



SPE 91436

## Design and Feasibility of Creating Gas-Storage Caverns by Using Acid to Dissolve Carbonate Rock Formations

James W. Castle, SPE, Clemson University; David A. Bruce, Clemson University; Scott E. Brame, Clemson University; Donald A. Brooks, SPE, DB Consulting; Ronald W. Falta, Clemson University; Lawrence C. Murdoch, Clemson University

Copyright 2004, Society of Petroleum Engineers Inc.

This paper was prepared for presentation at the 2004 SPE Eastern Regional Meeting held in Charleston, West Virginia, U.S.A., 15–17 September 2004.

This paper was selected for presentation by an SPE Program Committee following review of information contained in a proposal submitted by the author(s). Contents of the paper, as presented, have not been reviewed by the Society of Petroleum Engineers and are subject to correction by the author(s). The material, as presented, does not necessarily reflect any position of the Society of Petroleum Engineers, its officers, or members. Papers presented at SPE meetings are subject to publication review by Editorial Committees of the Society of Petroleum Engineers. Electronic reproduction, distribution, or storage of any part of this paper for commercial purposes without the written consent of the Society of Petroleum Engineers is prohibited. Permission to reproduce in print is restricted to a proposal of not more than 300 words; illustrations may not be copied. The proposal must contain conspicuous acknowledgment of where and by whom the paper was presented. Write Librarian, SPE, P.O. Box 833836, Richardson, TX 75083-3836, U.S.A., fax 01-972-952-9435.

### Abstract

The feasibility of creating gas-storage caverns by dissolving carbonate rock formations was examined based on process design, geologic factors, and preliminary economic analysis. The method involves drilling one or more wells, pumping acid into the formation, and then removing and treating the waste fluid. To enhance acid transport into the formation, the rock may be hydraulically fractured prior to pumping the acid.

To analyze the requirements for creating storage volume, the following were examined: weight and volume of rock to be dissolved; gas storage pressure, temperature, and volume at depth; solubility of acid-rock reaction products; and acid costs. Design considerations and economic calculations indicate that the new method will be applied most advantageously to carbonate formations deeper than approximately 4000 feet, with limestone at depths between 6000 and 9000 feet preferred. In order to identify potential sites for applying the new method to creating storage volume, a large amount of data from carbonate formations was compiled for six states: Ohio, Kentucky, Indiana, West Virginia, Pennsylvania, and New York. Based on GIS analysis, large areas of West Virginia, Pennsylvania, and New York were identified as potentially suitable for developing carbonate-cavern storage. Smaller areas that may be suitable were identified in Indiana, Ohio, and Kentucky.

The potential for application of this new method is very promising based on preliminary economic analysis that considered capital costs, well-design options and costs, waste treatment options, and cost comparison with other gas storage methods.

### Introduction

Because natural gas is in high demand in many regions of the United States, there is an increasing effort focused on

developing new methodologies that will make natural gas more readily available. Of particular interest are more efficient and safe means for storing large quantities of natural gas close to major pipelines or high usage areas. The primary focus of our investigation is to evaluate the feasibility of creating underground natural gas storage caverns in optimal locations by dissolving carbonate rock formations using acid. The analysis includes compilation of a large amount of data from carbonate formations in six states (Indiana, Ohio, Kentucky, West Virginia, Pennsylvania, and New York), which were selected based on location near major natural-gas markets and pipelines.

The basic concept that we propose for creating carbonate-cavern storage is to drill to depth, fracture the carbonate rock layer if needed, and then produce a cavern using an aqueous acid to dissolve the carbonate rock. Following waste-fluid removal, the resulting subsurface cavity can be used to store natural gas. Abundant carbonate rock formations worldwide make the method attractive to both industry and the consumer, especially when the facility is to be located near large gas markets where current gas storage capacity is insufficient to meet demand. An additional benefit of carbonate-cavern storage is its suitability for developing storage capacity of specific volume near industrial facilities or power-generating plants.

The first phase of our investigation has focused on developing guidelines and a cost estimate for creating gas storage caverns in carbonate rock formations that have negligible innate storage capacity (i.e., low permeability and/or porosity). There are two primary factors that determine the viability of creating an underground natural gas storage reservoir by acid dissolution of carbonate rock: the cost associated with dissolving large quantities of limestone with aqueous acids (dissolution economics) and the existence of carbonate rock formations at the appropriate location and depth (geology).

### Volumetric Analysis and Acid Selection

**Gas Storage Pressure, Temperature, and Volume.** Forecasting reservoir conditions is critical in determining the physical properties of the natural gas contained in storage as well as the cost for generating the storage facility via acid dissolution. The key parameters needed to evaluate gas properties at depth are temperature and pressure. For all of

our calculations a range of gas storage capacities were investigated: 0.25 billion cubic feet (BCF) to 2.0 BCF of natural gas at atmospheric conditions (STP, standard temperature and pressure). The depths investigated range from 500 to 12,000 ft, which are common depths to find carbonate rock formations in the study area. In estimating reservoir pressure and temperature a geophysical gradient was assumed and is expected to be reasonably accurate because of low tectonic stress due to little tectonic activity in the study area. A typical pressure gradient of 0.433 psi/ft was used for the hydrostatic pressure, and the pressure gradient needed to cause rock fracture was estimated to be 0.64 psi/ft. This value of 0.64 psi/ft is very conservative, as fracture gradients can exceed 1.0 psi/ft in many areas, which would allow for a greater volume of gas to be stored within a given cavity volume. Also, the fracture pressure gradient is not always linear and can vary locally depending on the geological conditions such as rock composition and stress.<sup>1,2,3</sup> For our storage calculations, it was assumed that the storage cavern could be pressurized to a value greater than the hydrostatic pressure at depth, but less than the pressure needed to cause rock fracture; thus, a pressure gradient of 0.55 psi/ft was selected for the storage facility.

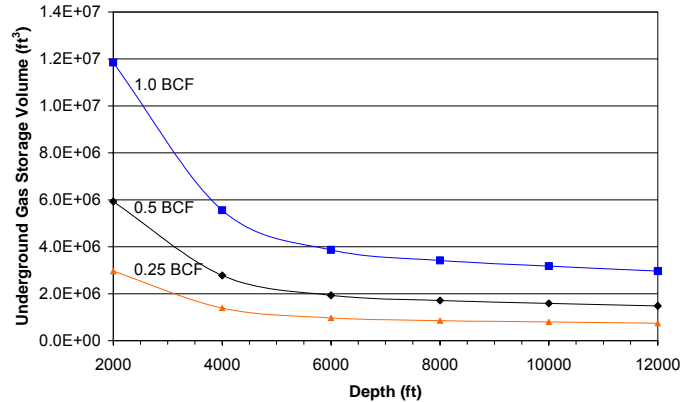
In our investigation a geothermal gradient of 20°C per kilometer and a surface temperature (actually 3 m deep) of 11°C were used to predict reservoir temperature.<sup>4,5</sup> Similar geothermal gradients (often linear) exist in various parts of North America. Although not accounted for, a slightly lower temperature than that assumed could exist because of the thick sedimentary strata found in the study area. Using these geophysical gradients, reservoir conditions can be established. For instance, an 8000 ft deep storage facility can be predicted to have a pressure of 4415 psi and a temperature of 140°F. Using these conditions, one may predict the physical behavior of the natural gas in containment and calculate the necessary cavity volume.

