

CARBON CAPTURE AND STORAGE

CO₂ Management Technologies

Editor

Amitava Bandyopadhyay, PhD



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Edited by
Amitava Bandyopadhyay, PhD



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CONTENTS

<i>Acknowledgment and How to Cite</i>	<i>ix</i>
<i>List of Contributors</i>	<i>xi</i>
<i>Introduction</i>	<i>xv</i>

PART I: Absorption, Adsorption and Membrane Based Separation Processes for CO₂ Capture

- 1. Amine Versus Ammonia Absorption of CO₂ as a Measure of Reducing GHG Emission: A Critical Analysis**..... **1**
Amitava Bandyopadhyay
- 2. CO₂ Capture in a Spray Column Using a Critical Flow Atomizer** **55**
Amitava Bandyopadhyaya and Manindra Nath Biswas
- 3. Characteristics of CO₂ Hydrate Formation and Dissociation in Glass Beads and Silica Gel**..... **85**
Mingjun Yang, Yongchen Song, Xuke Ruan, Yu Liu, Jiafei Zhao, and Qingping Li

Part II: Geological Sequestration of CO₂

- 4. Geological Carbon Sequestration: A New Approach for Near-Surface Assurance Monitoring** **105**
Lucian Wielopolski
- 5. Enzymatic Carbon Dioxide Capture**..... **121**
Alain C. Pierre
- 6. On the Potential for CO₂ Mineral Storage in Continental Flood Basalts—PHREEQC Batch- and 1D Diffusion-Reaction Simulations**..... **177**
Thi Hai Van Pham, Per Aagaard and Helge Hellevang
- 7. Experimental Study of Cement - Sandstone/Shale - Brine - CO₂ Interactions** **203**
Susan A. Carroll, Walt W. McNab, and Sharon C. Torres

PART III: Biological Sequestration of CO₂**8. Identification of a CO₂ Responsive Regulon in *Bordetella* 239**

Sara E. Hester, Mingsun Lui, Tracy Nicholson, Daryl Nowacki, and Eric T. Harvill

9. CO₂ Efflux from Cleared Mangrove Peat..... 267

Catherine E. Lovelock, Roger W. Ruess, and Ilka C. Feller

10. Soil Microbial Responses to Elevated CO₂ and O₃ in a Nitrogen-Aggrading Agroecosystem 277Lei Cheng, Fitzgerald L. Booker, Kent O. Burkey, Cong Tu,
H. David Shew, Thomas W. Rufty, Edwin L. Fiscus,
Jared L. Deforest, and Shuijin Hu**PART IV: Current Research Trends in CO₂ Capture using Ionic Liquids****11. Overview of Ionic Liquids Used as Working Fluids in Absorption Cycles 311**

Mehrdad Khamooshi, Kiyan Parham, and Ugur Atikol

12. CO₂ Capture in Ionic Liquids: A Review of Solubilities and Experimental Methods..... 325

Elena Torralba-Calleja, James Skinner, and David Gutiérrez-Tauste

PART V: Air Capture of CO₂**13. Capturing Carbon Dioxide From Air 363**

Klaus S. Lackner, Patrick Grimes, and Hans-J. Ziock

Author Notes..... 377**Index..... 383**

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INTRODUCTION

Carbon capture and storage (CCS) refers to a set of methods for the mitigation, remediation, and storage of industrial CO₂ emissions. This current book addresses the technologies currently being applied and developed, and those most in need of further research. The book as a whole discusses methods of carbon capture in industrial settings, while the various sections look at topics such as biological and geological approaches to carbon sequestration, introducing ionic liquids as a method of carbon capture, and new approaches to capturing CO₂ from ambient air.

Carbon dioxide (CO₂), one of the green house gases (GHGs), has been well known for more than a century. Its emission from the combustion of fossil fuels, in addition to other industrial sources, is adversely affecting the climate on earth. Climate change is emerging as a risk all over the world that has generated public concern. Estimates have indicated that power production contributes to the tune of 70% of the total CO₂ released into the atmosphere from fossil fuel combustion worldwide. Capturing and securely storing CO₂ from the global combustion systems thus constitutes an important and achievable target. A legion of researchers have thus far developed absorbents to remove CO₂ from combustion facilities that are currently recognized globally as most effective. The cost of capturing CO₂ can be reduced by finding a low-cost solvent that can minimize energy requirements, equipment size, and corrosion. Monoethanolamine is being used for removing CO₂ from the exhaust streams and is a subject inculcated over a period of about 80 years. A host of such amines are being investigated and put into practice. However, commercializations of such operating plants for capturing CO₂ from power plants in the world are few and far between. On the other hand, aqueous ammonia is the other chemical solvent for capturing CO₂ that has proven experimentally to be more effective than amine-based processes. Chapter 1, by Bandyopadhyay, aims at critically elucidating relative merits and demerits of ammonia and amine-based CO₂ capture options from the exhausts of coal-fired thermal

power plants (TPPs). It includes the life cycle CO_2 emissions for both the processes. Finally, it is estimated that a total emission of about 152 Mt CO_2 -equivalent could occur after use of 100 Mt ammonium bicarbonate (NH_4HCO_3) as synthetic N-fertilizer that is about 50% of the total CO_2 captured (315 Mt) for producing the fertilizer, NH_4HCO_3 . Clearly, this estimate demonstrates that the synthetic N-fertilizer, NH_4HCO_3 , produced by NH_3 scrubbing of CO_2 from fossil fuel (e.g., coal) fired TPP could have a significant beneficial environmental impact so far as GHG emission is concerned.

The emission of CO_2 into the atmosphere is causing the majority of the global warming, and thus various end-of-pipe treatment methods have evolved to capture CO_2 from fixed point sources. In Chapter 2, Bandyopadhyay and Biswas deal with CO_2 capture from a simulated gas stream using dilute NaOH solution in a spray column using a two-phase critical flow atomizer capable of producing very fine sprays with high degree of uniformity and moving at very high velocities. Experimentation was carried out to investigate the percentage removal of CO_2 as well as interfacial area as functions of different variables. The maximum percentage removal of CO_2 observed was about 99.96% for a QL/QG ratio of 6.0 $\text{m}^3/1000$ ACM (liquid flow rate of $1.83 \times 10^{-5} \text{ m}^3/\text{s}$ and gas flow rate of $3.33 \times 10^{-3} \text{ m}^3/\text{s}$) and for a CO_2 feed rate of 100 l/h, while the observed values of interfacial area were in the range of 22.62–88.35 m^2/m^3 within the framework of the experimentation. A simple correlation was developed for predicting the interfacial area as functions of various pertinent variables of the system. Experimental data fitted excellently well with the correlation. The comparison of the interfacial area observed between the present system and the existing systems revealed that the present system produced higher values of interfacial area than the existing systems and hence the performance of the system was better than the existing system.

