

Increasing emission of carbon dioxide (CO_2) has a major impact on global warning.

Significantly large quantities are created as exhaust gases from global industrial production – such as cement and steel industries, but mainly from fossil fuel driven electric power plants – but also as associated gas from oil and gas production. CO_2 has not only a negative impact on the environment as the so-called "Greenhouse Gas" – CO_2 at higher concentration is directly "lethal" for the human body.

The increase of energy consumption goes hand in hand with the increase of CO_2 emissions, and especially the decision to build more and more coal power plants is in contradiction to the overall demand to reduce CO_2 emissions.

Therefore – to reduce the emission of CO_2 into the atmosphere – the industry is aiming for a method to extract CO_2 from the exhaust gases and capture it in large quantities in artificial storages in subsurface geological formations. Such underground storages are already geologically very well known and sometimes applied as storages for natural gas in subsurface underground formations, e.g., saline aquifers. The problem with such natural storages even for temporary deposition of waste and toxic gases is to take sufficient measures to secure the stability of such storages and to avoid uncontrolled "escapes" of the captured media. The "sealing conditions" of such natural/artificial formations have to be properly investigated and determined but the most important tool to secure uncontrolled events is to install a powerful technical control and monitoring system which can help to identify hazardous and unpredicted events and predict deviations from normal operating conditions – in advance: An "Early Warning System" and "Risk Assessement System" for hazardous waste disposals.

The problem with those storages is the uncertainty of the cap rocks and the uncertainty of the geological and lithological sealing boundaries of the storage as well as the uncertainty of the inter-reactivity of different CO_2 phases with boundary spaces (Figure 1.1).

To minimize the risk of unpredictable events it is mandatory to develop methods which are able to monitor the flow and behavior of fluids inside the Carbon Capture Storage as well as lithological changes and induced boundary changes.



Figure 1.1 Phase Diagram CO₂. (Source: www.chemistry-blog.com).

In the public awareness, an artificial Carbon Capture Storage in subsurface geological formations is considered as "Waste Disposal of hazardous material" and consequently there is a very high degree of resistivity against such underground carbon capture storages – especially "not in my backyard". To achieve public acceptance, it is at least necessary to apply transparent monitoring technologies to reduce the uncertainty about the behavior of the technical storage conditions and the dynamics of the stored media.

Such method must be able to monitor any kind of "change of conditions" over the entire storage space and its boundaries continuously and permanently during the whole lifetime of the storage.

There is a fundamental difference – philosophically – in monitoring the fluid behavior in a tank or even in an oil reservoir – where operating parameters are monitored and measured – and monitoring the fluid behavior in an artificial storage of hazardous waste material where it is not enough to monitor the prevailing operating parameters because what actually has to be monitored is the "unpredictable" since it is assumed that something might happen beyond the operating parameters; something neither expected nor predicted. Nobody knows what will happen, or how/ when/where, but everybody expects that something could happen.

1.2 State of the Art Practice

Currently in Carbon Capture Storages observation wells are drilled mainly for permanent observation purposes and they are equipped with downhole sensors to measure pressure, temperature and other physical, chemical and electrical properties of the media surrounding the borehole.

6 CUTTING-EDGE TECHNOLOGY FOR CCUS

From the total data and gradients relating to all these parameters, models of the behavior of the stored media inside the storage are derived – and of course such models do not cater for the "unpredictable", which after all is the reason for monitoring and modeling.

These methods in connection with modeling techniques are very well known and very useful in application as long as the storage is a known system with stable physical and chemical properties and well defined stable boundary conditions.

A Carbon Capture Storage however represents a spatial distributed "dynamic system" with uncertain boundary conditions and the "test well monitoring concept" alone does not meet the given requirements.

The results of such monitoring methods are only reliable as long as the storage mechanism in the entire corpus behave "as modeled" but they are not able to detect phenomena beyond the models. For this reason, the classical parametric methods satisfy the control of "storage tank" working conditions but they are not suited to measure or predict the "unpredicted". Also the number of test wells is limited and so is the spatial resolution.

Another class of methods can be seen in ground penetrating radar or sonar systems but unfortunately the penetration depth and spectral properties of such methods are not suited for such applications.

A further method to identify structural and impedance changes could be seen in the application of time lapse reflection seismic (4D) – however, the penetration features and also the limited information as well as the requisite controlled source do not allow this method as a permanent and continuous monitoring tool for Carbon Capture Storages – not to mention the operation costs of such a method.

1.3 Marmot's CCSM Technology

As a solution for a permanent Carbon Capture Storage Monitoring system Marmot's CCSM provides a technical method which allows monitoring the fluid behavior inside the storage as well as structural changes using "noninvasive" technical means from the surface without penetrating mechanically into the storage space itself.

Two conditions are fundamental for such a monitoring system:

• The surveillance of the storage must be permanent and continuous and for any kind of measurement this needs a permanently and continuously operating signal source which should have no extra impact on the environment. • The source signal must have the energetic and spectral "properties" to allow the signal to reach any "element" of the storage system in space and time – including the boundaries and sealing spaces.