Natural gas is a highly compressible mixture having a density that varies significantly with changes in temperature and pressure and to a lesser extent with composition. It is preferable to use experimentally measured data for natural gas density over values predicted by ideal gas law or more complicated equations of state (e.g., Peng-Robinson). The original measurements for natural gas density were reported in various journal articles, but the collected data are presented in several useful reference sources, including the *Handbook of Natural Gas Engineering*. Experimental gas density data<sup>6</sup> illustrate that the average molecular weight of the gas, i.e., the composition, will affect the mixture density, especially at elevated pressures. The natural gas composition used for all calculations was 90% methane and 10% ethane, which yielded an average gas molecular weight of 17.3 g/mol, which corresponds to a 0.6 gravity gas (i.e., the specific gravity of the gas is 40% less than that of air at STP conditions).

The cavity storage volume required for a given quantity of natural gas is calculated using the gas density at STP and storage conditions (Equation 1):

$$\frac{V(\text{STP, ft}^3)}{\rho(\text{STP, lb/ft}^3)} = \frac{V(\text{storage T and P, ft}^3)}{\rho(\text{storage T and P, lb/ft}^3)} \dots \dots \dots (1)$$

The volume of underground gas storage needed at a specified depth for a given quantity of natural gas is shown in Figure 1.



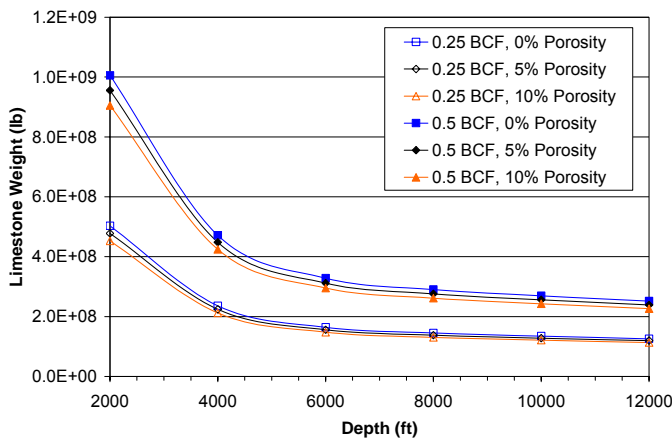
**Figure 1. Variations with depth in underground storage volume required for 0.25 to 1 BCF (STP or zero depth conditions) of total gas storage capacity. The plotted relationship depends heavily on pressure and temperature gradient assumptions.**

As illustrated in Figure 1, the high compressibility of natural gas makes it advantageous to develop a storage cavern at depths greater than 4000 ft, with optimal depth below 6000 ft. Below this depth the increase in gas density with depth is greatly reduced. Additionally, advantages gained by the increased gas density at depths below 6000 ft may be offset by higher drilling and operating costs.

**Weight and Volume of Rock to be Dissolved.** The volume of rock needing to be dissolved using aqueous acids is a function of the volume of gas to be stored in the reservoir (at STP conditions), gas density at depth, and the porosity of the carbonate rock formation:

$$V_{\text{Rock}} (\text{ft}^3) = \left[ \frac{V_{\text{gas}} (\text{STP, ft}^3) \cdot \rho_{\text{gas}} \left( \text{depth, } \frac{\text{lb}}{\text{ft}^3} \right)}{\rho_{\text{gas}} \left( \text{STP, } \frac{\text{lb}}{\text{ft}^3} \right)} \right] \left( 1 - \frac{\% \text{Rock Porosity}}{100} \right) \dots (2)$$

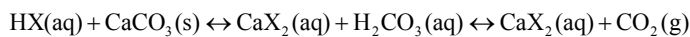
The mass of rock that must be removed for a given storage capacity is simply the volume of rock (accounting for rock porosity) multiplied by the density of the rock (limestone or dolomite). Using a calcium carbonate density of approximately 170 lb/ft<sup>3</sup>, Figure 2 illustrates how the mass of rock to be dissolved varies with depth, rock porosity, and total gas storage volume.



**Figure 2. Weight of limestone to be removed via acid dissolution for gas storage volume of 0.25 and 0.5 BCF and limestone porosities between 0 and 10%.**

**Rock Solubility and Acid Characteristics.** In order to dissolve large deposits of limestone using aqueous acids, two reaction fundamentals need to be considered: kinetics and equilibria. The reaction kinetics determine the rate at which dissolution can occur, and reaction equilibria combined with product solubility determine the theoretical yield and maximum concentration of species exiting from the dissolution process. One would prefer that the dissolution reaction rate be fast and that the reaction equilibria favor the formation of highly soluble salt products. Due to the common nature of the reagents involved in the dissolution process, much of the reaction kinetics, reaction equilibria, and reactant/product solubility data have already been measured and are readily available in the technical literature.

Limestone deposits can be dissolved in aqueous media using an appropriate acid via the reaction mechanism shown below:



There are several important considerations that must be taken into account before the optimal acid can be selected for creating carbonate-cavern storage. These parameters include:

- 1) acid cost and availability;
- 2) aqueous solubility of resulting calcium salts;
- 3) acid and/or salt toxicity;
- 4) waste remediation considerations;
- 5) corrosion characteristics;
- 6) the need for combustion and/or evaporation controls (for organic acids);
- 7) dissolution reaction rate;
- 8) dissolution reaction equilibrium constant;
- 9) pKa for acid dissociation in water; and
- 10) prior use in related oil and gas applications.

Criteria 1, 2, 4, and 8 above were the primary factors used to identify organic and inorganic acids that may prove economically and chemically viable for the dissolution process. Although the other criteria were also considered, they had less of an impact on the overall viability of the dissolution process.

**Reaction Equilibrium Constants.** Reaction equilibria (for the carbonate dissolution reaction shown previously) determine the thermodynamic limit to which reactants can be converted into products and can be calculated using the Gibbs free energy of formation for the reagents and products. Despite the elevated pressure at lower depths, some CO<sub>2</sub> would exist as a separate gas phase; however, for these initial calculations it was assumed that all of the CO<sub>2</sub> would remain in solution until the salt products were pumped to the surface. Additionally, the change in enthalpy (heat generation) with reaction can be calculated from the properties of similar pure components. These data (Table 1) and the relevant equations (Equations 3 and 4) relating them are shown below. These calculations reveal that the equilibrium reaction constant is high (favorable) for all of the listed acids except for acetic. Further, all of the dissolution reactions are exothermic; thus, localized heating effects could increase the rate of limestone dissolution.

