IMPROVED GEOLOGIC SEQUESTRATION USING CARBON DIOXIDE THICKENERS

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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 CO_2 thickeners, inducing 2-200 fold increases in viscosity at concentrations of 0.1-5.0 wt%. The fluoroacrylate content of the copolymer assures CO_2 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 CO_2 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, CO_2 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 CO_2 are sequestered each year in this manner. The technologies associated with the injection of CO_2 into subterranean porous media containing water, gas and oil have been studied for decades. Of particular relevance is the use of CO_2 to recover oil from sandstone or limestone formations. This CO_2 EOR technology provides a basis for understanding the phenomena involved in the flow of CO_2 in porous media. The 70 oil fields in the world that use CO_2 to displace oil from the formation sequester large volumes of CO_2 in the reservoir at the end of the project. The bulk of the CO_2 currently used for these EOR projects is derived from natural CO_2 reservoirs, however. It is expected that in the future, CO_2 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 CO_2 emissions. Worldwide emission has been estimated to be 21.8 Gt CO_2/yr, or 5.9 Gt C/yr (Rubin, et al. 1992). The US generates 4.8 Gt CO_2/yr, or 22% of these emissions. The US CO_2 output from all electric generating plants is 35% of this total, 0.46 GtC/yr, or 1.7 Gt/yr of CO_2, or 30.6 TSCF/yr of CO_2. 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 CO_2 (Winter and Bergman, 1993) -30 Gt CO_2 (Johnson, et al. 1992) for depleted oil and natural gas reservoirs. A worldwide estimate 320 Gt CO_2 has also been made (Koide, et al, 1992).

There is an aspect of CO_2 sequestration into geologic formations that may significantly diminish the capacity of aquifers and oilfields. Although the permeability or porous media to oil, water and CO_2 are of the same order of magnitude, the viscosity of the CO_2 is significantly less than the viscosity of oil or water. At sequestration conditions, the viscosity of CO_2 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 (CO_2) to the displaced fluid (water or oil) result in poor vertical sweep efficiency as the CO_2 preferentially flows through low permeability layers and poor areal sweep efficiency as viscous fingers of CO_2 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 CO_2 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 CO_2 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 CO_2 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 CO_2-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 CO_2, 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 CO_2 thickeners, semifluorinated trialkyltin fluorides, telechelic polyfluorourethane 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 CO_2-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 CO_2 solubility ands 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 fluoroacylate 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 CO_2 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 CO_2. 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, CO_2-thickener that is two orders of magnitudes less expensive that 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 CO_2-thickener can be identified for geologic sequestration applications. Our strategy for designing an inexpensive CO_2-thickener was (a) to identify a highly CO_2-philic polymer, (b) to maximize its molecular weight, and (c) to modify its structure to incorporation CO_2-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 CO_2 soluble, non-fluorous copolymer was obtained by copolymerizing CO_2 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 CO_2 using sterically hindered aluminum catalysts, Figure 1. Note that CO_2 is a raw material for the synthesis of the CO_2-thickening compound. Although this may result in a marginal increase in the amount of CO_2 sequestered in an aquifer, the foremost advantage is that lost cost of CO_2 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. ^{27}Al NMR showed that these catalysts exhibit only one Al species, unlike typical aluminum catalysts used in CO_2/oxirane copolymerizations that exhibit "multi-site" behavior. The extent to which CO_2 is incorporated into the polymer is a function of temperature, pressure, and catalyst type.

Phase results of mixtures of CO_2 and these new CO_2-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 CO_2 at the same temperature and pressure. The solution is shear-thinning at all concentrations. At 5 wt% in liquid CO_2, 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 mat be able to induce a 10-fold increase in solution viscosity at the low shear rates associated with CO_2 sequestration.

Copolymers of PO and CO_2 proved to be remarkably CO_2-philic; Figure 3 shows that a 250 repeat unit PO/CO_2 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 CO_2, the copolymer exhibits greater CO_2-solubility than PO, and the copolymer is more CO_2-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 CO_2 soluble moiety, has been addressed. The PO/CO_2 copolymer is one of several novel polymers that has demonstrated CO_2-philicity greater than one of the previously established CO_2 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 CO_2-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 CO_2 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/CO_2 copolymers, for example, exhibit solubility comparable to CO_2 fluorinated ethers of comparable repeat units. These non-fluorous copolymers must be modified, however, to make them effective thickeners.

