



CO₂QUEST

2ND INTERNATIONAL FORUM ON RECENT DEVELOPMENTS OF CCS IMPLEMENTATION

LEADING THE WAY TO A LOW-CARBON FUTURE

16TH - 17TH DECEMBER, 2015

ATHENS, GREECE



ST. GEORGE LYCABETTUS HOTEL

BOOK OF ABSTRACTS



ACKNOWLEDGEMENTS

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Abstracts submitted to this event by members of these projects acknowledge the above funding.

The organising and scientific committees would like to acknowledge and thank the IEAGHG for the associated International Journal of Greenhouse Gas Control Special Issue that will be published in 2017.

AGENDA

WEDNESDAY, 16 DECEMBER, 2015		
08:00	REGISTRATION/WELCOME COFFEE	Faidra / Parthenon rooms
08:30	Opening: Welcome and Introduction Dr. Nils Røkke (SINTEF, Norway) & Prof. Michael Fairweather (University of Leeds, UK)	Hedra meeting room
08:40	Plenary Lecture 1: Status of International Standardisation on CO ₂ Transportation Dr. Achim Hilgenstock (Hilgenstock Consulting, Germany) Chair: Dr. Marit Mazzetti (SINTEF, Norway)	
Session 1: Transport & Safety Chair: Dr. Marit Mazzetti (SINTEF, Norway)		
09:20	An Overview of the CO ₂ QUEST Project Haroun Mahgerefteh (UCL, UK)	
09:30	Design and Application of a Large-scale Experimental Pipeline for Studying the Release and Dispersion Characteristics of CO ₂ in Different Phase States Xingqing Yan (DUT, China)	
09:50	High Pressure CO ₂ CCS Pipelines: Comparing Dispersion Models with Multiple Experimental Datasets Chris Wareing (University of Leeds, UK)	
10:10	On Simulation of Dynamic Brittle Fracture of CO ₂ Pipeline Using Coupled Fluid–structure Modelling Approach Reza Hojjati-Talemi (OCAS, Belgium)	
10:30	Predicting the Atmospheric Dispersion of Carbon Dioxide from A Buried Ruptured Pipeline Jennifer Wen (University of Warwick, UK)	
10:50	COFFEE BREAK	Faidra / Parthenon rooms
Session 2: Transport & Safety Chair: Prof. Haroun Mahgerefteh (UCL, UK)		Hedra meeting room
11:10	Techno-economic Analysis of Gas Purification for CO ₂ Transport in Pipeline Networks and Injection for Storage Evgenia Mechleri (Imperial College London, UK)	
11:30	Impact of Impurities in CO ₂ Streams on Compression Strategies for Carbon Capture and Sequestration Sergey Martynov (UCL, UK)	
11:50	Computationally Efficient Simulation of Two-phase Flows of CO ₂ Mixtures Solomon Brown (UCL, UK)	Faidra / Parthenon rooms
12:10	LUNCH	
12:50	Plenary Lecture 2: CO ₂ Transport and Safety - An Industrial Perspective Mr. Michael Drescher (Statoil R&D, Norway) Chair: Dr. Evgenia Mechleri (Imperial College London, UK)	Hedra meeting room

Session 3: Process Optimisation and Techno-economic Considerations Chair: Dr. Evgenia Mechleri (Imperial College London, UK)		Hedra meeting room
13:30	Highlights of the IMPACTS Project – Ambition, Scope and Main Findings Marit Mazzetti (SINTEF, Norway)	
13:50	IMPACTS Recommendations for Safe and Efficient Handling of CO ₂ with Impurities Amy Brunsvold (SINTEF, Norway)	
14:10	The IMPACTS Toolbox for the Design and Operation of CCS Systems Filip Neele (TNO, The Netherlands)	
14:30	Techno-economic Evaluation on the Effects of Impurities for Conditioning and Transport of CO ₂ by Pipeline Geir Skaugen (SINTEF, Norway)	
14:50	Impacts of Impurities on CO ₂ Transport and Storage Heike Ruetters (BGR, Germany)	
15:10	Techno-Economic Analysis of CO ₂ Quality Impact on CCS Chains Charles Eickhoff (Progressive Energy Ltd., UK)	
15:30	COFFEE BREAK	Faidra / Parthenon rooms
Session 4: Process Optimisation and Techno-economic Considerations Chair: Dr. Halvor Lund (SINTEF, Norway)		Hedra meeting room
15:50	Operational Flexibility of CO ₂ Transport and Storage James Craig (IEAGHG, UK)	
16:10	The Multi-period Optimisation of Full CCS Chain for Flexible Operation: From a Gas-fired Power Station to Injection/Storage Evgenia Mechleri (Imperial College London, UK)	
16:30	CO ₂ Purity from Different Carbon Capture Applications and Associated Cost and Performance Richard Porter (UCL, UK)	
16:50	Assessment of CO ₂ Enhanced Oil Recovery Projects through Process Modelling Adekola Lawal (Process Systems Enterprise Ltd., UK)	
17:10	Quantification of the Water-Carbon-Energy Nexus for Carbon Negative Electricity Generation Mathilde Fajardy (Imperial College London, UK)	
17:30	CLOSE	

COCKTAIL DINNER

20:00 – 22:00: Cocktail dinner at the *Grande Balcon*

THURSDAY, 17 DECEMBER, 2015

08:00	REGISTRATION/WELCOME COFFEE	Faidra / Parthenon rooms
08:30	Plenary Lecture 3: Fracture Propagation in a CO₂ Pipeline – An Operator’s Perspective Russell Cooper (National Grid, UK) Chair: Dr. Amy Brunsvold (SINTEF, Norway)	Hedra meeting room
Session 5: Thermophysical Properties Chair: Dr. Amy Brunsvold (SINTEF, Norway)		
09:10	Thermodynamic Properties of a CO ₂ -rich Mixture CO ₂ +CH ₃ OH in Conditions of Interest for CCS Technology and Other Applications Sofía Blanco (UNIZAR, Spain)	
09:30	Experimental Speed of Sound in CO ₂ -rich Mixtures with Methanol. Extrapolation to Pure CO ₂ Javier Fernández López (UNIZAR, Spain)	
09:50	Investigation of Models for Prediction of Viscosity Properties for CO ₂ Mixtures Jacob Stang (SINTEF, Norway)	
10:10	Modeling of CO ₂ Solubility in Single and Mixed Electrolyte Solutions Using Statistical Associating Fluid Theory Ioannis Economou (Texas A&M University, Qatar)	
10:30	Development of a Novel Experimental Apparatus for Hydrate Equilibrium Measurements Panagiotis Kastanidis (NCSR Demokritos, Greece)	
10:50	COFFEE BREAK	Faidra / Parthenon rooms
Session 6: Thermophysical Properties Chair: Prof. Ioannis Economou (Texas A&M University, Qatar)		Hedra meeting room
11:10	Ionic Liquids for CO ₂ Capture using Molecular Simulation: Bulk and Permeability Properties Niki Vergadou (NCSR Demokritos, Greece)	
11:30	Simulation of Two-Phase Flow of CO ₂ Mixtures: Comparing Cubic and Reference Equations of State Halvor Lund (SINTEF, Norway)	
11:50	Iolicap Project Results George Romanos (NCSR Demokritos, Greece)	
12:10	Vapour-liquid Equilibrium Data for the Carbon Dioxide and Oxygen (CO ₂ +O ₂) System at 6 Isotherms Between the Freezing Point and Critical Temperature of CO ₂ Jacob Stang (SINTEF, Norway)	
12:30	Experimental Work at RUB and Tsinghua and a New Model Describing Thermodynamic Properties of CO ₂ -rich Mixtures Roland Span (Ruhr-Universität Bochum, Germany)	
12:50	Modeling Solid–Fluid Equilibria with Application to CO ₂ Mixtures Ilias Nikolaidis (NCSR Demokritos, Greece)	
13:10	LUNCH	Faidra / Parthenon rooms

13:50	Plenary Lecture 4: CCS Developments in North America Dr. Greeshma Gadikota (University of Columbia, USA) Chair: Dr. Filip Neele (TNO, The Netherlands)	Hedra meeting room
Session 7: Storage Chair: Dr. Filip Neele (TNO, The Netherlands)		
14:30	Reactive Transport Simulations of an Impure CO ₂ Flue Gas Injection into a Saline Aquifer on a 2D Reservoir Scale Dorothee Rebscher (BGR, Germany)	
14:50	Analysing the Effect of Impurities in the CO ₂ Stream Injected on Fractured Carbonates Miguel Angel Delgado (CIUDEN, Spain)	
15:10	Effect of SO ₂ Co-injection on CO ₂ Storage Marielle Koenen (TNO, The Netherlands)	
15:30	Comparison of Different Numerical and Modelling Approaches for Implementing SO ₂ as a CO ₂ Flue Gas Impurity in Geochemical Simulations in Saline Sandstone Aquifers Dorothee Rebscher (BGR, Germany)	
15:50	Thanks and End of Conference Haroun Mahgerefteh (UCL, UK)	
16:00	CLOSE	

The following posters will be presented throughout the event:

POSTERS
Potentiodynamic Anodic Polarisation for the Corrosion Study of Stainless Steel 304 and Ion in Aqueous Amine Solvents Paraskevi Gkanavara (Imperial College London, UK)
An Analytical Model for Blowdown of Pressurised CO ₂ Pipelines Wentian Zheng (UCL, UK)
TREND – A Software Package Providing Thermophysical Properties for the CCS community Stefan Herrig (Ruhr-Universität Bochum, Germany)
CO ₂ Capture and Purification Technology with Selective Removal of NO _x and SO ₂ Shaoyun Chen (DUT, China)
Simulation of Transient Flow in CCS Pipelines with Intermediate Storage Nor Daud (UCL, UK)
Investigating the Corrosion and Surface Passivation of Carbon Steel in Amine Blends Louis Yu (Imperial College London, UK)
Choice of Benchmark CCS Chains for Illustrating CO ₂ Quality Issues Charles Eickhoff (Progressive Energy Ltd., UK)
The European CCS Laboratory Infrastructure ECCSEL Paris Klimantos (NTNU, NO)

THE BOOK OF ABSTRACTS CAN BE DOWNLOADED

FROM: <http://goo.gl/sMknAX>

Status of International Standardization on CO₂Transportation

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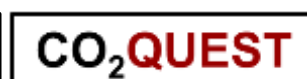
Abstract

Carbon Capture and Storage (CCS) technology plays an important role in reducing carbon dioxide emissions. Especially pipeline transportation is regarded as a major technology to transport large quantities of CO₂ from capture facilities to storage sites. Standards for natural gas transportation via pipelines exist but do not cover the different characteristics of CO₂ and its implications on design, construction and operation of pipeline systems. Therefore, the international standard ISO 27913 was derived, describing the state of the art for CO₂ transportation. The standard is considered to be a supplement to existing standards for natural gas and not to be a standalone standard.

The ISO Technical Committee (TC) 265 for Carbon dioxide capture, transportation and geological storage was founded in 2011 and started with a first TC meeting in June 2012 in Paris. Today 20 countries are participating members and 8 countries observing members in the ISO TC 265 with Canada and China as Secretariat. It comprises of six working groups (WG's) that deal with Capture (WG1), Transportation (WG2), Storage (WG3), Quantification and Verification (WG4), Cross-Cutting Issues (WG5) and Enhanced Oil Recovery (WG6). Working Group 2 on CO₂ Transportation met first time in June 2013 in Bonn to collect the current knowledge on CO₂ transportation, to develop a strategy and distribute topics to work on for experts around the world to derive a first Working Draft (WD). The second meeting in London in February 2014 and the third one in April 2014 in Berlin were used to compile and finalize the WD to distribute it for comments inside WG2. Fracture arrest assurance, corrosion and CO₂ stream composition were identified as most important issues for CO₂ transportation. Comments on WD were discussed and solved in a fourth meeting in Gelsenkirchen in August 2014 and the Committee Draft (CD) was submitted for comments to the ISO/TC 265 afterwards. WG2 met for a fifth meeting in Birmingham, Alabama in January 2015 to discuss and solve the comments on the CD and the provision of a Draft International Standard (DIS) ISO/DIS 27913 CO₂-Transportation for DIS Ballot. The Ballot was finalized with 100% pro votes. The sixth meeting, which took place in December 2015 in Kjeller just a week ahead of this conference was for DIS comments finalization. The worldwide participation at all stages of the development of the standard assures that the Standard represents the state of the art and provides a common understanding of the topic. DNV RP 201 was used as the initial basis for ISO 27913 and WG2 is grateful for that opportunity. Currently ISO 27913 is in the FDIS phase and will be published at latest in October 2016.

The definition of the scope of ISO 27913 was discussed with all working groups because it is key to define where a transport system starts and where it ends. The definition developed is as follows: "The system boundary [...] between capture and transportation is the point at the inlet valve of the pipeline, where the composition, temperature, and pressure of the CO₂ stream is within a certain specified range by the capture process or processes to meet the requirements for transportation as described in [this] International Standard. [...] The boundary between transportation and storage is the point where the CO₂ stream leaves the transportation pipeline infrastructure and enters the storage infrastructure." [1]. It seems simple, but it was a lot of work to find a common understanding.

The specific thermodynamic properties of CO₂ differ significantly from the properties of natural gas for standard operating conditions. Hence, CO₂ can be transported as a gas, as a liquid, or in the dense phase. Transport in liquid and dense phase and phase can result in hydraulic shocks which should be taken into account in the design and operational phase. Furthermore, the CO₂ decompression behavior and embrittlement due to the Joule-Thomson effect are promoting fracture propagation so that countermeasures like the use of special steel, fracture arrestors or the wall thickness need to be taken. In case fracture arrestors are not acceptable especially the wall thickness calculation plays an important role to assure a safe operation. One approach for wall thickness calculation for fracture arrest is the Battelle-Two-Curve-Model which is described in ISO 3183. But, due to the fact that the CO₂ decompression curve has a very long plateau, and the model has been shown not to be sufficiently conservative in full scale burst tests based on the current knowledge a modification by a correction factor is recommended in the new standard resulting in a higher



wall thickness. Specialist advice can be obtained to determine an alternative correction factor. In addition, for CO₂ streams with impurities the saturation pressure changes leading to an increase in wall thickness for fracture-arrest as shown in Figure 1. The composition of a CO₂ stream and its properties have a significant effect on design, construction, and operation.

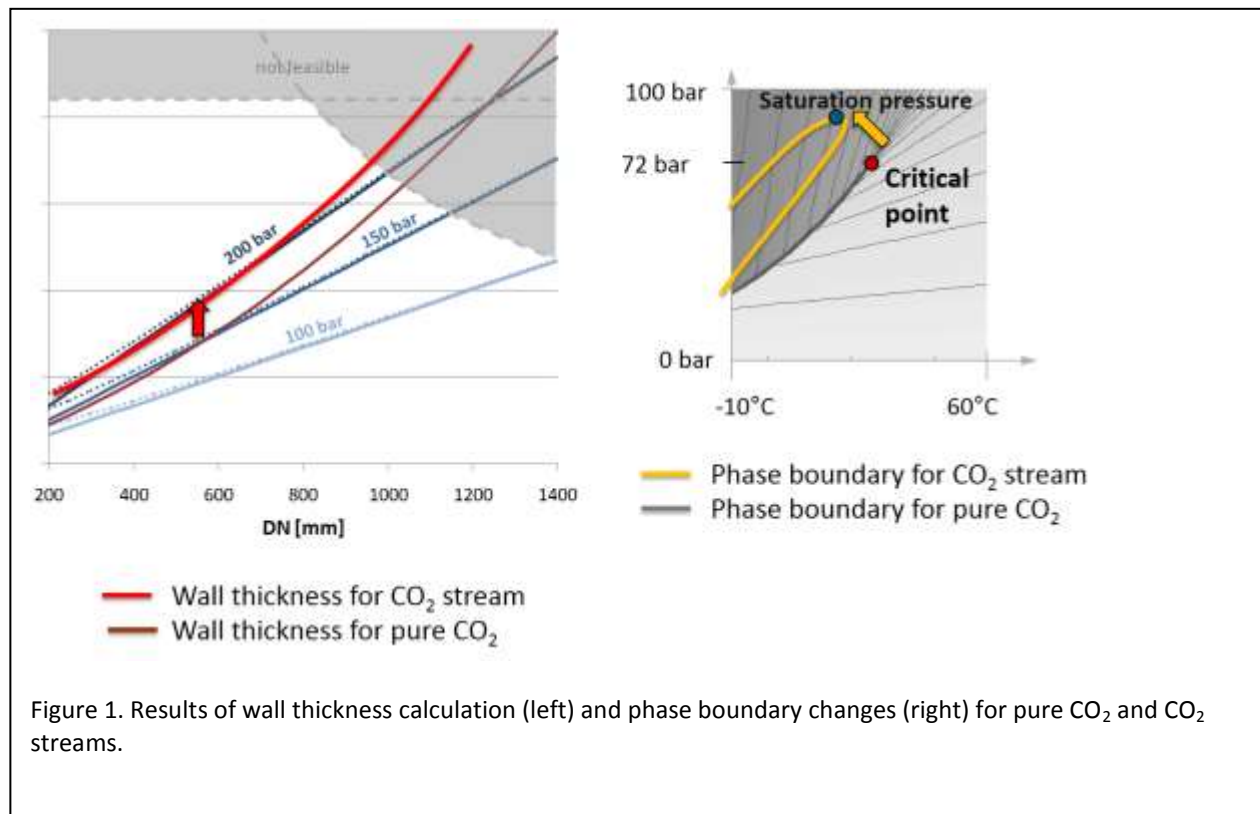


Figure 1. Results of wall thickness calculation (left) and phase boundary changes (right) for pure CO₂ and CO₂ streams.

Non-discriminatory grid access for everybody is possible, if the specification of the CO₂ stream is considered in the design process and meets the requirements of the operational envelope. In case of mixing of different CO₂ streams in a pipeline network from different sources of CO₂ (e.g. power plant, cement mill, etc.), it needs to be assured that the mixture of the individual compounds from different CO₂ streams do not cause undesired cross chemical reactions, or increases the risk of corrosion, or lead to an increase of the saturation pressure. A non-discriminatory grid access is not possible, if the CO₂ stream does not match the original design and operational criteria.

Internal corrosion is a significant threat for pipeline integrity. CO₂ pipelines should be designed for corrosion not to take place under normal operational conditions. For upset conditions a corrosion management plan shall be developed as part of the design. Its scope shall include internal corrosion and a plan to recover from failure of the control. Within the Standard there are two informative Annexes (Annex A, C) that give additional information.

Through efficient and multi-national co-operation solutions for the major issues have been found. Broad international participation in the ISO 27913 Standard development assures global acceptance. The Standard describes the state of the art and leaves the possibility of further development as the state of the art will develop in the future.

Concluding, the Standard ISO 27913 gives a good framework for design, construction and operation of CO₂ pipelines and supplements existing pipeline standards for natural gas.

References

1. ISO 27913 Carbon dioxide capture, transportation and geological storage — Pipeline transportation systems

Design and application of a large-scale experimental pipeline for studying the release and dispersion characteristics of CO₂ in different phase states

J. Yu¹, L. Guo², X. Yan^{*1}, S. Chen¹, Y. Zhang¹, H. Mahgerefteh², and C. Proust³

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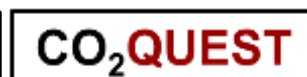
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Abstract

Large-scale release and dispersion experiments are essential for studying the safety issues resulting from CO₂ sudden release during CO₂ transportation by pipelines. Under the support of the European Union 7th Framework Programme (CO2QUEST), an industrial-scale pipeline with a total length of 258 m and an internal diameter of 233 mm (ϕ 273 × 20 mm) was set up to conduct CO₂ release experiments. A reinforcing device was built to prevent the possible movement of the pipeline due to the impulse and recoil forces during CO₂ sudden release. A heating system was used both for varying the initial temperature and increasing the initial pressure of CO₂ in the pipeline. A dual-disc device was designed to control the CO₂ sudden release precisely, simulating the intentional or accidental release from pipelines in real conditions. The pressures and temperatures of fluid in the pipeline, and the temperatures of the pipeline wall were recorded, together with the temperatures and CO₂ concentrations within the downstream dispersion region. A small weather station was built to measure the ambient temperature, ambient pressure, ambient humidity, and wind speed and direction. Sudden release experiments with initial pressure lower than 16 MPa and initial temperature from 0 to 40 °C are all available to be carried out by using this pipeline. The detailed variations of the fluid parameters during release and dispersion of CO₂ in different phase states could be obtained. The apparatus has been used several times in the research of CO2QUEST project. Experimental results from these tests indicate that the performance of this apparatus is good enough for the research requirement. Finally the release and dispersion characteristics were analysed, taking a release experiment of supercritical CO₂ for example.



High pressure CO₂ CCS pipelines: Comparing dispersion models with multiple experimental datasets

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Abstract

Carbon capture and storage (CCS) technology is designed to reduce carbon dioxide (CO₂) emissions from point sources of emission such as coal-fired power stations, in order mitigate greenhouse gas production. CCS technology involves capturing CO₂ and then storing it in a reservoir, instead of allowing its release to the atmosphere, where it contributes to climate change. Necessary transportation between points of capture and storage can be achieved in different ways, but it is commonly acknowledged that high pressure pipelines transporting liquid CO₂ will be the most reliable and cost effective choice. Safe pipeline operation is of paramount importance as routing will be unable to avoid populated areas and inventory could be several tens of thousand tonnes of CO₂, posing a number of dangers upon release due to its physical properties; it is a colourless, odourless asphyxiant which sinks in air and has a tendency to form cold solid (at -78.9 °C) upon release with subsequent sublimation. Gaseous CO₂ is directly toxic in inhaled air at concentrations around 5% and likely to be fatal at concentrations around 10%.

A number of projects have included experiments investigating the behaviour of high pressure CO₂ releases from pipelines simulating accidental or operational CCS scenarios. Typically these are dense phase pure CO₂ releases into air with varying levels of humidity. Data in the near-field, defined as within a few metres of the release point, is available in the public domain, either published in the scientific literature or freely downloadable, from the CO2PIPETRANS, CO2PIPEHAZ and CO2QUEST European-funded projects, from the industry-funded COOLTRANS research programme and from laboratory scale experiments e.g. [1].

At the previous CCS Forum meeting in March 2015, we reported initial jet centreline comparisons between available datasets and our state-of-the-art multi-phase heterogeneous discharge and dispersion model for pure CO₂. We now report refined journal-quality comparisons between extended experimental datasets and our improved discharge and dispersion model, shown in Figure 1. This model is capable of predicting both near and far-field fluid dynamic and phase phenomena and has been validated against a number of datasets for free releases [2,3], punctures of buried pipelines [4] and ruptures of buried pipelines [5,6]. Predictions are based on the solutions of the ensemble-averaged, density-weighted forms of the transport equations for mass, momentum, and total energy. Initial comparisons were performed with a compressibility-corrected k-turbulence model. The model now employs different equations of state (EoSs): (1) our original composite EoS [7] (consisting of Peng-Robinson [8] in the gas phase, Span and Wagner [9] in the liquid phase and DIPPR in the solid phase); (2) the Jager and Span EoS for solid phase CO₂ [10]; and (3) molecular SAFT-based models. The equation of state is also able to consider part-liquid and part-gas releases of CO₂ (Figure 1a), as well as impure releases of CO₂+N₂ and pure 100% CO₂ releases. The compressibility-corrected k-ε turbulence model is now also joined by a compressibility-corrected Reynolds-stress turbulence model with novel coefficients validated against air-jet releases. In this presentation and intended IJGGC journal paper, we compare this range of models to centreline (Figure 1a) and radial (Figures 1b and 1c) jet experimental data from a number of sources, for the first time demonstrating such a comparison and the importance of suitable equations of state, turbulence models and informed choice of initial release conditions. The results of these comparisons will inform far-field modelling of CO₂ release scenarios and entire chain CCS quantified risk analysis, benefitting academic, industry and regulatory stakeholders.



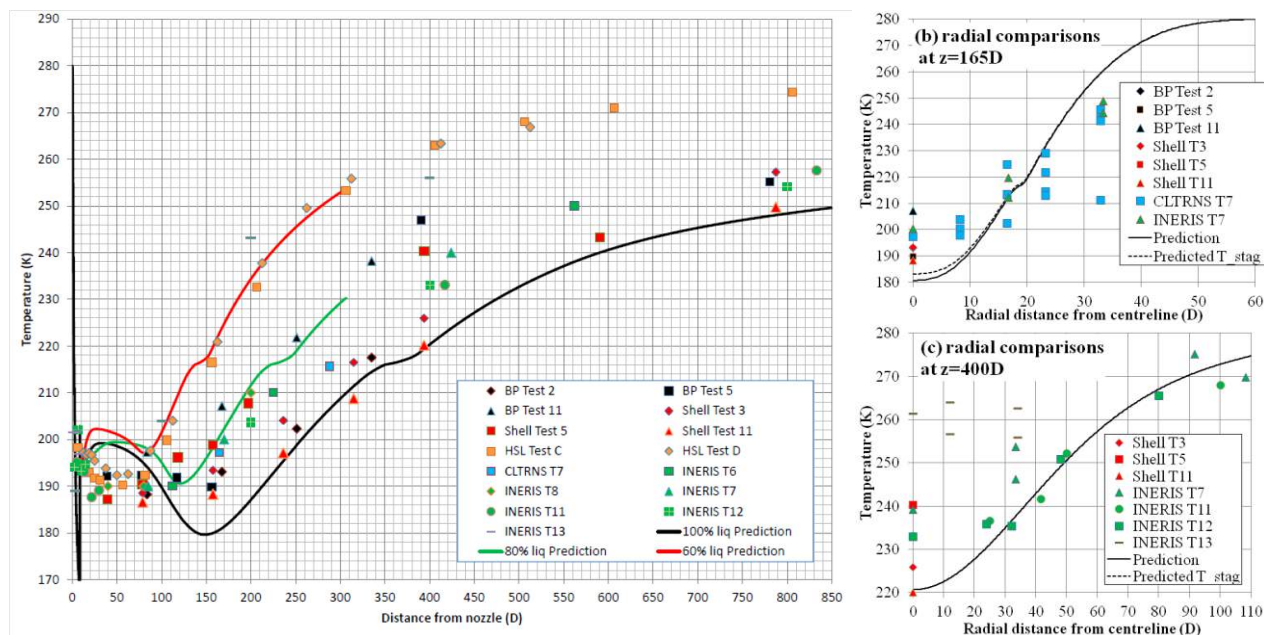


Figure 1. A comparison between experimental data and numerical predictions along the centreline of the jet (a) with 100% liquid prediction (black line), 80% liquid prediction (green line) and 60% liquid prediction (red line). Further radial comparisons are shown at 165D (b) and 400D (c) along the centreline from a 100% liquid prediction. The experimental data has an error of $\pm 5K$ throughout; error bars are omitted in the figure for clarity.

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On simulation of dynamic brittle fracture of CO₂ pipeline using coupled fluid–structure modelling approach

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Abstract

The deployment of Carbon Capture and Storage (CCS) is the cornerstone of the drive to reduce CO₂ emissions [1]. As part of the CCS chain, pressurised pipelines are widely recognised as the most practical and economical means of transporting the huge amounts of captured CO₂ from coal fired power plants for subsequent sequestration. Typically, such pipelines may cover distances of several hundred kilometres at pressures above 100 bars. Transport of CO₂ in dense phase presents a high potential for auto-refrigeration due to depressurisation, either during operations or due to equipment failure [2]. Concerns have been raised that low temperatures (-78 °C) induced by the expansion of dense-phase CO₂ to ambient pressure may result in embrittlement of the pipeline steels, increasing the risk of escalation of a small leak in a CO₂ pipeline into a fast-propagating brittle fracture [3, 4]. As such, to ensure safe operation of CO₂ pipelines, the risk for brittle fracture and its consequences need to be correctly assessed.

In the past several numerical and experimental studies have addressed the ductile mode of fracture propagation in pipelines, especially due to its relevance to the natural gas transmission pipelines. However, the brittle mode of pipeline failure has not received as much attention yet. Commonly, to prevent the brittle fracture in pipelines, the pipe wall material is selected based on the brittle to ductile transition temperature, which should be lower than the minimal pipe wall temperature encountered during the pipeline operation/ decompression. However, using this criterion may not provide economically efficient solution, leading to overdesign of the pipeline. Therefore, more accurate modelling of the pipeline decompression during the running fracture is required.

The present study develops a fluid-structure coupling methodology for simulation of scenarios of pipeline failure involving the brittle fracture propagation. The proposed model couples the fluid dynamics and heat transfer between the escaping fluid and pipe wall, and the fracture mechanics of the deforming pipeline exposed to the thermal stresses and pressure. To simulate the state of the fluid in the rupturing pipeline a one-dimensional compressible CFD model is applied. This model assumes the homogenous equilibrium nature of the flow and accounts for the propagation of the crack tip into the pipe at a speed predicted by the material failure model. The latter in its turn, is applied to calculate the crack propagation for the instantaneous state of stress and thermal conditions at the pipe wall as predicted by the CFD model. In terms of fracture model, a novel approach of eXtended Finite Element Method (XFEM)-based cohesive segment technique is used to model dynamic brittle fracture behaviour of pipeline steel. In this model the dynamic stress intensity factor and crack velocity are calculated at crack tip at each step of crack propagation. Figure 1 shows the section of the pipeline including the initial crack, discretised in a number of elements for the FEM simulations, and the schematic representation of the CFD/ crack propagation coupling algorithm.

To calibrate the brittle fracture model the data from the lab-scale Drop Weight Tear Test (DWTT) of X70 pipeline steel at -100°C is applied. Figure 2 (a) and (b) show the finite element mesh of the DWTT test sample and the comparison between the simulations and the measured data respectively. Figure 2 (c) shows the relation between crack propagation speed and normalized dynamic stress intensity factor extracted at crack tip from numerical model.

Using the methodology developed, a study is performed to evaluate the impact of CO₂ fluid phase and pipeline transportation conditions on the rate of brittle fracture propagation in a real-scale 48" OD pipeline. The model allows the quantitative prediction of the pipeline tendency to long running fractures in the form of the variation of crack length with crack velocity.



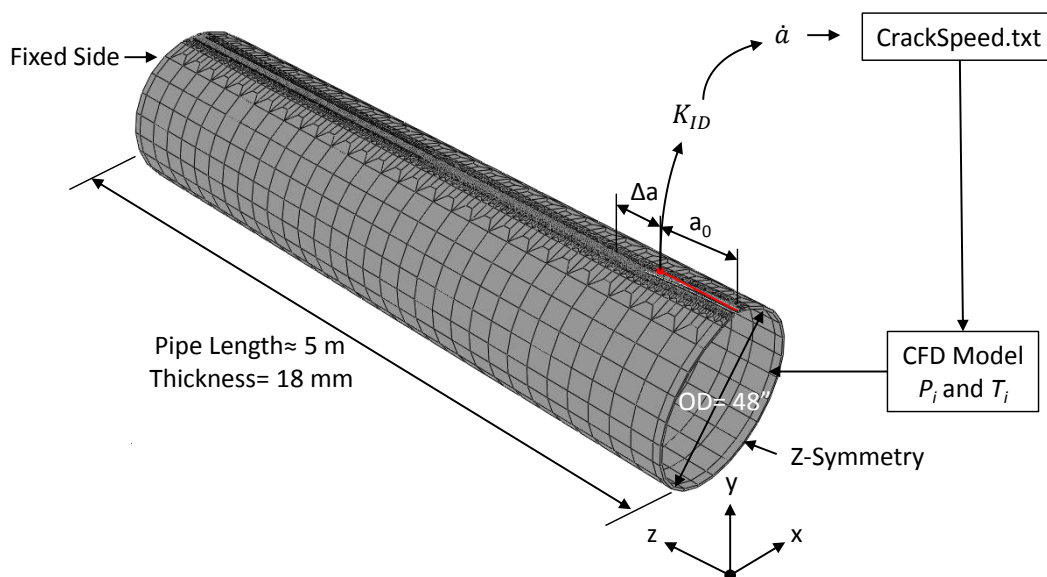


Figure 1. Advancing stationary crack in a pipeline using coupled fluid-structure interaction algorithm.

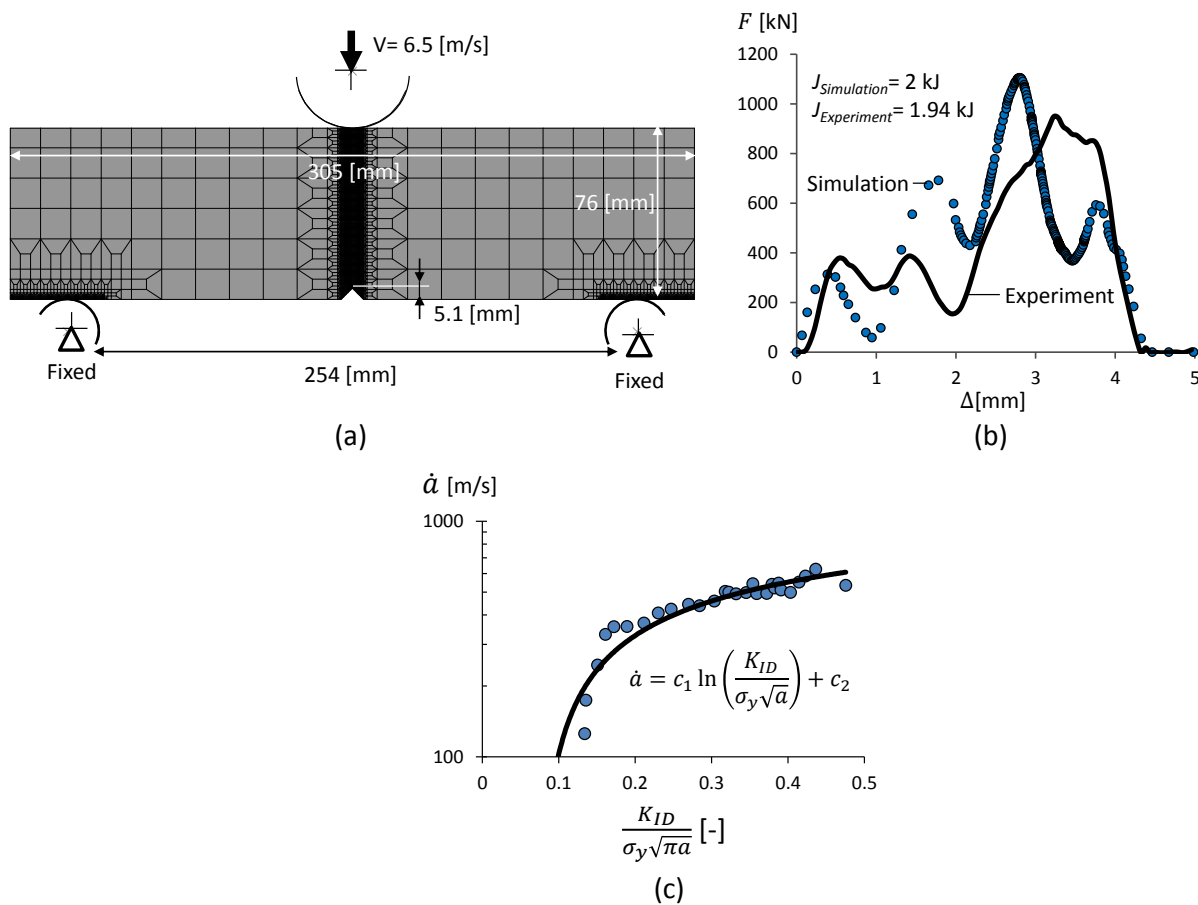


Figure 2. (a) Finite element mesh of DWTT, (b) comparison between simulation results and experimental observation and (c) Calculated crack velocity versus normalized crack tip dynamic stress intensity factor.

References

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Predicting the Atmospheric Dispersion of Carbon Dioxide from a Buried Ruptured Pipeline

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Abstract

At the 1st International Forum on Recent Developments of Carbon Capture and Storage (CCS) Implementation, the development and validation of CO₂FOAM, a dedicated Computational Fluid Dynamics (CFD) solver for carbon dioxide (CO₂) dispersion, developed within the framework of the open source CFD code OpenFOAM® [1] was presented. As a follow up, this presentation details further validation studies using Case Study 4 within the series of full scale tests commissioned by National Grid within the dense phase CO₂ Pipeline TRANSPORTation (COOLTRANS) research programme [2,3]. The test involved the release of dense phase CO₂ from a ruptured buried pipeline.

The numerical simulations used a pseudo source supplied by DNV GL to represent the release and provide the inlet boundary conditions. In reality, the flow is fully transient. Initially, the pressure fell to saturation and thereafter the flow stabilised. The pseudo source and atmospheric conditions supplied by DNV GL are listed in Table 1. These were calculated based on the approximate steady flow conditions after the flow had stabilised. The simulation represents the steady state that this steady flow would produce and therefore, the predictions can be compared with the experimental observations if the steady flow period dominated the release process.

Parameters		Case Study 4 Test 02
Mass Flow CO ₂ Vapour	kg/s	206.7
Mass Flow CO ₂ Condensed	kg/s	86.3
Mass Flow Air	kg/s	174.3
Total Mass Flow	kg/s	467.3
Total Mass Flow CO ₂	kg/s	293.0
Mass fraction of CO ₂ Vapour	%	44.233
Mass fraction of CO ₂ Condensed	%	18.468
Representative Crater Source Velocity	m/s	44.80
Representative Crater Source Diameter	M	2.145
Representative Crater Source Density	kg/m ³	2.887
Representative Crater Source Temperature	K	185.7

Table 1 The specified parameters for the pseudo source of the CO₂ release



Parameters		Value
Field Temperature averaged over 45 measurements	°C	17.7
Relative humidity (average over all test)	%	73
Dew temperature	°C	12.76
Average of wind speed measured at four locations	m/s	2.5
Average of wind direction measured at four locations	°	242

Table 2 The atmospheric conditions on the day of the test

Test 02 was selected from the experimental tests in Case Study 4 following recommendation from DNV GL about the reliability of the measurements. This test was carried out without the presence of any obstacles. The computational domain was determined based on the rupture scale in order to simulate the release cloud. The topographic data provided by DNV GL is used to mesh the realistic terrain and the data contains the local coordinates of the terrain at different locations with reference to the origin which is chosen as the centre of the release. The size of the domain is determined by taking into account the release mass flow rate, velocity and wind speed.