Calculation of Gibbs free energy of reaction from Gibbs free energy of formation values:

$$\Delta G_{rxn}^0 = \sum_{\text{products}} \beta_j G_{f,j}^0 - \sum_{\text{reactants}} \alpha_i G_{f,i}^0 \dots \dots \dots (3)$$

Calculation of reaction equilibrium constants (K<sub>eq</sub>) from Gibbs free energy of reaction data:

$$-\Delta G_{rxn}^0 = RT \ln K_{eq} \dots \dots \dots (4)$$

**Table 1. Gibbs free energy of reaction, enthalpy change with reaction, and equilibrium constant for several limestone acid dissolution reactions. The favorable reactions are shaded.**

Reaction	ΔG (kJ/mol)	ΔH (kJ/mol)	<sup>298</sup> K <sub>eq</sub>
CaCO <sub>3</sub> (s) + H <sub>2</sub> SO <sub>4</sub> (aq) ↔ CaSO <sub>4</sub> (s) + H <sub>2</sub> CO <sub>3</sub> (aq)	-58.8	-8.7	2.02 · 10 <sup>10</sup>
CaCO <sub>3</sub> (s) + 2HCl(aq) ↔ CaCl <sub>2</sub> (aq) + H <sub>2</sub> CO <sub>3</sub> (aq)	-47.9	-35.5	2.46 · 10 <sup>8</sup>
CaCO <sub>3</sub> (s) + 2HNO <sub>3</sub> (aq) ↔ Ca(NO <sub>3</sub> ) <sub>2</sub> (aq) + H <sub>2</sub> CO <sub>3</sub> (aq)	-47.8	-104.	2.45 · 10 <sup>8</sup>
CaCO <sub>3</sub> (s) + 2CH <sub>3</sub> COOH ↔ Ca(CH <sub>3</sub> COO) <sub>2</sub> (aq) + H <sub>2</sub> CO <sub>3</sub> (aq)	-6.79	-38.6	15.5

**Dissolution Product Solubility.** The aqueous solubility of the resulting carbonate salt is also a key factor in determining the ideal acid for dissolving limestone. A low calcium salt solubility would require much greater quantities of water (and acid) to be pumped through the underground formation in order to prevent the salt product from precipitating out of solution. Aqueous solubility data for selected acids are shown in Table 2. The solubility data show that most of the monoprotic inorganic acids (e.g., hydrochloric and nitric acid) yield calcium salts with high aqueous solubility, with the exception of orthophosphoric acid. In contrast, the calcium salts of the diprotic (e.g., sulfuric acid) and triprotic (e.g., citric acid – not shown) acids have a very low solubility in water. Finally, the monoprotic organic acids react to form calcium salts that have moderate (e.g., calcium acetate, calcium formate) to high (e.g., calcium hydroxypropionate)

solubility in water. In summary, the solubility of the calcium salts derived from reactions involving sulfuric and orthophosphoric acid are too low to yield a viable dissolution process. Thus, on the basis of calcium salt solubility alone, any acid yielding a calcium salt with aqueous solubility greater than 100 g/l is acceptable, although higher solubility is preferred.

**Table 2. Solubility of some common calcium salts in water at STP. Acids yielding reaction products having acceptable solubility are shaded.**

Acid	Calcium Salt	Solubility of Calcium Salts in 25°C Water (g/l)
nitric acid (HNO <sub>3</sub> )	calcium nitrate (Ca(NO <sub>3</sub> ) <sub>2</sub> )	1212
3-hydroxypropionic acid (C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> )	calcium hydroxypropionate (Ca(C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> ) <sub>2</sub> )	1000
hydrochloric acid (HCl)	calcium chloride (CaCl <sub>2</sub> )	745
acetic acid (CH <sub>3</sub> COOH)	calcium acetate (Ca(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> )	374
formic acid (HCOOH)	calcium formate (Ca(CHO <sub>2</sub> ) <sub>2</sub> )	162
orthophosphoric acid (H <sub>3</sub> PO <sub>4</sub> )	calcium orthophosphate (Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O)	18
sulfuric acid (H <sub>2</sub> SO <sub>4</sub> )	calcium sulfate (anhydrite, CaSO <sub>4</sub> )	2

**Acid Costs.** Current bulk sale prices for several candidate acids are shown in Table 3. These prices are for materials to be delivered in the northeastern U.S. and are for technical grade purity acids, with the exception of phosphoric acid (farm grade listed). Further significant reductions in acid cost could be realized following negotiations with acid producers and distributors. This is especially true given the quantity of acid to be purchased and the fact that high purity acids are not required for the dissolution process. The acid prices and purities, shown in Table 3, were used to calculate the cost for dissolving one pound of limestone, which provides a direct means for comparing the economic viability of the various acids. On a cost basis alone, any of the common inorganic acids appear to be a reasonable choice for the dissolution process, while the cost of most of the organic acids is prohibitive.

**Selection of the Optimal Dissolution Acid.** Several acids have been considered for the dissolution process (see lists in Tables 1-3), many of which have existing use in oil and gas operations, such as hydrochloric acid. Some of the advantages in using hydrochloric acid include: low cost, high acid solubility, fast reaction rates with carbonate rock, and highly soluble products (calcium chloride) that allow for the easy removal of calcium waste from the well. Furthermore, the high production of hydrochloric acid in the United States (approximately 4 million metric tons per year) is advantageous given the large quantities of acid needed to generate the proposed storage volumes, and there is an existing commercial market for the calcium chloride dissolution product. However,

**Table 3. Acid cost (Chemical Market Reporter, Dec. 2003). Acids with more favorable cost are shaded.**

Acid	Current Sale Price \$ US / ton (wt % acid)	Acid Cost per Pound of Limestone Dissolved, \$ US
orthophosphoric acid (H <sub>3</sub> PO <sub>4</sub> )	2.7 (52%, farm grade)	0.005
sulfuric acid (H <sub>2</sub> SO <sub>4</sub> )	25 (100%)	0.012
hydrochloric acid (HCl)	68 (22 °Be, 34%) <sup>a</sup>	0.075
nitric acid (HNO <sub>3</sub> )	215 (40 °Be, 68%) <sup>a</sup>	0.199
formic acid (HCOOH)	451 (85%)	0.244
acetic acid (CH <sub>3</sub> COOH)	910 (95%)	0.575
3-hydroxypropionic acid (C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> )	1100 (95%) <sup>b</sup>	0.918

