

BRITISH GEOLOGICAL SURVEY

Natural Environment Research Council

Fluid Processes Research Group

Technical Report WE/91/20/C

**A Preliminary Feasibility Study
for the Underground Disposal of
Carbon Dioxide in UK.**

D.W. Holliday*, G.M. Williams, S. Holloway*,
D. Savage and M.P. Bannon

*Tectonic and Database Research Group
Fluid Processes Research Group,

British Geological Survey, Keyworth

April 1991

Commercial-In-Confidence

Prepared for:-

British Coal Corporation
Coal Research Establishment
Stoke Orchard
Cheltenham GL52 4RZ

This report has been generated from a scanned image of the document with any blank pages removed at the scanning stage.
Please be aware that the pagination and scales of diagrams or maps in the resulting report may not appear as in the original

CONTENTS

1.	INTRODUCTION	1
2.	CARBON DIOXIDE PRODUCTION RATES	1
3.	CARBON DIOXIDE DISPOSAL UNDERGROUND	2
3.1	General considerations for underground disposal	2
3.2	Pressure - Temperature conditions underground	2
3.3	Carbon dioxide solubility in groundwater	3
3.4	Natural occurrence of carbon dioxide in the geosphere	4
3.5	Potential host formations in the U.K.	5
4.	POTENTIAL PROBLEMS OF UNDERGROUND DISPOSAL	6
4.1	General	6
4.2	Reaction with the host rock	6
4.3	Groundwater pollution	8
4.4	Ground Stability	9
4.5	Microseismic effects	9
4.6	Sterilisation of Earth resources	10
5.	SITE INVESTIGATION FOR SUITABLE FORMATIONS	10
5.1	General considerations	10
5.2	Use of fluid inclusions in CO ₂ reaction studies with the host rock	11
6.	DETAILS OF POTENTIAL U.K. HOST FORMATIONS	12
6.1	Man-made voids	12
6.1.1	Mine Workings	12
6.1.2	Artificial caverns	12
6.2	Aquifers	13
6.2.1	Introduction	13
6.2.2	Pre-Permian aquifers	14
6.2.3	Permo-Triassic aquifers	15
6.2.4	Jurassic-Cretaceous aquifers	16
6.3	Volume considerations	17
7.	CONCLUSIONS	17

8.	RECOMMENDATIONS FOR FURTHER STUDIES	19
9.	REFERENCES	20

LIST OF TABLES

Table 1	Physical properties of carbon dioxide.	3
---------	--	---

LIST OF FIGURES

Figure 1	Variations in pressure and temperature with depth below surface.	23
Figure 2	The phase diagram for carbon dioxide.	24
Figure 3	Minimum overpressure required to liquefy CO ₂ at different reservoir depths.	25
Figure 4	Reduced-variable phase diagram for carbon dioxide.	26
Figure 5	Variation in CO ₂ solubility in water with pressure	27
Figure 6	Solubility of CO ₂ at infinite dilution in NaCl solutions. K _H ^o is in units of fugacity (atm/molality). (From Drummond, 1981).	28

1. INTRODUCTION

The Association of the Coal Producers of the European Community are agreed that immediate action is required to reduce the build up of greenhouse gases in the atmosphere (Harrison, 1990). This is considered necessary even though the effect of these gases on global climate and the human race, are very uncertain mainly because the factors and processes affecting climatic change are poorly understood. Possible action that has been considered to reduce the emission of green house gases include:-

- (a) better efficiency of power generation.
- (b) cessation of CFC production
- (c) prevention of deforestation
- (d) control CO₂ release into the atmosphere by utilisation and disposal elsewhere.

The use of CO₂ as an intermediate feed stock in chemical industries is a possible means of reducing atmospheric emissions, but not all the CO₂ produced could be used in this way. Possible disposal options for the surplus CO₂ are as follows :-

- (1) Underground storage in exhausted oil and gas reservoirs, aquifers or other geological traps.
- (2) Gaseous dispersion at shallow depths in the ocean
- (3) Disposal in the deep ocean

In this report only the geological disposal of CO₂ is considered.

2. CARBON DIOXIDE PRODUCTION RATES

In Britain 82 million tonnes of coal are consumed per year for power production and approximately 180 million tonnes of CO₂ are produced and released into the atmosphere. For disposal underground, the CO₂ will need to be removed from the power stack emission by compressing the gas to a pressure of around 60 bars at ambient temperature (15°C). In these conditions the CO₂ will be a relatively pure liquid although there is some possibility that SO₂ and NO_x may be present in small quantities. In coal gasification power plants which are being considered in the future, potential contaminants will be HCl and H₂S.

3. CARBON DIOXIDE DISPOSAL UNDERGROUND

3.1 General considerations for underground disposal.

The basic concept for underground disposal is that the CO₂ should be contained and confined within a geological host formation and not find its way back to the surface - at least not for a very long time. For disposal to be feasible therefore, a receptor or host formation is required with adequate storage potential. In all cases it is essential that the host formation is capped by a low permeability seal to minimise the escape of the CO₂ and one of the major considerations in choosing a host formation is to determine its storage properties, to consider its confinement and if necessary to estimate the rate at which CO₂ may leak back to the surface. The low permeability seal confining the CO₂ is likely to be strata of dense unfractured rock, clay or shale. It is assumed that over very long periods of geological time the CO₂ will eventually be released either due to erosion of the ground above the host rock formation or as a result of CO₂ migration through existing pathways, or new pathways that may form at some time in the future.

Because of the large rate of production of CO₂ it is assumed that the primary consideration is to dispose of the CO₂ and not to consider retrievability for future use.

3.2 Pressure - Temperature conditions underground

The average geothermal gradient in the UK is about 25-26°C km⁻¹ depth. If it is assumed that the surface temperature is about 10°C then at depths of more than 800-850 m the temperature will be above the critical temperature of CO₂ which is 31.1°C. Above this temperature CO₂ cannot exist as a liquid. The critical pressure of CO₂ is defined as that pressure which is required to liquefy it at its critical temperature. For pure CO₂ this is 7.38 MPa (72.8 atmospheres) and by coincidence this hydrostatic pressure occurs at about the same depth as the critical temperature of CO₂ occurs (Figure 1). The presence of sulphur dioxide, hydrogen sulphide or methane will depress the critical point (Shepherd et al., 1985). Above the critical temperature, CO₂ exists as a supercritical fluid which is a gas-like compressible fluid that takes the shape of, and fills its container. It is not a liquid (an incompressible fluid that takes the shape of the bottom of its container) but has liquid-like densities (0.2 - 0.9 g/ml). Supercritical CO₂ is non-polar, is immiscible in water, and is a very good solvent for organic compounds. Consequently it has been used to "solvent extract" hydrocarbons in enhanced oil recovery operations.

At temperatures below 31.1°C, that is at depths shallower than 800 m below the surface, it may be possible to store CO₂ as a liquid providing the pressure is sufficient. The phase

diagram of CO₂ (Figure 2) shows the phases expected in relation to the temperature and pressure conditions. At depths shallower than 800 m it will be necessary to over-pressure the reservoir or host formation to produce liquid CO₂ (Figure 3). Over-pressuring, may be possible but consideration must be given to the geotechnical problems that may occur particularly in fracturing the rock and reducing the confinement provided by the rocks above the reservoir or host formation. For CO₂ disposal as a liquid at shallow depths it is essential to keep conditions to below the critical temperature of 31.1°C. Since, the temperature margin below the critical temperature will be much less than 20°C it is doubtful whether CO₂ disposal as a liquid will be feasible. CO₂ could however, be stored as a compressed gas at shallow depths, if sufficient storage capacity were available.

The density of CO₂ in relation to temperature and pressure is important in determining the storage potential for CO₂. A reduced-variable phase diagram showing the variation in CO₂ density with pressure and temperature is given in Figure 4 in which the axes (reduced temperature and reduced pressure), are the ratios of the actual pressure or temperature to the critical point pressure or temperature. The critical density is 0.468 g/mL.

Table 1 Physical properties of carbon dioxide

Phase	Density (g/mL)	Viscosity (poise)	Diffusivity (cm ² /s)
gas	0.001	0.00005 - 0.00035	0.1 - 1.0
supercritical fluid	0.2 - 0.9	0.0002 - 0.001	0.00033 - 0.00001
liquid	0.8 - 1.0	0.003 - 0.024	0.000005 - 0.00002

3.3 Carbon dioxide solubility in groundwater

In general, CO₂ is the prevalent carbon gas in the geological environment over a wide range of temperature and redox conditions. In most water-rock systems, CO₂ is the most abundant gas, but rarely exceeds 2 mole percent in solution (Ellis, 1959).