CO_2 hydrate formation and dissociation is crucial for hydrate-based CO_2 capture and storage. Experimental and calculated phase equilibrium conditions of carbon dioxide (CO_2) hydrate in porous medium were investigated in Chapter 3, by Yang and colleagues. Glass beads were used to form the porous medium. The experimental data were generated using a graphical method. The results indicated the decrease of pore size resulted in the increase of the equilibrium pressure of CO_2 hydrate. Magnetic reso-

nance imaging (MRI) was used to investigate the priority formation site of CO_2 hydrate in different porous media, and the results showed that the hydrate form firstly in BZ-02 glass beads under the same pressure and temperature. An improved model was used to predict CO_2 hydrate equilibrium conditions, and the predictions showed good agreement with experimental measurements.

There are two distinct objectives in monitoring geological carbon sequestration (GCS): Deep monitoring of the reservoir's integrity and plume movement and near-surface monitoring (NSM) to ensure public health and the safety of the environment. However, the minimum detection limits of the current instrumentation for NSM is too high for detecting weak signals that are embedded in the background levels of the natural variations, and the data obtained represents point measurements in space and time. In Chapter 4, Wielopolskie introduces a new approach for NSM, based on gamma-ray spectroscopy induced by inelastic neutron scatterings (INS). This technique offers novel and unique characteristics providing the following: (1) High sensitivity with a reducible error of measurement and detection limits, and, (2) temporal- and spatial-integration of carbon in soil that results from underground CO_2 seepage. Preliminary field results validated this approach showing carbon suppression of 14% in the first year and 7% in the second year. In addition the temporal behavior of the error propagation is presented and it is shown that for a signal at the level of the minimum detection level the error asymptotically approaches 47%.

In the past decade, the capture of anthropic carbonic dioxide and its storage or transformation have emerged as major tasks to achieve, in order to control the increasing atmospheric temperature of our planet. One possibility rests on the use of carbonic anhydrase enzymes, which have been long known to accelerate the hydration of neutral aqueous CO_2 molecules to ionic bicarbonate HCO_3^- species. In Chapter 5, by Pierre, the principle underlying the use of these enzymes is summarized. Their main characteristics, including their structure and catalysis kinetics, are presented. A special section is next devoted to the main types of CO_2 capture reactors under development, to possibly use these enzymes industrially. Finally, the possible application of carbonic anhydrases to directly store the captured CO_2 as inert solid carbonates deserves a review presented in a final section.

In Chapter 6, Pham and colleagues consider continental flood basalts (CFB) as potential CO_2 storage sites because of their high reactivity and abundant divalent metal ions that can potentially trap carbon for geological timescales. Moreover, laterally extensive CFB are found in many places in the world within reasonable distances from major CO_2 point emission sources. Based on the mineral and glass composition of the Columbia River Basalt (CRB), the authors estimated the potential of CFB to store CO_2 in secondary carbonates. They simulated the system using kinetic dependent dissolution of primary basalt-minerals (pyroxene, feldspar and glass) and the local equilibrium assumption for secondary phases (weathering products). The simulations were divided into closed-system batch simulations at a constant CO_2 pressure of 100 bar with sensitivity studies of temperature and reactive surface area, an evaluation of the reactivity of H_2O in scCO_2 , and finally 1D reactive diffusion simulations giving reactivity at CO_2 pressures varying from 0 to 100 bar. Although the uncertainty in reactive surface area and corresponding reaction rates are large, the article estimated the potential for CO_2 mineral storage and identified factors that control the maximum extent of carbonation. The simulations showed that formation of carbonates from basalt at 40°C may be limited to the formation of siderite and possibly FeMg carbonates. Calcium was largely consumed by zeolite and oxide instead of forming carbonates. At higher temperatures (60 – 100°C), magnesite is suggested to form together with siderite and ankerite. The maximum potential of CO_2 stored as solid carbonates, if CO_2 is supplied to the reactions unlimited, is shown to depend on the availability of pore space as the hydration and carbonation reactions increase the solid volume and clog the pore space. For systems such as in the scCO_2 phase with limited amount of water, the total carbonation potential is limited by the amount of water present for hydration of basalt.

Reactive-transport simulation is a tool that is being used to estimate long-term trapping of CO_2 , and wellbore and cap rock integrity for geological CO_2 storage. In Chapter 7, Carroll and colleagues reacted end member components of a heterolithic sandstone and shale unit that forms the upper section of the In Salah Gas Project carbon storage reservoir in Krechba, Algeria with supercritical CO_2 , brine, and with/without cement at reservoir conditions to develop experimentally constrained geochemical models for use in reactive transport simulations. The authors observed

marked changes in solution composition when CO_2 reacted with cement, sandstone, and shale components at reservoir conditions. The geochemical model for the reaction of sandstone and shale with CO_2 and brine is a simple one in which albite, chlorite, illite and carbonate minerals partially dissolve and boehmite, smectite, and amorphous silica precipitate. The geochemical model for the wellbore environment is also fairly simple, in which alkaline cements and rock react with CO_2 -rich brines to form an Fe containing calcite, amorphous silica, smectite and boehmite or amorphous $\text{Al}(\text{OH})_3$. Our research shows that relatively simple geochemical models can describe the dominant reactions that are likely to occur when CO_2 is stored in deep saline aquifers sealed with overlying shale cap rocks, as well as the dominant reactions for cement carbonation at the wellbore interface.

Sensing the environment allows pathogenic bacteria to coordinately regulate gene expression to maximize survival within or outside of a host. In Chapter 8, Hester and colleagues show that *Bordetella* species regulate virulence factor expression in response to carbon dioxide levels that mimic in vivo conditions within the respiratory tract. We found strains of *Bordetella bronchiseptica* that did not produce adenylate cyclase toxin (ACT) when grown in liquid or solid media with ambient air aeration, but produced ACT and additional antigens when grown in air supplemented to 5% CO_2 . Transcriptome analysis and quantitative real time-PCR analysis revealed that strain 761, as well as strain RB50, increased transcription of genes encoding ACT, filamentous hemagglutinin (FHA), pertactin, fimbriae and the type III secretion system in 5% CO_2 conditions, relative to ambient air. Furthermore, transcription of *cyaA* and *fhaB* in response to 5% CO_2 was increased even in the absence of BvgS. In vitro analysis also revealed increases in cytotoxicity and adherence when strains were grown in 5% CO_2 . The human pathogens *B. pertussis* and *B. parapertussis* also increased transcription of several virulence factors when grown in 5% CO_2 , indicating that this response is conserved among the classical bordetellae. Together, our data indicate that *Bordetella* species can sense and respond to physiologically relevant changes in CO_2 concentrations by regulating virulence factors important for colonization, persistence and evasion of the host immune response.

