

**Energiministeriets
Forskningsudvalg for
produktion og fordeling af
el og varme**

Deponering af CO₂ i under-
grunden belyst ud fra Linde-
boringen

ENS. J. Nr. 1323/93-0017

Fritz Lyngsie Jacobsen, Dan Olsen,
Karen Hvid Ipsen, Henrik Kruse og
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Deponering af CO₂ i Undergrunden

Dette projekt, "Deponering af CO₂ i undergrunden", er udført som et samarbejde mellem ELSAMPROJEKT A/S og Danmarks og Grønlands Geologiske Undersøgelse (GEUS) for at demonstrere, at det er muligt at bygge et sådant depot i Danmark. Der er hensigten at vise, der er muligt at udføre et sådant på et teknisk forsvarligt grundlag.

Linde strukturen beliggende i Nordjylland, NV for Holstebro, blev valgt som demonstrations lokalitet. Den er godt beskrevet og anført med en omhyggeligt udført moderne boring, hvorfra der findes godt bevarede materialer. Der er tidligere udført lignende, men mere bredt dækkende projekter af denne type. Dette projekt er bemærkelsesværdigt ved, at det giver en specifik beskrivelse af et projekt, der kan bruges som grundlag for et forsøgsanlæg, hvis det er ønskeligt. Desuden vurderes projektet på forsøgsmæssigt grundlag og med anvendelsen af kalk som en betydningsfuld sekundær barriere.

Resultaterne af projektet er blevet forelagt internationalt ved konferencen "Greenhouse Gases: Mitigation Options" den 22-25 august 1995 i London. Titelne på de to foredrag var: H. Kruse, M.E. Tekiela, T. D. Krom og K.H. Ipsen: "Consequences of Transporting CO₂ Waste Gas" og K.H. Ipsen og F.L. Jacobsen: "The Linde Structure, Denmark an Example of a CO₂-Depository with a Secondary Chalk Cap Rock". Foredragene blev vel modtaget og vedlægges i kopi.

En fuldstændig rapportering af projektet findes i Jacobsen, F.L.: "Subsurface disposal of carbon dioxide. The geological description of Linde No. 1" (Geological Survey of Denmark and Greenland. Report 1/96).

Geologisk beskrivelse af Linde nr. 1

Linde strukturen beliggende i det vestlige Jylland, syd for Limfjorden, er valgt som et eksempel på en deponeringsplads for CO₂-gasser. Denne struktur er lille, men giver en god mulighed for at vurdere den som et muligt forsøgsområde. Der er tidligere udført et godt bore- og logningsarbejde på stedet i 1979-1980.

Strukturen er en lille dome på toppen af en snæver salt struktur tæt ved Vejrum saltdomen. Linde boringen, udført i perioden 23. november 1979 til 24. januar 1980, har givet de væsentlige informationer til denne rapport.

Linde-boringens stratigrafi

0 - 168 m:	Kvartær. Glaciale aflejringer af grus, sand og ler.
168 - 397.5 m:	Øvre og mellem Oligocen. Marine ler, almindeligvis med glimmer i top og bund. Små gasmængder til stede.

397.5 - 518.5 m:	Øvre Eocæn. Mergel, gullig til lys olivengrå, marin. Mellem til nedre Eocæn. Overvejende plastisk ler, mørk grønlig grå til brun, marin. Nedre Eocæn. Ler, mørkegrå med lag af vulkansk aske, grå, marin.
518.5 - 717.5 m:	Paleocæn. "Selandian". Ler, mørkegrå og ved bunden af dette afsnit grøn mergel med glaukonit, marin. Danien. Kalk, lysegrå til hvid med flint, marin.
717.5 - 880.5 m:	Øvre Kridt. Maastricht. Kridt, hvidt til rødligt gråt med flint, marin.
880.5 - 905 m:	Campanian. Kalk, hvid, konsolideret, marin.
905 - 1002 m:	Santonian og Coniacian. Kalk, hvid til rødlig grå, hård, marin.
1002 - 1040 m:	Turon. Kalk, hvid til rødlig grå, hård og ved bunden af afsnittet, ler, mergel og skifre, marine.
1040 - 1050 m:	Cenoman. Kalk, rødlig grå, marin.
1050 - 1063.6 m:	Nedre Kridt. Rødby formationen. Ler og mergel, brune, marin.
1063.6 - 1120 m:	Vedsted formationen. Skifre og lersten, mørkegrå, marine.
1120 - ca 1200 m:	Øvre Jura. Bream formationen. 1120 - 1169 m: Frederikshavn member. Sektionen 1120 - 1145 m er sand- og siltsten, lys olivengrå og 1145 - 1169 m er en lersten, mørkegrå. Begge er marine. 1169 - ca 1200 m: Børglum member. Lersten, mørkegrå, marin.
Ca 1200 - 1338 m:	Nedre Jura. Fjerritslev formationen. Lersten som ovenfor.
1338 - 2242.6 m:	Afsnittet er ikke beskrevet i denne rapport.

Deponeringsbjergarten, Frederikshavn member i dybden 1120 - 1145 m består af sand- og siltsten. Tykkelsen af net (brugbart) sand er ca. 3 m. Porøsiteten er ca. 25% med maximum på ca. 30%. Den gennemsnitlige deponeringskapacitet i Linde Strukturen er ca. 455 000 t af CO₂ ved en fyldningsgrad på 2/3 af reservoiret. Ved en net sand på minimum 2 m og maximum 5 m og 30% porøsitet samt total fyldning vil depotet kunne rumme mellem 546 000 t og 1365 000 t CO₂-gas.

Lagene over reservoiret skal fungere som en tæt dækbjergart. Den primære dækbjergart vil være ler sektionen på 56 m. Dette anslås at være en tæt bjergart hvor der er målt meget lave permeabilitetsværdier. Som sekundær barriere vil den ca. 400 m tykke, højereliggende, kalk sekvens fungere. Dette vil fremgå af de følgende rapporter.

CO₂ strømningforsøg på kalkprøver fra boringen Linde nr. 1.

