ENERGY&FUELS
AN AMERICAN CHEMICAL SOCIETY JOURNAL
VOLUME 19, NUMBER 3 MAY/JUNE 2005

Reviews

Sequestration of Carbon Dioxide in Coal with Enhanced Coalbed Methane Recovery—A Review[†]

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Received May 7, 2004

This article reviews the storage of captured CO_2 in coal seams. Other geologic formations, such as depleted petroleum reservoirs, deep saline aquifers and others have received considerable attention as sites for sequestering CO_2. This review focuses on geologic sequestration of CO_2 in unmineable coalbeds as the geologic host. Key issues for geologic sequestration include potential storage capacity, the storage integrity of the geologic host, and the chemical and physical processes initiated by the deep underground injection of CO_2. The review topics include (i) the estimated CO_2 storage capacity of coal, along with the estimated amount and composition of coalbed gas; (ii) an evaluation of the coal seam properties relevant to CO_2 sequestration, such as density, surface area, porosity, diffusion, permeability, transport, rank, adsorption/desorption, shrinkage/swelling, and thermochemical reactions; and (iii) a treatment of how coalbed methane (CBM) recovery and CO_2-enhanced coalbed methane (ECBM) recovery are performed (in addition, the use of adsorption/desorption isotherms, injection well characterization, and gas injection are described, as well as reservoir screening criteria and field tests operating in the United States and abroad); (iv) leak detection using direct measurements, chemical tracers, and seismic monitoring; (v) economic considerations using CO_2 injection, flue gas injection, and predictive tools for CO_2 capture/sequestration decisions; (vi) environmental safety and health (ES&H) aspects of CO_2-enhanced coalbed methane/sequestration, hydrodynamic flow through the coal seam, accurate gas inventory, ES&H aspects of produced water and practices relative to ECBM recovery/sequestration; (vii) an initial set of working hypotheses concerning the chemical, physical, and thermodynamic events initiated when CO_2 is injected into a coalbed; and (viii) a discussion of gaps in our knowledge base that will require further research and development. Further development is clearly required to improve the technology and economics while decreasing the risks and hazards of sequestration technology. These concerns include leakage to the surface, induced seismic activity, and long-term monitoring to verify the storage integrity. However, these concerns should not overshadow the major advances of an emerging greenhouse gas control technology that are reviewed in this paper.

I. Introduction

The effect of increasing atmospheric carbon dioxide (CO_2) concentration on global warming is now recognized as one of the most important environmental issues facing society. The connection between anthropogenic emissions of CO_2 with increasing atmospheric CO_2 levels and temperatures has been well-established and well-accepted. This problem is being addressed internationally through the formation of organizations such as the United Nations Framework Convention on

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10.1021/ef040047w CCC: $30.25

Climate Change (UNFCCC) and the Intergovernmental Panel on Climate Change (IPCC). To stabilize atmospheric levels of greenhouse gases (GHGs) while minimizing the world economic impact, four options are being explored, which project the use of (1) less carbon-intensive fuels, (2) more-energy-efficient methods, (3) carbon sequestration, and (4) increased conservation. A successful stabilization program for atmospheric GHGs will, most likely, involve all four options.

To counteract the effect of increasing GHGs in the atmosphere during the 21st century, the U.S. Department of Energy (DOE) has established energy research and development programs in carbon sequestration science. This direction complements two long-standing program options directed toward generating energy in the future using (1) less carbon-intensive fuels and (2) more-energy-efficient methods to develop a "pathway to stabilization" of carbon emissions. A U.S. DOE Office of Fossil Energy Report[1] (and the wealth of international references within) provides an overview of the potential methods that have been suggested as routes to carbon sequestration.

A recent U.S. DOE "road map"[2] that was developed by the National Energy Technology Laboratory (NETL) suggests potential pathways for sustaining the near-term and midterm use of fossil energy while reducing the rate of growth of CO_2 levels. A White Paper[3] prepared for the National Climate Change Technology Initiative addresses the capture of CO_2 from present and planned fossil energy systems and the direct geological sequestration of CO_2. The objectives of the White Paper are (1) to describe current CO_2 capture and geologic storage activities, (2) to assess the reduction in GHG levels resulting from successful efforts with current activities, and (3) to envision new research and development (R&D) initiatives to accelerate technology development to provide other acceptable cost options for reduction of GHG levels. Carbon sequestration pathways implemented during the next 30 years must be both economically and environmentally attractive.