The solubility of CO₂ in water is given in Figure 5. Over the temperature range 0 - 120 °C, the solubilities at pressures below 200 MPa (300 - 700 atmospheres) decreased with increasing temperature. From 30 to 70 MPa (300 - 700 atmospheres) a solubility minimum is observed between 70 -80 °C, with solubilities increasing as temperature increases to 120°C.

Solubility data for carbon dioxide in water and salt solutions at temperatures to 450°C and pressures to 1400 bars have been reviewed by Drummond (1981) who derived a regression equation of the following form to describe its solubility:-

$$\ln KH^{\circ} = A + BT + CX + D/T + E/X + FXT + GX/T + HT/X \quad (1)$$

where KH° = fugacity (atm)/molality
 T = °Kelvin
 X = sodium chloride molality + 1.0

and A-H are regression coefficients as follows:-

A	=	20.244	E	=	0.4445
B	=	-0.016323	F	=	0.0012806
C	=	-1.0312	G	=	255.9
D	=	-3629.7	H	=	-0.001606

Drummond (1981) observed that CO₂ solubility decreases (i.e. K_H increases) sharply from 25° to 150°C and that addition of NaCl decreases CO₂ solubility by a factor of 4 for a 6 molal solution (Figure 5). In general, the salinity of groundwaters present in British aquifers are less than 5 molal NaCl (Edmunds, 1986).

3.4 Natural occurrence of carbon dioxide in the geosphere.

Carbon dioxide is ubiquitous in the geosphere, and is intimately associated with hydrocarbon deposits of oil and gas. Large natural CO₂ deposits also exist without hydrocarbons, as a result of hydrothermal or volcanic activity.

Large, naturally-occurring sources of CO₂ have been used for flooding oil reservoirs in enhanced oil recovery processes (Matthews, 1989). In the USA, these occur at Bravo Dome, New Mexico (6 tcf); McElmo Dome, SW Colorado (10 tcf at 97% CO₂); Jackson Dome, Mississippi (3-5 tcf); LaBarge-Big Piney, S W Wyoming (20 tcf at 70-80% CO₂).

The Herste gas field in Westphalia, Germany, which contains dry CO₂, is thought to have originated from volcanic heating. Volcanic activity often produces large amounts of CO₂. One example with catastrophic consequences was the release of CO₂ from Lake Nyos in the Cameroon in 1986 and the loss of 1700 lives due to asphyxiation (Anderson, 1987).

3.5 Potential Host formations in the UK

Potential host formations in the United Kingdom include:-

- (1) Exhausted oil fields on land and offshore.
- (2) Reservoir rocks with aquifer properties.
- (3) Existing man made voids such as salt cavities, or newly engineered voids.

In general there are few large cavernous voids underground which could receive CO₂, and disposal into geological formations must rely on the intergranular pore space within the rock, that is its porosity, and the ability of the fluid to permeate the rock (its permeability). The capacity for rocks to store fluids may be due to intergranular porosity, which is the space that exists between the mineral grains, or from fractures, joints, bedding planes or solution channels within the rock. Most subsurface space is occupied by water which may be highly mineralised. Since water is relatively incompressible, injection of CO₂ necessitates displacement of the water.

The conditions of pressure and temperature within the host formation determine the form of the CO₂ particularly its density and therefore the mass that can be accommodated. The extent and physical properties of the host formation, particularly the effective porosity and permeability to the CO₂ will be important in estimating the storage volume available. The composition of the rock and the fluids present are important to determine possible chemical reactions with the CO₂ which may lead to rock dissolution or mineral precipitation.

Unfortunately not all the porosity of the rock is available for storage. Total porosity may be made up of an effective or interconnected porosity and a non-connected porosity or dead end pores. Fluids in "dead end pores", exchange only slowly, by diffusion, with the interconnected pores, and it is difficult to displace fluid from them. Therefore, when a fluid such as CO₂ invades the rock it will not displace all the water from the pores. Even after large volumes of CO₂ have been pumped the rock still retains a residual amount of water. This residual water varies between 15 -30 % of the pore space in typical aquifers. At a scale much larger than the pore size, similar effects occur due to the heterogeneity of the formation in terms of its physical properties. Formation heterogeneity is the subject of current research since if it is understood, wells to remove oil may be located in optimum positions, and better estimates of hydrocarbon recovery can be made. Conversely, the amount of CO₂ that can be injected into a reservoir depends on the heterogeneity of the formation at a range of scales.

4. POTENTIAL PROBLEMS OF UNDERGROUND DISPOSAL

4.1 General

As a result of past experience with the injection of liquid wastes into the ground, the following problems have been identified:-

- (a) Reaction of CO₂ with host rock and groundwater
- (b) Groundwater pollution
- (c) Ground stability
- (d) Micro-seismic events
- (e) Sterilisation of earth resources

4.2 Reaction with the host rock

Injecting a potentially reactive fluid into a reservoir rock may result in a number of mineralogical changes leading to mineral dissolution or mineral precipitation which may clog the pores and reduce access to the pore space. Research into the use of CO₂ as a miscible gas to increase oil recovery from geological reservoirs began in the 1950's (Matthews, 1989). The process consists of injecting gaseous CO₂ via a borehole, alternating with water injections from the same borehole, to 'sweep' oil to a recovery borehole. In most flooding operations, the reservoir temperature is above the critical point, and carbon dioxide exists as a supercritical fluid.

Problems encountered during carbon dioxide flooding relevant to CO₂ storage in aquifers include corrosion and scaling. Scaling occurs in production wells due to the sudden release of CO₂ from aqueous solution as pressure is reduced in the well bore region. These scales consist predominantly of carbonates. 'Formation damage' may occur as a result of the removal of carbonate cements from reservoir sandstones due to the increased P_{CO₂} in pore fluids.

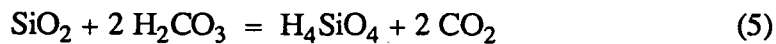
Since supercritical carbon dioxide is non-polar, it is unlikely that it will cause appreciable reaction with the host rock, although supporting evidence from the geological literature is lacking and a study of fluid inclusions in cores taken from CO₂ reservoirs may provide useful information on mineral stability. It is considered that the principal mechanism of interaction with the reservoir/aquifer host rock will result from CO₂ dissolved in groundwater.

The solubility of CO₂ in water has been discussed previously. Dissolved CO₂ as carbonic acid, (H₂CO₃), will dissolve carbonate minerals (calcite, dolomite, ankerite, siderite) present

Although both the above mass balances imply relatively minor changes in solids volume, the production of considerable amounts of kaolinite could constrict pore throats in the aquifer and thus reduce its permeability and hence, the efficiency of the injection of carbon dioxide. This could be evaluated in laboratory experiments by flooding rock cores of candidate aquifers with carbon dioxide and measuring the resulting permeability change.

The aluminosilicate mineral content of most sandstone aquifers is minor relative to quartz. It is considered that quartz would be relatively unreactive under conditions of high P_{CO_2} in the fluid phase. The rate of dissolution and magnitude of solubility of quartz is known to be independent of pH at pH <7 under conditions appropriate to shallow burial (70°C, atmospheric pressure - e.g. Knauss and Wolery, 1988), and under these conditions is more inert than the common aluminosilicates (Lasaga, 1984).

However, there is circumstantial evidence from some petrographic studies of sandstone diagenesis that carbonate cements precipitated under conditions of high P_{CO_2} may be corrosive or replacive towards detrital quartz grains (e.g. Hurst, 1981). This reaction may involve release of carbon dioxide from solution as follows:-



There are no experimental data to confirm the hypothesis that quartz dissolution is sensitive to variations in P_{CO_2} and this reaction may only progress if the CO_2 produced is removed from the system. The high activity of CO_2 in the system as a result of injection, may prevent the reaction proceeding significantly to the right.

4.3 Groundwater pollution

The pollution of fresh or worthwhile reserves of groundwater by CO_2 injection is not likely to be considered as a direct result of the CO_2 injection operation. Groundwater pollution would occur if CO_2 escaped as a result of a failure in the confining barriers to the host rock or if previously unidentified pathways existed. Failure in the borehole casing allowing CO_2 to escape at shallow depths into potable aquifers is an obvious situation which could result in groundwater contamination.

