

MANAGING GREENHOUSE GAS EMISSIONS: STRATEGIES AND DEVELOPMENTS IN AUSTRALIA

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KEYWORDS

Greenhouse gas emissions, Australia's abatement programs, renewable energy

ABSTRACT

Australia is only a minor contributor to greenhouse gas (GHG) emissions globally but is a major contributor on a per capita basis. Owing to its dependence on coal-fired electricity generation, its energy intensive industries such as mining, aluminium, iron and steel, as well as its agriculture and land clearing practices, Australia's GHG emissions have already risen to 111% of the baseline 1990 levels. Consequently the Australian Government has moved from its previous 'no regrets' GHG abatement policies to issue new initiatives ranging from incentives and assistance programs on renewable energy, energy efficiency and alternative fuels, to a mandated target of 2% increase in renewable-based power generation (from 10% to 12%). Given the Government commitment of almost AUD\$1 billion over four years, these programs focus on the implementation of technologies available in the short-term rather than funding major long term development of new GHG abatement technologies.

INTRODUCTION

Australia, a large land mass approximately the area of continental USA containing about 19 million people, is rich in minerals and agricultural resources. It exports each year substantial quantities of raw and semi-processed minerals and metals as well as agricultural products. As a consequence of these factors, its energy use is high; for example, its electricity generation has increased from 155 TWh in 1990 to 179 TWh in 1998, with a further projected increase of over 40% by 2010. Australian energy use by source is shown in Table 1.

Greenhouse gas emissions worldwide exceed 41,000 million metric tons (tonnes) CO₂ equivalent annually, of which Australia's contribution is very small, about 1.4%. However, on a per capita basis at 26.7 tonnes CO₂ equivalent, Australia is amongst the highest emitters, 25 % higher than the USA and 2-3 times the annual per capita emissions of other developed countries, e.g. Germany at 12.6 tonnes. Further, by 1996, greenhouse gas emissions in Australia had increased to 111% of its 1990 baseline levels, already exceeding the emission target of 108% of 1990 baseline levels assigned at the Kyoto Greenhouse Summit in December 1997.

Australia in 1992 implemented a National Greenhouse Response Strategy, involving the voluntary cooperation and input by different levels of government, industry and the community for pursuing reduction of greenhouse gas (GHG) emissions. Shortly before the Kyoto meeting Australia moved from this "no-regrets" voluntary approach, e.g. the Greenhouse Challenge Agreement, to a more proactive strategy to combat and control the rising greenhouse gas emissions. In November 1997, the Prime Minister, Hon. John Howard announced a major policy statement entitled, *Safeguarding the Future: Australia's Response to Climate Change*, that included a AUD\$180 million package for addressing climate change and GHG emission issues. Since this announcement the Australian Government has expanded its initiatives and funding, to near AUD\$1 billion over 4-5 years, for a range of GHG emissions reduction projects.

This paper highlights various Government initiatives and programs. It also provides insight into selected key projects aimed at arresting Australia's continuing rise in CO₂ emissions.

GREENHOUSE ABATEMENT POLICIES/PROGRAMS

Underlying Australia's greenhouse abatement policies are the following premises:

1. Australia's competitive position in international markets should not be disadvantaged by policies and measures to reduce GHG emissions
2. Nuclear power is not a politically acceptable option in the short to medium term based on prevailing community attitudes.

The November 1997 Statement highlighted a range of financial incentives for energy efficiency and renewable energy programs along with mandating a 2 % increase in power generation from 'new' renewable energy sources. These policies and programs have subsequently been supplemented and expanded. The Australian Greenhouse Office (AGO) was formed to coordinate and implement the various greenhouse programs and measures, including the National Greenhouse Strategy (NGS).

Programs now being supported by the Australian Government include:

- Greenhouse Challenge – an expanded registry of companies, organizations and government authorities giving voluntary commitments to reduce their GHG emissions
- Renewable Energy Showcase Projects
- Renewable Energy Commercialisation Program
- Household Photovoltaic Scheme
- Alternative Fuels Conversion Program and Diesel Fuel/Alternative Fuels Grant
- Cities for Climate Protection™
- Efficiency Standards for Power Generation
- Bush (i.e. Outback) for Greenhouse
- International Greenhouse Partnerships (previously Activities Implemented Jointly)

The measure requiring a 2% increase in the use of 'new renewables' for power generation over existing levels by 2010 has also been strengthened to include a penalty of AUD\$40/MWh for non-attainment of the target.

The State and Local governments in Australia, having a degree of autonomy on energy and GHG matters, have strongly supported the Australian Government national programs as well as initiating State programs such as:

- The Green Power Program offering higher priced but renewables-based electricity
- Cogeneration and biomass generation incentives
- Energy efficiency labeling for household appliances
- Energy Smart programs and awards for companies, schools and other organizations

While the impact of these measures is difficult to quantify, there is general agreement that more action is required if Australia is to achieve its GHG targets. Carbon credit trading is an additional measure that various jurisdictions see as having potential to assist Australia meet its Kyoto obligations. The AGO has issued four discussion papers on the topic and is assessing the responses. Meanwhile the Sydney Futures Exchange is setting up electronic trading systems for a carbon credit market.

A major element of carbon trading schemes in Australia is sequestration credits from forestry activities. Forestry is largely a State responsibility and these carbon credit schemes vary from State to State. However, most State governments are actively pursuing forestry management programs and encouraging investment in future carbon sequestration credits. For example, TEPCO of Japan has significant forestry investments in NSW and Tasmania.

The Australian Government has also recently announced a model for a greenhouse trigger that would apply to actions or development projects that are likely to generate GHG emissions of over 500,000 tonnes of CO₂ equivalent in any 12 month period. This trigger could be applied under the Commonwealth's new Environment Protection and Biodiversity Act 1999. The proposed emissions threshold corresponds to approximately 10% of the average annual rise in Australia's total GHG emissions (1).

The current emphasis of the Australian Government funded greenhouse abatement programs is in maximising reductions in GHG emissions via demonstration, commercialisation and enhanced market acceptance of available or near-term renewable energy and energy efficiency technologies. A more detailed report summarising the various programs and including pertinent web sites, has been published elsewhere (2).

RENEWABLE ENERGY DEVELOPMENTS

2% Renewable Energy Target: The mandated 2% Renewable Target has been defined as 9500 GWh (about 2800MW) of green power that electricity suppliers are required to obtain from new renewable sources. Currently some 10 % of Australia's electricity is generated from renewable sources. Table 2 gives a breakdown of renewable energy sources for 1998

Beginning in 2001 with an additional 400 GWh of new renewables-based electricity, the measure will be phased in steps reaching 9500 GWh in 2010. As a minimum, the target amount is to be maintained through the period 2010-2020.

This 2% Target measure has already provided a significant boost to developing the renewable energy industry in Australia, and could stimulate at least AUD\$2 billion investment. Hence it is a major driver to develop new renewable energy sources for reducing GHG emissions.

SWERF Waste-to Energy Facility in NSW: Energy Developments Limited (EDL) is constructing a Solid Waste Energy Recycling Facility (SWERF) in Wollongong, NSW following a Renewable Energy Showcase Grant of \$2 million from the AGO. Based on 10 years development, the SWERF project will convert household trash to 'green' electricity with the potential for consuming 90% of the waste collected by Wollongong City Council currently going to landfill. Assuming a yield of 85% organic pulp (putrescibles, organics, paper, plastic), it is estimated that 100 tonnes of municipal solid waste will generate 90 MWh of electricity (3).

The EDL facility, costing AUD \$10 million for initial development, has been designed to separate recyclable materials, such as metals and glass, from unsorted household garbage and gasify the organic-based remainder using the Brightstar Environmental gasification technology. The gas is burned in reciprocating engines to generate electricity that is sent to the grid. The facility, having four 1.35 MW Gen-sets currently, is to be commissioned in July-August 2000. This demonstration phase will process some 20,000 tonnes per annum and, depending on a successful outcome, will be followed by two more distinct phases - 75,000 tonnes per annum and 150,000 tonnes per annum. The latter will generate up to 16 MW of electricity and substantially reduce the pressure on landfill sites.

Landfill-Gas to Electricity: EDL also operates 16 landfill-gas power generation facilities around Australia with a combined capacity of 72 MW. The conversion into electricity of methane gas resulting from anaerobic digestion of organic refuse avoided the release of 1.84 million tonnes of CO₂ in the 1998-99 financial year.

Bagasse/Wood Waste Generation: The construction of Australia's largest biomass project, costing AUD\$50 M, at Rocky Point Sugar Mill, Queensland, is scheduled for May 2000. The completed facility is to generate 30 MW of 'green' electricity from bagasse (typically 20-weeks sugarcane crushing season per year) and wood waste/green waste for use by consumers as well as steam and electricity for industrial users including the sugar mill and a nearby ethanol distillation plant.

The project is being jointly developed by the Heck Group (Rocky Point Sugar Mill owners) and Stanwell Corporation (power generator) supported by an AGO Showcase Grant of AUD \$3 million (4).

BP Solar Olympic Athletes Village: BP Solar, now BP Solarex following the merger of BP Oil with Amoco, is completing the installation of a 1 kW solar cell on each roof of the 650 houses at the Athletes Village for the 2000 Olympics in Sydney. The 12 solar laminates on each roof incorporate BP Solarex's high efficiency (17 %) Laser Grooved Buried Grid mono-crystalline technology.

In Australia, BP Solarex manufactures solar cells from multi-crystalline and mono-crystalline technology. The Solarex facility in 1999 received a Renewable Energy Commercialisation Grant of AUD \$482,000 to upgrade its multi-crystalline solar cell fabrication facility (4). By the end of year 2000, the company will be producing 13 MW of solar cell panels from its Sydney factory, with a projected output of 20 MW by the end of 2001.

CONCLUSIONS

The Australian Government has made a major commitment of almost \$1 billion towards achieving its Kyoto obligations through its financial support of diverse renewable energy and energy efficiency programs. The focus of the programs is on maximising reductions in GHG emissions via the demonstration, commercialisation and improved market acceptance of renewable energy and energy efficient technologies.

It is widely accepted that further measures will be needed for Australia to achieve its Kyoto targets. Options could include carbon credit trading, setting efficiency targets for major GHG emitters, and minimising the GHG impact of major development projects.