U.S. DOE initiatives complement other national and international programs that are directed toward understanding the magnitude of the GHG problem and possible mitigation options. These include the IEA Greenhouse Gas R&D Program and other programs in Australia, Belgium, Canada, Denmark, Finland, France, Japan, Korea, The Netherlands, New Zealand, Norway, Poland, Sweden, Switzerland, the United Kingdom, the United States of America, Venezuela, and the Commission of the European Communities.

Long-term storage of CO_2 in coal seams is just one option under investigation. Other options may include storage of CO_2 in active or depleted oil and gas fields with enhanced oil recovery (EOR), deep saline aquifers, gas-rich shales, methane hydrate formations, salt caverns, other geological formations, or the ocean. The successful sequestration strategy will take advantage of most, if not all, of these potential sinks. Oceanic sequestration may be a viable option for the storage of CO_2 from large, stationary sources near the coast; however, it is probably not the best option for CO_2 from sources in the continental interior. Geological sequestration is probably the best option for CO_2 from those sources. Among the geological sequestration options, those that allow the production of a value-added product such as methane (CH_4) or petroleum are the options that are the most attractive and will likely be developed first. These value-added processes include sequestration of CO_2 in gassy coalbeds with the simultaneous recovery of CH_4 and EOR with CO_2. To our knowledge, the storage of CO_2 in coal with concomitant enhanced coalbed methane recovery has not been extensively reviewed, although brief reviews have appeared in English[4] and Japanese.[5]

Bachu defines geological sequestration as "the capture of CO_2 directly from anthropogenic sources and disposing of it deep into the ground for geologically significant periods of time."[6] Sequestration of CO_2 in geological formations is a storage process. Here, coal seam sequestration is defined as the storage of CO_2 from anthropogenic sources into deep, unmineable coal seams for geologically significant times with or without the concomitant recovery of natural gas. According to Byrer and Guthrie, "unmineable coals are either too thin, too deep, or too unsafe" to mine. "In recent times, historically mined coals may also be too high in sulfur or mineral matter or too low in BTU value to be economically profitable."[7]

As far as can be determined, the concept of coal seam sequestration was first proposed by Macdonald of Alberta Energy during discussions with Gunter and coworkers in 1991.[8] They performed a "proof of concept" study to verify their hypothesis. Even though Macdonald seems to have been the first to have proposed the storage of CO_2 in coal seams for sequestration purposes, the concept of enhanced coalbed methane (ECBM) recovery using CO_2 predates that proposal considerably. In 1972, Every and Dell'osso[9] found that CH_4 was effectively removed from crushed coal by flowing a stream of CO_2 at ambient temperature through the coal. ECBM is defined as the process of injecting a gas or mixture of gases into a coal seam with the purpose of enhancing the desorption of coalbed methane (CBM) and increasing the recovery of CH_4 from the coal. In 1980, Fulton and others showed that a rapid loss of CH_4 from coal occurred when CO_2 was injected in three cycles during 90 days.[10,11] Arri et al. of BP−Amoco showed that CH_4 could be displaced from coal using CO_2.[12] The BP−Amoco Corporation demonstrated, in a

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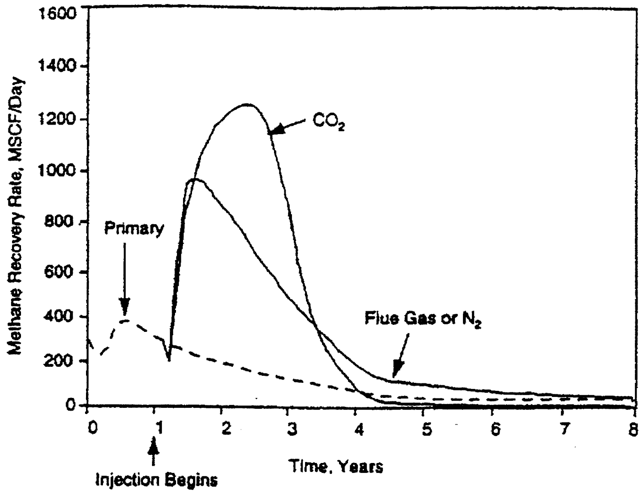