CO_2 emissions from cleared mangrove areas may be substantial, increasing the costs of continued losses of these ecosystems, particularly in

mangroves that have highly organic soils. In Chapter 9, Lovelock and colleagues measured CO_2 efflux from mangrove soils that had been cleared for up to 20 years on the islands of Twin Cays, Belize. The authors also disturbed these cleared peat soils to assess what disturbance of soils after clearing may have on CO_2 efflux. CO_2 efflux from soils declines from time of clearing from $\sim 10\,600 \text{ tonnes km}^{-2} \text{ year}^{-1}$ in the first year to $3000 \text{ tonnes km}^{-2} \text{ year}^{-1}$ after 20 years since clearing. Disturbing peat leads to short term increases in CO_2 efflux ($27 \text{ umol m}^{-2} \text{ s}^{-1}$), but this had returned to baseline levels within 2 days. Deforesting mangroves that grow on peat soils results in CO_2 emissions that are comparable to rates estimated for peat collapse in other tropical ecosystems. Preventing deforestation presents an opportunity for countries to benefit from carbon payments for preservation of threatened carbon stocks.

Climate change factors such as elevated atmospheric carbon dioxide (CO_2) and ozone (O_3) can exert significant impacts on soil microbes and the ecosystem level processes they mediate. However, the underlying mechanisms by which soil microbes respond to these environmental changes remain poorly understood. The prevailing hypothesis, which states that CO_2 - or O_3 -induced changes in carbon (C) availability dominate microbial responses, is primarily based on results from nitrogen (N)-limiting forests and grasslands. It remains largely unexplored how soil microbes respond to elevated CO_2 and O_3 in N-rich or N-aggrading systems, which severely hinders our ability to predict the long-term soil C dynamics in agroecosystems. Using a long-term field study conducted in a no-till wheat-soybean rotation system with open-top chambers, Chapter 10, by Cheng and colleagues, showed that elevated CO_2 but not O_3 had a potent influence on soil microbes. Elevated CO_2 ($1.5\times\text{ambient}$) significantly increased, while O_3 ($1.4\times\text{ambient}$) reduced, aboveground (and presumably belowground) plant residue C and N inputs to soil. However, only elevated CO_2 significantly affected soil microbial biomass, activities (namely heterotrophic respiration) and community composition. The enhancement of microbial biomass and activities by elevated CO_2 largely occurred in the third and fourth years of the experiment and coincided with increased soil N availability, likely due to CO_2 -stimulation of symbiotic N_2 fixation in soybean. Fungal biomass and the fungi:bacteria ratio decreased under both ambient and elevated CO_2 by the third year and also coincided with increased

soil N availability; but they were significantly higher under elevated than ambient CO_2 . These results suggest that more attention should be directed towards assessing the impact of N availability on microbial activities and decomposition in projections of soil organic C balance in N-rich systems under future CO_2 scenarios.

The cycle performance of refrigeration cycles depends not only on their configuration, but also on thermodynamic properties of working pairs regularly composed of refrigerant and absorbent. The commonly used working pairs in absorption cycles are aqueous solutions of either lithium bromide water or ammonia water. However, corrosion, crystallization, high working pressure, and toxicity are their major disadvantages in industrial applications. Therefore, seeking more advantageous working pairs with good thermal stability, with minimum corrosion, and without crystallization has become the research focus in the past two decades. Ionic liquids (ILs) are room-temperature melting salts that can remain in the liquid state at near or below room temperature. ILs have attracted considerable attention due to their unique properties, such as negligible vapor pressure, nonflammability, thermal stability, good solubility, low melting points, and staying in the liquid state over a wide temperature range from room temperature to about 300°C . The previously mentioned highly favorable properties of ILs motivated Khamooshi and colleagues in Chapter 11 to carry out the present research and review the available ILs found in the literature as the working fluids of absorption cycles. Absorption cycles contain absorption heat pumps, absorption chillers, and absorption transformers.

The growing concern of climate change and global warming has in turn given rise to a thriving research field dedicated to finding solutions. One particular area which has received considerable attention is the lowering of carbon dioxide emissions from large-scale sources, that is, fossil fuel power. Chapter 12, by Torralba-Calleja and colleagues, focuses on ionic liquids being used as novel media for CO_2 capture. In particular, solubility data and experimental techniques are used at a laboratory scale. Cited CO_2 absorption data for imidazolium-, pyrrolidinium-, pyridinium-, quaternary-ammonium-, and tetra-alkyl-phosphonium-based ionic liquids is reviewed, expressed as mole fractions (X) of CO_2 to ionic liquid. The following experimental techniques are featured: gravimetric analysis, the pressure drop method, and the view-cell method.

The goal of carbon sequestration is to take CO_2 that would otherwise accumulate in the atmosphere and put it in safe and permanent storage. Most proposed methods would capture CO_2 from concentrated sources like power plants. Indeed, on-site capture is the most sensible approach for large sources and initially offers the most cost-effective avenue to sequestration. For distributed, mobile sources like cars, on-board capture at affordable cost would not be feasible. Yet, in order to stabilize atmospheric levels of CO_2 , these emissions, too, will need to be curtailed. Chapter 13, by Lackner and colleagues, suggests that extraction of CO_2 from air could provide a viable and cost-effective alternative to changing the transportation infrastructure to non-carbonaceous fuels. Ambient CO_2 in the air could be removed from natural airflow passing over absorber surfaces. The CO_2 captured would compensate for CO_2 emission from power generation two orders of magnitude larger than the power, which could have instead been extracted from the same airflow by a windmill of similar size. The authors outline several approaches, and show that the major cost is in the sorbent recovery and not in the capture process. Air extraction is an appealing concept, because it separates the source from disposal. One could collect CO_2 after the fact and from any source. Air extraction could reduce atmospheric CO_2 levels without making the existing energy or transportation infrastructure obsolete. There would be no need for a network of pipelines shipping CO_2 from its source to its disposal site. The atmosphere would act as a temporary storage and transport system. The authors also discuss the potential impact of such a technology on the climate change debate and outline how such an approach could actually be implemented.

