

**Carbon Dioxide Capture for Storage
in Deep Geologic Formations –
Results from the CO₂
Capture Project**

**Geologic Storage of Carbon Dioxide
with Monitoring and Verification**

Volume 2

Elsevier Internet Homepage – <http://www.elsevier.com>

Consult the Elsevier homepage for full catalogue information on all books, major reference works, journals, electronic products and services.

Elsevier Titles of Related Interest

AN END TO GLOBAL WARMING

L.O. Williams

ISBN: 0-08-044045-2, 2002

FUNDAMENTALS AND TECHNOLOGY OF COMBUSTION

F. El-Mahallawy, S. El-Din Habik

ISBN: 0-08-044106-8, 2002

GREENHOUSE GAS CONTROL TECHNOLOGIES: 6TH INTERNATIONAL CONFERENCE

John Gale, Yoichi Kaya

ISBN: 0-08-044276-5, 2003

MITIGATING CLIMATE CHANGE: FLEXIBILITY MECHANISMS

T. Jackson

ISBN: 0-08-044092-4, 2001

Related Journals:

Elsevier publishes a wide-ranging portfolio of high quality research journals, encompassing the energy policy, environmental, and renewable energy fields. A sample journal issue is available online by visiting the Elsevier web site (details at the top of this page). Leading titles include:

Energy Policy

Renewable Energy

Energy Conversion and Management

Biomass & Bioenergy

Environmental Science & Policy

Global and Planetary Change

Atmospheric Environment

Chemosphere – Global Change Science

Fuel, Combustion & Flame

Fuel Processing Technology

All journals are available online via ScienceDirect: www.sciencedirect.com

To Contact the Publisher

Elsevier welcomes enquiries concerning publishing proposals: books, journal special issues, conference proceedings, etc. All formats and media can be considered. Should you have a publishing proposal you wish to discuss, please contact, without obligation, the publisher responsible for Elsevier's Energy program:

Henri van Dorssen

Publisher

Elsevier Ltd

The Boulevard, Langford Lane

Kidlington, Oxford

OX5 1GB, UK

Phone: +44 1865 84 3682

Fax: +44 1865 84 3931

E.mail: h.dorssen@elsevier.com

General enquiries, including placing orders, should be directed to Elsevier's Regional Sales Offices – please access the Elsevier homepage for full contact details (homepage details at the top of this page).

Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO₂ Capture Project

**Geologic Storage of Carbon Dioxide
with Monitoring and Verification**

Edited by

Sally M. Benson

*Lawrence Berkeley Laboratory
Berkeley, CA, USA*

and Associate Editors

Curt Oldenburg¹, Mike Hoversten¹ and Scott Imbus²

*¹Lawrence Berkeley National Laboratory
Berkeley, CA, USA*

*²Chevron Texaco Energy Technology Company
Bellaire, TX, USA*

Volume 2



ELSEVIER

2005

Amsterdam – Boston – Heidelberg – London – New York – Oxford
Paris – San Diego – San Francisco – Singapore – Sydney – Tokyo

ELSEVIER B.V.
Radarweg 29
P.O. Box 211, 1000 AE Amsterdam
The Netherlands

ELSEVIER Inc.
525 B Street, Suite 1900
San Diego, CA 92101-4495
USA

ELSEVIER Ltd
The Boulevard, Langford Lane
Kidlington, Oxford OX5 1GB
UK

ELSEVIER Ltd
84 Theobalds Road
London WC1X 8RR
UK

© 2005 Elsevier Ltd. All rights reserved.

This work is protected under copyright by Elsevier Ltd, and the following terms and conditions apply to its use:

Photocopying

Single photocopies of single chapters may be made for personal use as allowed by national copyright laws. Permission of the Publisher and payment of a fee is required for all other photocopying, including multiple or systematic copying, copying for advertising or promotional purposes, resale, and all forms of document delivery. Special rates are available for educational institutions that wish to make photocopies for non-profit educational classroom use.

Permissions may be sought directly from Elsevier's Rights Department in Oxford, UK: phone (+44) 1865 843830, fax (+44) 1865 853333, e-mail: permissions@elsevier.com. Requests may also be completed on-line via the Elsevier homepage (<http://www.elsevier.com/locate/permissions>).

In the USA, users may clear permissions and make payments through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA; phone: (+1) (978) 7508400, fax: (+1) (978) 7504744, and in the UK through the Copyright Licensing Agency Rapid Clearance Service (CLARCS), 90 Tottenham Court Road, London W1P 0LP, UK; phone: (+44) 20 7631 5555; fax: (+44) 20 7631 5500. Other countries may have a local reprographic rights agency for payments.

Derivative Works

Tables of contents may be reproduced for internal circulation, but permission of the Publisher is required for external resale or distribution of such material. Permission of the Publisher is required for all other derivative works, including compilations and translations.

Electronic Storage or Usage

Permission of the Publisher is required to store or use electronically any material contained in this work, including any chapter or part of a chapter.

Except as outlined above, no part of this work may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without prior written permission of the Publisher.

Address permissions requests to: Elsevier's Rights Department, at the fax and e-mail addresses noted above.

Notice

No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made.

First edition 2005

Library of Congress Cataloging in Publication Data

A catalog record is available from the Library of Congress.

British Library Cataloguing in Publication Data

A catalogue record is available from the British Library.

ISBN: 0-08-044570-5 (2 volume set)

Volume 1: Chapters 8, 9, 13, 14, 16, 17, 18, 24 and 32 were written with support of the U.S. Department of Energy under Contract No. DE-FC26-01NT41145. The Government reserves for itself and others acting on its behalf a royalty-free, non-exclusive, irrevocable, worldwide license for Governmental purposes to publish, distribute, translate, duplicate, exhibit and perform these copyrighted papers. EU co-funded work appears in chapters 19, 20, 21, 22, 23, 33, 34, 35, 36 and 37. Norwegian Research Council (Klimatek) co-funded work appears in chapters 1, 5, 7, 10, 12, 15 and 32.