Kerneprøver fra kalksekvensen i Linde boringen blev anvendt for at undersøge ændringerne i bjergarten når den blev udsat for påvirkning af CO₂. Ved den undersøgelse forventedes det, at ændringer i kalken ved deponering af CO₂, der eventuelt trænger frem til kalken, kan forudsiges.

Fra to kerner fra Linde nr. 1 boringen, kerne nr. 6 (boret dybde 881 - 887.2 m og optaget kerne 38.1%) og kerne nr. 7 (boret dybde 962.2 - 970.0 m og optaget kerne 93.5%) blev udtaget prøver til laboratorieundersøgelser under reservoirbetingelser. Der blev til eksperimenterne udtaget plugs på 1.5" i diameter. Disse prøver blev undersøgt for permeabilitet for gas og væske samt analyseret for porøsitet, kernevægtfylde, kerneoverflade, topografi og porevæskes forandring når de blev udsat for CO₂. I alt blev 5 forsøg under reservoirbetingelser udført.

Ved indflydelse af CO₂ findes det, at gaspermeabiliteten stiger med et statistisk signifikant beløb. Væskepermeabiliteten blev fundet til at forblive uændret eller til at aftage. I nogle af prøverne var faldet i væskepermeabiliteten statistisk signifikant. Hverken porøsitet eller kernevægtfylden viste nogen væsentlige ændringer ved påvirkning af CO₂.

Stigningen i gaspermeabiliteten viser, at der sker en opløsning af materiale under CO₂-forsøget. Massebalance betragtninger og den uvæsentlige ændring af porøsiteten udelader muligheden af en større opløsning af prøven. Det synes sandsynligt, at den tiltagen i permeabiliteten for gas skyldes en foretrukket opløsning i zoner med høj permeabilitet. Dette bekræftes af svage tegn på opløsning ved analyse af SEM-billederne optaget af prøver udtaget ved tilførselsenden af en CO₂ forsøgsprøve. SEM-optagelser fra den centrale del af en prøve viser ingen tegn på opløsning. Opløsning ved tilførselsenden af prøven kan muligvis have fundet sted ved CO₂ injektionen i prøven, hvilket giver høje strømningshastigheder ved CO₂ tilførselsventilen. Ved analog betragtninger til mulige fremtidige CO₂ injektioner i kalksektioner må man forvente en tiltagende kalk opløsning ved høj strømningshastighed, dvs. i nærheden af deponeringsbrønden.

Den fundne aftagen i væskepermeabiliteten ved CO₂ forsøget er forsøgsvis forklaret som blokering af porerne af småpartikler, der er blevet frigjort ved opløsningen under CO₂-forsøget. Sådanne småpartikler blev konstateret ved CO₂-forsøgene fra alle prøver. Den efterfølgende tiltagen af gaspermeabiliteten er forsøgt forklaret ved udskylning af småpartikler under rensningen før den endelige måling af gaspermeabilitet.

Under CO₂ strømningsforsøget blev der med mellemrum udtaget prøver til kemisk analyse. Disse analyser viser forandringerne i den kemiske sammensætning, der finder sted i porerne på prøverne under CO₂ belastningen. Brugen af disse resultater i forbindelse med den termodynamiske modelanalyse og dens konklusion er beskrevet i næste afsnit.

Termodynamik og kinetik af kalk-vand-CO₂ systemet

Denne del af rapporten indeholder en kort termodynamisk beskrivelse af gassen, salt formationsvand og bjergarten ved CO₂-injektionen i et underjordisk lager. Som i de andre dele af rapporten er Linde Strukturen i det vestlige Jylland valgt som model.

CO₂ vil ved reservoirforhold (140 Bar og 50°C) være en superkritisk fluid. Den er ikke blandbar med vand, men Linde saltvandet vil være i stand til at opløse lidt mere en 3 vægt-% CO₂.

I et dybt underjordisk reservoir vil den opløste CO₂ danne kulsyre og resultere i en lavere pH. Dette resulterer i opløsning af karbonat mineralerne. Den sekundære cap rock, som beskrevet tidligere, i Linde strukturen består af kalk og kridt, som begge kan udsættes for et kemisk angreb af en sur opløsning. Imidlertid viser den termodynamiske ligevægts model, at kun en mindre del af kalken opløses af den CO₂-holdige opløsning. Dette giver ingen væsentlig risiko for en svækkelse af cap rock.

Kalkens opløsning kinetik i forsøgsarbejdet anses for at være diffusionskontrolleret og temmelig langsom. Af den grund er den kemiske ligevægt ikke blevet nået i nogen af de udførte forsøg.

Konsekvens beregning af lækager på en CO₂ gasledning

I denne del af rapporten er den økonomiske og miljøtekniske konsekvens af transport af CO₂ i en trykrørledning på 30 km blevet undersøgt. Denne del af rapporten beskæftiger sig med transporten af CO₂ fra brændingsanlægget til deponeringslokaliteten.

To grundlæggende lækagetyper er blevet modelleret ved brug af gasdispersions modellen DEGADIS+: Et konstant udslip som følge af et hul på rørledningen og en øjeblikkeligt dannet gassky i tilfælde af sprængning af rørledningen.

Beregningerne viser, at det værst tænkelige uheld sker ved sprængning af gasledningen. Der er udført sikkerhedsberegninger ved at bestemme CO₂-koncentrationen i luften for afstande på 5, 10, 15 og 30 km mellem sikkerhedsventilerne. Disse ventiler bruges for at reducere udslippets størrelse fra gasledningen og dermed reducere risikoen.

Indåndingen af 50 000 ppm CO₂ i 1 minut er den kritiske værdi ved maximum sikkerhedsbelastning, da uønskede helbredspåvirkningen finder sted over denne grænse. Sikkerhedsafstanden er mellem 150 og 750 m på begge sider af rørledningen, afhængig af afstanden mellem sikkerhedsventilerne og gas-væske-tilstanden af CO₂-gassen. Den aktuelle sikkerhedsafstand til gasledningen vil såfremt den bliver bygget, derfor afhænge af disse faktorer.