At this stage, there is no substantial government funding of high risk R&D projects as is common in USA, Japan and Germany. The Australian Government, however, supports fundamental greenhouse research activities through several CSIRO Divisions (e.g. global warming and climate change at the Division of Atmospheric Research; carbon fixing in forests and crops at the Division of Forestry) and various Cooperative Research Centres (e.g. CRC for Greenhouse Accounting; CRC for Renewable Energy; CRC for Clean Power from Lignite).

Increased joint government and industry funding of innovative technical solutions will be required to make further reductions in GHG emissions from Australia's particular energy generation and resource use as we move closer towards the Kyoto target dates of 2008-2012 and beyond.

ACKNOWLEDGMENTS

The authors express their thanks to New Energy and Industrial Technology Development Organization (NEDO), Sydney Representative Office, Australia for funding the Report (2) on which this paper is essentially based.

REFERENCES

- (1) Environment Australia: www.environment.gov.au, May 2000.
- (2) Allardice, D.J. and Young, B.C. *Greenhouse Gas Fixation and Utilisation Policy and Technology in Australia*, Report to NEDO (Sydney Representative Office): March 2000, 76p.
- (3) Toms, P. *Sustainable Utilisation of Green Waste and Urban Biomass – A Case Study of Wollongong's Electricity Plant and Solid Waste to Energy Recycling Facility*, IIR Conference on Waste Minimisation and Recycling 31 Aug – 1 Sep 1999, 17p.
- (4) Australian Greenhouse Office: www.greenhouse.gov.au/renewable/recp.
- (5) ABARE: *Australian Energy: Market Developments and Projections to 2014-15*, Canberra, 1999.
- (6) Schaap, H. *Data: Electricity Supply Association of Australia*, Melbourne, 1998.

Table 1. Australian Energy Use 1997-1998*

Source	Amount (%)
Crude oil	34
Black coal	29
Brown coal	13
Natural gas	18
Renewables	6

*Source: ABARE (5)

Table 2. Mix of Renewable Energy sources in Australia in 1998*

Source	Capacity (MW)	Generation (GWh)
Large hydro	7580	16,000
Small hydro	200	700
Biomass	330	800
Landfill gas	15	20
Sewage gas	49	90
Black liquor	6	40
Wind	2.7	4.8
Grid photovoltaic	0.14	0.3
Solar thermal	0.045	<1
Remote area power systems	14	<2
TOTAL	8,200	17,700

*Source: ESAA data (6)

A LIFECYCLE ASSESSMENT FRAMEWORK FOR EVALUATING THE REDUCTION OF CARBON DIOXIDE THROUGH INJECTION IN ACTIVE OR DEPLETED RESERVOIRS

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Keywords: CO₂ storage, enhanced oil recovery, depleted reservoirs

Abstract

Several industries are conducting research to reduce their greenhouse gas (GHG) emissions because of the growing concerns over the GHG's effect on the atmosphere. In the petroleum industry, sequestration in active or depleted reservoirs seems a feasible solution towards lowering these emissions. Furthermore, injection in depleted reservoirs is said to offer important storage capacity, whereas injection in active reservoirs for enhanced oil recovery (EOR) combines GHG storage with the production of additional oil.

This paper presents a systematic approach to investigating and comparing the benefits of CO₂ storage in depleted versus EOR reservoirs. The benchmark is the potential for net CO₂ sequestration over the lifetime of the reservoir. An example applying a lifecycle assessment to an ARCO (now BP Amoco) project in West-Texas is described. The analysis on depleted reservoir storage is still in progress. However, preliminary results with EOR suggest GHG emissions from this power intensive process are small compared to the storage capacity of the formation, leading to a significant reduction of GHG emissions.

Introduction

With the burning of fossil fuel, arise anthropogenic emissions of greenhouse gases which enhance the natural greenhouse effect and could contribute to changing global climates. The petroleum and power industries are considering projects to reduce their emissions. Solutions include the offset of emissions by reforestation and forest management projects, as well as the reduction in emissions through energy efficiency improvements at their facilities, and sequestration of greenhouse gases in the oceans or underground in aquifers or fossil fuel reservoirs.

Fossil fuel reservoirs are very attractive as storage for greenhouse gases (especially carbon dioxide) because of existing infrastructure and/or a good understanding of the reservoirs. Two types of reservoirs can be used for that purpose: depleted reservoirs and reservoirs still active where enhanced oil recovery (EOR) can be applied.

Depleted reservoirs have not been employed for the storage of carbon dioxide yet. However, for many years now, they have been an essential link in the supply chain to ensure uninterrupted availability of natural gas during periods of high-energy demand such as winter. When the demand is low and excess capacity occurs, natural gas is stored in depleted reservoirs. It is recovered later on when necessary. In 1997, there were at least 410 underground reservoirs in the United States used for natural gas storage, with a total working gas capacity of 108 billion cubic meters (Thompson, 1997). Depleted reservoirs are located throughout the U.S. All areas of the United States with known oil and gas reservoirs also have depleted reservoirs. Both depleted oil reservoirs and depleted gas reservoirs can be used for storage of carbon dioxide and it is estimated the storage potential for these formations is around 794 billion metric tonnes worldwide (Stevens and Taber, 1999). This is a large potential for storage compared to the 6.6 billion metric tonnes of greenhouse gases in carbon dioxide equivalent emitted by the U.S. in 1997 (adapted from EPA, 1999).

For the case of active reservoirs, enhanced oil recovery is initiated when pumping techniques no longer produce enough oil for the fields to remain economically attractive. Supercritical carbon dioxide (CO₂) is injected in the reservoir and serves as an efficient solvent by reducing the viscosity of the oil, and thus enabling the oil to flow more readily to the producing wells. The carbon dioxide usually originates from naturally occurring CO₂ reservoirs, and in some cases CO₂ comes from processing plants. Reservoirs suitable for EOR are mostly located in the Permian Basin, TX, but can also be found in Alaska, California, Kansas, Oklahoma and the Texas Panhandle (Moritis, 1998). The current production from CO₂ EOR accounts for about 30 thousand cubic meters of oil per day from a total of 63 projects, or about 3% of total U.S. oil production (Moritis, 2000). Typically, an average of 530 to 1750 cubic meters of CO₂ is injected per cubic meter of oil recovered (Beike and Holtz, 1996). The overall storage potential in EOR reservoirs is estimated to about 129 billion metric tonnes (Stevens and Taber, 1999). Therefore, reservoirs using CO₂ for enhanced oil recovery present the advantage of being able to store large quantities of CO₂ while providing the economic incentive of oil production.

This presentation will compare the two storage options (depleted reservoirs versus EOR reservoirs) following a life cycle assessment methodology. Based on a currently operated EOR reservoir in the Permian Basin, we will investigate the storage potential as well as the emissions generated by the energy intensive process which includes the injection of the CO₂, its separation, capture and compression. The EOR reservoir analysis reflects the actual data from the case study with CO₂ originating from natural reservoirs and from the recycled CO₂-rich stream of the processing plant (attached to the EOR process for the treatment of the produced gas stream). The depleted reservoir case is a virtual case, a modification of the same reservoir to fit a depleted situation.

Methods –Life Cycle Assessment

To determine the environmental burden associated with the injection of CO₂ in active or depleted reservoirs, we chose to use a life cycle assessment (LCA) in order to capture the impacts from “cradle to grave.” The LCA can be used for product/process comparison, pollution prevention or simply for understanding one process/product’s impacts on the environment. An LCA’s major strength is the objectivity of the environmental analysis, and the elimination of externalities in project management regarding environmental issues.

The LCA follows a very structured methodology. We focused our efforts here on the inventory analysis and the impact analysis. Simply, the process is broken down into small entities, therefore facilitating the determination of input streams (resource requirement) and output streams (emissions) for each entity. The impact analysis provides a quantitative or qualitative characterization of the streams into and out of the system.

This presentation will be limited to greenhouse gas emissions and to the boundary of the facility. The scope of this work includes the extraction of oil/gas from the reservoir, the processing of the gas phase (extraction and separation of the usual components such as CO₂, H₂S, natural gas liquids), compression of the separated CO₂ stream, and underground injection in the reservoir either for use in EOR or simply for long term storage. Because we are investigating an existing reservoir under EOR, the study will be limited to the estimated 40-year lifetime of the reservoir.

A functional throughput unit was selected as a normalizing factor in order to allow for comparison among alternative approaches. In the case of EOR, and other methods of oil production in general, the net quantity of crude oil produced is the valued commodity. Therefore, releases to the environment and resources needed throughout the processes are quantified and indexed to the quantity of crude oil produced by the facility.

This LCA analysis uses specific site data for field emissions and storage as well as for electricity generation. The data used to determine the emissions are in part from direct sampling, and in part estimates based on applicable emission factors (E&P Forum, 1994; EPA, 1998; AP-42, 1998; IPCC, 1996). To remain conservative, the results presented below rely mainly on the E&P Forum emission factors or the EPA emission factors when no corresponding E&P Forum emission factors were available. The storage capacity is determined by performing a mass balance on the amount of CO₂ injected and the amount of CO₂ produced along with the oil.

Results and Discussion

A significant part of a life cycle assessment has to do with resource utilization or the use of natural resources to perform the process or obtain the desired product. Resources include both the natural resources used directly by on-site devices and indirect resources for generation of the grid power used by the facility. In our example, the resources consist of gas and coal, but remain regional variables and would be different for other part of the US. For the oil recovery process linked to enhanced oil recovery the resources also include CO₂. This paper is not going to discuss this aspect in order to better focus on emissions and storage.

The greenhouse gases emitted by the EOR processing can be divided into the direct and indirect emissions. Indirect emissions are attributable to electricity generated outside of the facility boundaries and transported through the grid to power equipment within the system investigated. In our case study, we found indirect emissions account for 13.5% of total CO₂ emissions, about 0.1% of CH₄ emissions, and approximately 0.8% of N₂O emissions.

Direct emissions originate from the use of on-site equipment fired by natural gas. On-site fired equipment demands more power than equipment receiving electricity from the grid and therefore emissions are higher. Direct emissions account for 59.2% of CO₂ emissions, approximately 2% of methane emissions, and 84.1% of N₂O emissions.

The rest of the on-site emissions are accounted for by process equipment leakage and routine maintenance that could result in fugitive methane emissions. In addition, flaring associated with the separation plant is also included and constitutes the remaining of the emissions presented. The system's total CO₂ emissions amounted to 0.3 kg / kg of oil produced. The EOR process also emitted 0.0015 kg of methane / kg of oil produced, and 2.1 10⁻⁵ kg of N₂O / kg of oil produced.