In Figure 1, the realistic terrain is represented by the inner area enveloped by the red line. It is approximately 330 m long and 200 m wide. The specified realistic terrain data is mainly plotted as five lines located at the X coordinates of -200 m, -110 m, -30 m, 30 m and 120 m respectively. The CO₂ source (i.e. point of release) is located at the origin of the coordinate system.

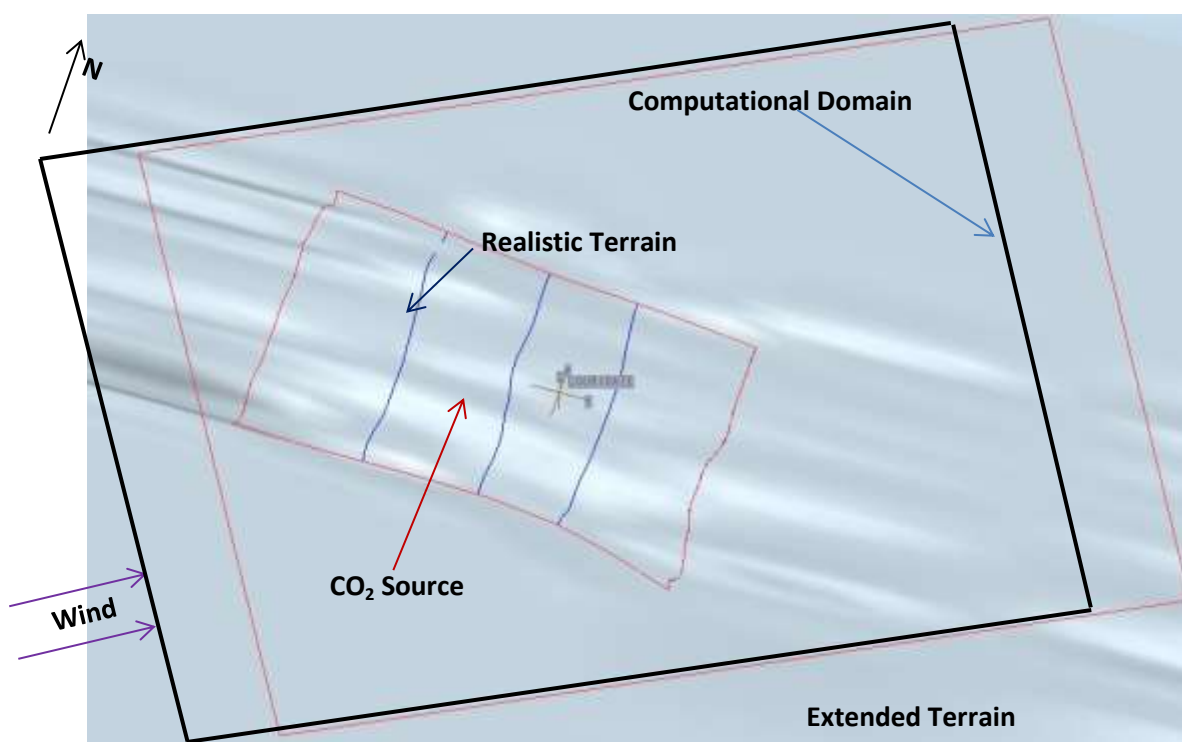


Figure 1. The computational domain for Case Study 4 – Test 02.

Figure 2 shows the mesh at ground level in which the surface mesh on the ground with realistic terrain is emphatically displayed and the unevenness of the ground is clearly shown. The structured mesh is used to discretise the computational domain. A finer resolution is used around the CO₂ source while coarser grids are used further away from the source to save computational time. Overall the mesh contains 3,633,280 grid cells. This resolution was used following a preliminary grid sensitivity study to identify the optimum analysis setup.

The simulations are conducted in two steps. Firstly, computations were performed to predict the steady state wind flow before the CO₂ release to establish the windy environment in which the CO₂ was released. This was then followed by simulating the dispersion of the CO₂ cloud.

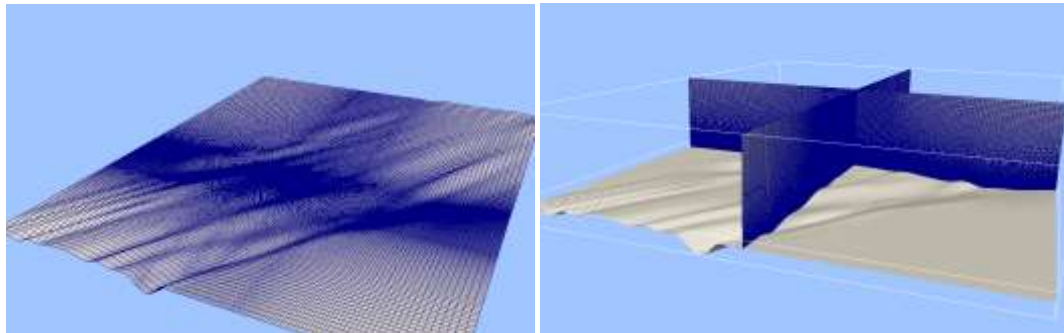
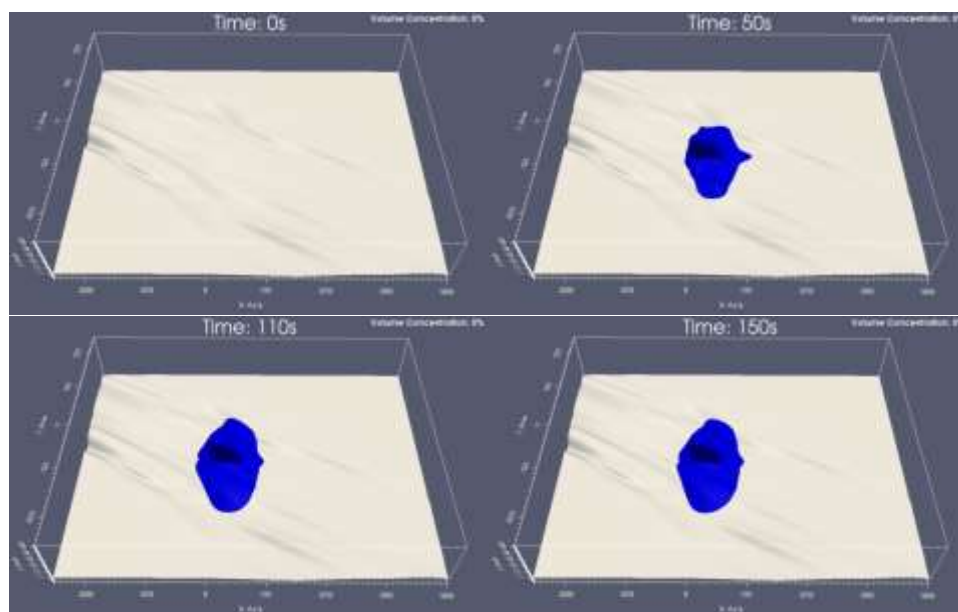


Figure 2. The computational mesh for Case Study 4 dispersion calculations.

Figure 3 displays the CO₂ cloud footprint (with a volume concentration level of 5%). The CO₂ cloud nearly stabilizes after 120 seconds following the release. The stable cloud covers a length of 105 m in the wind direction (25 m and 80 m at the upstream and downstream directions respectively) and a width of 225 m in the crosswind direction (110 m and 115 m at the positive and negative Y direction, respectively). The area covered is approximately half of the area of CO₂ cloud with a concentration level of 3%.



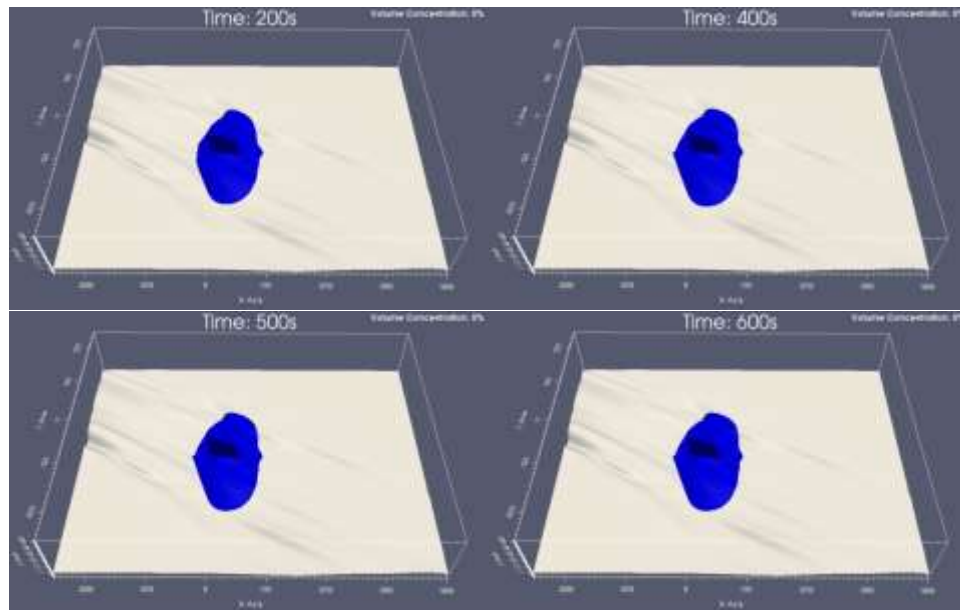


Figure 3. The footprint of CO₂ cloud (volume fraction 5%) for Case Study 4 – Test 02.

Further results will be presented to show the comparison between the predictions and the measurement for CO₂ concentrations at different locations.

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Techno-economic analysis of gas purification for CO₂ transport in pipeline networks and injection for storage

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Abstract

The IEA Energy Technology Perspectives 2014 stated that Carbon Capture and Storage (CCS) is a crucial component in capping the world's average surface temperature increase by 2 °C [1] and, if applied to the power generation and heavy industry sectors, could reduce cumulative emissions by 14% in 2050 [2]. In addition, when considering the decarbonisation of the heavy industry sector, CCS is currently the only available option. Therefore, it is imperative that the CCS process be optimised to run smoothly through each stage of operation and that its costs be minimised in order to accelerate its global financial and political acceptance. In view of these issues, this paper focuses on the operational modelling of a CO₂ capture process, modelling and quantifying the economic benefits resulting from a CO₂ transport network system and the cost reduction ensuing from CO₂ capture plant clusters.

Oxy-combustion capture comprises of two energy intensive sections: the air separation unit (ASU) and the CO₂ purification and compression unit (CO₂CPU). The CO₂CPU brings the raw flue gas from a low purity atmospheric CO₂ stream to a high purity, high pressure CO₂ stream suitable for transport. So far little has been discussed regarding the optimal design and operation of the CO₂CPU [3]. This work focused on minimising the capital and operational costs involved in the CO₂CPU while prioritising an EOR suitable end product. Three CO₂ compression and purification units processing flue gas from a pulverised fuel oxy-combustion plant were modelled in Aspen HYSYS. These CO₂CPU models build on similar separation processes presented by Posch et al. [4] and Pipitone et al. [5].

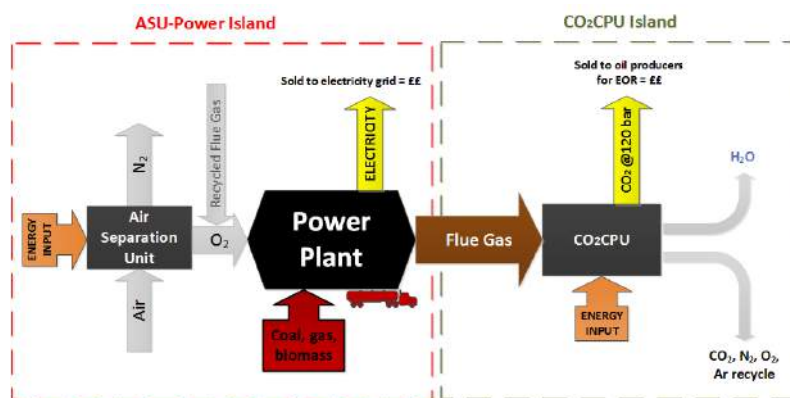


Figure 1. Illustrative diagram of the oxy-combustion capture process highlighting the main energy intensive units and revenue sources and outputs for each island: the ASU island and the CO₂CPU island

It was established that, as the CO₂CPU models increased in complexity and purity of the produced CO₂ stream, they increased in operational and capital costs but decreased in capture efficiency i.e. increase the amount of CO₂ vented to the atmosphere. The capital and operational costs for each process model were translated into a price for each stream of CO₂ marketed for EOR. A non-monotonic and non-linear relationship between CO₂ price and CO₂ purity was observed. A CO₂-EOR suitable product stream, requiring a very high purity, led to a price of £20 per tonne, while the least complex system provides a stream that is suitable for transport, but not for injection, at a price of £11 per tonne.

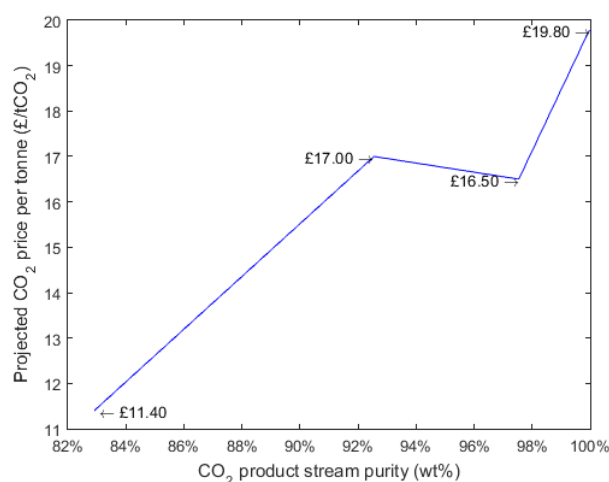


Figure 2. Graph showing the price of CO₂ per tonne if marketed assuming a 20% minimum return on investment on the CO₂CPU

In addition, this paper discusses the possibility of having one CO₂ capture plant for a cluster of power and/or industrial plants as opposed to several smaller capture plants. Modelled in Aspen HYSYS, it was found that instead of having 4 CO₂CPU with a 5 Mt. CO₂ yearly capacity, having one large CO₂CPU with a yearly capacity of 20Mt. CO₂ reduces capital expenditure by 16% and yearly operational expenditure by 4%.

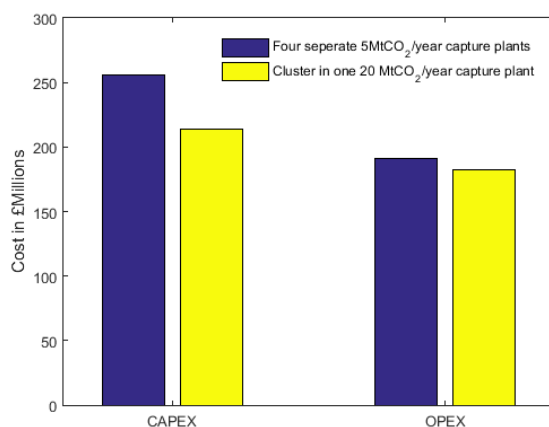


Figure 3. Bar chart showing the CAPEX and OPEX for one large CO₂CPU processing 20 Mt CO₂/year compared with four CO₂CPU plants each with a 5Mt CO₂/year throughput

As CCS is deployed on a large scale, we will deploy transport networks, as opposed to a large number of single point-source to sink links. It is therefore vital to understand how these complex networks will behave, and indeed contribute to the flexibility of these systems. Therefore, a second part of this work considers a hypothetical UK-based network of CO₂ sources connecting to a single sink in the North Sea [6]. The CO₂ sources considered include combined cycle gas turbine (CCGT) plants, coal fired power plants and industrial plants. The CO₂ transport network allows for high purity sources of CO₂ derived from post-combustion capture power plants to be combined with less expensive, lower purity sources of CO₂ using oxy-combustion capture, to produce a CO₂ stream which is suitable for injection, i.e., a CO₂ stream composed of > 96 wt% CO₂. This led to a 17% reduction in the price of CO₂.

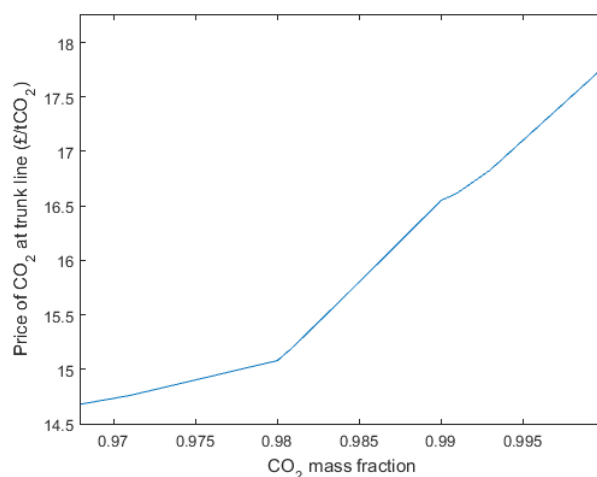


Figure 4. Graph showing the price of CO₂ at the end of the trunk line as a function of the purity achieved by mixing streams from different capture options

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Impact of impurities in CO₂ streams on compression strategies for Carbon Capture and Sequestration

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Abstract

The efficacy of Carbon Capture and Sequestration (CCS) as a means to mitigate the CO₂ gas emissions from various industrial sectors, including fossil fuel operated power plants, requires the minimisation of the costs associated with compression and transportation of the captured CO₂. For high-pressure compression and transportation of CO₂, several strategies have been recommended for high-purity CO₂ streams [1, 2]. However, given that CO₂ captured from emission sources will contain notable amounts of impurities that may significantly affect the thermodynamic properties of the mixture, while their removal would significantly reduce efficiency of CCS process, the costs of compression should also be balanced with the costs of CO₂ purification. As such, evaluation of strategies and power requirements for compression of CO₂ mixtures containing impurities becomes particularly important.

This paper applies a thermodynamic analysis method to determine the power requirements for compression of CO₂ streams carrying up to 15% of impurities originating from various capture technologies (Table 1), to a dense-phase fluid state for pipeline transportation. The multistage compression is modelled as a sequence of idealised isentropic compression and isobaric cooling steps, which bring the stream from a given initial state to the final pressure and temperature conditions (151 bar and 38°C). The analysis is performed for three different types of industrial multistage compressors (Table 2), applied to compress ca. 156.4 kg/s of CO₂ emitted from a coal-burning 900 MW power plant. In order to evaluate the thermodynamic properties of CO₂ mixtures involved in the multistage compression model, the Peng-Robinson equation of state is applied [3].

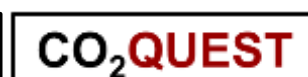
	Oxy-fuel			Pre-combustion	Post-combustion
	Raw/dehumidified	Double flashing	Distillation		
CO ₂ (% v/v)	85.0	96.70	99.30	98.07	99.8

Table 1. Purity of CO₂ streams captured in oxy-fuel, pre-combustion and post-combustion technologies [4].

Option	Compression technology
A	Conventional integrally geared centrifugal compressors
B	Advanced supersonic shockwave compression
C	Compression combined with liquefaction and pumping

Table 2. Multistage compression technology options.

Figure 1 illustrates the variation of the energy demand for multistage compression of CO₂ streams of various purity captured from the oxy-fuel combustion process. As can be seen from this figure, the compression power generally increases with a decrease in purity of CO₂ stream. This can be explained by the fact that compression power is inversely proportional to the fluid density which progressively decreases with the existence of impurities. On the contrary, the impact of CO₂ stream purity on the intercooling pump work is non-linear.



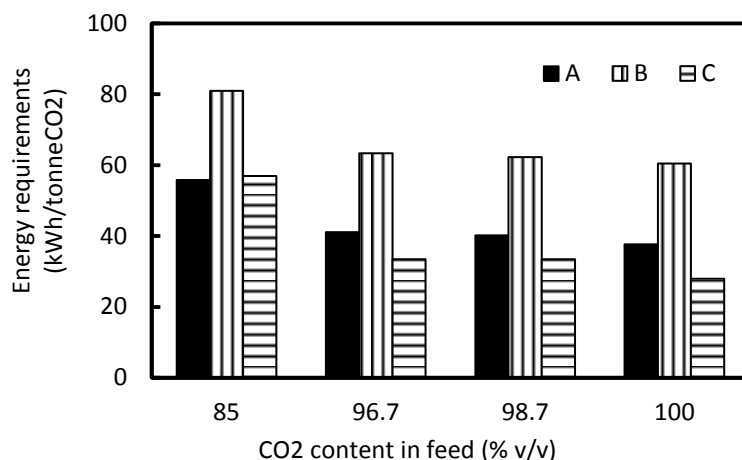


Figure 1. Energy requirements of multistage compression options A, B and C (Table 2) for pure CO₂ and the oxy-fuel mixtures (Table 1).

Based on the results of the present study, several recommendations for selection of suitable temperature and pressure conditions for multi-stage compression of impure CO₂ streams can be made. In particular, in the case of CO₂ streams carrying less than 5% impurities, multistage compression combined with liquefaction using utility streams and subsequent pumping from ca. 62.5 bar pressures can potentially offer higher efficiency than conventional gas-phase compression. In the case of relatively large amount of impurities, typical for raw/dehumidified oxy-fuel based CO₂, which has a significantly lower boiling temperature than pure CO₂, liquefaction should be performed at higher pressures and would require using refrigeration systems utilising part of CO₂ stream or cryogenic coolants such as R134-a. Implications of the results of the thermodynamic analysis for the design and operation of compressors for CO₂ streams of various impurities are discussed.

Acknowledgement

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Computationally efficient simulation of two-phase flows of CO₂ mixtures

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Abstract

As the only practical means of transporting the large amounts of CO₂ captured following the large-scale deployment of Carbon Capture and Storage, the construction of significant pipeline infrastructure is inevitable [1]. The most efficient use of these pipelines to connect the wide variety of CO₂ emitters, from fossil fuel power plants to cement production [2], to suitable storage sites is the development of collection networks [3]. Given the differing capture technologies and processing that may be applied, the CO₂ stream fed into the transportation may contain a number of impurities and vary in composition. It is well established that the presence of impurities has important impacts on many aspects of pipeline design, not least the propensity of the pipeline to ductile fracture [4] and the release rate in the case of loss of containment [5]. The ability to simulate these processes in the presence of impurities is therefore of great value for assessing the safety of such pipelines.

Given that CO₂ will be transported in the dense-phase or supercritical state, the pipeline decompression, as a result of its accidental failure, will inevitably result with the phase change in the fluid, and hence two-phase flow. The most commonly used, and simplest, model for the simulation of such flows, is the homogeneous equilibrium model, which relies on the ability to evaluate the phase equilibria of the mixture in question. While the equations of state used for modelling the phase equilibria and the techniques for their calculation are naturally evaluated using the pressure and temperature (P-T) using so called isothermal 'flash' calculations, the conservation laws that are used to model the fluid flow are naturally posed in terms of the density and internal energy (p-U). To obtain the data required for the p-U in question, a so called isochoric-isoenergetic flash is needed. Since existing isochoric-isoenergetic flash algorithms rely on an iterative loop over the P-T variables, their practical application necessarily adds a great deal of computational weight but is also susceptible to numerical instabilities in the underlying isothermal flash algorithms.

In this work a robust method for efficiently performing isochoric-isoenergetic flashes, for the purposes of two-phase flow calculations, is presented. The technique is based on adaptive inverse interpolation and can be applied independently of the equation of state and the specific mixture under consideration. This makes it ideal for the implementation of the complex, computationally heavy equations of state that are required for the accurate prediction of the thermodynamic properties and phase equilibria of CO₂ mixtures.

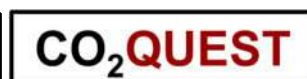
Following an analysis of its accuracy, the method is coupled with a flow model, and a number of tests are performed to establish the robustness and computational efficiency of the method in the presence of rapid transients. This coupled flow model is then used to predict the decompression of several mixtures and the results are compared against experimental data. It is found that the with an appropriate sampling an interpolant can be built which not only provides a robust thermodynamic model for use in flow models but also greatly reduces the computational weight of the two-phase flow simulations for which it is needed.

Acknowledgement

The research leading to this work has received funding from the European Union 7th Framework Programme FP7-ENERGY-2012-1-2STAGE under grant agreement number 309102.

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CO₂ Transport & Safety – An industrial perspective

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Abstract

The world's need for energy is increasing while at the same time the greenhouse gas emissions must be reduced. For reducing the carbon footprint and combating climate change Statoil's approach is to be a low-emission producer of oil and gas focussing on energy efficiency as well as reducing methane emissions. In addition, Statoil sees the potential in replacing coal with gas as energy source as one of the most important and immediately available ways to reduce emissions. Gas power plants are seen as a valuable lower carbon partner to support growth in renewables as gas power plants can flexibly balance the irregular electricity output of wind and solar power. Finally, decarbonized gas production, i.e. with the use of CCS is seen as a viable solution as an energy carrier.

However, the investment in CCS projects is still costly and there is a investment threshold offshore. Decreasing this threshold Statoil's aim is to lower the uncertainty for design and operation of CCS facilities as this decreases the need for safety margins and hence costs. One solution is seen in the availability of a reliable "toolbox" which can be applied for the safe, robust and economical design and operation. For CO₂ transport this toolbox should typically consist for instance of models and tools for flow assurance and safety risk assessment. Per today, tools for these applications are limitedly available and to a large extend not properly assessed and qualified. This partly accounts for tools for simulating pure CO₂ but even more so for tools handling CO₂ with impurities.

CO₂ transport R&D is considered as open innovation in Statoil and its goal is to contribute to the development of experimentally verified tools. Statoil focuses on the development of reliable flow assurance models for transient operations in pipeline and wells as well as on the improvement of tools for safety risk assessment. Statoil contributes by building and operating test facilities for providing experimental data sets as well as supporting suppliers.

Ongoing experimental activities within CO₂ transport in Statoil are the investigations of temperature and pressure behaviours in pipelines during start-ups, shut-ins and pressure release using pure CO₂ as well as CO₂ with impurities [1]. For these test activities Statoil's CO₂ transport test facility at its R&D centre in Trondheim, Norway is used. Further plans are to extend the current test facility which comprises of a 140 m horizontal flow circuit with a 150 m vertical flow circuit and execute investigations to collect experimental data for steady-state and transient flows as well as study efficient well kill operations for CO₂ blow-outs [2]. In addition to flow assurance, Statoil contributes to the execution of large scale CO₂ dispersion experiments for the development and validation of dispersion models and risk analyses of CO₂ pipelines.

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Highlights of the IMPACTS Project – Ambition, Scope and Main Findings

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Abstract

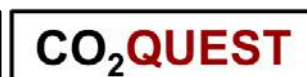
IMPACTS is a PAN European research project where researchers from academia and industry from nine different countries collaborates on investigating impact of impurities in CO₂ captured from power plants and other CO₂-intensive industries on CO₂ transport and storage. The goal is to develop the CO₂ quality knowledge base required for defining norms and regulations to ensure safe and reliable design, construction and operation of CO₂ pipelines and injection equipment. This encompasses fluid properties, phase behaviour and chemical reactions occurring both in the infrastructure complex and at the storage reservoirs. The successful outcome of IMPACTS will allow closing the knowledge gap regarding these issues which is paramount for ensuring reliable design, construction and operation of CO₂ pipelines and injection equipment, and safe long-term geological storage of CO₂. IMPACTS has generated a large amount of new knowledge in this area and is an example of how wide reaching research programs where different groups look into different aspects of the same topic brings the knowledge base forward while ensuring that the results are aligned.

Fundamental properties of CO₂ mixtures relevant for CO₂ transport are investigated both experimentally and theoretically. Both large scale experiments for injection and corrosion, as well as fundamental experiments on thermo-physical, chemical and physical effects of impurities have been performed. The behaviour of different CO₂ mixtures was then established and the subsequent consequences for relevant CO₂ value chains were determined with respect to economy, safety and possible environmental impact (HSE). The main findings from IMPACTS include:

- Fundamental vapour-liquid equilibrium data have been established for CO₂-N₂, CO₂-O₂ and CO₂-Ar mixtures. These are of a better accuracy than experimental data available in the literature until now. These data can be used to improve the state-of-the art equations of states currently used for CO₂ mixtures. An example of these results is given in Figure 2. The data for the CO₂-N₂ system is published in [2], whereas the two other systems are to be published.
- An overview of knowledge regarding corrosion of pipelines in CO₂ service has been established and experimental work has determined effect of CO₂ supercritical mixtures on corrosion of pipeline materials. An example results from such corrosion tests is given in Figure 3. The results have e.g. been used to establish the expected corrosion rate in terms of [mm/yr] in pipelines used to transport specific CO₂ mixtures. Impurity levels varied from 1100 to 3000 ppm, under temperatures ranging from 40 to 75 °C and pressures ranging from 8 to 12 MPa.
- A better equation of state has been developed for CO₂ mixed with all the potential contaminants expected in captured CO₂. In [3], an improved EOS is presented which especially performs well for the important CO₂-H₂O mixture.

7 representative CCS chains have been formulated to be used in the IMPACTS analysis, evaluation and recommendations. These cover the full range of compositions likely to be encountered in CCS projects over the next 10-25 years. These are ready for use in the analysis of economic, operational and risk effects of impurities. A start has been made on the construction of the economic model.

The three year IMPACTS project is coming to its end in December 2015. In the concluding part of the project the overall working goal is to use the established technical knowledge base for developing future standards, protocols, techno-economical analysis, and developing practices for design and operation of CO₂ pipelines and storage site infrastructures. This work will be performed and published in the coming months, and will be reported upon in the final



paper following this abstract. The results are scheduled to be presented to the standardization committees, such as the ISO committee on CO₂ transport for possible implementation into the new ISO Standard on CO₂ transport..

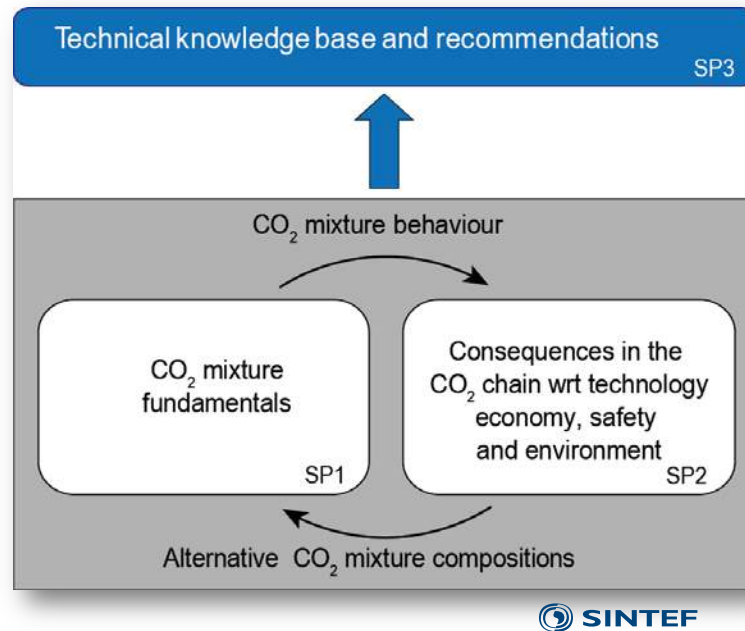


Figure 1. The concept of the IMPACTS project. CO₂ mixture fundamental properties will be established through experimental and theoretical work,

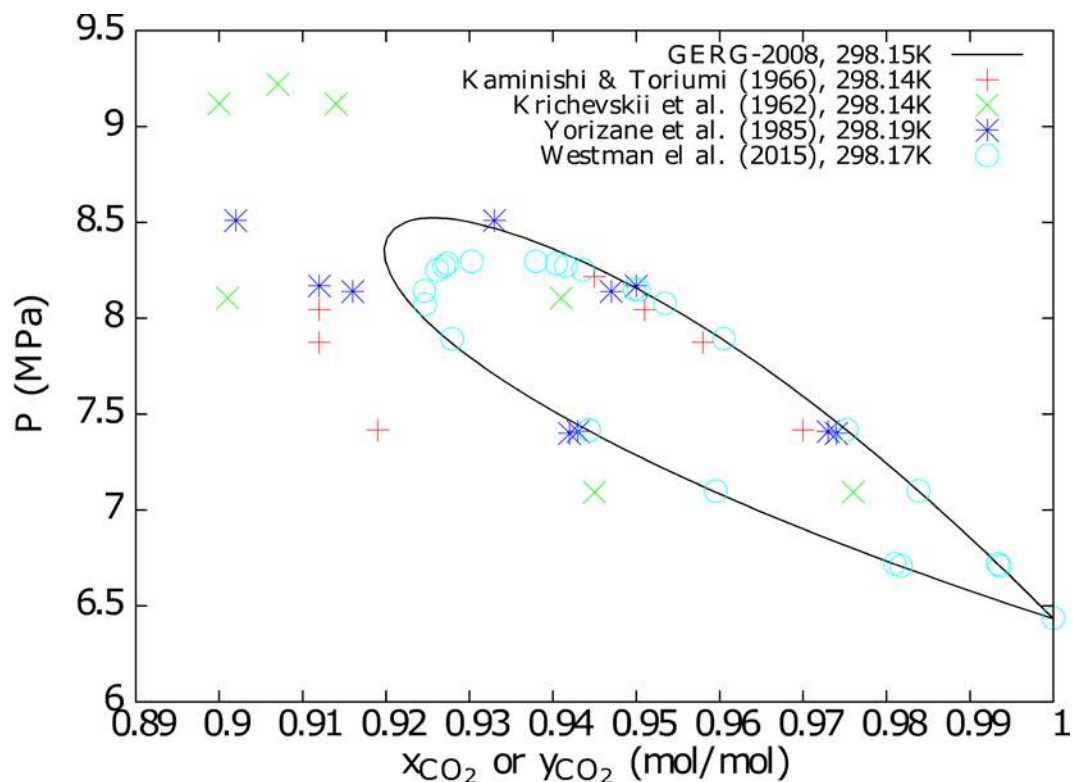


Figure 2. Isothermal VLE data for a CO₂-N₂ system. Data are from literature, EOS calculations at mean temperature $T = 298.17$ K, and measurements with estimated uncertainties from present work in the IMPACTS project (Westman et al.).

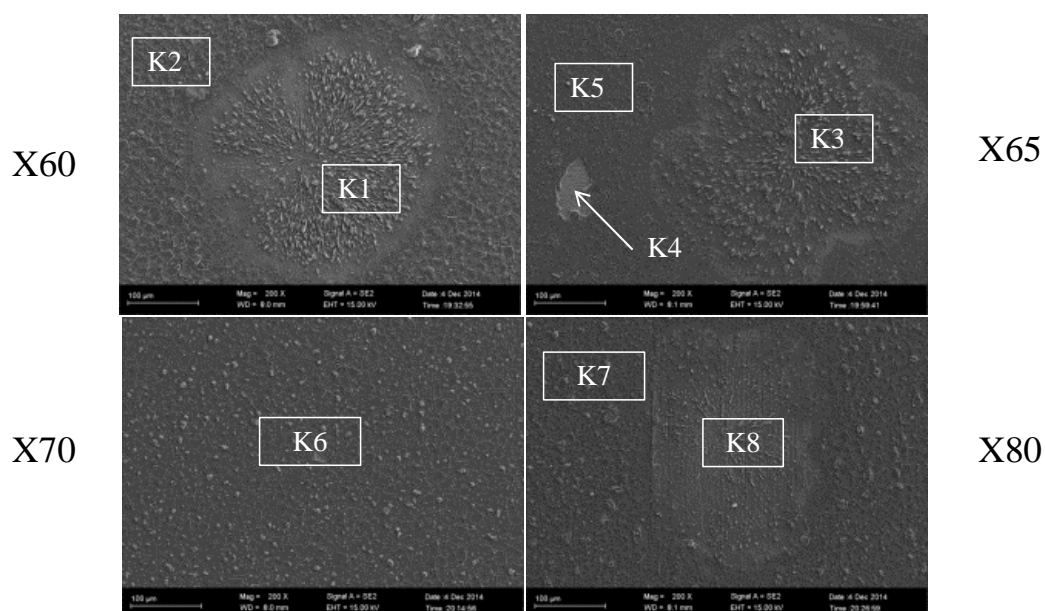


Figure 3. SEM images of four different corroded steel samples after exposure to a CO₂-H₂O-O₂-SO₂ mixture. Tests were used to establish corrosion rates in [mm/yr]. Tests were carried out by Tsinghua University.

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IMPACTS recommendations for safe and efficient handling of CO₂ with impurities

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Abstract

We know that CO₂ captured from power plants and industrial sources will not be purely CO₂, but will contain chemical impurities. But how will these impurities affect the design and operation of a CCS chain, which will include capture, conditioning, transport, injection and permanent storage?

The EU CCS Directive requires that the captured CO₂ consists "overwhelmingly" of CO₂, which is often translated to a minimum concentration of 95% CO₂. For most CCS systems, the CO₂ concentration is in the range of 95-99% CO₂, but there could be many different combinations of the chemical impurities (e.g. nitrogen, argon, carbon monoxide, NO_x, SO_x, hydrogen sulphide, etc.) depending on the CO₂ source and the CO₂ capture method. And as large CO₂ pipeline networks develop worldwide, many CO₂ streams with varying compositions could potentially be mixed together as they are transported to storage locations.

So is the requirement of "overwhelmingly" CO₂ enough to ensure safe transport and storage? Is it pure enough for the transport pipelines to withstand corrosion? Is it pure enough to ensure that there are no phase changes (i.e. change to solid phase) of the CO₂ mixture that could lead to damaged equipment and poor performance? And what if the costs of the entire project could be reduced by purifying the CO₂ stream before transport and storage? Or what is the trade-off of transporting lower purity streams and implementing corrosion-preventing measures? There are a multitude of questions and factors at play and there is no one-size-fits all approach to designing and operating all CCS systems. Until now there has been no established method to discover the relationship between the CO₂ stream quality and the cost of safe transport and storage.

