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NOVEL SORPTION/DESORPTION PROCESS FOR CARBON DIOXIDE CAPTURE (FEASIBILITY STUDY)

TOPICAL REPORT

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ABSTRACT

Western Research Institute and the University of Wyoming Enhanced Oil Recovery Institute have tested a novel approach to carbon dioxide capture in power plants and industrial operations. This approach is expected to provide considerable cost savings, in terms of regeneration of the sorbent. It is proposed that low molecular weight, low volatility liquid fluorocarbons be utilized to absorb CO_2 due to their unusual affinity for the gas. The energy savings would be realized by cooling the fluorocarbon liquids below their melting point where the CO_2 would be released even at elevated pressure. Thus, the expense of heating currently used sorbents, saturated with CO_2, under low pressure conditions and then having to compress the released gas would not be realized. However, these fluorinated materials have been shown to be poor carbon dioxide absorbers under conditions currently required for carbon capture. The project was terminated.

DISCLAIMER

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EXECUTIVE SUMMARY

Western Research Institute developed a novel approach to carbon dioxide capture in power plants and industrial operations. This approach was expected to provide considerable cost savings, in terms of regeneration of the sorbent. It is proposed that low molecular weight, low volatility liquid fluorocarbons be utilized to absorb CO_2 due to their unusual affinity for the gas. The energy savings would be realized by cooling the fluorocarbon liquids below their melting point at which point the CO_2 would be released even at elevated pressure. Thus, the expense of heating currently used sorbents, saturated with CO_2, under low pressure conditions and then having to compress the released gas would not be realized. In order to test this concept, collaboration was proposed with The University of Wyoming, Enhanced Oil Recovery Institute which has the appropriate sorption/desorption measuring apparatus and skilled operators. Feasibility of this approach chiefly rests on how much carbon dioxide will be absorbed by the fluorocarbons. The technical literature reports conditions under which fluorocarbons become miscible with carbon dioxide but there is little or no data on absorption of CO_2 under our conditions of interest. Unfortunately, our tests revealed that the absorption of CO_2 in fluorocarbons was too low for this approach to be practical and the project was cancelled.

INTRODUCTION/BACKGROUND

UW/WRI proposed using novel absorption materials, crystalline fluorocarbon surfactants to capture carbon dioxide in power plant flue gasses and industrial operation which produce large amounts of carbon dioxide. Fluorocarbons have unusual affinity for CO_2 and are actually miscible in the pure liquid. We would want to use fluorinated surfactants to minimize the vapor pressure of these liquids thus minimizing loss in separation systems and at the same time keeping the molecular weight low so as to maximize the solubility with CO_2. Choosing a crystallizable system could lead to a novel, low energy regeneration procedure. Carbon dioxide should dissolve easily in the surfactant when it is in a liquid state (above its melting point). Upon cooling below the crystallization temperature, the material will solidify and reject the dissolved gas. It is possible that the gas could be released into a high pressure environment thus lessening the energy requirements for compression of the separated gas. Thus energy requirements for regenerating the crystalline, fluorosurfactant absorbent would be much lower than for amine systems due to no heating requirements and lower compression costs.

The technical literature reports conditions for CO_2 solubility of different fluorinated materials but there is little or no data on CO_2 absorption. The goal of this program would be to collect absorption and desorption data on several commercial fluorosurfactants. Temperatures and pressures would be chosen to bracket the conditions to be experienced in industrial environments where capture is desired. These data would be used to assess the feasibility of using fluorosurfactants as CO_2 sorbents. An additional goal would be to acquire like data for other pure gases that are present in mixtures with CO_2 and from which separation is desired. Knowledge of the solubility and diffusivity of CO_2 and gases from which it is to be separated could then be used to assess the practicality of using fluorosurfactants (or related materials) as components of a membrane separation device.

Professors Maciej Radosz and Youqing Shen of the University of Wyoming Enhanced Oil Recovery Institute made carbon dioxide absorption/desorption measurements on several fluorinated materials supplied by WRI using a Rubotherm gas sorption measuring system. Measurements were made at several temperatures and pressures simulating field conditions.

OBJECTIVES

The overall objective is to determine the feasibility of saving energy in a fluorocarbon/CO_2 capture technology by absorbing large quantities of the gas and releasing it at lower temperatures and higher pressures through crystallization. If feasibility is demonstrated, the next step is to start optimization of the molecular structure for maximum capture efficiency.

RESULTS AND CONCLUSIONS

Initial sorption/desorption measurements were made on an ionic phosphate fluorosurfactant. This is a commercial material produced by the Dupont Company with the tradename, Zonyl UR. Its chemical structure is:

$$(R_fCH_2CH_2O)_xP(O)(OH)_y$$

where $R_f = F(CF_2CF_2)_z$; x = 1 or 2; y = 2 or 1; x + y = 3; z = 1 to about 7. The molecular weight is 700 Daltons. At ambient pressure, this material should melt at about 70°C and recrystallize at about 40°C.

Measurements were made at 25 and 75°C and pressures of 1 and 10 bar. At 25° the fluorinated surfactant was solid and at 75° it was liquid. CO_2 sorption was low under all conditions. At 1 bar, the absorption was less than 0.1% at both 25° and 75°C. At 10 bar, absorption was slightly higher at about 1% for both temperatures. This fluorinated phosphate surfactant does not appear to have the chemical structure needed for sufficient carbon dioxide absorption.

Because this fluorinated phosphate surfactant does not appear to have the chemical structure needed for sufficient carbon dioxide absorption we have evaluated a model fluorinated compound, poly(chlorotrifluoroethylene), PCTFE. PCTFE is miscible with liquid carbon dioxide (unpublished data) and was therefore chosen as a model material to determine the maximum absorption by a fluorinated chemical. The highest equilibrium CO_2 absorption for PCTFE was 4.0 wt% occurring at 25°C and 15 bar. The table below summarizes the equilibrium absorption (wt %) at every condition tested.

	1 bar	**10 bar**	**15 bar**
25°C	1.9	3.5	4.0
75°C	1.2	1.6	1.7

This data indicates that fluorinated materials probably do not absorb carbon dioxide at sufficiently high levels for the conditions appropriate for this project and we will discontinue work on these types of materials.

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