Volume 2: The Storage Preface, Storage Integrity Preface, Monitoring and Verification Preface, Risk Assessment Preface and Chapters 1, 4, 6, 8, 13, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33 were written with support of the U.S. Department of Energy under Contract No. DE-FC26-01NT41145. The Government reserves for itself and others acting on its behalf a royalty-free, non-exclusive, irrevocable, worldwide license for Governmental purposes to publish, distribute, translate, duplicate, exhibit and perform these copyrighted papers. Norwegian Research Council (Klimatek) co-funded work appears in chapters 9, 15 and 16.

© The paper used in this publication meets the requirements of ANSI/NISO Z39.48-1992 (Permanence of Paper).

Printed in The Netherlands.

Working together to grow
libraries in developing countries

www.elsevier.com | www.bookaid.org | www.sabre.org

ELSEVIER

BOOK AID
International

Sabre Foundation

Chapter 15

CO₂ CONDITIONING AND TRANSPORTATION

Geir Heggum¹, Torleif Weydahl², Roald Mo¹, Mona Mølsvik² and Anders Austegaard²

¹Reinertsen Engineering, Trondheim, Norway
²SINTEF Energy Research, Trondheim, Norway

ABSTRACT

The aim of the CO₂ Conditioning and Pipeline Transportation project is to advance the development of cost effective and safe methods for CO₂ compression and pipeline transportation. Optimized design for the compression process and pipeline system requires accurate and reliable predictions of fluid properties, particularly density and water solubility.

Existing CO₂ pipeline transportation systems (onshore USA and Canada; offshore Norway) are reviewed in terms of operational parameters, particularly drying specifications. Based on calculations of water solubility for a selected case, it is found that the most stringent drying requirements (e.g. 50 ppm proposed for Hammerfest LNG) may be relaxed to ~600 ppm (present USA Kinder Morgan specification). Today there is little experience with subsea pipelines for CO₂ transportation, particularly in deep waters and over long distances. The intension of this study is to build up confidence in the technology and save costs for future projects.

Thermodynamic models and tools for calculating properties for CO₂ and CO₂-rich mixtures have been verified against experimental data. For CO₂ density the Lee–Kesler model is in satisfactory agreement with National Institute of Standards and Technology (NIST) data both in gas and liquid phase. For solubility of water in pure CO₂, the Soave–Redlich–Kwong equation of state with adjusted binary coefficient to 0.193 in van der Waals mixing rule can be applied, and gives a good approximation to the data collected from literature. Adding impurities as CH₄, N₂, H₂S and amines to the CO₂ mixture will affect the solubility of water, e.g. adding 5% methane lowers the water solubility in the liquid phase considerably. However, very little experimental data on water solubility in these mixtures is available in the literature.

In order to inhibit hydrate formation and prevent excessive corrosion rates for carbon steel, no free water should be allowed in the pipeline. Thus, water removal is usually required upstream of the pipeline inlet. For a typical case, theoretical calculations show that the limit for free water precipitation at supercritical conditions in the pipeline averages ~1300 ppm. This suggests that water content requirements might be relaxed and opportunities for alternative, more cost-effective water removal solutions are provided.

INTRODUCTION

Project Background

The overall goal of this study is to support the development of cost effective and safe methods for CO₂ compression and transportation. The combined effort by SINTEF, Reinertsen and IFE is aimed at qualifying state-of-the-art process engineering, material selection and pipeline engineering methods to ensure optimal design of CO₂ compression and pipeline systems.

Unlike natural gas, CO₂ will be in the liquid or supercritical state, quite close to the critical point in the pipeline. In this state, the CO₂ density may be three times higher than the corresponding density of natural gas (molar densities) at same temperature and pressure. The density is an important property with respect to the prediction of the static pressure gain in the pipeline flow.

The water solubility in CO₂ is dependent on the temperature and pressure, and these characteristics can be utilized in the drying process. Free water in the pipeline will cause hydrate formation and corrosion problems under certain conditions, and must hence be avoided. Accurate estimations of the water solubility are consequently an important issue, which is addressed in the present work. The density and the solubility of water in CO₂ will also vary as a function of other gases in the CO₂ such as hydrocarbons, nitrogen and other impurities.

Experience with CO₂ Transportation

Onshore transportation and injection of CO₂ for enhanced oil recovery (EOR) has been going on for three decades in the United States, providing much experience on issues regarding on-shore facilities. Conversely, offshore experience is very limited.

Onshore

Kinder Morgan (KM) is a US based company with more than 30 years of experience in CO₂ transportation and injection for EOR. In 2002, 17 Mt CO₂ was transported in their pipeline system [1].

The Cortez pipeline is the largest example, with a diameter of 30 in. and a capacity of 12.2 Mt CO₂/yr. The CO₂ for this pipeline is produced from the McElmo field, which contains 97 mole% of pure CO₂. Before the CO₂ is pumped down the pipeline, it is cleaned, dehydrated and compressed to supercritical pressure (145 bar). To achieve the required pressure for CO₂ transportation, KM makes use of pumps rather than compressors, which reduces operational costs. No chemicals are necessary in the transportation systems. Dehydration is necessary to obtain the requirements for using carbon steel. According to KM, the requirement for CO₂ pipelines, used for EOR in the US, is maximum 600 ppm water [2]. Due to the rather relaxed water requirement, diethylene glycol (DEG) can be used for dehydration, instead of TEG (triethylene glycol, since the boiling point is lower, DEG is less effective than TEG). The transportation of CO₂ is in the liquid phase, below the supercritical point for CO₂ (below critical temperature, but above critical pressure).

