## **TNO Built Environment and Geosciences**

Princetonlaan 6 P.O. Box 80015 3508 TA Utrecht The Netherlands

www.tno.nl

TNO report

2008-U-R781/B Is Carbon Dioxide in Case of Natural Gas Storage a Feasible Cushion Gas? T +31 30 256 42 56 F +31 30 256 44 75 info@nitg.tno.nl

Date 1 August 2008

Author(s) L.G.H. van der Meer, A. Obdam

Assignor

CATO 3.1/2.3 034.62127

Project number

Classification report Title Abstract Report text Appendices

Number of pages 17 (incl. appendices) Number of appendices

All rights reserved. No part of this report may be reproduced and/or published in any form by print, photoprint, microfilm or any other means without the previous written permission from TNO.

All information which is classified according to Dutch regulations shall be treated by the recipient in the same way as classified information of corresponding value in his own country. No part of this information will be disclosed to any third party.

In case this report was drafted on instructions, the rights and obligations of contracting parties are subject to either the Standard Conditions for Research Instructions given to TNO, or the relevant agreement concluded between the contracting parties. Submitting the report for inspection to parties who have a direct interest is permitted.

© 2008 TNO

# Summary

Demand for natural gas is generally seasonal in nature: more natural gas is required in the winter than in the summer, and therefore prices in the winter are generally higher. Operators of natural gas storage facilities have the opportunity to arbitrage these seasonal price differences. Furthermore, gas buffer volume close at the consumer's site of the delivery chain makes it possible to optimize gas production and long distance transport. Each storage location has its own physical characteristics (porosity, permeability, retention capability) and economics (site preparation and maintenance costs, deliverability rates, and cycling capability), which govern its suitability to particular applications.

Two of the most important characteristics of an underground storage reservoir are its capacity to hold natural gas for future use and the rate at which gas inventory can be withdrawn its deliverability rate. Total gas in storage is the volume of storage in the underground facility at a particular time. This volume consists of both base gas and working gas. Base gas (or cushion gas) is the volume of gas intended as permanent inventory in a storage reservoir to maintain adequate pressure and deliverability rates throughout the withdrawal season. Working gas is available to the marketplace.

This cushion gas may represent more than half the total gas volume, and possible up to 70% of the initial investment for the storage facility. Experimental studies performed in the last 30 years, backed up by field experience, have shown that at least 20% of the cushion gas can be replaced by a less expensive inert gas. In this report we evaluate the possibility to employ  $CO_2$  as a cheap cushion gas with as main aim to improve the economics of a storage operation with the added benefit of greenhouse gas reduction.

# Contents

	Summary	
1	Introduction	
1.1	Natural gas storage	
1.2	Storage Measures	7
1.3	Natural Gas Storage Capacity	
2	CO <sub>2</sub> a cushion gas?	
2.1	Introduction	
2.2	Gas Mixing	
2.3	Physical interactions between CO <sub>2</sub> and methane	
2.4	CO <sub>2</sub> Storage Potential	
3	Conclusions	
4	References	
5	Signature	

## 1 Introduction

### 1.1 Natural gas storage

Demand for natural gas is generally seasonal in nature: more natural gas is required in the winter than in the summer, and therefore prices in the winter are generally higher. Operators of natural gas storage facilities have the opportunity to arbitrage these seasonal price differences. Furthermore, gas buffer volume close at the consumer's site of the delivery chain makes it possible to optimize gas production and long distance transport. Natural gas-may is stored in a number of different ways. It is most commonly held in inventory underground under pressure in three types of facilities. These are: (1) depleted reservoirs in oil and/or gas fields, (2) aquifers, and (3) salt cavern formations. (Natural gas is also stored in liquid form in above ground tanks. A discussion of liquefied natural gas (LNG) is beyond the scope of this report. Each storage type has its own physical characteristics (porosity, permeability, retention capability) and economics (site preparation and maintenance costs, deliverability rates, and cycling capability), which govern its suitability to particular applications. Two of the most important characteristics of an underground storage reservoir are its capacity to hold natural gas for future use and the rate at which gas inventory can be withdrawn its deliverability rate

Most existing gas storage in the United States, the county with the largest storage capacity, is in depleted natural gas or oil fields that are close to consumption centres. Conversion of a field from production to storage duty takes advantage of existing wells, gathering systems, and pipeline connections. Depleted oil and gas reservoirs are the most commonly used underground storage sites because of their wide availability.