IMPACTS, a three-year collaboration project under the EU 7th framework programme for research, aimed at deciphering the impact of impurities in captured CO₂, from power plants and other CO₂-intensive industries, on CO₂ transport and storage. IMPACTS has established a novel methodology and framework (see Figure 1) with a diverse team of experts consisting of three main features: 1) experiments and verified property models for mixtures of CO₂ and impurities, 2) techno-economic assessments of CCS chains with impurities to understand the effect of impurities on materials, equipment, processes, operation and safety procedures on transport and storage, and 3) resulting guidelines for safe and cost efficient CO₂ transport and storage with impurities.

Based on the knowledge and tools developed in IMPACTS, various recommendations have been elucidated for optimized operation of safer and more efficient handling of CO₂ with impurities along full CCS chains. In this work, an overview of the main challenges and resulting consequences leading to the quality requirements are outlined. In addition, competing issues (e.g. purity, longevity and cost) are addressed and suggestions for appropriate ranges of impurity levels and examples of optimized impurity levels are presented. Furthermore, guidelines for material selection in equipment along the CO₂ infrastructure are proposed, as are considerations to be made regarding the impact of CO₂ impurities on storage injection and integrity.



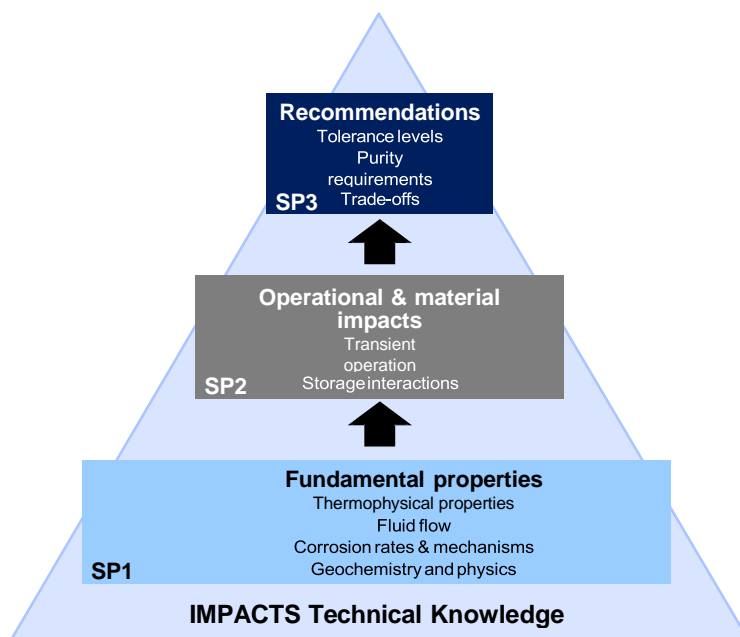


Figure 1 : Illustration of the overall strategy of the IMPACTS project

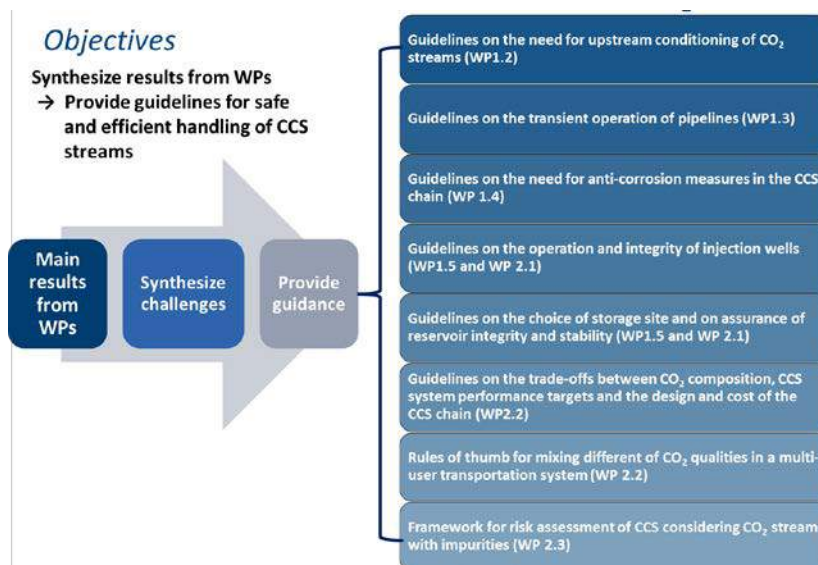


Figure 2: IMPACTS project flow chart leading to recommendations on safe and efficient transport and storage of CO₂ with impurities

The IMPACTS Toolbox for the design and operation of CCS systems

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Abstract

Impurities in captured CO₂ affect the properties of the CO₂ flow and its behaviour when in contact with materials and processes. The design and operation of a CCS system, from capture, through to transport, injection and storage, depends on these properties and behaviour of the CO₂. The effects, which can be highly significant, cover a broad range including deterioration of materials, reduction in efficiencies, increased risks and health and safety implications.

The IMPACTS project has studied the relation between the purity of the CO₂ stream and the design and operation of a CCS system. Using measurements, experiments and modelling focused on elements of the CCS chains, as well as on specific physical and chemical processes that can take place within a CCS system, the project has developed a holistic approach to investigating the impact of impurities on CCS systems.

During the project, a wealth of results, guidelines and tools have been derived relating the interaction of the CO₂ stream, its composition and the requirements on and performance of a CCS system or of elements of a CCS system.

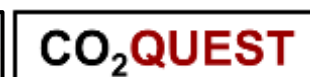
One example of these results is found in the area of storage capacity. To a first approximation, impurities will affect storage capacity through the fact that they displace some of the volume dedicated to CO₂. However, for some impurities there are other effects that play a role that can be non-linear, as well as depth-dependent. Table 1 shows that for realistic CO₂ compositions significant deviations from expected storage capacity can occur, if initial calculations were based on pure CO₂. The table shows that the storage capacity deviations can be much larger than the amount of impurities in the CO₂.

The IMPACTS Toolbox contains the results such as those reported in Table 1 related to CO₂ storage. The table shows that storage capacity can be significantly different for real CO₂ mixtures, when compared with estimates derived on the assumption of storing pure CO₂. Figure 1 shows a similar result, for the cost of CCS as a function of N₂ content, due to the effect of N₂ on storage capacity. Other elements of the Toolbox are conclusions and guidelines from many other areas including transport, mixing of CO₂ streams from different sources and optimisation and cost of the CCS system.

The Toolbox is expected to become a useful reference for CCS system design and operation, for both future operators and regulators. The quality of CO₂ from future participants in a multi-user CCS network and the impact on design choices for today's transport and storage systems is only one area in which the results from the IMPACTS project and the Toolbox will be highly relevant. The Toolbox will be made publicly available through the IMPACTS project website.

Depth (m) reservoir	Selexol based adsorption (CO ₂ purity 98%) Oil field			Post combustion ammonia (CO ₂ purity 99.8%) Aquifer			Natural gas processing (CO ₂ purity 95%) Gas reservoir		
	Storage capacity (Mt)			Storage capacity (Mt)			Storage capacity (Mt)		
	Pure	Mixture	Diff (%)	Pure	Mixture	Diff (%)	Pure	Mixture	Diff (%)
800	9.2	4.7	-48.9	14.1	13.9	-1.4	6.0	3.1	-48.3
900	5.2	3.9	-25	15.9	15.7	-1.3	5.2	3.3	-36.5
2000	4.9	4.7	-4.1	34.2	34.2	0	5.0	4.5	-10.0
3400	4.0	3.9	-2.1	57	56.8	-0.3	4.0	3.8	-5.0

Table 1. The effect of CO₂ purity on storage capacity (Mt), for CO₂ streams from three different capture technologies, stored in three types of storage reservoir. Results are shown for several depths; the maximum effects are observed at depths near 800 m.



Effect of Nitrogen on CCS chain storage capacity with depth

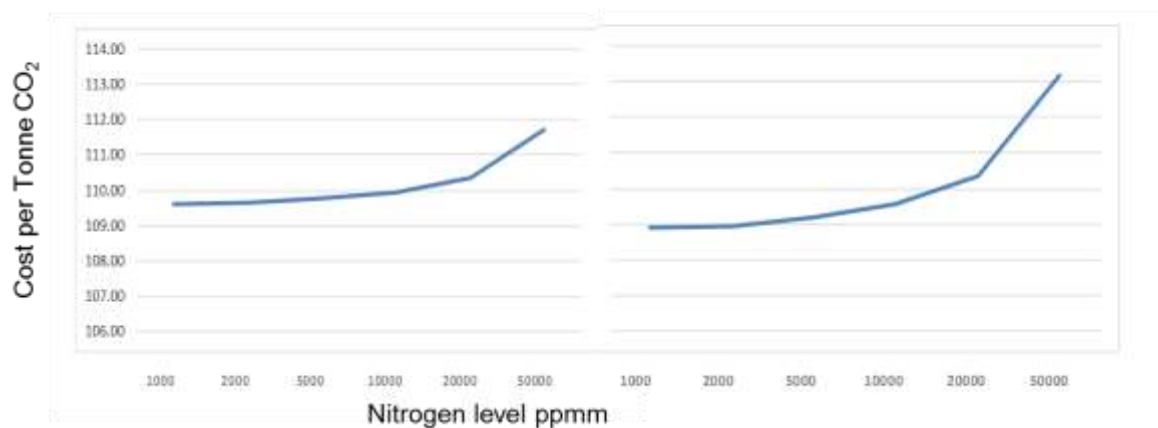


Figure 1. The effect of N₂ in the captured CO₂ stream on total CCS cost as a result of the impact of the N₂ content on storage capacity.

Techno-economic Evaluation on the Effects of Impurities for Conditioning and Transport of CO₂ by Pipeline

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Abstract

Techno-economic assessments that utilize fundamental knowledge of the thermo-physical properties of the CO₂ stream are crucial for enabling energy and cost efficient design of CO₂ transport and storage infrastructure. A number of projects have been established and are in progress on various aspects of CO₂ transport. Among these are projects focusing on acquiring experimental data for CO₂ rich mixtures with impurities (KPN CO₂MIX), projects on simulation of CO₂ flow in transport pipes (KPN CO₂ DYNAMICS, FME BIGCCS SP2), projects on transport infrastructure optimization (FME BIGCCS SP4), and projects on safety and cost assessment of various transport options (FME BIGCCS SP4, EU IMPACTS, EU CO₂ QUEST). However, more work is still needed on the development of thermodynamic models for CO₂ with impurities, on the analysis of the effects of impurities, as well as model uncertainties upon the process design and operation costs and energy efficiency.

In this work, a methodology for integrated techno-economic assessment [1, 2] is applied on selected case studies for CO₂ transport with varying impurity levels in the CO₂ feed stream.

The design and techno-economic analysis of the transport and storage infrastructure must be based on robust and reliable models for CO₂ with impurities. The effect of 5 mole% N₂ in a CO₂ stream at 90 bar and ~33 °C, both density and dynamic viscosity will decrease by nearly 45% compared to pure CO₂. The consequence of this is that although the friction factor is decreased, the pressure drop and the theoretical power consumption could be increased by 182% due to the higher flow velocity caused by the reduction in density. It is therefore important to know the effect of impurities on all thermo-physical properties in order to avoid operation in an especially unfortunate pressure and temperature range. It is also necessary to include the variation of properties with temperature and pressure when CO₂ are to be transported over long distances. The variation of density is illustrated in Figure 1. From the state-of-the-art review of techno-economic models predicting the costs of CO₂ pipeline transport [3] it is shown that many previous studies use constant values for the fluid density either as pure CO₂ or for a given mixture in one state point. Other comprehensive studies [4] seem to use a constant pressure drop gradient when calculating the pressure loss and required pumping power over the pipeline distance.

The case study that is presented here includes the conditioning (for transport) and transport of pressurized CO₂ over 500 km by pipeline. The feed gas for the case study is humid CO₂ at atmospheric conditions and includes impurities from two possible capture processes. The two feed stream specifications are related to: a) capture from oxy-fuel combustion (OXY-feed) and b) natural gas sweetening process (GAS-feed). The OXY-feed used in the study will have 3% N₂ and 2% O₂ in addition to 7% H₂O while the GAS-feed will have 1% N₂ and 9% Methane. The base case is a feed stream with pure CO₂ saturated with water vapour (93% CO₂ and 7% H₂O). Examples of the conditioning route in a pressure-enthalpy diagram are shown in Figure 2. The green dew-point lines come from varied amounts of saturated water vapour that are removed from the feed in the different compression and separation stages used in the conditioning process.

The transport pressure is set to be 150 bar and four different pipeline diameters (18,22,24 and 28") are studied with respect to required number of booster stations and maximum pressure loss. In this study, the various thermo-physical properties are calculated locally along the pipeline and the total energy consumption is found by integrating the local pressure loss and specific power. Heat transfer between the gas and the surroundings is also included. The results show that in a 24" pipeline with 4 booster stations, the consumed power increases by 7.0 and 15.0% for the conditioning and 47.8 and 83.3 % for the transport part compared to the base case for the OXY-feed and the GAS-feed respectively. The calculated specific power consumption and required number of booster stations are shown in Figure 3



The result the energy requirements for the conditioning and transport of CO₂ with impurities are coupled to a cost model based on the NOAK (Nth Of A Kind) principle [5] where the investments costs, maintenance and operating costs for both the conditioning and for the transport are included. As a key performance indicator the CO₂ avoided transport costs that approximate the average discounted CO₂ tax or quota during the duration of the project that would be required as income to match the net present value of the additional capital and operating costs. The annual avoided amount of CO₂ transported is defined as the CO₂ transported minus the amount of CO₂ generated from electricity consumption in the conditioning and transport process.. In the case study the economic consequences of transporting CO₂ with impurities in a pipeline designed for (almost) pure CO₂ are discussed. The results showing the calculated costs for conditioning and transport in a 24" pipeline is shown in Figure 4.

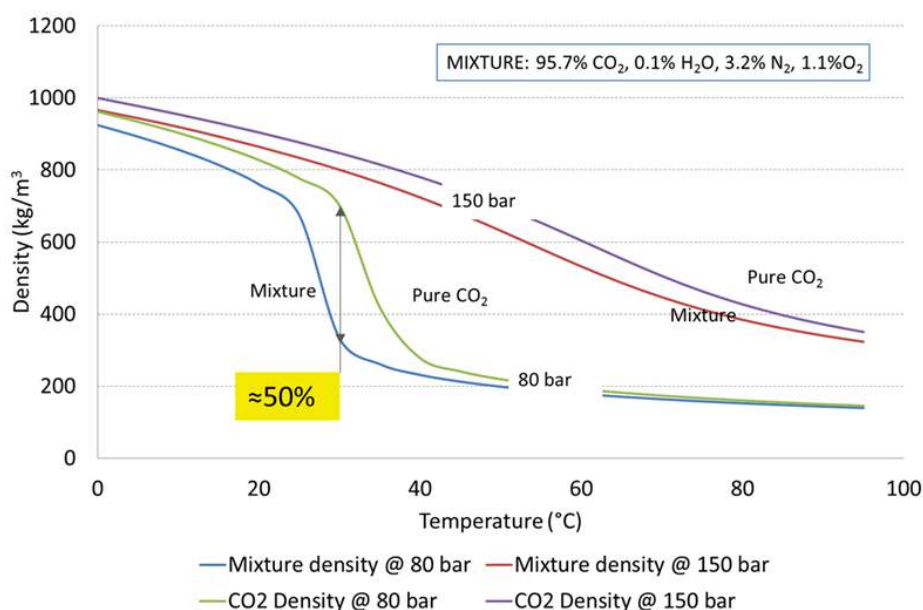


Figure 1: Illustration of the variation of density with temperature and pressure for pure CO₂ and CO₂ with 5% impurities from N₂, O₂ and H₂O

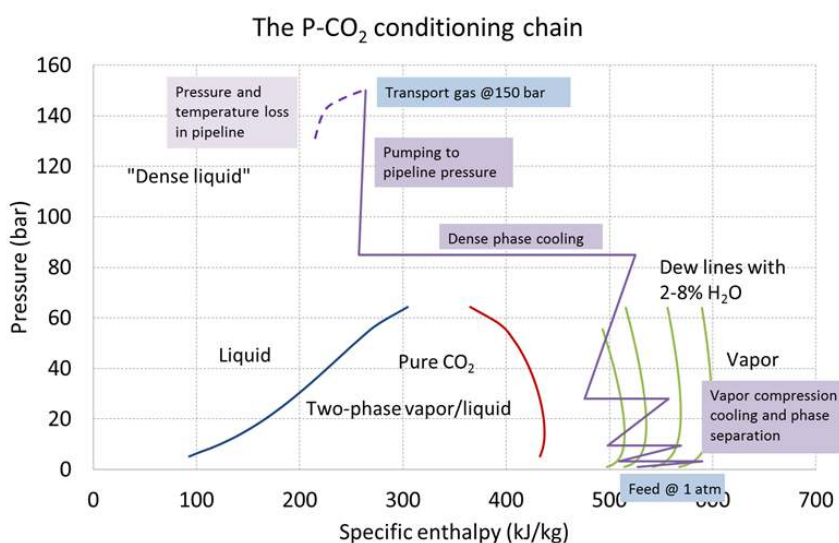


Figure 2: Example of the conditioning route in a pressure enthalpy diagram for the case study for pipeline transport (BASE cases)

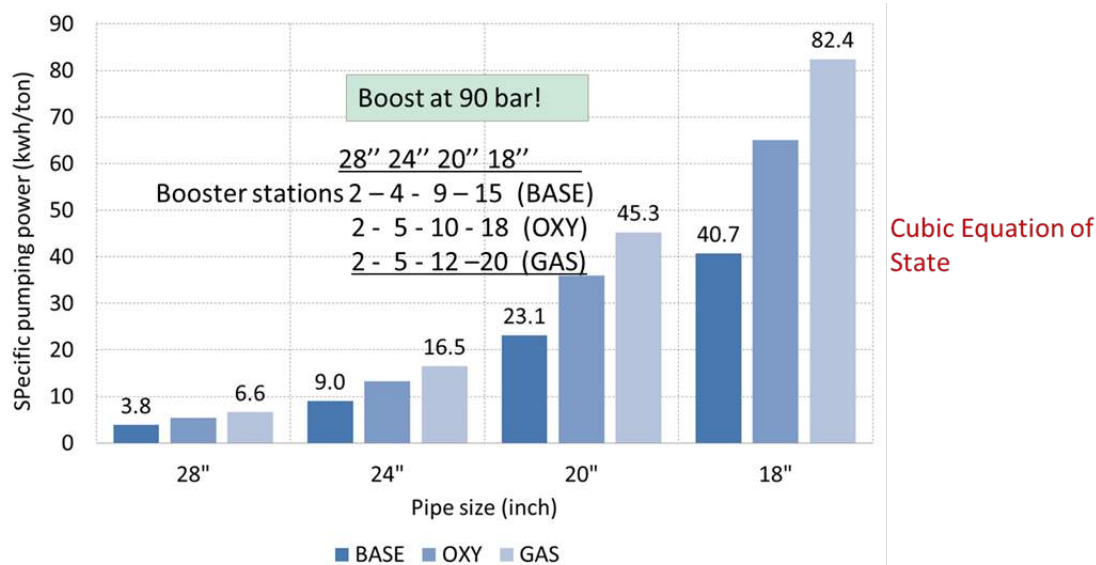


Figure 3: Required energy consumption and number of booster stations for transport of CO₂ in a 500 on-shore pipeline with different (outer) diameter for the BASE, OXY and GAS cases

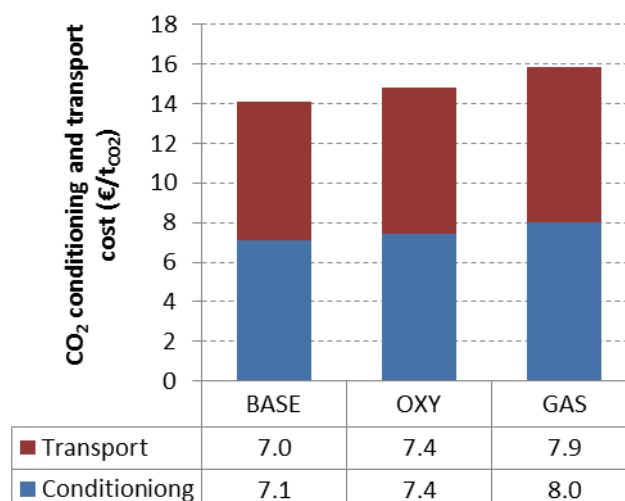


Figure 4: CO₂ conditioning and transport cost of the BASE, OXY and GAS cases with 24" pipeline diameter

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Impacts of impurities on CO₂ transport and storage

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Abstract

Carbon dioxide (CO₂) streams captured from power stations or industrial plants may contain various associated incidental substances ("impurities") such as SO_x, NO_x, O₂, N₂, etc. Compositions of captured CO₂ streams vary in relation to the emitter, the capture technology, and the application of further purification steps [1]. The presence of impurities may impact CO₂ transport, injection, and geological storage in two ways: Firstly, physical fluid properties such as phase behavior, viscosity, density, interfacial properties etc. may be modified affecting CO₂ transport and injection behavior as well as storage capacity. Secondly, chemical properties of the CO₂ stream may be changed with implications for corrosion of pipeline steels or plant components, and for geochemical reactions in the storage reservoir that, in turn, may affect injectivity, geomechanical rock properties, and long-term trapping of CO₂.

In the collaborative project "CO₂ purity for capture and storage (COORAL)" potential impacts of various impurities in CO₂ streams on different processes in the individual parts of the CCS chain were investigated to define requirements for CO₂ purity along the entire CCS chain. More specifically, data on phase behavior, viscosities, and densities were measured experimentally using binary to quaternary mixtures of CO₂ with N₂, O₂ and/or Ar. Capital and operating costs for several pipeline design options were assessed. To study impacts of specific impurities and impurity combinations and to inform material selection, corrosion of selected metal-based materials was investigated in different CO₂ streams at conditions mimicking compression, transport, or injection conditions. From these investigations, e.g., acceptable water contents were defined. Applicable dehydration technologies were selected and respective (additional) costs were compared. Also, implications of different impurities on phase behavior during injection were modeled to define feasible operational modes. Geochemical reactions as affected by the reactive impurities SO_x, NO_x, O₂ and/or H₂ and effects of mineral reactions on geomechanical rock properties were investigated by laboratory experiments and numerical simulations.

Results for the individual parts "source/capture", "transport", "injection", and "geological storage" were synthesized and illustrated using two generic single source - single sink CCS chain scenarios. In either scenario, a coal-fired power plant (thermal capacity of 1600 MW) is the emitter at which 137 kg CO₂/s (or 4.32 Mt CO₂/yr) are captured by pre-combustion capture or from oxyfuel combustion resulting in two contrasting CO₂ stream compositions (Tab. 1).



Tab. 1: CO₂ stream compositions considered in CCS scenarios (contents after compression; [1]). ("PreC" = CO₂ stream composition resulting from pre-combustion capture, "Oxy" = CO₂ stream composition resulting from oxyfuel technology).

Component	Pre-Combustion Capture ("PreC")	Oxyfuel ("Oxy")
CO ₂	97.95 vol.%	96.65 vol.%
O ₂	–	0.81 vol.%
N ₂	0.9 vol.%	1.96 vol.%
Ar	300 ppmv	0.57 vol.%
H ₂ O	600 ppmv	100 ppmv
NO _x	–	100 ppmv
SO ₂	–	50 ppmv
SO ₃	–	20 ppmv
H ₂	1.0 vol.%	–
H ₂ S/COS	100 ppmv	–
CH ₄	100 ppmv	–
CO	400 ppmv	750 ppmv

The following key parameters were defined for the scenarios [2]:

Scenario A: transport option: pipeline; transport distance: 50 km; transport of CO₂ at temperature (T) > T_{Crit}; injection in a saline aquifer (Rotliegend reservoir; depth: 3000 m; porosity: 10%, permeability: 40 mD; reservoir temperature: 363 K; initial reservoir pressure: 32 MPa; one injection well).

Scenario B: transport option: pipeline; transport distance: 500 km; transport of CO₂ at T < T_{Crit}; injection in a saline aquifer (Buntsandstein reservoir; depth: 1500 m; porosity: 20%, permeability: 300 mD; reservoir temperature: 328 K, initial reservoir pressure: 15 MPa; one injection well).

Calculations on pipeline design indicated a significant impact of CO₂ stream purity on transport economics when impurity levels exceed approx. 1.5 vol.%. In addition, costs of pipeline transport depend on the pressure and temperature conditions selected. Differences in capital costs for the transport of CO₂ streams of compositions "Oxy" and "PreC" were only calculated in scenario A, since over this short transport distance capital costs are mainly related to compressor costs. Capital costs for transporting a CO₂ stream of composition "Oxy" were higher than the respective costs for a CO₂ stream of composition "PreC". In scenario A, also operating costs were found to be higher for transporting a CO₂ stream of composition "Oxy" in comparison to composition "PreC", whereas in scenario B the difference in operating costs related to the CO₂ stream composition was very small (Fig. 1). The influence of CO₂ stream composition on total pipeline transport costs (capital plus operating costs) diminished with increasing transport distance. Overall, a minimum CO₂ content of 95 vol.% is recommended in CO₂ streams for pipeline transport.

Combining CO₂ streams from different emitters and sharing of CO₂ transport and storage infrastructure is one option to reduce the costs of the CCS technology (e.g., [3]). According to the Directive 2009/31/EC, CO₂ streams must meet "reasonable minimum composition thresholds" to be fed in a common pipeline network. As of today, it is not known how such composition thresholds may be defined and which impurity levels may be viable in practical application. The dynamic interplay of CO₂ streams from different emitters – both in terms of mass fluxes and compositions – will influence corrosion of, e.g., pipeline material and plant components, as well as geochemical alterations of cap rocks and reservoir rocks. These influences are studied in the recently launched collaborative project "CLUSTER" based on a model scenario of a regional cluster of different CO₂ emitters feeding into a joint trans-regional pipeline network. In addition, issues and processes are investigated for an overall design of a "cluster CCS system", such as setting up of CO₂ stream mixing schemes and facilities, and the potential need for interim CO₂ storage arising from the coupling of process steps of different flexibilities and loading capacities. Overall, the project aims to set up criteria and respective recommendations for (maximum) tolerable quantities, acceptable variability (in terms of composition and mass flux) and "critical" combinations of individual impurities in the captured CO₂ streams for their combined handling in a common transport and storage infrastructure.



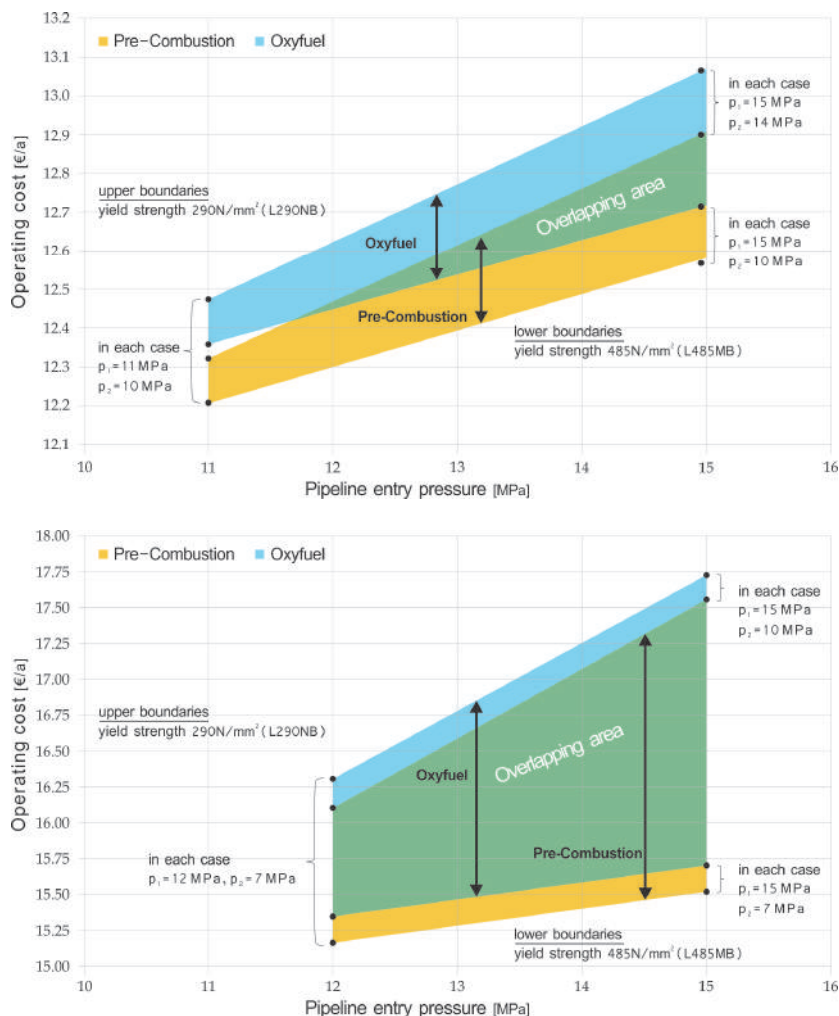


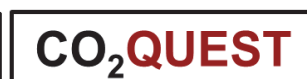
Fig. 1: Comparison of operating costs for scenarios A (top) and B (bottom) as function of pipeline entry pressure ([4]; entry pressure = design pressure; CO₂ stream compositions: Pre-Combustion = “PreC” and Oxyfuel = “Oxy”). Black dots indicate minimum and maximum operating costs at selected pipeline entry and exit pressures p_1 and p_2 , respectively, for CO₂ stream compositions “Oxy” and “PreC”. Black arrows mark the data range of each CO₂ stream composition.

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Techno-Economic Analysis of CO₂ Quality Impact on CCS Chains

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Abstract

The techno-economic analyses carried out in the IMPACTS project are derived from a standard economic model which has been adapted to include the detailed influences of impurities in the CO₂ stream, derived elsewhere within the project, on typical CCS chains.

The IMPACTS CCS chain economic model is designed to allow the user to model the cost consequences of impurities in the CO₂ stream flowing through a chosen CCS chain and to look at the economic consequences of varying the impurity levels on the overall project economics for the chain. The model is written in Excel, chosen to make it readily accessible and adaptable by all partners and results are provided in tabular and graphical forms. The CCS chain required can be specified by the user and the model will do various continuity checks and provide a graphical representation of the chain (see Figure 1) for the user to check. Typical output economic measures would be the overall project return or the cost per tonne of capturing and storing CO₂.

The main tool within the model to achieve this are Cost Functions which are used to vary the costs of CCS chain elements associated with differing levels of impurity in the CO₂ stream. If the level of an impurity in the model varies from the standard benchmark level, the model uses the relevant Cost Functions to determine the changes in costs to be used and these are then incorporated into the overall project economic data. Cost Functions can reflect additional costs in providing a purer CO₂ stream from the capture plant, or may also represent the costs of changing downstream materials or conditions to cope with impurities, such as using different qualities of steel, for example.

An illustration of a Cost Function is given in Figure 2, where the level of H₂O derived from the capture process is normally 250ppmm and reduction requires the installation of a methanol drying process at a Capex of €10m in steps of 100ppmm down to 10ppmm and an additional running cost of €1m/a/100ppmm reduction on a pro-rata basis. Examples of the impact of such cost functions on the resulting economic output are given in Figure 3 for reductions in nitrogen and water for a pre-combustion capture case.

When the model is populated with both upstream and downstream Cost Functions, it is possible to flex individual impurities throughout the CCS chain to look for optimal positions where the resulting project is economically optimised for the balance between cleaning up the CO₂ stream and dealing with the consequences. The optimised results contribute to the IMPACTS Toolbox and the project recommendations.

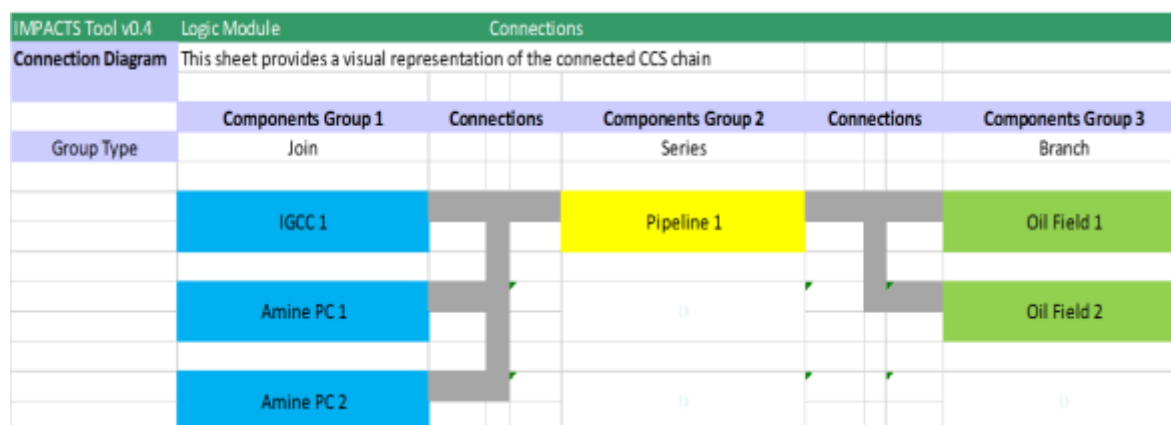


Figure 1. Diagrammatic representation of CCS chain in the IMPACTS model

Capex	
H ₂ O ppm	CF (€m)
2000	0
250	0
249	10
200	10
199	20
150	20
149	30
100	30
99	40
50	40
49	50
10	50

Opex	
H ₂ O ppm	CF (€m/a)
2000	0
250	0
10	2.4

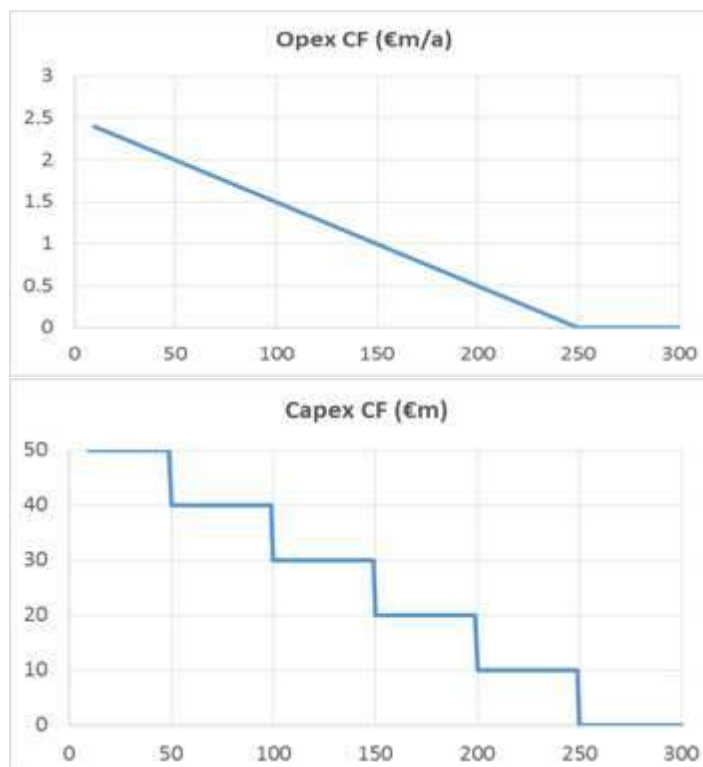


Figure 2. Illustrating the derivation of a Cost Function for varying impurity level (ppmm)

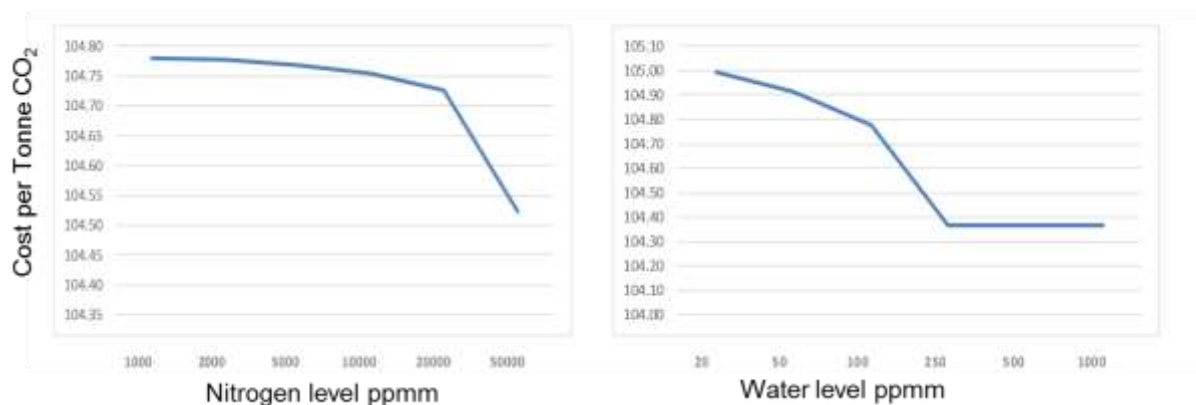


Figure 3. Effect of Nitrogen & Water reduction on Pre-combustion capture costs

Operational Flexibility of CO₂ Transport and Storage

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Abstract

The optimisation of carbon capture and storage (CCS) projects in terms of cost and efficiency requires one or more large scale point sources of captured CO₂ which can be transported via a pressurized CO₂ pipeline to reservoirs. There are a series of factors which could either reduce or disrupt the supply of CO₂ to a reservoir notably the intermittency of different sources and the presence of impurities particularly water. The implications for reservoir properties and operation may also be affected. IEAGHG commissioned a review of CO₂ pipeline transport from varied industrial sources, and the implications for CO₂ storage, which are summarised in this paper.