In Western Canada, acid gas (a mixture of H₂S and CO₂) is removed from the natural gas. Typically, a four-stage compression process from 0.80 to 60 barg is used with cooling below 20 °C. The acid gas is then in liquid phase, provided the methane content is no greater than 1–2%. Selection of material for the acid gas injection line between the plant and the injection well is generally related to whether or not the acid gas has been dehydrated. For dehydrated gas, sour service carbon steel materials could be used, such as CSA-Z662 Grade 359 Category II [3]. If dehydration by glycol is used to ensure that no free water drops out, it should be installed after the second or third compression stage, since the solubility of glycol is lowest in the pressure range of 40–55 bar [4].

Offshore

At Sleipner Vest, operated by Statoil in the North Sea, CO₂ removal and injection is done offshore. Amine separation is used to remove CO₂ from the gas stream. The CO₂ is injected into a saline aquifer, called the Utsira formation, 800 m below seabed. The purpose of the CO₂ removal system on Sleipner Vest is to reduce the CO₂ content in the export gas from maximum 8.95 to 2.5 vol% to meet sales gas specifications and to avoid taxed emissions to the atmosphere [5]. The gas injection system is designed for a gas rate of 1.7 MSm³/d. CO₂ is separated by an amine absorber. The separated CO₂ is saturated with water at operating conditions (0.1 barg at 70 °C). Water is condensed in a CO₂ water wash column operating directly counter-current with cooled re-circulated water. No further drying is implemented before the CO₂ compressor train.

The CO₂ gas is compressed to 80.0 barg in four stages. An aftercooler is installed downstream the compressor on stage 1–3, which cools the gas to 30 °C. The condensed liquid (mainly water) is removed in a suction scrubber on each stage. The water content is 3.9 mole% for the 1st stage compressor and 0.3 mole% for the 3rd stage. The solubility of water in CO₂ is lower at the third stage pressure of 32 barg than at the wellhead pressure of 80 barg. This ensures robustness with respect to hydrate formation.

EXPERIMENTAL/STUDY METHODOLOGY

In the present work both commercial and in-house calculation tools have been used to calculate thermodynamic properties of CO₂ and CO₂ mixtures. The commercial tools are the flowsheet programs

PRO II 6.0 [6] and HYSYS 3.0.1 [7]. In addition some in-house tools to calculate solubility in binary and ternary mixtures have been developed. These tools solve the general equations for predicting solubility and density of CO₂ mixtures. The reader is referred to Refs. [9,10] for a comprehensive description of the equations of state (SRK, LK and BWRS) and mixing rules presented in this chapter. This study is limited to the simple van der Waals mixing rule.

The CO₂ compression and drying process is calculated in HYSYS. For CO₂ pipeline transport, a program that calculates the wellhead pressure for a mixture consisting mainly of CO₂ has been developed. The program solves the distributed mass, momentum and heat balance equations for one or two-phase stationary flow in a one-dimensional pipeline. A more detailed description of the program is found in Ref. [8]. The output from the calculations are the stationary temperature, pressure, density and void fraction profile in the pipeline in addition to the temperature distribution in the pipeline material.

RESULTS AND DISCUSSION

Properties for CO₂ Pipeline Transportation

In this section, the thermodynamic models and tools are discussed through comparison with available experimental data.

Properties for pure CO₂

Regarding thermodynamic properties of pure CO₂, much research has been carried out and accurate measurements are available. The National Institute of Standards and Technology (NIST) [11] provides properties such as densities, enthalpy and viscosity for CO₂, from 216 to 1100 K, and for pressures up to 8000 bar. These data are used as reference densities when comparing computations with experiments.

Figure 1 shows the comparison between NIST data and various models. The sudden increases in density with increasing pressure are due to the phase transition from gas to liquid. As seen in the figure, all models compare well with the NIST data in the gas phase, but not as well as in the liquid phase, especially at temperatures close to the critical point ($T_c = 31\text{ }^\circ\text{C}$, $P_c = 73.8\text{ bar}$). The Benedict–Webb–Rubin–Starling

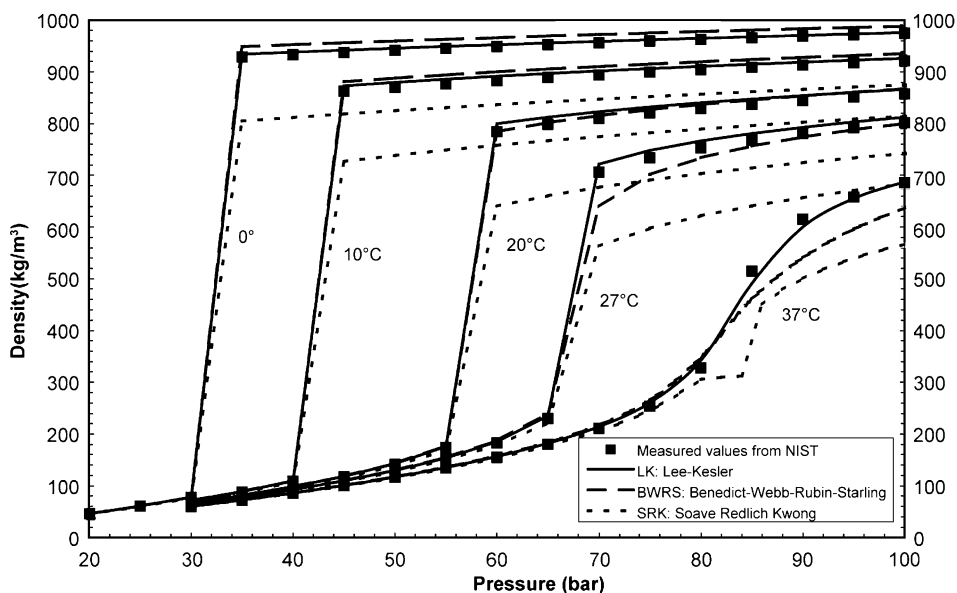


Figure 1: Calculations and experiments for CO₂ density as a function of pressure at selected temperatures.