PART I

ABSORPTION, ADSORPTION, AND MEMBRANE BASED SEPARATION PROCESSES FOR CO₂ CAPTURE

CHAPTER 1

AMINE VERSUS AMMONIA ABSORPTION OF CO₂ AS A MEASURE OF REDUCING GHG EMISSION: A CRITICAL ANALYSIS

AMITAVA BANDYOPADHYAY

1.1 INTRODUCTION

The report published by the Inter Governmental Panel on Climate Change (IPCC 1990) clearly demonstrates that human activities result in the generation of four greenhouse gases (GHGs) into the atmosphere. These gases are carbon dioxide (CO₂), methane (CH₄), chlorofluorocarbons (CFCs), and nitrous oxide (N₂O) that are contributing to the global warming phenomena considerably. The global warming caused by the increased levels of these gases is one of the most serious environmental threats to the human race at present (Yeh and Bai 1999). CO₂ emitted into the atmosphere is assumed to cause the greatest adverse impact on the observed green house effect accounting for approximately 55% of the observed global warming (IPCC 1990).

The risks associated with the climate change are increasing. The growing awareness of this fact has brought the interests of researchers for the abatement of CO₂ since 1989 (Diao et al. 2004). Besides CO₂ abatement that is commonly known as the CO₂ capture, the importance of its sequestration is also being gradually addressed all around the globe. The Kyoto Protocol to the United Nations Framework Convention on Climate Change (UNFCCC 1997) put forth an embargo on the major contributing nations to reduce CO₂ emissions by 6% below the level as was in 1990. That the protection of the climate system should occur “on the basis of equity and in accordance with Parties” was noted categorically by the UNFCCC. The leadership role in combating climate change and its adverse impacts should be taken by the industrialized nations as the majority of the historical cumulative emissions were caused by them. Therefore, they were given specified commitments for the reduction of emissions in the Kyoto Protocol (Harald et al. 2002). Furthermore, the Kyoto Protocol has also elucidated scientific and economic aspects at length (Bolin 1998; Banks 2000). The arithmetic aspect under the scientific regime based on the CO₂ emission intensity levels were estimated by Sun (2003). The emissions of CO₂ from coal were decreased, not only in their relative share but also in their absolute value due to its supply in the total fuel pool was reduced (Sun 2002, 2003). However, attention on researches on the flue gas emitted from the thermal power plants (TPPs) is growing because 30% of the total global fossil fuel is used for power generation that emits considerable amount of CO₂. It is estimated that around 6 billion tons of carbon emission occur globally by burning fossil fuels out of which about 1.8 billion tons is contributed from TPPs alone (Martin and Meyer 1999). It is further estimated from 1995 database (Sun 2002) that the USA is the largest emitter of CO₂ in the world amounting to 23.7% of the total CO₂ emission while China stands second place making up 13.6%. Considering the seriousness and urgency involved in the matter, the reduction of CO₂ emission from burning fossil fuels assumes considerable importance so as to slow down the trend of global warming.

Legions of researches are being carried out over the past few decades to reduce the CO₂ emission into the atmosphere. These studies came up with suggestive strategies for CO₂ emission reduction, for instance, fuel alternative, energy conservation, and improving efficiencies of TPPs (Blok

et al. 1993; Huang 1993; Bai and Wei 1996). Implementation of these strategies, however, may have a subtle impact on the CO₂ emission reduction. As a result, various end-of-pipe treatment methods have been given serious attention to capture/reduce and recover CO₂ from the flue gas streams. These methods are chemical (gas-liquid) absorption, physical adsorption, cryogenic separation, membrane separation, biological fixation, and oxy-fuel combustion with CO₂ recycling (Wolsky et al. 1994; Kimura et al. 1995; Nishikawa et al. 1995). The chemical absorption among these methods has been studied extensively for reducing CO₂ emission from fossil fuel-fired TPPs considering it as a reliable and relatively low cost method (Chakma 1995). Ostensibly, very limited technologies are available commercially for CO₂ capture suitable for TPPs. None of these technologies has so far been deployed at typical base loaded plant since these are not cost effective. The major researches that were carried out on amine and on ammonia-based absorption systems for CO₂ capture are briefly discussed here. Yeh and Bai (1999) experimentally investigated on the evaluation of two reagents viz. aqueous NH₃ and monoethanolamine (MEA) for scrubbing of CO₂. The performances of these two solvents were compared in terms of CO₂ removal efficiency and absorption capacity. They showed experimentally that both the CO₂ removal efficiency and absorption capacity using NH₃ as a solvent were better than those of MEA as a solvent under similar operating conditions chosen in their investigation. Ciferno et al. (2005) reported on a technical and economic scoping analysis that compared two different CO₂ absorption processes, viz. NH₃ absorption of CO₂ and MEA-based CO₂ absorption processes. This analysis was based on the research into aqueous NH₃-based CO₂ capture conducted under the aegis of National Energy Technology Laboratory (NETL). An economic scoping study was conducted to quantify the potential benefits of aqueous NH₃-based technology developing heat and material balances for a pulverized coal (PC)-fired TPP. Estimated were also the differences in capital and operating costs relative to the base case amine for CO₂ capture for the PC-fired TPP of same size. Reportedly, NH₃-based system achieved much better performance than the MEA-based system. McLarnon and Duncan (2005) reported that Powerspan developed performances of CO₂ capture processes based on MEA and aqueous NH₃ as solvents. In aqueous NH₃-based CO₂ absorption process, the rich solvent was stripped off to regenerate

NH₃ and to release CO₂. Ammonia was thus not consumed in the scrubbing process, and no separate by-product was created. A 1-MW pilot plant demonstration was scheduled to begin in 2008, which would produce 20 tons (ca.) of sequestration-ready CO₂ per day. The objective of the pilot was to demonstrate on CO₂ capture through integration with the multi-pollutant control process, i.e., CO₂ capture undertaken after SO₂ and fine particulates were captured. Also performance of MEA-based process was compared with that of the NH₃-based process that clearly indicated the superiority of the NH₃-based system over the MEA-based system in terms of performance. Dave et al. (2009) presented results of ASPEN simulations of a CO₂ removal and recovery plant that was intended for capturing CO₂ from a 500-MW conventional coal-fired TPP flue gas stream. They investigated into the performance of CO₂ capture process with aqueous solutions of 2-amino-2-methyl-1-propanol (AMP), methyldiethanolamine (MDEA), and NH₃ as solvents and compared the performances of each solvent with the conventional 30% by weight of MEA solution. A laboratory scale wetted wall gas–liquid contactor was further, experimentally investigated by them to generate mass transfer data so as to validate the simulated process condition for CO₂ capture by aqueous NH₃. The ASPEN-derived results further showed that 30% by weight of AMP-based process had the lowest overall energy requirement amongst the solvents chosen in their investigation. However, they did not investigate into aspects like refinement of product CO₂, its compression, transportation, and storage. Aspects of economics derived from the merits and demerits of amine and NH₃-based processes were also not reported. Thus, AMP-based process apparently looked energetically favorable, but intrinsically this study is falling short of a complete process.