The effect of CO_2 on groundwater quality depends on the buffering capacity of the system. In cases where significant buffering capacity exists eg in carbonate dominated systems then, dissolution of the rock and an increase in bicarbonate concentration of the groundwater would result as shown in equation (2)

Similar situations occur around landfill sites where methane and CO₂ released from waste biodegradation migrates into shallow aquifers and produces a hardness halo of bicarbonate ions in the groundwater. As the buffering capacity is depleted, or where buffering is poor, the groundwater may become acid to pH, oxygen may be depleted, and cations especially iron, manganese and heavy metals which are more soluble in lower pH or in lower redox conditions may enter solution. Geochemical modelling of such systems is possible to establish the mineral speciation in solution and the possibility of mineral dissolution/precipitation.

Over-pressuring a formation with CO₂ may displace other fluids (saline groundwater or hydrocarbons) which may migrate and pollute other groundwater reserves. If abandoned oil field are used problems may be encountered in leakage of CO₂ back to the surface or to shallower formations through unplugged or poorly sealed oil or gas wells. Such wells can be difficult to locate and difficult to seal.

4.4 Ground Stability

The stability of the ground may be affected if minerals are dissolved, or if pressures greater than those *in situ* are applied. Over-pressuring may result in fracturing of the formation which will increase permeability / porosity but may also disrupt the integrity of the confining barrier. Over pressures may raise the level of the ground surface; mineral dissolution may allow the surface to subside. The greater the depth of the repository then the less the effects may be on the surface.

If mineral dissolution occurs the structural support of the formation is weakened. The pressure of fluid within the formation will prevent the formation collapsing under the pressure of the overlying rock, providing the fluid is relatively incompressible. If the fluid is compressible then the formation may collapse and irreversible changes may occur in the structure of the rock such that it may be impossible to regain the original porosity on increasing the fluid pressure again.

4.5 Microseismic effects

There have been several instances where the injection of liquid into the ground has resulted in stress release and movement of faults. In fact, water injection into fault planes has been used to release rock stresses in earthquake zones in a controlled way rather than allow stress to build up and for the energy to be released catastrophically. In any host formation the natural *in situ* stresses on the rock would need to be considered so as to evaluate the potential for its release following fluid injection, and the possible environmental effects. Although Britain

does not lie in a tectonically active zone (Brereton and Muller, 1991), rock stresses may be high in the vicinity of faults and could be released by fluid injection. With any injection operation microseismic events are likely to occur but by definition may be minor and have little consequence.

4.6 Sterilisation of Earth resources

A number of earth resources could conceivably be sterilised by CO₂ disposal. Mineral resources such as oil or gas, or mineral ores are obvious examples, but geothermal energy or highly mineralised groundwater which contains dissolved constituents which may at some time in the future become economically viable to extract, may also be affected.

The sterilisation of mineral resources is a potential problem, and preference needs to be given to areas where no mineral reserves are likely to exist. However, potential reservoir structures for CO₂ disposal would also be those situations where oil or gas may be trapped. The use of exhausted oil or gas fields would therefore be sensible, since the fact that hydrocarbons exist confirms that there is both a reservoir rock and suitable confinement. If a potential trap structure is found which does not contain hydrocarbons, it may mean that conditions were unfavourable for oil genesis ie. that there was no source rock, or that hydrocarbons were formed but they were not contained by the structure. The geological environment and thermal history of the sediments are important in answering some of the questions about the potential for oil and gas to exist.

Mineralised groundwaters, although not regarded as a groundwater resource may have dissolved constituents which at some time in the future may be extracted economically.

5. Site investigation for suitable formations

5.1 General considerations

Evaluating the structure of deep formations which may have potential for CO₂ storage is expensive, and is not offset by the likelihood of finding hydrocarbon reserves. Deep seismic profiling is an obvious technique for identifying oil bearing structures, but drilling is very expensive to confirm their suitability. As already mentioned, the need to confirm the existence of a reservoir rock and the degree of confinement is the main objective of the site investigation. Hydrocarbon traps prove the existence of a reservoir rock with confinement, but confinement, is more difficult to establish if there are no hydrocarbon reserves present. Pressure profiles measured during drilling, and water chemistry relationships between aquifers above and below a potentially confining layer may provide circumstantial evidence

of confinement integrity. Geological faults are likely to constitute pathways for fluids to migrate from the reservoir and evidence of hydrocarbon migration and mineralisation along fault zones may also hold important clues to fluid migration in the past. Gas emissions from fault zones may also provide clues as to the depth to which fluids circulation in fault planes. Evidence of $^3\text{He}/^4\text{He}$ which is released from the mantle may indicate the depth to which faults provide fluid pathways.

5.2 Use of fluid inclusions in CO_2 reaction studies with the host rock

Fluid inclusions can be described as crystal imperfections in the form of liquids, solids and vapours trapped in minerals, and are generally less than 100 μm in size. 'Primary' fluid inclusions are those which formed when, and have not been altered since, the mineral was formed. Primary fluid inclusions are samples of the actual fluids from which the mineral was formed, for example diagenetic or hydrothermal fluids, and can provide valuable information on the physical and chemical processes involved in the mineral formation.

Fluid inclusions may be studied by non-destructive techniques using normal optical microscopes, or by a variety of destructive techniques where the contents of the inclusion are analysed chemically.

The most widely used non-destructive technique is thermometric analysis, which involves the use of a 'heating-freezing stage' in conjunction with an optical microscope. The temperatures of phase changes which occur within inclusions as they are heated and cooled can be related to the chemical composition of the inclusion, and indicate the temperature and pressure of mineral formation.

A technique which is used for the identification of hydrocarbon bearing inclusions is the use of an ultra-violet microscopy. Fluid inclusions containing hydrocarbons fluoresce at various intensities depending on the composition and wavelength of the UV illumination. The presence of hydrocarbon bearing inclusions in diagenetic minerals such as quartz overgrowths and calcite can therefore be used for the identification of migration pathways of hydrocarbon-bearing fluids.

Studies of fluid inclusions provide information on temperature and pressure regimes and fluid chemistry which existed during mineral formation, and on migration pathways of hydrocarbon bearing fluids. Furthermore they allow phase changes which occur for various chemical compositions within the inclusions to be studied conveniently and inexpensively.

6. DETAILS OF POTENTIAL UK HOST FORMATIONS.

6.1 Man-made Voids

These include both abandoned mine workings and artificially created caverns.

6.1.1 Mine Workings

The most abundant and voluminous underground mine workings in Britain are for coal. Most coal workings are onshore, but in coastal areas workings commonly project out a few kilometres under the sea. Modern longwall methods of extraction allow the workings to collapse and thus create no long-term storage space. Abandoned older workings by the pillar and stall method, which retain a large void-space, are widespread. For the most part these are less than 1 km deep. However, except locally, they are not in closed or sealed structures. Thus they are unlikely to be able to retain any fluid or be able to provide long-term disposal of significant amounts of CO₂.

Evaporites (gypsum, anhydrite, salt, potash) and their associated beds are largely impermeable and some old mine workings could provide sealed voids. However, these are too limited in number and extent to provide a general method of CO₂ storage. The only major salt (Cheshire) and potash (North Yorkshire) mines in the country are currently active. Many old gypsum and anhydrite workings are at relatively shallow depths, where liquid CO₂ might be stored. However, this would probably require reservoir pressure to be considerably higher than hydrostatic pressure, and consideration must be given to the effects of overpressure on the seal.

6.1.2 Artificial Caverns

It is technically feasible to construct large man-made caverns in hard impermeable rocks. However, it is unlikely that their excavation could be undertaken economically or on the necessary massive scale.

The technology to excavate caverns in rock salt by pumping water down boreholes is well advanced. Salt is produced in this way from the Triassic rocks of the Cheshire basin. Storage caverns for North Sea gas have been constructed in this manner in Permian salt deposits on the east Yorkshire coast. Similar caverns could also be created at depths suitable to hold CO₂ in the supercritical fluid phase, but they would need to be kept relatively small to avoid collapse and subsidence. The high cost of offshore drilling probably limits the feasibility of creating a system of sub-sea caverns. It is probable that only a small proportion of the CO₂ produced could be stored in this way. Another disadvantage is the need to drill a new borehole for each cavern.

6.2 Aquifers

6.2.1 Introduction

Although groundwater is obtained at relatively shallow depth from rocks of widely different ages in the British Isles, aquifers in which intergranular porosity and permeability play a significant role in regional groundwater flow, are limited in number. Deeply buried (>1 km) formations, in which most joints and fissures are closed, and which are capable of storing and retaining groundwater or other fluids, are restricted both in numbers and in their geographical extent.