Simultaneously, the process contributed to storing 3 kg of CO₂ / kg of oil produced, and 0.18 kg of methane / kg of oil produced. Table 1 provides a summary of the emissions from the EOR process per kg of crude oil produced. The mass balance for carbon dioxide exhibits process emissions as positive quantities, while the amount stored in the reservoir is shown as a negative number. This highlights the CO₂ storage potential of an oil reservoir.

Table 1 Mass balance of greenhouse gas emission for the EOR process (kg / kg of oil produced)

	Carbon Dioxide		Methane		Nitrous Oxide	
	On-site	Off-site	On-site	Off-site	On-site	Off-site
Emission	0.31	0.05	0.002	1.5 x10 ⁻⁶	2 x10 ⁻⁵	1.6 x10 ⁻⁷
Storage	3		0.2			
Balance	-2.6		-0.2		2 x10 ⁻⁵	

Our results suggest the EOR process using CO₂ as a solvent contributed to limiting the amount of greenhouse gases reaching the atmosphere over the lifetime of the reservoir (40 years). This table includes both the CO₂ recycled and the CO₂ originating from natural reservoirs. Only the recycled CO₂ would have been vented under normal EOR operations. Close to 45% of the CO₂ injected in the reservoir over the 40 year period

came from the recycling plant. We found that all of the CO₂ recycled is ultimately stored in the formation and 20% of the CO₂ purchased from natural CO₂ reservoirs is stored again in the EOR reservoir.

The part of the analysis related to storage of carbon dioxide in depleted reservoirs is still in progress. Therefore, we are unable to provide a comparison of both types of storage at this time, but will present the complete results of the study at the conference. However, we expect emissions for depleted reservoir storage to be in the same order of magnitude than for the EOR process. The depleted reservoir storage capacity should be significantly higher because EOR requires injection of additional fluids in the reservoir, like water, to boost production. Also injection in depleted reservoir is easier to monitor because nothing is actually removed from the reservoir.

Conclusion

The first part of the analysis demonstrates the CO₂ storage potential of an oil reservoir in the Permian Basin, TX, through the use of enhanced oil recovery. Concurrent with the storage possibilities in an active reservoir, we estimated the greenhouse gas emissions originating from the range of equipment used and from flaring practices and fugitive emissions. The results suggest the EOR process is not only a major CO₂ user, but could also be a significant way to store the CO₂ underground. This study, so far, also illustrates that the overall sequestration efficiency could be enhanced by utilizing captured and recycled CO₂ from process vents and stack effluents, instead of using CO₂ from natural reservoirs.

The second part of the study on injection of CO₂ in depleted reservoirs will be presented at the conference. We will analyze and compare both storage options focusing on storage capacity and emissions associated with separation and compression of the CO₂ stream. Incentives might play a significant role in the implementation and widespread use of these storage options.

Acknowledgements

The authors acknowledge fruitful discussions with Bruce Johnson, Tom Krawietz, Margaret Lowe, Barry Petty, Joe Sinner, and Clifton Yocom from ARCO Permian, TX, and thank them for providing data for this case study and for their support throughout this research.

References

- Beike, D.K., M.H. Holtz. 1996. "Integrated geologic, engineering, financial assessment of gas displacement recovery in Texas." Proceedings of the Permian Basin Oil and Gas Recovery Conference, Midland, Texas, 27-29 March. SPE 35167.
- E&P Forum. 1994. Methods for estimating atmospheric emissions from E&P Operations. Report No 2.59/197, September 1994.
- EPA. 1998. Inventory of US greenhouse gas emissions and sinks 1990-1996. Environmental Protection Agency, March 1998.
- EPA. 1999. Inventory of US greenhouse gas emissions and sinks 1990-1997. Environmental Protection Agency, March 1999.
- IPCC, 1996. Revised 1996 IPCC Guidelines for national greenhouse inventories. The Intergovernmental Panel on Climate Change.
- Moritis, G. 2000. "EOR weathers low oil prices." *Oil and Gas Journal*. March. 20.

Stevens, S.H., J.J. Taber. 1999. "Barriers to overcome in implementation of CO₂ capture and storage (disused oil and gas fields)." IEA Report PH3/22.

Thompson, J. M. 1997. "U.S. underground storage of natural gas in 1997: existing and proposed." Energy information administration, Natural Gas Monthly September 1997.

A TOOL TO FACILITATE MODELING AND PILOT PROJECTS FOR SEQUESTRATION OF CARBON DIOXIDE IN SALINE FORMATIONS

Keywords: greenhouse gasses, capture and storage

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ABSTRACT

Saline water-bearing formations that extend beneath much of the continental United States are attractive candidates for disposal of CO₂ produced during power generation or by other industrial processes. We have quantified the characteristics of saline formations that assure that gas can be efficiently injected into the selected subsurface unit and that it will remain sequestered for suitably long time periods. A GIS data base of these geologic attributes of 21 saline formations is available to support data analysis and comparison with CO₂ source locations. Attributes include depth, permeability, formation thickness, net sand thickness, percent shale, sand-body continuity, top seal thickness, continuity of top seal, hydrocarbon production from interval, fluid residence time, flow direction, CO₂ solubility in brine (P, T and salinity), rock mineralogy, water chemistry, and porosity. Variations in formation properties should be considered in order to match a surface greenhouse gas emissions reduction operation with a suitable subsurface disposal site.

INTRODUCTION

For CO₂ sequestration to be a successful component in U.S. emission-reduction strategies requires a favorable intersection of a number of variables such as the market for electricity, fuel source, power and industrial plant design and operation, a suitable geologic host for sequestration, and a suitable pipeline or right-of-way from the plant to the injection site. The concept of CO₂ sequestration in saline water-bearing formations (saline "aquifers") isolated at depths below potable aquifers became of widespread interest several years ago (Bergman and Winter, 1995) and continues to evolve. Saline formations are attractive because large volumes of prospective sink underlie many parts of the United States. Significant barriers remain, however, including high costs and potential citizen concerns about the safety and effectiveness of this process. Our contribution to the U.S. effort to reduce greenhouse gas emission via underground sequestration is a data base of formations that may have potential for sequestering CO₂. This data base can be used to (1) match CO₂ sources with prospective sinks, (2) conduct preliminary feasibility analysis, and (3) build various types of economic and process models. Our goal is to provide low-cost but realistic data that can support the search for viable options for CO₂ sequestration.

The scope of our investigations is saline water-bearing formations outside of oil and gas fields. We are accepting the concept of hydrodynamic trapping (Hitchon, 1996), in which the CO₂ is isolated from the atmosphere and potable water supplies by very long (>1,000 yr) travel times between the injection site and these environments. A structural trap for the CO₂ is not required. We are also focusing on onshore sites near large or closely spaced commercial power plants and other industrial centers with point-source emissions of CO₂. This definition allows exploration for large volumes of saline formations that may be optimal injection sites near sources where sequestration could be undertaken at minimal cost.

METHODS

In the feasibility phase of our project, we (1) mapped the 1996 carbon emissions of power plants to identify basins where sinks would be useful, (2) collected informal information on the areal distribution of industrial CO₂ sources, (3) identified 16 parameters that describe the properties of reservoirs and seals in potential sinks, and (4) tested the feasibility of collecting these data in saline formations.

During Phase II of our project, we compiled regional scale information and quantitatively mapped the 16 parameters for at least one target saline formation in 21 basins. This data compilation is based entirely on literature review, employing regional summaries, water-supply papers, state survey and U.S. Geological Survey maps and publications, oil and gas resource assessments, waste injection literature, and unpublished data sources including theses and contract reports. We used recent stratigraphic overviews to identify at least one potential saline

aquifer in areas with CO₂ sources. Then we conducted a literature search using GeoRef (<http://georef.cos.com/>) and other online resources and consulted local experts to locate, acquire, and compile the required information. We ranked the quality of data for each parameter as follows: (1) detailed data digitized from the cited source, (2) generalized or schematic data from the cited source, (3) detailed data interpreted during this project, (4) sparse or descriptive data interpreted during this project, and (5) little or no data, values based on analog data.

Raw data showing the spatial distribution of each parameter was digitized. In most basins, the raw data consisted of one or more paper maps, which were scanned and georeferenced using Cartesian projection and latitude-longitude as calibration points, digitized using NDS Mapper software, attributed, and imported into ESRI ArcView GIS (geographic information system). One source of error in the data base lies in unknown projection and imprecise registration of the source maps. A few data sets were obtained in digital format (for example, from N. Gupta Battelle Memorial Institute, USGS online sources, and an unpublished oil field data base compiled by M. Holtz, Bureau of Economic Geology).

Data were then manipulated in GIS and spreadsheet software to standardize highly variable raw data. Once in ArcView the maps were reprojected in meters and in Albers Equal Area projection, and the spreadsheet data were standardized into common units. Variability in original data is the major source of error in the data set; however, standardization is necessary for interbasinal comparisons, and we think that the precision is adequate for the intended purpose of supporting the search for CO₂ sequestration options. Site-specific follow-up studies will be required at any potential sequestration prospect to confirm relationships observed at a regional scale.

We did not attempt a comprehensive survey of potential saline formations. Saline formations were selected using the following informal criteria: (1) the formation has geographic and geologic potential to serve as a sink for areas of point-source CO₂ emissions, (2) sufficient data were located to map some of the parameters, and (3) inclusion of the formation contributes a geologically diverse set of potential sinks to be used for modeling experiments.

RESULTS

During the feasibility phase of evaluation of parameters that describe the properties of reservoirs and seals in potential sinks, we decided that the state of the science was too immature to determine which variables are critical. We therefore decided to compile diverse data. Variables were selected either because other workers have used them for models or basin assessment (for example Hendriks and Blok, 1995; Holloway and van der Straaten, 1995; Koide and others, 1995; Hitchon, 1996; van der Meer, 1996; Weir and others, 1996; Gupta and others 1998) or because they are commonly used in reservoir evaluation or for underground waste disposal site evaluation. These diverse data sets will then facilitate further evaluation and modeling.

Six parameters were selected primarily to describe injectivity. Injectivity controls how fast CO₂ can be injected into the saline formation without excessive pressure buildup. Depth is a primary constraint on the density of the injected CO₂. At typical temperature and pressure 800 m approximates the critical point, below which CO₂ requires less volume, which improves injectivity. Permeability and formation thickness are the rock variables that determine the flow rate from a well. Net sand (net high permeability strata) describes the thickness of the strata that accept fluid and are used for capacity assessment. Percent shale and sand-body continuity are indexes to the internal heterogeneity of the injection unit; they are needed to model the behavior of the CO₂ after it is injected.