Large point sources of CO₂ emissions can deliver relatively pure 99.7% CO₂ after scrubbing and dehydration. However, it is important to recognise that many large-scale industrial processes that generate CO₂ emissions are cyclical and intermittent, for example coal fired power generation and cement plants. To ensure a consistent and reliable CO₂ supply integrated pipeline networks will be necessary. Experience from the United States clearly demonstrates that CO₂ with a high level of purity can be delivered for widespread enhanced oil recovery (EOR). Most of this CO₂ comes from natural sources but two oil refineries, one in Europe and another in the USA are now delivering CO₂ to pipeline networks.

Networks can be a useful means to control flow in a pipeline. They can also act as a buffer by supplying CO₂ from several sources to a number of different sinks. Multiple sources also mean that there is less reliance on a single source and intermittent supply can be accommodated. Pipeline design and controlled operation, using Supervisory Control and Data Acquisition (SCADA) systems, can be used to ensure that CO₂ is delivered to storage sites at an optimum rate. CO₂ can also be temporarily compressed or 'packed' into pipelines as a short term measure.

This investigation has revealed that most CO₂ pipelines currently in existence in North America are overdesigned for their current application. They are designed for higher flow rates and operating pressures through the use of thicker walls and larger diameters. For example, the Denbury Greencore Pipeline began operation with a capacity of 0.96 M tonnes / year but was designed to carry up to 13.9 M tonnes /year. Future pipeline networks can take advantage of this experience.

Impurities N₂, CH₄, and H₂ can have negative impacts on pipelines including fracture propagation, non-metallic component deterioration and the formation of hydrates and clathrates. The density and viscosity of fluids can also be affected. However, compression and transport of CO₂ for CO₂-EOR use in the United States has shown that impurities are not likely to cause transport problems provided CO₂ stream composition standards are maintained and pressures are kept significantly over the critical point (≥ 10.3 MPa). The most significant effect on transport and injection of CO₂ is the water content. Hydrate formation can lead to the most dramatic interruption to flow but the condition is generally preventable using multistage compression and knock out systems plus the inclusion of monoethylene glycol.

Intermittent flow can have an impact on wellbore integrity, fatigue and corrosion. Changes in gas pressure can result in deleterious phase behaviour including segregation of the component gases leading to corrosive effects. Maintaining sufficient pressure is possible onshore with compressor plants but this option is not possible offshore. Lengthy offshore pipelines may need to be larger in diameter than their onshore equivalents so that pipeline pressure can be maintained.



CO₂ injected into oil reservoirs can be a highly effective means for increasing oil production (EOR). Much of the gas is then permanently retained within the reservoir. However, CO₂-EOR relies on controlling pressure and flow rate conditions to optimise oil recovery. Restricted injection caused by wells being shut in can result in deleterious changes in reservoir pressure and oil miscibility. Under these conditions attendant drops in oil production could occur and in some circumstances the precipitation of minerals or asphaltenes or changes in formation fluid saturation properties. Reservoir permeability can be reduced as a result. This investigation has found that experienced operators can plan for intermittency and apply mitigation strategies.

In contrast, large scale CO₂ storage in depleted oil fields, and large saline aquifers, needs to maximize reservoir capacity with potentially long term injection over several years, and at higher pressure, compared with CO₂-EOR. The reservoir pressure needs to be controlled to avoid damage to the caprock or cause instability in faults. Pressure can be managed by using multiple wells and water pumping to control and relieve excess pressure, and control plume geometry. In both cases careful planning is required to ensure that the pressure/ temperature conditions of the CO₂ are compatible with the reservoir.

CO₂ injection programmes for large scale geological storage into deep saline aquifers and CO₂-EOR will have different objectives. Historically, the driver for using CO₂ for CO₂-EOR has been economic rather than environmental. The CO₂ injection rate needs to be optimized to enhance production without causing early breakthrough. The initial stages of injection will require much more CO₂ than in the later stages of recovery, as the reservoir is saturated and the CO₂ produced with the oil is recycled back into the reservoir. Therefore, the timing of the availability of the CO₂ is crucial. There is extensive experience of the use of CO₂ for CO₂-EOR, mainly in the United States, which has provided relevant detailed background for this investigation.



The multi-period optimisation of full CCS chain for flexible operation: From a gas-fired power station to injection/storage

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Abstract

The transition to a low carbon electricity system presents challenges for electricity system resilience. Three leading options for decarbonising the electricity sector are: renewable energy, nuclear power and applying carbon capture and storage technologies to fossil fuel-based power generation. Renewables and nuclear provide a much less flexible supply of electricity than fossil fuel plant. Nuclear provides a constant base load, but generation cannot be increased efficiently in response to peaks in demand, and supplies of renewable electricity are inherently intermittent. Therefore, the ability of CCS plants to operate in a flexible, load-following manner will command an increasing premium as we transition towards a low carbon energy system [1].

As pointed out by Bui et al. [2], there is a knowledge gap associated with how a decarbonised plant will operate to exploit the differential between peak and off-peak electricity prices. Previous work in this area, has considered a model of a super-critical coal-fired power plant integrated with an amine-based CO₂ capture process in which several decoupling options between these two units were assessed in order to maximise profitability taking into account electricity price daily fluctuations [3]. This work, based on a similar approach, focuses on the modelling of the whole CCS chain from power generation to storage. The full CCS chain model was implemented in the gCCS modelling environment [2]. The model includes the different CCS elements, starting from a gas-fired power plant, an amine-based post-combustion capture plant, the compression train, the pipeline, moving into the injection wells and storage, as it is illustrated in Figure 1.

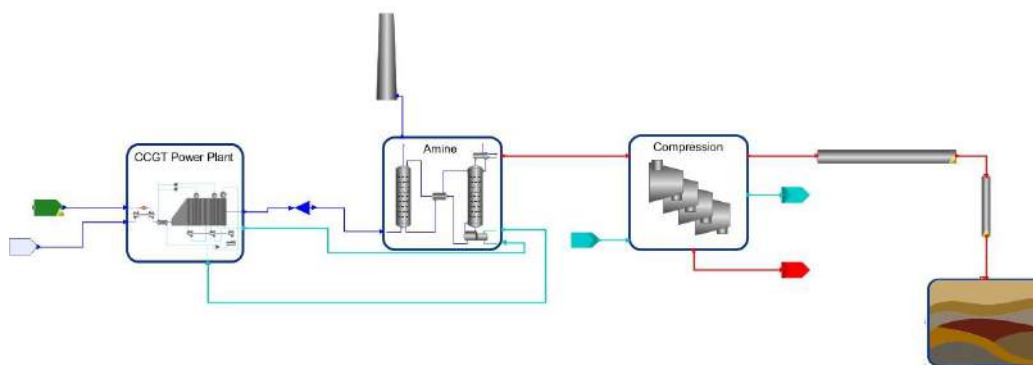


Figure 1. Carbon capture and storage network

Aiming at decoupling both power and capture plants to exploit the price variation of the electricity market, a multi-period dynamic optimisation problem was formulated and solved using this model. Four distinct scenarios were evaluated: load following, solvent storage, exhaust gas by-pass and time-varying solvent regeneration [4]. In the load following scenario the power plant ramps up and down the capture plant's operation is tightly integrated with that of the power plant.

Figure 2 illustrates some results for the optimal solution of solvent storage compared to the load following scenario. In this scenario, the possibility of storing CO₂ in the capture plant during high electricity price periods was considered. During high-price periods, part of the solvent from the absorber is by-passed from the stripper into a storage tank, maximising the power output in these periods. In order to maintain an overall capture rate of 90% at the end of each day, the accumulated CO₂ inventory is stripped along with the regular captured CO₂ from the absorber during low-price

periods. This is done by adding some flow from the storage tank to the solvent from the absorber before it reaches the stripper column. The plots shows an optimal regenerated CO_2 flow larger than the load-following case during low-price periods (between the first 6 hours and between 10h and 16h), while the opposite happens during the other remaining periods, which shows that the solvent storage does afford the power plant a slight advantage over the load following base case.

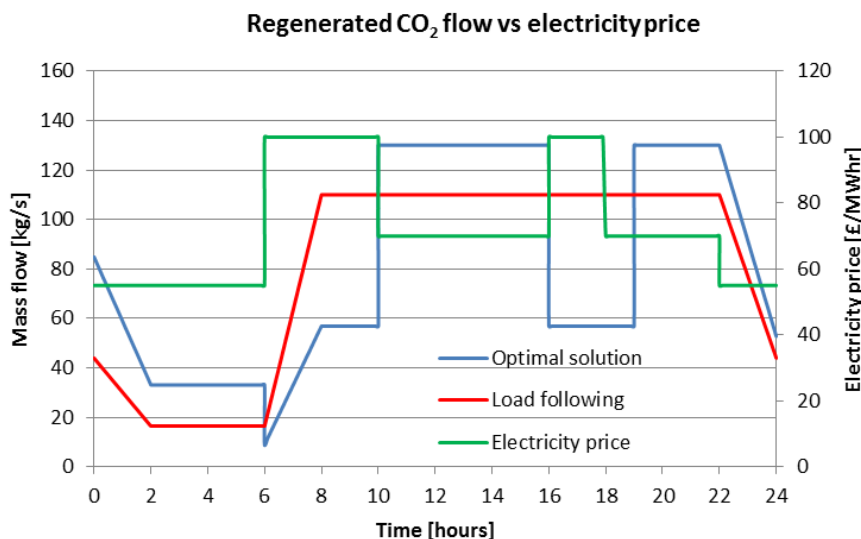


Figure 2. Daily cycle CO_2 mass flow regenerated from a load-following capture plant against optimal solvent storage for a given price electricity variation

Figure 3 shows the compression system discharge CO_2 and injected flow into the reservoir for both load-following and optimal solvent storage cases for a 2-day cycle. It can be observed that, although the long pipeline network (around 200 km) introduces a significant delay in response, the injected CO_2 flow varies similarly with its source (capture/compression) from full load (110 kg/s) to part-load (19 kg/s). On the other hand, for the optimal solvent storage case, although the compressed flow varies more significantly than the load following case (between 130 and 15 kg/s), there is a higher stability in the injected flow (between 40 and 90 kg/s). Although the compressed CO_2 has more variability, the duration of those peaks is smaller, resulting into an increase in the stability (and safety) of the injection operation.

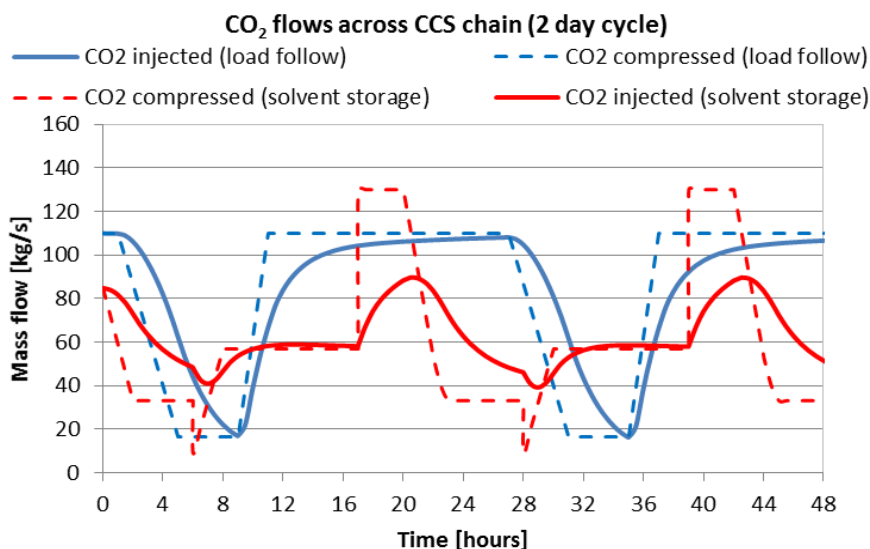


Figure 3. Two-day cycle of the CO_2 mass flow across the transmission and injection system for both load-following and optimal solvent storage cases

The solvent storage scenario compared to the load following has proven to be more beneficial to both power-capture and compression-injection, since it leads to higher capture rates and also at stability at the injection part of the CCS chain. Same comparisons have been derived for the other scenarios as well as a cost comparison between the different options.

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CO₂ purity from different carbon capture applications and associated cost and performance

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Abstract

A range of impurities can exist in CO₂ streams captured from combustion-based power generation, including combustion by-products, air derived gases and other process fluids [1]. The purity of the final CO₂ product is dependent on a number of factors including the fuel composition, the purity of oxygen from Air Separation Units (ASU) if using, the mode of operation of the power plant, including levels of oxygen excess, levels of air-ingress, location of flue gas recycle and recycle ratio, and the selection of post-combustion pollution control devices, but mostly on the selection of the CO₂ purification strategy. The ultimate composition of the CO₂ streams captured from fossil fuel power plants or transported to storage sites using high pressure pipelines will be governed by safety, environmental and economic considerations. Even though from a technological perspective, very high purity CO₂ from fossil fuel-fired power plant flue gas is achievable, it may not be required for some transport and storage applications, and so the associated increase in cost in achieving high purity levels may be avoided. Therefore the optimum levels of CO₂ purification for carbon capture processes with due consideration of purification costs and the downstream impurity impacts on pipeline transport and geological storage must be determined.

In this study, the trade-off between the cost of carbon capture and the purity of the product CO₂ stream from coal-fired power sector CCS plants is analysed using a scenario based approach. Techno-economic modelling approaches have been used to calculate various performance factors and costs of CCS plants. The three main types of power sector CCS plants of oxyfuel combustion, pre-combustion and post-combustion capture with different process scenarios have been considered and the impact on cost and product composition of CO₂ was assessed.

In modelling oxyfuel combustion capture plants, Aspen HYSYS [2] was used to undertake detailed simulation of the CO₂ Compression and Purification Unit (CPU) section of the plant which can deal with the removal of non-condensable components of N₂, O₂ and Ar, and compression of the product stream to high pressures (> 100 bar). Based on the same composition and flow rate of raw oxyfuel CO₂ flue gas, three different compression and purification process strategies were considered: 1) CO₂ compression and dehydration only, 2) 'Double flash' purification system, and 3) Distillation purification system. Important parametric information results from the oxyfuel compression and purification scenario analysis, including the CPU's total capital and operating costs calculated through Aspen cost functions, the product stream composition and the CPU energy requirement (in kWh/tonne of CO₂ captured). This information was used to calculate the impact of the different CO₂ compression and purification strategies on the overall power plant costs using the Integrated Environmental Control Model (IECM) [3] developed by Carnegie Mellon University for typical plants that produce a similar flowrate and composition of raw oxyfuel CO₂ flue gas.

In pre-combustion capture, different solvents are used that have different performance and cost impacts. The impact of the use of two solvents of SelexolTM and Rectisol[®] on plant performance, cost and CO₂ purity was assessed for separate capture scenarios (CO₂ and H₂S being removed in separate streams with H₂S further processed to a more easily handleable form). The impact of using SelexolTM in the co-capture configuration (CO₂ and H₂S being removed together in the same product stream) was also assessed. To do this, cost and performance models for each process scenario were developed, using IECM along with necessary assumptions and literature values for the three cases.

The cost and performance of plants fitted with post-combustion capture technology using monoethanolamine (MEA) solvent as the CO₂ capture medium were assessed. For similar sized plants and using the same coal as the oxyfuel combustion and pre-combustion power plants. Two different scenarios were investigated within the IECM framework. The first consists of a plant equipped with pollution control devices of Electrostatic Precipitator (ESP)



particulate control system, In-furnace NO_x controls, hot-side Selective Catalytic Reduction (SCR) and wet Flue Gas Desulfurisation (FGD) SO₂ control. The second plant is only equipped with an ESP particle control system and therefore supplies a flue gas with higher quantities of impurities to the post-combustion CO₂ capture plant.

The results of the study as illustrated in figure 1 show that the technology with the lowest Cost of Electricity is pre-combustion capture using SelexolTM physical solvent with co-capture of impurities. With the present assumptions, this technology produces CO₂ with an estimated purity of 97.64 mol% but with high estimated levels of H₂S (at 3974 ppm_v). Conversely, the highest cost technology in this analysis is found to be pre-combustion capture using Rectisol solvent and with separate capture of sulfur impurities. The CO₂ stream produced by this technology is dry with low levels of other contaminants such as CO and H₂. The technologies that jointly produce the highest grade of CO₂ are post-combustion capture with NO_x and wet FGD environmental control and oxyfuel combustion plant with CO₂ purification by distillation, both producing 99.99 mol% CO₂ product, but with post-combustion capture by lowest cost. The three analysed oxyfuel combustion capture technologies produce the widest range of CO₂ purity with the compression and dehydration only system, that doesn't include any additional purification of the raw CO₂ flue gas stream producing the lowest grade CO₂ stream that contains 77.69 mol% CO₂ and high levels of non-condensable species (O₂, N₂ and Ar) plus acid gas species. The present study should facilitate further analysis of whole CCS chain techno-economics and process configuration.

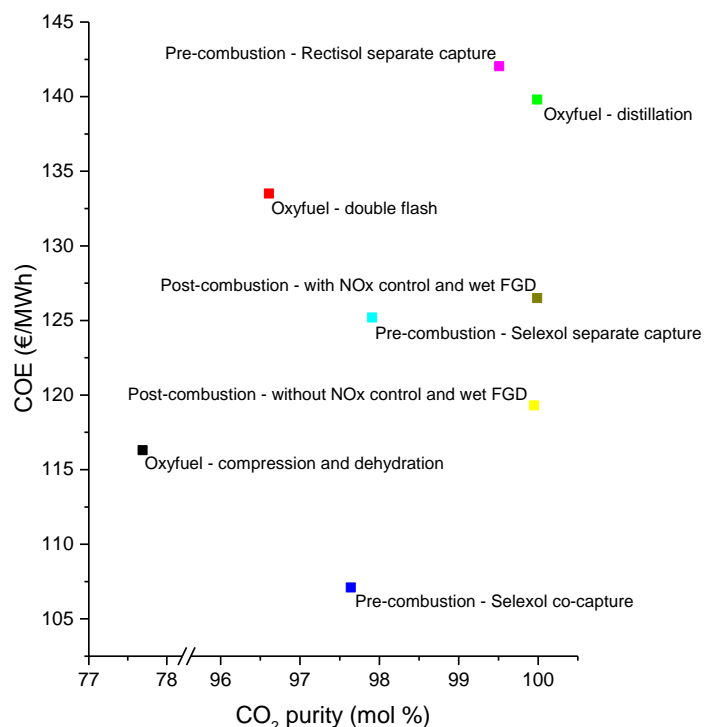


Figure 1. Cost of Electricity (constant 2014 €/MWh) versus CO₂ purity for different CO₂ capture technologies

Acknowledgement

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Assessment of CO₂ Enhanced Oil Recovery Projects through Process Modelling

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Abstract

The commercial implementation of carbon capture and storage (CCS) still faces significant challenges. Supercritical CO₂ is particularly effective for Enhanced oil recovery (EOR) operations in reservoirs deeper than 2000 ft. with oil viscosities less than 20 cP at reservoir conditions [1]. At high pressures (implying reservoirs deeper than ~2500 feet), CO₂ is miscible with oil and effectively swells the oil, reduces its viscosity and possibly reduces the surface tension with the reservoir rock enabling further production of hydrocarbons. Incremental oil production from EOR operations is typically around 5 -15% of the original oil in place. This can provide significant benefits towards improving the business case for CCS investments. With time, the CO₂ injected also “breaks through” and is produced with the incremental oil and gas. Gas treating facilities can be built to separate the produced CO₂ with the aim of recycling it for injection and reducing the requirement for fresh supply of CO₂.

The Boundary Dam CCS project, the world’s first post-combustion coal-fired CCS project, transports CO₂ via pipeline to nearby oil fields in Southern Saskatchewan where it is used for Enhanced Oil Recovery [2]. The Weyburn CO₂ flood in Canada has been injecting CO₂ from the North Dakota Gasification plant at Beulah since 2005.

There are a number of challenges faced during CO₂ EOR operations. These include:

1. Predicting the performance of the reservoir with CO₂ injection
2. Predicting the composition of the produced fluids (which will change over the lifetime of the project)
3. Designing facilities to handle the produced gas over the lifetime of the asset
4. Understanding the changes in CO₂ supply requirements with increased use of recycled CO₂.

This study presents results based on a tool developed to address these challenges - a CO₂ EOR extension to gCCS. gCCS was developed in a £3m project was commissioned and co-funded by the ETI and project participants, who comprise E.ON, EDF, Rolls-Royce, CO2DeepStore, Process Systems Enterprise (PSE) and E4tech. The project was aimed at delivering a robust, fully integrated tool that could be used across the whole CCS chain [4]. This tool was released as a commercially-supported software product in December 2014.

A case study based on a published paper discussing a large scale CO₂ flood along the Texas Gulf Coast [3] is presented. A summary of the specification for this development is given in Table 1. The flowsheet used for the study is shown in Figure 1.

A dynamic simulation of the project life was carried out. For the base case, it was assumed that the entire field was developed simultaneously. The purchased CO₂ supply requirements based on increasing CO₂ recycle rates were assessed. In addition, the impact of the capacity of the gas treating facilities on natural gas revenues was analysed. Finally, based on assumed project cost information and simulation results, the capital and operating expenditure as well as the expected revenues were estimated and analysed within gCCS. This was used to carry out an economic analysis of the project. The results were compared with another case where the field development was assumed to be staged. Figures 2 to 4 show some of the results.



Parameter	Unit	Value
Estimated number of patterns		70
Area of pattern	Acre	80
Depth of reservoir	ft	5600
Oil (specific gravity) API	° API	31
Original oil in place (OOIP) per pattern	MMstb	9.3
Absolute permeability	mD	1000
Target Average reservoir pressure	psia	3000
Oil viscosity	cP	0.385
CO ₂ injection rates per pattern	rb/day	7500
Total CO ₂ injection rates	MMscfd	1050
Purchased CO ₂ arrival pressure	Bar	100
Three phase separator pressure	psia	800
Natural gas maximum H ₂ S content for sale	ppmv	10

Table 1. Key parameters of the CO₂ EOR flowsheet [3].

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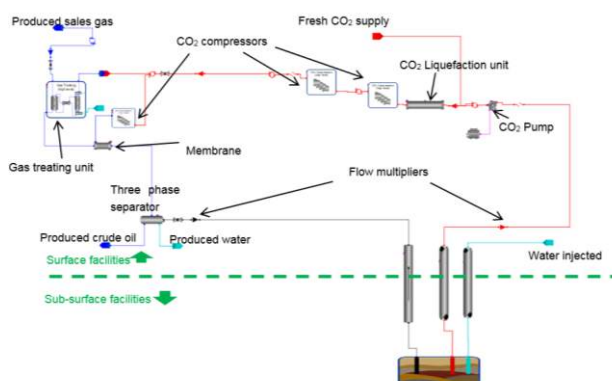


Figure 1. Representation of the CO₂ EOR flowsheet

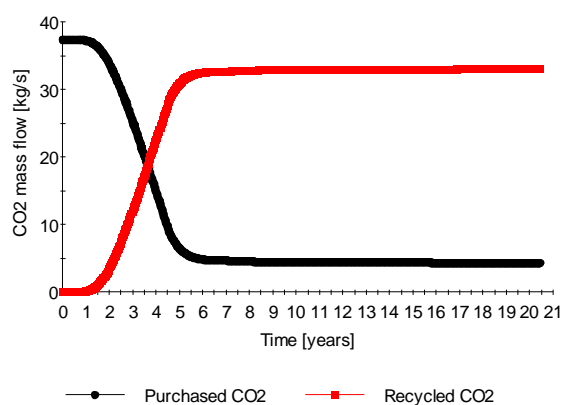


Figure 2. Purchased and recycled CO₂ flows

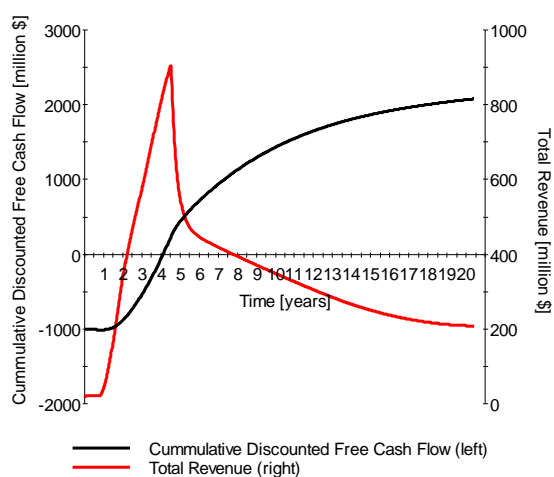


Figure 3. Project economic analysis

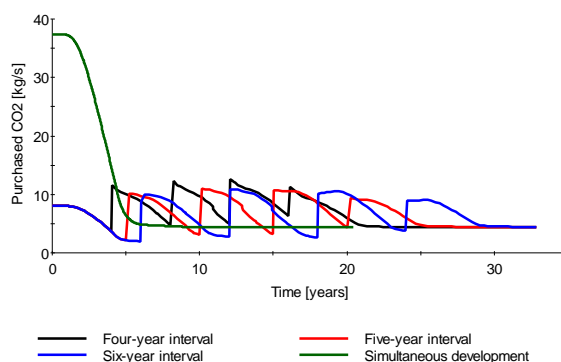


Figure 4. Purchased CO₂ flows for simultaneous and staged developments

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Quantification of the water-carbon-energy nexus for carbon negative electricity generation

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Abstract

Combining biomass co-firing for power generation and carbon capture and storage, BECCS (Bio-energy and CCS) appears as a promising carbon negative solution to meet UK's 2050 mitigation targets [1], consistent with the Intergovernmental Panel for Climate Change (IPCC) carbon concentration scenarios [2]. Because water scarcity intensifies with global warming, the carbon concern cannot be dissociated from the water concern: a comprehensive investigation of both carbon and water intensity of BECCS's whole value chain (see figure 1) is necessary for a proper assessment of its potential.

The main parameters selected for this analysis were the biomass type, geographical location, amount of co-firing, power plant cooling system, implemented CCS technology and amount of CCS. Cooling systems (wet cooling tower, once-through, dry cooling), co-firing and CCS technologies (post-combustion and oxy-combustion) were studied with the IECM software (Berkenpas et al. [3]). Both CCS systems were considered to assess the power plant's cost, efficiency, water and carbon intensity. Regarding the feedstock, five different types of biomass - among agricultural residues (wheat straw and sugarcane bagasse) and energy dedicated crops (miscanthus, willow and switch grass) - were considered for this analysis, in nine different locations. Their embodied water – mainly the water required during their growth in m³/tons (wet basis) - was calculated using the green, blue, and grey water terminology and methodology (Chapagain et al. [4], Allen et al. FAO [5]), according to their growing region and climate, growth cycle, yields and fertilizer application rate. Embodied energy and carbon footprint were also evaluated and compared using a Life Cycle Assessment approach similar to the Farm Energy Analysis Tool (FEAT) (Camargo et al. [6], [7]) encompassing farming methods and inputs, short distance transportation and biomass drying and densification.

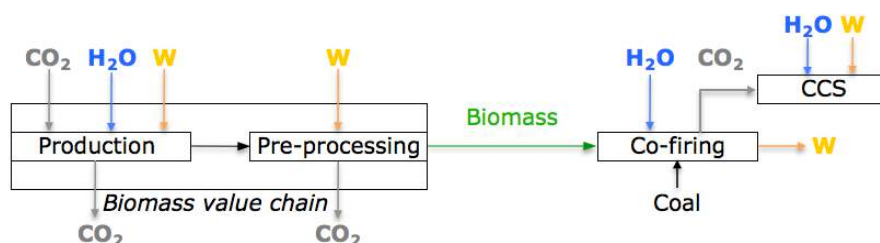


Figure 1: BECCS value chain with CO₂, H₂O and power inputs and outputs.

Results indicated that embodied water and energy were mostly sensitive to yield and moisture content at harvest. Among agricultural residues, bagasse from sugarcane was found to be more promising than wheat straw regarding water requirement, but not regarding energy, for bagasse's high moisture content (50% as

opposed to 10% for straw) requires a high energy input for drying. Similarly, with a higher yield, miscanthus looked promising at the farming stage, but was overall as energy efficient as switch grass due to its high moisture content.

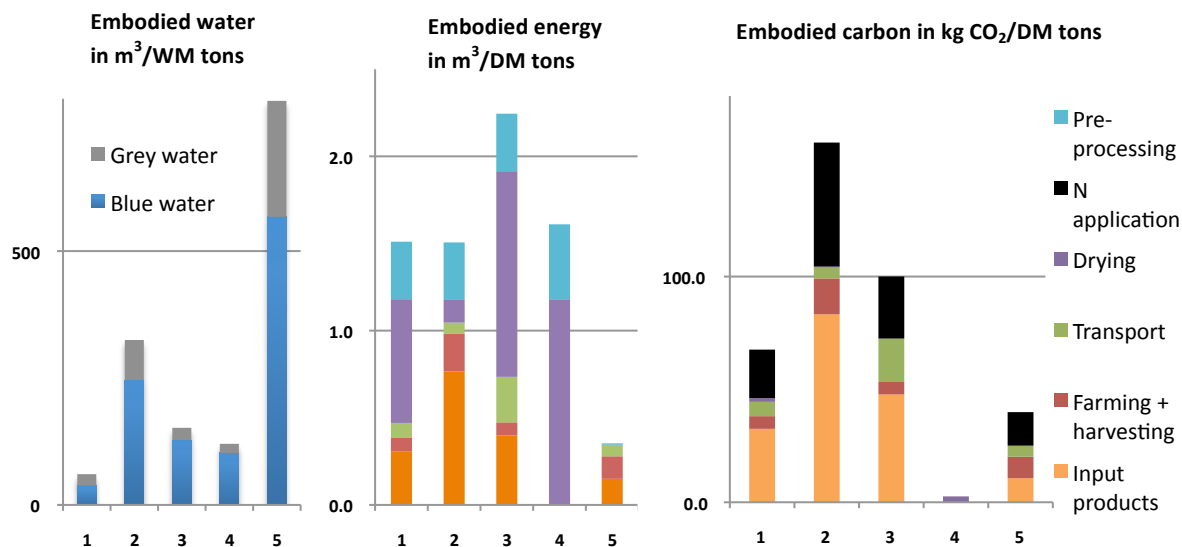


Figure 2: (from left to right) **Embodied water, energy and carbon of energy dedicated crops** (*miscanthus*: 1, *switch grass*: 2, *willow*: 3) and **agricultural residues** (*sugarcane bagasse*: 4, *wheat straw*: 5)

Logically, carbon intensity decreased with the amount of co-firing and CCS, while water intensity increased. The main factors contributing to this increase were the embodied water in biomass and the CCS cooling water, which justified the need to have a closer look at the biomass feedstock and cooling systems. Wet cooling towers were found to be the more energy efficient and less water and carbon intensive.

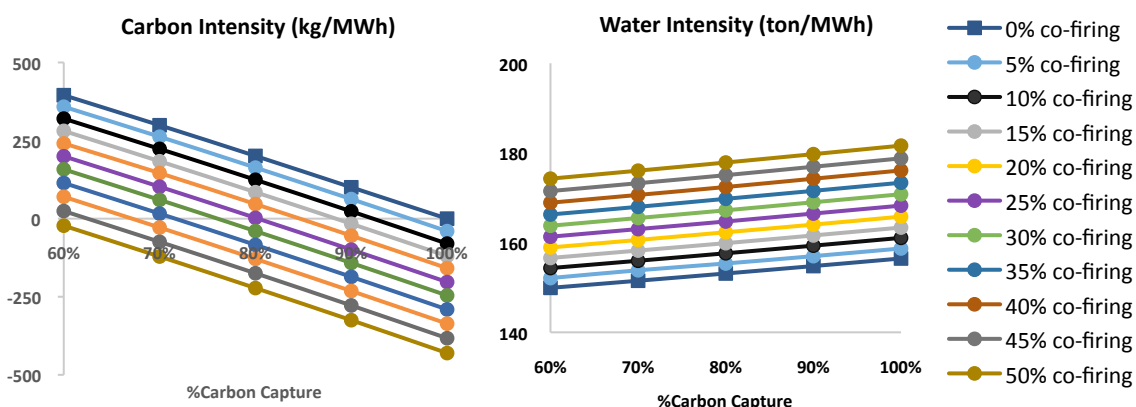


Figure 3: (from left to right) **Carbon and water intensity of a 500 MW supercritical power plant with wet tower cooling, as a function of the amount of oxy-combustion CCS, and for different % of co-firing.**

As expected, the plant's efficiency decreased with the amount of co-firing and CCS. But biomass' high moisture content being its main contributor, a higher overall efficiency was obtained by recovering the steam from the flue gas (see figure 4).

The cost analysis showed a break-even time of fifteen years for a co-firing and CCS system, with a possible reduction of two years with subsidies (see figure 5).

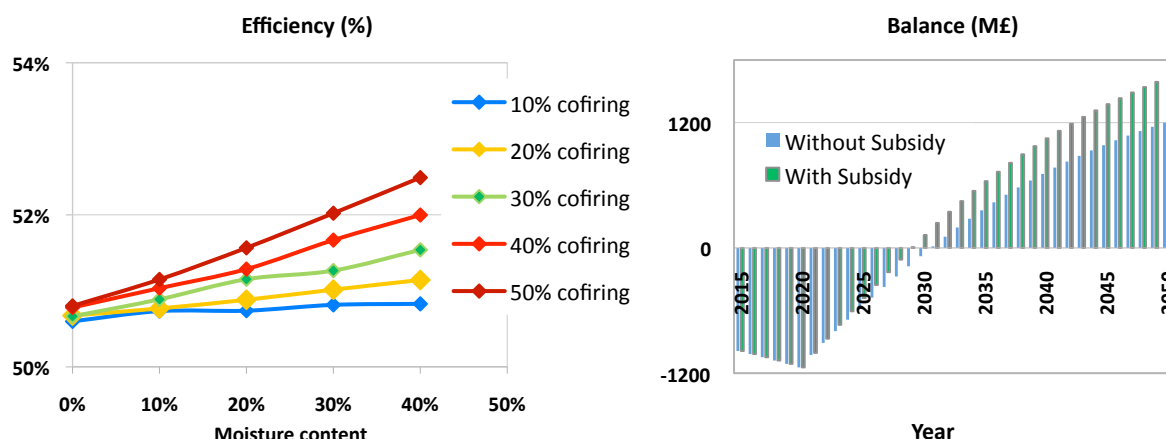


Figure 4: Efficiency of a supercritical 500 MW plant with 90% oxy-combustion CCS and heat recovery as a function of the biomass moisture content and for different amounts of co-firing.

Figure 5: Discounted Cash flow analysis of the same system with 25% co-firing (no heat recovery).

Overall, using oxy-combustion CCS on a co-firing power plant showed to be cheaper, more energy efficient and less carbon and water intensive than using post-combustion.

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Fracture Propagation in a CO₂ Pipeline – An Operator's Perspective

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Abstract

National Grid is working with Capture Power Limited to develop the White Rose Carbon Capture and Storage (CCS) Project. This is an oxy-fuelled power and CCS Demonstration Project of up to 426 MWe gross output. The standalone power plant would be located at the existing Drax Power Station site near Selby, North Yorkshire in the UK. National Grid is responsible for the carbon dioxide (CO₂) pipeline, transportation infrastructure and store. The White Rose CCS Project will use the common pipeline and storage infrastructure that National Grid is developing for the Humber cluster.

The Yorkshire and Humber project would involve the construction of a cross country pipeline and a sub-sea pipeline to transport CO₂ from fossil fuel power stations and industrial plants in the region to a permanent geological storage site beneath the North Sea.

CO₂ is a hazardous substance which, in the unlikely event of an accidental release, could cause harm to people. Compliance with UK health and safety legislation requires that pipelines are designed, constructed, operated and maintained in accordance with recognised pipeline codes. A primary element of pipeline codes for pipelines transporting hazardous gas and high vapour pressure fluids is fracture control. Dense phase CO₂ is a high vapour pressure fluid, so fracture control is a key requirement of the material selection and design process for pipelines transporting it. The codes require that the pipeline material is sufficiently tough to prevent running brittle fractures and to arrest running ductile fractures. The widely used model for ductile fracture arrest in gas pipelines, the semi-empirical Two Curve Model, has not been validated for applications involving dense phase CO₂ or CO₂-rich mixtures.

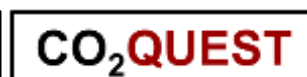
The proposed Yorkshire and Humber CCS Cross-County Pipeline has a diameter of 610 mm (24 inch) and a wall thickness of 19.1 mm. It would be constructed using Grade L450 line pipe steel (i.e. it has a specified minimum yield strength of 450 N/mm²) with a specified minimum average full-size Charpy V-notch impact energy of 250 J. It would transport CO₂-rich mixtures in the dense phase. The National Grid entry specification for pipeline transportation specifies a maximum saturation pressure of 80 barg.

Fracture propagation is a complex phenomenon and, to this day, it is not fully understood. The methods for estimating the toughness required to arrest a running ductile fracture are semi-empirical. Consequently, when new grades of line pipe steel are developed (e.g. L555 (X80) and L690 (X100)) or when pipelines are to be used to transport new types of fluids (e.g. rich gas or CO₂) or to transport fluids at higher pressures or higher design factors, full-scale fracture propagation tests are required to extend the range of validity of the existing semi-empirical methods. These tests are expensive, but necessary.

Experimental and Analytical Studies

National Grid has conducted extensive small and large scale tests and analytical work to investigate fracture propagation in CO₂ pipelines. This work included two full-scale fracture propagation tests with dense phase CO₂-rich mixtures that were conducted for National Grid by the DNV GL Spadeadam Test & Research Centre, Cumbria, UK. The full-scale tests used Grade L450 line pipe steel with a diameter of 914 mm (36 inch) and a wall thickness of 25.4 mm. The first test was conducted on 21 April 2012 and the second on 13 October 2012. Predictions made using the Two Curve Model and the (notionally conservative) Wilkowski et al. (1977) correction factor were incorrect and non-conservative. An additional correction factor was required in order to conservatively predict the results of the two tests.