Critical appraisal of these comparative studies indicates that CO₂ absorption (capture/removal) using aqueous NH₃ solution classically meets the demands of the GHG mitigation options compared to that of amine-based system under similar hydrodynamic conditions despite both these methods were having their own advantages and limitations. An attempt has, therefore, been made in this article to assess critically the relative merits and demerits of these two chemical absorption systems for CO₂ capture as a measure of reducing the GHG emission. While critically elucidating the aforesaid relative merits and demerits of NH₃-based and MEA-based CO₂

absorption processes, investigations carried out by earlier researchers to compare their performances will be analyzed elaborately. However, in this analysis, the study reported by Dave et al. (2009) will not be considered further due to the shortcomings associated with it as mentioned earlier.

1.2 AMINE-BASED CO₂ ABSORPTION PROCESS

The CO₂ absorption from the mixture of sulfur-containing acidic gases had been a subject in the history of chemical engineering since early part of the last century. The concept of separating CO₂ from flue gas streams was commenced in the 1970s as an economic source of CO₂ especially for enhanced oil recovery (EOR) operations rather than as an option for the GHG emission reduction. In the USA, several CO₂ capture plants were constructed for commercial applications in the late 1970s as well as in early 1980s (Kaplan 1982; Pauley et al. 1984). All these CO₂ capture plants were based on the chemical absorption processes using MEA-based solvent. MEA is a homologue of alkanolamines. The credit for developing alkanolamines as absorbents for acidic gases goes to Bottoms (1930). He was granted a patent in 1930 for such application. The historic development of CO₂ removal using aqueous amines are classically elucidated by Kohl and Nielsen (1997). Thus, this technology was developed over 80 years ago as a general, non-selective solvent to remove acidic gas impurities like, hydrogen sulfide (H₂S), CO₂ from refinery operations as well as sweetening of natural gas streams (Kohl and Nielsen 1997). Some of the initial developers of MEA-based CO₂ capture technology were Fluor Daniel Inc., Dow Chemical Co., Kerr-McGee Chemical Corp. and ABB Lummus Crest Inc. This technology is capable of capturing typically about 75–90% of the CO₂ and producing a nearly pure CO₂ (>99%) in the product stream.

Besides, the absorption of CO₂ in alkali was developed since middle of the last century in studying various aspects of mass transfer in chemical engineering (Lynn et al. 1955). Development of devices for carrying out gas–liquid mass transfer operations is still important to the researchers. Developing such devices means improving the intrinsic mass transfer design parameters like interfacial area of contact and true gas side as well

as liquid side mass transfer coefficients. CO₂ absorption in various alkaline solutions had been shown to perform excellently well in determining the intrinsic mass transfer design parameters, for instance, the interfacial area of contact and true liquid side mass transfer coefficient. In these deterministic studies, researchers have classically demonstrated the uses of reactions of CO₂ with various alkaline solutions like generic amines, mixture of amines, hindered amines, sodium hydroxide (NaOH), and sodium carbonate/sodium bicarbonate (Na₂CO₃/NaHCO₃) mixture or potassium carbonate/potassium bicarbonate (K₂CO₃/KHCO₃) mixture (Danckwerts and Sharma 1966; Astarita 1967; Danckwerts 1970). Since this section is aimed at assessing the applicability of amines as a solvent for CO₂ removal, the discussion will be restricted within the amine-based solvents only.

In the amine-based CO₂ capture plant, the flue gas is contacted with the amine such as MEA, in a packed bed absorption tower. The principal reactions occurring when solutions of MEA are used to absorb CO₂ may be represented (Kohl and Nielsen 1997) by ionization of water (Eq. 1), hydrolysis as well as ionization of dissolved CO₂ (Eq. 2), protonation of alkanolamine (Eq. 3), and carbamate formation (Eq. 4) as given below:



All the above reactions account for the principal species present in aqueous alkanolamine treating solutions. Additional reactions, however, may occur, which produce species other than those specified, but these are not considered important in the CO₂ absorption process. The flue gases after absorber are washed to recover any residual MEA and exhausted to the atmosphere. The CO₂-rich solvent is passed through a desorber in

which a counter-current steam stripped off CO₂ from the solvent producing a stream of H₂O and CO₂. The H₂O is condensed out leaving a stream of CO₂ (purity >99%) that is ready for compression. The CO₂-lean solvent, on the other hand, is cooled in a condenser and recycled back to the absorber.

Although these reactions relate specifically to primary amines, such as MEA, they can squarely be applied to secondary amines, such as diethanolamine (DEA), by suitably modifying the structural formula of the amine. However, tertiary amine undergoes reactions 1 through 4, but cannot react directly with CO₂ to form carbamates by reaction 4 due to the absence of α -H atom. If the reaction 4 is predominant, as it often occurs with primary amines, then the carbamate ion ties up with an alkanol-ammonium ion produced in reaction 3. As a result, the capacity of the solution for CO₂ is almost limited to 0.5 mol of CO₂/mol of amine. This is true even at relatively high partial pressures of CO₂ in the gas to be treated. This limitation is attributed to the high stability of the carbamate and its relatively low rate of hydrolysis to bicarbonate. In contrast, a ratio of 1 mol of CO₂/mol of amine can theoretically be achieved for the tertiary amines which are unable to form carbamates. In order to overcome this difficulty of operation as in the case of MDEA, it is necessary to add an activator, typically another amine, which increases the rate of hydration of dissolved CO₂. This has, therefore, given birth to the absorption of CO₂ in mixed amines as described later.