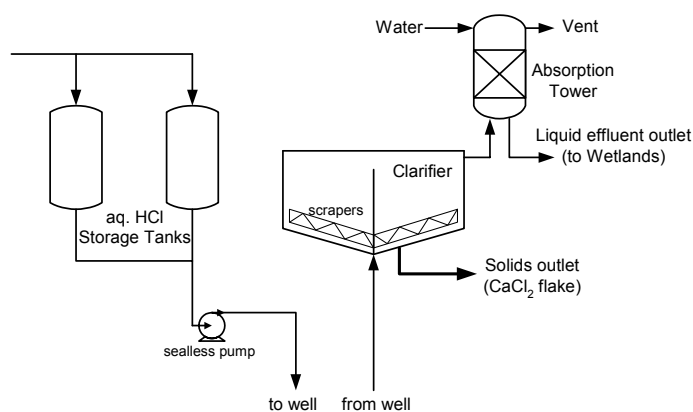
a Degrees Baume (°Be) is a measure of specific gravity based on a 10% NaCl solution having a value of 10. The specific gravity (i.e., purity) at 60 °F for a fluid denser than water can be expressed as sp.gr. = 145/(145-Baume).

b Projected sales price in 2006 (Cargill).

hydrochloric acid is corrosive to drilling equipment and the resulting waste products require greater post-removal processing. Other acids that have been used previously for limestone dissolution include acetic and formic acid. Both of these organic acids are highly miscible with water, have low viscosities, are more environmentally friendly, and less corrosive to equipment. However, there are disadvantages to using acetic and formic acid: moderate reaction rates with carbonates (due to the low pKa of the acids in water), slightly less soluble calcium salt products, and moderately high acid costs. Despite the organic acids offering certain advantages over the inorganic acids, the cost of using any of these materials is prohibitive. Thus, at this time we conclude that hydrochloric is the most suitable acid to use for the dissolution process.

### Process Design and Economics

The process that we propose for creating carbonate-cavern storage, shown in Figure 3, involves pumping hydrochloric acid into a carbonate formation, where it will react rapidly and dissolve the carbonate. The products of this reaction, calcium chloride and carbonic acid, are highly soluble in water and will be removed, leaving behind a gas storage cavern capable of high rates of gas deliverability. Some of the key components of the process are: 1) an acid collection and storage facility, 2) an acid pumping station, 3) a clarifier for evaporating water and collecting crude CaCl<sub>2</sub> product, 4) an absorption tower to remove residual amounts of unused acid, 5) a secondary waste treatment facility, and 6) a CaCl<sub>2</sub> packaging facility (not shown).



**Figure 3. Simplified process flow diagram for acid dissolution of carbonate rock to create storage caverns.**

**Well Design Options and Costs.** There exist several options for the number and placement of wells for the acid dissolution process for creating gas storage in carbonate rock. A single concentric tube design is possible and would likely yield a spherical or elliptical shaped gas storage cavern (Figure 4A). With this design, fresh acid would be pumped down the well between the inner and outer casing, similar to the pumping of water to create salt caverns. Soluble salt products would be removed from the well using the smaller casing. However, there are also two-well and multi-well designs that could be used to rapidly produce an underground gas storage cavern. For the two-well designs (two-well with vertical fracture and two-well dogbone design), one well would be used to pump down fresh acid, while the other well would be used to remove spent acid products (Figure 4B). These two-well designs differ in how a water-flow channel is developed between the two wells. In one case, the carbonate rock is fractured (vertical fractures below approximately 2000 ft), while in the other case a horizontally drilled hole connects the two wells. A description of the two-well designs is listed below:

#### Two-well with Vertical Fracture:

*Description:* Drill two wells and fracture vertically to connect the wells.

*Method:* Drill the first well, log, perform microfracture and injection tests, drill the second well, and fracture the rock between the two wells.

*Restrictions/Comments:* A small amount of initial porosity is needed to fracture the rock

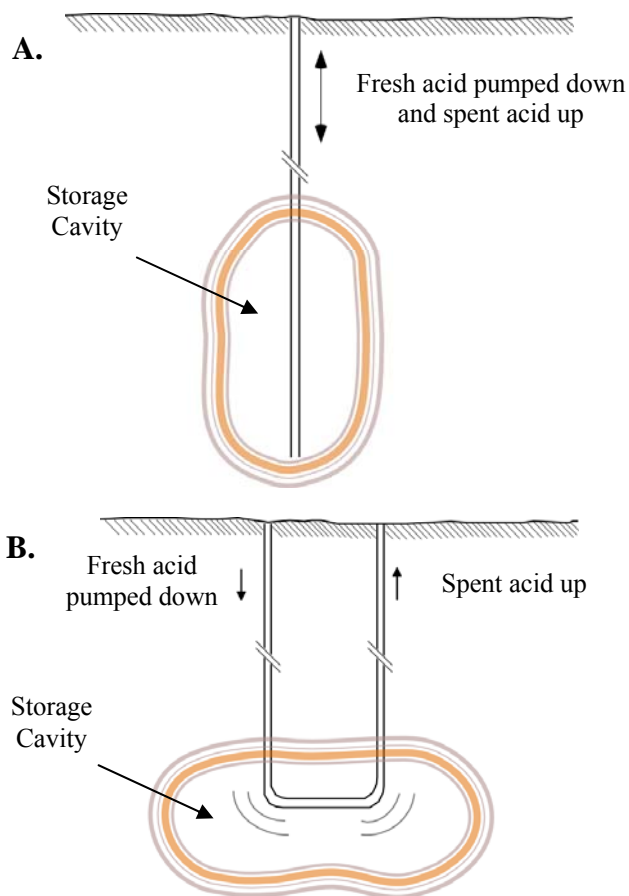
#### Two-well Dogbone Design

*Description:* Two vertical wells with a horizontal connector.

*Method:* Drill the first well, log, drill the second well, and finally drill the horizontal connector between wells.

*Restrictions/Comments:* Most dissolution will probably occur at the corners. Distance between wells will depend on storage capacity. No initial porosity is needed.

For cost estimation purposes, a vertical-fracture two-well design was selected, and the cost for this type of design is listed in Table 4 for a range of depths.



**Figure 4. Well designs for creating gas-storage caverns by acid dissolution of carbonate rock. A) Single-well design; B) Two-well dogbone design.**

**Table 4. Approximate estimated drilling and fracturing costs in the Northeastern U.S.**

Depth (ft)	Estimated Costs in Thousands of Dollars US				
	Inlet Well <sup>a</sup>	Outlet Well <sup>b</sup>	Additional Completed Costs		
			Horizontal Connector <sup>c</sup>	Acid Fracture <sup>d</sup>	Hydraulic Fracture <sup>e</sup>
4,000	250	150	50	20	30
8,000	1,000	500	100	100	75
12,000	2,500	1,000	150	150	200

a Completed injection/withdrawal storage well, 7 inch, high deliverability flow string to bottom.

b Additional slim hole well to assist in cavity building. Flow string set at total depth.

c Directionally drilled connection between wells at total depth.

d Five thousand gallon gelled acid breakdown to initiate cavity building process.

e Hydraulic fracture with proppant to initiate/accelerate cavity building process.