Specielle forhold, som lavninger i terrænet, vejrforhold eller tæt beplantede områder vil ændre sikkerhedsafstandene. Dette vil ske både med forøgelse og reduktion af dens forhold til et eventuel gasudslip. Disse forhold vil blive medtaget ved planlægningen af rørledningens placering.

THE LINDE STRUCTURE, DENMARK AN EXAMPLE OF A CO₂ - DEPOSITORY WITH A SECONDARY CHALK CAP ROCK

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Abstract - The Danish Linde Structure is being investigated with respect to be used as a depository of CO₂. The structure has been drilled with a comprehensive coring and logging program thus making the structure suitable to use as a model structure. The reservoir rock is sand, while the primary cap rock is claystone, with chalk as a secondary cap rock. In the case of the Linde reservoir, when carbonic acid may react with the calcite secondary cap rock, or with carbonates cementing the reservoir sandstone, the gas/brine/rock chemistry is also extremely important. Dissolution and weakening of the cap rock may put an effective stop to the utilization of an otherwise interesting formation for CO₂ storage.

I. INTRODUCTION

In a presentation given by Thomas D. Krom [1-2] in Oxford, U.K. and in Essen, Germany in the Spring of 1993, the possibilities of construction of a CO₂ - depository were discussed. A number of structures large enough to be used as depository sites were drilled for oil exploration in the 1950'es and were logged using the methodology of that time. In 1979-80 ELSAM drilled a well on the small Linde structure and carried out high quality logging and a extensive coring program. The well provides a good example of a possible depository site, a comprising sandstone depository, with a claystone primary cap rock and a secondary chalk cap rock.

2. GEOLOGICAL SETTING

The Linde structure is small, Fig. 1 [3] resting upon a small pillow of Zechstein salt at the base. Movements of salt and the initial formation of the pillow probably occurred in late Triassic to the Jurassic time. However, only a small salt pillow was formed due to the influence of the neighbouring Vejrum Structure which used nearly all of the salt. Later intermittent movement has occurred on the structure but only in a small scale. The resulting domal shaped structure is very regular and provides good possibilities for studying a test reservoir. The structure is demonstrated on a profile (Fig. 2) close to direction E-W and including the Vejrum Salt dome. The Linde-1 well is situated off-center. In connection with this publication a schematic description is given [4,5] but only for the section above 1338 meters, which in this case includes

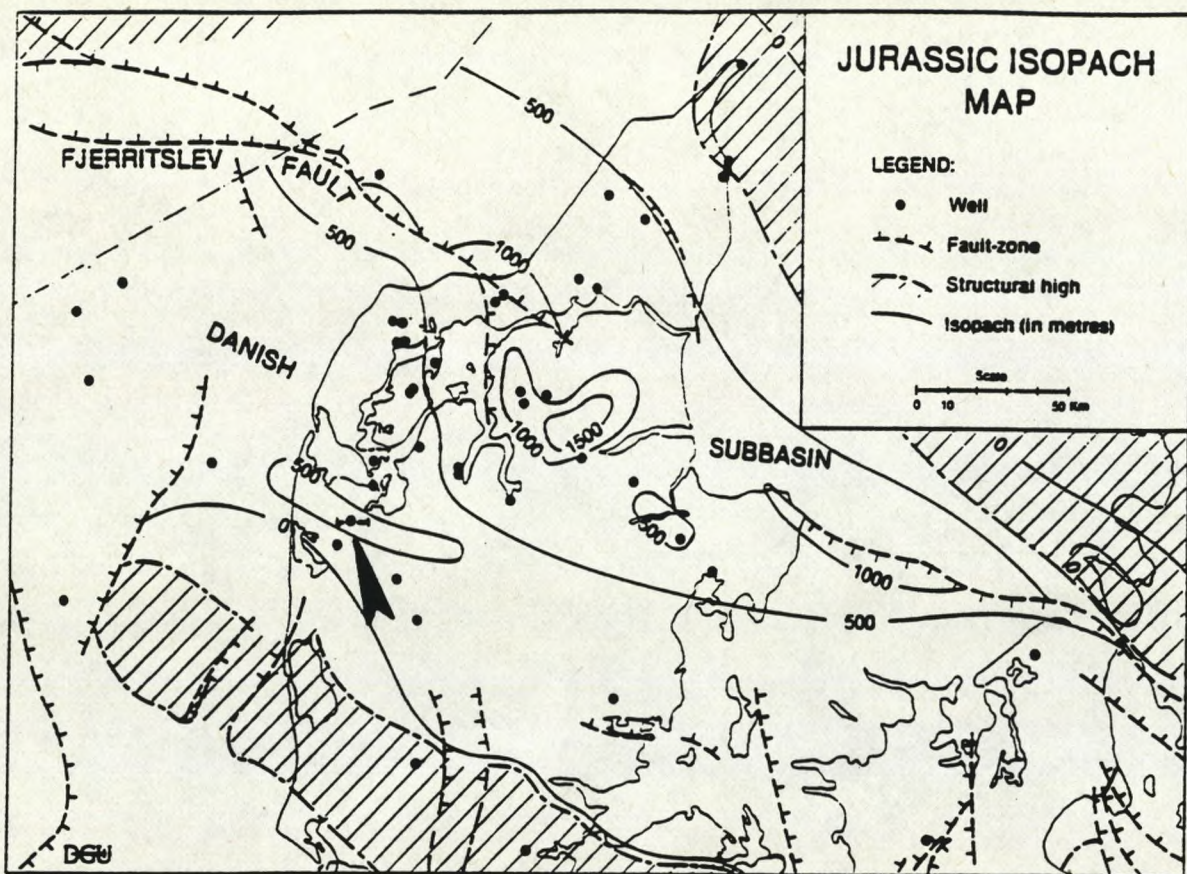


Fig. 1. Generalized isopach map of the Jurassic sequence in the Danish Subbasin [3]. Well locations are indicated. Linde 1 well is indicated by an arrow, as well as location of profile in Fig. 2.