Ten parameters were collected primarily to assess how effective the unit would be at trapping the CO₂. Under most conditions, CO₂ at critical point will be buoyant in brine. The top seal is defined as the low-permeability unit above the prospective injection unit that will limit leakage of the injected CO₂ upward into potable water and the atmosphere. The thickness of the top seal as well as its continuity can be used to calculate the rate of escape of CO₂ to assure that trapping will be effective. Production of oil or gas from the interval can provide a pathway for more rapid release of CO₂ to the atmosphere; pragmatically it raises issues of mineral rights. Injection of CO₂ in producing intervals can be beneficial to production, maintaining pressure and helping to mobilize oil. Use or reuse of hydrocarbon reservoirs for CO₂ sequestration has been considered in a number of studies, such as Holtz and others (1999), and is therefore not the focus of our study. Because we are using a hydrodynamic trapping assumption, fluid residence time

and flow direction are important in assessing effectiveness of lateral trapping in the formation and identifying potential short lateral paths for leakage to fresh water or the atmosphere. Temperature, pressure, and salinity are major variables in calculating CO₂ solubility in brine. Mineral trapping, in which CO₂ reacts with minerals in the rock, can also provide a very long term trapping mechanism (Hitchon, 1996); therefore, we compiled rock mineralogy and brine chemistry to permit assessment of the role of this process. Porosity is a simple variable for assessing the total volume of storage in the saline formation.

We identified 21 candidate formations in onshore U.S. basins, including Los Angeles, Powder River, Sevier, Mojave, South Carolina, Alabama, North Carolina, Appalachian, Illinois, Texas Gulf Coast, East Texas, Florida, Black Warrior, Denver, Williston, Michigan, San Juan, Palo Duro, and Anadarko. Data sets of 16 parameters for the target saline formation in each basin have been compiled and digitized. In many basins, several potential prospects were identified. We selected one or two formations to characterize in this study and note the potential for additional resource in overlying and underlying formations.

DISCUSSION

When we proposed this study, we thought that saline formations were generally poorly known because they are unused. We expected to have to interpolate information from oil and gas producing areas and aquifers. However, during the feasibility phase as well as the assessment phase, we found that data describing saline formations at a regional scale are moderately abundant. Data are derived from regional studies integrating areas productive for resources as well as assessment of saline formations themselves for potential for deep well injection of waste or saline water resources. In many places more detail can be extracted from sources such as well records and regulatory information from various types of injection, including waste and gas storage.

Capacity for CO₂ sequestration in different basins is highly variable. Primary causes of variability are formation thickness and permeability. For example, much larger volumes of CO₂ could be injected into thousands of feet of high-permeability sand typical of the Tertiary of the Gulf Coast than in the few hundred feet of older and less permeable basal Cambrian sandstones of the Midwest. In addition, quality of seals varies greatly, from thick, ductile mudstones to brittle and potentially highly fractured carbonate rocks. Many areas contain layered seal and permeable strata that may have the potential for greater protectiveness than a single thick seal. However, feasibility of implementing a sequestration project may not require optimal geologic conditions; other variables may bring a lower capacity sink into use.

We did not attempt a comprehensive survey of potential saline formations; therefore, our study is not intended as a refinement of the total volume assessment of Bergman and Winter (1995) or as a tool for evaluating all the sequestration options at a given site. It is, however, suitable for meeting our goal to provide realistic data that can support the search for viable options for CO₂ sequestration. In addition, our study provides a template for additional data compilation to create a detailed national assessment of capacity. This flexible data base can be used for construction of other scenarios, for example, combination of CO₂ utilization and geologic sequestration.

The data base is available to researchers in ArcView format from the Bureau of Economic Geology (contact us at <http://www.beg.utexas.edu>).

CONCLUSIONS

Variations in formation properties should be considered in order to match a surface greenhouse gas emissions reduction operation with a suitable subsurface disposal site. In this environment, where cost is a critical limiting factor, matching CO₂ capture processes with an optimal subsurface site for sequestration can be essential. This data base provides a vehicle for assessing the interaction between surface variables such as the nature of the source and type of capture and infrastructure and subsurface geologic variables.

ACKNOWLEDGMENTS

This project was funded by DOE under contract number DE-AC26-98FT40417.

REFERENCES

Bergman, P. D., and Winter, E. M., 1995, Disposal of carbon dioxide in aquifers in the U.S.: *Energy Conversion and Management*, v. 36, p. 523-526.

- Gupta, Neeraj, Naymik, T. G., and Bergman, Perry, 1998, Aquifer disposal of carbon dioxide for greenhouse effect mitigation: Proceedings of the 23rd International Conference on Coal Utilization and Fuel Systems, March 9-13, Clearwater, Florida.
- Hendriks, C. A. and Blok, K., 1995, Underground storage of carbon dioxide: Energy Conversion and Management, v. 36, p. 539-542.
- Hitchon, Brian, ed., 1996, Aquifer disposal of carbon dioxide: hydrodynamic and mineral trapping – proof of concept: Alberta, Canada, Geoscience Publishing Ltd, 165 p.
- Holloway, Sam, and van der Straaten, Rieks, 1995, The Joule II project: the underground disposal of carbon dioxide: Energy Conversion and Management, v. 36, no. 6-9, p. 519-522.
- Holtz, M. H., Nance, P. K., and Finley, R. J., 1999, reduction of greenhouse gas emissions through underground CO₂ sequestration in Texas oil and gas reservoirs, The University of Texas at Austin, Bureau of Economic Geology final report prepared for EPRI through the Department of Energy, WO4603-04, 68 p.
- Koide, H., Takahashi, M. Tsukamoto, H. and Shindo, Y, 1995, Self-trapping mechanism of carbon dioxide in aquifer: Energy Conversion and Management, v. 36, p. 505-508.
- van der Meer, L. G. H., 1996, Computer modeling of underground CO₂ storage: Energy Conversion and Management, v. 37, no. 6-8, p. 1155-1160.
- Weir, G. J., White, S. P., and Kissling, W. M., 1996, Reservoir storage and containment of greenhouse gasses: Transport in Porous Media: v. 23, p. 37-60.

ANALYSIS OF VISCOUS FINGERING IN TWO-DIMENSIONAL FLOW CELL BY FRACTAL DIMENSION

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KEYWORDS: Fractal dimension, Viscous fingering, CO₂ sequestration

INTRODUCTION

The potential global warming effects of increased carbon dioxide (CO₂) in the atmosphere have recently gained national and international attention. Consequently, the search for different ways to reduce CO₂ emissions has increased, and among the options available is sequestration of CO₂ by injection into deep brine formations. However, when a less viscous fluid, such as CO₂ is used to displace a more viscous fluid, such as brine, a flow instability phenomenon known as viscous fingering occurs. During this type of flow, the less viscous fluid forms fingers extending into the more viscous fluid. This phenomenon is significant to CO₂ sequestration in brine-saturated formations, because it will govern how much volume is available for CO₂ storage. Researchers desire to maximize the saturation of sequestered CO₂. A greater understanding of the flow patterns might yield insight that could ultimately lead to the increase of CO₂ sequestered. One way of observing the complex flow patterns that occur during immiscible displacements is to use an artificial porous medium made by etching channels of random width into glass plates. Since this medium is transparent, images of the flow can be recorded and used to characterize the geometry of the flow. Fractal dimension is one method that has been used to describe random geometries, including porosity (Hildgen et al, 1997), aggregates formed in different fluid mechanical environments (Logan and Kilps, 1995), and characterization of waste water treatment systems (Bellouti et al, 1997). The fractal dimension is used in this study to characterize relative saturations of air under different fluid flow conditions.

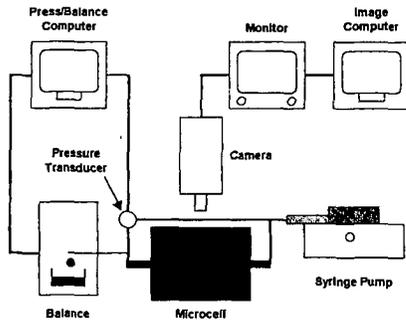


Figure 1: Experimental flow system

EXPERIMENTAL

The experimental flow system (see Figure 1) consists of a micro flow cell, which simulates the porous medium; a syringe pump, which provides a constant-volume-rate injection of fluid into the flow cell; a pressure transducer for measuring the pressure drop across the flow cell; and a balance for measuring the mass of the displaced fluid. The flow cell is made by etching channels of random width into a glass plate and fusing a second, flat plate to it, thereby creating a network of enclosed channels connected to inlet and outlet manifolds. A picture of one of the micro flow cells having random distribution of different channel widths used in this study is shown in Figure 2.

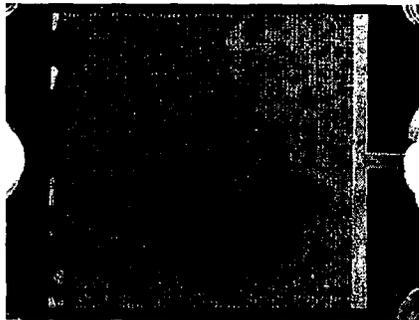


Figure 2: Flow cell showing pattern formed by injection of air into a water-saturated cell. The cell inlet is on left and the outlet on right.

Channel widths for cell #1 are in the range of 175-575 μm and for cell #2 are in the range of 260-1305 μm . In the experiment, the cell was first flooded with water to residual gas saturation. Then air was injected while the pressure drop across the cell and the mass of water displaced were recorded. Digital images of the cell were taken at regular intervals, usually 5 seconds, with a CCD camera. A computer program was developed to analyze the images for saturation and relative permeability calculations. Experiments were performed at different capillary numbers by use of different flow rates.

ANALYSIS

We use the box counting method (Aker, 1997) to analyze the pattern formed by the viscous fingers. In this method the image is covered with an array of square boxes, each box of size L , and the number of those boxes N that cover the injected-air pattern is counted. The relationship between N and the size of the box can be represented by

$$N(L) \sim L^{-d} \quad (1)$$

where d is the box-counting dimension and is a function of the geometry of the pattern. For example, if all the channels of the cell were filled with air, N would be proportional to L^{-2} . Or, if the air were to flow straight across the cell from entrance to exit filling only one channel, N would be proportional to L^{-1} . Since the actual pattern of the air flow is somewhere between these two extremes, N will be proportional to L^{-d} , where $1 < d < 2$. A log-log plot of the box counts can be used to determine d , as shown in Figure 3.