The results of the first and second tests cannot be used directly to set the toughness requirements for the Yorkshire and Humber CCS Cross-County Pipeline, because: i) the non-conservatism in the theoretical estimates is not fully



understood or quantified, and ii) there is (unknown) uncertainty associated with extrapolating to a different diameter and wall thickness. Therefore, a third full-scale test was necessary to evaluate the fracture arrest capability of the pipe to be used to construct the proposed pipeline.

The Project-Specific Full-Scale Test

The third full-scale fracture propagation test was conducted at the Spadeadam Test & Research Centre on 25 July 2015.

The third test used Grade L450 line pipe steel with a diameter of 610 mm (24 inch) and a wall thickness of 19.1 mm, i.e. identical to that for the proposed Yorkshire and Humber CCS Cross Country Pipeline.

The results of the first and second tests were used to estimate the conditions that might be required for arrest. The third test was designed to provide confirmation (or otherwise) of this empirical prediction.

The test section consisted of an initiation pipe and then, either side of the initiation pipe, one transition pipe and two production pipes. The (in total) four production pipes are representative of the type of line pipe that would be used in the proposed Yorkshire and Humber CCS Cross Country Pipeline.

A running ductile fracture was successfully started in the initiation pipe. The fracture propagated through the transition pipes on either side of the initiation pipe at a speed of approximately 100 m.s⁻¹ before it arrested on entering the production pipes. The rapid arrest on entering the production pipes suggests that the toughness of these pipes was significantly higher than that required to arrest a running ductile fracture.

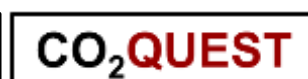
Conclusions

The full-scale fracture propagation test has confirmed that a running ductile fracture will arrest in the proposed Yorkshire and Humber CCS Cross County Pipeline. Fracture arrest will occur at a saturation pressure of 80 barg in 610 mm (24 inch) diameter, 19.1 mm wall thickness, Grade L450 line pipe with a specified minimum average toughness of 250 J.

Three full-scale fracture propagation tests in two different pipe geometries have been conducted by National Grid, in addition to analytical studies. Nevertheless, the state-of-the-art is, that if a future project requires a pipe geometry, grade or saturation pressure of the CO₂-rich mixtures that differs significantly from that in the three full-scale tests, then a project-specific full-scale test would be required to confirm that a fracture will arrest.



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Thermodynamic properties of a CO₂-rich mixture CO₂+CH₃OH in conditions of interest for CCS technology and other applications

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Abstract

Methanol can be an impurity in transported and stored anthropogenic CO₂ in CCS technology. Moreover SCCO₂ is the most widely used supercritical solvent and methanol is one of the most common modifiers used in SCCO₂ processes. Despite the importance of the system CO₂+CH₃OH and the need of data for its thermodynamic properties, it must be pointed out that although vapour-liquid equilibrium, *VLE*, has been widely studied in literature, there is little information about volumetric behaviour at $T \leq 313$ K and mole fraction $x_{\text{CO}_2} > 0.75$. No data for speed of sound, c , isobaric specific heat capacity, c_p or Joule-Thomson coefficient, μ_{JT} , were found. Accurate experimental data for these properties of CO₂+impurity mixtures are needed to obtain a reference model, especially equation of state (EoS), for CCS technology, which is one of the most critical future challenges. In addition, pressure-density-temperature, $p - \rho - T$, and *VLE* experimental data are necessary to evaluate several parameters related to transport, injection and storage, as pipeline size, booster power, permeation flux, ...[1]. Besides, c allows controlling aspects such as pressure drops, leak detection, composition changes and the performance of seismic studies. c_p and Joule-Thomson coefficient, μ_{JT} , data are required to estimate temperature variations which can be produced at various stages of the process.

The aim of this work was to conduct an extensive thermodynamic study of a CO₂-rich mixture with methanol ($x_{\text{CO}_2} = 0.9700$). With this purpose, by means of a double path pulse-echo method at 5MHz, we experimentally measured the speed of sound for the system CO₂+CH₃OH with $x_{\text{CO}_2} = 0.9700$ at six T ranged from 263.15 to 313.15 K and at pressures from 3.28 up to 194.49 MPa (Figure 1). The overall standard uncertainty of c , u_c , was $5.9 \times 10^{-4} \cdot c$. Density, ρ , at the same temperatures and up to 20.00 MPa, (Figure 2) and bubble point (p_b , ρ_L), between 263 to 304 K, were obtained for the same mixture using a vibrating-tube densimeter with $u_\rho = 0.2 - 0.4$ kg/m³.

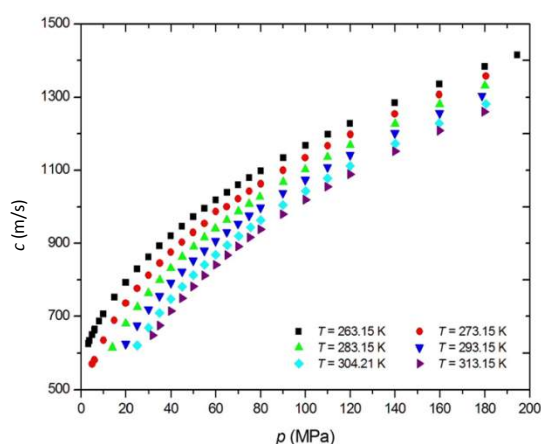


Figure 1. Experimental speeds of sound, c , versus pressure, p , for CO₂ + CH₃OH with $x_{\text{CO}_2} = 0.9700$ at several temperatures.

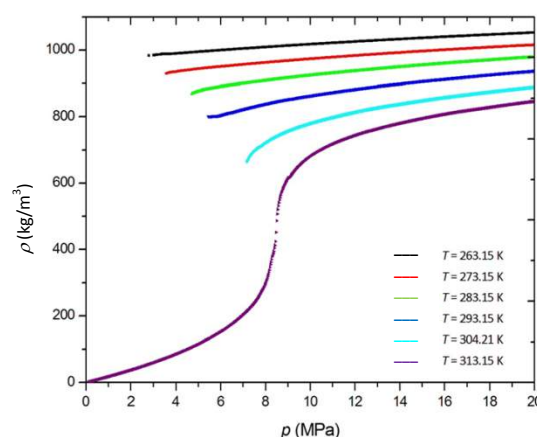


Figure 2. Experimental densities, ρ , versus pressure, p , for CO₂ + CH₃OH with $x_{\text{CO}_2} = 0.9700$ at several temperatures.



Our experimental results were compared with those calculated using two different formulation EoS: PC-SAFT [2, 3] and GERG [4]. The Mean Relative Deviation obtained for each property, $MRD_x(\%)$, is shown in Table 1. The obtained deviations allow us to validate the EoS to represent the experimental thermodynamic behavior of the mixture.

EoS	$MRD_c(\%)$	$MRD_\rho(\%)$	$MRD_{p_b}(\%)$	$MRD_{\rho_L}(\%)$
PC-SAFT	2.77	4.07	2.23	6.04
GERG	2.65	0.64	5.67	1.37

Table 1. Comparison between our experimental results and values from the PC-SAFT and the GERG EoSs. Properties: c , at pressures up to $p = 194.49$ MPa; ρ , up to $p = 20.00$ MPa; p_b and ρ_L .

From our c and ρ experimental values, and from calculated c_p , at the reference pressure of 14 MPa, we obtained ρ , c_p , and μ_{JT} , of the $\text{CO}_2 + \text{CH}_3\text{OH}$ mixture with $x_{\text{CO}_2} = 0.9700$ from 263.15 to 313.15 K and up to 195 MPa (Figures 3 and 4). For this, we used a calculation method based on numerical integration of partial differential equations that relate c with other thermodynamic properties [5]. This method has thus far been applied to only liquids systems. We adapt this method to mixtures containing compressed gases, and we confirm our results via comparison with values from the PC-SAFT and the GERG EoSs (validated above).

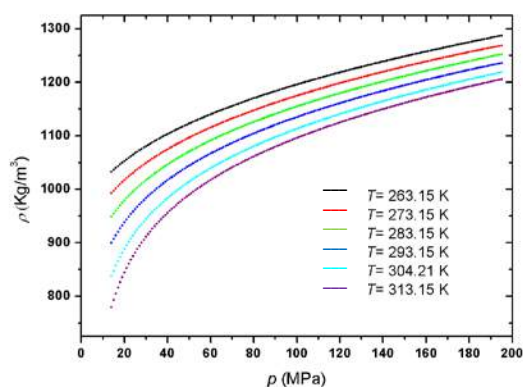


Figure 3. Calculated densities, ρ versus pressure, p , for the mixture $\text{CO}_2 + \text{CH}_3\text{OH}$ with $x_{\text{CO}_2} = 0.9700$ at several temperatures.

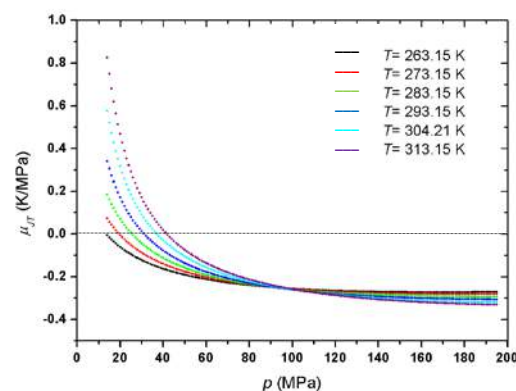


Figure 4. Calculated Joule-Thomson coefficients, μ_{JT} versus pressure, p , for the mixture $\text{CO}_2 + \text{CH}_3\text{OH}$ with $x_{\text{CO}_2} = 0.9700$ at several temperatures.

The comparison of our calculated ρ , c_p and μ_{JT} values with those from the PC-SAFT and the GERG EoSs was done at temperatures from 263.15 to 313.15 K and pressures from 14 to 195 MPa. The deviations thus obtained, are expressed as $MRD_x(\%)$ or AAD in Table 2 and they validate the calculation method.

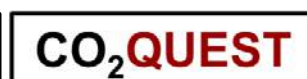
EoS	$MRD_\rho(\%)$	$MRD_{c_p}(\%)$	$AAD_{\mu_{JT}}(\text{K/MPa})$
PC-SAFT	1.90	10.3	0.056
GERG	0.46	2.47	0.013

Table 2. Comparison between values for several calculated properties and those obtained using the PC-SAFT and the GERG EoSs, for the $\text{CO}_2 + \text{CH}_3\text{OH}$ mixture with $x_{\text{CO}_2} = 0.9700$ from 14 to 195 MPa at several T .

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Experimental speed of sound in CO₂-rich mixtures with methanol. Extrapolation to pure CO₂.

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Abstract

Many thermodynamic properties of pure CO₂ have been accurately determined in wide ranges of temperature and pressure, but speed of sound, c , data are scarce, mostly in the conditions of interest for CCS technology. Experimental determination of speed of sound in pure dense CO₂ presents serious difficulties, due to its high opacity at relatively high frequencies. Using sufficiently low-frequency techniques the signals can be obtained, but it requires a large volume of fluid and therefore, a large apparatus, which, in high-pressure techniques, is not advisable for operation and safety. Lin [1] obtained speed of sound results for pure CO₂ at 0.5 MHz, but the signals were difficult to interpret and the uncertainty could not be estimated. Our speed of sound installation uses a double-path pulse-echo method at a frequency of 5 MHz. In this installation, we did not obtain signal at all for pure CO₂ or for several CO₂-rich mixtures of interest in CCS technology. Nevertheless, we found that the addition of small amounts (doping) of methanol to the fluids modifies their acoustic behaviour and allows measuring in wide ranges of pressure and temperature, both in pure CO₂ and in CO₂-rich mixtures. Lin and Trusler [2] doped pure CO₂ with propane, and they obtained good signals at 2 MHz, and, from these measurements, they extrapolated the speed of sound in pure CO₂. In our 5 MHz apparatus, CO₂+propane is opaque for mole fraction of propane below 0.2. However, methanol is suitable for our device's frequency, chemically compatible with the installation, well known as a modifier in supercritical extraction, used in industrial processes as Rectisol and which can occur as an impurity in anthropogenic CO₂ or added to it as a desiccant and/or hydrate inhibitor.

Thus, the aim of this work is to test the suitability of methanol as doping agent in order to obtain reliable values of speed of sound at 5 MHz in pure CO₂ and, in the future, in CO₂-rich mixtures of interest for CCS. For this purpose, we measured the speed of sound in several CO₂-rich mixtures with methanol, we obtained extrapolated values in pure CO₂, (using the same method that Lin and Trusler [2]) and we evaluated the effect of the dopant on c . In addition, the obtained values of c , at wider composition range than needed for doping, are useful for the development and improvement of the equations of state necessary to the design of the processes in CCS technology. The experimental results were used to validate PC-SAFT [3, 4] and GERG [5], two EoS of different formulation.

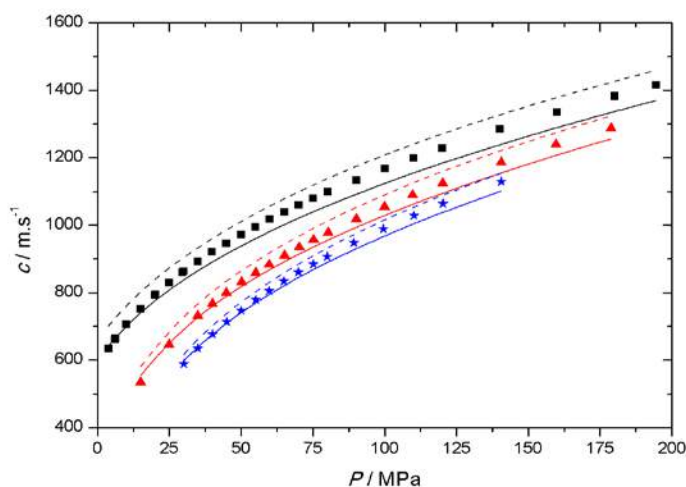


Figure 1. Experimental speeds of sound, c , in the CO₂ + CH₃OH mixture with $x_{\text{CO}_2}=0.9503$.

■ $T = 263.15 \text{ K}$
▲ $T = 298.15 \text{ K}$
★ $T = 323.15 \text{ K}$
Solid line, PC-SAFT EoS
Dashed line, GERG EoS



So, in this work, we determined the speed of sound for the system CO₂+CH₃OH at seven compositions [x_{CO_2} = 0.8005, 0.9025, 0.9503, 0.9700, 0.9794, 0.9845, 0.9898], at three temperatures [T = 263.15 K, 298.15 K and 323.15 K], and up to approximately 200 MPa. (Except the mixture with x_{CO_2} = 0.9700 at 263.15 K, that was previously measured by us [6]). Figure 1 shows the three isotherms for the mixture with x_{CO_2} = 0.9503. The standard relative uncertainty of the experimental c , u_c , was calculated elsewhere [6] and was u_c = 0.059%.

The results for each isotherm and isopleth were fitted to the equation

$$(P - P^\#) = \sum_{i=1}^3 a_i (c - c^\#)^i \quad (1)$$

where $P^\#$ = 70 MPa and $c^\#$ is the speed of sound at $P^\#$. Coefficients for a selected mixture are shown in Table 1. Using eq. 1 speed of sound data can be obtained at round values of P at each T . In this way, we calculated values of c for the five CO₂-richest reported mixtures [x_{CO_2} = 0.9503, 0.9700, 0.9794, 0.9845, 0.9898], at the studied ranges of pressure and temperature. These values, at each T and P , were fitted to the following equation

$$c(x_{\text{CO}_2}) = c_0 + c_1(1 - x_{\text{CO}_2}) + c_2(1 - x_{\text{CO}_2})^2 \quad (2)$$

where $c(x_{\text{CO}_2} = 1) = c_0$ is the speed of sound in pure CO₂. Therefore, by extrapolation to infinite dilution we obtained values of c in pure CO₂ at those P and T (Table 2, Figures 2 and 3). The overall standard relative uncertainty of the speed of sound in pure CO₂, $u_r(c_0)$, was calculated by combining u_c with the relative standard deviation in the calculation of c_0 determined with eq. (2). The value obtained was $u_r(c_0)$ = 0.12%, similar to that obtained by Lin and Trusler (0.10%) using the same procedure but with different dopant (propane) and frequency (2 MHz) [2], and also lower than 0.5% - 2% presented by the reference EoS for pure CO₂ (Span and Wagner [7]).

x_{CO_2}	T/K	$10 \times a_1$ MPa.m ⁻¹ .s	$10^4 \times a_2$ MPa.m ⁻² .s ²	$10^8 \times a_3$ MPa.m ⁻³ .s ³	MRD_c %
0.9503	263.15	2.5039	2.543	7.33	0.019
	298.15	2.1649	2.271	7.40	0.012
	323.15	2.0001	2.127	7.10	0.004

Table 1. Coefficients of the equation 1 for the mixture CO₂ + CH₃OH with x_{CO_2} = 0.9503 at temperatures T , and mean relative deviations.

T / K	P MPa	$c / \text{m.s}^{-1}$					c_0 m.s^{-1}	c_1 m.s^{-1}	c_2 m.s^{-1}	$u_{\text{r}}(c_0)$ %
		$x_{\text{CO}_2} =$								
		0.9503	0.9700	0.9794	0.9845	0.9898				
298.15	25	648.39	650.03	652.10	652.94		657.7	-346	3214	0.18
	50	830.58	833.85	836.02	838.07	837.87	840.7	-236	619	0.21
	75	956.32	959.83	961.93	963.83	963.75	966.4	-215	230	0.16
	100	1056.03	1059.48	1061.49	1063.13	1063.01	1065.2	-175	-238	0.14
	125	1140.13	1143.42	1145.35	1146.75	1146.57	1148.5	-139	-587	0.12
	150	1213.62	1216.71	1218.56	1219.77	1219.53	1221.1	-112	-817	0.11
	175	1279.35	1282.22	1284.00	1285.06	1284.76	1286.2	-91	-948	0.11
	200	1339.10	1341.75	1343.46	1344.39	1344.05	1345.3	-77	-1002	0.11

Table 2. Speeds of sound calculated using equation 1 for the CO₂ + CH₃OH mixtures at T = 298.15 and pressures P . Coefficients of equation 2 at the same conditions. c_0 is the derived speed of sound in pure carbon dioxide, and $u_r(c_0)$ is its overall relative uncertain.

We compared these extrapolated values of speed of sound in pure CO₂ with the data from literature. Mean relative deviations (MRD_c) were 0.61% and 0.44% when our results were compared with direct measurements by Pitaevskaya and Bilevich [8] and Lin [1], respectively, at the common temperatures. Al-Siyabi results [9] are consistent with ours, but not directly comparable due to the different temperatures. MRD_c was 0.21% from derived values obtained using propane as a dopant at 2 MHz by Lin and Trusler [1, 2], at the common temperatures. Figures 2 and 3 show a good agreement between the whole set of data, without trends with temperature or pressure. Finally, our extrapolated values showed a MRD_c = 0.43% from values calculated using Span and Wagner EoS [7]. Figure 4 presents the relative

deviations of speeds of sound in pure CO₂ obtained in this work and found in the literature from the values obtained using SW EoS [7].

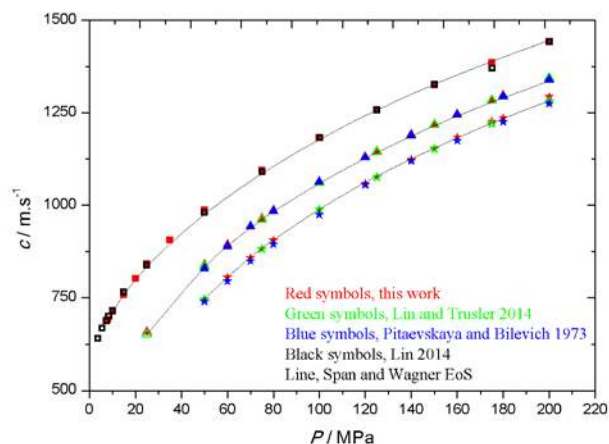


Figure 2. Speed of sound, c , in pure CO₂ versus pressure, P , at several temperatures, T . ■, $T = 263.15$ K; ▲, $T = 298.15$ K; ★, $T = 323.15$ K.

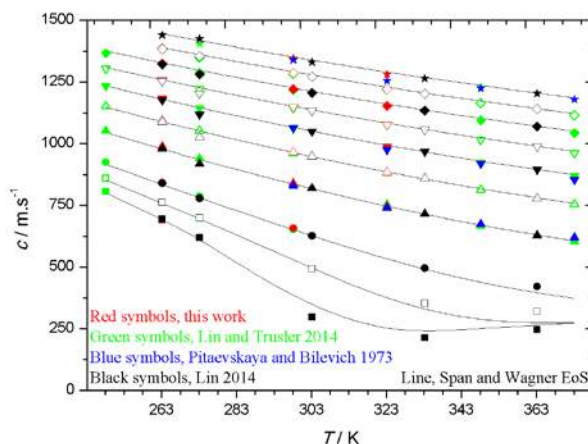


Figure 3. Speed of sound, c , in pure CO₂ versus temperature, T , at several pressures, P . ■, $P = 8$ MPa; □, $P = 15$ MPa; ●, $P = 25$ MPa; ▲, $P = 50$ MPa; △, $P = 75$ MPa; ▼, $P = 100$ MPa; ▽, $P = 125$ MPa; ◆, $P = 150$ MPa; ◇, $P = 175$ MPa; ★, $P = 200$ MPa.

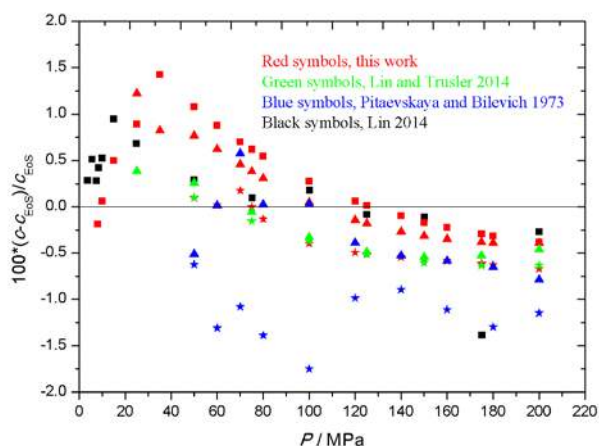


Figure 4. Relative deviations of speeds of sound in pure CO₂ obtained in this work and found in the literature, c , from the values obtained using Span and Wagner EoS, c_{EoS} . ■, $T = 263.15$ K; ▲, $T = 298.15$ K; ★, $T = 323.15$ K.

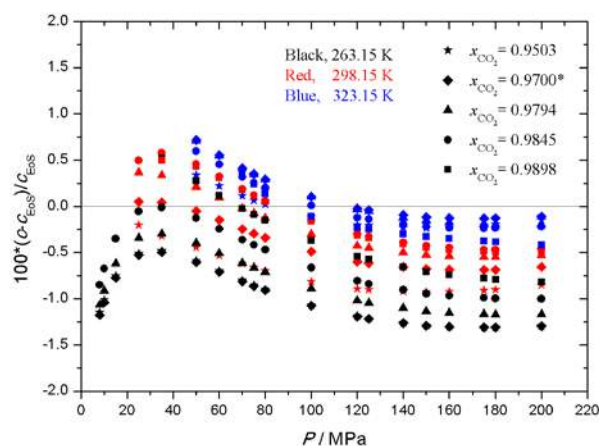


Figure 5. Relative deviations of this work experimental speeds of sound in the mixtures CO₂ + CH₃OH, c , from the speeds of sound in pure CO₂ calculated by the Span and Wagner EoS, c_{EoS} . *At 263.15 K, ref. [6].

The addition of only 1% in mole of methanol made the sound echoes appear clear at 5 MHz in the studied ranges of pressure and temperature, with relative deviations between -0.82% and +0.52% with respect to the SW EoS for pure CO₂ (Fig. 5). Doping between 1% and 5%, the relative deviations range from -1.31% to +0.72%, with an overall MRD_c of 0.52%. In any case, the error when the mixtures are taken as pure CO₂ remains within the tolerance margin of the SW EoS, with the exception of $P < 10$ MPa at 263.15 K for the three methanol-richest mixtures, where it is only slightly higher.

The results for the binary mixtures were compared with those calculated using the PC-SAFT and GERG EoS (Fig. 1 and 6, Table 3). PC-SAFT: average deviations for each isotherm and isopleth range between 1.60% and 5.01%, with an overall average value of 2.8%. GERG: This EoS overestimated speed of sound at all the studied temperatures, pressures and compositions, obtaining higher deviations at lower working pressures and at higher concentrations of methanol. Average deviations of each isotherm and isopleth range from 0.64% to 12.9%, being 4.97% the overall average MRD_c .

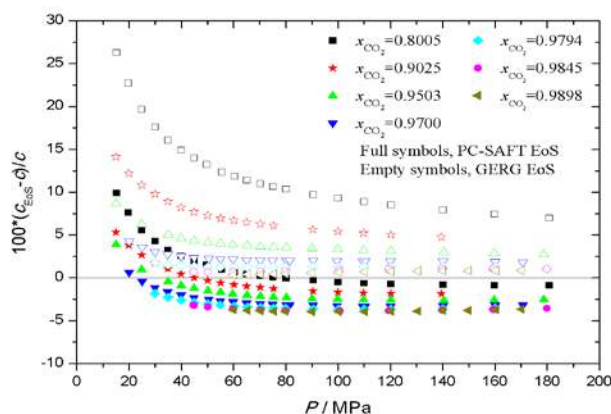


Figure 6. Comparison between this work experimental speeds of sound in the CO₂+CH₃OH mixtures, c , and the values calculated using the PC-SAFT and GERG EoS, c_{EoS} , at $T = 298.15$ K.

x_{CO_2}	$MRD_c(\%)$ $T = 263.15$ K		$MRD_c(\%)$ $T = 298.15$ K		$MRD_c(\%)$ $T = 323.15$ K	
	PC-SAFT	GERG	PC-SAFT	GERG	PC-SAFT	GERG
0.8005	2.12	11.7	2.09	12.9	2.16	11.0
0.9025	2.56	7.12	1.60	7.65	1.57	6.49
0.9503	2.82	4.95	2.05	4.23	1.55	3.16
0.9700	3.08*	3.62*	2.61	2.29	2.56	1.40
0.9794	3.98	2.15	3.22	1.34	2.95	0.86
0.9845	4.32	1.55	3.66	0.85	3.09	0.74
0.9898	5.01	0.80	3.86	0.64	3.15	0.65

Table 3. Comparison between this work experimental speeds of sound for CO₂+CH₃OH and those calculated using the PC-SAFT and GERG EoS. *Ref. [6].

Acoustic measurements are needed for proper design and monitoring of transport and storage of anthropogenic CO₂, however, the special features of CO₂ and CO₂-rich mixtures can make difficult and even impossible their determination. The addition of small amounts of methanol as doping agent enables the experimental obtaining of c in CO₂ at 5 MHz, and the effect of the dopant has been quantified. In the future, we will extend this method to opaque CO₂-rich mixtures of interest for CCS technology.

Acknowledgements: The research leading to these results has received funding from Ministry of Economy and Competitiveness of Spain ENE2013-44336-R and from Government of Aragon and the European Social Fund.

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Investigation of models for prediction of viscosity properties for CO₂ mixtures

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Abstract

When calculating movement of gases and liquids, transport of heat and speed of chemical reactions (for fast reactions) one need the transport properties of the mixture. The transport properties describe the transport of momentum (viscosity), of internal energy (thermal conductivity) and of components (diffusivity). Here different mathematical models for viscosity are compared with experimental data collected from literature for binary mixtures of CO₂ with impurities from: Ar, CH₄, CO, H₂, N₂, N₂O, O₂ or SO₂. These mixtures are relevant for transport of Carbon dioxide and in the CCS (Carbon Capture and Storage) chain. All the data is plotted and compared with different models.

Several models for viscosity that are suggested in the literature are investigated and compared with collected experimental data on mixtures of CO₂. Binary mixtures of CO₂ with the impurities Ar, CH₄, CO, H₂, N₂, N₂O, O₂ or SO₂ in temperature, pressure and concentration range relevant for transport, capture and storage. The standard models available in the NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP Version 9.0) [1] are also included in the comparisons.

New regressed parameters for existing models are also presented.

The transport properties measured through viscosity, thermal conductivity and diffusivity give details about transport of momentum, thermal energy and components. The physical processes are quite equal and of that reason they are treated with the same modelling approach.. For calculation of heat transfer it is important to have an accurate value of these properties, and it will help modelling and designing process units like heat exchangers and separators and to estimate friction and heat losses during pipeline transport of CO₂ containing residual components.

This study focuses on relevant mixtures for the transport of CO₂ coming from various CO₂ capture processes. According to Li et. al. [2], a pressure range from 0.5 bars to 500 bars and a temperature range from -55°C to 1350°C are interesting

Temperature area	Max pressure	Application
-55 °C to 40°C	200	Transport and purification
4 °C to 150 °C	500	Storage
150 °C to 1350 °C	80	CO ₂ capture, pre-combustion

Table 1 Temperature and pressure range of interest.

For single component at low pressure the viscosity is only a function of temperature, and one can do direct curve fitting of experimental data of viscosity as function of temperature. Zeberg-Mikkelsen[3] have done curve fitting for argon, hydrogen, methane, neon, nitrogen and oxygen.

Chung et.al[4] have made a general model for viscosity. It requires critical temperature and volume, acentric factor and dipole moment (in Debyes) for all materials. For polar substances it requires a special correction depending on the number of -OH groups. Poling[5] give a table over deviation for given gases.

In addition Lucas [6], Reichenberg[7] have proposed alternative models based on the corresponding state principle for pure components. Lucas has not included associate gases and Reichenberg is only focussing on organic gases.

For mixture at low pressure one can use individual viscosity models for each of the components or find average values for the input parameters like the acentric factor and the critical parameters and use that in the chosen viscosity model. When the viscosities for the each of the components in the mixture is calculated this will give more flexibility when choosing a specific prediction model for the components.



The viscosity for a mixture at higher pressure can be estimated by getting average values of the parameters like critical pressure and temperature and then use a model for a pure component to calculate viscosity. Another method is to use viscosity at low pressure for a mixture and then extend it to higher pressure.

The TRAPP[8] method is an extended corresponding state method for prediction of density and transport properties like viscosity and thermal conductivity for pure components and mixtures. The method is described by Poling[5] and Huber[9] and is shown in Eq. (1)

$$\eta_m(T, \rho, x) = \eta_m^0(T, x) + F_{\eta_m}(\eta^R(T_0, \rho_0) - \eta^{R0}(T_0)) + \Delta\eta^{\text{ENSKOG}}(T, \rho, x) - \Delta\eta^{\text{ENSKOG},0}(T, x) \quad (1)$$

Here the variables are:

η_m Viscosity for the mixture

η_m^0 Viscosity for the mixture at low pressure. Here one selects a model in section **Error! Reference source not found.**

η^R Viscosity for the reference fluid, Propane is at a scaled temperature and density.

$T_0 = T/f_m$ The temperature is divided on a factor f_m to get the temperature of the reference fluid that gives similar properties.

$\rho_0 = \rho h_m$ The density is multiplied with a factor h_m . The factors h_m and f_m are based on the evaporating pressure.

η^{R0} Viscosity for reference fluid at low pressure

$\Delta\eta^{\text{ENSKOG}}(T, \rho, x)$ Enskog addition that accounts for the situation where one molecule is much larger than the other molecule. $\Delta\eta^{\text{ENSKOG}}=0$ for pure components.

$\Delta\eta^{\text{ENSKOG},0}(T, x)$ Enskog term at low pressure.

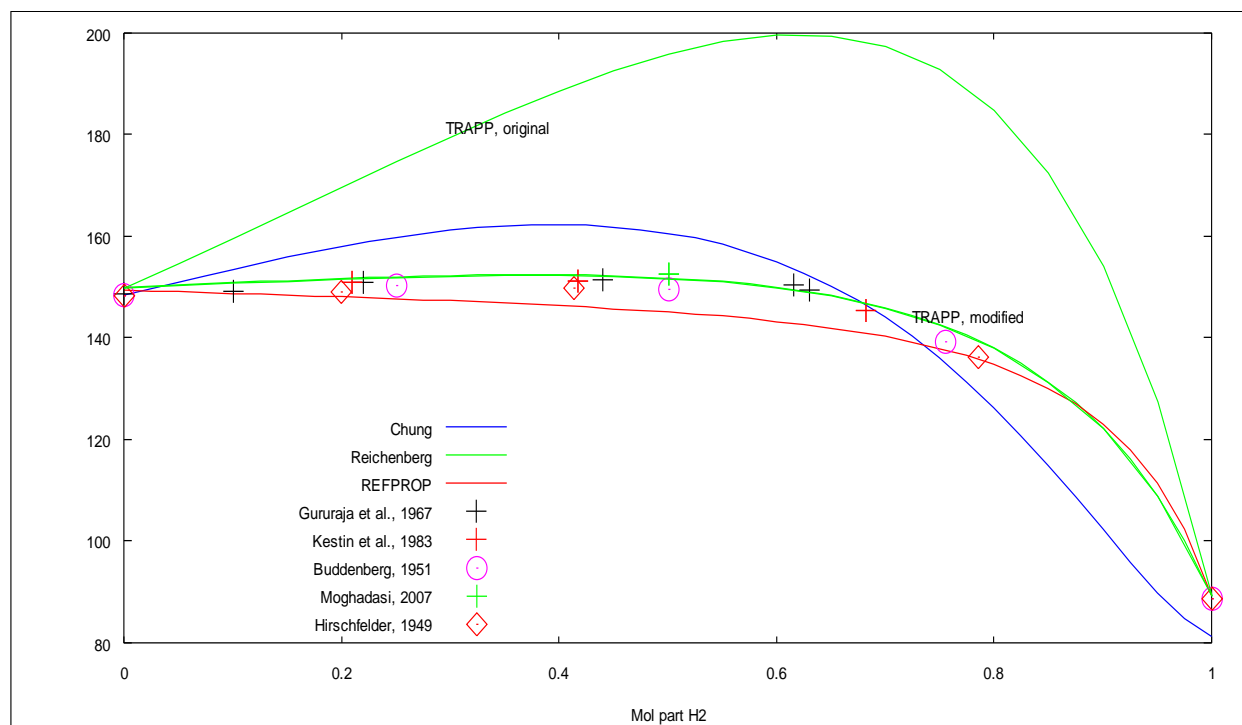


Figure 1 The TRAPP method applied with and without subtraction of the term $\Delta\eta^{\text{ENSKOG},0}$ compared to experimental values [10], [11], [12], [13], [14] and prediction from REFPROP v9.0

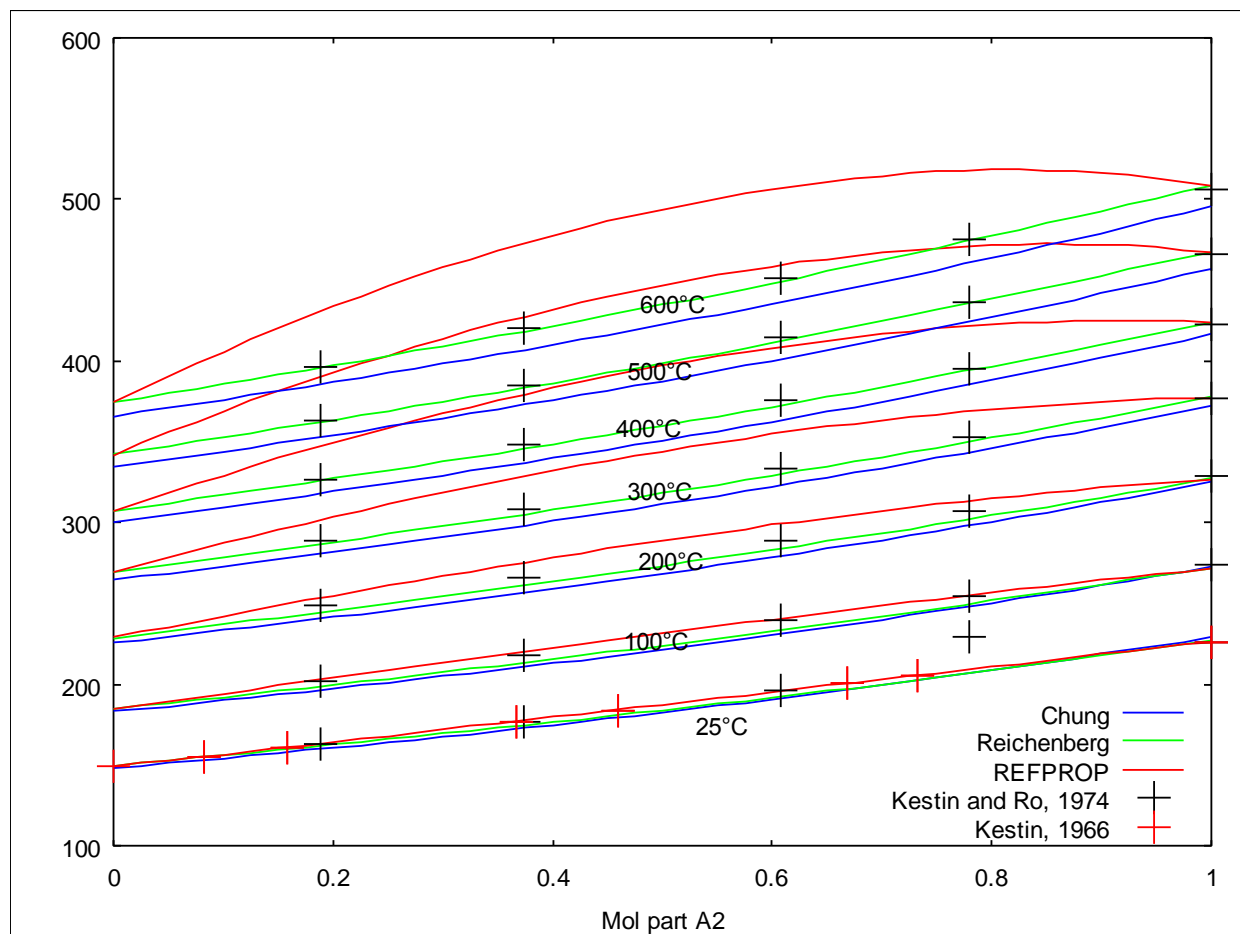


Figure 2 : Viscosity for mixture CO₂-Ar [15, 16]

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Modeling of CO₂ Solubility in Single and Mixed Electrolyte Solutions Using Statistical Associating Fluid Theory

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Abstract

The geologic sequestration of CO₂ in underground formations, primarily in saline aquifers, is a promising approach for the reduction of CO₂ emissions. Understanding the behavior of CO₂ in electrolyte solutions and brines is of great importance to the design of a CO₂ geologic sequestration process. At the temperature and pressure conditions of geological CO₂ storage, thermodynamic properties of CO₂ - H₂O and CO₂ - H₂O - electrolytes mixtures are quite complex and modeling of such systems is extremely challenging.