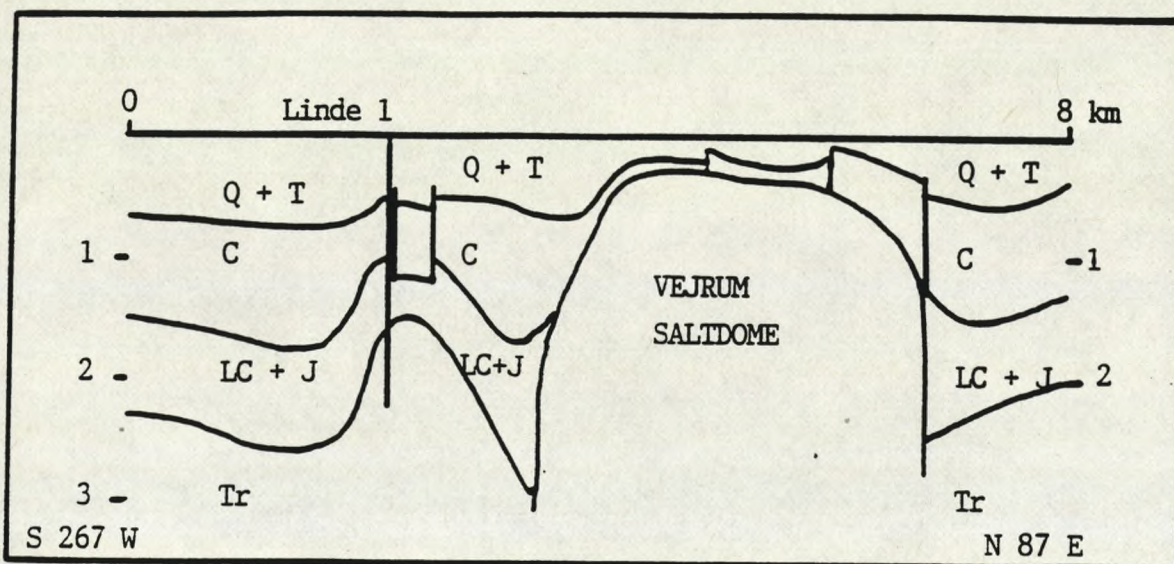


Fig. 2. Schematic section of the Linde structure and the Vejrum salt dome. Q+T: Quaternary and Tertiary rocks, C: Upper Cretaceous rocks, LC+J: Lower Cretaceous and Jurassic Rocks and Tr: Triassic rocks.

the max. depository depth. Location of the profile is demonstrated on Fig. 1 and depths of the rocks are exemplified below.

3. LITHOLOGICAL DESCRIPTION

Description of the drilled rocks are given below. All depths are given in meters below surface.

- 0 - 168 Quaternary. Glacial deposits of clays, sands and gravel. All the rocks are unconsolidated.
- 168 - 397.5 Oligocene. 168-277: Marine, micaceous clays, brownish black to black with a decreasing content of clays with depth. 277 - 370.5: Branden Formation. Clays, brownish black at top to dark greenish grey and olive grey to dark greenish grey and to light greenish grey and light sandy in the lower 20 meters. 370.5 - 389: Hvornum Member. Clauconitic clay olive black to olive grey. All the sections above are Upper Oligocene. 389 - 397.5: Viborg Formation, Middle Oligocene. Clay, olive grey to greenish grey with glauconite.
- 397.5- 518.5 Eocene. 397.5 - 440: Soevind Formation, Upper Eocene. Marl, yellowish grey to light olive grey. 440 - 489: Lillebelt and Roesnaes Formation Middle-Lower Eocene. Clays, varicoloured, dark greenish grey and moderately brown. 489 - 518.5: Lower Eocene. Clay, dark grey to greyish black with volcanic, ash beds, 0.5 to 11.0 cm thick. All Eocene beds are marine.
- 518.5- 717.5 Paleocene. 518.5 - 563.5: Selandian Formation. Clay, dark grey to medium dark grey at bottom of a section. The basal part is developed as marl. 563.5 - 717.5. Darian Formation. Chalk to Calcisiltite, medium light grey, light grey, white to pinkish grey with little clay decreasing towards bottom. Flint is found in various amounts. All the rocks are marine.
- 717.5- 1120 Cretaceous. (717.5 - 1050 Upper Cretaceous, and 1050 - 1120 Lower Cretaceous).
717.5 - 880.5: Maastrichtian chalk, very soft to soft, unconsolidated to consolidated, pinkish grey to white. Flint, black to light grey occur occasionally from top of the section to 770 m. 880.5 - 905: Campanian? chalk, white, medium hard, consolidated, common fractures. 905 - 1002: Santonian and Coniacian? chalk, white to pinkish grey, medium hard to hard, slightly porous to tight, fractured. 1002 - 1040: Turonian chalk, white to pinkish grey with flint, bluish white. 1034 - 1038: Clay and marl, slightly silty, light to dark greenish grey. 1038 - 1040: Shale, dark grey, slightly silty. 1040 - 1050: Cenomanian chalk, pinkish grey with trace muscovite, medium hard, consolidated and tight. Some hairline fractures and interbedded with clay, medium grey. 1050 - 1063.6: Roedby Formation, Lower Cretaceous. Clay and marl, light brown, moderately brown to yellowish brown slightly silty. 1063.6 - 1120: Vedsted Formation. Shale and claystone, dark grey to greyish black and olive grey, slightly silty, common fractures with slickensides. All beds are marine.
- 1120 - 1338 Jurassic. (1120 - approx. 1200 Upper Jurassic, and approx. 1200 - 1338 Lower Jurassic).
1120 - 1169. Bream Formation, Frederikshavn member, Upper Jurassic. 1120 - 1145: Sand and siltstone, pale olive to light olive grey with 85-90% quartz, angular to subangular. Slightly consolidated with a porosity 20-25%. 1145 - 1169: Siltstone and claystone, medium grey to medium light olive grey, micaceous and with microlignite. 1169 - approx. 1200: Bream Formation, Boerglum Member. Claystone, greyish black to medium light grey, silty, micaceous with trace of pyrite and microlignite. Thin dispersed beds of

dolomite/calcite. Approx 1200 - 1338: Fjerritslev Formation. Claystone, as above. All beds are marine.