In some areas, most notably the Midwestern United States, natural aquifers have been converted to gas storage reservoirs. An aquifer is suitable for gas storage if the water bearing sedimentary rock formation is overlaid with an impermeable cap rock. While the geology of aquifers is similar to depleted production fields, their use in gas storage usually requires more base (cushion) gas and greater monitoring of withdrawal and injection performance. Deliverability rates may be enhanced by the presence of an active water drive.

Salt caverns provide very high withdrawal and injection rates relative to their working gas capacity. Base gas requirements are relatively low. The large majority of salt cavern storage facilities have been developed in salt dome formations located in the Gulf Coast states. Salt caverns have also been leached from bedded salt formations in North-eastern, Midwestern, and South-western states. Cavern construction is more costly than depleted field conversions when measured on the basis of dollars per thousand cubic meters of working gas capacity, but the ability to perform several withdrawal and injection cycles each year reduces the per-unit cost of each thousand cubic meter of gas injected and withdrawn.

There have been efforts to use abandoned mines to store natural gas, with at least one such facility having been in use in the United States in the past. Further, the potential for commercial use of hard-rock cavern storage is currently undergoing testing. None are commercially operational as natural gas storage sites at the present time.

Figure 1 is a cartoon type of representation of the various types of underground storage facilities, while Figure 2 shows the location of the nearly 400 active storage facilities in the US.



Figure 1. Types of Underground Natural Gas Storage Facilities



Figure 2. Underground Natural Gas Storage Facilities in the US.

### 1.2 Storage Measures

There are several volumetric measures used to quantify the fundamental characteristics of an underground storage facility and the gas contained within it. For some of these measures, it is important to distinguish between the characteristic of a facility such as its capacity, and the characteristic of the gas within the facility such as the actual inventory level. These measures are as follows:

- Total gas storage capacity is the maximum volume of gas that can be stored in an underground storage facility in accordance with its design, which comprises the physical characteristics of the reservoir, installed equipment, and operating procedures particular to the site.
- Total gas in storage is the volume of storage in the underground facility at a particular time.
- Base gas (or cushion gas) is the volume of gas intended as permanent inventory in a storage reservoir to maintain adequate pressure and deliverability rates throughout the withdrawal season.
- Working gas capacity refers to total gas storage capacity minus base gas.
- Working gas is the volume of gas in the reservoir above the level of base gas. Working gas is available to the marketplace.

Deliverability is most often expressed as a measure of the amount of gas that can be delivered (withdrawn) from a storage facility on a daily basis. Also referred to as the deliverability rate, withdrawal rate, or withdrawal capacity, deliverability is usually expressed in terms of normal cubic meter per day (Nm3/day). Occasionally, deliverability is expressed in terms of equivalent heat content of the gas withdrawn from the facility, most often in Btu per day The deliverability of a given storage facility is variable, and depends on factors such as the amount of gas in the reservoir at any particular time, the pressure within the reservoir, compression capability available to the reservoir, the configuration and capabilities of surface facilities associated with the reservoir, and other factors. In general, a facility's deliverability rate varies directly with the total amount of gas in the reservoir is most full and declines as working gas is withdrawn.

Injection capacity (or rate) is the complement of the deliverability or withdrawal rate-it is the amount of gas that can be injected into a storage facility on a daily basis. As with deliverability, injection capacity is usually expressed in Nm3/day, although Btu/day is also used. The injection capacity of a storage facility is also variable, and is dependent on factors comparable to those that determine deliverability. By contrast, the injection rate varies inversely with the total amount of gas in storage: it is at its lowest when the reservoir is most full and increases as working gas is withdrawn.

None of these measures for any given storage facility are fixed or absolute. The rates of injection and withdrawal change as the level of gas varies within the facility. Additionally, in practice a storage facility may be able to exceed certificated total capacity in some circumstances by exceeding certain operational parameters. But the facility's total capacity can also vary, temporarily or permanently, as its defining

parameters vary. Further, the measures of base gas, working gas, and working gas capacity can also change from time to time. This occurs, for example, when a storage operator reclassifies one category of gas to the other, often as a result of new wells, equipment, or operating practices (such a change generally requires approval by the appropriate regulatory authority). Also, storage facilities can withdraw base gas for supply to market during times of particularly heavy demand, although by definition, this gas is not intended for that use.