In this work, the statistical associating fluid theory (SAFT) is used to model CO₂ solubilities in single and mixed electrolyte solutions. The proposed SAFT model implements an improved mean spherical approximation, which uses a parameter K to correct the excess energies, namely KMSA, in the primitive model to represent the electrostatic interactions between ions. The proposed SAFT2-KMSA model is able to describe accurately mean ionic activity coefficients and liquid densities of electrolyte solutions including Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, Br⁻ and SO₄²⁻ from 298.15 K to 473.15 K using mostly temperature independent parameters, with sole exception being the volume of anions. CO₂ is modeled as a non-associating molecule, and temperature-dependent CO₂ - H₂O and CO₂ - ion cross interactions are used to obtain CO₂ solubilities in H₂O and in single ion electrolyte solutions. Without any additional fitting parameters, CO₂ solubilities in mixed electrolyte solutions and synthetic brines are predicted, in good agreement with experimental measurements. A representative example is shown in Figure 1.

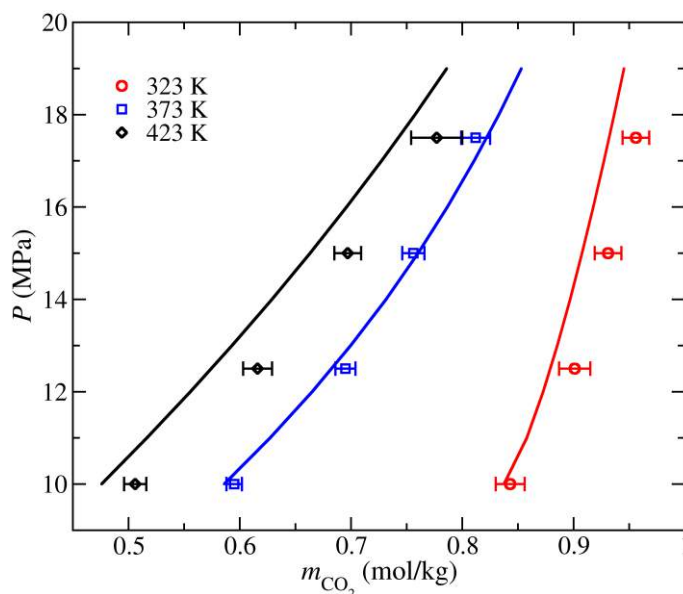


Figure 1. CO₂ solubility in a synthetic brine of ionic strength $I = 1.712$ mol/kg at 323 K, 373 K and 423 K. Symbols are experimental data (Zhao *et al.*, *Environ. Sci. Technol.*, **49**, 1972, 2015) and lines are SAFT2-KMSA predictions.

Development of a Novel Experimental Apparatus for Hydrate Equilibrium Measurements

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Abstract

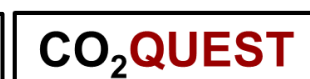
The current study reports our recent efforts to design and construct a novel experimental apparatus to be used for measuring the three-phase (Hydrate–Liquid water–Vapor; H–Lw–V) equilibrium conditions of pure gas and gas-mixture hydrates. The experimental apparatus can operate at pressures up to 20 MPa. The different parts of the experimental set-up are discussed and analyzed. Calibration issues are addressed and validation experimental measurements are reported at pressure conditions below 7.5 MPa for the case of pure gas hydrates.

In addition to measuring the three-phase equilibrium pressure and temperature conditions with the current experimental apparatus, liquid phase analysis measurements are reported. In particular, the solubility of the gas in the aqueous phase is measured under three-phase equilibrium conditions.

Gases of interest to the current study include CH₄, and CO₂. Both gases are of significant importance in industrial gas-storage and transportation applications, as well as gas-mixture separation applications. Table 1 presents equilibrium points and the respective solubilities for the systems CO₂-H₂O and CH₄-H₂O and Figure 1 gives a view of the good convergence of our results as compared to the literature.

Exp. No	System	Method	P (MPa)	T (K)	T _{CSMGem} (K)	X (molar fraction)	X _{CSMGem} (molar fraction)	Dev. (%)
6**	CO ₂ – H ₂ O	IPS	4.04 ± 0.02	281.8	282.258	0.0292 ± 0.0008	0.0274	6.55
8**	CO ₂ – H ₂ O	PBD	3.41 ± 0.02	281.0	281.148	0.0292 ± 0.0009	0.0257	13.88
9**	CO ₂ – H ₂ O	PBD	3.52 ± 0.02	281.0	281.351	0.0275 ± 0.0005	0.027	1.89
10**	CO ₂ – H ₂ O	PBD	2.33 ± 0.02	278.6	278.328	0.0236 ± 0.0004	0.0213	10.7
12**	CH ₄ – H ₂ O	IPS	7.04 ± 0.02	282.7	282.893	0.00197 ± 0.0002	0.00186	5.80
13**	CH ₄ – H ₂ O	IPS	5.36 ± 0.02	280.0	280.117	0.00183 ± 0.0002	0.00158	16.14
14**	CH ₄ – H ₂ O	PBD	7.07 ± 0.02	282.5	282.936	0.00194 ± 0.0002	0.00185	4.73

Table 1. Experimental measurements of the solubilities of CO₂ and CH₄ in H₂O three-phase (H–Lw–V) equilibrium conditions, and comparison with the calculations using CSMGem [1].



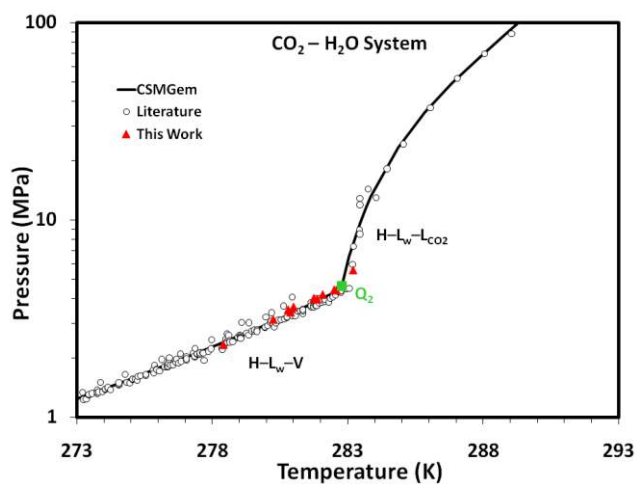


Figure 1. Pressure vs. Temperature at three-phase equilibrium conditions for the system $\text{CO}_2 - \text{H}_2\text{O}$. Comparison between experimental data obtained in this work (triangles) and values from literature [1], with calculations using CSMGem [1] (solid line). The green square denotes the upper quadruple point, Q2.

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Ionic Liquids for CO₂ Capture using Molecular Simulation: Bulk and Permeability Properties

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Abstract

Ionic liquids (ILs) are organic salts with melting points usually near room temperature (RTILs). They are characterized by extremely low vapor pressures, wide liquid ranges, non-flammability, thermal stability, tunable polarity, good electrolytic and solvation properties and easy recycling. In combination with the aforementioned properties, several ILs exhibit also an unexpectedly large CO₂ absorption capacity and selectivity [1] and are, therefore, classified among the most attractive candidate sorbents for CO₂ capture and separation from post-combustion flue gases [2]. In parallel, task-specific ILs fulfill many environmental aspects of the post combustion CO₂ capture (PCC) technology, such as reducing the parasitic energy load, the reduced water use and (near-) zero release of solvents to the environment. Gas absorption capacity of ILs depends on their chemical and molecular structure, especially of the anions. The huge number of possible structures of ILs available for investigation demands the unfolding of the microscopic mechanisms that are responsible for the ILs macroscopic behavior and the development of screening strategies based on accurate molecular modelling of sorbate / sorbent interactions.

The present work focuses on the molecular simulation of imidazolium-based [TCM⁻] ionic liquids and their permeability and selectivity to gases using a classical force field that has been optimized and extensively validated [3]. Long molecular dynamics (MD) simulations of the 1-alkyl-3-methylimidazolium tricyanomethanide ([C_nmim⁺][TCM⁻], *n* = 2, 4, 6, 8) IL family have been performed [3] at various temperatures and at atmospheric pressure in order to calculate the thermodynamic, structural and transport properties of the pure ILs, exploring, simultaneously, the intrinsic characteristics and mechanisms of the systems under study at the atomistic level [4-5].

Predictions on density extracted from molecular dynamics simulations are in very good agreement with experimental data with a deviation less than 1.2% (Figure 1). The spatial organization of these systems was thoroughly studied. The calculated radial distribution and radial-angular distribution functions between the ions' centers of mass revealed that ILs exhibit organization at much longer distances compared with conventional liquids with the anion-cation interaction being stronger than the other two interactions at all temperatures (Figure 2a). The effect of the alkyl tail length on these properties was also investigated and tail aggregation phenomena, which become more evident for the longer alkyl chain lengths, were detected by calculating radial distribution functions between different sites on the ions (Figure 2b). The ions' translational motion was analyzed along specific axes in order to investigate anisotropy phenomena in the ions diffusion while the presence of heterogeneities in the dynamics was investigated by detecting deviations from the expected Gaussian behaviour. Shear viscosity calculations were performed using the following Green-Kubo relation and the agreement between the experimental and the predicted values is reasonably good with the temperature dependence of the viscosity being captured well for all ILs. Ions' self-diffusion coefficients were calculated in the Fickian regime using the Einstein relation. The predicted diffusivities are in very good agreement with experimental NMR measurements for the cation.



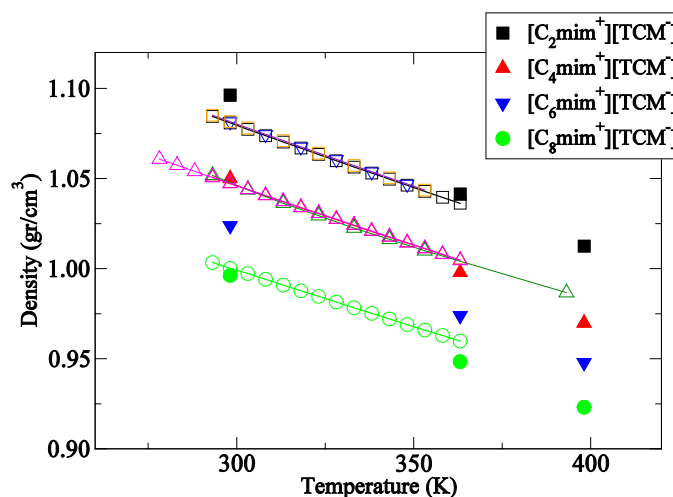


Figure 1. MD predictions for the density of $[C_n\text{mim}^+][\text{TCM}^-]$, $n = 2, 4, 6, 8$ (full points). The lines with open points are experimental data for $[C_2\text{mim}^+][\text{TCM}^-]$ ^{7,9-11}, $[C_4\text{mim}^+][\text{TCM}^-]$ ^{6-7,11} and $[C_8\text{mim}^+][\text{TCM}^-]$ ⁸.

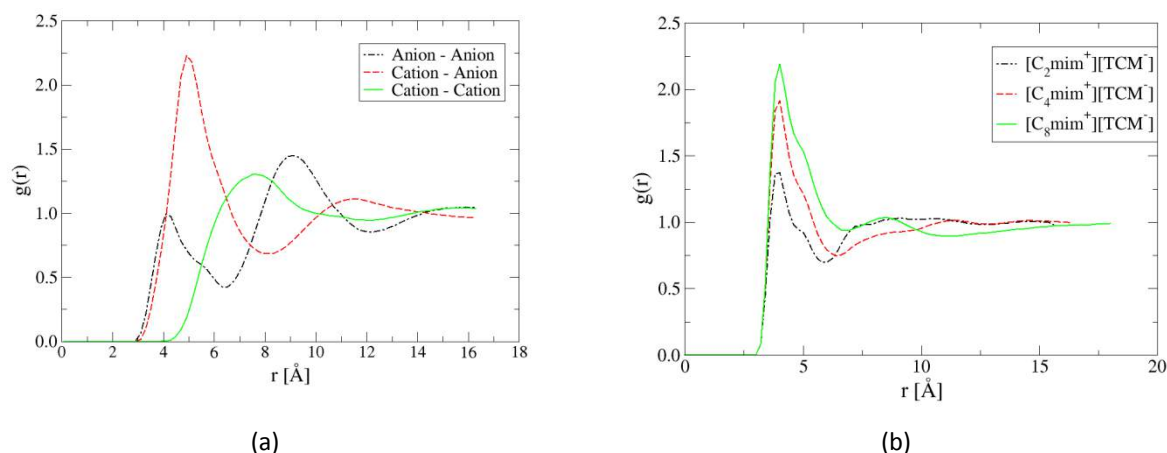


Figure 2. (a) Radial distribution function $g(r)$ for the anion-anion (black), anion-cation (red) and cation-cation (green) center of mass of $[C_4\text{mim}^+][\text{TCM}^-]$ at 298.15 K and (b) Radial distribution function $g(r)$ between the terminal carbon atoms in the cation's alkyl chain of $[C_2\text{mim}^+][\text{TCM}^-]$ (black), $[C_4\text{mim}^+][\text{TCM}^-]$ (red) and $[C_8\text{mim}^+][\text{TCM}^-]$ (green) at 298.15K.

Gas (CO_2 , N_2 , CH_4 , Ar , SO_2 , H_2S , CO and O_2) permeability has been studied [12] by performing additional very long MD simulations for the prediction of gas diffusivity while gas solubility has been calculated in the infinite dilution regime using the Widom test particle insertion method. All gases appear to have comparable diffusivities in each IL system studied and for that, the solubility is expected to control the selectivity properties of these ILs, a fact that is also supported by experimental results [13]. Experimental measurements for CO_2 and N_2 are in excellent agreement with the predicted values and from the extracted data can be concluded that $[\text{TCM}^-]$ ILs are highly selective with $[C_4\text{mim}^+][\text{TCM}^-]$ being identified as the most selective for CO_2/N_2 separation. Gas absorption selectivities (solubilities and diffusivities) were also calculated for the widely used imidazolium-based $[\text{Tf}_2\text{N}^+]$ IL family. The comparison between the imidazolium-based $[\text{Tf}_2\text{N}^+]$ and $[\text{TCM}^-]$ families (Figure confirms that $[\text{TCM}^-]$ ILs are very promising candidates for use in gas separation technologies.

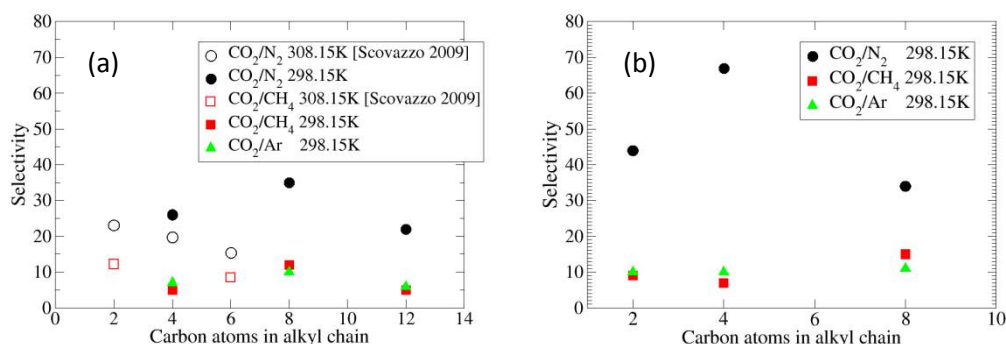


Figure 3. Selectivity for the gas pairs CO₂/N₂, CO₂/Ar, CO₂/CH₄ at room temperature and at atmospheric pressure of (a) [C_nmim⁺][Tf₂N⁻], $n = 4, 8, 12$, and (b) [C_nmim⁺][TCM⁻], $n = 2, 4, 8$. Experimental selectivities [14] of CO₂/N₂ and CO₂/CH₄ in [C_nmim⁺][Tf₂N⁻] are also plotted (open points).

Acknowledgements

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Simulation of Two-Phase Flow of CO₂ Mixtures: Comparing Cubic and Reference Equations of State

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Abstract

In a carbon capture and storage (CCS) infrastructure, CO₂ transport is an essential component. CO₂ can be transported using either pipelines or ships, depending on the location of the source and the most appropriate storage site. The captured CO₂ mixture will most often contain some impurities such as oxygen, nitrogen, argon, carbon monoxide and hydrogen.

Impurities can significantly alter the thermodynamic properties of the CO₂ mixtures, depending on the concentration of each impurity. To describe such mixtures accurately, an accurate equation of state (EOS) is needed, which relates pressure and temperature to other quantities like density, heat capacity and composition of the liquid and vapour phases. The EOSCG equation of state (1) has been developed at Ruhr-Universität Bochum (RUB) to accurately describe CO₂ mixtures.

In this work, we compare the results from EOSCG, GERG-2008 (2) and simpler, cubic equations of state for transient cases that are relevant for CO₂ pipeline transport. More specifically, we consider quantities that are relevant for depressurisation of a pipeline. A depressurisation may occur either due to a controlled emptying of the pipe, or due to an accident where the pipe ruptures. In such incidents, the speed of sound and the phase envelope of the mixture are especially important. The speed of sound governs the speed of pressure waves, which has an impact on the risk of running fractures (3). The phase envelope affects how low temperatures can be expected during a depressurisation. Too low temperatures may cause damage to the pipe steel or other equipment. The phase envelope also governs at what temperatures and pressures two-phase flow will appear, which one seeks to avoid in normal pipeline operation. Finally, accurate density prediction is essential to allow accurate fiscal metering of CO₂ transport, i.e. to determine the mass flow of CO₂ in a pipeline. We consider a number of relevant impurities such as nitrogen, oxygen, hydrogen, methane and ethane.

The results show that there are significant differences between EOSCG/GERG-2008 and the cubic equations of state. As an example, for a depressurisation of a 5km pipeline with a mixture of 95% CO₂ and 5% N₂, the Soave-Redlich-Kwong (SRK) cubic EOS estimates a significantly higher sound velocity than EOSCG, as shown in Figure 1. It also predicts a lower saturation pressure than EOSCG, seen in Figure 2. These two effects could lead to wrong conclusions about whether there is a risk for running fractures or not. On the other hand, SRK estimates a lower temperature than EOSCG, and is hence more conservative in this respect, as seen in Figure 4. The density prediction by SRK is also significantly lower, as seen in Figure 3.

Our results illustrate the importance of using accurate thermodynamic models when simulating two-phase flow of CO₂ mixtures, since impurities can greatly affect critical parameters like speed of sound, temperature, pressure and density.

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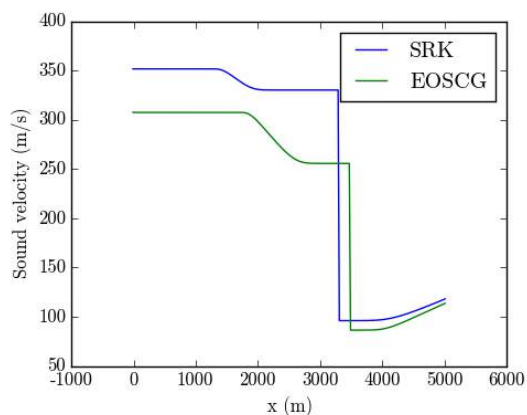


Figure 1. Speed of sound during depressurisation of a 5km pipeline filled with 95% CO₂, 5% N₂.

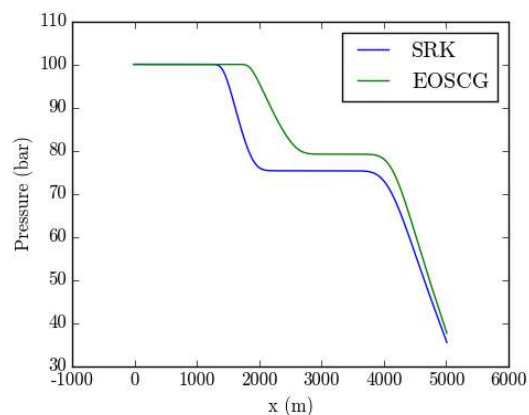


Figure 2. Pressure during depressurisation

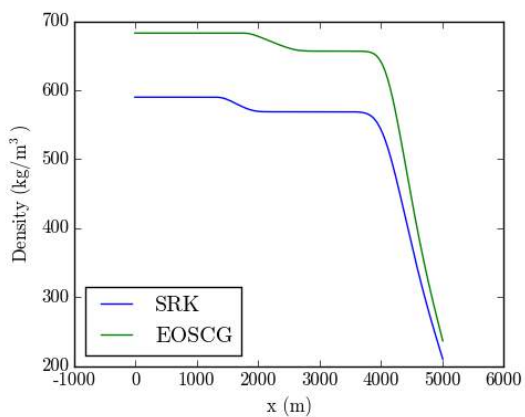


Figure 3. Density during depressurisation

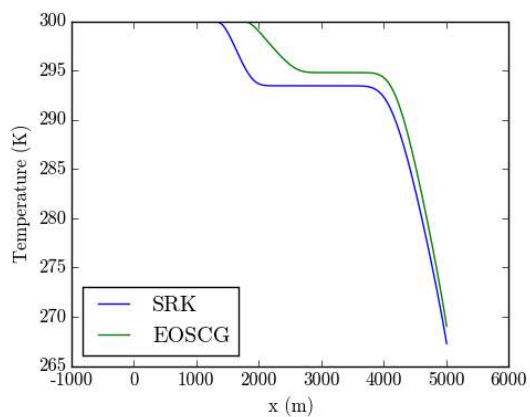


Figure 4. Temperature during depressurisation

Iolicap Project Results

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Abstract

The presentation reports on the most important results of the Iolicap project (FP7-ENERGY-2011-1, 283077). The report encompasses the output and main conclusions on the synthesis and thermophysical properties of Ionic Liquids (ILs), including also properties such as their corrosiveness and toxicity.

The application potential of ILs as solvents for CO₂ capture with the conventional scrubbing stripping process is critically reviewed and alternative novel applications are proposed including the immobilisation of ILs on to porous materials and monoliths for the development of efficient absorbents and membranes. Moreover, the presentation provides an overview on our efforts to enhance the experimental accuracy of advanced analytical techniques regarding the definition of thermophysical and physicochemical IL's properties and gives an insight on our capacity to predict important properties of ILs via molecular simulation studies and via the development of accurate EoS models.

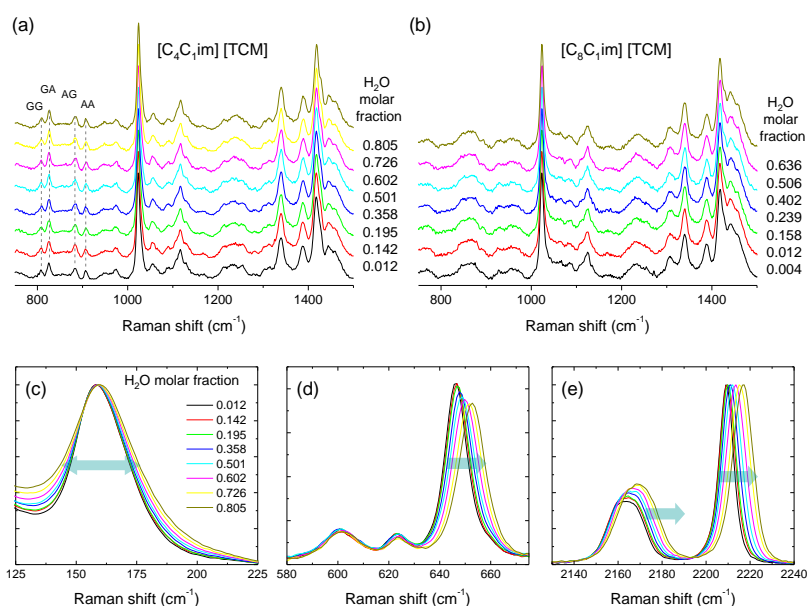


Figure 1. Advanced analytical techniques such as Raman analysis unveil the mechanism behind the positive effect of water on the CO₂ capture by tricyanomethanide anion ILs [1].

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Vapour-liquid equilibrium data for the carbon dioxide and oxygen (CO₂+O₂) system at 6 isotherms between the freezing point and critical temperature of CO₂

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Abstract

A setup for the measurement of vapor-liquid phase equilibria of CO₂-rich mixtures relevant for carbon capture and storage (CCS) transport conditions is presented. An isothermal analytical method with a variable volume cell is used. The apparatus is capable of highly accurate measurements in terms of pressure, temperature and composition, also in the critical region. Vapor-liquid equilibrium (VLE) measurements for the binary system CO₂+O₂ are reported at 6 isotherms between the freezing point and critical temperature of CO₂, with estimated standard uncertainties of maximum 6 mK in temperature, maximum 3 kPa in pressure, and maximum 0.0006 in mole fractions of the phases. These measurements are verified against existing data. Although some data exists, there is little trustworthy data around critical conditions, and our data indicate a need to revise the parameters of existing models. A fit made against our data of the vapor-liquid equilibrium prediction a cubic EOS is presented. The critical region of the isotherm are fitted using a scaling law, and high accuracy estimates for the critical composition and pressure are found.

Detailed knowledge about phase behaviour, under different conditions is relevant for all parts of the CCS-chain. Currently there are still gaps in the available data for thermophysical data. One important property for calibration and verification of equations of state (EOS) is phase equilibrium data. The present paper reports the results of VLE measurements on the CO₂+O₂ binary system, with measurements covering the whole VLE pressure region at the 6 isotherms between the freezing point and critical temperature of CO₂. At conditions where, high quality literature data exist for this system, some data points are repeated to confirm the operation of the experimental setup. Furthermore, several measurements were taken at conditions where no previous data or only data of dubious quality could be found, for instance at pressures close to the critical point of the binary mixture at the measured temperatures. Additionally, measurements were performed at temperatures close to the critical temperature of CO₂. The results are compared to existing EOS models, and new fits are presented.

The experimental setup is shown in Figure 1 a more detailed description could be found in [1] The vapor-liquid equilibrium measurements were carried out using an isobaric isothermal analytical method with a variable volume cell, as described by [2] This method involves analysis of the equilibrium composition of both phases. The content of the cell is loaded with the the syringe pumps, and then brought to equilibrium with the stirrer at constant temperature. A constant pressure is used as an indicator of equilibrium. After a constant pressure is achieved the stirrer is turned off to let the cell settle before sampling of vapour and liquid is done.



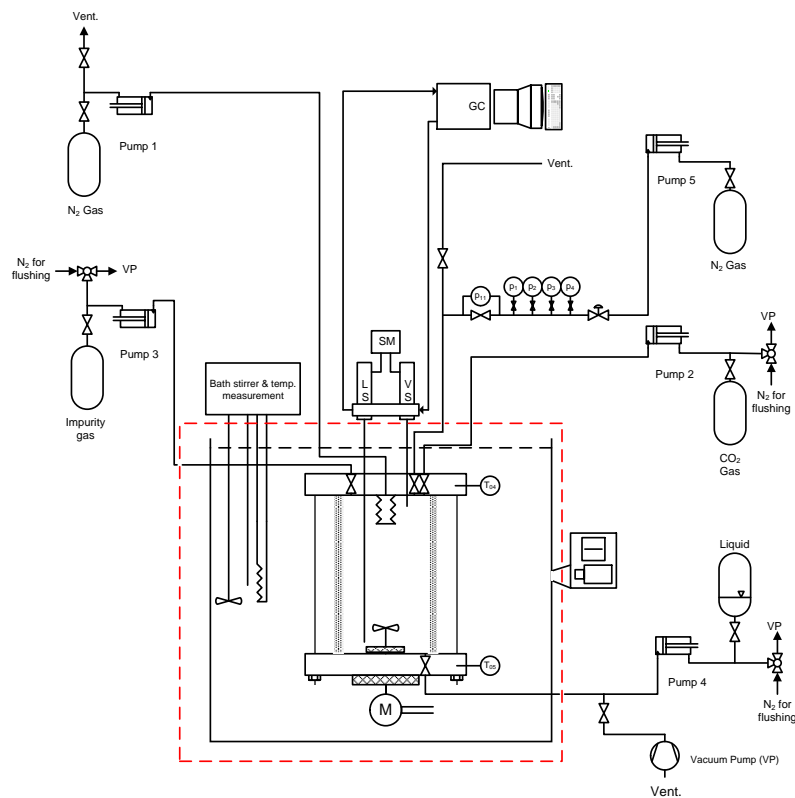


Figure 1 Principal diagram of cell and auxiliary apparatus. LS: Liquid sampler, VS: Vapor sampler, M: Motor for stirrer inside cell. T04: Top flange temperature. T05: Bottom flange temperature.

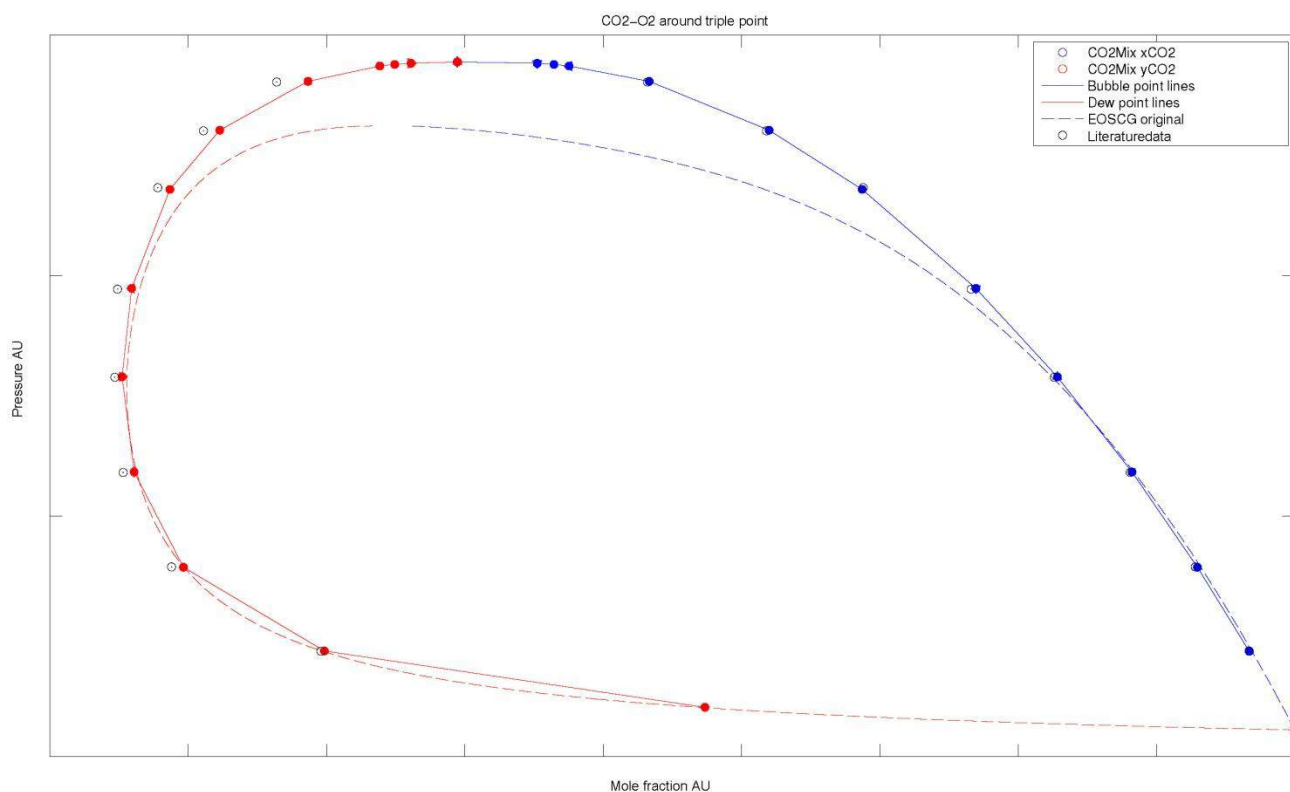


Figure 2 CO₂-O₂ isotherm around triple point of CO₂

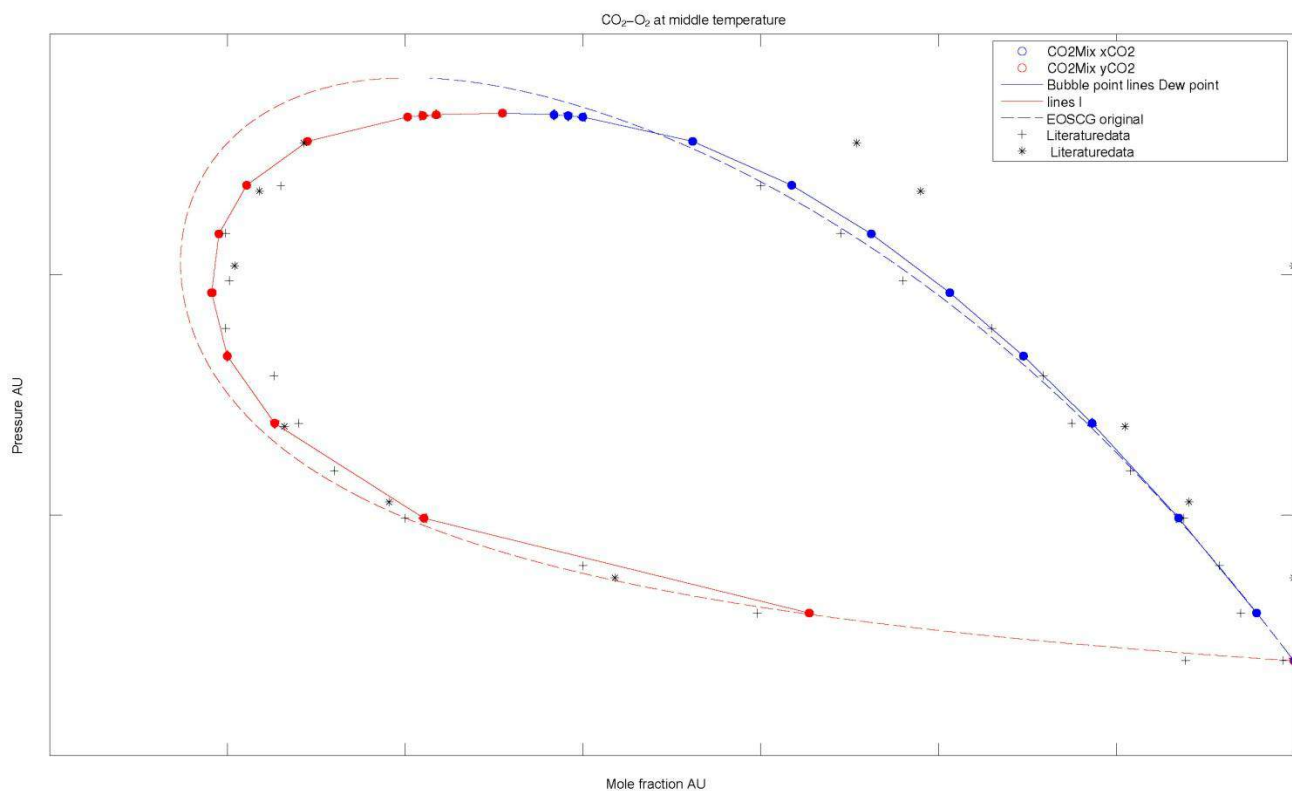


Figure 3 CO₂-O₂ isotherm around the midpoint between triple point and critical temperature of CO₂

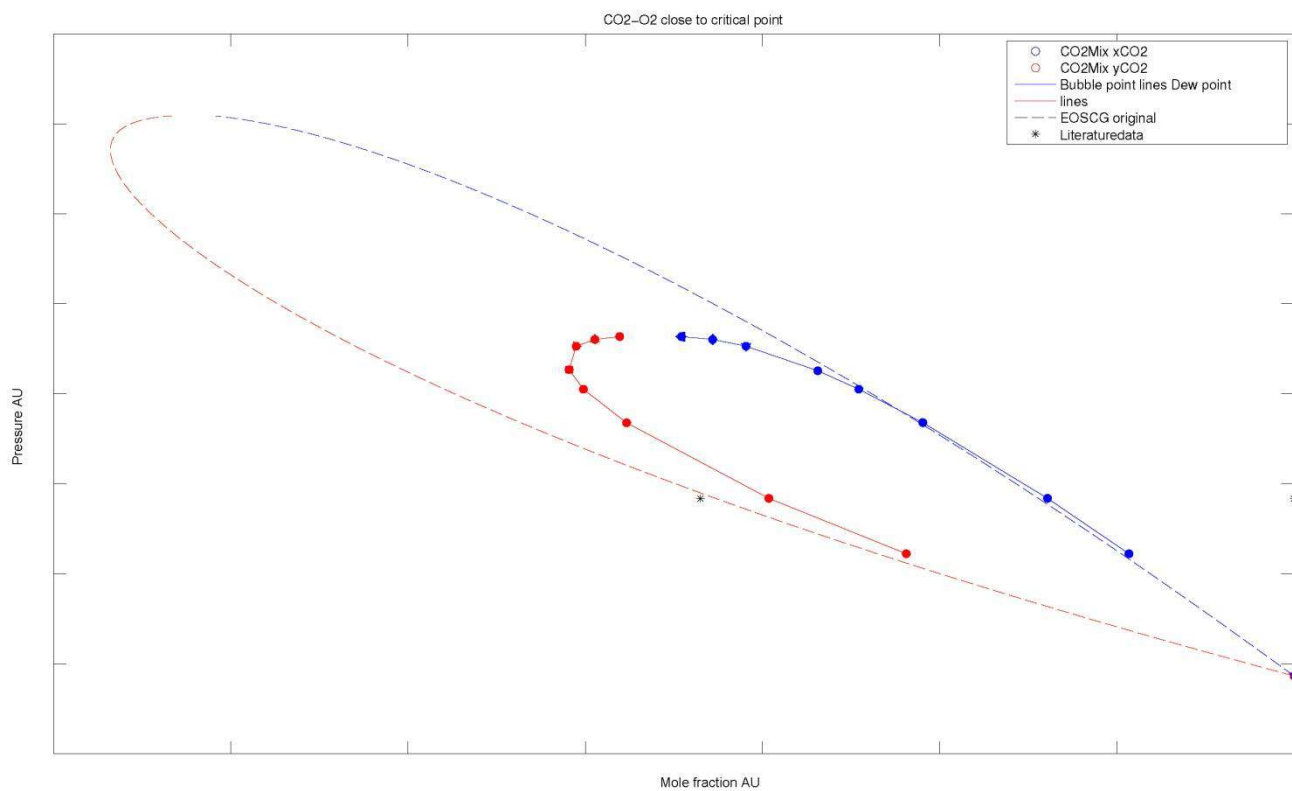


Figure 4 CO₂-O₂ isotherm close to the critical point of CO₂

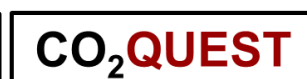
Three selected isotherms are shown in this abstract, in general the measurements shows good agreement with literature data. The isotherm at around the critical point of CO₂ have very little literature data available. New regression models will also be presented at the conference.