Below the depth 1338 to the total depth of 2243 metres, the formations in the well are Triassic sandstones, claystones and salt.

The reservoir rock, the Frederikshavn Member, located at the depth 1120 - 1145 metres comprises sand and siltstone. The sand is well known in Northern Jutland, the upper 2 to 3 metres often developed as a coarser sand. The porosity is 20-25% and with quarts as the major mineral. The section above 1034 - 1120 m. is the cap rock section with clay as the dominating rock forming mineral and with minor beds of marl as well as beds with a varying content of silt. A seal strength test yielded very low permeability.

Above the clay section is very thick (400 + m), and laterally extensive calcareous formation which is believed to act as a secondary cap rock. This is discussed later in the paper.

4. PHYSICAL ASPECTS

Carbon dioxide has a critical pressure of 73.8 bar and a critical temperature of 304.1 K. At Linde reservoir conditions, which are approximately 140 bar, 50°C, CO₂ exists as a supercritical fluid, that is, it is neither a gas nor a liquid, but possesses some characteristics of both: Like a gas, it is compressible and will fill its container, but the density is liquid-like [6].

Supercritical CO₂ fluid is immiscible with water, however water will dissolve small amounts of both subcritical CO₂-gas as well as the supercritical fluid. Typically, the solubility of subcritical CO₂-gas in fresh water is less than 6% by weight [7]. The solubility of a gas in a liquid is generally a strong function of pressure, and to a lesser degree, of temperature and chemical composition; increasing temperature and salinity will lower the solubility. CO₂-solubility in water and brine is suggested calculated from the Krichevsky-Ilinskaya equation [8], [9], rather than the simple Henry's constant model, since this will take into account the change in CO₂ activity coefficient as a function of composition. Based on this, the amount of CO₂ soluble in pure water, and in brines with different total dissolved solids content has been calculated, and is graphed in Figure 1. The solubility of CO₂ in water and brine increases significantly from atmospheric pressure up to approx. 80 bars, above which practically no more dissolution will occur, and a strong salting-out effect on CO₂ solubility in brine is seen.

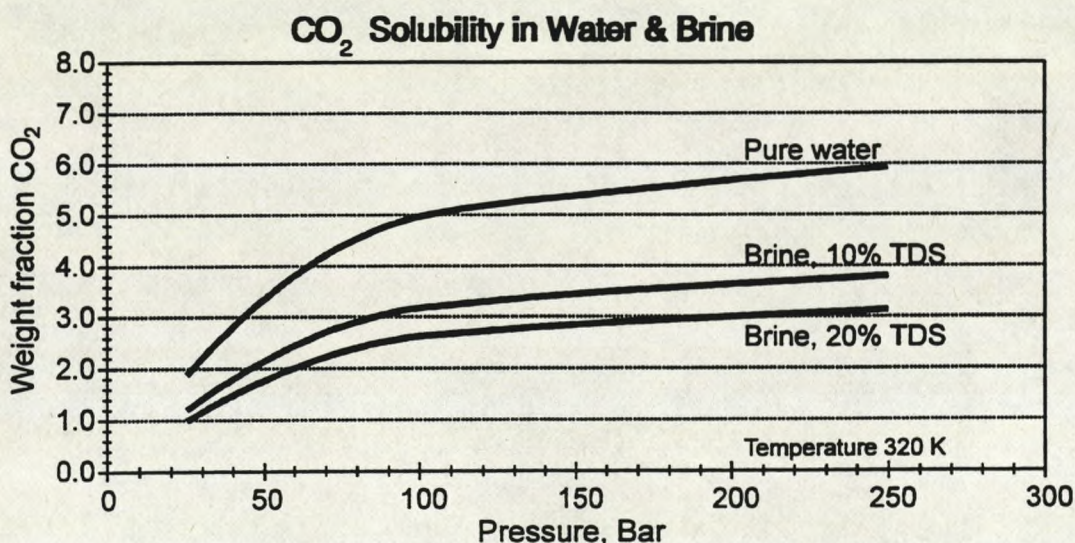


Fig. 3. CO₂ solubility in water and brine with 10-20% Total Dissolved Solids.

Due to the relatively low solubility of CO₂ in water, the viscosity of the brine is assumed to be almost independent of carbon dioxide saturation, but a slight increase in viscosity may be found for water fully saturated with carbon dioxide [7]. The CO₂ fluid viscosity is 52 micropoise at reservoir conditions, but is expected to vary within the 30-70 micropoise range, sensitive to both variations in temperature and pressure [10].

The density of carbon dioxide and water systems in equilibrium is a weak linear function of pressure at constant temperature, but the effect of CO₂ dissolution will be marginal compared to the effect of the salt content. When CO₂ goes into solution, a slight amount of brine swelling may be expected between 2 and 7% [7].

5. CHEMICAL ASPECTS

The introduction of a chemical species, such as CO₂, into a ground water system in thermodynamic equilibrium will create disequilibrium. The ground water system will respond to this by distributing the new species between the various phases of the system, striving to attain equilibrium anew. Thermodynamic equilibrium exists between the brine sampled at the Linde well, and calcite. The injection and subsequent dissolution of CO₂ into the brine, forming large amounts of carbonic acid, will cause calcite to dissolve until equilibrium is once again attained at the actual carbon dioxide partial pressure.

The dissolution of calcite has been calculated using a computer model, PHRQPITZ from the U. S. Geological Survey [11], [12], which is capable of performing geochemical calculations in brines and other electrolyte solutions to high concentrations using the Pitzer virial-coefficient approach for activity-coefficient corrections.

The Linde brine is an intermediate salinity brine, the chemical analysis of which is given in table 1. Calcite dissolution in the Linde brine as a function of CO₂ partial pressure is graphed in figure 4.

Table 1. Chemical composition of formation brine, [mg/l].