RESULTS AND DISCUSSION

Results from three experiments are discussed in this paper. These were conducted using two flow cells, and fixed injection rate Q and slightly different mobility ratios M . The mobility ratio is defined as ratio of the viscosity of the displaced fluid to that of the displacing fluid. The experimental conditions are shown in Table 1.

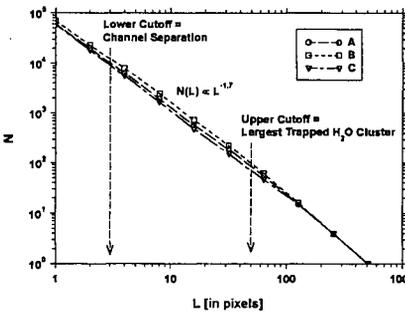


Table 1. Experimental Conditions

Experiment	Flow Cell	Fluids	Channel Width [μm]	Q [ml/min]	M
A	#1	Water and gas	175-575	0.87	53.76
B	#2	Water and gas	260-1305	0.90	53.76
C	#1	Nacl soln. and CO_2	175-575	0.91	72.53

The fractal dimensions of the flow patterns for these experiments are presented in Figure 3. The data plotted are for the ultimate flow patterns observed at the end of each experiment. The plots of data from the dynamic phase of the experiment, when the flow patterns are changing, are parallel to the plots of the ultimate values. Fractal dimensions of 1.7 were obtained with water and air as the immiscible fluids. When a sodium chloride solution and CO_2 were used (experiment C), no change in d was observed. We also noted that the injection rate does not change the value of d over the range of injection rates used.

Thus, in our work we found that d does not depend on the physical properties of the flow cell; the mobility ratios, although the two mobility ratios are relatively close; and on the level of air saturation of the cell. This implies that d is more of a characteristic of the flow patterns than any other parameter. The values of d obtained in our studies characterize viscous fingers for diffusion-limited aggregation (DLA) (Meakin, 1983). Figure 4 shows the correlation between fractal dimension and saturation.

CONCLUSIONS

These experiments demonstrate that fractal dimension is a function of fluid saturation but is independent of physical properties of the porous media. This analysis will be useful for

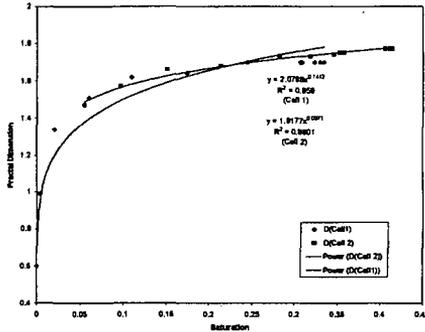


Figure 4: Fractal Dimension as a Function of Saturation

determining the fraction of the porous media that the displacing fluid will occupy. This is critical in the case of CO_2 sequestration into brine-saturated formations, because the more volume of space occupied by CO_2 during sequestration the more effective the process is.

Acknowledgments: Olubunmi Ogunsola was a National Research Council Sr. Associate. Her associateship and this work were funded by the Office of Fossil Energy, U.S. Department of Energy.

References

1. Bellouti, M. *Wat. Res.* **1997**, 31, 1227.
2. Aker, E. *PhD Dissertation, University Institute Oslo*, 1997.
3. M. Ferer, M.; G. Bromhal, and D. H. Smith, "Pore-Level Modeling of Carbon Dioxide Sequestration in Deep Aquifers," *Fuel Division preprint*, Washington, DC, August 20-24, 2000.
4. B.E. Logan and J. R. Kilps, *Wat. Res.* **1995**, 29, 443.
5. P. Meakin, *Phys. Rev. A* **1983**, 27, 2616.
6. M. Rahman, *J. of Food Engineering* **1997**, 32, 447.
7. P.Hildgen et al, *Physica. A* **1997**, 234, 593.

Pore-Level Modeling of Carbon Dioxide Sequestration in Deep Aquifers

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KEYWORDS: CO₂ sequestration, Pore-level modeling; Immiscible drainage

ABSTRACT

Underground injection of gas is a common practice in the oil and gas industry. Injection into deep brine-saturated formations is a commercially proven method of sequestering CO₂. However, it has long been known that the immiscible displacement of a connate fluid by a less-dense and less-viscous fluid produces gravity override and unstable displacement fronts. These phenomena allow only a small fraction of the pore volume of a brine-saturated formation to be available for sequestration. A better understanding of the fluid displacement process could lead to reduced capital and operating costs by increasing CO₂ sequestration in deep aquifers.

We have developed a pore-level model of the immiscible injection of a non-wetting fluid (CO₂) into a porous medium saturated with a wetting fluid (brine). This model incorporates a distribution of different "pore-throat" radii, the wettability of the formation (i.e., the gas-liquid-solid contact angle), the interfacial tension between the fluids, the fluid viscosities and densities, and all other parameters that appear in the capillary pressure or the capillary, Bond, or fluid-trapping numbers. The computer code for the model maintains a constant injection velocity to within a few percent.

This model has been used, with experimental values of viscosities and interfacial tensions, to study the high-pressure injection of carbon dioxide into brine-saturated porous media. Results are presented for the applied pressures, fluid-front geometries, residual saturations, and numbers of blocked throats.

INTRODUCTION

The possible effects of rising atmospheric concentrations of carbon dioxide on global climate are of worldwide concern. The U. S. Department of Energy and its National Energy Technology Laboratory have instituted programs to study various methods of sequestering CO₂. [1], [2] Underground injection of gas has long been a common practice in the oil and gas industry. [3] Injection into deep brine-saturated formations is a commercially proven method of sequestering CO₂. [4] However, it has long been known that the immiscible displacement of a connate fluid by a less-dense and less-viscous fluid produces gravity override and unstable displacement fronts. [5] These phenomena allow only a small fraction of the pore volume of a brine-saturated formation to be available for sequestration. [6] A better understanding of the fluid displacement process could lead to new technologies for alleviating these mobility control problems [5] and to reduced capital and operating costs for CO₂ sequestration in deep aquifers.

We have developed a pore-level model of the immiscible injection of a non-wetting fluid (CO₂) into a porous medium saturated with a wetting fluid (brine). [7] This model, which is an extension of an earlier model for two miscible fluids, [8] incorporates a distribution of different "pore-throat" radii, the wettability of the formation (i.e., the gas-liquid-solid contact angle), the interfacial tension between the fluids, the fluid viscosities and densities, and all other parameters that appear in the capillary pressure or the capillary, Bond, or fluid-trapping numbers. This model has been used, with experimental values of viscosities [9] and interfacial tensions, [10] to study the high-pressure injection of carbon dioxide into brine-saturated porous media. Results are presented for a variety of capillary numbers, showing trends in the applied pressures, fluid-front geometries, and residual saturations.

DESCRIPTION OF THE MODEL

This pore-level model of injection of carbon dioxide into a water-wet porous medium incorporates, as realistically as possible, both the capillary pressure blocking the invasion of narrow throats and the viscous pressure drop in a flowing fluid. The two-dimensional model consists of a square lattice of pore bodies with unit volume at the lattice sites and connecting throats, which are of unit length and have randomly chosen cross-sectional areas between 0 and 1. We choose to inject the carbon

dioxide along a diagonal; if we had chosen to inject along one side of the square lattice, we would have the artificial situation of one-half of the throats perpendicular to the average pressure gradient, making them more susceptible to capillary blocking because of a reduced pressure drop. This model is similar in spirit to other recent modeling efforts; but our model has some features which should make it more physical than other models: e.g. pore throats with real volumes, pore bodies with finite volume, constant velocity (giving a meaningful capillary number), and multiple checks on whether pores are blocked or unblocked.[11],[12],[13]

When the interface is in one of the pore throats, the radius of curvature, R , of the meniscus is fixed by contact angle, θ , and the radius of the pore throat, r ;

$$R = r / \cos\theta. \quad (1)$$

Therefore, the pressure drop across the meniscus is fixed at the capillary pressure

$$P_{cap}(R) = \frac{2\sigma \cos\theta}{r}, \quad (2)$$

where σ is the surface tension. Thus the flow velocity is given by the throat conductance times the total pressure drop across the throat, see Fig. (1a).

$$q = g_{throat} (P_{nw} - P_w - P_{cap}). \quad (3a)$$

Here, pressure P_{nw} is the pressure in the non-wetting, CO_2 -filled pore body, and P_w is the pressure in the wetting water-filled pore body. The transmissibility (conductance) of the throat is given by Poiseuille's law [14]

$$g_{throat} = \frac{1}{8\pi\mu_w} \frac{A_{throat}^2}{(x + (1-x)/M)} \quad (3b)$$

where μ_w is the viscosity of water, A_{throat} is the cross-sectional area of the throat, (randomly chosen from a uniform distribution between 0 and 1), x is the fraction of the throat of length 1 which is water-filled, and M is the ratio of the water viscosity to that of the carbon dioxide. From Eq. (3a), the CO_2 advances if the pressure difference between the CO_2 -filled pore and the water-filled pore exceeds the capillary pressure. Otherwise the CO_2 will retreat.

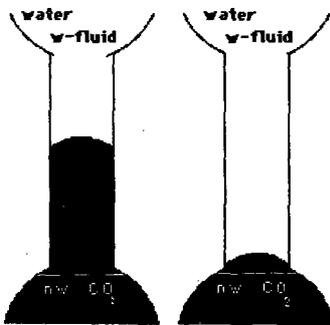


Fig. 1a Meniscus in throat
Fig. 1b Meniscus at inlet
Blocking is possible in 1.b (see Eq. (5))

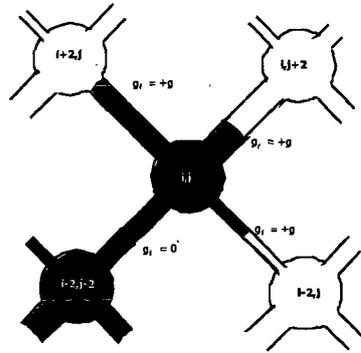


Fig. 2 Example for determining g_f in Eq. (6).