Methyldiethanolamine (MDEA) has gained considerable importance as a nonselective solvent for removing high concentration of CO₂ owing to its low energy requirements, high capacity, excellent stability, and other associated factors. Its chief disadvantage is its low rate of reaction with CO₂ that has resulted in the low absorption rate as well. Investigation showed that the addition of primary or secondary amines, for instance MEA and DEA, had increased the rate of CO₂ absorption significantly without diminishing the previously noted advantages of MDEA (Mshewa and Rochelle 1994). Their model calculations over a wide range of temperatures and partial pressures predicted that the overall gas phase mass transfer coefficient for CO₂ absorption in a solution containing 40% MDEA and 10% DEA was 1.7–3.4 times greater than that for CO₂ absorption in a 50% MDEA solution under typical absorption column conditions. The relevant

kinetic data of DEA had taken from the available literature for the purpose of the model predictions.

TABLE 1: Commercial anthropogenic CO₂ capture facilities as of June 2009

Commercial CO ₂ source	Type of operation	Use	CO ₂ capture capacity	
			TPD	MTPA
IMC Global Soda Ash Plant (USA)	Coal fired power plant	Soda ash production	800	0.3
Warrior Run Power Plant (USA)	Coal fired power plant	Food/beverage	330	0.1
Schwarze Pumpe Pilot Plant (Germany)	Coal fired oxyfuel combustion	Various	202	0.1
Shady Point Power Plant (USA)	Coal fired power plant	Food/beverage	200	0.1
Great Plains Synfuels Plant (USA)	Coal gasification	EOR	5,480	2.0
Sumitomo Chemicals Plant (Japan)	Natural gas-fired power plant	Various	200	0.1
Prosint Methanol Production Plant (Brazil)	Methanol	Food/beverage	90	0.0
Enid Fertilizer Plant (USA)	Fertilizer	Urea, EOR	1,850	0.7
Indian Farmers Fertilizer Company (India)	Fertilizer	Urea, NPK, DAP, NP	900	0.3
Ruwais Fertilizer Industries (UAE)	Fertilizer	Urea	400	0.1
Luzhou Natural Gas Chemicals (China)	Fertilizer	Urea	160	0.1
Petronas Fertilizer (Malaysia)	Fertilizer	Urea	160	0.1
Shute Creek Natural Gas Processing Plant (USA)	Natural gas processing	EOR	15,870	5.8
Val Verde Natural Gas Plants (USA)	Natural gas processing	EOR	3,970	1.4
In Salah Natural Gas Production Facility (Algeria)	Natural gas processing	Geologic storage	3,290	1.2
Sleipner West Field (North Sea, Norway)	Natural gas processing	Geologic storage	2,740	1.0
Snohvit LNG Project (Barents Sea, Norway)	Natural gas processing	Geologic storage	1,920	0.7
DTE Turtle Lake Gas Processing Plant (USA)	Natural gas processing	EOR/geologic storage	600	0.2

TABLE 2: Commercial CO₂ scrubbing solvent

Solvent type	Solvent		Process conditions
	Proprietary name	Chemical name	
Physical solvents	Rectisol	Methanol	−10/−70°C, >2 MPa
	Purisol	N-2-methyl-2-pyrrolidone	−20/+40°C, >2 MPa
	Selexol	Diemethyl ethers of polyethyl- eneglycol	−40°C, 2–3 MPa
	Fluor solvent	Propylene carbonate	Below ambient temperatures, 3.1–6.9 MPa
Chemical solvents	Organic (amine based)		
	MEA	2.5N MEA and inhibitors	40°C, ambient-inter- mediate pressures
	Amine guard	5N MEA and inhibitors	
	Econamine	6N Diglycolamine	80–120°C, 6.3 MPa
	ADIP	2-4N Diisopropanolamine, 2N MDEA	35–40°C, >0.1 MPa
	MDEA	2N MDEA	
	Flexsorb, KS-1, KS-2, KS-3	Hindered amine	
	Inorganic		
	Benfield and versions	Potassium carbonate and catalysts. Lurgi and Catacarb processes with arsenic trioxide	70–120°C, 2.2–7 MPa
Physical/ chemical solvents	Sulfinol-D, Sulfinol-M	Mixture of DIPA or MDEA, water and tetrahydrothiopene or diethylamine	>0.5 MPa
	Amisol	Mixture of methanol and MEA, DEA, diisopropylamine or dieth- ylamine	5/40°C, >1 MP

A different class of absorbents known as the sterically hindered amines has reported in the literature to control the CO₂/amine reaction (Goldstein 1983; Sartori and Savage 1983; Chludzinski et al. 1986). Some of the sterically hindered amines reported for CO₂ absorption are AMP, 1,8-p menthenediamine (MDA), and 2-piperidine ethanol (PE). The CO₂ absorption characteristics of sterically hindered amines are sufficiently similar to those of the alkanolamines although they are not necessarily alkanolamines. The hindered amines are used as promoters in hot K₂CO₃ systems as

component of organic solvent and as the principal agent in aqueous solutions for the selective absorption of CO₂. Sterically hindered amine with a specifically designed molecular configuration can yield independent performance based on their individual selectivity toward CO₂ absorption. The pilot and commercial plant data revealed that substantial savings in capital and operating cost could be achieved with the hindered amines.

A comprehensive assessment of the commercially available CO₂ capture technologies as of June 2009 was reported by Dooley et al. (2009). Such commercially operating plants and commercial CO₂ scrubbing solvents are furnished in Tables 1 and 2 for the benefit of our improved understanding.

1.2.1 CO₂ CAPTURE FROM FLUE GAS OF TPPS BY AMINE

The special report of IPCC on Carbon Dioxide Capture and Storage (IPCC 2005) has classically reviewed various methods for CO₂ capture in the light of GHG emission reduction that includes CO₂ capture from flue gas of thermal power plants also. Besides other processes, application of MEA- or amine-based process for CO₂ absorption was discussed therein. It was, however, mentioned earlier in this article that amine-based absorption of CO₂ was not developed for removing CO₂ from the flue gas stream of TPP. In fact, such an amine-based CO₂ absorption process can be adopted for flue gas of TPP, if the quality of the flue gas is similar to the feed gas being treated for the conventional amine-based CO₂ absorption process. However, such a quality matching seldom occurs and as a result, the flue gas of TPP requires special treatment prior to its introduction into the amine-based CO₂ absorption process. Therefore, the aspects of conventional amine-based CO₂ absorption and its restriction on application toward CO₂ capture for TPPs need special attention which is described in this section for improving our understanding. The flue gas of a coal-fired TPP may contain several contaminants, like sulfur dioxide, SO₂ = 300–3,000 ppmv, oxides of nitrogen, NO_x = 100–1,000 ppmv, and particulate matter = 1,000–10,000 mg/m³. In contrast, natural gas-fired power plants generate contaminants at considerably lower levels and the concentrations here are SO₂ < 1 ppmv, NO_x = 100–500 ppmv, and particulate matter =