Figure 1. Comparison of methane recovery rates for a fully methane-saturated coalbed for primary pressure depletion, for pure CO_2 injection, for pure N_2 injection, and for flue gas injection, where injection and production wells are arranged in a five-spot pattern. An injection pressure of 2000 psia, a reservoir pressure of 1500 psia, a permeability of 10 mD, a porosity of 0.5%, a coalbed thickness of 10 ft, and a drainage area of 46 acres were assumed. (From Gunter et al.,[292] after Chaback et al.[13])

series of patents, that CH_4 could be effectively removed and recovered from deep, unmineable coals using CO_2 and other gases.[13−15] Chaback et al. explained, using a modeling and simulation study, that CH_4 was removed from the coal by displacement chromatography as CO_2 is transported through the coalbed.[13] Chaback et al. simulated the effects of injecting pure nitrogen (N_2), pure CO_2, or a simulated, dry flue gas composed of 15% CO_2 and 85% N_2 on production as well as modeling primary production. The simulation results they obtained for recovery of CH_4 are shown in Figure 1.[13] When ECBM is performed using CO_2, the term becomes CO_2-ECBM, and when the objective is to also sequester CO_2, in addition to producing CH_4, the name becomes CO_2-ECBM/sequestration. CO_2-ECBM/sequestration and EOR using CO_2 injection are the only sequestration options that produce a value-added product (CH_4 and oil, respectively).

Coal seam sequestration with simultaneous recovery of natural gas is a particularly appealing way of addressing the increase in the atmospheric concentration of CO_2, and it offsets the cost of capture, compression, transportation, and storage of CO_2 by producing natural gas. Thus, among the possible scenarios for long-term storage of CO_2, those techniques that offer production of a byproduct such as natural gas or petroleum are expected to be the first commercially practiced sequestration technologies. Deep, unmineable coal seams are convenient sinks, because they are widespread and exist in many of the same areas as large, fossil-fuel fired, electric-power-generating stations.[6,16]

The expertise required to inject CO_2 into geological formations already exists. Industry has been practicing EOR and enhanced gas recovery (EGR) for years. In December 1993, BP−Amoco performed a small pilot CO_2-injection experiment in the San Juan basin coal from the Fruitland Formation in Colorado.[8] Conoco-Phillips and the Bugas Division of Radoil used a diesel engine to burn fuel to produce a gas stream that was O_2 depleted and consisted of 83% N_2 and 12% CO_2. The diesel power was then used to compress the gas and inject it into the San Juan coal.[17] As far as could be determined, this is the first documented example of the injection of raw combustion gases into a coal seam to generate CH_4. Burlington Resources did perform CO_2-ECBM in deep, unmineable coal seams in the San Juan basin coals in New Mexico starting in 1996.[18] Reeves[19] recently wrote a report entitled "The Coal-Seq Project—Field Studies of ECBM and CO_2 Sequestration in Coal". The project has several near-term objectives related to ECBM field studies in the San Juan basin, but one of the medium-term objectives is to assess the potential for coal seam sequestration across the United States. A group of partners performed a CO_2-ECBM/sequestration project using the Manville coals at the Fenn Big Valley in Alberta in 1997.[20] Thus, coal seam sequestration can be accomplished with off-the-shelf technology, which should make rapid commercialization possible. Researchers from The Netherlands have completed a study of the technical and economic feasibility of using CO_2-ECBM/sequestration in Dutch coal.[21,22] Researchers in Belgium have begun to consider the possibilities of sequestering CO_2 in coals in the Westphalian Campine coal basin.[23] These and other projects will be discussed in greater detail later.

