CATO-2 Deliverable WP 3.5-D01

Progress report on:

Numerical model data and reports on the effect of seasonal CO2 delivery on storage efficiency and capacity

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(CATO-2 Director)

1 Executive Summary (restricted)

T3.5.1 CO_2 buffering; seasonal storage and production
Seasonal storage: CO_2 from the Pernis refinery is currently supplied to farmers to increase the rate of grow of vegetables within greenhouses and to soft drink producers. This amount of required CO_2 depends on the weather and also on the season. For example: during the summer the farmers may need additional CO_2 than the refinery or electrify producer can provide, while during wintertime they ay not need any CO_2. A possible solution may be the temporal storage the gas into a depleted gas field (during wintertime) or other underground structures, followed by reproduction during the pick demand periods. Several aspects need to be investigated:

- CO_2, tends to dissolve compositions such as water, hydrocarbons and maybe even radioactive elements. This could lead to well integrity issues (moist CO_2) Reproduced CO_2 may also not have enough purity for use in the various applications. Possibly the reservoir is cleaned after several cycles of injection and reproduction.
- The reservoir may dry out as a result of the repeated cycles of injection of dry and reproduction of wet CO_2.

Activities year 1: Carry out geological, physical modelling and numerical simulation studies of the effects of seasonal variations of CO_2. Simulate CO_2 storage scenarios with quantitative predictions of responses.

This activity will be ceased after year one in according to the reduction of activities caused by budget cuts.

Summary of the activities:

- Started with a literature study on potential sites for seasonal storage:
  - Small gas fields
  - Salt caverns
- Discussion on effects on reservoirs by CO_2-injection and – production:
  The cleaning effect, i.e. removal of resins near the well was found to improve flow rates in the GdF-TNO field test in a previous storage program.
- Discussions together with members from SP1, SP2 and SP3 to make an inventory on supply, demand and transport capacities for CCS. (meeting SP1, SP2, SP3 on 26/02/10)
  A summary of this meeting, with consequences is provided here below. The minutes of the meeting are in the appendix.

Conclusions:

- A reservoir may dry out as a result of the repeated cycles of injection of dry and reproduction of wet CO_2.
- Reproduced CO_2 has a reduced purity for use in the various applications. Moreover, it may cause unwanted:
  - corrosion, and mineralization in the transport system.
  - and multi-phase flow.
- Advantage: possibly the reservoir is cleaned after several cycles of injection and reproduction.

Seasonal storage will cause significant technical problems during second stage transport.

Distribution List

(this section shows the initial distribution list)

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Document Change Record

(this section shows the historical versions, with a short description of the updates)

Version	Nr of pages	Short description of change	Pages

Table of Content

2 Applicable/Reference documents and Abbreviations

2.1 Applicable Documents

(Applicable Documents, including their version, are documents that are the “legal” basis to the work performed)

	Title	Doc nr	Version date
AD-01	Beschikking (Subsidieverlening CATO-2 programma verplichtingnummer 1-6843	ET/ED/9078040	2009.07.09
AD-02	Consortium Agreement	CATO-2-CA	2009.09.07
AD-03	Program Plan	CATO2-WP0.A-D.03	2009.09.29

2.2 Reference Documents

(Reference Documents are referred to in the document)

	Title	Doc nr	Issue/version	date
	See below in Appendix			

2.3 Abbreviations

(this refers to abbreviations used in this document)

	None

3 General Text

Task 3.5.D01: CO_2 buffering; seasonal storage and production.

Activities year 1:

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Considerations regarding transportation, impurities and consequences:

Limitations of gas quality on transport, using conventional and/or existing transport systems.

Impurity	Limit	Reason
H2O	500 ppm	Technical limitation: below solubility limit of H2O in CO2 / Corrosion
O2	Aquifer < 4 vol %, EOR 100 – 1000 ppm	
Hydrocarbons	<4% non-condensables	Capacity

H2S SOx NOx	200 PPM 100 ppm 100 ppm	Health and safety consideration / geochemistry
H2 N2 Ar	<4% non-condensables	Capacity
CO	2000 ppm	Health and safety consideration
Glycol	To be investigated	
Amines	To be investigated	

Transport problems for multi-phase flow:
- A shift in density as a function of the pressure causes a shift in the pressure drop over a pipeline. (T_{pipe} ca. 5℃, $P_{g/l}$ pure CO_2 ca 40 bar.)
- Impurities could result in two-phase flow, which is unacceptable for transport.