If the interface is at the entrance to a throat Fig. (1b), the throat will be blocked if the pressure difference is positive but not large enough to overcome the capillary pressure in Eq. (2). In this case, the positive pressure difference creates a meniscus with a radius of curvature, R , satisfying the equation

$$P_{cap}(R) = \frac{2\sigma \cos\theta}{R} = P_{nw} - P_w, \quad (4)$$

where this radius of curvature is larger than the radius R in Eq. (1) needed to enter the throat. Therefore the throat is blocked ($q = 0$) whenever a positive pressure drop is too small to push the meniscus into the throat, i.e., whenever

$$0 < P_{nw} - P_w < \frac{2\sigma \cos\theta}{r} \quad (5)$$

If the pressure drop in Eq. (5) is negative (q is negative ; $q = g_{throat} (P_{nw} - P_w)$), the water re-invades the pore body ; and if the pressure drop exceeds the capillary pressure, the non-wetting fluid advances; q is positive and given by Eq. 3a.

Volume conservation of the incompressible fluid dictates that the net volume flow, q , out of any pore body must be zero. Using the above rules for the flow velocities, requiring that the net flow out of pore body (i,j) be zero leads to the following equation for $P_{i,j}$:

$$(g_{i-2,j-1} + g_{i,j+1} + g_{i-1,j} + g_{i+1,j})P_{i,j} = (g_{i-2,j-1} P_{i-2,j-2} + g_{i,j+1} P_{i+2,j+2} + g_{i-1,j} P_{i-2,j} + g_{i+1,j} P_{i+2,j}) + (gf_{i-2,j-1} P_{cap,i-2,j-1} + gf_{i,j+1} P_{cap,i,j+1} + gf_{i-1,j} P_{cap,i-1,j} + gf_{i+1,j} P_{cap,i+1,j}) \quad (6)$$

Here the array gf is zero if there is no meniscus in the throat; for a meniscus in the throat $gf = +g$ or $-g$ depending on the direction of CO_2 advance in the throat (Fig. 2).

To determine the pressure field one iterates (Eq. 6) until stability is achieved (the residual is less than some small value); i.e. until

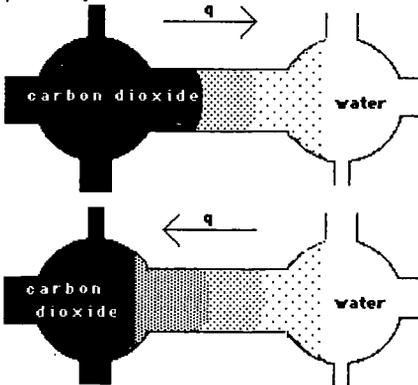
$$R = \sum (P_{new} - P_{old})^2 < \varepsilon, \quad (7)$$

where ε is chosen to be small (e.g. $10^{-6} > \varepsilon > 10^{-9}$). This value of ε was adjusted to minimize run-time without seriously sacrificing mass-conservation.

At a given time step, once the pressure field is determined for the initial choice of conductances, the interface is scanned to determine if there are changes in the throat blockages because of changes in the pressure drops. With these new conductances, the pressure field is re-determined by iterating Eq. (6). With the new pressure field, changes in the blockages are re-determined. This procedure continues until there are no further changes in the blockages, or until the changes occur only in throats that have alternated (blocked to unblocked) three times or more.

Once the pressure field has been determined and there are no more changes in throat blockage (excluding the oscillating blockages discussed above), we know the pressure field that will advance the interface. We choose a time interval that will advance the fluid one-half unit volume through the throat with the largest flow velocity.

Flow can increase the amount of non-wetting fluid (CO_2) within the pore throat, or through the pore throat into the pore body (Fig. 3a). Similarly, backflow can cause the interface to retreat within the pore throat (Fig. 3b) or through the pore throat into the pore body.



Flow Rules: Fig. 3a) Top ; 3b) Bottom
 Fig. 3a) flow can advance the interface through the throat into the pore body
 Fig. 3b) the interface can retreat from a pore body into the throat and into the next pore body

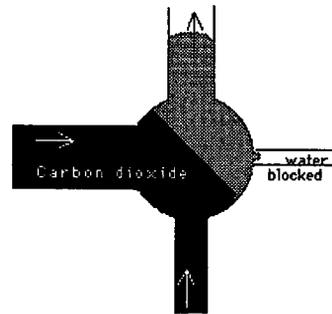


Fig. 4 If the flow over-fills a pore body at a given step, the over-filling is shared by the unblocked throats

If the pore body becomes over-filled by carbon dioxide, the excess fluid is shared proportionally by the outflow throats (Fig. 4). However, if at these pressures the

carbon dioxide is blocked from entering any throats, the last time interval is recalculated so that the fluid will just fill the pore body with an excess of 5% or less. Similarly, if the water backflow fully re-invades a pore body, the excess water is shared by the outflow throats.

If the carbon dioxide occupies two adjacent pores, without fully occupying the throat between them, there is a trapped plug of water in the throat. This plug will remain trapped in the throat unless the pressure drop across the throat is large enough to mobilize the plug of wetting fluid. The pressure drop across the throat must be larger than the capillary pressure to push the water out of the throat. If the pressure drop is large enough, we allow this water to reside in the pore until such a time as that pore is fully re-invaded by water. This assumption that the water remains in the pore is unphysical, because it is more favorable to have the wetting fluid re-invade the narrower throats filled with non-wetting fluid. The fraction of wetting fluid (water) participating in this unphysical process is calculated in the program. On the other hand, if water re-invades two adjacent pore bodies, without re-invading the connecting throat, the non-wetting carbon dioxide is moved to the low-pressure pore body.

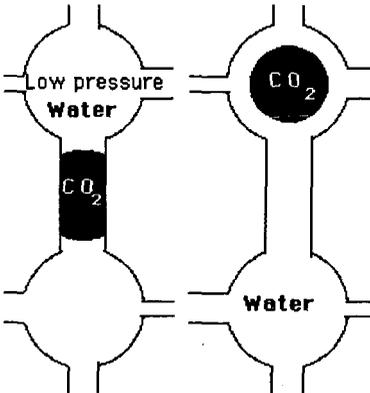


Fig 5a) Trapped CO_2 will be moved to the lower pressure pore body.

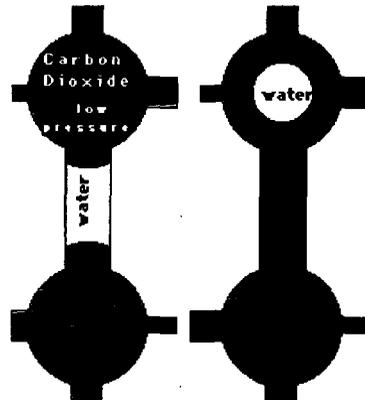


Fig. 5b) Trapped water will be moved to the low pressure pore body for a pressure drop exceeding the capillary pressure

A throat is considered to be on the interface, if the pore body at one end contains some water and if the pore body at the other end is fully invaded by carbon dioxide (or was fully invaded and is not yet fully re-invaded by water due to backflow).

RESULTS

We have chosen parameters appropriate to high-pressure injection of carbon dioxide injection into a typical brine saturated reservoir: an interfacial tension, $\sigma = 21 \frac{\text{dynes}}{\text{cm}}$, a contact angle of $\theta = 0^\circ$, and a viscosity of the high pressure CO_2 , $\mu = 0.05 \text{ cp}$. [9,10,15]

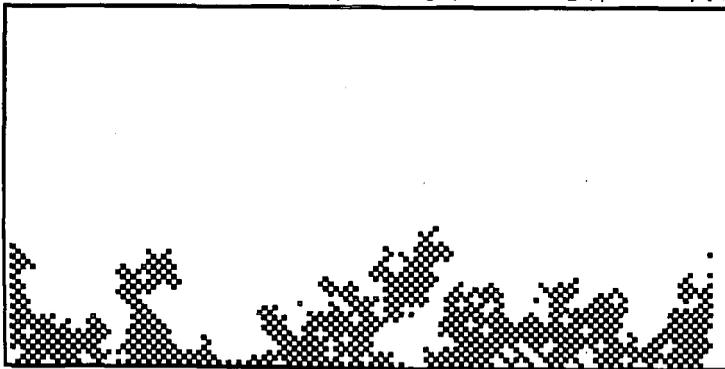


Figure 6) The flow pattern, the black pores are occupied by carbon dioxide.

We chose the scale of the medium (length of a typical throat) to be $\ell = 100 \mu\text{m}$; thus, in our model porous medium, the largest throats will have a radius of $56 \mu\text{m}$, and the smallest capillary pressure (in this largest throat) will be $P_{\text{cap,min}} = 7500 \frac{\text{dyne}}{\text{cm}^2}$. Using these values of the parameters, we have run this program on a 70×70 square lattice array, adjusting the pressure drop, ΔP , to maintain a constant flow velocity $q = \frac{q^* \ell^3}{8\pi \text{ sec}}$ with $q^* = 116.0 \pm 1.4$. For these parameters the capillary number is 3×10^{-5} .

Figure 6 shows the flow pattern after 10,000 time steps. The black areas are invaded by carbon dioxide. At this time the saturation is 24%.

As mentioned, the velocity is approximately constant; small variations are within a standard deviation of less than 2%. To maintain this constant velocity, the pressure drop shows wide variations (see Fig. 7).

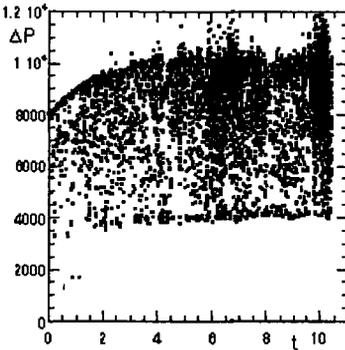


Figure 7) Pressure drop across the porous medium as a function of injection time.

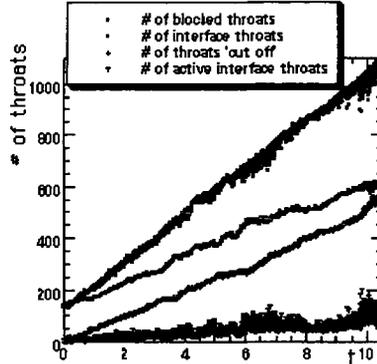


Figure 8) Number of throats of different types as a function of injection time.

Figure 8 shows the dramatic effect of capillary blocking of the throats, near the end of this simulation there are 600 throats on the interface. Of these 600 throats, only 90 are active with the rest being blocked. The total number of blocked throats consists of the 510 interfacial throats that are blocked and the 560 throats that have trapped, immobilized water (as in Fig. 5b, with the pressure drop being too small to mobilize the trapped water).