Understanding and quantifying the gas-coal interactions is an important area of research. Predictions concerning the long-term stability of the sequestered gas require a knowledge of how the gas is held in place and what factors might induce its release. Reliable estimates of the gas-retention capacity of coal seams are needed

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for economic assessments of the viability of candidate seams. CH_4 production from coalbeds has led to extensive investigations into factors that affect its adsorption capacity, both to determine the gas-in-place accurately and because of safety issues in coal mining.[24−26] However, studies of the CO_2 capacity of coals under in-seam conditions have been limited. The more recent proposal—that the injection of CO_2 into coal seams is a viable option to mitigate the increasing worldwide CO_2 emissions[27]—has stimulated interest in developing a better understanding of the coal−CO_2 interactions and the adsorption capacity of a candidate coal seam for CO_2.

Estimated CO_2 Storage Capacity of Coal Basins. Coals have a substantial capacity to store gases by adsorption on their surfaces and within their porous structures. The storage capacity is directly related to the pore pressure. Estimates of the capacity of deep, unmineable coal seams to imbibe CO_2 are crude and unrefined. Rough estimates exist for the capacity of some gassy coal seams to sequester CO_2. Stevens et al.[18] estimated the combined capacity of the San Juan, Uinta, and Raton basins at 8.5 gigatons (Gt) of CO_2, and the combined Bowen and Sidney basins in eastern Australia at 11.2 Gt of CO_2.[18] The Cambay basin in western India and the Kuznetsk basin in Russia are estimated to have CO_2 storage capacities of 3.8 and 13.6 Gt, respectively.[18] Note that only those basins containing significant amounts of methane were considered. When other deep, unmineable coal seams are considered, the cumulative potential CO_2 storage capacity is expected to be much larger. In toto, the estimated CO_2 storage capacity of all the aforementioned gassy coal seams is estimated to be 37.8 Gt of CO_2. Reeves has revised some of the capacity estimates of the CO_2 sequestration potential of various gassy coal seams throughout the world. These revised results are presented in Table 1.[28] The table contains information on the CO_2 sequestration potential and the CO_2-ECBM reserves for coal formations throughout the world and ranks them according to their potential reserves, resource concentration, producibility, development costs, and CO_2 availability.

Geological assessment of several major international coal basins was completed by Wong et al.[29] to identify the best coal basin in each of four countries for CO_2-ECBM development. Using market potential, production potential, CBM/CO_2 storage potential, CO_2 supply potential, and site infrastructure costs (financeability), they further ranked these major coal basins from highest to lowest for CO_2-ECBM potential: (1) the Bowen basin (Australia), (2) the Qinshui basin (China), (3) the Upper Silesian basin (Poland), and (4) the Cambay basin (India).

Table 1. Ranking of World's Most Prospective Coal Deposits for CO_2-Enhanced Coal Bed Methane Recovery/Sequestration for 13 Coal Basins[a]

		Ranking[b]									
coal basin/region	country	potential reserves	concentration of resources	ECBM producibility	development costs	gas sales market	CO_2 availability	overall score	ranking of basin[c]	CO_2-enhanced reserves[c] (Tcf)	CO_2 sequestration potential[d] ($\times 10^6$ tons)
San Juan	United States	5	5	5	5	4	5	29	1	13.0	1400
Kuznetsk	Russia	5	4	4	3	4	4	24	3	10	1000
Bowen	Australia	5	4	4	4	4	3	24	4	8.3	870
Ordos	China	4	3	4	3	2	2	18	13	6.4	660
Sumatra	Indonesia	4	3	3	3	4	4	21	8	3.5	370
Uinta	United States	2	3	5	5	4	5	24	2	2.2	230
Western Canada	Canada	4	2	3	4	3	3	19	9	1.6	170
Sydney	Australia	4	4	3	3	4	4	22	7	1.4	150
Raton	United States	2	3	4	5	4	5	23	5	0.8	90
Cambay	India	3	5	3	4	5	3	23	6	0.7	70
Donetsk	Ukraine/Russia	1	5	2	3	4	4	19	11	0.3	30
NE China	China	2	4	2	3	4	4	19	12	0.2	20
Damodar Valley	India	2	3	2	4	4	4	19	10	0.1	10
								Total High-Potential Basins:		48.5	5070

[a] From ref 28. [b] The ranking scale is 1 (lowest) to 5 (highest). [c] Estimated amounts of additional CH_4 that can be recovered due to CO_2 injection. Estimated reserves in addition to pressure-depleted recovery. [d] Estimated amounts of CO_2 that can be stored.