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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., Vejtasa, S., Pelline, J., Biasca, F., Simbeck, D., and Dickensen, R., 1992, "Screening Analysis of CO_2 Utilization and Fixation," US DOE Report DOE/FE/61680-H2, SFA Pacific, Inc., Mountain View, CA.

Koide, H., Tazaki, Y., Noguchi, S., Nakayama, S., Iijims, 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., Styranec, T., Beckman, E., "Non-fluorous Polymers with Very High Solubility in Supercritical CO_2 Down to Low Pressures," Nature405 (2000)165-168.

Shi, C.; Huang, Z.; Kilic, S.; Xu, J.; Enick, R.; Beckman, E.;Carr, A.; Melendez, R.; Hamilton. A.; " The Gelation of CO_2: 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, I-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 CO_2 and Propylene Oxide

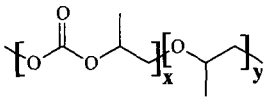
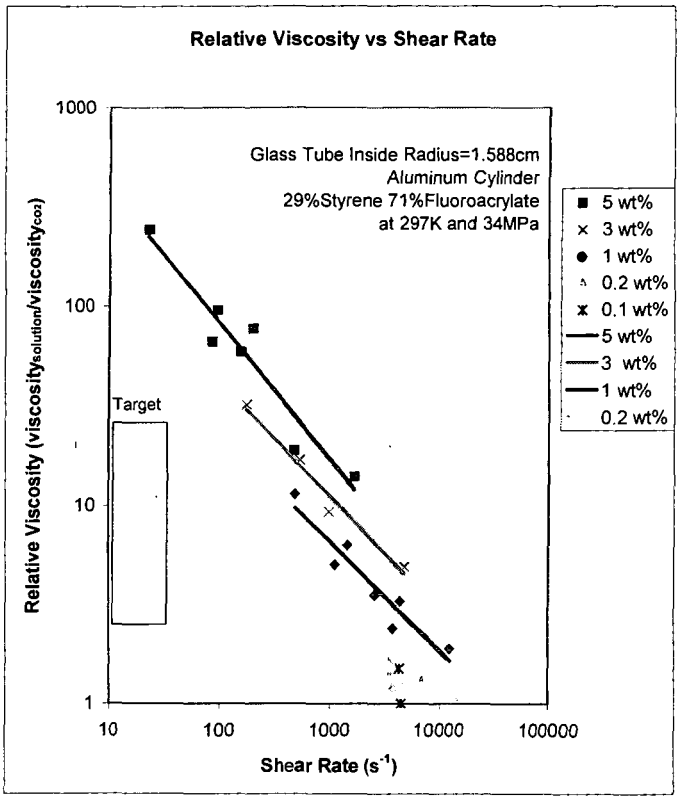


Figure 2. Effect of Shear Rate and Copolymer Concentration on Solution Viscosity of Fluoroacrylate-Styrene Copolymer/CO_2 Mixtures



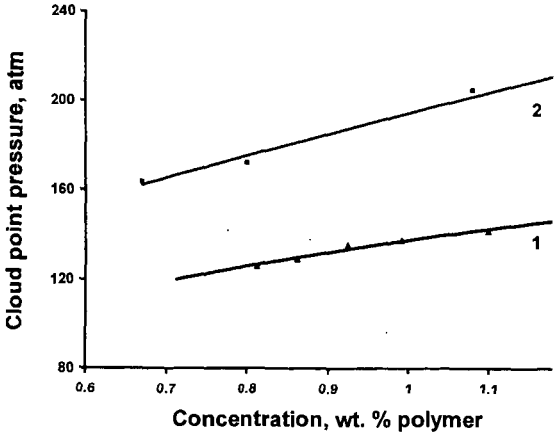


Figure 3. 295K, Cloud point pressure vs concentration in CO_2 for 1. PO/CO_2 copolymer with 250 repeat units and 2. polyperfluoropropyleneoxide polymer with 175 repeat units