(BWRS) model is calculated with PRO II, the Soave–Redlich–Kwong (SRK) and Lee–Kesler (LK) models are calculated with in-house codes. The LK model gives the most accurate result with a maximum error of 4.7% for the results in figure, even when CO₂ is close to the critical point. For these results the SRK and the BWRS model have a maximum error of 26 and 12%, respectively.

Water solubility in pure CO₂

The solubility of water in CO₂ vapor at a given temperature decreases to a minimum as pressure is increased (see Figure 2). When the pressure is further increased, a phase transition to liquid occurs and the solubility increases again. These physical properties of CO₂ are important to consider when dehydrating the CO₂, as the minima in water solubility is the best operating point when “knocking out” water.

The binary coefficient between water and CO₂ is adapted to 0.193 for the standard van der Waals mixing rule with SRK equation of state. With this adaptation of the model the mean absolute error between calculations and experiments is 6.3%. The results in the liquid phase are much more sensitive to the binary interaction parameter than the results in the gas phase as shown in Figure 2. Three different binary coefficients are plotted in the figure, where 0.0392 and 0.23 are the default values for HYSYS and PRO II, respectively. It is important to note that the optimum binary coefficient for solubility of water in CO₂ is different from the coefficient for solubility of CO₂ in water. Because the commercial programs only operate with a single default binary coefficient for the CO₂–H₂O system, the calculations will not fit the results properly, unless the parameter is adjusted (Figure 2).

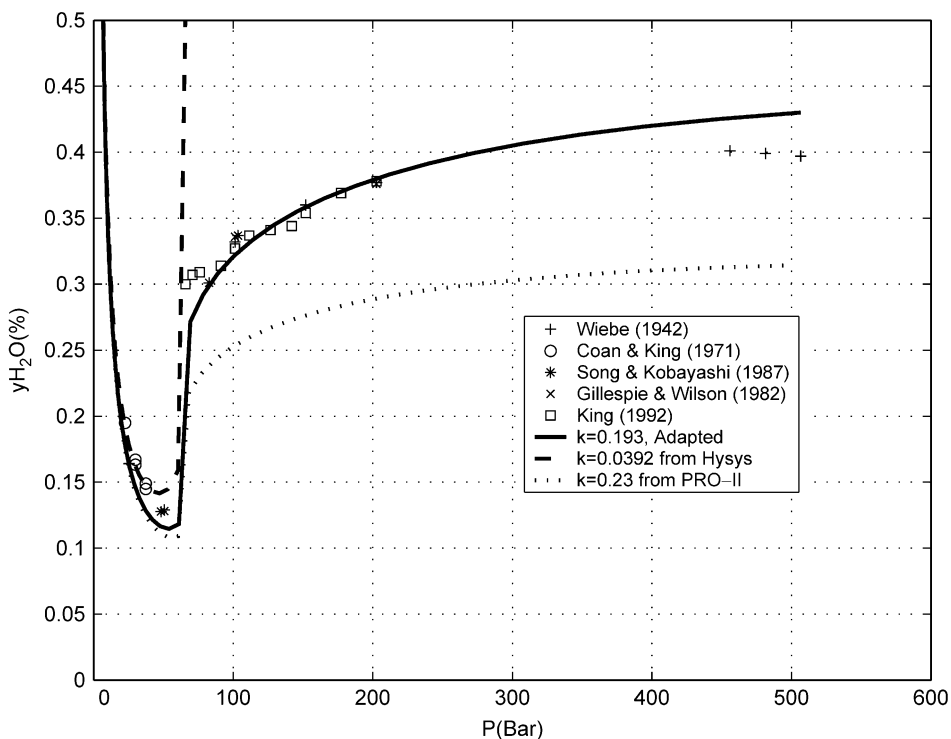


Figure 2: Comparison of model calculations using SRK with van der Waals mixing rule and various binary coefficients (k) at 26 °C with measurement data (from 24 to 28 °C) for solubility of water in CO₂. Given in molar percent (1% = 10,000 ppm). The experimental data are found in Refs. [12–16].

Solubility of water in CO₂ mixtures

Figure 3 shows experiments and calculations for solubility of water in pure CO₂ (solid line) and in CO₂ with 5.3% intermixture of methane (dotted line and the experiments of Song and Kobayashi [17]). The solubility of water in CO₂ and CO₂-CH₄ mixtures is about the same in the gas phase. The difference is however much larger in the liquid phase, where the solubility of water in a mixture of CO₂ and CH₄ is much lower than in pure CO₂. A practical consequence is that, to avoid free water precipitation, the gas must be dried to a lower water level, which again increases the cost. As can be seen from Figure 3, the pressure where liquid appears is also higher in a mixture of CO₂-CH₄ (71 bar) than in pure CO₂ (65 bar).