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A NOVEM report estimated that ~8 Gt of CO_2 could be stored in Dutch coals,[21,22] and the estimate for coal seam sequestration capacity in the Belgium Westphalian Campine coal basin is 0.21 Gt of CO_2.[23] Gunter et al. estimated the capacity of deep coalbeds in Alberta, Canada for sequestration at ~20 Gt of CO_2.[8] Lastly, Kuuskraa et al. estimated the total global capacity of coalbeds to sequester CO_2 to be 82−263 Gt of carbon or ca. 300 to 964 Gt of CO_2.[30,31]

In 1996, the Energy Information Agency (EIA) estimated the coal resources to a depth of 6000 feet (1829 m) in the United States to be almost 60 trillion tons (60 000 Gt) with ~90%, or 54 trillion tons (54 000 Gt), being unmineable.[32] According to Cook et al., coals can store up to 0.06 tons of CO_2 per ton of coal at 5 MPa (50 atm) pressure.[33] Thus, under ideal conditions and using all the unmineable coal reserves in the United States, an upper limit on the amount of CO_2 that could be stored can be estimated at 324 Gt of CO_2. It must be emphasized that this value represents an upper limit and the actual practical CO_2 storage capacity of U. S. coals is, most probably, lower. Stevens et al. recently estimated the worldwide coalbed CO_2 sequestration capacity to be 225 Gt of CO_2.[18] They further estimate, using cash flow analysis, that 5−15 Gt of CO_2 could be sequestered at a profit, assuming CH_4 production by CO_2-ECBM, with another 60 Gt of CO_2 sequestered at a cost of less than $50 per ton of CO_2, and another 150 Gt of CO_2 sequestered at a cost of between $100 and $120 per ton.

The aforementioned estimates are uncertain,[34] but they begin to establish preliminary limits on the potential CO_2 sequestration capacity of unmineable coalbeds. As noted by Bergman and Winter, estimates of the capacity of a geological sink to sequester CO_2 are tentative and are dependent on the set of assumptions applied and the general approach used.[35] Benson noted that it is "important not only to account for the storage volume that is available for sequestration, but also to determine what fraction of the available storage space will be occupied by CO_2. This will depend strongly on the formation's heterogeneity and the complex interplay of viscous and gravitational forces."[36] The sequestration efficiency refers to the portion of pore volume in a geological formation that is actually used to store CO_2. Currently, it is estimated that only 1%−10% of the available pore volume is used to store CO_2.[1] Obviously, the sequestration efficiency of a geological formation will have a major effect on its sequestration capacity.

CO_2 storage capacity estimates are uncertain and based upon many assumptions and other estimates. For example, the definition of a "deep unmineable coal" is important. In the United States, coals have been mined to ~3000 feet. Some of the estimates of storage capacity in the literature may include more-shallow coal seams. Economic considerations have an impact on CO_2 capacity estimates. There is a lack of data on seam thickness, lateral continuity, depth of the seam, CH_4 content, and CO_2 adsorption isotherm measurements. To obtain global CO_2 storage capacity estimates, many of these parameters are themselves estimated.

Estimated Amounts of CH_4 in Coal. There has been active exploration for coalbed gas in the United States, due, in part, to a federal tax credit for its production. The Section 29 tax credits[37,38] available for CBM production from qualifying coal seams between 1980 and 1992 were a major factor in the quadrupling of onshore natural gas drilling. These tax credits have expired. Between 1986 and 1990, new gas well completions went from 400 to 1600 per year, and there was a 15-fold increase in CBM production from 1989 to 2000.[38−40] Progress in CBM technology such as improved geological knowledge and well completion practices led to higher reserves per well, and more-efficient production and drilling practices also played a major role in increased CBM production. U.S. CBM production for 2001 was 1.56 Tcf (0.044176 Tm^3).[41] (Note: Tcf denotes trillion cubic feet, whereas Tm^3 denotes trillion cubic meters.)