Additional computer runs will lead to a greater understanding of the role of capillary trapping in CO_2 sequestration and of the effectiveness of different sequestration schemes.

1. U. S. Department of Energy, Office of Fossil Energy. *Carbon Sequestration*, February 1999.
2. U. S. Department of Energy, National Energy Technology Laboratory. *Carbon Sequestration*, June 1999.
3. Hadlow, R. E. In *Proc. 67th Annual Tech. Conf. Soc. Petrol. Engrs.*, Washington, DC, 1992, SPE 24928.
4. Hanisch, C. *Environ. Sci. Tech.* **1998**, 32, 20A-24A.
5. Smith, D. H., ed. *Surfactant-Based Mobility Control: Progress in Miscible-Flood Enhanced Oil Recovery*, American Chemical Society, Washington, DC, 1988.
6. Hendriks, C. *Carbon Dioxide Removal from Coal-Fired Power Plants*, Kluwer Academic Publishers, Dordrecht, 1994.
7. Ferer, M., G. S. Bromhal and D. H. Smith. In *Proc. Pittsburgh Coal Conference*, Pittsburgh, PA, September 11-14, 2000, paper # 53.
8. Ferer, M., J. Gump and D. H. Smith. *Phys. Rev. E* **1996**, 53, 2502-2508.
9. Michels, A., A. Botzen and W. Schurman. *Physica* **1957**, 23, 95-102.
10. Chun, B.-S. and G. T. Wilkinson. *Ind. Eng. Chem. Res.* **1995**, 34, 4371-77.
11. van der Marck, S. C., T. Matsuura & J. Glas. *Phys. Rev. E* **1997**, 56, 5675-5687.
12. Pereira, G. *Phys. Rev. E* **1999**, 59, 4229-4242.
13. Akers, E. *A Simulation for Two-Phase Flow in Porous Media*, Dissertation, Univ. of Oslo, Oslo, Norway (1996) www.fys.uio.no/~eaker/thesis/thesis.html.
14. Lenormand, R., E. Touboul and C. Zarcone. *J. Fluid Mech.* **1988**, 189, 165-187.
15. Vesovic, V. and W. A. Wakeham. *J. Phys. Chem. Ref. Data* **1990**, 19, 763-808.

IMPROVED GEOLOGIC SEQUESTRATION USING CARBON DIOXIDE THICKENERS

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KEYWORDS: geologic sequestration, carbon dioxide, viscosity

ABSTRACT

The sequestration capacity of deep saline aquifers and abandoned oils reservoirs may be increased if dense carbon dioxide can be thickened. Random copolymers of 71 mol% fluoroacrylate and 29% styrene are the most effective CO₂ thickeners, inducing 2-200 fold increases in viscosity at concentrations of 0.1-5.0 wt%. The fluoroacrylate content of the copolymer assures CO₂ solubility, while the π - π stacking of the phenyl groups induces substantial viscosity increases. Non-fluorous analogs of these thickeners are being developed to dramatically reduce their cost.

INTRODUCTION

The focus of this paper is the sequestration of CO₂ in geologic formations, such as oil reservoirs, gas reservoirs, aqueous formations and deep and unmineable coal formations (DOE 1999). This mode of sequestration has already been initiated Sleipner West off the coast of Norway. At this site, CO₂ is separated from a natural gas off-shore production well, and then re-injected into an aquifer 1000 m under the North Sea. About 1 million tonnes of CO₂ are sequestered each year in this manner. The technologies associated with the injection of CO₂ into subterranean porous media containing water, gas and oil have been studied for decades. Of particular relevance is the use of CO₂ to recover oil from sandstone or limestone formations. This CO₂ EOR technology provides a basis for understanding the phenomena involved in the flow of CO₂ in porous media. The 70 oil fields in the world that use CO₂ to displace oil from the formation sequester large volumes of CO₂ in the reservoir at the end of the project. The bulk of the CO₂ currently used for these EOR projects is derived from natural CO₂ reservoirs, however. It is expected that in the future, CO₂ derived from power plant flue gas may be used for EOR.

Another advantage of geologic sequestration is that a significant capacity for geologic sequestration exists in the US. Although estimates of the capacity for geologic sequestration can vary widely, they indicate a substantial potential for sequestration relative to anthropogenic CO₂ emissions. Worldwide emission has been estimated to be 21.8 Gt CO₂/yr, or 5.9 Gt C/yr (Rubin, et al. 1992). The US generates 4.8 Gt CO₂/yr, or 22% of these emissions. The US CO₂ output from all electric generating plants is 35% of this total, 0.46 GtC/yr, or 1.7 Gt/yr of CO₂, or 30.6 TSCF/yr of CO₂. These sequestration capacity estimates for domestic geologic formations include 1-130 GtC for deep saline aquifers (Bergman and Winter, 1995), 10-25 GyC for natural gas reservoirs, 0.3GtC/yr for active gas fields (Baes, et al. 1980), 0.14 Gt/yr for depleted and abandoned oil reservoirs (DOE, 1993), 3 Gt CO₂ (Winter and Bergman, 1993) -30 Gt CO₂ (Johnson, et al. 1992) for depleted oil and natural gas reservoirs. A worldwide estimate 320 Gt CO₂ has also been made (Koide, et al. 1992).

There is an aspect of CO₂ sequestration into geologic formations that may significantly diminish the capacity of aquifers and oilfields. Although the permeability or porous media to oil, water and CO₂ are of the same order of magnitude, the viscosity of the CO₂ is significantly less than the viscosity of oil or water. At sequestration conditions, the viscosity of CO₂ will be on the order of magnitude of 0.1 cp. Oil viscosity can be 0.2-20 cp, while brine viscosity is on the order of 1 cp. These low ratios (less than unity) of the displacing fluid (CO₂) to the displaced fluid (water or oil) result in poor vertical sweep efficiency as the CO₂ preferentially flows through low permeability layers and poor areal sweep efficiency as viscous fingers of CO₂ bypass oil in each layer. These effects become more pronounced as the viscosity ratio becomes smaller. A substantial reduction in the effective volume for sequestration may occur because of the poor sweep efficiency of CO₂ in an aquifer. For example, a comparison of the sequestration capacity estimates of The Netherlands indicated that a reduction of about an order-of-magnitude reduction of the sequestration capacity of an aquifer may occur if the effects of the low-viscosity of CO₂ on sweep efficiency are accounted for (van Engelenberg and Blok, 1991; van der Meer, 1992, van der Meer, et al. 1992). Therefore, if the viscosity of the CO₂ could be increased to a value

comparable to that of the fluid being displaced (water or oil), a significant increase in the sequestration capacity of aquifers and oilfields could be realized. An inexpensive CO₂-thickener that is capable of elevating the M to a value of unity would enhance the sequestration capacity of aquifers and oilfields. The ideal thickener would be effective in dilute concentrations, easy to dissolve in CO₂, inexpensive, non-volatile, readily available in large quantities, environmentally benign and safe. Carbon dioxide thickeners had not been designed and synthesized until the late 1990's (Enick, 1998).

MATERIAL AND METHODS

Four novel types of CO₂ thickeners, semifluorinated trialkyltin fluorides, telechelic polyfluoro-urethane ionomers, fluorinated small hydrogen bonding compounds (Shi et al. 1999) and fluoroacrylate-styrene copolymers (Huang, et al. 2000) have been recently identified. Only the fluoroacrylate-styrene copolymers have exhibited the ability to induce dramatic increases in viscosity at dilute concentrations, however. The fluoroacrylate-styrene copolymer was composed of two monomers, a fluoroacrylate and styrene. These monomers were bulk-polymerized. The fluoroacrylate portion of the random copolymer imparted significant carbon dioxide solubility to the polymer. The styrene was relatively CO₂-phobic and interacted with the styrene functionalities of neighboring polymers in solution via "π-π stacking". These intermolecular associations lead to the formation of macromolecular structures in solution that can induce tremendous increases in solution viscosity. The optimal composition of the copolymer was 29 mol% styrene-71 mol% fluoroacrylate. Greater concentrations of styrene led to marked decreases in CO₂ solubility and viscosity enhancement. Falling cylinder viscometry results for this copolymer were measured in a high pressure, windowed, variable volume view cell manufactured by D.B. Robinson.

Unfortunately, these types of fluoroacrylate-styrene copolymers suffer an inherent disadvantage. The copolymer is predominantly fluoroacrylate and this fluorinated monomer is currently *very expensive*. Once injected into the aquifer, the thickener cannot be recovered and recycled, therefore all of the thickener will be "lost" to the reservoir. 3M uses fluoroacrylate monomers in their products, and the lowest price of their fluoroacrylate polymers is on the order of \$50-100/lb. Even at \$50/lb, the 0.1wt% (1000 ppm) copolymer would add approximately \$100/ton CO₂ injected in chemical costs alone. At a concentration of 0.01 wt% (100 ppm) the added cost of this chemical would be \$10/ton, and at 0.001 wt% the cost would be \$1/ton CO₂. The economics of sequestration would therefore require this type of thickener to be effective at concentrations as low as 0.001 wt% (1 ppm). Although it is reasonable to expect a significant viscosity increase at 0.1wt%, it is highly unlikely that *any* thickener can be effective at concentrations of 0.01 wt% or less.

Therefore our objective was to identify an environmentally benign, CO₂-thickener that is two orders of magnitudes less expensive than the fluoroacrylate-styrene copolymer. Clearly, the copolymer must contain *no fluorine*, and preferably it should be composed of *only carbon, hydrogen and oxygen*. If this can be achieved, it is quite reasonable to expect that an affordable CO₂-thickener can be identified for geologic sequestration applications. Our strategy for designing an inexpensive CO₂-thickener was (a) to identify a highly CO₂-philic polymer, (b) to maximize its molecular weight, and (c) to modify its structure to incorporate CO₂-phobic functional groups that lead to viscosity-enhancing macromolecular structures in solution. The results of the first step (a) will be presented. An example of a highly CO₂ soluble, non-fluorous copolymer was obtained by copolymerizing CO₂ and a cyclic ether to form an ether-carbonate copolymer (Sarbu, et al. 2000). This was done by copolymerizing either propylene oxide (PO), ethylene oxide (EO), or cyclohexene oxide (CHO) with CO₂ using sterically hindered aluminum catalysts, Figure 1. Note that CO₂ is a raw material for the synthesis of the CO₂-thickening compound. Although this may result in a marginal increase in the amount of CO₂ sequestered in an aquifer, the foremost advantage is that lost cost of CO₂ will lower the price of this copolymer. Polymerizations using these aluminum catalysts give yields in the range of 200 - 1200 g polymer/g catalyst. The polymerizations are typically living in character, with molecular weight distributions less than 1.5 (typically 1.1) and absolute molecular weights governed by the ratio of monomer to initiator. ²⁷Al NMR showed that these catalysts exhibit only one Al species, unlike typical aluminum catalysts used in CO₂/oxirane copolymerizations that exhibit "multi-site" behavior. The extent to which CO₂ is incorporated into the polymer is a function of temperature, pressure, and catalyst type.