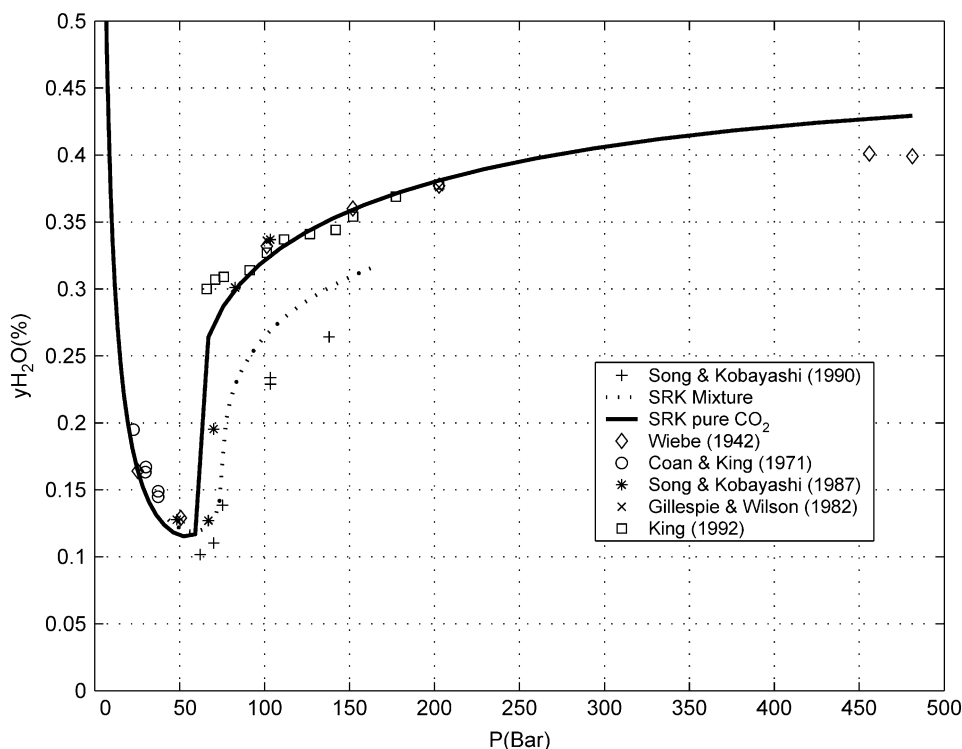


Figure 3: Comparison of model calculations at 26 °C with measurement data (from 24 to 28 °C) for solubility of water in CO₂ (solid line and Refs. [12–16]) and in a mixture of CO₂ and 5.3% CH₄ (dotted line and Ref. [17]).

A binary coefficient of 0.52 is used for the methane–water system. With this binary coefficient, the water solubility in the ternary mixture is overestimated in the liquid phase according to the experimental data. The coefficient can be further adjusted to fit the data better, but generally the amount of data is too sparse to draw any conclusions regarding model performance. The SRK with Huron Vidal mixing rule (Huron et al. [18]) is a better model for this mixture. Work in progress is to apply more advanced models to this mixture.

The effect of water solubility with intermixture of N₂ in CO₂ has not been properly verified due to lack of experimental data. A paper by Seo et al. [19] describes the three phase equilibrium conditions (aqueous liquid-hydrate-vapor) for binary mixtures of CO₂ and N₂, but does not measure the water solubility in this mixture. According to Carroll [20] no data exist for water solubility in a mixture of CO₂ and H₂S. However,

we can assume that very small amounts of H₂S will not have a major effect on the water solubility in a CO₂ mixture. The phase behavior of H₂S and CO₂ is qualitatively similar [21]. The solubility in water is slightly larger for H₂S than for CO₂. Amines, from an amine separation process, will mainly occur in a liquid or aqueous phase (high boiling point), and will only affect the liquid/water phase in the mixture and not the gas phase.

System Design

The transportation system proposed includes a process facility for conditioning the CO₂ gas mixture, primarily compression, and pipeline(s) for transportation to the injection/deposition point. Typically, CO₂ is separated from hydrocarbon gas by amine absorption and may contain up to 5% CH₄, 5% N₂, 0.5% water, 100 ppm H₂S and a small amount of amines as it is fed to the compression process.

Compression process

In order to inhibit hydrate formation and prevent excessive corrosion rates for carbon steel, no free water should be allowed in the pipeline. Thus, water removal usually is required upstream the pipeline inlet.

The base case for the compression process includes compressors with coolers and scrubbers between each compression stage in order to reduce the gas temperature and knock out free water. In order to increase the pressure of CO₂ from 1 to 150 bar (pipeline requirement), four compression stages are considered. The “pure compression process” is shown schematically in Figure 4.

Water removal. By using coolers with seawater at 9 °C as a cooling medium, the gas temperature can be reduced to approximately 15 °C between each compression stage. For this case, theoretical calculations show that the water content in the CO₂ mixture can be reduced to approximately 600 ppm (mole), only by compression, intermediate stage cooling and scrubbing for dehydration.

Additional drying. The water content in the gas depends on the available cooling media temperature. In areas with air temperature at 20 °C as the only available cooling media, the CO₂ temperature could be reduced to approximately 30 °C after the coolers. In this case, the lowest theoretically achievable water content in CO₂ is approximately 1600 ppm [2].

If precipitation of free water in the pipeline is possible and/or likely, additional drying may be required. In general, the following type of dryers can be utilized for water removal in CO₂:

- Adsorption units using, e.g. molecular sieves (MSA).
- Absorption with TEG or DEG as an absorber medium.

Molecular sieve adsorption is the recommended drying method due to low investment costs, compact design, low maintenance rate and generally, good operating experience. In order to reduce size, a MSA downstream the 2nd stage scrubber is recommended.

Gas condensation. Typically, compression to a point above the bubble point pressure is required, prior to transportation. Hence, in the compression process, the gas is condensed (to liquid phase). For pure CO₂, the bubble and dew point curves coincide and the pressure during condensation is constant (at constant temperature). Intermixture of CH₄ in CO₂ leads to a higher bubble point pressure, compared to pure CO₂, and the bubble point pressure is above the dew point pressure. Between these two pressures, is the two-phase region, with gas and liquid in equilibrium. As can be seen from Figure 5 (95% CO₂ and 5% CH₄), if the temperature is kept constant at 15 °C and the gas is pressurized, droplets will start to condense out at 50 bar and complete condensation is reached at 62 bar.