~10 mg/m³ (Chakravarti et al. 2001). The temperatures of flue gases generated from a fossil-fueled power plants are usually above 100°C, which means that they need to be cooled down to the temperature levels required for the absorption process (IPCC 2005). This can be done in a cooler with direct water contact, which also acts as a flue gas washer with additional removal of fine particulates. In addition to the above, flue gas from coal combustion will contain other acid gas components such as NO_x and SO₂. Flue gases from natural gas combustion will mainly contain NO_x as the contaminant as pointed out earlier. These acidic gases, similar to CO₂, will have a chemical interaction with the amine as solvent. This is not desirable as the irreversible nature of this interaction leads to the formation of heat stable salts, and hence a loss in absorption capacity of the solvent and the risk of formation of solids in the solution. It also results in an extra consumption of chemicals to regenerate the amine and the production of a waste stream such as sodium sulfate (Na₂SO₄) or sodium nitrate (NaNO₃). Therefore, the pre-removal of NO_x and SO₂ to very low values before CO₂ capture becomes essential. For NO_x, it is the NO₂ which leads to the formation of heat stable salts. In addition, careful attention must also be paid to fly ash and soot present in the flue gas as they might plug the absorber if their concentration levels are too high. The operation of some demonstration facilities of CO₂ capture plant to coal-fired TPP caused several problems associated mainly with these contaminants. It was further suggested (IEA 2007) that the flue gas of the TPP for CO₂ capture should be pretreated to avoid amine degradation so as to achieve the following compositions of the contaminants prior to introducing into the amine-based CO₂ absorption systems:

1. SO₂ concentration: 10–30 mg/Nm³ [3.82–11.46 ppmv]
2. NO₂ concentration: 40 mg/Nm³ [21.26 ppmv]
3. particulate matter: <5 mg/Nm³.

Therefore, the MEA-based CO₂ capture process requires very low SO₂ in the flue gas at its inlet. Since most commercially available SO₂ scrubbing systems, commonly called as the Flue Gas Desulphurization (FGD) systems are not efficient enough to attain such a lower value of SO₂ concentration in the flue gas prior to being introduced into the CO₂ capture system.

The situation is further complicated on a system having FGD installed previously. Because such a system would, therefore, require an auxiliary SO₂ scrubbing system to make the flue gas stream ready for the CO₂ capture system and in turn increase the capital cost of the CO₂ capture system (McLarnon and Duncan, 2009).

Oxygen present in the flue gas would cause another problem of rapid degradation of some of the alkanolamines used for amine absorption. The degradation byproducts lead to corrosion problems and cause significant deterioration in the overall separation performance. For instance, the mixture of MEA and MDEA cannot be made to be oxygen resistant (Nsakala et al. 2001). Therefore, while this process potentially offers an improved system from the standpoint of solvent regeneration as well as energy requirement, it is imperative to separate the excess oxygen from the flue gas stream. This purification has been tested in demonstration plant facilities by converting the O₂ present in the flue gas by burning it with natural gas over a De-Oxy catalyst upstream of the solvent contactor into CO₂. The de-oxygenated flue gas thus leaving the De-Oxy system is introduced to the MEA/MDEA absorption system where CO₂ is removed (~90%+). The constituents thus present in the flue gas leaving the MEA/MDEA absorption system are N₂, H₂O vapor, CO₂, and relatively small amounts of NO_x, SO₂, and CH₄ that are discharged to the atmosphere through stacks above the absorber.

A key feature of post-combustion CO₂ capture process based on absorption is the high energy requirement and the resulting efficiency penalty on power cycles. This is primarily due to the heat necessary to regenerate the solvent (steam stripping) and to a lesser extent the electricity required for liquid pumping, the flue gas fan, and finally compression of the CO₂ product. Therefore, the CO₂ removal/capture plant should be designed in such a way so that the generation of CO₂ from the energy required for operating the CO₂ capture plant should be less than the amount of CO₂ it is programmed to remove with the purpose of classically meeting the basic philosophy of GHG emission reduction.

In the absence of a complete design data for a typical CO₂ capture process using MEA, the range of data generated from a large number of simulated runs reported by Rao (2002) is presented in this article. He has simulated CO₂ capture process using ProTreat, a software package. This

package is generally used for simulating processes for the removal of CO₂, H₂S, and mercaptans from a variety of high and low pressure gas streams by absorption into thermally regenerable aqueous solutions containing single or blended amines. The package deals with the separation as a mass transfer rate process through the use of column model. A large number of process simulation runs were conducted to cover a reasonable range of values for the parameters that described the CO₂ capture process. The CO₂ capture and separation system consists of a flue gas compressor, cooler, absorber, heat exchangers, regenerator, sorbent circulation pumps, etc. Values of model parameters estimated are presented in Table 3.

TABLE 3: Typical range of simulated values of parameters for CO₂ capture process by MEA

No	Parameter	Type	Range
1	CO ₂ content in the flue gas (mol%)	Input	3.5–13.5
2	Flue gas flow rate, G (kmol/h)	Input	9,000–24,000
3	Inlet flue gas temperature (°C)	Input	40–65
4	MEA concentration (wt%)	Input	15–40
5	Solvent flow rate, L (kmol/h)	Input	16,000–70,000
6	L/G ratio, dimensionless	Input	0.73–5.56
7	Reboiler heat duty, Q (GJ/h)	Input	95–664
8	Q/L (MJ/kmol)	Input	2.4–22.5
9	CO ₂ removal efficiency (%)	Output	41.2–99.9
10	CO ₂ product flow rate (kmol/h)	Output	333–2,840
11	Lean sorbent CO ₂ loading (mol CO ₂ /mol MEA)	Output	0.05–0.34
12	Rich sorbent CO ₂ loading (mol CO ₂ /mol MEA)	Output	0.27–0.55
13	Absorber diameter (ft)	Output	26–42
14	Regenerator diameter (ft)	Output	12–42
15	Exhaust flue gas temperature (°C)	Output	40.4–71.6
Parameters held constant were			
Absorber height		40 ft	
Absorber packing		Rasching rings, metallic, 1-inch packing size	
Inlet flue gas pressure		3 psi	
Solvent pumping pressure		30 psi	
Number of trays in regenerator		24 (tray spacing = 2 ft, weir height = 3 inches)	
Compressor efficiency		60–100%	

1.2.2 CURRENT STATUS OF RESEARCH ON THE SELECTIVITY OF AMINES FOR CO₂ CAPTURE FROM EXHAUST STREAMS

Critical appraisal of the available literature on the classical amine-based CO₂ absorption systems coupled with the suggested requirements of the level of contaminants for the CO₂ capture plant as described earlier indicates that the CO₂ capture plant would require specially designed amine absorption system, in which the classical amine-based CO₂ absorption systems developed, based on acid gas treatment cannot be replicated to the CO₂ capture plants augmented to the TPPs due to various constraints as described before.