The technical conclusion from these conditions is to use a broadband acoustic noise as source signal which is powerful and stable and generated by a permanent continuous source.

Such source signal exists in the omnipresent and omnidirectional natural seismic background – noise [1].

The principle of analysis follows here the principles of analyzing the behavior of a technical dynamic system by pulse response or "white noise" response [18].

The technical method is to record and analyze from the surface the spectral deformation of the seismic background and its changes in a frequency range between 0.1 and 30 Hz.

Any seismic signal can be construed as a convolution of a series of filters [2]:

$$W(t) = S_{1}(t) * A_{2}(t) * A_{3}(t) * A_{4}(t) * I_{5}(t)$$

where

- W(t) Recorded signal
- $S_1(t)$ Undisturbed source signal
- $A_2(t)$ Filter characteristic of the storage
- $A_3(t)$ Filter characteristic of the cap rock
- $A_4(t)$ Filter characteristic of the transition zone between cap rock and surface
- $I_5(t)$ Instrument characteristic

It is a fundamental criterion for a complex "Storage System" like CCS that all geological, lithological, geophysical, geochemical and physical rock properties are very well known – otherwise it doesn't make sense to select this system and use it as a Carbon Capture Storage – as opposed to a hydrocarbon reservoir under development. And for this reason, based on the detailed knowledge of all storage properties it is possible to associate the system elements and its filter characteristics to the signal pattern components.

Marmot's CCSM technology is a spin-off of the ULF-PSSM – 5D Quantum Monitor [3] for permanent monitoring of producing oil fields and "Time Variant Visualization of Fluid and Non-Fluid Reservoir Dynamics". This technology is based on the spectral analysis of the omnipresent and omnidirectional seismic background noise of the earth (RSSN = Random Spread Spectrum Noise).

This ULF – PSSM technology is noninvasive using the seismic background noise as source signal – it is operated with surface or near surface broadband signal converter (Resonance Spectrometer) and it delivers a broad spectrum of information from which in reservoir monitoring the following phenomena are observed and used as processing parameter:

- Frequency conversion power caused by fluid saturation parameter in porous media (non-linear transfer function for a limited frequency band)
- Stochastic resonances caused by secondary permeability fluid spaces which act as $\lambda/4$ resonators and indicate rock properties [22, 23]
- Spectral anomalies indicating complex faulting systems or/ and spatial rock unconformities which transform mechanical energy into chemical energy [24]
- SLSE Short Life Single action Events indicating spontaneous lithological changes.

The creation of side bands caused by frequency conversion at non-linear transfer elements is a well-known effect in communication instruments and electronic devices [19] but the same theory applies for acoustic wave



Figure 1.2 Principle of the ULF-PSSM Analysis.

propagating in anisotropic geological formations. A fluid saturated porous "body" is a frequency converter in a distinct frequency window building lower and higher sidebands from the incoming Random Spread Spectrum Noise (RSSN) of the seismic background. At the surface, these conversion products can be recorded but because of non-symmetric wave propagation in the lithosphere only the lower sidebands make a significant contribution and can be used for the calculation of fluid saturation because conversion power and fluid saturation are directly related.

The second phenomenon which contributes to the analysis of rock properties – secondary permeability – is the appearance of stochastic resonances caused by fluid prone fractures where the fluid column is acting as a $\lambda/4$ Resonator due to its geometrical and fluid properties. Each reservoir or storage has a characteristic resonator pattern depending on the rock properties (Figure 1.3).

Figure 1.3 also shows two more phenomena which are used as monitoring tools and reservoir or storage characterization. Spectral anomalies as emission or absorption spectra indicate changes in the fluid-rock system which may occur in space or even in time, when system properties are changing.

The next indicator which is very important especially in CCS monitoring is the SLSE which provides a huge amount of information including indication of micro seismic or micro tectonic events caused by micro fractures or macro fractures (in case of macro fractures we have to expect landslides, earthquakes or avalanches).

In case of a CCS system or in general a "disposal system" these events are crucial and they have to be "captured" with 100% reliability and each of these events may happen only once – only once in the whole lifetime of the storage or the system – and one of those events can be the trigger for



Figure 1.3 Frequency Conversion – Stochastic Resonances – Spectral Anomalies and SLSE.

the system collapse or can predict the system collapse and for this reason *permanent monitoring* is mandatory for system control. This is the same in oil reservoir monitoring but there the direct hazardous component is missing – the task is different.

1.4 Principles of Information Analysis

Principally we have to distinguish between signal analysis and information analysis. From the continuous signal stream information elements are separated and from those information elements an information vector

$$(x, y, z, A_1, A_2, A_3, ..., A_n)$$

is created. A manifold of these information vectors over time builds a socalled "event space" from which each (finite) element is attributed with a "probability"

$$\{(x, y, z, P_1, P_2, P_3, ..., P_n)\}(t)$$

The projection from the event space into the initial 3D cube allows the dynamic visualization of the storage "MODEL".



Figure 1.4 Signal – Information Flow.