Element	Linde formation brine
Na ⁺	44,000
K ⁺	320
Ca ²⁺	1,700
Mg ²⁺	870
Cl ⁻	70,500
HCO ₃ ⁻	123
SUM	117,400

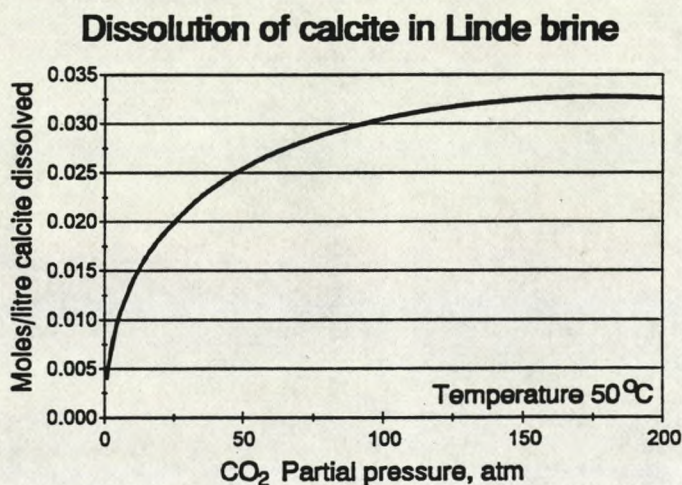
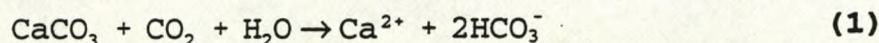


Fig. 4. Calcite dissolution.

The net dissolution of calcite is as follows,



however, calcite dissolution is the product of several chemical reactions, any of which may be the rate controlling step, depending on the chemical environment and the proximity to equilibrium [13].

Precipitation/dissolution reactions are quite complex. Several mechanisms can be identified, may control the rate of transfer of reactants between the solid and the solution. Transport mechanisms such as diffusion of reactants to and from the solid, and surface reactions, such as adsorption and desorption reactions at the solid surface. Generally, surface reactions are most important near equilibrium, while transport mechanisms tend to control the reaction rate as the disequilibrium increases. Laboratory investigations of interactions between brine, CO₂, and core samples from the Linde well is currently well under way, and will be reported subsequently.

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CALCULATING THE CONSEQUENCES OF A CO₂-PIPELINE RUPTURE

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Abstract - Focusing on the costs and consequences of large-scale CO₂ transport in steel pipes, transport in liquid form is superior to gaseous form. A modelling study was performed on the basis of a 350 MWel coal-fired power plant, with CO₂ removal amounting to 70 kg CO₂ per sec for disposal. An aquifer disposal site at an injection pressure of 200 bar and a transport distance of 30 km is the study baseline. Both economic evaluations and a risk assessment of a pipe rupture showed that liquid transport of CO₂ from the power plant to the injection site was optimal at a pressure of 60 bar.

1. INTRODUCTION

Extracting CO₂ from power plant flue gas is one option for reducing the Danish emissions of CO₂ - thus contributing to mitigate the accumulation of greenhouse gasses in the atmosphere. This paper is the result of a case study of the economic costs and risk assessment of an underground pipeline.

The CO₂-gas will be transported from a power plant in a pressurized buried pipeline to a disposal site either as a gas or as a liquid depending on the temperature and pressure in the pipe. This paper describes an investigation of the optimum conditions for this transport (pressure, pipe diameter, etc.), taking into account the economic consequences and health hazards incurred by a pipeline rupture. The economic assessments are estimates intended to show the difference in construction and operating costs for transport in either gaseous or liquid form. Calculation of the CO₂ concentrations in the vicinity of the pipe in case of a rupture illustrates the consequences to human health. The investigation has determined safety distances from the pipeline which will ensure that the CO₂-concentration beyond these distances does not imply serious health hazards to the neighbouring population.

A dense gas model, the US-EPA DEGADIS+ [1], has been used to estimate the transport and dispersion of the CO₂-gas in the atmosphere. Maximum possible emissions have been assumed in the calculation of the initial CO₂ cloud released by an accidental rupture, the calculations thus illustrate the consequences of a worst case emission from the transmission system. The health risk is evaluated by comparing the calculated concentrations with a human tolerance limit for CO₂ where the concentrations and exposure time are of decisive importance.

2. TRANSMISSION SYSTEM

Preliminary investigations to locate CO₂ disposal sites have concluded that an inland disposal site relatively close to the CO₂ generating plant is the most likely solution for Danish conditions [2]. Thus the pipeline modelled in the calculations was 30 km long and transported a CO₂ flow of 250 ton/h over a period of 30 years.

When compressing CO₂ it has to be taken into account that the gas will liquify at a given pressure and temperature. Two phase flow in the pipeline has been disregarded as being difficult to control, and therefore the costs of transporting the CO₂ as either a gas or a liquid were examined. Following the extraction process and before entering the pipeline, the CO₂ undergoes pressurisation and to some extent temporary storage to minimize flow fluctuations in the pipe. At other industrial uses of CO₂ this storage facility is typically pressurised to 15 bar. The CO₂ leaving this system is the reference point of the following estimate of energy use and economic evaluations. In both cases the CO₂ has to be kept within a certain pressure and temperature range to ensure that phase transmission does not occur in the pipe.

Taking into account the price of steel pipes and the energy loss because of internal friction in the pipeline it is possible to estimate the unit cost of CO₂ transport at various transport pressures and diameters in either liquid or gaseous form. Hence it was found that a pipe diameter of 0.65 m for gaseous transport and 0.40 m for liquid transport (table 1) would be the best options as they give the lowest total costs of energy consumption and pipe construction costs.

The cost of steel pipes, pipeline construction as well as auxiliary equipment - pumps, compressors and valves - has been based on supplier information and written off over a 10-year period with an annual interest of 5%. Costs of transport and pressurization to injection pressure (200 bar) include the energy required for the transport process at the production price of energy which is assumed to be constant at 220 DKK/MWh. Surveillance and maintenance have been calculated as a percentage of the total construction costs for the pipe system.

The energy analysis shows that the pressure loss in both cases is of minor importance due to the relatively short transport distance, see table 1. Although the energy required for initial liquefaction is higher, it is compensated for by the lower friction loss during transportation and a lower demand for energy to reach injection pressure thus resulting in an overall lower energy demand for liquid transport.