Because N₂ is more volatile than CH₄, introduction of N₂ leads to an even higher bubble point pressure. For a mixture of 95% CO₂, 2% CH₄ and 3% N₂, complete condensation at 15 °C requires a pressure of approximately 70 bar [2].

If the content of volatile components (N₂ and CH₄) in the gas is low, typically less than 5%, the pressure fluctuation during condensation is moderate and condensation of the CO₂ mixture is feasible. In this case,

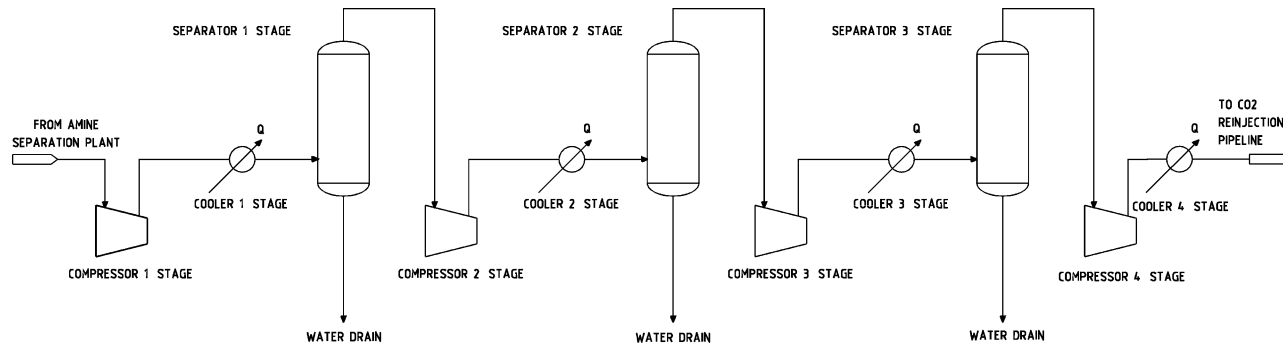


Figure 4: Four stage compression process with interstage cooling and scrubbing.

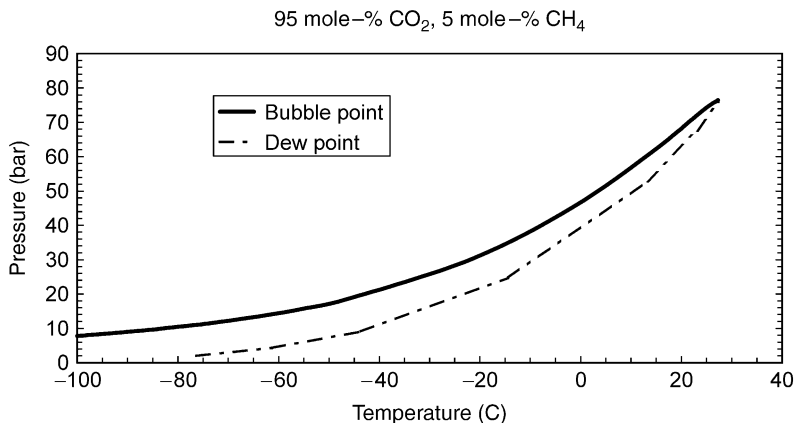


Figure 5: Dew point and bubble point curve for CO₂ mixed with CH₄, calculations in HYSYS with SRK equation of state.

the last compression stage may include a pump instead of a compressor. By pumping, the power consumption and hence, the operational costs will be reduced in the order of 10% compared to a pure compression process.

Pipeline transportation

Water content and drying requirements. For hydrocarbon pipelines, a requirement to dry the gas to 50 ppm water is often used in order to ensure that no free water is in the pipeline. The requirement for CO₂ pipelines, used for EOR in the United States (New Mexico), is maximum 600 ppm water (Kinder Morgan) [2]. Experiments performed at IFE, with CO₂ and carbon steel, show low/insignificant corrosion rates for water content below 600–700 ppm (mole), over a wide range of temperatures [22].

For a typical case, the minimum temperature and pressure in the pipeline is 5 °C and 85 bar, respectively. Theoretical calculations indicate a lower critical limit for free water precipitation of approximately 1300 ppm (mole) in this case. Even if the pressure is reduced to 70 bar, the water solubility is considerably higher than 600 ppm [2]. Thus, free water precipitation is unlikely.

Based on this consideration, it is concluded that a maximum water content of 50 ppm may be too stringent a requirement. For typical CO₂ pipeline transportation, it is considered that a maximum water requirement of 600 ppm may be suitable and sufficient to prevent free water precipitation (see Seiersten, this volume).

Onshore/offshore pipeline transportation. In general, the fluid properties, such as density and water solubility, depend on pipeline pressure and temperature. For long pipelines the fluid will be cooled down to ambient temperature, typically 5 °C for deep water pipelines. For an onshore pipeline, the fluid temperature will be close to the air temperature. As the fluid is cooled down and the pressure is reduced, water tends to precipitate out of the gas. For example, Figure 2 shows that the solubility of water in CO₂ is at a minimum at a pressure of approximately 50 bar. For a deep water pipeline, the static head contributes to increased pressure and increased water solubility, and therefore tends to keep the pipeline dry (no free water).

The compression/pumping requirement at the inlet of the transportation pipeline depends not only on the reservoir pressure, but also on the reservoir depth at the injection point. Deep water combined with a deep reservoir results in a large static pressure in the pipeline/well, which again contributes to obtaining the required injection pressure. Thus, if the water and reservoir depths are large, the boosting requirement at the pipeline inlet is reduced, resulting in reduced capital and operational costs for compression/pumping.