This publication has been produced with support from the research program CLIMIT and the BIGCCS Centre, performed under the Norwegian research program Centres for Environment-friendly Energy Research (FME). The authors acknowledge the following partners for their contributions: Gassco, Shell, Statoil, TOTAL, GDF SUEZ and the Research Council of Norway (193816/S60 and 200005/S60).

The research leading to these results has also received funding from the European Community's Seventh Framework Programme (FP7-ENERGY-20121-1-2STAGE) under grant agreement n° 308809 (The IMPACTS project). The authors acknowledge the project partners and the following funding partners for their contributions: Statoil Petroleum AS, Lundin Norway AS, Gas Natural Fenosa, MAN Diesel & Turbo SE and Vattenfall AB.

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Experimental work at RUB and Tsinghua and a new model describing thermodynamic properties of CO₂-rich mixtures

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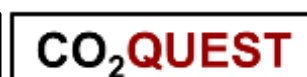
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Abstract

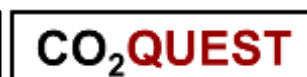
Work Package 1.2 of the IMPACTS project, “Thermophysical Behaviour of CO₂ Mixtures”, aims at an improved description of thermodynamic and transport properties of mixtures relevant for the transport of CO₂. The work package covers the evaluation of existing transport property models, phase-equilibrium measurements for relevant binary systems, density measurements for relevant binary systems, and the development of an improved thermodynamic property model based on or validated by the experimental results. The work on transport property models and on phase equilibrium measurements is presented in separate talks. This presentation will briefly show results of density measurements carried out at Ruhr-University in Bochum [1-4] and at Tsinghua University in Beijing [5-7] and of dew point measurements carried out at Ruhr-University [8, 9]. The main focus of the presentation will be on development and performance of an improved multiparameter equation of state model, which was recently finalised as part of the IMPACTS project [10], and on current developments aiming at the description of relevant components that have not been considered in accurate property models yet. The theoretical work on thermodynamic properties in IMPACTS is closely related to activities funded from different sources [11-13]. Results both from IMPACTS and from these related projects could be implemented in the “Tool Box” provided by IMPACTS. In this way, users interested in an assessment of the impact of impurities are enabled to accurately describe thermodynamic properties of CO₂-rich mixtures relevant for CO₂-transport by pipeline and by ship. As element of the IMPACTS Tool-Box the thermodynamic property software “TREND” is described in detail during the poster session of the workshop.

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Modeling solid – fluid equilibria with application to CO₂ mixtures

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Keywords: solids, CCS, PC-SAFT

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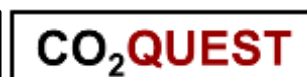
Abstract

Carbon Capture and Sequestration (CCS) has grown in recent years from lab and pilot scale activity to a full blown industrial process. Preliminary conceptual design, detailed design, simulation and optimization of a CCS process require, among others, accurate knowledge of the physical properties of the chemical system involved. CO₂ is typically captured from fossil fuel power plants and is transported to the appropriate storage location. This fluid stream contains different chemical impurities in various concentrations, that depend on the initial process and the type of pre-treatment imposed to the stream prior to transportation. Identifying solid - fluid equilibria conditions and their dependence on impurities are critical to the design and operation of CO₂ pipelines and storage facilities. The reason is that the formation of dry-ice resulting from solid-fluid equilibria can largely affect the safety of CCS facilities during equipment depressurization, process shutdown or other process upsets.

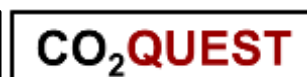
Solid-fluid equilibria properties can be predicted by a variety of methods. The challenge in developing a solid-fluid model lies on selecting and combining thermodynamic models for each phase which are both accurate and computationally efficient not only for pure CO₂ but also for multi-component mixtures. The models developed in this work use cubic (SRK, PR) and more advanced (PC-SAFT [1]) equations of state to account for fluid (vapor or liquid) properties and either simple thermodynamic models or more complex empirical correlations to account for the pure CO₂ solid phase. Three solid-fluid models of increasing complexity have been developed and validated. The first model is based on the equilibration of chemical potentials between the solid and fluid phases at the same temperature and pressure, where the pure CO₂ saturation pressure is provided from accurate correlations fitted to experimental data [2]. The second model is based on a thermodynamic integration method proposed by Seiler et al. [3] and uses experimentally accessible pure component properties to calculate the solid-fluid equilibrium. The most complex model involves combination of the empirical equation of state proposed by Jäger and Span [4] for solids with a fluid EoS. The models are validated against experimental data for pure CO₂ and CO₂ mixtures at solid-liquid-vapor equilibrium conditions [5]. The accuracy varies substantially, as one goes from simple to more accurate models for the solid state, but also depends on the accuracy of the description of the fluid phase from the EoS.

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CCS Developments in North America

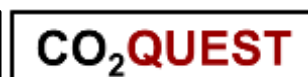
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Abstract

Rising concentration of atmospheric CO₂ is attributed to the increasing consumption of fossil fuels. North America which accounts for 19% of the CO₂ emissions is the second largest emitter after China, which accounts of 27% of the emissions. Efforts to limit the rising atmospheric concentrations of CO₂ have led to the development of technologies for carbon capture and storage (CCS). In this contribution, an overview of CCS developments that span fundamental research to implemented technologies in North America will be discussed. A wide range of technologies that include niche approaches for integrating sustainable energy production with CCS to large scale CCS demonstration projects and their inherent challenges and opportunities will be considered.



Reactive transport simulations of an impure CO₂ flue gas injection into a saline aquifer on a 2D reservoir scale

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Abstract

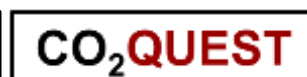
Numerical simulations of reactive transport prove to be a useful tool evaluating the potential impact of injecting impure CO₂ flue gas into deep saline aquifers [1-3]. A first approach to numerically simulate the geochemical reactive processes in the subsurface is a one dimensional, radial grid, representing shallow reservoirs with a relatively small thickness of the targeted storage formation. For other storage systems with a thickness larger than a few meters and where buoyancy effects in the CO₂ plume migration have to be considered, a two dimensional grid becomes inevitable. However, for the proper description of short term transport processes occurring close to the injection, small cells are required. Hence, the introduction of a 2D grid, spanning horizontal and vertical direction, leads to a significant increase in the total number of grid cells. Naturally, the computational effort increases and consequently computational time, too. Careful revision of the chosen parameters allows for some simplifications of the model in order to keep total computational time reasonable, grid optimization is advisable.

Based on our previous 1D studies embedded in the CO2QUEST project [4, 5], 2D simulations of impure CO₂ injection were performed. Reservoir and caprock characteristics, as wells as injection scenario reflect the CCS test site Heletz, Israel. Mineralogy and petrophysical parameters are derived from in-situ and laboratory experiments implemented within the MUSTANG Project [6]. Geophysical input values are assigned as follows: temperature (66 °C, isothermal), pressure (14.7 MPa), and salinity (0.055). The reservoir complex under investigation can be divided into four layers, i.e. sandstone, shale, sandstone, and a lower shale caprock, refer Table 1 and Figure 1. The mineralogy of these two sandstones consists mainly of quartz, in addition with feldspars, clay minerals, carbonate (ankerite), and pyrite, whereas the shale and caprock mineralogy is dominated by feldspars and clay minerals, and in some minor extent of carbonates (calcite and ankerite). While the sandstone layers are highly permeable, the permeabilities of the clay-rich shale and caprock layers are lower by three to four orders of magnitude.

layer	height [m]	porosity [%]	horizontal permeability [mD]	vertical permeability [mD]	quartz [%]	feldspar [%]	clay minerals [%]	carbonates [%]	other minerals [%]
caprock	2	9.5	0.1	0.1	3	50	35	8	4
sandstone	2	21.3	700	100	70	16	8	4	2
shale	3	9.5	0.1	0.1	3	50	35	8	4
sandstone	9	15.6	700	100	70	16	8	4	2

Table 1. Geological and mineralogical characteristics.

The entire 2D radial grid spans 30 km in horizontal and 16 m in vertical direction. The total vertical extent of 16 m is represented by 48 cells of equal height, whereas the horizontal grid division is non-equidistant. As noted above, the inner section of the grid needs a higher grid resolution, in this case, expanding horizontally to 2000 m, see Figure 1. Here, the grid consists of 220 cells, exponentially increasing in size from 0.22 m to 49 m. Subsequently, the periphery is depicted as a grid with larger increasing cell sizes in the horizontal direction (30 cells in total). In the vertical direction, five cells represent 16 m. This yields a 2D grid with 10710 cells in total, which is capable of simulating both geochemical transport processes on a small scale close to the injection site and proper pressure dissipation on a large scale. Hence, this concept provides the needed detail on the one hand, but ensures on the other hand that the computational effort on standard workstations remains manageable.



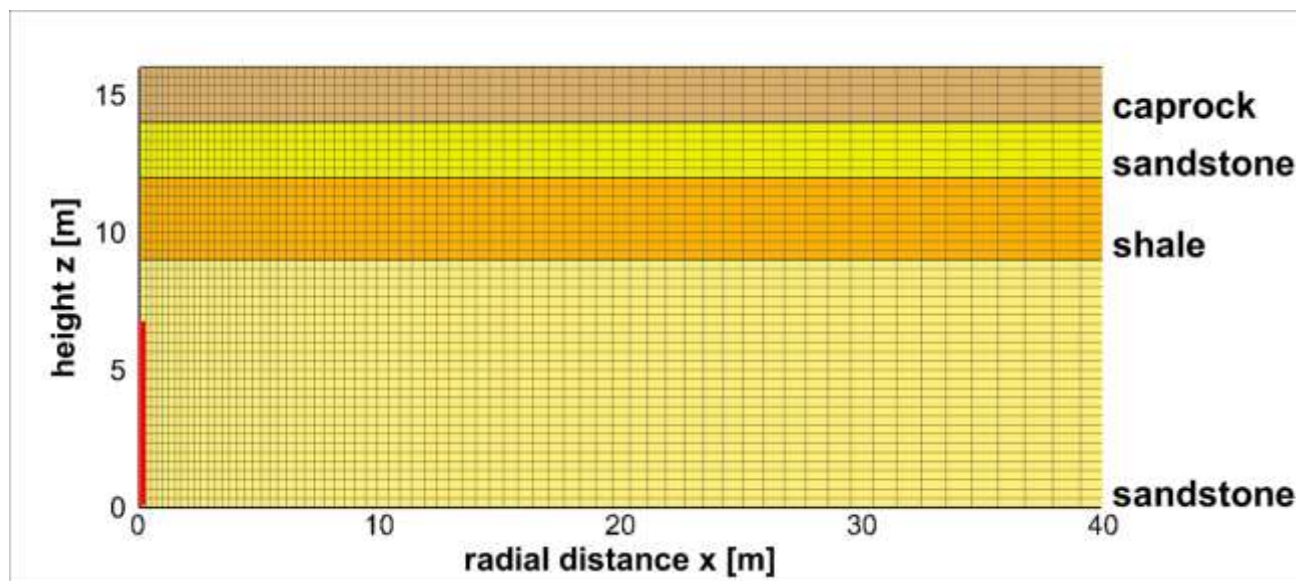


Figure 1. Section of the layered 2D model representing the Heletz saline aquifer reservoir. The whole 2D radial symmetric model covers a horizontal distance of 30 km. The injection takes place in 20 cells at the very left, marked in red.

The injection into the lowest sandstone is assigned to a column of 20 cells located at the lower left corner of the radial symmetric 2D model. Numerical simulations were performed using the parallel code TOUGHREACT V3.0-OMP [7]. The 99 %:1 % mixture of CO₂ and SO₂ is injected with a rate of 9 kg/s. After a 10 year injection period, a CO₂ plume develops in the lowest sandstone layer. Figure 2 shows the situation up to 240 m from the injection site. The horizontal extent of the gas phase reaches up to 2500 m. This maximal distance is located within the lower sandstone, just beneath the shale layer. At a horizontal distance of approximately 400 m from the injection well, nearly the whole thickness of this sandstone layer is influenced by CO₂. The fully dried out zone expands for approximately 75 m.

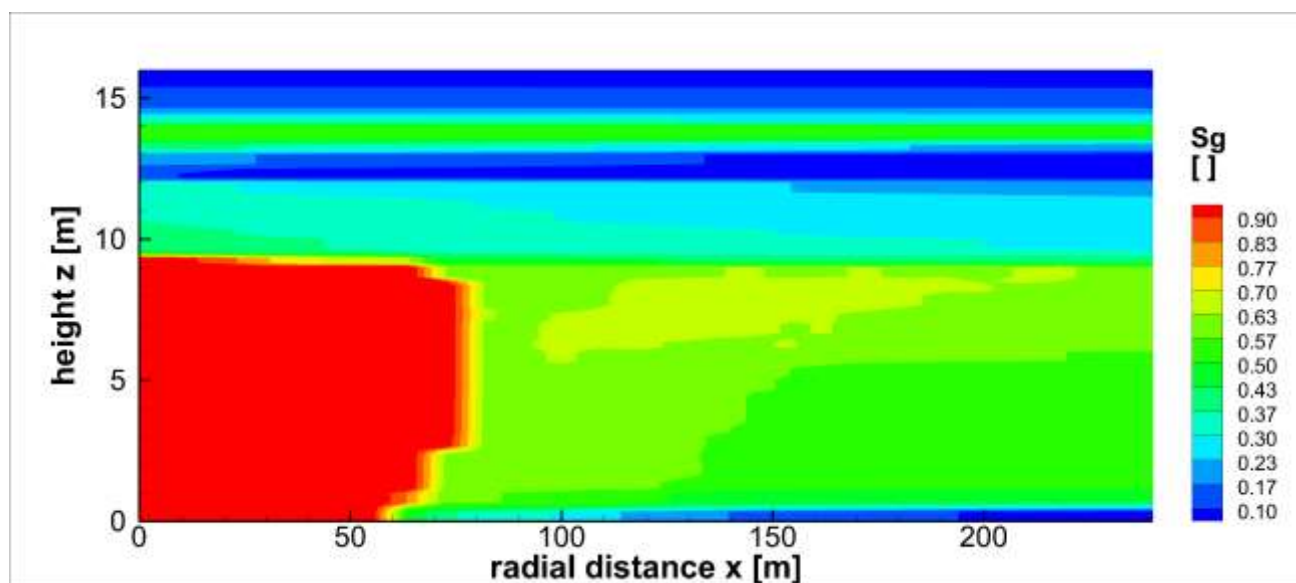


Figure 2. Simulated CO₂ gas saturation S_g after 10 years of CO₂ stream injection at a rate of 9 kg/s, including 1 % SO₂.

The excerpt in Figure 3 illustrates the difference in porosity relative to the starting situation after 10 years of injection as a result of geochemical processes. Several observations can be made from the spatial pattern of the porosity change. First of all, a distinct front of increased porosity developed from 100 m at the bottom to 200 m at the

top of the lower sandstone layer. This is mainly due to dissolution of ankerite and its spatial profile overlaps nicely with the SO₂ gas phase distribution. At the bottom of the shale layer evolves a small region (blue band in Figure 3) of porosity decrease, which is based on the transformation of calcite to anhydrite and their difference in molar volumes. This is consistent with the potential self-sealing capacity of caprocks [8]. The minerals in the upper parts of the reservoir (upper shale, sandstone, and lower caprock) are nearly unaffected, although they are flooded by CO₂, as well. However this CO₂ stream contains no significant amount on SO₂ due to the precipitation of anhydrite. The porosity change pattern in its entirety reflects the interdependency between multiphase, multi-component transport, reactivity, residence times, and flow pattern. This complex interplay and its impact on operation and geochemical management of impure CO₂ injections will be discussed in more detail in the presentation.

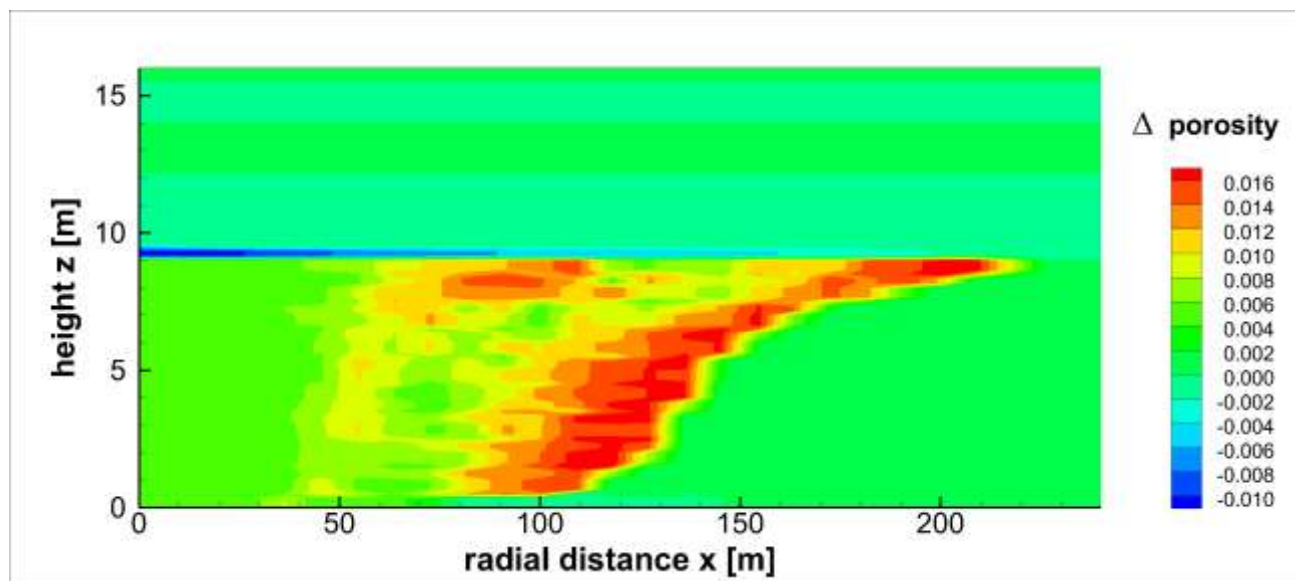
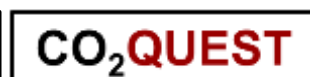


Figure 3. Simulated porosity difference after 10 years of CO₂ stream injection at a rate of 9 kg/s, including 1 % SO₂.

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Analysing the effect of impurities in the CO₂ stream injected on fractured carbonates

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Abstract

The only way to limit global warming to less than two degrees (i.e. 2DS or two degrees scenario) is to combine energy efficiency with renewable energy apart from a large expansion in the use of carbon capture and storage (CCS) (Christian, 2015). CCS is recognized one of the key existing technologies to reduce the global emissions of CO₂ into the atmosphere (International Energy Agency (IEA), 2013). Regarding technical aspects, the technology has “a green light” although there are some important uncertainties to be solved (Delgado, Diego, & Alvarez, 2014).

The *Fundación Ciudad de la Energía* (CIUDEN) has successfully completed the full CCS chain, being the CO₂ captured in the Technology Development Centre in *Cubillos del Sil* (León, Spain) whereas the CO₂ is geologically injected in the deep saline aquifer located in the Hontomín Pilot (Burgos, Spain) (Fernandez, De Dios, & Marín, 2015).

As regards on CO₂ storage, one of the most important uncertainties of the technology is to understand the physicochemical processes that take place in the rock-brine-CO₂ system within the storage, during and after CO₂ injection, and the changes induced on operational processes due to impurity effects (Brosse, Magnier, & Vincent, 2005) (Michael, et al., 2015). CIUDEN's activities focused on this issue include the accomplishment of experiments in lab scale and field scale, always taking into account that the impurity compositions used in lab scale are higher than in field scale due to following reasons: the identification of operational changes and geo-chemical effects depends on the composition of impurities in the CO₂ stream and the avoidance of situations that could cause damages to the facility.

Regarding lab works, static tests and dynamic tests were carried out; in both cases, a pressure of 150 barg and a temperature around 45 °C were selected. In order to study the effects of impurities, a comparison between the pure CO₂ injection (to define a baseline) and the binary mixtures injection (e.g. CO₂ with 5% of SO₂) in reservoir conditions were conducted (IEAGHG, 2011/04). Helium porosity and gas permeability were measured previously and after each test, as well as X-ray fluorescence spectrometry and X-ray diffraction were also conducted for knowing the chemical and the geological composition. Finally, computerized tomography scanner (CTS) and scanner electron microscopy SEM were also performed. The table and figure below illustrate some results achieved for a carbonate sample (surface analogue):

	Before	After
L (mm)	56.27	56.14
D (mm)	37.16	37.19
m (g)	126.94	126.46
Φ (%)	23.2	23.4
N ₂ Perm (mD) (Klink)	2.07	0.887

Table 1. Physical properties for the sample B1.4.9 pre and post CO₂+SO₂ injection



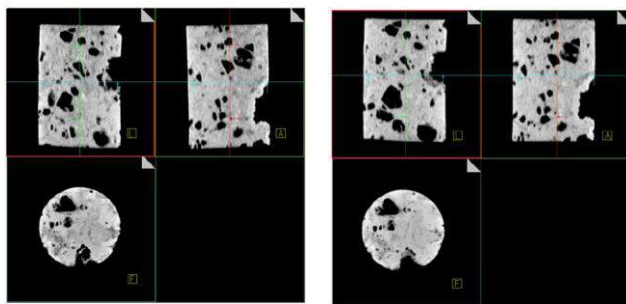


Figure 1. Computerized tomography results for the sample B1.4.9 pre and post CO₂ + SO₂ injection.

In the field tests conducted in Hontomín Pilot, up to 150 tons of CO₂ and synthetic air (5 % v of N₂ and O₂) were co-injected on fractured carbonates (i.e. Hontomín), comparing the operational parameters (Liebscher & Möller, 2013) with the baseline where 1,500 tons of pure CO₂ were injected during the reservoir hydraulic characterization. Besides this, the analysis of the geochemical reactivity of CO₂ with impurities injected on the rock matrix and its correlation with the results from laboratory were done. To achieve these goals, during two months after injection, samples of fluids from reservoir were extracted using different DOT's, being the gas phase analyzed in a MIR-FT (Multigas Infra Red Fourier Transform analyzer by Environnement S.A.; hereinafter, FTIR) whereas the liquid phase was analyzed using liquid chromatography (METROHM model automatic processor 850 professional IC).



Figure 2. Injection of CO₂ and synthetic air: (a) air cylinder racks; (b) sample DOT's obtained from the U-tube

In order to advance some differences in relation with the operational parameters between the two situations (with and without impurities), two figures are included.

Figure 3 shows the bottom hole pressure and the well head pressure (hereinafter, BHP and WHP) evolution with the time; apart from that, other data such as the CO₂ temperature and the mass flow rate was included.

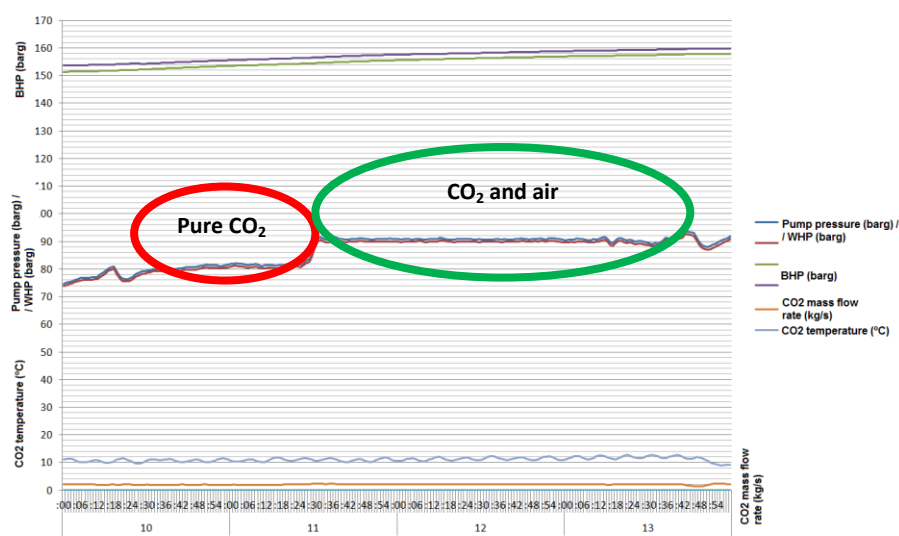


Figure 3 BHP and WHP for the injection of pure CO₂ and CO₂ with air

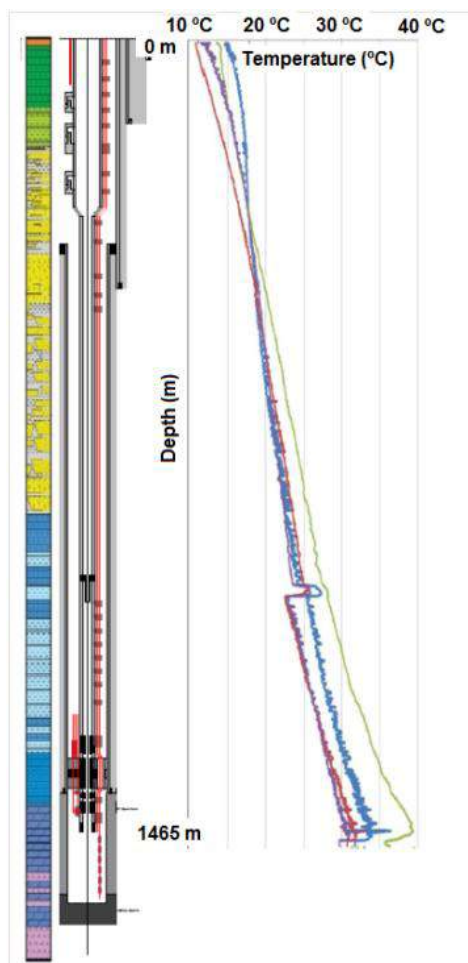


Figure 4. DTS as a function of the depth for different fluids: green colour before any injection (base line), blue colour for the

The figure 4 presents the temperature along the injection tubing measured by the DTS (distributed temperature sensing) as a function of the depth for different fluids.

Finally and focused on the gas phase contained in the DOTs, moisture, CO₂, CO, SO₂, CH₄, NO_x and O₂ were measured in the FTIR. In particular, for the base case, following graph was obtained (see figure 5):

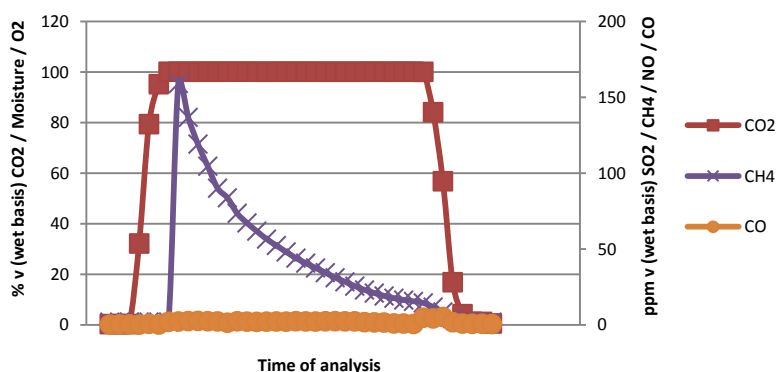


Figure 5. Gas phase for the base case (CO₂ injection without impurities)

As a general conclusion, the effects of impurities on carbonates for geological storage of carbon dioxide are addressed in this paper, presenting the results obtaining both in lab scale and field scale and its correlation. For the first case, SO₂ and NO₂ were studied as impurities whereas in the second, synthetic air was selected.

Acknowledgement

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7-ENERGY-20121-1-2STAGE) under grant agreement n° 308809 (The IMPACTS project). The authors acknowledge the project partners and the following funding partners for their contributions: Statoil Petroleum AS, Lundin Norway AS, Gas Natural Fenosa, MAN Diesel & Turbo SE and Vattenfall AB.

The sole responsibility of this publication lies with the author. The European Union is not responsible for any use that may be made of the information contained therein.

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Effect of SO₂ co-injection on CO₂ storage

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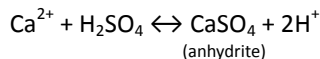
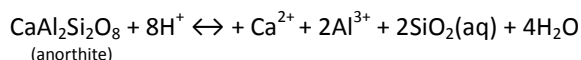
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Abstract

Removing impurities from a captured CO₂ stream, such as N₂, NO_x, SO_x, H₂S, H₂, O₂, and Ar, is a costly and energy-intensive process. Leaving these impurities in the gas would lower the costs for carbon capture. Yet, the potential negative impact of these impurities on transport and geological storage of CO₂ requires investigation. The IMPACTS (The impact of the quality of CO₂ on transport and storage behaviour) project aims at developing knowledge and technology on CO₂ quality to support implementation of safe and cost-efficient CCS.

We investigated the physicochemical behaviour of CO₂-SO₂ mixtures and corresponding effects on storage capacity. In addition, we assessed geochemical reactions of co-injected SO₂ on a sandstone reservoir, shale caprock, and wellbore cement to evaluate potential negative effects which would require additional prevention and/or mitigation measures and corresponding costs. Storage capacity calculations were performed using the storage module of the ECCO tool (Loeve et al. [1]) and the NIST REFPROP database with state-of-the-art PVT behaviour of gas mixtures (Lemmon et al. [2]). PHREEQC version 3 (Parkhurst and Appelo [3]) was used to simulate geochemical interactions of the gas mixtures with the pore waters and subsequently with reservoir, caprock and cement mineralogy. Comparison of CO₂ and SO₂ solubility calculations using adapted Henry's constants for high pressure, temperature, and salinity conditions with calculations via the Peng-Robinson EOS, as implemented in PHREEQC, showed similar results. In order to allow constant supply of CO₂ and SO₂ from the gas phase instead of a single dissolution phase, the Peng-Robinson EOS was used in our simulations.

The results of the storage capacity calculations show that the capacity of an aquifer at a depth of 800 m decreases by 3.5% compared to a pure CO₂ stream if 5% SO₂ is present. Since SO₂ requires 5% of the pore space volume, the capacity decrease of 3.5% implies a density *increase* of the impure stream compared to pure CO₂. At greater depth, the storage capacity for the impure stream decreases beyond 5%. At a depth of 3.4 km the capacity decreases by 7%, implying a *decrease* in gas density. In addition to a decrease in storage capacity, the presence of 5% SO₂ has significant effects on the geochemical reactions in a sandstone aquifer compared to pure CO₂. This is especially true if plagioclase is present in the host rock which consists of the calcium end-member anorthite (CaAl₂Si₂O₈). Dissolution of SO₂ into the formation water decreases the pH dramatically to a value close to 0. This causes fast dissolution of anorthite and the subsequent formation of anhydrite:



Assuming infinite SO₂ supply near the injection well, the more anorthite is present, the more anhydrite can form. Anorthite was the only calcium-containing mineral in our simulations, but other minerals, such as calcite, could also act as a source of calcium. In a worst case scenario with complete dissolution of the CO₂ and SO₂, and complete mixing of the formation water, significant porosity decreases can occur within the time frame of the injection phase due to the formation of anhydrite. At lower, more realistic SO₂ concentrations of e.g. 1% or 0.01%, the porosity decreases simulated are much less, and are much more similar to the pure CO₂ case (Figure 1). Including these results on porosity decrease into the storage capacity calculations, considering a maximum allowable pressure increase at the end of the injection phase, give significant additional reduction in the storage capacity for a SO₂ concentration of 5% (Figure 2). This effect will be even larger at greater depth than 800 m, due to the lower density as explained above.

The sealing components of the storage complex, the caprock and the annular wellbore cement, need to retain their sealing integrity on a long time scale. For both caprock and cement we can assume that diffusion of dissolved species is the only migration process into and out of the reservoir. We developed 1D diffusion models to simulate the effects of



SO₂ co-injection. The dissolved CO₂ and SO₂ and dissociated species slowly migrate upward into the shale caprock and are partially sequestered as carbonates and anhydrite respectively. This causes a reduction in porosity and corresponding decrease in diffusion rate. SO₂ enhances this effect and is therefore beneficial for the sealing integrity of the caprock. Like for the reservoir models, the potential for anhydrite precipitation depends on the SO₂ concentration and the amount of calcium released during the dissolution of primary minerals present in the caprock (Figure 3). Reactions in wellbore cement in the presence of carbonized brine are in general much faster than in siliciclastic rocks, and they are highly complex. Mineral reactions and inward and outward diffusing species result in several reaction zones, which progress inward with time. The simulated zones are in general similar to the zones described in literature (e.g. Kutchko et al. [4]; Rimmelé et al. [5]). Since cement contains various Ca-rich minerals (e.g. portlandite and C-S-H), which are unstable in acid conditions, the presence of SO₂ in the CO₂ stream results in the formation of small amounts of anhydrite, at the expense of calcite. Overall, the porosity changes with time and space are very similar to a pure CO₂ case. Hence, the presence of SO₂ does not seem to have a negative impact on the sealing capacity of cement.

Overall, we can conclude that with increasing SO₂ concentration the injection rate and storage capacity are predicted to go down because of pore clogging by primarily anhydrite, provided that a calcium source is present in the reservoir rock. This would have significant consequences for the overall costs for CO₂ storage. Either less CO₂ can be stored or measures need to be taken to mitigate clogging, e.g. by acid stimulation techniques. With regard to sealing integrity of caprock and wellbore cement, negative impacts of the presence of SO₂ are not expected.

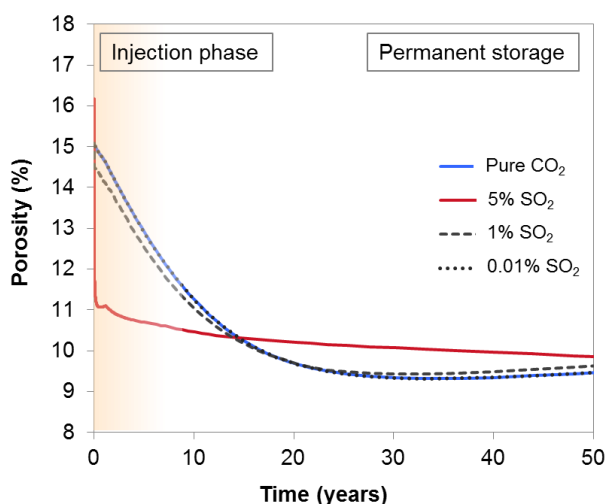


Figure 1. Simulated porosity change in the reservoir with time for CO₂ with various SO₂ concentrations.

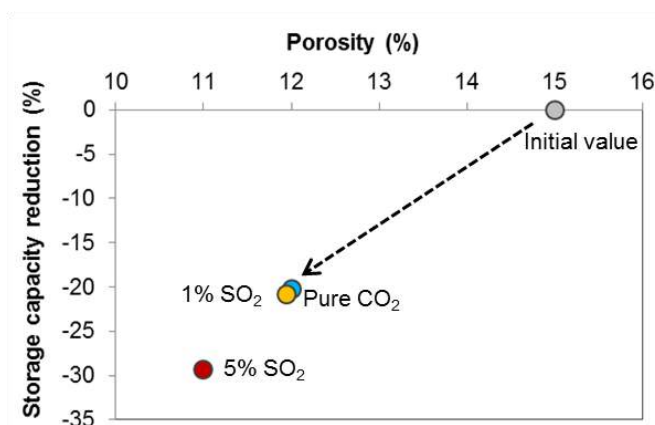


Figure 2. Porosity change and corresponding decrease in storage capacity for CO₂ with various SO₂ concentrations at a depth of 800 m.

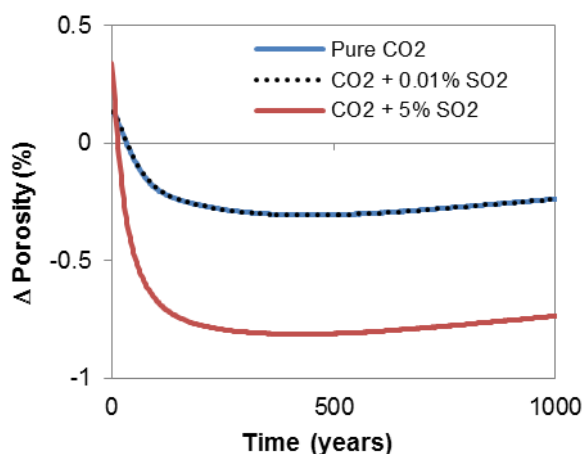


Figure 3. Porosity change in the caprock close to the reservoir contact where geochemical interactions are considered most severe, for CO₂ with various SO₂ concentrations.