In the last three decades exploration for oil and gas, and, to a lesser extent, for low enthalpy geothermal energy, has been intense and considerable study has been made of deep British aquifers. Many of the results of this work are publicly available.

In addition to the requirements that the aquifer should be deeper than approximately 1 km (ie. at temperatures above the critical point of CO₂) and have good reservoir properties, it should have a proven closure which can be defined by the presence of producing or abandoned oil and/or gas fields. These are likely to have major cost advantages for the disposal of CO₂ (e.g. existing infrastructure, no exploration costs) compared to other closed structures of the same size.

In the absence of proven closure, exploration to define closed structures would have to be undertaken, with no guarantee that such structures exist. In the oil industry this is usually done using seismic surveys. The major sedimentary basins in England and Wales are at least partially covered by seismic surveys, which could probably be purchased or traded. This would be cheaper than acquiring new data.

Park (1991) has reviewed the possibility of disposing of CO₂ in Britain's offshore oil and gas fields. The formations which contain our oil and gas reserves range from Devonian to Eocene in age and range geographically from south of 53°N to nearly 62°N, a distance of almost 1000 km. Because of the high cost of exploration and development offshore, particularly in the deeper waters of the northern and central North Sea, it is most likely that CO₂ disposal into producing or abandoned fields, with their existing infrastructure, will be much cheaper than, for example, installing new platforms. The best strategy for an offshore area feasibility study might be to study the fields on an individual basis, bearing in mind that it may be possible to use additional "satellite" non-hydrocarbon-bearing closures near existing fields, particularly in the southern North Sea gas basin. This possibility is discussed further below, under Permo-Triassic reservoirs.

6.2.2 Pre-Permian Aquifers

For all practical purposes Lower Palaeozoic and Precambrian rocks can be discounted from this discussion. They are not important aquifers at outcrop, having very low intergranular porosity and permeability, and there is no reason to suppose that their performance will improve with depth.

The recent review of Devonian and Carboniferous rocks by Holliday (1986) has concluded that they have poor potential as deep aquifers and as a source of low enthalpy geothermal energy. For the most part they are hard, compact rocks with relatively low porosities and permeabilities. A few exceptions were noted where Devonian and Carboniferous formations form excellent shallow aquifers, in particular the late Devonian Knox Pulpit Sandstone of the Midland Valley of Scotland and the Lower Carboniferous Fell Sandstone Group of Northumberland. It was suggested by Holliday (1986) that these might prove to have deep aquifer/low enthalpy geothermal potential, but this has not been supported by such new data (mainly confidential) as has come to hand in the last few years. Nevertheless, the location of much of Britain's urban population and related industrial centres, and all of the country's coal production, in areas underlain by Carboniferous strata, suggests that these rocks may warrant further examination in the present context. This view is strengthened by the occurrence of around 20 active or exhausted oil fields in the East Midlands, in which the reservoir rocks are Upper Carboniferous sandstones, and by the abundant evidence of deep regional groundwater circulation, in many parts of the country, in the limestones of Lower Carboniferous age.

The East Midlands oilfields stand as models for the CO₂ storage capacity of Carboniferous rocks in the rest of the country. They provide a good indication of the likely capacity of closed structures elsewhere. Their typical porosity (<15%) and permeability values (<50 mD) are probably characteristic of Carboniferous sandstones in other parts of the country. Carboniferous rocks of the UK onshore have the following advantages as possible sites of CO₂ storage.

- (1) They contain numerous sandstone bodies.
- (2) They have been deformed to produce many small to medium-sized, potentially closed structures.
- (3) There is commonly more than one sandstone in any closure.
- (4) They are located close to the source of CO₂ production.

They also have the following main disadvantages:-

- (1) The closed structures are generally limited in size.
- (2) The rocks generally have low porosities and permeabilities.
- (3) An extensive programme of exploration and drilling would be required before the storage capacity of each structure could be quantified.

The oil industry experience provides only a partial model for CO₂ storage. In the East Midlands, for every oil-bearing structure there are between ten and twenty which proved to be "dry". In most fields only one sandstone in the sequence contains oil whereas the others are water-bearing. Thus, in the East Midlands alone, there are probably a hundred or more small to medium size structures capable of storing CO₂, with capacities ranging up to perhaps as much as 5 x 10⁶ tonnes. Based on the density of hydrocarbon exploration drilling elsewhere in the country, there are probably fewer closed structures in other areas of Carboniferous rocks.

6.2.3 Permo-Triassic Aquifers

Permo-Triassic sandstones are important sources of shallow groundwater in many parts of the UK. Despite the effects of increasing cementation, these sandstones commonly retain good porosities and permeabilities at depths in excess of 1 km (Smith, 1986).

Downing & Gray (1986) concluded that Permo-Triassic sandstones were the best deep aquifers in the country and designated them as the principal targets for low enthalpy geothermal energy. They are also extremely important hydrocarbon reservoirs. Lower Permian sandstones are the main reservoir formation in the Southern North Sea gas fields. Onshore, they have been found to contain small sub-economic gas accumulations. The Sherwood Sandstone Group is also an important gas reservoir in the Southern North Sea (Esmond, Forbes, Gordon and Hewitt fields) and in the Irish Sea (Morecambe field). Onshore, it forms the principal reservoir in the Wytch Farm Oilfield in Dorset (Colter & Havard 1981, Dranfield et al. 1987), and in the Southampton Geothermal Scheme.

Those features of the Permo-Triassic sandstones favourable to the oil and geothermal industries are also likely to be favourable for the underground storage of CO₂. Thus the Permo-Triassic sandstones are likely to be the main reservoirs for underground storage of CO₂, whether onshore or in the Southern North Sea.

Lower Permian sandstones, locally known as Penrith Sandstone, Collyhurst Sandstone, Bridgnorth Sandstone, Basal Permian Sands and (offshore) Rotliegendes, are commonly of aeolian origin. There are six main areas of England and Wales where Permian sandstones occur at depths below 1 km; the Wessex Basin, the Worcester Basin, the Cheshire Basin, West Lancashire, the Carlisle Basin, and East Yorkshire/Lincolnshire. However, they have little known potential in the Wessex Basin and are not sealed from the overlying Triassic Sherwood Sandstone over parts of the Cheshire Basin and the Worcester Basin. In the other areas they are likely to be well sealed by overlying (Zechstein) mudstones and evaporites. Reservoir properties of the Permian sandstones in these areas are detailed by Smith (1986).

Early Triassic sandstones of the Sherwood Sandstone Group (Bunter Sandstone of offshore areas) were mainly deposited by braided rivers. There are three areas of the onshore UK where the Sherwood Sandstone aquifer occurs below 1 km depth; the Wessex and southern Worcester Basins, East Yorkshire and Lincolnshire, and a small area in the Cheshire Basin (Whittaker 1985). Aquifer properties and seal are likely to be adequate over at least parts of the Wessex Basin and Cheshire Basin and all of the East Yorkshire/Lincolnshire area (Penn et al. 1987, Downing & Gray 1986). At depth, the Sherwood Sandstone is usually well sealed by the overlying Mercia Mudstone Group.

There are some very large non-hydrocarbon-bearing closures on the Sherwood Sandstone in the southern North Sea gas basin, associated with salt swells in the underlying Zechstein evaporites. In the majority of cases these are sealed from the Rotliegend sandstone by the Zechstein evaporites and mudstones, and it is generally considered that this, rather than poor seal on the Sherwood Sandstone, accounts for the absence of gas in these structures. Some of these are near or above existing fields in the Rotliegend sandstone. Many of these could perhaps be used for CO₂ disposal where they are buried sufficiently deeply. The size of such structures is not publicly documented; such detail that is available suggests that they could be at least an order of magnitude bigger than those in the related hydrocarbon-bearing reservoir (cf. France 1975; Gray 1975).

6.2.4 Jurassic-Cretaceous Aquifers

There are a number of deep aquifers of significance in the Jurassic and Cretaceous rocks of the UK onshore area, though none were regarded by Downing & Gray (1986) as having any great low enthalpy geothermal potential. In some cases, eg. the Lower and Upper Greensand, this is more because burial rarely or never reaches 1 km. For this reason they would also not be considered initially for CO₂ disposal. Other formations are commonly tight and compact at depth, with only low or modest porosity and permeability. In the Wessex Basin of southern England, oil has been found in a number of formations of Jurassic age. The most important of these are the Lower Jurassic Bridport Sands and the Middle Jurassic Great Oolite Group.