The amount of CH_4 available in the major coal basins in the United States has been estimated at 400−700 Tcf (11.33−19.82 Tm^3). One estimate is shown in Figure 2 and Table 2.[42−44] Of this amount, ~150 Tcf (4.25 Tm^3) are believed to be technically recoverable, using current or near-term technology, and ~29 Tcf (0.821 Tm^3) are considered "proved reserves".[41] The recoverable CBM estimates may include mineable coalbeds that are not suitable for CO_2 sequestration. Kim published a technique to estimate the CH_4 content of coals in place.[45] Gunter et al. stated that estimates of CBM resources in the United States range between 275 and 649 Tcf (7.787−18.377 Tm^3).[8] U.S. CBM proved reserves for 2000 were estimated at 15.7 Tcf (0.444 Tm^3), representing 8.9% of the estimated 177.4 Tcf (5.023 Tm^3) of U.S. natural gas proved reserves for 2000.[39] U.S. production

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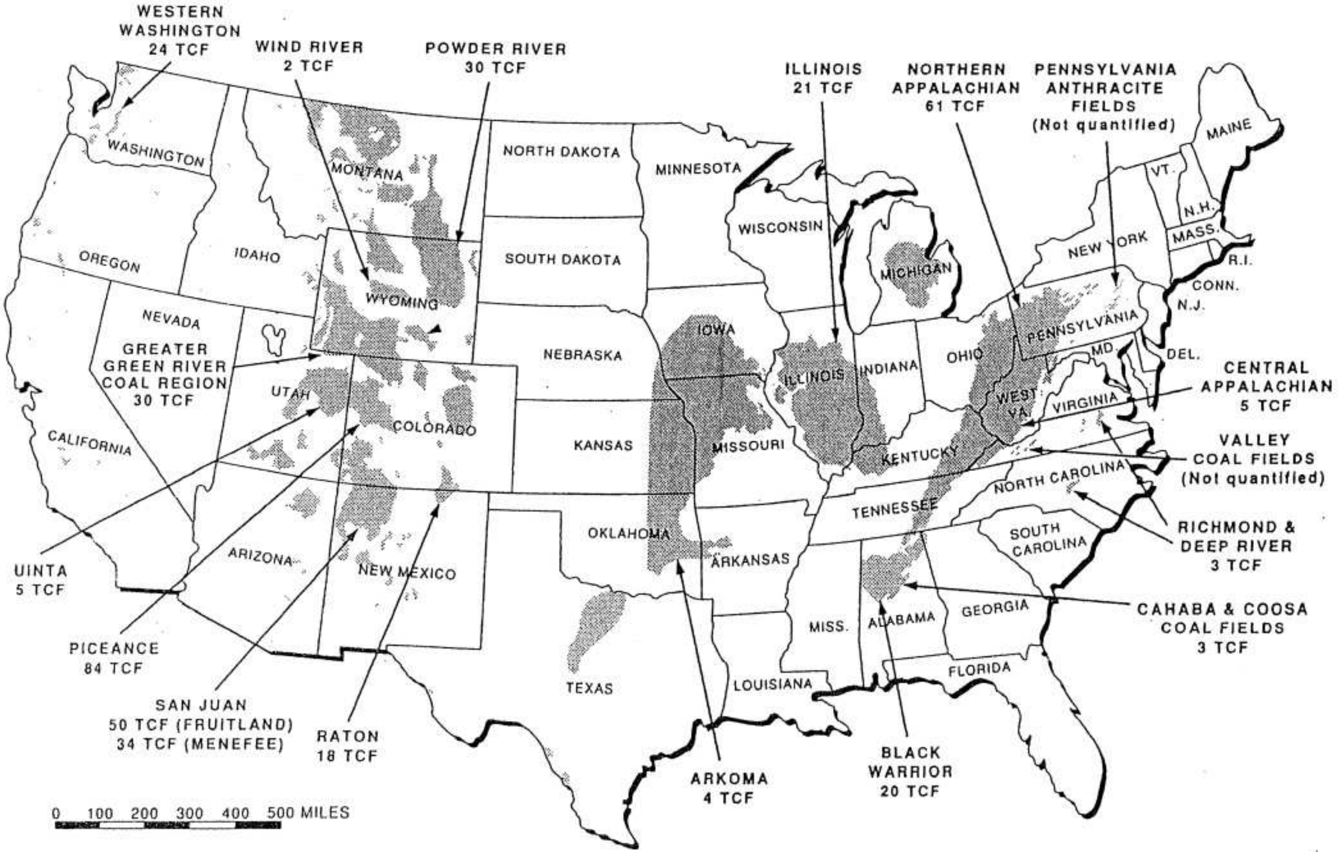

Figure 2. Methane in major coal basins in the United States. (From ref 43.)