**Waste Treatment.** The limestone dissolution reaction with aqueous hydrochloric acid yields calcium chloride and carbonic acid as products. These products are highly soluble in water and can be easily removed from the underground storage cavity. Upon exiting the well, these dissolution

products are to be treated using two above-ground process elements: a clarifier and a secondary wastewater treatment system. The design includes an absorption tower. The initial liquid/slurry will be sent to an enclosed cylindrical clarifier equipped with scrapers, where the water will evaporate and solid calcium chloride product will be isolated. The calcium chloride can be sold in both liquid and solid form in the northern U.S., where it is the preferred deicing agent for roads ( $\text{CaCl}_2$  is effective as a deicing agent at temperatures as low as  $-15^\circ\text{C}$ ). Current production of  $\text{CaCl}_2$  is achieved by reacting HCl with quarried limestone. The sale of this product stream will also enhance the profitability for the dissolution project by offsetting the cost for hydrochloric acid.

Although various options for secondary treatment of the wastewater are possible, a constructed wetland treatment system provides important economic and environmental benefits. Principles of natural wetlands will be applied to constructing a treatment system designed to ensure the desired reactions at predictable rates. This is a proven approach that has been used successfully for the treatment of various waste fluids, including refinery effluent and brines produced from oilfields.<sup>7,8,9,10,11,12</sup>

Since large quantities of dissolved carbon dioxide will be generated by this process (e.g., the formation of 1 BCF of gas storage at 4000 ft would produce 234 thousand tons of carbon dioxide - approximately 6% of what a typical coal power plant releases annually), the wetlands treatment system is expected to greatly contribute to the reduction of carbon dioxide emission from the process due to the uptake of carbon dioxide (in the form of carbonates) by the plants. These plants are resilient to moderate levels of salts, such as calcium chloride, and have proven to be highly effective in applications involving the treatment of aqueous waste streams from power plant boilers and scrubbing towers. Thus, the waste treatment options described are expected to help reduce the emission of carbon dioxide and provide a revenue source that is derived from the calcium chloride product from the dissolution process.

**Fixed Capital Cost Estimation.** Fixed capital costs, including both direct and indirect costs, were estimated for a limestone dissolution process that would use hydrochloric acid to create a 0.5 to 1 BCF gas storage reservoir. The various costs were calculated using Lang factors (Table 5), which relate the costs of construction to total purchased equipment costs. The Lang factors used for our investigation were obtained from the process design text by Peters and Timmerhaus<sup>13</sup> and are specifically for processes built in the U.S. that require both liquids and solids handling. For this cost estimate, *delivered* equipment costs were used to estimate fixed capital costs, and these values are shown in Table 6. The key equipment items include corrosion resistant pumps, hydrochloric acid holding tanks (20,000 gal tanks), a clarifier and absorber for isolating calcium chloride products, and a wetlands wastewater treatment area for carbonic acid removal. Since these economic calculations are for only a moderately well defined process, the contingency factor (36) is higher than would be used for a process where a detailed piping and instrumentation diagram had been developed. These calculations yield a fixed capital cost of \$3,270,529 US.

**Table 5. Estimated fixed capital cost factors for a 0.5 to 1 BCF gas storage facility created via acid dissolution of limestone using hydrochloric acid. The purchased equipment cost is from Table 6.**

Operation	Lang Factors	Cost (\$ US)
Direct Costs		
Purchased Equipment	100	799,640
Installation	39	311,860
Instrumentation	13	103,953
Piping	31	247,888
Electrical	10	79,964
Buildings	29	231,896
Yard Improvements	10	79,964
Service Facilities	55	439,802
Land	2	15,993
Indirect Costs		
Engineering & Supervision	32	255,885
Construction Expenses	34	271,878
Contractor's Fee	18	143,935
Contingency	36	287,871
<b>Total Fixed Capital Investment</b>	<b>409</b>	<b>3,270,529</b>

**Table 6. Estimated delivered equipment costs for a 0.5 to 1 BCF gas storage facility created via acid dissolution of limestone using hydrochloric acid.**

Purchased Equipment	Cost (\$ US)
Clarifier/Absorber	449,640
Sealless, acid-resistant centrifugal pumps	85,000
Hydrochloric acid storage tanks	265,000
<b>Total Equipment Costs (delivered)</b>	<b>799,640</b>

**Chemical Pricing.** The purchase cost of hydrochloric acid and the fair market value of the calcium chloride products were derived from up-to-date pricing information in *Chemical Market Reporter*, which provides industry average pricing for most commodity chemicals. In order to emphasize the need for developing gas storage at depths greater than 4000 ft, variations in the total cost of hydrochloric acid as a function of storage depth are shown in Figure 5. Because of the large quantities of acid required, it is estimated that the negotiated price for acid would be 10 to 50% less than the current market price for technical grade hydrochloric acid. Additionally, the current sales prices for a variety of calcium chloride products are 250, 289, 377, and 356 US dollars/ton of  $\text{CaCl}_2$  product in the form of 80% flake, 95% flake, 35% aqueous, and 45% aqueous (all wt %), respectively. It was assumed for the overall cost estimate that only 75% of the calcium chloride product could be recovered and sold as 80% flake product. The exact purity and form of the calcium chloride product leaving the clarifier could vary with process conditions and with the location of the storage facility (i.e., the presence of

impurities in the underground limestone could affect the purity of the precipitated CaCl<sub>2</sub> product).

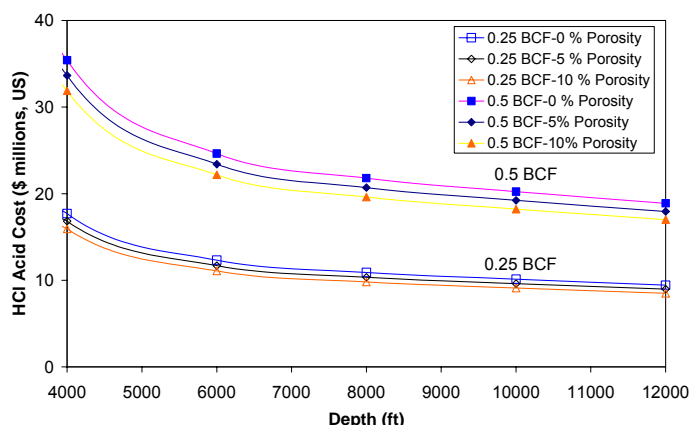


Figure 5. Cost of aqueous HCl (33 wt % solution) needed for a 0.25 or 0.5 BCF natural gas storage facility at varying depths (in limestone of varying porosity - 0, 5 or 10%) in the northeastern U.S.