In the northern and central North Sea, Jurassic, Cretaceous and Tertiary aquifers reservoir hydrocarbons in numerous major oil and gas fields. In many of these fields the rocks are highly overpressured, i.e. pore pressures are greater than the hydrostatic pressures at those depths. Detailed enumeration and discussion of these is beyond the scope of the present report.

6.3 Volume Considerations

Park (1991) has made a preliminary estimate of the potential for aquifers in current UK oil and gas fields to store CO₂, based on figures quoted in the Department of Energy's "Brown Book". His estimate of 4750 x 10⁶ tonnes of CO₂ storage capacity may prove to be an underestimate, since only hydrocarbon-bearing structures and reservoirs are included. His figures do not take into account other closures that are probably sealed but which do not contain economic hydrocarbons. These, however, would be expensive to exploit as new drilling and pumping/pipeline infrastructures would be necessary. Another possibility is the potential of water-bearing aquifers in the same closure as the hydrocarbon-bearing reservoirs.

With the exception of the Wytch Farm Oilfield, all onshore hydrocarbon discoveries in the UK are at least an order of magnitude smaller than offshore fields. No detailed calculations have been made for the onshore to compare with Park's (1991) offshore figures. Preliminary estimates suggest that all known onshore oilfields, excluding Wytch Farm, could collectively store around 5 x 10⁶ tonnes of CO₂ in the hydrocarbon-bearing reservoirs. The biggest of these fields, Welton (Rothwell & Quinn 1987), could hold around 10⁶ tonnes. These figures might be increased by an order of magnitude by utilising other non-hydrocarbon-bearing aquifers in the same structures. Recoverable reserves of oil at Wytch Farm, which extends offshore into Bournemouth Bay, are said to be 37.6 x 10⁶ tonnes. This implies a storage capacity for CO₂ of the order of 30 x 10⁶ tonnes. The capacity of other onshore non-hydrocarbon-bearing closures in Permo-Triassic sandstones is unknown, but it is unlikely than any of these will exceed that of Wytch Farm.

7. CONCLUSIONS

Based on a preliminary assessment the following conclusions can be made with respect to the feasibility for the disposal of CO₂ underground in UK.

1. At depths of more than 800 m below ground the temperature will be above the critical temperature of CO₂ (31.1°C) which means that it will exist as a supercritical fluid.
2. At shallower depths than 800 m where the temperature is between 10 - 30°C, it may be possible to store CO₂ in liquid form, providing the geological formations are over-pressured. However, the narrow temperature range and the possibility that over-pressuring may fracture the containment medium, makes liquid CO₂ storage within 800 m of the surface appear unattractive and will need to be considered carefully.

3. Compressed gas storage in shallow depth is possible but will probably not be sufficient to hold the quantity of CO₂ that needs to be disposed.
4. Potential problems with deep disposal of CO₂ include dissolution of the host rock, groundwater pollution, ground stability due to fracturing of the formation or subsidence, initiation of microseismic events, and the sterilisation of mineral or geothermal reserves.
5. Characterising the confinement and volumes of potential CO₂ reservoirs will be more expensive if the reservoir is not associated with hydrocarbon accumulations which prove the geological trap, and confirmation of integrity may always be associated with a degree of uncertainty.
6. Aquifers provide the best means of underground storage.
7. There are many potential host formations suitable for CO₂ disposal in the UK, particularly if the continental shelf is included.
8. Permo-Triassic sandstones provide the best potential storage capacity onshore and in the southern North Sea; a number of younger formations would be suitable in the northern North Sea.
9. Existing oil and gas fields offer initial advantages because closure and seal is already demonstrated, and an existing infrastructure of pipelines and wellheads may currently be in existence.
10. Numerous non-hydrocarbon-bearing closures, that are probably sealed, occur both onshore and offshore, but would require detailed preliminary investigation.
11. The main potential for storage in aquifers is offshore, where the proven hydrocarbon fields are larger.
12. Onshore storage potential is more limited, but has the advantage of location closer to the source of CO₂ production, with smaller pipeline or drilling costs.
13. Man-made voids have limited storage potential.

8. RECOMMENDATIONS FOR FURTHER STUDIES

This preliminary study suggests that aquifers could prove an important means of underground disposal of CO₂, particularly by making use in the first instance of current or abandoned hydrocarbon fields. However, much remains to be done before this can be demonstrated as a practical, viable means of disposal.

We propose that the following topics be given priority:-

1. The CO₂ phase diagram imposes constraints on the depths and pressures at which disposal can take place. A detailed study of the implications of the phase diagram should be carried out.
2. CO₂ is presently injected into reservoir rocks in many oil fields to enhance recovery. A review of CO₂-based enhanced oil recovery technology and experience would provide important data relevant to future underground CO₂ disposal. Studies may already have been undertaken on the reaction of CO₂ with the host rock leading to pore clogging and limiting the ability for CO₂ to permeate the rock. Additional questions for which enhance oil recovery experience may at least have partially provided insight include:- potential for rock fracturing, microseismic events, volumes that can be invaded, corrosion effects, costs.
3. It is probable that CO₂, in any phase, will react with some of the minerals in the host reservoir. A laboratory investigation of these changes and their effects on the character of the reservoir is required. The study of fluid inclusions in cores from natural CO₂ reservoirs may provide useful information on mineral stability.
4. A more detailed review of the distribution and character of the main onshore and offshore aquifers, and of the distribution of hydrocarbon fields and other closed structures, is required.
5. Following the suggested aquifer review, it should be possible to propose some locations for a preliminary pilot field study, where the technical problems and economics of CO₂ disposal in aquifers can be evaluated. While in the long run most disposal is likely to be in offshore aquifers, a pilot scheme more probably could be better located onshore adjacent to a source of CO₂. One of the East Midlands Oilfields would seem to be a strong possibility. A major study to select the optimum location of a preliminary pilot study should be instigated.

9. REFERENCES

- Anderson, I., (1987). Nyos: the danger may not be over. *New Scientist*, 5 th February.
- Brereton N R and Muller B, 1991. European stress: Contributions from borehole breakouts. Royal Society - Discussion Meeting on Origin and Distribution of Tectonic Stress in the Lithosphere, 10/11 April 1991.
- Burley, S. D. (1984). Patterns of diagenesis in the Sherwood Sandstone Group (Triassic), United Kingdom. *Clay Minerals* 19: 403-440.
- Colter, V.S. & Havard, D.J. (1981). The Wytch Farm Oil Field, Dorset. Pp. 494-503 in: Illing, L.V. & Hobson, G.D. (Eds). *Petroleum Geology of the Continental Shelf of North-West Europe*. Heyden, London.
- Downing, R.A. & Gray, D.A. (Eds) (1986). *Geothermal Energy – The potential in the United Kingdom*. HMSO, London, 186pp.
- Dranfield, P., Begg, S.H. & Carter, R.R. (1987). Wytch Farm Oilfield: Reservoir characterisation of the Triassic Sherwood Sandstone for input into reservoir simulation studies. pp. 149-160 in: J. Brooks, & K.W. Glennie (Eds), *Petroleum Geology of north west Europe*. Graham and Trotman, London.
- Drummond, S.E. (1981). Boiling and mixing of hydrothermal fluids: chemical effects on mineral precipitation. PhD thesis, Pennsylvania State University, 380pp.
- Edmunds, W. M. (1986). Geochemistry of geothermal waters in the UK. In 'Geothermal energy - the potential in the United Kingdom' (eds RA Downing and DA Gray), HMSO, 187pp.
- Ellis, A. J. (1959). The solubility of calcite in carbon dioxide solutions. *Amer J Sci* 257: 354-365.
- France, D.S. (1975). The geology of the Indefatigable gas-field. pp. 233-239 in: Woodland, A.W. (ed) *Petroleum and the continental shelf of north west Europe: Volume 1 Geology*. Applied Science Publishers, Barking.
- Gray, I. (1975). Viking gas-field. Pp. 241-247 in: Woodland, A.W. (ed) *Petroleum and the continental shelf of north west Europe: Volume 1 Geology*. Applied Science Publishers, Barking.

Harrison, J. (1990). Global warming; the Coal Industry view. *New Scientist* 1st. September 1990.

Holliday, D.W. (1986). Devonian and Carboniferous Basins. pp.84–110 in: Downing, R.A. & Gray (Eds) *Geothermal Energy – The potential in the United Kingdom*. HMSO, London.

Hurst, A. R. (1981). A scale of dissolution for quartz and its implications for diagenetic processes in sandstones. *Sedimentology* 28: 451-459.

Knauss, K. G. and Wolery, T. J. (1988). The dissolution kinetics of quartz as a function of pH and time at 70°C. *Geochim Cosmochim Acta* 52: 43-54.