Table 2. United States Coal Bed Methane Resources[a]

coal basin/region	state(s)	gas-in-place (Tm^3)
Arkoma Basin	Oklahoma, Arkansas	0.06−0.11
Black Warrior Basin	Alabama, Mississippi	0.57
Cahaba Coal Field	Alabama	0.06
Central Appalachian Basin	Tennessee, Kentucky, West Virginia, Virginia	0.14
Coosa Coal Field	Alabama	0.03
Greater Green River Coal Region	Wyoming, Colorado	0.03−0.85
Illinois Basin	Illinois, Indiana, Kentucky	0.14−0.59
Northern Appalachian Basin	Pennsylvania, Maryland, West Virginia, Ohio, Kentucky	1.73
Pennsylvania Anthracite Fields	Pennsylvania	NQ[b]
Piceance Basin	Colorado	2.38
Powder River Basin	Montana, Wyoming	0.85
Ratan Basin	Colorado, New Mexico	0.23−0.51
Richmond and Deep River Basins	Virginia, North Carolina	0.06−0.08
San Juan Basin		
Fruitland Formation	Colorado, New Mexico	1.42
Menefee Formation	Colorado, New Mexico	0.62−0.96
Uinta Basin	Utah, Colorado	0.03−0.14
Valley Coal Fields	Virginia	NQ[b]
Western Washington Coal Region	Washington	0.03−0.68
Wind River Basin	Wyoming	0.03−0.06
	total	8.4−11.2

[a] From ref 43. [b] Not quantified.

of CBM in 2000 was 1.4 Tcf (0.0396 Tm^3) of the 19.2 Tcf (0.5936 Tm^3) of the total natural gas production.[39] Global CBM resources have been estimated to range from 2980 to 9260 Tcf (84.38−262.21 Tm^3)[30,31,44,46,47] and were reviewed by Davidson et al.[48] Kuuskraa recently made a country-by-country estimate of the global CBM for both gas-in-place and "technically recoverable resources" (see Table 3). Based on the assumption that two moles of CO_2 are sorbed onto coal for every mole of CH_4 released (see discussion in the sections entitled "Adsorption Isotherms of Gases on Coals," "CO_2-ECBM," and "Burlington Resources, Allison Unit CO_2-ECBM Pilot", given later in this review) the global CO_2 storage capacity of coalbeds was estimated to be 82−263 Gt of carbon (see the previous section, "Estimated CO_2 Stor-

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(47) Dhir, R.; Dern, R. R. J.; Mavor, M. J. *JPT, J. Pet. Technol.* **1991**, *43*, 1424−1433.

(48) Davidson, R. M.; Sloss, L. L.; Clarke, L. B. Coalbed Methane Extraction; Report No. IEACR/76, 1995.

Table 3. International Coalbed Methane (CBM) Resources[a]

country	CBM Resources (Tcf) in-place	CBM Resources (Tcf) recoverable
Russia	550−1550	N/A
China	350−1150	70
United States	500−1730	150
Australia	310−410	60
Canada	570−2280	140
Indonesia	210	30
Western Europe	120	N/A
Southern Africa[b]	100	20
India	90+	20
Poland/Czech Republic	70	N/A
Turkey[b]	50	10
Ukraine	50	N/A
Kazakhstan[b]	40	10
total	3010−7840	510

[a] From Kuuskraa.[43] In 1998, Kuuskraa published a country-by-country estimate for global coalbed methane, both for in-place and for technically recoverable resources. He estimated a CBM in-place value of 3000−8000 Tcf and a technically recoverable value of 510 Tcf. Kuuskraa's 1998 estimate for recoverable CBM resources is double his value published in the early 1980s. His most-recent estimates were based on a combination of detailed CBM basin studies and information on the rank and depth of coal basins around the world. [b] Assumes 20% gas-in-place recovery.