**Estimation of Total Facility Costs.** The total gross-earnings cost for developing an underground gas storage facility via the acid dissolution of limestone equals the difference between total income derived from the sale of calcium chloride salts and the total development cost. The total development cost for the gas storage facility can be estimated by summing the direct production costs, fixed charges, and facility overhead charges. The factors for these various costs were taken from the text by Peters and Timmerhaus<sup>13</sup> and are a primarily a function of the hydrochloric acid cost and the total capital investment cost. These economic factors are reported in Table 7 and the total gross-earnings cost for a 0.25 or 0.5 BCF gas storage facility in limestone is shown in Figure 6 as a function of limestone porosity at depth. Although no data are presented in this paper on dolomite dissolution costs (for brevity), these costs were evaluated and found to be approximately 6% more than that for limestone formations. This is primarily due to the higher density of the dolomite rock as compared to limestone.

**Comparison of Gas Storage Costs.** There exist several possibilities for increasing the availability of natural gas storage near major use markets. Some (but not all) of the possibilities include: 1) construction of new above-ground gas storage vessels of varying size, 2) use of abandoned mines for underground gas storage facilities, 3) conversion of existing aquifers to gas storage facilities, 4) conversion of oil and gas reservoirs to storage, and 5) the development of new underground gas storage facilities by the dissolution of carbonate rock, as we are proposing, or by the dissolution of salt. With each of these methods there are both economic and safety considerations. The construction of large numbers of above ground gas storage vessels introduces considerable risk in the modern era of terrorism. The most feasible way to store gas above ground is to liquefy it, which is expensive, and then store it in insulated tanks as liquefied natural gas (LNG).

Table 7. Estimated total production cost factors for a 0.5 to 1 BCF gas storage facility created via acid dissolution of limestone using hydrochloric acid.

Item	% Total Development Cost
<b>Direct Production Costs</b>	
Raw Materials	49
Labor	14
Utilities	8
Maintenance	3
<b>Fixed Charges</b>	
Depreciation - Fixed Capital Cost	9
Taxes	1.5
Insurance	0.5
Plant overhead	8
<b>General Expenses</b>	
Administration Costs	2
Distribution and selling costs	5
<b>Total</b>	<b>100</b>

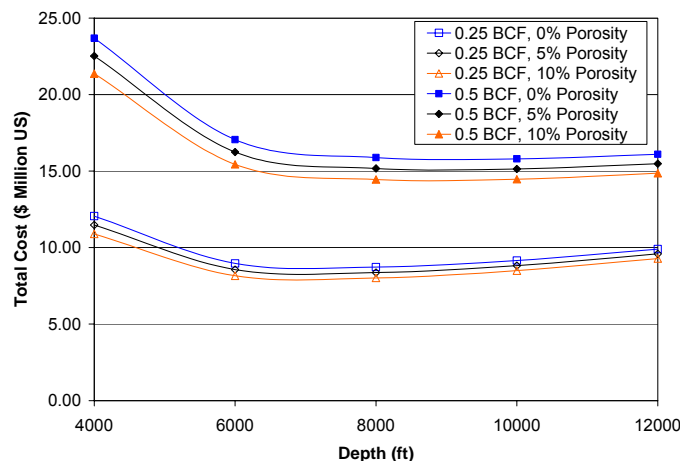
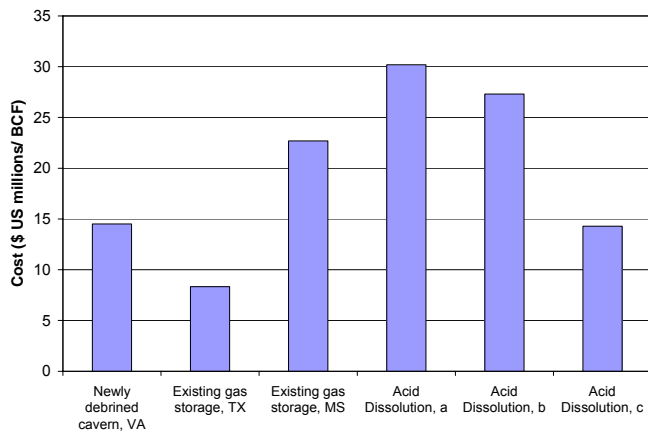


Figure 6. Total cost for a 0.25 and 0.5 BCF natural gas storage facility in limestone of 0, 5, and 10% porosity at varying depths in the northeastern U.S.

The conversion of abandoned mines to underground gas storage facilities suffers from the fact that the mines may not be located near existing gas storage pipelines or population centers. Additionally, these mines may not be suitable for storing the natural gas because of the many containment issues of abandoned mines.

In order to help evaluate the economic feasibility of the limestone dissolution process, cost comparisons were made to existing or newly created gas storage facilities. Figure 7 shows cost comparisons between salt storage and carbonate-cavern storage created by acid-dissolution. The total gross-earnings cost analysis shows that reductions in cost are achieved with increases in rock porosity and are significantly influenced by the price of hydrochloric acid and calcium chloride.



**Figure 7. Cost comparison of various underground gas storage methods. Acid Dissolution, *a* for 1 BCF, 0% porosity, listed acid cost, 75% CaCl<sub>2</sub> sold, 8000 ft.; *b* for 1 BCF, 10% porosity, listed acid cost, 75% CaCl<sub>2</sub> sold, 8000 ft.; *c* for 1 BCF, 5% porosity, 65% of listed acid cost, 75% CaCl<sub>2</sub> sold, 8000 ft.**

If hydrochloric acids costs can be negotiated to a value lower than the average list sales price, then the new process is even more competitive with other means for creating underground gas storage. Such reductions in acid cost are very likely given the quantity of acid to be purchased and the ability to use low purity hydrochloric acid. For example, Reed Business Information's Online Purchasing Magazine lists hydrochloric acid sales prices as low as \$58 per metric ton for technical grade acid, which represents a 23% reduction in acid cost over that used for our primary cost estimates.

### Geologic Criteria for Creating Carbonate-Cavern Storage

**Optimum Rock Formations.** The gross earnings costs clearly indicate the advantages of developing limestone storage caverns at depths greater than 4000 ft, where natural gas densities are near their maximum. Additionally, the increased density of dolomite requires that more acid be used to develop storage in these rock formations. Based on the conservative pressure gradients that we used, the preferred rock formation is one made of limestone at depths between 6000 and 9000 ft. Further cost savings (up to 9%) can be achieved by developing gas storage in limestone with increased porosity (up to 15%). Such limestone formations exist in many regions of the U.S., and conventional gas storage fields have been developed within this depth range.<sup>14</sup>

**Identification and Correlation of Carbonate Units.** A regional survey was conducted to identify stratigraphic units consisting of predominantly carbonate rock that are likely candidates for developing carbonate-cavern gas storage in the following states: Indiana, Ohio, Kentucky, West Virginia, Pennsylvania, and New York. Thick, laterally continuous carbonate sequences underlie major portions of these states. To identify the regional extent of each of these stratigraphic units, a series of maps was produced using existing data.