Lasaga, A. C. (1984). Chemical kinetics of water-rock interactions. *J Geophys Res* 89: 4009-4025.

Matthews, C. S. (1989). Carbon dioxide flooding. In 'Enhanced oil recovery', (eds E.C. Donaldson, G.V. Chilingarian and T.F. Yen), *Developments in Petroleum Science* 17B, Elsevier, Amsterdam, 129-156.

Miller, J. P. (1952). A portion of the system $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ with geological implications. *Amer J Sci* 250: 161-203.

Park, R.S. (1991). A preliminary estimate of the capacity of UK oil and gas fields for the storage of carbon dioxide. Unpublished report for British Coal.

Penn, I.E., Chadwick, R.A., Holloway, S., Roberts, G., Pharaoh, T.C., Allsop, J.M., Hulbert, A.G. & Burns, I.M. (1987). Principal features of the hydrocarbon prospectivity of the Wessex–Channel Basin, UK. Pp. 109–118 in: J. Brooks & K.W. Glennie (Eds) *Petroleum Geology of north west Europe*. Graham & Trotman, London.

Ross, G.D., Todd, A.C. and Tweedie, J.A. (1981). The effect of simulated CO_2 flooding on the permeability of reservoir rocks. In 'Enhanced oil recovery', (F.J. Fayers, ed), *Developments in Petroleum Science* 13, Elsevier, Amsterdam, 351-366.

Rothwell, N.R. & Quinn, P. (1987). The Welton Oilfield. Pp. 181–190 in: J. Brooks & K. Glennie (Eds) *Petroleum Geology of north west Europe*. Graham and Trotman, London.

Segnit, E.R., Holland, H.D. and Biscardi, C.J. (1962). The solubility of calcite in aqueous solutions. *Geochim Cosmochim Acta* 26: 1301-1331.

Sharp, W. E. and Kennedy, G. C. (1965). The system $\text{CaO-CO}_2\text{-H}_2\text{O}$ in the two phase region calcite and aqueous solution. *J Geol* 73: 391-403.

Shepherd, T.J. Rankin, A.H. and Alderton, D.H.M. (1985). A practical guide to fluid inclusion studies. Blackie. New York. pp 239.

Smith, I.F. (1986). Mesozoic Basins. Pp. 42-83 in: Downing, R.A. & Gray, D.A. (1986). *Geothermal Energy – The potential in the United Kingdom*. HMSO, London.

Whittaker, A. (Ed) (1985). *Atlas of onshore sedimentary basins in England and Wales: Post-Carboniferous tectonics and stratigraphy*. Blackie, Glasgow, 68pp.

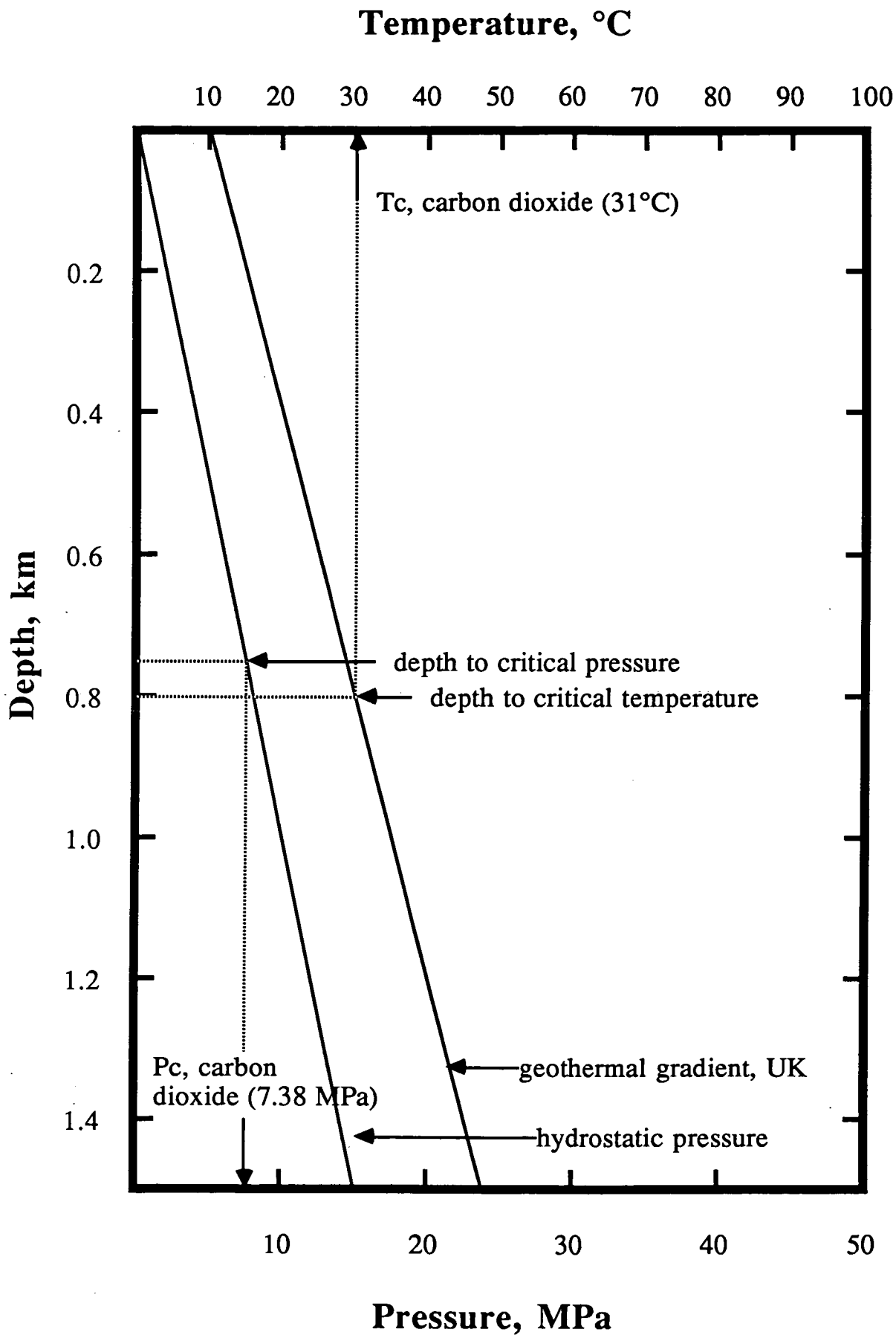


Figure 1 Variations in pressure and temperature with depth below surface.