Table 1. Comparison of costs for gaseous and liquid transport, 30-year period.

		Gaseous	Liquid
Basic assumptions			
Transport pressure	Bar	35	60
Internal diameter	m	0.65	0.40
Soil temperature	°C	0-7	
Injection pressure	bar	200	
Pressure loss (friction)	bar	3-4	2
Costs			
Pipeline and construction	DKK/ton	2.4	2.1
Auxiliary equipment	DKK/ton	1.1	1.0
Transport and injection	DKK/ton	5.7	4.1
Surveillance and maintenance	DKK/ton	2.4	2.1
Total costs	DKK/ton	11.6	9.2

The transport costs of one ton of CO₂, summarized in table 1, speak in favour of liquid transport. The total costs must, however, be evaluated together with the consequences of a pipeline rupture as the environmental impact is likely to increase as the transport pressure in the pipeline increases. Guidelines to be followed for such a piping system [3] suggest that there shall be no more than 30 km between two check valves which in this case study means that the pipeline may be constructed without check valves at all. Due to the large amount of CO₂ transported in this project, it is preferred to place check valves at shorter intervals given the potential hazards for the neighbouring population. In the calculations of the consequences of a pipeline rupture, a calculation was included where the distance between the valves was as short as 5 km.

3. CONSEQUENCES OF RUPTURE

Threshold values.

A threshold value for CO₂ was used for determining the safety distance to the pipe and has been evaluated on the basis of the physiological impact of CO₂ at elevated concentrations [4,5]. Under normal pressure and temperature CO₂ is a colourless and odourless gas even at high concentrations.

In concentrations of approximately 5% (50,000 ppm) the gas causes an increase in respiration along with a number of other symptoms, such as headache, breathing difficulty, palpitation, dizziness and weakness. Consequently, 5% concentrations are assumed to be the lower limit for adverse human effects. Above 10 vol% (100,000 ppm) the gas causes instantaneous unconsciousness and will be lethal unless the victim is quickly removed. Consequently, 10% can be considered as the upper limit for survival. If the concentration is 20% the gas is instantaneously fatal [4,5].

Immediately after release the concentration will be highest in the centre of the gas cloud with falling gradients to the sides because of intensive mixing with ambient air. Due to the wind the plume is dispersed the most at the rear edge, whereas high concentration gradients persist at the front edge of the plume. The criterion for a safe distance to the pipeline is based on the time dependence concentration profile shown in figure 1, where the lower limit (50,000 ppm) as well as the time of exposure for this concentration are emphasized. During the time of exposure concentrations higher than 50,000 ppm will occur. In order to prevent serious adverse effects the maximum exposure time is not to exceed a defined maximum of 1 minute for concentrations higher than 50,000 ppm, regardless of the distance from the pipeline

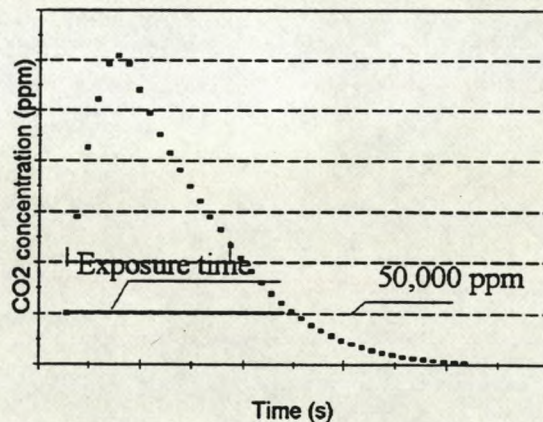


Fig. 1 Example of the change in concentration with time at a given receptor, for instantaneous CO₂ release.

Defining source strength.

The emission from the pipeline has been determined on the basis of physical and thermodynamic calculations of the gas/liquid as it escapes the pressurised pipeline. As a rupture is in effect a large leak, the period of time taken for a large amount of CO₂ to be discharged would be short, i.e. adiabatic expansion of the CO₂ occurs. In the modelling studies a worst-case emission is assumed, defined by a complete pipe rupture right between two check valves causing outflow from two pipe ends.

If a rupture occurs when transported in gaseous form, the CO₂ will initially escape by pushing the overlying soil upwards at an explosion-like speed. The cavity, which is excavated from the expansion of the gas, will immediately be filled with atmospheric air thus contributing to initial mixing of gas and air. The expansion of CO₂ will occur at sonic speed and will continue to do so until the pressure ratio between the CO₂ and the ambient air is down to about 1.9. The temperature of the escaping gas will fall drastically as a result of the expansion and a cloud of cold gas will form which is then dispersed and slowly mixed with ambient air. The rate of emptying the pipeline will

be controlled by the cross-section area of the pipe and the speed of the escaping gas, which again will be controlled by the difference in pressure between the pipeline and the atmosphere. Therefore the mass flow will be largest immediately after the accident with an exponential decay in time.

Transported in liquid form the CO₂ escape scenario is not very different. Initially there will be a large pressure drop in the pipeline as the liquid is virtually incompressible, the pressure will fall until the liquid becomes a mixture of saturated vapour/liquid. In the vicinity of the rupture, liquid CO₂ will escape and immediately vaporize and expand, some of the liquid will even sublimate into dry ice, which will precipitate onto the ground. This will take place over a very short period of time. After the pressure fall the flow profile of the escaping gas will almost be as described for gaseous CO₂ transport.

Whether the pipeline segment is 30 km or only 5 km, the segment is equipped with check valves at both ends. Along the pipe sensor devices are installed registering the rupture, which will cause actuators to seal the pipe and throttle down the compressors. Until the valves are completely shut, gas/liquid will continue to flow into the damaged segment. This flow has been disregarded in the calculations because it will have no influence on the amount included in the initial puff. However, it will increase the total amount released from the segment.