Distance. Knowledge about the distance from the capture plant to the injection point is needed in order to establish the pressure and boosting requirements at the pipeline inlet. Increased pipeline length results in higher frictional pressure loss and increased costs for compression/pumping. Alternatively, the pipe diameter can be increased in order to reduce the flow velocity and thus, reduce the pressure drop. In this case, the capital costs for the pipeline will increase.

In principle, high water content in the CO₂ mixture can be handled either by

- sufficient drying (water removal) downstream in the capture process, or
- using corrosion resistant materials for pipeline and process equipment.

The distance from capture to injection may influence the strategy for handling high water content, i.e. drying vs. corrosion resistant materials. If the pipeline is long, an ordinary carbon steel pipeline is considered to be the only realistic alternative due to cost. In this case, sufficient drying (water removal) upstream of the pipeline is required in order to prevent free water and excessive corrosion rates. On the other hand, if the pipeline is short, the use of corrosion resistant materials should be considered. For short pipelines, the costs for corrosion resistant materials may be less than the costs for installing and operating a separate drying unit.

Materials evaluation and corrosion protection

The corrosion rates in carbon steel pipelines strongly depend on the water content and the water solubility in the CO₂ mixture (see Seiersten [22] and this volume). If free water exists in the pipeline, it will be saturated with CO₂ and the corrosion rate will be significant for carbon steel. For a free water phase without inhibitor the corrosion rate due to CO₂ may be several mm/yr. If free water is expected to occur frequently or normally, MEG or a commercial corrosion inhibitor like, e.g. “Dynea KI-350”, may be used to obtain acceptably low corrosion rates (less than 0.1 mm/yr). If MEG or corrosion inhibitor is not used, and free water is present, corrosion resistant alloys will be required.

In general, it is recommended to dry the gas sufficiently in order to inhibit precipitation of free water in the pipeline. For long pipelines, water removal is considered to be the most cost-effective solution, since ordinary CMn steel (e.g. API X65) can be used in this case.

The minimum operating temperature for ordinary CMn steel is $-46\text{ }^{\circ}\text{C}$. If the pipeline leaks and the ambient pressure is low/atmospheric, the liquid CO₂ may be transformed to dry ice (solid CO₂), with a temperature of approximately $-79\text{ }^{\circ}\text{C}$ and low temperature steel may be required to avoid further failure.

In general, equipment in the compression train can be made from carbon steel. However, for the following components, corrosion resistant alloys may be required:

- piping at the inlet of the compressors as well as critical components in the compressors,
- coolers and piping just downstream of the coolers, and upstream of the scrubbers, and
- scrubbers.

Alternatively, if acceptable from a mechanical point of view, such components can be made from carbon steel with a certain internal corrosion allowance added to the required wall thickness.

CONCLUSIONS

Documentation about existing CO₂ pipeline transportation systems is provided. Today’s onshore systems are primarily CO₂ pipelines used for EOR in the US and acid gas removal in Western Canada. The only existing offshore injection is at Sleipner Vest in the North Sea, operated by Statoil. Drying requirements for the CO₂ pipelines for EOR, operated by Kinder Morgan, is 600 ppm. At the LNG plant at Hammerfest in Norway, CO₂ will be removed from the natural gas. The drying requirement for this plant is 50 ppm water, which is the engineering practice for transportation of natural gas. Based on theoretical calculations as well as experimental data from IFE, it is concluded that a maximum water content of 50 ppm may be a too stringent requirement. A maximum of 600 ppm water may be a suitable and sufficient requirement for CO₂ pipelines.

Typically, the gas mixture out of the capture plant may contain up to 5% CH₄, 5% N₂, 0.5% water, 100 ppm H₂S and an unknown amount of amines. The pure compression process, as opposed to less expensive pumping, is considered to be robust with respect to handling likely composition ranges. High water content in the gas is handled by the scrubbers. Because there is no phase transition, pressure fluctuation due to condensation is eliminated. The water content in the CO₂ mixture can be reduced to approximately 600 ppm (mole), by compression, intermediate stage cooling and scrubbers for dehydration. In this case, it is assumed that seawater at approximately 10 °C is available as a cooling medium. Theoretical calculations indicate a lower/critical limit for free water precipitation of approximately 1300 ppm (mole) in the pipeline. Thus, precipitation of free water is not likely in this case.

In order to inhibit hydrate formation and prevent excessive corrosion rates for carbon steel, sufficient water removal is required upstream the pipeline inlet. The CO₂ pipeline can be made from CMn steel (e.g. API X65), provided that no free water is present and that the minimum operation temperature will not drop below -46 °C. If free water precipitation in the pipeline is possible/likely, additional drying may be required, preferably by molecular sieve adsorption.

Accurate and reliable predictions of fluid properties, particularly density and water solubility, are critical with respect to process and pipeline design. Thermodynamic models and tools for calculating properties for CO₂ and CO₂-rich mixtures have been verified against experimental data. For CO₂ density the Lee–Kesler model is in satisfactory agreement with NIST data both in gas and liquid phase.

RECOMMENDATIONS

For solubility of water in pure CO₂, the SRK model with adjusted binary coefficient to 0.193 in van der Waals mixing rule gives the best approximation to the data collected from literature. Adding impurities as CH₄, N₂, H₂S and amines to the CO₂ mixture will affect the solubility of water, i.e. adding 5% methane lowers the water solubility in the liquid phase considerably. However, very little experimental data is available in the literature for these mixtures. More experimental data is needed in order to verify the model performance.

In the case of a sudden pressure drop to atmospheric pressure (worst case), liquid CO₂ may transform to dry ice (solid CO₂), with a temperature of approximately -79 °C. Thus, low temperature steel materials should be considered for onshore and shallow water pipelines. In future work, criteria for minimum design temperature and material selection for CO₂ pipelines should be established.