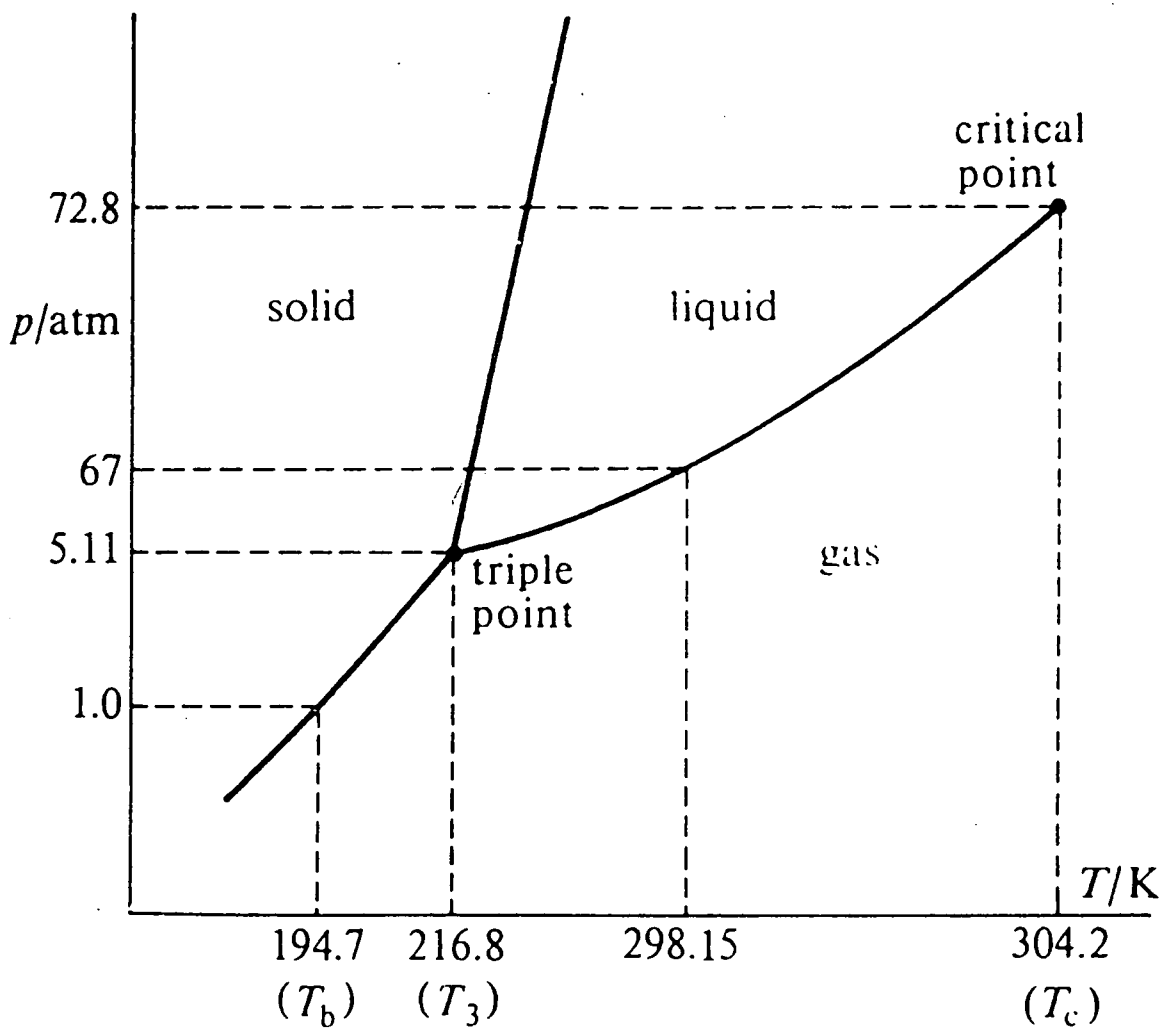


Figure 2 The phase diagram for carbon dioxide.

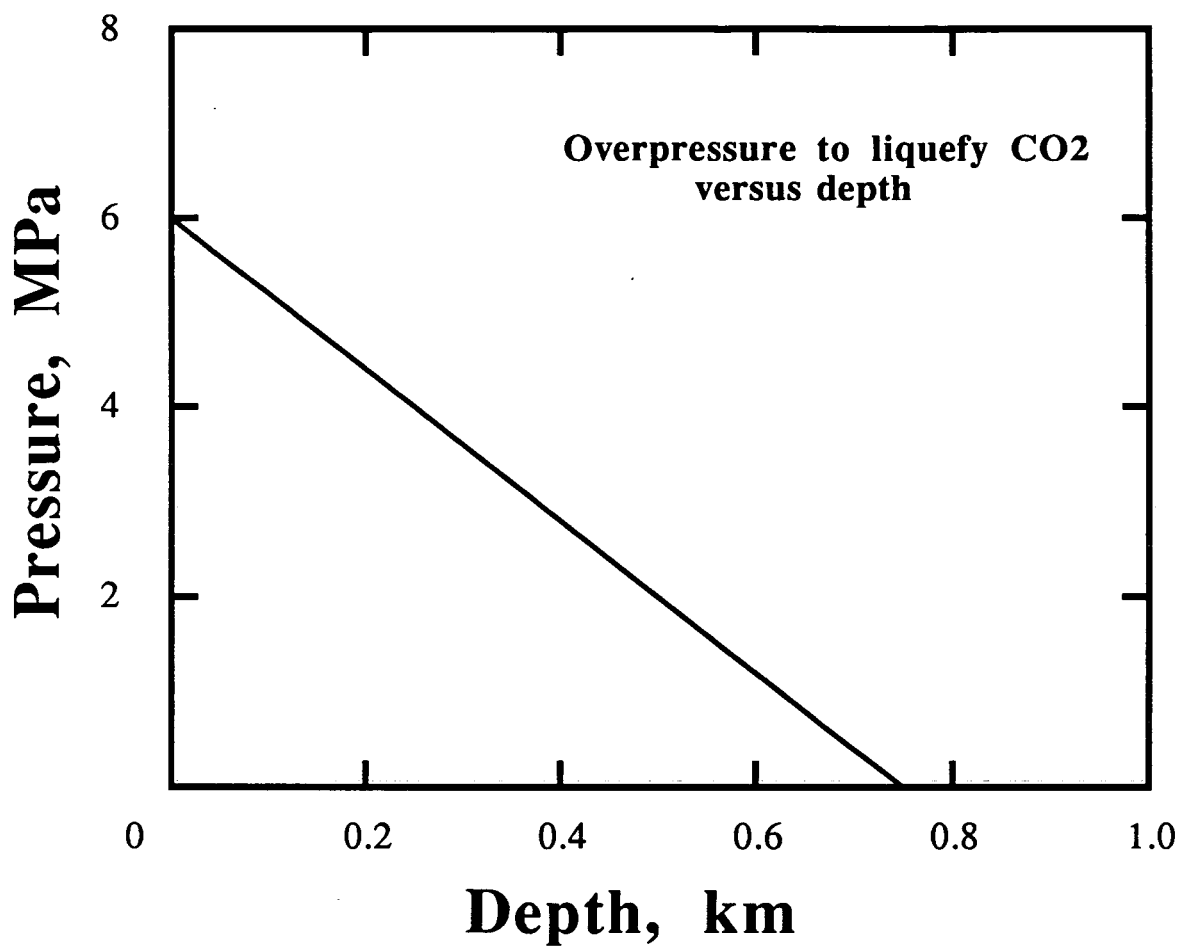


Figure 3 Minimum overpressure required to liquefy CO₂ at different reservoir depths.

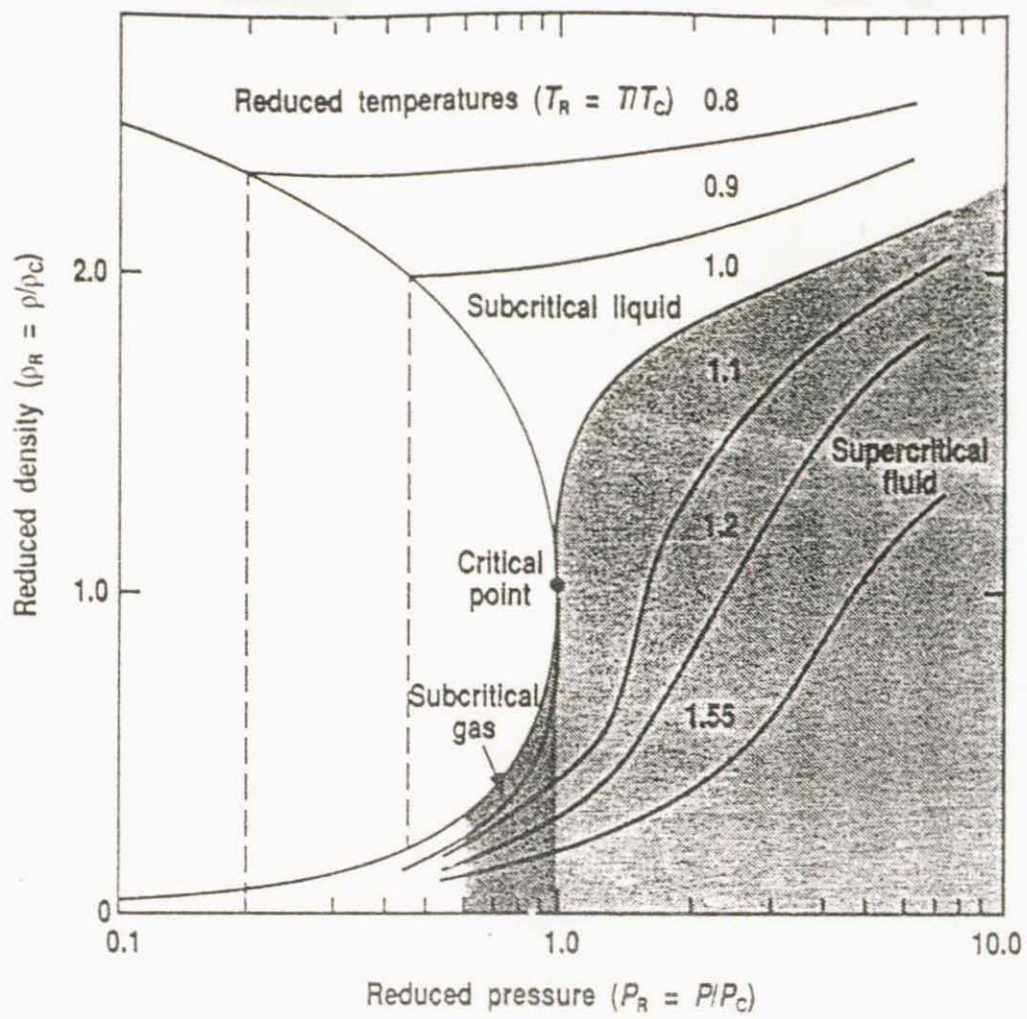


Figure 4 Reduced-variable phase diagram for carbon dioxide.