Recent literature (Aronua et al. 2009) also reveals that alkanolamines reported for CO₂ absorption are still deficient for CO₂ absorption due to inherent problems associated with their use in CO₂ capture process. Legion of factors affect the efficacy of a solvent to be selected for CO₂ absorption. The factors for selecting a solvent are solubility, vapor pressure, molecular weight, foaming tendency, degradation properties, and corrosivity. Other associated factors include reaction kinetics, heat of reaction, energy of regeneration, and the capacity of cyclic use of amine. Finally, the environmental and cost factors are also to be taken into consideration. Therefore, the solvent selection is more dependent on techno-enviro-economic feasibility rather than a simple techno-economic feasibility in such applications.

Aronua et al. (2009) further investigated performances of various solvents for CO₂ capture, which were compared to MEA that was chosen as the base case for all comparisons. Solvents selected for their investigation were AMP (1.0, 2.5, and 5.0 M), mixture of 0.42 M N,N'-di-(2 hydroxyethyl) piperazine (DIHEP) and 0.58 M N-2-hydroxyethylpiperzine (HEP), 2.5 M AMP, mixture of 2.5 AMP and 0.5 M piperizine (PZ), 1.0 M tetraethylenepentamine (TEPA), and 2.5 M potassium salt of sarcosine (KSAR) (prepared by neutralizing equimolar amounts of sarcosine). A rapid screening apparatus was used for performing a relative comparison of the CO₂ absorption potentials of the aforementioned selected solvent systems. Experimental results showed that besides absorption data, desorption data were also squarely important to assess the performance of solvents for CO₂ absorption, since different solvents exhibit different de-

sorption behaviors. The absorption–desorption studies reported by them are summarized below:

1. The capacity of MEA in mol CO₂/mol amine was found to decrease with increase in concentration while its CO₂ removal per cycle increases with concentration.
2. The “0.42 M DIHEP + 0.58 M HEP” mixture has shown the lowest CO₂ absorption potential of all the systems investigated despite its best desorption ability.
3. 2.5 M KSAR showed a similar behavior to 2.5 M MEA; however, it was found to have slightly lower performance.
4. The performance of CO₂ absorption in AMP was enhanced with PZ, and the combination also showed high desorption ability.
5. TEPA showed outstanding CO₂ absorption potential by removing a large amount of CO₂ per cycle among the various solvents investigated. For example, 1.0 M TEPA removed three times more CO₂ per cycle than what was removed by 1.0 M MEA per cycle. Such higher absorption capacity was attributed due to presence of five amine (two primary and three secondary) sites in it. However, working with TEPA at higher concentration more than 1.0–2.0 M may be challenging owing to its higher viscosity.

Hakka and Ouimet (2006) developed absorbent based on tertiary amines that also includes a promoter to yield sufficient absorption rates to be used for low pressure flue gas streams. The use of oxidation inhibitors enables this process to be operative in oxidizing environments as also where limited concentrations of oxidized sulfur exist. They have claimed that this process can also simultaneously remove SO₂. The process comprises selecting absorbent from the following tertiary amines either alone or in combination as a mixture:

- methyldiethanolamine (MDEA),
- N,N'-di-(2-hydroxyethyl) piperazine (DIHPA),
- N,N'-di-(3-hydroxypropyl) piperazine,
- N,N,N',N'-tetrakis (2-hydroxyethyl)-1,6-hexanediamine,
- N,N,N',N'-tetrakis (2-hydroxypropyl)-1,6-hexanediamine,
- tertiary alkylamine sulfonic acids,
- triethanolamine (TEA).

The tertiary alkylamine sulfonic acid is selected from the group as given below either alone or in combination as a mixture:

- 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid,
- 4-(2-hydroxyethyl)-1-piperazinepropanesulfonic acid,
- 4-(2-hydroxyethyl)-1-piperazinebutanesulfonic acid,
- 4-(2-hydroxyethyl) piperazine-1-(2-hydroxypropanesulfonic acid),
- 1,4-piperazinedi (ethanesulfonic acid).

The chief advantage of this invention is the stability of certain tertiary amines used in the process that may also be used to remove SO₂ from the flue gas. Thus, the flue gas entering into the CO₂ capture system may contain SO₂ that would not degrade the absorbent as would occur for other generic amine-based absorbents described earlier. For example, pretreatment step is not required, if the flue gas would contain SO₂ under the present circumstances for reducing its concentration to avert excessive absorbent degradation. Simultaneously, the presence of SO₂ may be exploited to restrict oxidative degradation of the absorbent. This process is developed in such a way so that sufficient SO₂ may be either slipped from an upstream SO₂ removal process or added to the feed gas to the process to maintain sufficient sulfite in the CO₂ absorbent to scavenge and react with molecular oxygen effectively which is absorbed from the feed gas. As a result, the molecular oxygen would be unavailable for oxidizing the amine-based solvent. Accordingly, the feed gas undergoing CO₂ capture may be allowed to contain SO₂ ranging between 0 and 1000 ppmv. The process developed for recovering SO₂ and CO₂ from a flue gas stream comprises the following steps of operation:

1. SO₂ scrubbing loop: Treating the flue gas stream in an SO₂ scrubbing loop with a first absorbent stream to obtain a SO₂-rich stream and a SO₂-lean stream. Subsequent treatment of the SO₂-rich stream to obtain a first regenerated absorbent stream which is used back for SO₂ scrubbing;
2. CO₂ scrubbing loop: Treating the SO₂-lean stream in a CO₂ scrubbing loop with a second absorbent stream to obtain a CO₂-rich stream. Subsequent treatment of the CO₂-rich stream to obtain a