Corrosion of pipelines and other equipment:
- Existence of free water.
- Hydrate formation
- H_2S and O_2 increase corrosion speed in presence of free water.

Impurities affect transport capacity:
- The usual limit for non-condensable impurities is 4vol.%.

HSE:
- Release of impure CO_2 into the environment, impurities (H_2S) may have an effect on health, safety and the environment.

Considerations regarding storage:
- CO_2 tends to dissolve compositions such as rock minerals, hydrocarbons, creating moist CO_2 and gases such as H_2S.

Conclusions:

- A reservoir may dry out as a result of the repeated cycles of injection of dry and reproduction of wet CO_2.
- Advantage: possibly the reservoir is cleaned after several cycles of injection and reproduction.
- Reproduced CO_2 has a reduced purity for use in the various applications. Moreover, it may cause unwanted:
  - corrosion, and mineralization in the transport system.
  - and multi-phase flow.

Seasonal storage will cause significant technical problems during second stage transport.

Appendix

CATO2 Meeting on impurities in CO_2 flows: 26-2-2009

Place: TNO Princetonlaan,Utrecht
Date: 26-2-2009 11.00-15.00
Present: Joost de Wolff (KEMA): WP4 Monitoring/ETS
Karl-Heinz Wolf (TUDELFT): SP3 Storage
Marielle Koenen (TNO): SP3 Storage
Cor Hofstede (TNO): SP3 Storage
Hans Kamphuis (KEMA): SP1, modelling PowerPlants
Patrick van Hemert (TUDELFT): WP3.2 Storage
Ton Teunissen (Electrabel): WP1.1 interface capture/transport/storage
Mohammad Ahmad (Gasunie/KEMA): WP2.1 transport
Wim Mallon (Gasunie/KEMA): SP2
Albert van den Noort (Gasunie/KEMA): WP2.1 transport

Introduction

Within workpackage 2.1 of the CATO2 program, investigations are made on the technical aspects of CO_2 transport. From a first scan of the critical aspects for the design of a pipeline it is learned that impurities in the CO_2 flows can play an important role. Especially the physical properties of CO_2 with impurities influence the design of the system, since they form the basis of all design simulations. For these physical properties few validated models are available.

It is therefore important that assumptions are made on the possible composition of CO_2 flows in the CCS process, because it influences Capture, Transport and Storage. In the meeting representatives of the Capture, Storage, Transport and Safety subprograms were asked to give their point of view on impurities in CO2 flows based on their respective areas of interest. In the meeting the impact of possible impurities was discussed and knowledge on available data was shared. The goal of the meeting was to:
- Set a typical composition for CO_2 flows as a proposal for a standard to be used in $CATO_2$.
- An inventory on available data/models on physical properties of CO_2 within $CATO_2$.

This document describes the discussion and forms the start point for further research on this topic.