The course of the outflow has been modelled on the basis of a relatively simple equation [6,7].

$$Q_m = A \cdot c_1 \sqrt{p_t \cdot \rho_t \cdot c_2}$$

- Q_m = Outflow (kg/sec) (1)
 A = Cross sectional area (m²)
 P_t = Time dependent pressure in pipe (bar)
 ρ_t = Time dependent density in pipe (kg/m³)
 c_2 = Material constant (-)
 c_1 = Coefficient of discharge (-)

The principle is to calculate the amount of CO₂ escaping from the pipe during a time period dt and subsequently determine the values of the physical basic parameters in the pipe. The method is of an indicative nature as conditions in the pipe will not change instantaneously. In reality the outflow will be slightly delayed.

Fig. 2 gives an example of a CO₂ release time sequence on the basis of a 30 km pipeline with a diameter of 0.65 m. It can be seen that with two ends of the pipe exposed (worst case) the outflow will be practically exponential being halved within 54 seconds, meaning the pipe will be 90% empty within 163 seconds.

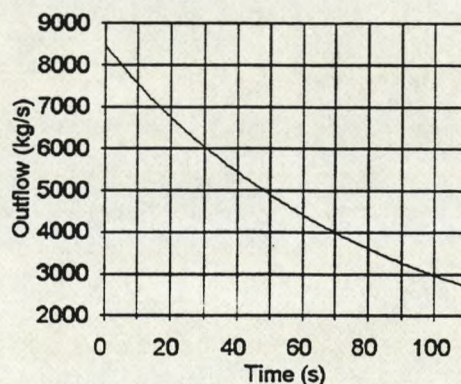


Fig. 2 Modelling gas outflow from 30 km pipe segment as a function of time

Dense gas modelling.

The DEGADIS+ model [1] is capable of calculating the effect of a continuous release (steady-state) or the effect of an instantaneously released gas cloud. However, the time dependent exponential outflow cannot be handled by the model and had to be converted into a puff (instantaneous) release. The amount of gas contained in a puff was determined by using the decay period ($T_{1/2}$), i.e. the time it takes for the outflow per time unit to be halved. This method assumes that the outflow of gas at the highest rate will be considered to be a puff. Using this method it is possible to treat the outflow from pipeline segments of varying length uniformly.

During the period equal to $T_{1/2}$ the gas will be transported a certain distance downwind. Farther away than the distance travelled during $T_{1/2}$ the CO_2 plume can be considered as a puff with a given initial size. Therefore, the dispersion of the discharge will be modelled as a puff for the distances beyond the radius of the area initially impacted by the CO_2 cloud. This radius is $T_{1/2}$ times the horizontal component of the wind, which in this case study has been chosen to be 5 m/sec. The gas discharged after $T_{1/2}$ is ignored in the calculations.

The amount of gas released in both cases is listed in table 2. The outflow from the pipe with liquified CO_2 is smaller than the gaseous CO_2 for two reasons. First the liquified CO_2 is transported in a pipe with a smaller diameter. From equation (1) the outflow is dependent on the cross-section area of the pipe and therefore the square of the diameter. Secondly the pressure drops from liquid state to saturated vapour which at 7°C equals a drop from 60 bar to 41.5 bar, making the outflow smaller than could be expected. The mass of the initial outflow of liquid CO_2 , causing the pressure drop, is included in the instantaneous release.

Model parameters.

As the DEGADIS+ model assumes constant meteorological parameters throughout the calculation period, it was assumed that stable meteorological conditions exist with an average ambient temperature of 20°C and surface temperature of 15°C . Adiabatic expansion of the released CO_2 will cause the temperature to decrease to -56°C (triple point), but as the outflow is modelled as a puff, an average temperature of -20°C has been used assuming some mixing with ambient air. Flat terrain has been assumed because the DEGADIS+ model is not capable of including terrain variations.

Affected area.

The results from the dispersion modelling is listed in table 2 together with some of the important model basis.

Table 2. Parameters and results from dense gas modelling.

		Gas		Liquid	
		30	5	30	5
Distance between valves	km	30	5	30	5
Period of decay	sec	54	10	52	10
Amount of CO_2 in puff	ton	346	63	229	42
Max. distance to threshold value	m	750	250	600	150

Table 2 shows that the health hazards are less when the CO_2 is transported as a liquid compared to gaseous transport because of the smaller distance to areas with CO_2 concentrations below the threshold value. Not surprisingly, there is a clear difference between the values of a 5 and a 30 km pipeline segment, the shorter the pipeline segment, the lower the CO_2 emission and safety distance.

4. SUMMARY

Two separate issues have been addressed: A cost estimate and a model of the outflow and dispersion resulting from a pipeline rupture. Both parts point to liquid transport as being preferable both in terms of economy and safety.

According to the economic estimates even the higher initial investment incurred by liquefaction of the CO₂-gas will be offset by lower operating costs (energy consumption) throughout the lifetime of the pipeline. Due to its low operating costs liquid transport is to be preferred.

The model study of the pipeline rupture is made up of two parts, the first assessing the outflow from the pipeline, and the second calculating the dispersion of the CO₂ plume. However, this cannot be performed without difficulties as the outflow from the pipeline is neither instantaneous nor continuous. A method describing the course of the outflow has been developed and was used to determine the size of an instantaneous puff, assuming maximum outflow from the pipeline with two ends emitting gas simultaneously. In the calculations a pressure of 35 bar was assumed for gaseous transport and 60 bar for liquid transport, both determined by the equation of state of CO₂.

The results of the model calculations for 30 km segments point at safety distances up to 750 m for gaseous transport and 600 m for liquid transport. The difference in distance is primarily caused by the differences in pipe diameters, which are highly decisive to the outflow. The safety distance is defined as the distance at which concentrations of min. 5% CO₂ will occur for 60 seconds.

One part of the survey was to examine the consequences inherent in having shorter distance between sensor and safety installations. The study shows a clear consequence if the ruptured piece of pipeline is isolated. In the model study 5 km segments were used, which would make the installation somewhat more expensive, but also be a great improvement in terms of safety.

Safety distances up to 750 m are difficult to realize in densely populated areas such as Western Europe. If a high safety rating is desired, the passive safety factors, such as distance between sensors, safety valves, marking, pipeline thickness, etc. must be increased.

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