Little data exists on the behavior of wet CO₂ gas in scrubbers. In the present work, the process considerations for CO₂ dehydration are based on theoretical calculations. The results of the calculations have not been verified by operational or experimental data. In order to clarify this uncertainty, it is recommended to collect data from existing CO₂ facilities and compare the data against model simulations.

NOMENCLATURE

T_c	Critical temperature
P_c	Critical pressure
K	Kelvin
Pa	Pascal (Unit for pressure)
M	Mega (one million)
SRK	Soave–Redlich–Kwong (equation of state)
LK	Lee–Kesler (equation of state)
BWRS	Benedict–Webb–Rubin–Starling
NIST	National Institute of Standards and Technology
EOR	Enhanced oil recovery
TEG	Triethylene glycol
MSA	Molecular sieve absorption

DEG	Diethylene glycol
CMn	Carbon manganese
API	American Petroleum Institute
IFE	Institute for Energy Technology
NorCap	The Norwegian part of CCP (CO ₂ Capture Project)

ACKNOWLEDGEMENTS

The authors are grateful to CCP and the Norwegian Research Council for financial support, as well as Institute for Energy Technology (IFE) for providing experimental data and expertise. The authors also would like to thank Bjørn Berger, Geir Owren, Trond Soligard, Lars Volden and Rune Meidal for important contributions to the project.

REFERENCES

1. Kinder Morgan homepage: <http://www.kindermorgan.com/>.
2. T. Weydahl, A. Austegaard, M.J. Mølnvik, R. Mo, G. Heggum, CO₂ Capture Project—An Integrated, Collaborative Technology Development Project for Next Generation CO₂ Separation, Capture and Geologic Sequestration—CO₂ Conditioning and Pipeline Transportation, CCP Report 50058, 2004.
3. G. Moritis, EOR dips in U.S. but remains a significant factor, *Oil Gas Journal*, September 26, 2004.
4. O. Bolland, S. Sæter, M. Hyllseth, O. Lunde, Gas Fired Power Plant with Reduced Emissions of Carbon dioxide, *SINTEF Report*, December 1991.
5. A. Baklid, R. Korbøl, G.A. Owren, Sleipner Vest CO₂ injection in shallow underground aquifer. Society of Petroleum Engineers, *71st Annual Technical Conference and Exhibition*, October 6–9, 1996, Denver, Colorado, USA.
6. PRO II, Version 6.0, <http://www.simsci.com/>.
7. HYSYS, Version 3.0.1, <http://www.hyprotech.com/>.
8. A. Austegaard, User Manual—CO₂ Wellhead Pressure Calculator, Version 2.1. *SINTEF-Report TR F5698*, Trondheim, Norway, 2002.
9. R.C. Reid, J.M. Prausnitz, B.E. Poling, *The Properties of Gases and Liquids*, fourth ed., New York: McGraw-Hill, 1987 (ISBN: 0-07-051799-1).
10. J.M. Prausnitz, R.N. Lichtenthaler, E.G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, third ed., Prentice Hall International Series in the Physical and Chemical Engineering Sciences, 1999.
11. National Institute of Standards and Technology (NIST), <http://webbook.nist.gov/chemistry/>.
12. R. Wiebe, The Binary System Carbon Dioxide—Water Under Pressure, *Chem. Rev.* **29** (1942) 475–481.
13. C.R. Coan, A.D. King Jr., Solubility of Water in Compressed Carbon Dioxide, Nitrous Oxide and Ethane. Evidence of Hydration of Carbon Dioxide and Nitrous Oxide in the Gas Phase, *J. Am. Chem. Soc.* **93** (8) (1971).
14. K.Y. Song, R. Kobayashi, Water Content of CO₂ in Equilibrium with Liquid Water and/or Hydrates, *SPE Formation Evaluation*, December 1987.
15. P.C. Gillespie, G.M. Wilson, Vapor–Liquid and Liquid–Liquid Equilibria: Water–Methane, Water–Carbon Dioxide, Water–Hydrogen Sulfide, Water–*n* Pentane and Water–Methane–*n* Pentane, *Research Report RR-48*, Wiltec Research Co., Inc., Provo, UT, 1982.
16. M.B. King, A. Mubarak, J.D. Kim, T.R. Bott, The mutual solubilities of water with supercritical and liquid carbon-dioxide, *J. Supercrit. Fluids* **5** (4) (1992) 296–302.
17. K.Y. Song, R. Kobayashi, The water content of a CO₂-rich gas mixture containing 5.31 mol% methane along three-phase and supercritical conditions, *J. Chem. Eng. Data* **35** (3) (1990).
18. M.-J. Huron, J. Vidal, New mixing rules in simple equations of state for representing vapour–liquid equilibria of strongly non-ideal mixtures, *Fluid Phase Equilib.* **3** (1979) 255–271.
19. Y.T. Seo, S.P. Kang, H. Lee, C.S. Lee, W.M. Sung, Hydrate phase equilibria for gas mixtures containing carbon dioxide: a proof-of-concept to carbon dioxide recovery from multicomponent gas stream, *Korean J. Chem. Eng.* **17** (2000) 659–667.

20. J.J. Carroll, Phase equilibria relevant to acid gas injection: part 1—non-aqueous phase behaviour, *J. Can. Petrol. Technol.* **41** (2002) 25–31.
21. J.J. Carroll, Phase equilibria relevant to acid gas injection: part 2—aqueous phase behaviour, *J. Can. Petrol. Technol.* **41** (2002) 39–43.
22. M. Seiersten, K.O. Kongshaug, Material selection for capture, compression, transport and injection of CO₂, Technical Report, Institute for Energy Technology, 2003.