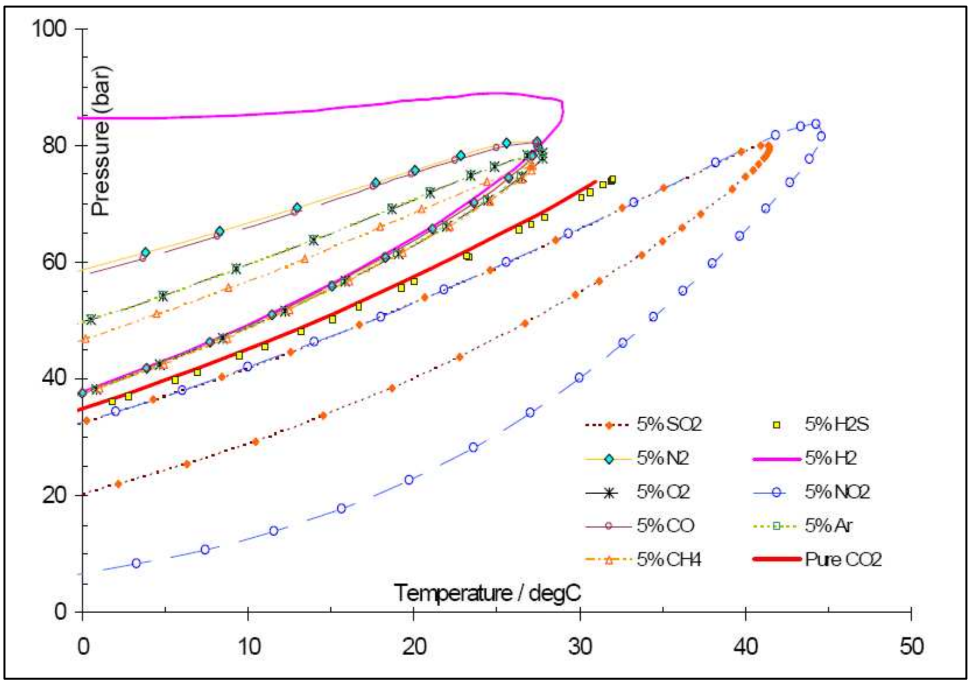
Storage

Karl-Heinz Wolf gave a global description of the work performed in SP3 regarding the Storage. Key issues for storage are:
- There is a variety of different storage locations with different specific conditions and chemical properties of the source and cap rock. Also pressures differ, aquifers are in this respect completely different from empty gas fields (10-30 bar) and rising in stead of high and constant. It is therefore difficult to give general guidelines for impurities allowed in the underground and (requested) conditions of the CO_2 at the wellhead (injectivity)
- The subject of injectivity is important and will need a different meeting for specific attention to cover all aspects and investigate possibilities for injection temperature, pressure and flow

- Impurities could be added to the CO_2 to actively steer the CO_2 flow in compartments in the store.
- Kinetics of CO_2+impurties+rock chemistry is very slow and hard to model. Time-scaling is essential in these experiments (temp x 10 => kinetics x 2)

Experiments are/will be conducted at TU-Delft:

- small setup cm3, large setup up to 1 meter cell. Focuses on pure CO_2 (=>99% CO_2) other setups at UU and TNO Rijswijk
- Experiments of Patrick van Hemert: 99,9996 % pure CO_2, if impurities (99,7% pure CO_2) are added measurement errors up to 100% are found near the critical point. Setup not suitable for CO_2 + impurities
- Issue from experiment: difficult to get the setup tight (for CO_2). Plastics are permeable for CO_2.
- Quote Karl-Heinz: "CO_2 with NOx and SOx can be injected without problems, however causing rock-fluid-gas interactions". Patrick and Marielle are not sure if this is true (experiments are lacking)
- Issue with water: corrosion on casing. Statement: as long as the water content is sufficient for the pipeline, it is also sufficient for the casing => limitation of water content will be imposed by the transport part of the CCS chain.

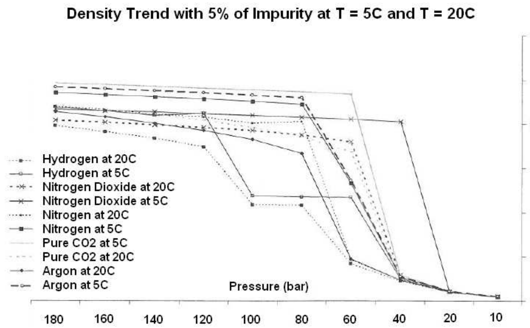


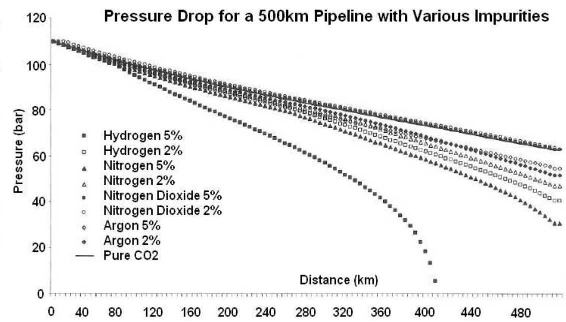
Transport

For the transport system impurities will have an influence on the design of the system. A number of aspects are:

- The phase diagram varies with composition. In pipeline transport, the pressure must exceed the critical pressure to prevent two-phase flow. Another option is to transport in the gaseous phase in all circumstances, which would mean a much lower transport capacity. The figure below shows simulations of the effect of impurities on the phase diagram of CO_2. NOTE: these are results from simulations, not validated by experiments!

- The effect of this envelope in the phase diagram is clearly seen on the density as a function of the pressure in the plot below. A shift in density as a function of the pressure will cause a dramatical shift in the pressure drop over a pipeline. Note that at typical temperatures in the pipeline (5℃) the boiling temperature of fluid pur e CO_2 is (approx) 40 bar. Including the impurities could result in two-phase flow, which is unacceptable.





- Corrosion of pipelines and other equipment depends on the existence of free water.
- Free water is needed for corrosion
- Hydrate formation
- H_2S and O_2 can increase the corrosion speed in presence of free water
- Impurities affect transport capacity.
- The usual limit for non-condensable impurities is 4% by volume.
- Lastly, when CO_2 is released into the environment, the impurities (H_2S) may have an effect on health, safety and the environment.

Note: The current limits on water of 40 ppm seem to be too strict a demand, based on above mentioned free water criterion. This may result in a far higher allowable water content, up to 1000 ppm or more.

Capture

Source of impurities

Typical values:

	Oxyfuel	Postcombustion	Precombustion
CO_2	90		
H_2O	0.2 (~=2000ppm)		
H_2S	1.5		
NOx	0.25 (~=2500ppm)		
SOx			
Ar	6 (!)		
O_2	2		
NH_3		?	
H_2			?

- PVT models (EOS's) are used to model capture plants
    - pvti
    - Aspen (WP1.1 Earl Goetheer?)
    - Span & Wagner (commercial ~ €5000, Patrick?)

Note: There is an issue with the effect of a combination of chemical elements.

Conclusions

- Antropogeneous from the capture processes will include impurities. The effect of these impurities on the physical properties and reactivity with the underground is not fully understood.
- Storage and Transport use pure CO_2 for models/calculations at the moment. Capture uses some impurities in models (ASPEN, Spang&Wagner)

Critical components in CO_2 flows:

- Transport:
- Free water – corrosion
- H_2S – Safety
- Storage
- Free water – corrosion casing
- Components with sulfur (reactivity with rock)
- Capture
- Inerts (N_2, H_2, CxHy) influence the capacity of the transport and storage system and influence the phase-behaviour.

The suggestion was made to formulate a research issue covering all WP's on the PVT issue, each WP specific for the conditions that are encountered in this are of interest

The capture plant

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SOx	100 ppm	Health and safety consideration/ geochemistry
NOx	100 ppm	Health and safety consideration/ geochemistry
H2	<4% non-condensables	Capacity
N2	<4% non-condensables	Capacity
CO	2000 ppm	Health and safety consideration
Ar	<4% non-condensables	Capacity
Glycol	Needs to be investigated	
Amines	Needs to be investigated	

After the meeting the idea was formed to draft a 1st of typical CO_2 composition based on e.g. functionality (what is the effect of the impurity) or on technical parameters (what comes out which process)

Define typicals

E.g. typicals based on functionality
- Typical 1: pure CO_2 → current know how and measurement
- Typical 2: CO2 + 4% inerts (eg N2 or Ar) → Volume / capacity limit
- Typical 3: CO2 + water + H2S + inerts → corrosion limit

Or:
Technical typicals
- Typical: pure CO_2 (post-combustion)
- Typical: typical oxyfuel
- Typical: typical pre-combustion

What we need:
- pvt data for CO_2 + impurities (EOS)
- viscosity/heatcapacity etc.
- maximum allowed values for sulfur components