So, it is very clear that in seasonal modulation storage of natural gas, in for instance an aquifer, a varying fraction of the injected gas, the base or cushion gas cannot be recovered. This cushion gas may represent more than half the total gas volume, and possible up to 70% of the initial investment for the storage facility. Experimental studies performed in the last 30 years, backed up by field experience, have shown that at least 20% of the cushion gas can be replaced by a less expensive inert gas. In these considerations a variety of gasses and gas mixtures have been considered with the emphasis on low production cost of the gas. Different methods are available to produce an inert gas that meets the specifications required. Recovery of natural gas combustion products (mixtures of 88% N2 and 12% CO<sub>2</sub>) and physical separation of air components (more or less pure N2) have been considered. In this report we will concentrate on CO<sub>2</sub> as cushion gas in the light of CO<sub>2</sub> storage to prevent the emission of CO<sub>2</sub> into the atmosphere in the context of removing a greenhouse gas.



Figure 3. Typical Monthly Natural Gas Storage Measures

#### 1.3 Natural Gas Storage Capacity

The following table gives a good idea about the present practical storage capacity. In order to produce this insight we have used the 2006 figures for the whole of the U.S., a country with a long standing gas storage history.

Year	2006	
Total Storage Capacity [10 <sup>6</sup> Nm <sup>3</sup> ]	235,871	
Salt Caverns	7,418	
Aquifers	38,405	
Depleted fields	190,047	
Total Number of Active Fields	397	
Salt Caverns	31	
Aquifers	44	
Depleted fields	322	
Average storage by field [10 <sup>6</sup> Nm <sup>3</sup> ]	594	
Salt Caverns	239	
Aquifers	872	
Depleted fields	590	

Table 1. Underground Natural Gas Storage Capacity for the U.S.

Source: The US Energy Information Administration

# 2 $CO_2$ a cushion gas?

### 2.1 Introduction

We can consider the use of  $CO_2$  as cushion gas in natural gas storage projects possible from two focal points, namely:

- To improve the economics of a natural gas storage operation by replacing a part of the valuable natural gas cushion gas by cheap CO<sub>2</sub>, or
- To use the gas storage location to store the greenhouse gas CO<sub>2</sub> from the point of view of the Carbon Capture and Storage option (CCS).

It will be clear that for both cases the ultimate  $CO_2$  storage volume is limited. For both cases it is important to study the possible physical differences and possible interaction between of natural gas and  $CO_2$ . During Natural gas storage both gases are injected into the same reservoir and at certain times natural gas is produced instead of injected.

#### 2.2 Gas Mixing

Verbal communication with people involved with a large gas storage operation in the South of Germany reported hardly any mixing effects. In the past several types of gasses were injected in the original natural gas reservoir. In the early days coal gas was injected followed by low- and high caloric Groningen gas to be followed by Russian gas. The fact that these gasses mainly consisted of methane gas which all having nearly the same gas and flow properties must be large reason for the very sharp interface seen between the gasses. It was reported that the transition between one gas to the other was observed in the observation well within 24 hours every time within a production or injection cycle. In general this is a logical effect. On the other hand if the properties of the gasses in the reservoir differ complex gas interfaces may be observed. In the case of  $CO_2$  as cushion gas these complex situations may occur.

Oldenburg at al (2001) have carried out numerical simulations of the mixing of carbon dioxide  $(CO_2)$  and methane  $(CH_4)$  in a gravitationally stable configuration using the multicomponent flow and transport simulator TOUGH2/EOS7C. The purpose of the simulations is to compare and test the appropriateness of the advective-diffusive model (ADM) relative to the more accurate dusty-gas model (DGM). The configuration is relevant to carbon sequestration in depleted natural gas reservoirs, where injected CO<sub>2</sub> will migrate to low levels of the reservoir by buoyancy flow. Once a gravitationally stable configuration is attained, mixing will continue on a longer time scale by molecular diffusion. However, diffusive mixing of real gas components CO2 and CH4 can give rise to pressure gradients that can induce pressurization and flow that may affect the mixing process. Understanding this coupled response of diffusion and flow to concentration gradients is important for predicting mixing times in stratified gas reservoirs used for carbon sequestration. Motivated by prior studies that have shown that the ADM and DGM deviate from one another in low permeability systems, we have compared the ADM and DGM for the case of permeability equal to 10-15  $m^2$  and 10-18 m<sup>2</sup>. At representative reservoir conditions of 40 bar and 40°C, gas transport by advection and diffusion using the ADM is slightly over predicted for permeability equal to 10-15 m<sup>2</sup>, and substantially over predicted for permeability equal to 10-18 m<sup>2</sup> compared to DGM predictions. This result suggests that gas reservoirs with permeabilities larger than approximately 10-15  $m^2$  can be adequately simulated using

the ADM. For simulations of gas transport in the cap rock, or other very low permeability layers, the DGM is recommended.