Phase results of mixtures of CO₂ and these new CO₂-philic functional groups will be presented. Solubility was determined using standard, non-sampling, visual cloud point determination via isothermal compressions and expansions of a mixture of specified overall composition. The same view cell used for the viscometry was employed for the solubility measurements.

RESULTS

A comprehensive falling cylinder viscometry study was conducted with the 29 mol% styrene-71 mol%fluoroacrylate copolymer. Figure 2 illustrates the effect of shear rate and polymer concentration on relative solution viscosity. The relative solution viscosity is the ratio of solution viscosity to the viscosity of neat CO₂ at the same temperature and pressure. The solution is shear-thinning at all concentrations. At 5 wt% in liquid CO₂, a 250-fold increase was observed at low shear rates. Even at concentrations as low as 0.2 wt%, a significant increase in the viscosity was detected at very high shear rates. The sequestration target area for desired viscosity increase and shear rate in the formation are also illustrated in this figure. It is apparent that this copolymer may be able to induce a 10-fold increase in solution viscosity at the low shear rates associated with CO₂ sequestration.

Copolymers of PO and CO₂ proved to be remarkably CO₂-philic; Figure 3 shows that a 250 repeat unit PO/CO₂ copolymer with 15.4% carbonate units exhibits lower miscibility pressures [8] than a fluoroether (poly(hexafluoropropylene oxide) whose chain length is significantly lower (175 repeats). It should be noted that a PO homopolymer of 250 repeat units would exhibit miscibility pressures beyond the capacity of our instrument. Therefore this copolymer is composed of two readily available monomers, one of the monomers is CO₂, the copolymer exhibits greater CO₂-solubility than PO, and the copolymer is more CO₂-soluble than fluoroether polymers of comparable length.

DISCUSSION

Although fluorinated copolymers are effective carbon dioxide thickening agents, their high cost will prohibit their implementation in large-scale geologic sequestration projects. Non-fluorous copolymers have therefore been proposed as means of reducing the cost of the thickening agent. The first of three steps required for developing an effective thickener, the identification of a highly CO₂ soluble moiety, has been addressed. The PO/CO₂ copolymer is one of several novel polymers that has demonstrated CO₂-philicity greater than one of the previously established CO₂ fluorinated ethers of a comparable number of repeat units. The next steps in the development of a thickening agent, increasing the MW of the copolymer and introducing CO₂-phobic associating functionalities, have not been completed.

CONCLUSIONS

Fluoroacrylate-styrene copolymers remain the most effective carbon dioxide thickening agent yet identified. Extrapolations of high shear rate falling cylinder viscometry results demonstrated that 2-20 increases in CO₂ viscosity may be realized at concentrations of 0.1 wt%. Process economics dictate that the maximum concentration of this fluorinated copolymer be only 0.001 wt%. Despite the effectiveness of this thickening agent, it is not a viable candidate for increasing the capacity of geologic sequestration formations. Non-fluorous copolymers may be viable, however, because of their significantly lower cost. PO/CO₂ copolymers, for example, exhibit solubility comparable to CO₂ fluorinated ethers of comparable repeat units. These non-fluorous copolymers must be modified, however, to make them effective thickeners.

ACKNOWLEDGMENTS

We would like to thank the US DOE National Petroleum Technology Office, the US DOE National Energy Technology Laboratory, Air Products, Cabot Oil and Gas, and Normex International for their financial support of this work.

REFERENCES

- Baes, C., Beall, S. and Lee, D., 1980, "The Collection, Disposal and Storage of Carbon Dioxide," 495-519 in *Interactions of Energy and Climate*, Bach, W., Pankrath, J. and Williams, J., eds., D. Riedel Publishing.
- Bergman, P. and Winter, E., 1995, "Disposal of Carbon Dioxide in Aquifers in the US," *Energy Consers. Mgmt.* 36:523-526.
- DOE, July 1993, "A Research Needs Assessment for The Capture, Utilization and Disposal of Carbon Dioxide from Fossil Fuel-Fired Power Plants," Volume II Topical Reports, DOE/ER-30194.
- DOE, Feb. 1999, "Carbon Sequestration, State of the Science," Office of Science, Office of Fossil Energy, US Department of Energy
- Enick, 1998, A Literature Review of Attempts to Increase the Viscosity of Dense Carbon Dioxide, DOE report DE-AP26-97FT25356
- Z. Huang, C. Shi, S. Kilic, J. Xu, E. Beckman, and R. Enick, "Fluoroacrylate-Styrene Copolymers as Thickening Agents for Liquid Carbon Dioxide" *Macromolecules* (in press)
- Johnson, H., Vejtas, S., Pelling, J., Biasca, F., Simbeck, D., and Dickensen, R., 1992, "Screening Analysis of CO₂ Utilization and Fixation," US DOE Report DOE/FE/61680-H2, SFA Pacific, Inc., Mountain View, CA.
- Koide, H., Tazaki, Y., Noguchi, S., Nakayama, S., Iijima, M., Ito, K., Shindo, Y., 1992, "Subterranean Containment and Long-Term Storage of Carbon Dioxide in Unused Aquifers and in Depleted Natural Gas Reservoirs," *Energy Conversion and Management*.
- Rubin, E., Cooper, R., Frosch, R., Lee, T., Marland, G., Rosenfeld, A., Stine, D., "Realistic Mitigation Options for Global Warming," 1992, *Science* 257, 148.
- Sarbu, T., Styrance, T., Beckman, E., "Non-fluorous Polymers with Very High Solubility in Supercritical CO₂ Down to Low Pressures," *Nature* 405 (2000)165-168.
- Shi, C.; Huang, Z.; Kilic, S.; Xu, J.; Enick, R.; Beckman, E.; Carr, A.; Melendez, R.; Hamilton, A.; "The Gelation of CO₂: A Sustainable Route to the Formation of Microcellular Materials," *Science* 286, 19 Nov. 1999, 1540-1543.
- van der Meer, L., "Investigations Regarding the Storage of Carbon Dioxide in Aquifers in the Netherlands," 1992, *Energy Conversion and Management*.
- van der Meer, L., Griffioen, J, Geel, C., Feb. 1992, "Investigations regarding the Storage of Carbon Dioxide in the Netherlands," IGG-TNO report OS.92-24-A, 1-105.
- van Engelenberg, B. and Blok, K., 1992, "Prospects for the Disposal of Carbon Dioxide in Aquifers," Department of Science, Technology and Society, Univ. of Utrecht, The Netherlands, Report No. G-91006.
- Winter, E. and Bergman, P., "Availability of Depleted Oil and Gas Reservoirs for the Disposal of Carbon Dioxide in the United States," presented at the 29-31 Mar 1993 IEA Carbon Dioxide Disposal Symposium, Oxford, UK.

Figure 1. Copolymer of CO₂ and Propylene Oxide

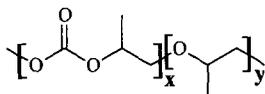


Figure 2. Effect of Shear Rate and Copolymer Concentration on Solution Viscosity of Fluoroacrylate-Styrene Copolymer/CO₂ Mixtures

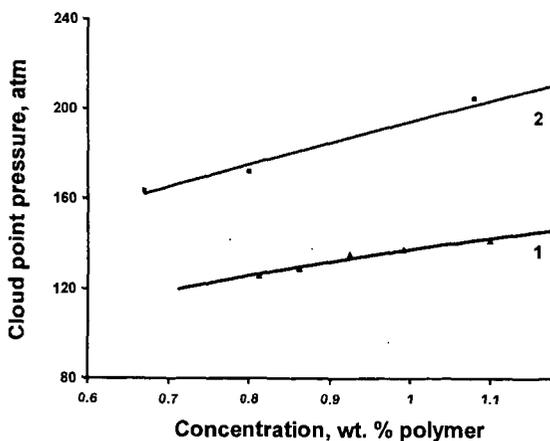
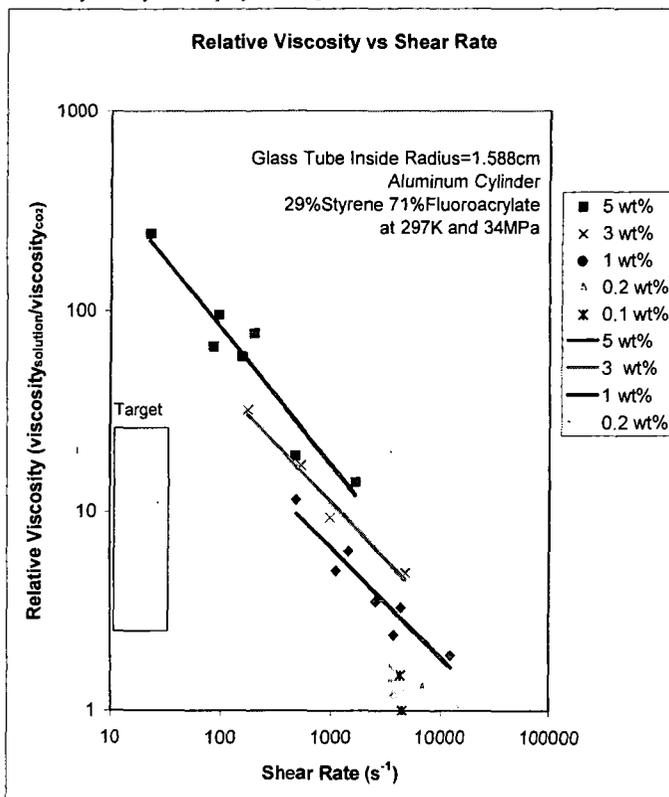


Figure 3. 295K, Cloud point pressure vs concentration in CO₂ for 1. PO/CO₂ copolymer with 250 repeat units and 2. polyperfluoropropyleneoxide polymer with 175 repeat units