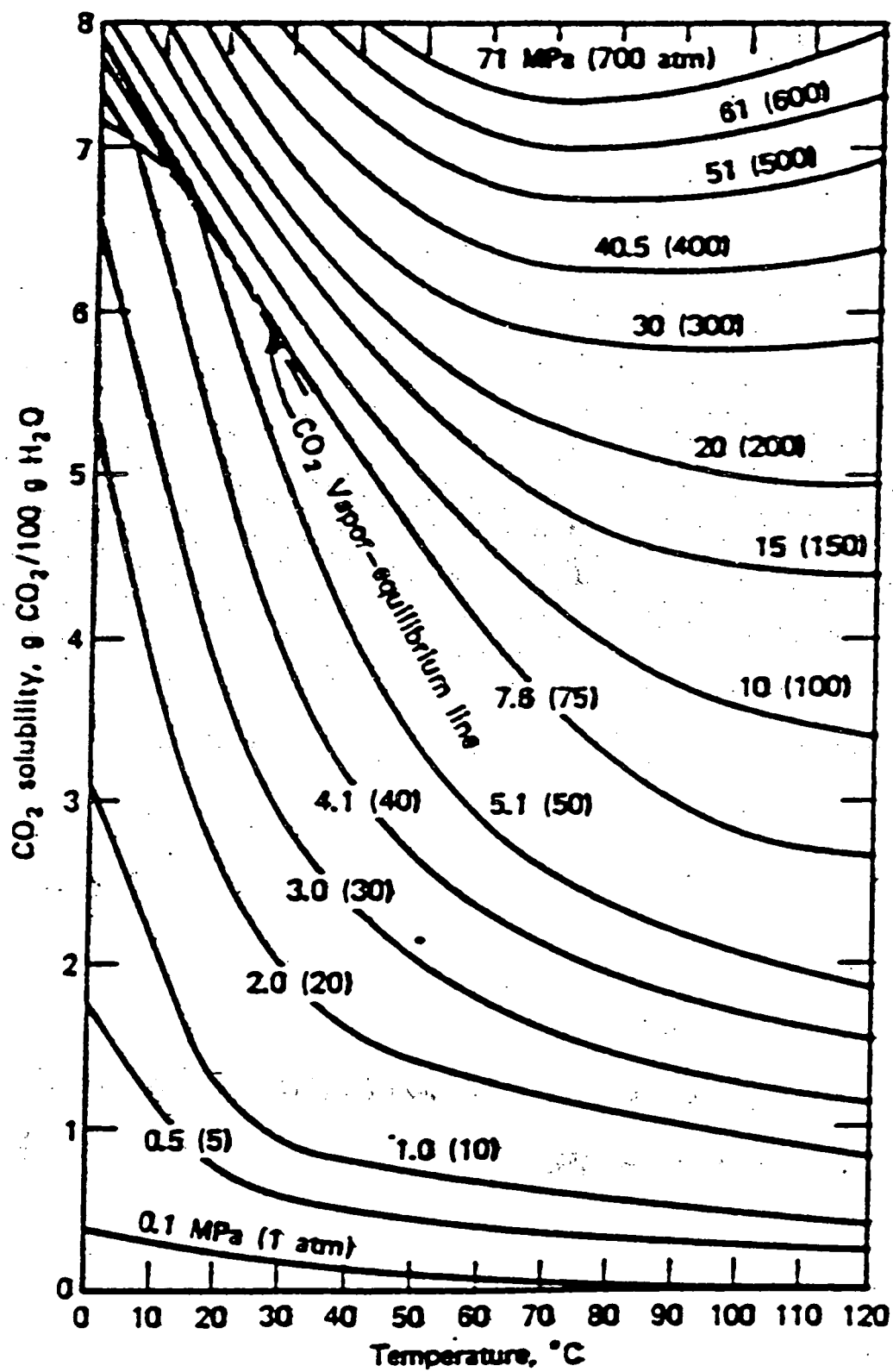


Figure 5 Variation in CO₂ solubility in water with pressure

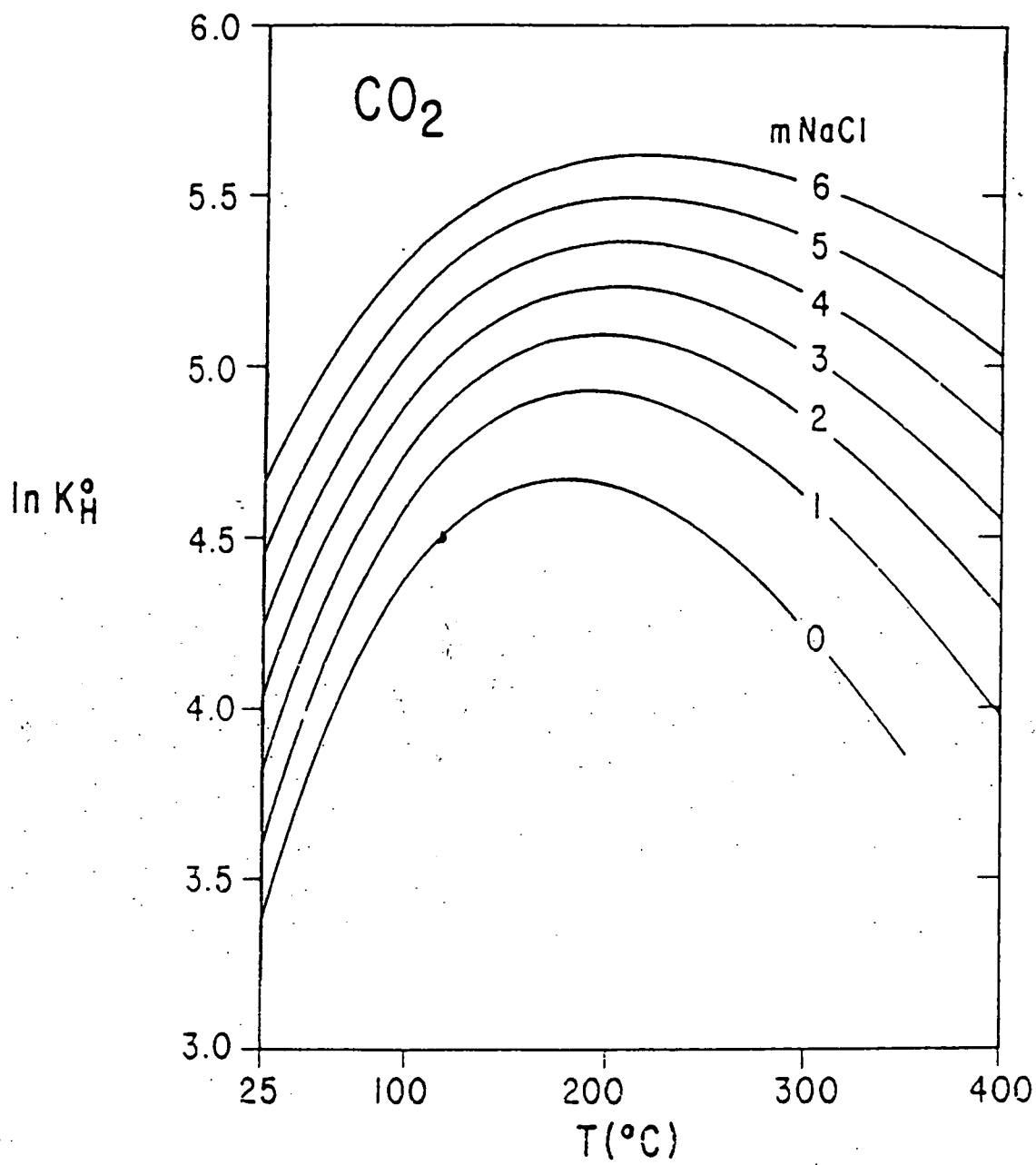


Figure 6 Solubility of CO_2 at infinite dilution in NaCl solutions.

K_H^o is in units of fugacity (atm/molality). (From Drummond, 1981).