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Comparison of different numerical and modelling approaches for implementing SO₂ as a CO₂ flue gas impurity in geochemical simulations in saline sandstone aquifers

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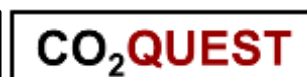
Abstract

Compositions of CO₂ flue gas streams assigned for geological storage have to be adequate both for transport and storage. Hence, the impact of impurities contained in these streams is gaining interest in recent years. Addressing related questions is the focus of the EU funded CO2QUEST project and the German BMWi (Federal Ministry for Economic Affairs and Energy) funded COORAL project [1]. One method for studying the long-term effects of impure CO₂ on reservoir rock minerals is provided by numerical simulation of geochemical systems [2]. Here, two different modelling approaches have been proven useful. (a) Zero-dimensional batch calculations, which examine geochemical systems with restricted complexity and give valuable information concerning time-dependent behaviour, mineral dissolution and precipitation reactions. In addition, they enhance the understanding about coupling and interaction of different mineral phases. Those calculations can be efficiently computed by applying different programmes, a widely used simulation code is PHREEQC V3 by the US Geological Survey [3]. (b) Another simulation approach is to consider multiphase multicomponent transport processes occurring during the CO₂ injection and operation of a storage reservoir. Thus, at least one-dimensional reactive transport simulations in the aqueous and CO₂ rich phases need to be incorporated in the model to address separation and localize reaction fronts correctly [4]. For such simulations, again a number of programmes exists to facilitate this necessary demand. The recent release of TOUGHREACT V3.0-OMP [5] is capable of including reactive transport simulations and injection of impure CO₂ [6].

In order to consider the influence of petrophysical and mineralogical properties on qualitative and quantitative results, three different scenarios were evaluated in the simulations of this study. Representative compositions of Bunter sandstone and Rotliegend sandstone were selected, as they are potentially suitable target formations in the North German Basin. In addition, the Lower Cretaceous sandstone from Heletz, Israel, typical for the Southern Mediterranean Coastal Plain, was included in the investigations. For the numerical simulations, measured and calculated data were derived for mineral composition, in situ p-T-s conditions, and formation water chemistry [7, 8]. Table 1 shows a selection of the main parameters.

base model	porosity [%]	p [MPa]	T [°C]	S []	brine	quartz [%]	clay minerals [%]	feldspars [%]	carbonates [%]	others [%]
Bunter	20	15.0	55	0.231	NaCl	63	6	16	9	6
Rotliegend	10	32.0	90	0.250	NaCl	63	9	11	10	7
Heletz	20	14.7	66	0.055	NaCl	69	9	16	4	2

Table 1. Main parameters used in the geochemical batch and 1D radial reactive transport simulations.



The simulations performed in this study focus on SO₂ as an impurity of the CO₂ stream due to its high dissolution potential, the ability to form highly reactive sulfuric acid, as well as its redox state facilitating oxidation or reduction reactions. The high solubility of SO₂ in water compared to CO₂, results in its preferential partitioning into the aqueous phase, accompanied by an SO₂ depletion of the CO₂ phase [4]. All reactive transport simulations were computed assuming 1 % SO₂ is coinjected with CO₂ at a constant total rate of 9 kg/s. The batch calculations were performed for a constant volume of the impure CO₂ stream. Figure 1 shows the evolution in time of selected carbonate minerals of the Bunter sandstone scenario under the influence of CO₂ and SO₂. The quantitative changes of this simulation represent to a certain degree the maximum chemical impact of the impurity, as an infinite reaction time is simulated.

For comparison, figure 2 depicts mineral fractions calculated for a geochemical scenario identical to figure 1 computed with the reactive transport simulator TOUGHREACT V3.0-OMP. The main difference between the two simulation approaches lies in the fact that at a specific distance from the injection site, the duration of chemical reactions, induced for instance by SO₂, is limited. On the one hand it takes a certain amount of time for the SO₂ containing (not yet SO₂ depleted) CO₂ plume to reach this distance. On the other hand, once the total dry out zone arrives at this radial distance, nearly all remaining water (except some residual pore water) is eventually expelled and all reactions between minerals and the aqueous solution come to an end. This development explains the in general identical transformation of the Ca²⁺ bearing carbonates calcite and dolomite to anhydrite [9], which is observed with PHREEQC and TOUGHREACT simulations. But in addition, it justifies the different quantitative amount of converted carbonate minerals as well. Hence, the spatial profile of carbonates and anhydrite in figure 2 mainly reflects the growing reaction times with increasing distance, which are connected to a slower expansion velocity of the CO₂ plume. The comparison of the different modelling approaches allows for estimating the possible ranges of rock alteration due to the injection of impure CO₂ into a storage aquifer. However, it should be noted that the results obtained from this study are exemplary. They cannot replace site specific simulations for the injection of CO₂ streams at real sites potentially suitable for geological storage.

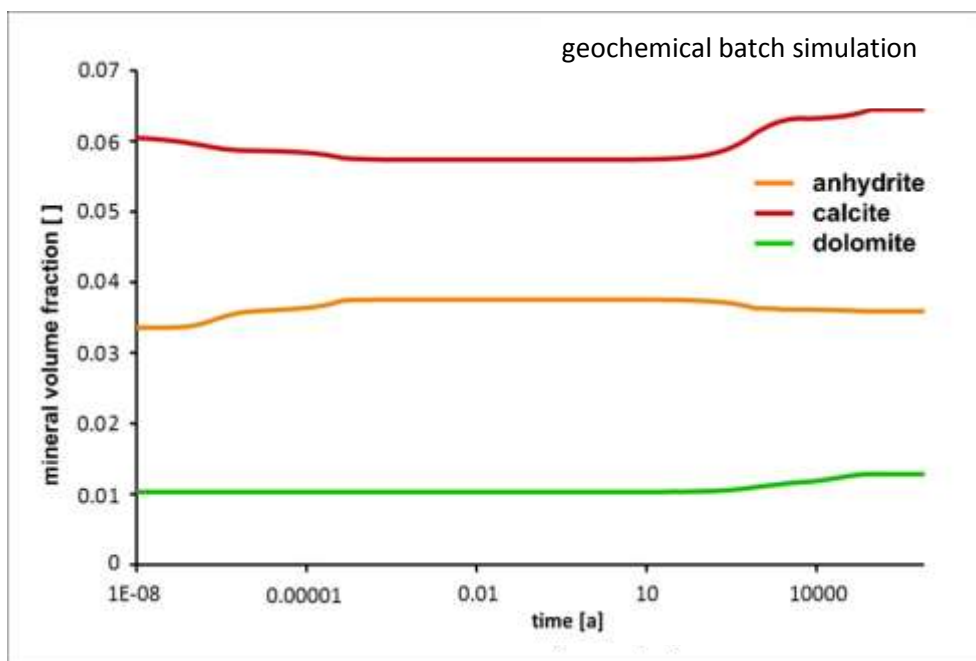


Figure 1. Evolution in time of Ca²⁺ bearing carbonate and sulfate minerals after 800000 years of injection of CO₂ including 1 % SO₂ derived from batch simulation using PHREEQC V3. Starting at approximately 80 years after injection, the initial trend of calcite dissolution and anhydrite precipitation is reversed to calcite (and dolomite) precipitation.

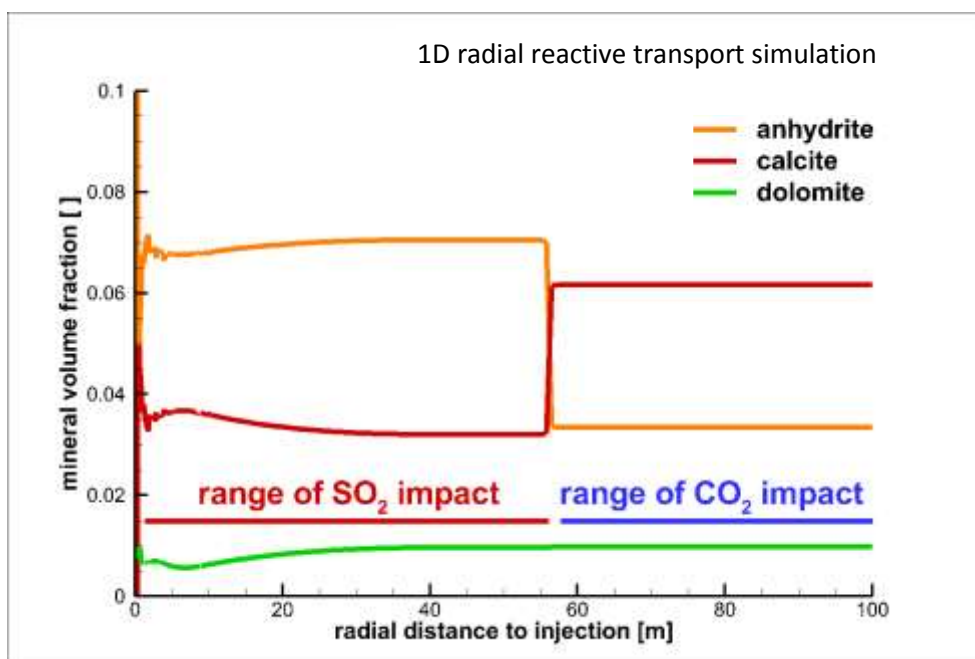


Figure 2. Spatial profiles of Ca²⁺ bearing carbonate and sulfate minerals after 10 years of injection of CO₂ including 1 % SO₂ using the simulation code TOUGHREACT V3.0-OMP. Within the range of SO₂, which spreads within the first 57 m in the Heletz base model, a significant transformation of Ca²⁺-bearing carbonates to anhydrite can be observed.

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Potentiodynamic anodic polarisation for the corrosion study of stainless steel 304 and iron in aqueous amine solvents

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Corrosion is a significant concern in post-combustion carbon capture (PCCC) plants. The corrosion mechanisms at the interface of the metal and the gas-loaded amine solution have recently become an area of research interest. A significant proportion of current knowledge of amine induced corrosion is based on industrial accounts in natural gas sweetening applications. This work has highlighted monoethanolamine, due to its popularity as well as some other amines. It has been shown that among the amines, monoethanolamine is the most corrosive while methyldiethanolamine the least. More recently, studies^{1,2} have also demonstrated the impact of experimental variables (i.e. temperature, solution velocity) on the corrosion rates obtained. A general trend observed is that higher amine concentration and CO₂ loading results in higher corrosion rates. However cases have been reported where the gas contamination leads to passivation. Tests conducted with amine mixtures provided useful information on corrosion control due to the different properties of the amines employed. This work is focused on the corrosion behaviour of iron, as representative for the vast range of carbon steels, and stainless steel 304 (SS304) in aqueous amine solutions. The latter metal is a popular construction steel which is associated with resistance against corrosion, due in great part to the chromium content.

A three-electrode corrosion cell was tested with both a SS304 and iron rotating disk (working) electrode (Pine); Pt counter and Ag/AgCl reference were employed. Aqueous solutions of monoethanolamine (MEA) and methyldiethanolamine (MDEA) were each tested at 1, 3 and 5M solutions, 3M will be highlighted herein. Solutions were purged with nitrogen and bubbled with carbon dioxide until saturation was achieved. Potentiodynamic anodic polarization experiments (EC-Lab SP200) were run, at ambient temperature and pressure, to determine corrosion rates of stainless steel and iron in the different solutions.

The corrosion rates were determined for cases before and after carbon dioxide (CO₂) loading by assessing the polarization curves obtained. The effect of CO₂ loading results in higher corrosion rates than in any unloaded solutions for all cases tested (Table 1) with rates comparable to those previously reported¹⁻³. However, there is more to note than simply the corrosion rate, as will be discussed herein. Critically, in cases without CO₂ loading a single passivation stage is observed. The stage itself exhibits little change in passivation current density as a function of the potential (i.e. it appears vertical), thus indicating that the dissolution rate of the passive film proceeds with a low rate. In contrast, multiple stages are observed when the solution is loaded with CO₂. This is demonstrated

System	Corrosion potential (V)	Corrosion rates (mm y ⁻¹)
Iron in 3M MEA	-0.89	14.72
Iron in 3M MEA +CO ₂	-0.77	88.69
Iron in 3M MDEA	-0.78	2.90
Iron in 3M MDEA+ CO ₂	-0.80	11.50
SS 304 in 3M MEA	-0.66	2.65
SS 304 in 3M MEA +CO ₂	-0.75	33.83

Table 1 Corrosion potential and rate as determined using Tafel method

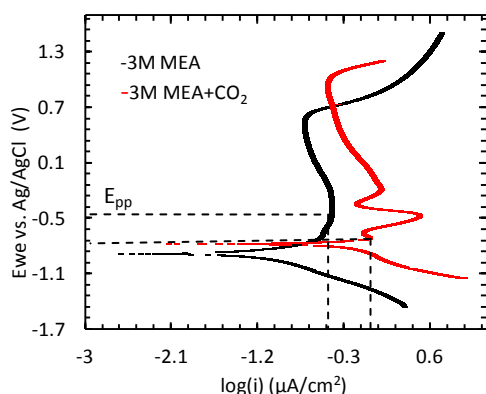


Figure 1: Effect of CO₂ on iron in 3M MEA

regardless of solvent or working electrode used (Figures 1 - 3). Interestingly, for both 3M MEA and 3M MDEA on iron, two initial unstable passivation layers form. The third, and final, passivation layer exhibits substantially more stability, than the first two. This final layer can be contrasted with the single layer formed in the cases of no CO₂ loading. The passivation current density shows greater change in this range and suggests a decrease in the dissolution rate of the passive film.³ This distinction is far more pronounced in the case of MDEA (Figure 2), than MEA (Figure 1).

In addition, all cases demonstrated that the CO₂ loading caused an apparent increase in current density seen in the polarization curves, which is indicative of increasing difficulty in passive layer formation. A range of species are likely formed in the various passivation layers observed. Although MEA and MDEA do not react with CO₂ using the same reaction mechanism, formation of

bicarbonate ions (HCO_3^-) takes place for both amines. It is in MDEA though where this formation is predominant due to the reaction mechanism of the amine that promotes the hydrolysis of CO_2 to HCO_3^- . Bicarbonate ions are significant oxidizers for the $\text{RNH}_x/\text{H}_2\text{O}/\text{CO}_2$ system.

Thus, the presence of them in the solution triggers further oxidation and reduction processes that result in the corrosion of the sample. However, the primary passive potential for all the specimens appears earlier in the CO_2 loaded amine solution. It has been shown⁴ that the presence of CO_2 can under some pH and potential conditions result in passivation. Thus, it could be assumed that the later (compared to the un-loaded case) collapse of the passive film occurs due to the presence of the passive layer.

In contrast to MEA, MDEA demonstrates significantly lower corrosion rates with and without CO_2 loading, respectively (Table 1). Although the value of the corrosion potential is almost the same for iron in both MEA and MDEA saturated solutions, the corrosion behaviour of the sample in the MDEA system shows an intriguing difference. The corrosion potential with CO_2 loading is slightly smaller than without. This suggests that corrosion in the un-loaded MDEA solution starts earlier than its loaded counterpart. This is likely due to the formation of a FeCO_3 layer on the sample surface, in the presence of CO_2 .⁵

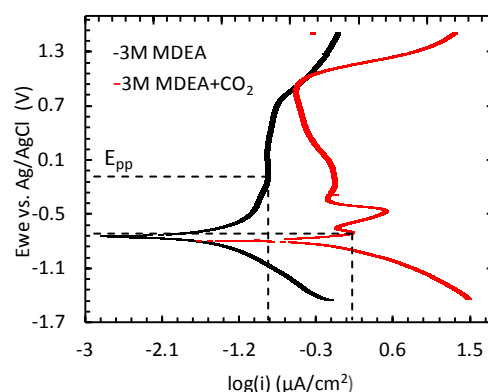


Figure 2: Effect of CO_2 on iron in 3M MDEA

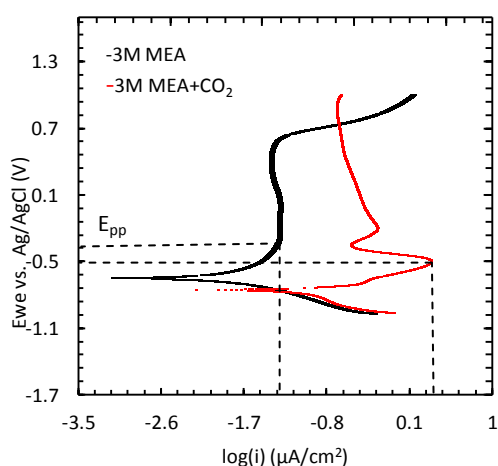


Figure 3: Effect of CO_2 on SS 304 in 3M MEA

Using SS304, the experiments were replicated on what is traditionally viewed as a relatively corrosion-resistant alloy. Similarly to the MDEA case, in the CO_2 saturated solution a lower E_{corr} in relation to the pure amine is observed. This suggests that corrosion of the specimen starts earlier when no CO_2 is loaded to the system. The initial passivation potential of loaded and unloaded 3M MEA on SS304 shows a smaller difference compared to iron in the corresponding amine solutions. This behaviour suggests that the effect of CO_2 on the ability of stainless steel to form passive layers is weaker compared to iron. Although the first passive film breaks very soon it reflects that the first attempt to passivation in the CO_2 -contaminated environment occurs almost simultaneously with the free- CO_2 system. Further polarization of the sample results in the second final passive region where the current densities reduce. Unlike the previous cases, SS304 forms a strong passive layer in two stages. The span of this region extends over a considerable potential range. What should be underlined is that the span of this region is the largest of all solutions and samples tested and dictates that it is easier to keep stainless steel in the passive region, due to chromium in the SS304's composition.

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An analytical model for blowdown of pressurised CO₂ pipelines

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Abstract

As part of Carbon Capture and Sequestration (CCS) chain, pressurised pipelines provide the most efficient and economically viable solution for long-distance transportation of the captured CO₂ to the sequestration site [1]. According to the International Energy Agency [2], over 100,000 km of CO₂ pipelines will be built across the world. Inevitably, some of these will be routed close to populated areas. Due to the fact that at high concentrations CO₂ is an asphyxiant, a comprehensive safety assessment must be conducted to quantify the risks and hazards arising from the unlikely event of a pipeline rupture. Central to such assessment is the determination of the transient outflow and evolution of temperature, pressure and fluid phases within the system. The transient outflow data serves as the source term in atmospheric dispersion modelling which is in turn used to determine minimum safety distances. The in-pipe fluid pressure, temperature and phases on the other hand are the essential input parameters required for modelling fracture propagation.

In recent years significant progress has been made in developing transient flow models for simulating depressurisation of high pressure pipelines [3][4]. However, given the absence of an analytical solution, all such models have been based on numerical solution of the conservation equations. Given the enormous number of calculations and iterations involved the corresponding computational workload can easily become prohibitive. This is especially the case for pipeline puncture failures. For example, the simulation of the complete depressurisation of a typical 100 km, 0.8 m diameter pipeline at 80 bar pressure experiencing a 50 mm puncture can take as long as 5 days using a relatively fast desktop computer.

In this study, a multispecies multiphase analytical depressurisation model incorporating the Homogeneous Relaxation Model (HRM) [5][6] based on the approximation of the pipeline as a depressuring vessel is presented. Given that the model is analytical, the computational run times become relatively insignificant.

This model accounts for the metastability of the stratified liquid phase. Interphase mass transfer is modelled explicitly based on the deviation of the stratified liquid phase gas quality from thermal equilibrium and the relaxation time. The pertinent fluid thermo-physical properties are calculated using the Helmholtz free energy equation of state with quadratic mixing model. The validation of the vessel model is first performed based on the comparison of its predictions against real data for the puncture induced depressurisation of stratified CO₂/N₂ mixture in a 2 m³ spherical vessel [7]. Following this, the range of applicability of the analytical model is determined through comparison against the rigorous but computationally expensive numerical pipeline depressurisation model.



Acknowledgement

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TREND – A Software Package providing thermophysical properties for the CCS community

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Abstract

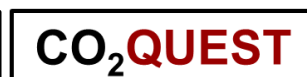
Understanding the impact of impurities in CO₂-rich mixtures on the process chain of Carbon Capture and Storage (CCS) requires various interdisciplinary contributions to enable process simulations, geological research, material science, or safety analyses. At a certain point, all these efforts demand the knowledge of thermodynamic properties of the involved mixtures. Nowadays, the most accurate way to determine these properties is by means of highly accurate equations of state explicit in the Helmholtz free energy. Within the IMPACTS project, the development of an accurate equation of state for CO₂-rich mixtures including CCS relevant components is one of the main targets. However, the calculation of thermodynamic properties from such multiparameter models is challenging since it requires complex derivatives as well as algorithms evaluating the results at a given state point. This aspect is of particular interest when a specified mixture splits into two or more phases. Stability analyses and phase equilibrium calculations belong to the most complex numerical problems in thermodynamics. In the presented research, the development of new stability analysis and phase equilibrium algorithms was consequently as important as providing new accurate equations of state. The resulting algorithms additionally enable the prediction of solid phases of CO₂ and water as well as of gas hydrates.

It is not surprising that neither the application of these algorithms nor the calculation of thermodynamic properties from equations of state can be individually handled by typical users. For this reason, the software package TREND by Span et al. [1] is an important element of the "IMPACTS Toolbox", which contains all relevant results, conclusions, and guidelines of the project. Since 2009, TREND has continuously been improved and extended. It enables straightforward calculations of thermophysical properties of pure substances and mixtures by means of highly accurate Helmholtz equations of state and other types of models. All results obtained on thermodynamic property models obtained in IMPACTS are implemented in TREND. The flash algorithms of TREND automatically employ the adequate equations, if the calculation of a specified state point requires a hydrate or solid phase model. Fluid phases in equilibrium with pure solid phases or hydrates are described by means of Helmholtz equations of state, a feature that is not provided by any other software package.

The implementation of the most accurate equations of state as well as the prediction and calculation of complex phase equilibria are remarkable achievements for the calculation of CCS processes. For this reason, TREND is a valuable tool for the CCS community.

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CO₂ Capture and Purification Technology with Selective Removal of NO_x and SO₂

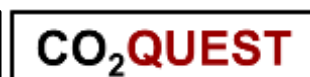
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Abstract

The intensive CO₂ emissions from combustion of fossil fuels had drawn great attention in the CCS research field. However, the traditional amines for CO₂ capture are easy to be poisoned by SO₂ and NO_x, which lead to ineffective CO₂ capture. Large amount of energy consumption and operational cost were lost due to this cause. An integrated technology for simultaneous removal of NO_x and SO₂ and CO₂ capture has been developed to solve this problem. In this process, NO_x and SO₂ will be 100% removed by wet absorption without any loss of CO₂ in the flue gas and then CO₂ will be captured using AEEA (amine) solution. The NO_x and SO₂ were turned to nitrate and gypsum, respectively. The 98% (by volume, dry basis) CO₂ released from AEEA solvent consuming around 1.6-2.0 tons of medium-high pressure steam. The released CO₂ can be then compressed to around 3 MPa before liquidation and distillation. After distillation, the light gas impurities like N₂ and O₂ could be removed and the product CO₂ can reach to 99.99% or even higher purity.



Simulation of Transient Flow in CCS Pipelines with Intermediate Storage

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Abstract

It is now widely accepted that for CCS to have a significant role in reducing the impact of global warming, the technology must include all the major industrial emission sources such as cement, steel, chemical processing and oil refineries as well as fossil power plants. CCS clusters comprising a collection of emission sources connected to a main pipeline network employed to transport the captured to a single or a number of storage sites offer the most practical option. However the safe and economic implementation of such systems presents a number of technical, operational and safety challenges.

Such pipeline networks should be designed to ensure smooth operation and minimise the impact of inevitable fluctuations in the CO₂ pressure and flow rates in the network on the rate of CO₂ delivery to the sequestration sites.

Given that existing commercial applications of CO₂ storage are operated at a base load, i.e. no specific flexibility is envisaged [4], designing a self-regulating CO₂ pipeline transport/ capture system enabling the steady-state delivery of CO₂ to the sequestration sites becomes important. In particular, using the temporary storage of dense-phase CO₂ in a tank has recently proved to be useful in reducing the energy penalty for the amine capture process and saving the compressor power demand [1,2,3]. However, the use of intermediate buffering storage for control of the flow in the CO₂ pipeline networks has not been explored in detail.

In the present study, a mathematical model is developed for simulating the pressure and flow dynamics within the transport CO₂ pipeline incorporating intermediate storage. The modelling employs the Method of Characteristics (MOC) with the non-linear DNSQE solver to resolve the conservation equations. It also accounts for the use of a compressor for injecting the CO₂ from storage tank into the pipeline.

Results based on the application of the model to hypothetical operational scenarios are presented to demonstrate the effectiveness of intermediate storage as a means for compensating a temporal drop in the captured CO₂ loading from any of the emission sources in the CCS cluster.

Acknowledgement

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Investigating the Corrosion and Surface Passivation of Carbon Steel in Amine Blends

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Abstract

Amine solvents have been widely used in post-combustion carbon capture for their economy, availability and utility. Some research has been conducted on the corrosive behaviour on a small selection of amines, extensive knowledge is limited except for monoethanolamine (MEA) which is one of the most corrosive amines used in industry [1]. An industrial study of carbon steel in an aqueous methyldiethanolamine (MDEA) solution found that the formation of a siderite (FeCO_3) product layer can inhibit corrosion [2]. Previous electrochemical experiments on carbon steel (C1018) in amine blends of MEA, MDEA, piperazine (PZ) and 2-amino-2-methyl-1-propanol (AMP) ranked MEA+PZ, MEA+AMP, MEA+MDEA, MDEA+PZ and AMP+PZ in decreasing corrosiveness [3]. Critically, with increasing popularity of amine blends, there is a significant need to understand these additionally complex cases. This work uses long-term corrosion experiments (representative of the stripper) to explore the influence of single amines and amine blending on carbon steel.

Aqueous amine solutions of MEA, MDEA, AMP and aminoethylpiperazine (AEPZ) were selected to represent the diversity of relevant amine chemistries. Solutions of 1, 3, and 5M were tested at 120°C and saturated with CO_2 prior to starting the experiment. A continuous flow of $20\text{mL}\cdot\text{min}^{-1}$ was maintained for the duration (7, 14, 21 days). Solution samples were taken at regular intervals and coupons removed upon completion of the experiment. Iron ion concentration in solution was measured using ICP-AES; the metal sample surface was imaged using SEM and assessed with EDX and XRD. Aqueous blends were prepared with 70 weight% DI water (Table 1). Blended amines were run for 10 days with an additional 20 day experiment in limited cases.

Solutions containing only MEA or AEPZ showed significant corrosion, as determined by weight change of the samples, as well as high iron ion concentration in solution. An increase in solvent molarity demonstrates an increase in corrosion rate. Interestingly, fluctuation in iron ion concentration in solution suggests metal dissolution into solution and re-precipitation. On the surface, SEM and XRD suggests a porous layer comprised of hematite ($\alpha\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4). There is no evidence of corrosion protection from this product layer, rather that continuous oxidation of iron is occurring underneath.

By contrast, corrosion rates for solutions containing MDEA or AMP were lower than either MEA or AEPZ by several orders of magnitude. Additionally, the rate decreases with longer exposure. A densely packed crystalline layer of siderite covers the coupon surfaces. Crystal habits generated in MDEA were packed more densely in comparison to the elongated crystals in AMP, suggesting variable crystal growth mechanisms. As solution iron ion concentration remained relatively low and constant, this layer clearly restricts continued iron oxidation.

Corrosion rates amongst the four amine blends were observed to decrease with a decreasing proportion of corrosive amine (Figure 1). The iron ion concentration for the four blend ratios shows a maximum on day 2 and subsequently converge to a common minimum, as is seen in the blend of MEA+MDEA (Figure 2). This suggests passivation

Table 1. Amine blend ratios with 175mL water and remainder by wt%.

Weight%	MEA	AEPZ	MDEA	AMP
MEA	10	-	90	-
+	25	-	75	-
MDEA	50	-	50	-
	75	-	25	-
MEA	10	-	-	90
+	25	-	-	75
AMP	50	-	-	50
	75	-	-	25
AEPZ	-	10	90	-
+	-	25	75	-
MDEA	-	50	50	-
	-	75	25	-
AEPZ	-	10	-	90
+	-	25	-	75
AMP	-	50	-	50
	-	75	-	25

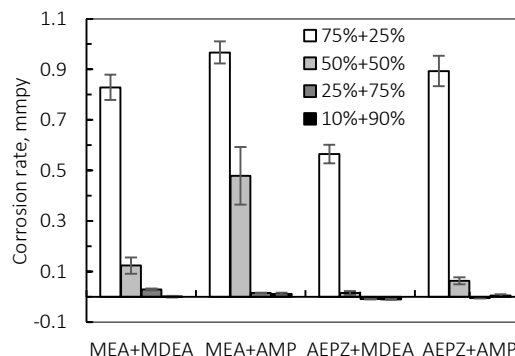


Figure 1. Amine blend corrosion rates.

is occurring. The growth of the product layer creates a physical barrier between the solution and metal substrate thereby preventing further oxidation of iron. In solution this results in a reducing flux of iron ions into solution, which causes overall concentration of iron ions in the bulk to reduce dramatically. Analysis of the MEA+MDEA surfaces using SEM and XRD identified morphology transitions with changing blend ratios (Figure 3). At a high corrosive amine concentration, the product layer was composed of hematite and magnetite. As the corrosive amine component was reduced, both iron oxide and siderite were predominant. This development suggests that the two species are competing not only in surface reaction, but also in capture of carbon dioxide. At the lowest corrosive amine concentration, a pure siderite product layer is observed to passivate the steel, which is in agreement with the low corrosion rate and iron ion concentration. Corrosion passivation for MEA+AMP exhibited similar behaviour. However, more variable siderite crystal growth was observed, similar to the behaviours seen in individual AMP experiments. Evidence of this less well established crystal growth is seen in iron ion concentration, where more deviation is observed.

Similarly, for AEPZ+MDEA and AEPZ+AMP blends, the iron ion concentration was observed to peak at day 2 and then decrease to a minimum. A discernible feature of AEPZ blends is the presence of siderite at all mixture ratios, where the reduction of AEPZ content improves the purity of siderite layers.

Across the four blends, similarities in solution behaviour and product layer formation suggest that capture mechanisms competing for dominance are a determining factor in which corrosion products are formed. The chemical structures of tertiary (MDEA) and sterically hindered (AMP) amines follow a CO₂ capture mechanism that promotes the formation of carbonate species which precipitate with Fe²⁺ to form siderite. Increasing the concentration of carbonate promoting amines in a blend may reduce the ion saturation time and therefore produce siderite at a faster rate. The quantity of promoter amines in blends is significant as it infers control over the degree of corrosion passivation. The findings of this study can be applied in fine tuning amine blends to optimise CO₂ loading while minimising corrosion.

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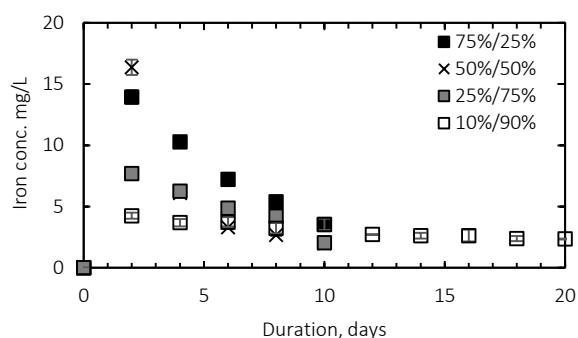


Figure 2. Iron ion concentration in MEA+MDEA blend.

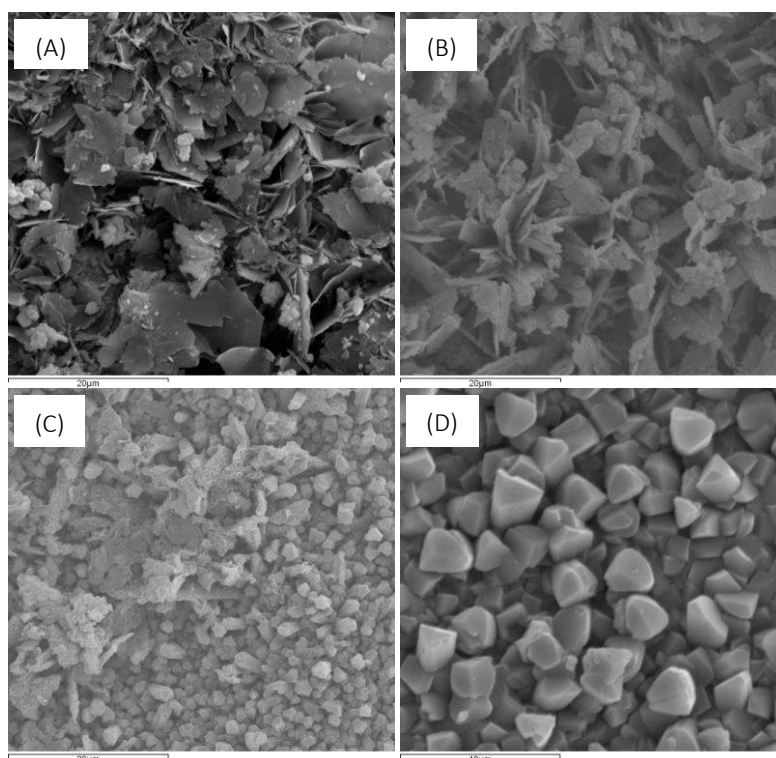


Figure 3. Transition of product species in MEA+MDEA at weight ratios of (A) 75%+25%, (B) 50%+50%, (C) 25%+75% and (D) 10%+90%.

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Choice of Benchmark CCS Chains for Illustrating CO₂ Quality Issues

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Abstract

Reference CCS chains are established in the IMPACTS project in order to provide a comprehensive benchmark from which to measure both the impact of CO₂ impurities on CCS chain performance and changes to the chain economics due to introduction of possible mitigations within the CCS chain.

In order to cover a reasonably comprehensive range of CCS chain conditions, the chosen CCS chains need to represent a sufficiently broad set of the CCS chains that can be envisaged as being commercially and technically plausible within the planning horizon of the IMPACTS project, assumed to be 10-20 years. To achieve this, the set of CCS chains cover both standard source-to-sink simple examples with both power and industrial sources and also a more complicated example covering combinations of sources and sinks (ie clusters) and, in particular, the mixing of CO₂ streams with differing levels of impurities.

In choosing the reference CCS chains, account has been taken of particular issues which are known to the project partners as being of interest in the design and operation of prospective / operating chains. Also, where possible, chains with features expected to occur widely in the European CCS context have been chosen. Table 1 lists some of these points and Figure 1 illustrates typical chain elements.

It has also been important to establish ranges of impurities that are of interest to the project by reviewing plausible levels of impurities which could arise from the various technologies being covered. Table 2 sets out the ranges of impurity levels which are the priority for the further analytical work in IMPACTS. For each identified impurity a benchmark level is given, which is intended to reflect the typical levels which would currently be achieved using standard equipment; maximum and minimum levels are also set out giving an overall range. The general case is based on post-combustion capture technology in ppm or %; where these levels differ significantly from the general case for alternative capture technologies, different data are set out in the subsequent rows.

Results arising from specific characteristics of the various chains will be highlighted in the presented results.

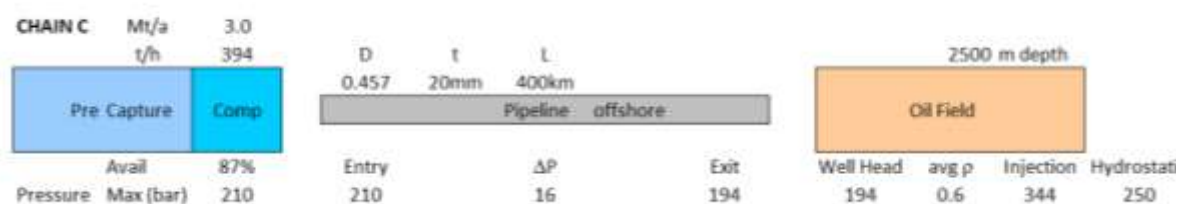


Figure 1. Diagram of a typical CCS chain used in IMPACTS

Element	Issue	Aspect
Capture	Variety of capture sources including: <ul style="list-style-type: none"> • Post-combustion power • Pre-combustion power • Oxyfuel power • Energy-intensive industry (steel, cement, glass etc) 	Use range to cover all the issues relating to the most demanding impurity levels

Transport	Main expected routes including: <ul style="list-style-type: none"> • Pipeline • Ship / barge • Road haulage 	Conditions vary considerably between different possible types of transport in terms of pressure and temperature (and physical state)
Storage	Range of storage locations: <ul style="list-style-type: none"> • Saline aquifer • N Sea oil field • Depleted gas field • Onshore and off-shore • Include chalk structures 	Physical and chemical environments vary greatly across storage sites as do the possible interactions of the CO ₂ stream impurities on the storage site
Health and Safety	Impurities harmful to human health within the CO ₂	Impact relative to the harmful effects of the CO ₂ itself

Table 1. Some of the key issues to be included in Benchmark CCS chains

Impurity	H ₂ O	N ₂	O ₂	Ar	NO _x	SO _x	CO	H ₂ S	H ₂	CH ₄	C2+	Cl	NH ₃
General limits (some only applicable in specific cases) including Post-combustion:													
Max	1000	5%	300	600	250	250	200	200	5000	1000	2000	20	300
Benchmark	100	2000	100	20	100	100	20	100	50	500	1000	5	50
Min	0.001	100	2	1	20	20	10	20	20	20	100	1	10
Adjusted For Oxyfuel:													
Max		5%	5%	5%			1500						
Benchmark		2%	3%	2%			50						
Min		1%	2	100			10						
Adjusted For Pre-combustion:													
Max		5%	30	600	250	250	1500		2%	100			
Benchmark		2%	10	200	10	10	400		1%	50			
Min		1%	2	100	10	10	50		20	20			
Adjusted For Gas Processing:													
Max										5%			
Benchmark										4%			
Min										20			

Table 2. Impurity ranges of interest to the IMPACTS project