Seven major carbonate units were identified and correlated for mapping (Table 8). These carbonate units are generally separated by non-carbonate (siliciclastic or evaporite)

formations, which may help provide an overlying seal for creating carbonate-cavern storage by acid dissolution. The only common exception to the presence of non-carbonate directly overlying the carbonate unit is the contact between Units 5 and 6. In a few areas, Unit 6 directly overlies Unit 7. Not all of the carbonate units are present over the entire study area because of regional variations in deposition and erosion.

**Table 8. Carbonate units mapped in the study area. Regional correlations and formation names after Patchen et al.<sup>15,16</sup> and Rupp.<sup>17</sup>**

Unit	Age	Example Formations/Groups
1	Lower Mississippian	Greenbrier Group (Big Lime)
2	Middle Devonian	Onondaga Limestone
3	Upper Silurian – Lower Devonian	Helderberg Limestone
4	Silurian	Lockport Dolomite
5	Upper Ordovician	Trenton Limestone
6	Upper Ordovician	Black River Group
7	Upper Cambrian – Lower Ordovician	Knox Group

**GIS Analysis and Mapping.** The goal of the data collection process was to obtain an even distribution of wells, with data from approximately 200 to 300 wells for each state. Well data, including formation tops, were obtained from the state geological surveys. Data were arranged in a consistent format, checked, and loaded into ArcView, which is a Geographic Information System.

Maps showing depth from the ground surface to the top of each carbonate unit were constructed within GIS using map algebra techniques. Carbonate unit elevation (structural) tops were interpolated into surfaces, and the resulting surfaces were subtracted from digital elevation models to produce maps showing the depth to the top of each carbonate unit. The thickness of each unit was then interpolated. Depth and thickness values were contoured for visual examination.

**Assessment of Geological Suitability.** In order to identify areas that are potentially suitable for creating storage caverns in carbonate rock using acid dissolution, a series of suitability maps was produced using the depth and thickness criteria (carbonate formations deeper than 4000 ft, with preference for limestone thicker than 300 ft and at depths between 6000 and 9000 ft). Maps were made for each state using various subranges of depth (e.g., Figs. 8-11).

The suitability maps show that there are carbonate units at a suitable depth present within some areas of all six states examined (Table 9). Large areas of Pennsylvania, West Virginia, and New York are potentially suitable for developing gas storage by dissolving carbonate formations. Smaller areas with the optimum thickness and depth of carbonate formations are present in the other states. In general, the most extensive formations consisting of predominantly limestone at a suitable depth and thickness are the Helderberg Limestone, Trenton Limestone, and Black River Group. The Greenbrier Group and Onondaga Limestone are suitable over a smaller regional extent. The Lockport Dolomite and Knox Group consist of predominantly dolomite within the study area. Before applying the new method for creating storage capacity in any specific area, geologic properties of the carbonate formations



within that area should be examined in greater detail than was done in our regional analysis.

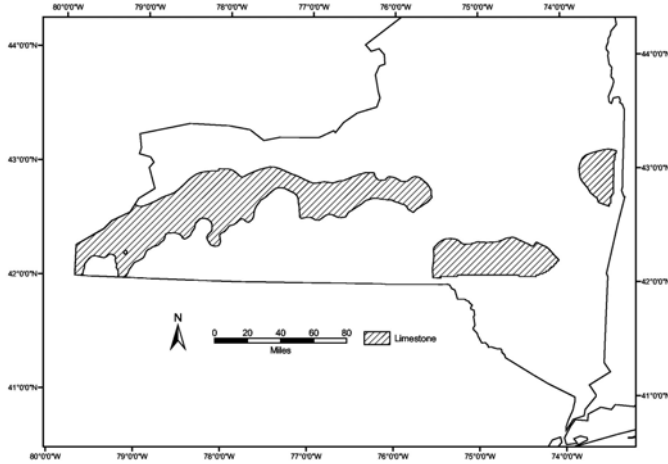


Figure 8. Limestone in New York that is in the 4000 to 6000 ft depth range and over 300 ft in thickness (Units 3, 5 and 6).

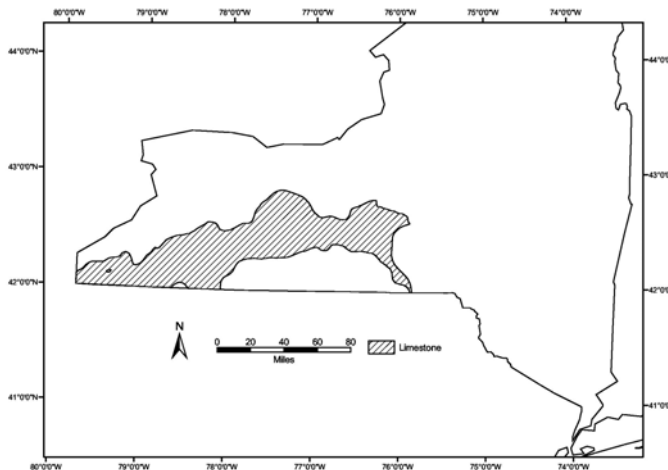


Figure 9. Limestone in New York that is in the 6000 to 8000 ft depth range and over 300 ft in thickness (Units 5 and 6).

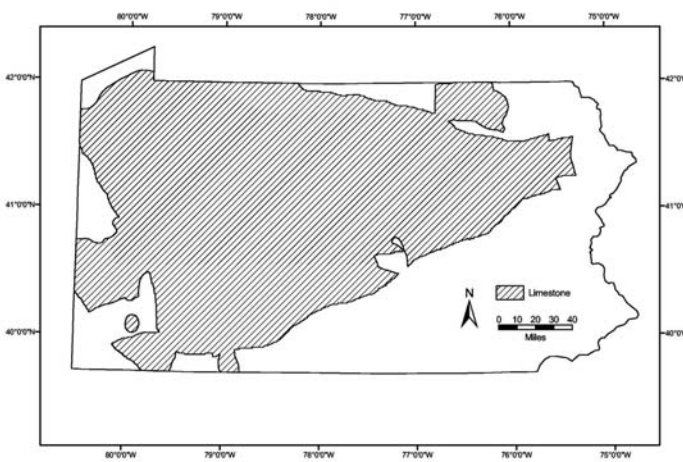


Figure 10. Limestone in Pennsylvania that is in the 6000 to 8000 ft depth range and over 300 ft in thickness (Units 2, 3, 5 and 6).



Figure 11. Limestone in West Virginia that is in the 6000 to 8000 ft depth range and over 300 ft in thickness (Units 3, 5 and 6).

Table 9. Carbonate units that meet suitability criteria for developing caverns by acid dissolution based on regional GIS mapping of depth and thickness. Typical formation names within each unit are listed in Table 8.