In reality it will not be a gravitationally stable configuration especially not if commercial  $CO_2$  injection rates are used. In the next section we will try to evaluate the possible physical differences between  $CO_2$  and methane in relation to their possible interaction in case of cushion gas competition between the two gasses.

### 2.3 Physical interactions between CO<sub>2</sub> and methane

#### 2.3.1 $CO_2$ and methane density

The density difference of fluids is the cause for the tendency for buoyancy or descending in case the fluids meet. For example  $CO_2$  has a buoyant tendency if injected in water and a descending tendency if injected in a methane reservoir. The density ratio of  $CO_2$  compared to methane is shown in Figure 4. At the expected storage temperature of 60 °C the density ratio is about 4 – 7. This will hamper the mixing of the two gases. The picture shows clearly that methane will always be less dense than  $CO_2$  and will eventually be on top of the  $CO_2$  in site of the reservoir.



Figure 4. Density ratio of CO<sub>2</sub> and methane as function of pressure and temperature

#### 2.3.2 CO<sub>2</sub> and methane viscosity

The ratio of  $CO_2$  viscosity to methane viscosity is of interest as the well Injection Index for a gas is a function of the inverse of the viscosity of the gas concerned. Usually the production capacity of a gas production well is known. For use of such a well for  $CO_2$ injection the Well Injection Index can be transformed to  $CO_2$  Injection Index by dividing by the  $CO_2$  / methane viscosity ratio as is shown in Figure 5.



Figure 5. Viscosity ratio of CO<sub>2</sub> and methane as function of pressure and temperature

#### 2.3.3 Practical Application of CO<sub>2</sub> injection

With the main physical differences between the two gasses shown we can start making an operational plan to introduce the  $CO_2$  as a cushion gas. As can be seen from the figures 4 and 5, reservoir temperature plays an imported role. So, the local or reservoir specific conditions could influence the final storage conditions. Here we will try to give a possible solution for the normal range of operational conditions. The density differences getting smaller by increasing temperatures while the viscosity ratio increases by decreasing temperature. In general it can be stated that we want to inject the  $CO_2$  as far away as possible from the methane injection/production location this to prevent the production of CO<sub>2</sub> cushion gas and subsequently pollute the production gas stream. Furthermore, large migration paths could stimulate miscibility. From a density point of view, the v will have a tendency to settle between the methane gas and the water i.e. at the gas-water contact (GWC). So, a  $CO_2$  injection location away from the methane operation area with perforations close or on top of the GWC will be probably the best configuration. The best possible CO<sub>2</sub> injection location could be created if this location could be combined with an area with the lowest fluid flow properties i.e. low permeability. As seen in many numerical simulation studies, CO<sub>2</sub> injection can deflect the water table, giving rise to the repressurization at large distance from the injection well.

Strongly layered storage reservoirs are less suitable for the implementation of  $CO_2$  as part of the cushion gas configuration. High permeable layers could cause  $CO_2$  to drawn to the production area with a large chance to interact with the working gas of the storage and even result in early breakthrough in the production wells resulting in a low quality production gas. The effects of reservoir heterogeneity on the total gas storage operation and fluid flow in the reservoir could be studied by numerical simulation.

In the past, Gas de France has studied (Laille (1986, 1988), Moegen (1989)) all kind of gas storage field manipulations, from complete conversions to inert gas injection. They

used the same methodology to simulate the planned operation. First simplified models were used to provide an approximate performance of the reservoir during the injection of inert gas. This was followed by the 3D compositional modeling to provide for more detailed and reliable prediction. The objective of this work was determining several operating parameters crucial to the design of the cushions gas replacement project. These were:

- The quantity of inert gas that can be substituted without consecutive troubles concerning the heating value or the gas produced during winter.
- The number of wells required for inert gas injection and their location.
- The conversion timing i.e. when to inject the CO<sub>2</sub>, probable in the summer when methane has to be injected to restore pressure.
- The schedule of inert gas injection.

Furthermore, they concluded that some 20 % of the methane cushion gas could be replaced with an inert gas, that a detailed geological description and the physical parameters related to mixing are necessary before physical performance can be simulated on a computer.

The introduction of  $CO_2$  as cushion gas is largely driven by economical reasoning. An important parameter is the gas price and the possible gas price development in the future. A low gas price period could be used to displace high quality gas (storage conversion). By definition, the cushion gas is never lost. By the ending of the storage functionality of the storage field, nearly all gas is recoverable as in case of a normal gas field. The use of  $CO_2$  as partial cushion gas could spoil the end production of an abandoned natural gas storage project. This is not the case if the gas storage installation includes  $CO_2$  gas removal equipment. In this case  $CO_2$  can possibly be recycled. But in all cases the economical indicators must be positive. This will be locally dependable and all parameters defining the local situation have to individually determent for the local circumstance.

### 2.4 CO<sub>2</sub> Storage Potential

As already shown in section 1.3 the average methane storage capacity by storage field is not extremely large. Let's take a rather optimistic view assuming a total methane gas storage capacity to be 3 x  $10^9$  Sm<sup>3</sup> for our calculation example. Furthermore, let's assume that of this gas  $^2/_3$  (66 %) is cushion gas and that some 20 % of this cushions gas can be replaced by CO<sub>2</sub>. So, this will result in some 200 x  $10^6$  Sm<sup>3</sup> of natural cushion gas can be replaced with CO<sub>2</sub>. And, if we further adopt a reservoir pressure of 150 bars and an average reservoir temperature of 70 °C than we can with the help of figure 6 estimated the CO<sub>2</sub> storage potential. The figure shows that for these reservoir values some 3.71 Mton of CO<sub>2</sub> can replace for each billion ( $10^9$ ) SM3 of CH<sub>4</sub>. In this example only 0.2 billion Sm3 could be replaced by CO<sub>2</sub> which will result in a CO<sub>2</sub> storage capacity of some 0.742 Mton of CO<sub>2</sub>. If we compare this amount of CO<sub>2</sub> with the average yearly CO<sub>2</sub> production of a 500 Mw coal power station of some 3.2 Mton, we can say that such a CO<sub>2</sub> storage option is difficult to consider a serious CO<sub>2</sub> mitigation proposal.



Figure 6. Volumetric comparison between  $CO_2$  and  $CH_4$  as function of reservoir pressure for several temperatures.

# 3 Conclusions

In natural gas storage some amount of cushion gas can be replaced with carbon dioxide. Design of such an operation has to concentrate on an effort to maximize the separation of working gas volume with the  $CO_2$  cushion gas bubble. I case the  $CO_2$  in the reservoir is in super critical state and the reservoir is highly homogeneous the  $CO_2$  will settle at the gas-water contact as a result of gravity segregation. A normal type of reservoir simulation coning study could give indication of the possibility of  $CO_2$  pollution of the working gas volume. Mixing of the methane gas and the  $CO_2$  has to minimize. Several studies have shown that layered reservoirs with large permeability contrasts are not suitable for conversion.

By definition, the cushion gas is never lost. By the ending of the storage functionality of the storage field, nearly all gas is recoverable as in case of a normal gas field. The use of  $CO_2$  as partial cushion gas could spoil the end production of an abandoned natural gas storage project.

Furthermore, it can be concluded that from a greenhouse gas sequestration point of view, the combined use of methane gas storage reservoir with  $CO_2$  as cushion gas and as a storage place for  $CO_2$  is not very attractive. Simply, the total amount of  $CO_2$  that can be sequestered is rather small with a more or less high risk of  $CO_2$  contamination of high valuable natural gas.

# 4 References

- Oldenburg, C.M., K. Pruess, and S.M. Benson, (2001): Process modeling of carbon sequestration with enhanced gas recovery, *Energy and Fuels*, in press.
- Laille, J.P., C. Coulomb, M.R. Tek (1986):Underground Storage in Cerville-Velaine, France: A Case History in Conversion and Inert Gas Injection as Cushion Substitute. SPE15588.
- Moegen, de H., H. Clouse (1989): Long-Term Study of Cushion Gas Replacement by Inert Gas, 19754.
- Laille, J.P., J.E. Molinard, A Wents (1988): Inert Gas Injection as Part of the Cushion of Underground Storage of Saint-Clair-Sure-Epte, France, SPE 17740.

# 5 Signature

Utrecht, 1 August 2008

TNO Built Environment and Geosciences

O.A. Abbink Head of department L.G.H. van der Meer, A. Obdam Author