State	Carbonate Units deeper than 4000 ft and thicker than 300 ft	Limestone Units from 6000-9000 ft and thicker than 300 ft
Indiana	1,3,4,6,7	6
Kentucky	4,5,6,7	5,6
New York	3,4,5,6,7	5,6
Ohio	6,7	6
Pennsylvania	2,3,4,5,6,7	2,3,5,6
West Virginia	3,4,5,6,7	3,5,6

**Conclusions**

Analysis of the process design, preliminary economics, and geologic suitability suggests that our proposed method of creating underground caverns in carbonate formations is a viable technology for developing gas storage capacity. The process appears to be competitive when compared with other means of creating underground gas storage. The creation of caverns in carbonate formations using the proposed process has the advantage of being applicable to many different locations because of the widespread occurrence of carbonate rock, offers high deliverability because of cavernous geometry, and will require a low volume of cushion gas. The method has the potential for leading to commercialization of new gas-storage capacity near major markets. Since depleted gas reservoirs and salt formations are nearly non-existent in many areas, the creation of caverns in carbonate rock offers an attractive alternative to conventional methods of gas storage.

The next phase of our investigation will include modeling of the processes involved in creating storage capacity by acid dissolution of carbonate rock. Specific areas will be selected for more detailed geologic characterization relevant to applying the new technology. A final design will be prepared to facilitate field demonstration of the new technology, with the goal of eventual full-scale deployment.

## Acknowledgments

We thank the personnel of the state geological surveys (Indiana, Kentucky, Ohio, Pennsylvania, New York, and West Virginia) from which data were obtained. In particular, we appreciate the time and assistance of the following individuals: Katharine Lee Avary (West Virginia Geological Survey), Justin Deming (New York State Museum), John Harper and Cheryl Cozart (Pennsylvania Geological Survey), Dave Harris (Kentucky Geological Survey), and John Rupp (Indiana Geological Survey).

Helpful discussions and data contributions from Columbia Natural Resources (CNR), Cabot Oil & Gas Corporation, and Halliburton are gratefully acknowledged. We especially thank Ed Rothman (CNR), John Abshire and Philip Towey (Cabot), and Gary Rodvelt and Greg Kozera (Halliburton) for their time and helpful suggestions. Also, we are grateful to Tom Blake for his interest in the project and valuable comments.

We thank John Rodgers (Clemson University) for very helpful discussions regarding constructed wetland treatment systems, and we greatly appreciate the contributions of Yang Yang, graduate research assistant at Clemson University, who worked diligently on constructing the GIS database and producing the maps.

Funding for this project is provided by the U.S. Department of Energy through the National Energy Technology Laboratory, Morgantown, West Virginia, under contract number DE-FC26-02NT41299. We gratefully acknowledge the helpful suggestions of James R. Ammer, USDOE.

## Nomenclature

°Be	= Baume
BCF	= billion cubic feet
°C	= degrees Celcius
lb	= pounds mass
°F	= degrees Fahrenheit
ft	= feet
psi	= pounds per square inch
%	= percent
aq	= aqueous solution
s	= solid
$C_i$	= concentration of species $I$
STP	= standard temperature and pressure
g	= gas
T	= temperature
$\Delta G^\circ_{\text{rxn}}$	= Gibbs free energy of reaction
$G^\circ_{f,i}$	= Gibbs free energy of formation
V	= volume
$K_{\text{eq}}$	= reaction equilibrium constant
wt	= weight
P	= pressure
X	= anion
$P_{\text{cri}}$	= critical pressure
$\rho$	= density
R	= ideal gas constant
GIS	= Geographic Information Systems
USDOE	= United States Department of Energy

## References

- Zoback, M.D. and J.H. Healy, "Friction, faulting and in-situ stress": *Annales Geophysicae*, **2**, p. 689-698. 1984.
- Fjær, E., R.M. Holt, P. Horsrud, A.M. Raaen, and R. Risnes, *Petroleum-Related Rock Mechanics: Developments in Petroleum Science 33*, Elsevier Science. 1992
- Rocha, L.A. and A.T. Bourgoyne, "A new simple method to estimate fracture pressure gradient": *SPE Drilling and Completion*, **11**, p. 153 - 159. 1996.
- Lillie, R.J., *Whole Earth Geophysics*: Prentice Hall, Upper Saddle River, NJ. 1999.
- Eckstein, Y. and G. Maurath, "Terrestrial heat-flow density", in *Geology of Pennsylvania*: Schultz, C.H., ed., Pennsylvania Geological Survey, p. 334-337. 1999.
- Standing, M.B. and D.L. Katz, "Density of natural gases": *Trans. AIME*, **146**, p. 140. 1942.
- Moshiri, G.A. (ed.), *Construction Wetlands for Water Quality Improvement*: Lewis Publishers, Ann Arbor, Michigan. 1993.
- Hawkins, W.B., J.H. Rodgers, Jr., W.B. Gillespie, Jr., A.W. Dunn, P.B. Dorn, and M.L. Cano, "Design and construction of wetlands for aqueous transfers and transformations of selected metals": *Ecotoxicology and Environmental Safety*, **36**, p. 238-248. 1997.
- Gillespie, W.B., Jr., W.B. Hawkins, J.H. Rodgers, Jr., M.L. Cano, and P.B. Dorn, "Transfers and transformations of zinc in constructed wetlands: mitigation of a refinery effluent": *Ecological Engineering*, **14**, p. 279-292. 2000.
- Huddleston, G.M. III, W.B. Gillespie, Jr., and J.H. Rodgers, Jr., "Using constructed wetlands to treat biochemical oxygen demand and ammonia associated with a refinery effluent": *Ecotoxicology and Environmental Safety*, **45**, p.188-193. 2000.
- Moore, M.T., J.H. Rodgers, Jr., S. Smith, Jr. and C.M. Cooper, "Mitigation of metolachlor-associated agriculture runoff using constructed wetlands in Mississippi, USA": *Agric. Ecosystems and Environ.*, **84**, p. 169-176. 2001.
- Murray-Gulde, C.L., J.E. Heatley, T. Karanfil and J.H. Rodgers, Jr., "Performance of a hybrid reverse osmosis-constructed wetland treatment system for brackish produced water": *Water Research*, **37**, p. 705-713. 2003.
- Peters, M.S. and K.D. Timmerhaus, *Plant Design and Economics for Chemical Engineers*, McGraw-Hill, New York, 4<sup>th</sup> ed. 1991.
- American Gas Association, *2001 Survey of Underground Storage of Natural Gas in the United States and Canada*, American Gas Association, Washington, DC.
- Patchen, D.G., K.L. Avary, and R.B. Erwin, *Northern Appalachian Region Correlation Chart*: American Association of Petroleum Geologists, Correlation of Stratigraphic Units of North America (COSUNA) Project, 1 sheet. 1984.
- Patchen, D.G., K.L. Avary, and R.B. Erwin, *Southern Appalachian Region Correlation Chart*: American Association of Petroleum Geologists, Correlation of Stratigraphic Units of North America (COSUNA) Project, 1 sheet. 1984.
- Rupp, J.A., *Structure and Isopach Maps of the Paleozoic Rocks of Indiana*: Special Report 48, Indiana Geological Survey, Bloomington, IN. 1991.