age Capacity of Coal Basins"), or ca. 300−964 Gt of CO_2.[31] For low-rank coals, including lignite, the adsorption capacity for CO_2 may be as much as 10 times more for CO_2 than it is for CH_4.[34] Thus, the aforementioned estimate of CO_2 storage capacity may be low by a considerable amount. A wealth of additional information involving all aspects of CBM can be found in The Society for Organic Petrology (TSOP) Coalbed Methane Reference List.[49]

The estimates of CBM resources are further complicated by difficulties in obtaining samples of fresh coal that have not lost any CH_4 during the sampling process, as well as complications with both the field and laboratory determination of coal gas content.[50] For example, depending upon the sampling and analytical protocols, some CH_4 can remain in the coal matrix during analysis and, thus, escape measurement. Variables that can affect CH_4 expulsion from the coal during laboratory analysis include the coal particle size, moisture content, pressure, maceral composition, and degree of thermal maturation.[51−53] Multiple experimental techniques to determine the gas content of coal exist. Mavor critically evaluated the accuracy and comparability of some of these methods using freshly cut coals.[54] Specifically, the direct method developed by the U.S. Bureau of Mines, the Smith and Williams method, and the BP−Amoco methods were evaluated.[54] The direct method includes removing a core sample of coal from the coalbed in a pressure canister and measuring the amount of CH_4 desorbed from it, and the indirect method involves estimation of the adsorption capacity of a coal from adsorption isotherms. The direct method of analysis was determined to be the most accurate.

In making estimates of the methane reserves present in coal seams, there is the problem of obtaining a reliable and accurate measurement of the amount of total gas and methane in a coal sample. There is also the larger problem of taking the experimentally measured values obtained on a core sample and extrapolating those values over an entire coal seam. Determining the gas-in-place is a significant element of the evaluation of a reservoir.[53] Nelson recently evaluated the accuracy of "commonly used reservoir property analysis methods"[55] and identified six major sources of errors that contribute to overall estimation inaccuracies. Many of the commonly used methods of analysis were determined to have inherent errors that result in underestimation of the gas-in-place by 50% or more. In a more-recent side-by-side comparison of methods to determine the gas-in-place present in coal core samples, the use of conventional core desorption and pressure core-based desorption showed an error range of <20%.[56]

Marine shales are often found at the roof of coalbeds. These shales serve as an excellent sealing material to prevent CH_4 from migrating away from the coal seam, as it accumulates in the coal.[57] During the preparation of an environmental assessment for a CBM project in Wyoming, Zander showed that over-and-underlying shales act as confining materials that hold both water and CH_4 in the coal. Zander simulated the coalbed and confining shale layers using a modular three-dimensional finite-difference groundwater flow model (MODFLOW) to predict the extent of groundwater drawdowns, and then completed two wells—one in the coal formation and one into the sand aquifer above the coal. The wells were equipped with continuous monitoring devices placed in strategic locations. The experiment showed that the assumption that the shale layers were acting as barriers to both CH_4 and H_2O migration was correct.[57] According to Deul, one of the fathers of CBM recovery, "the variability of mineral matter content, coal petrography and other physical properties is so great that the most reliable indicator of CH_4 content" and CO_2 sequestration capacity will be established by using the 'direct method' on coal cores extracted by drilling.[58]

Composition of Coalbed Gas. Coalbed gas is primarily composed of hydrocarbons from C_1 to C_4. The absolute concentration of each hydrocarbon varies from coal to coal. The fraction of gases greater than C_2 can vary from zero to 70% and is referred to as the degree of wetness or the percentage of ethane and higher hydrocarbons.[46,50] However, CH_4 is usually the major constituent (88%−98%), with the higher hydrocarbons and CO_2 present in lesser amounts.[59] The CO_2 content

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(49) The Society for Organic Petrology. Coalbed Methane (full list). The Society for Organic Petrology, 2001. (Available via the Internet at http://www.tsop.org/refs/cbmfull.htm.)

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(56) Kuuskraa, V. A. Error Range of Methods for Determination of Gas-in-Place in Coal; personal communication, August 26, 2003.

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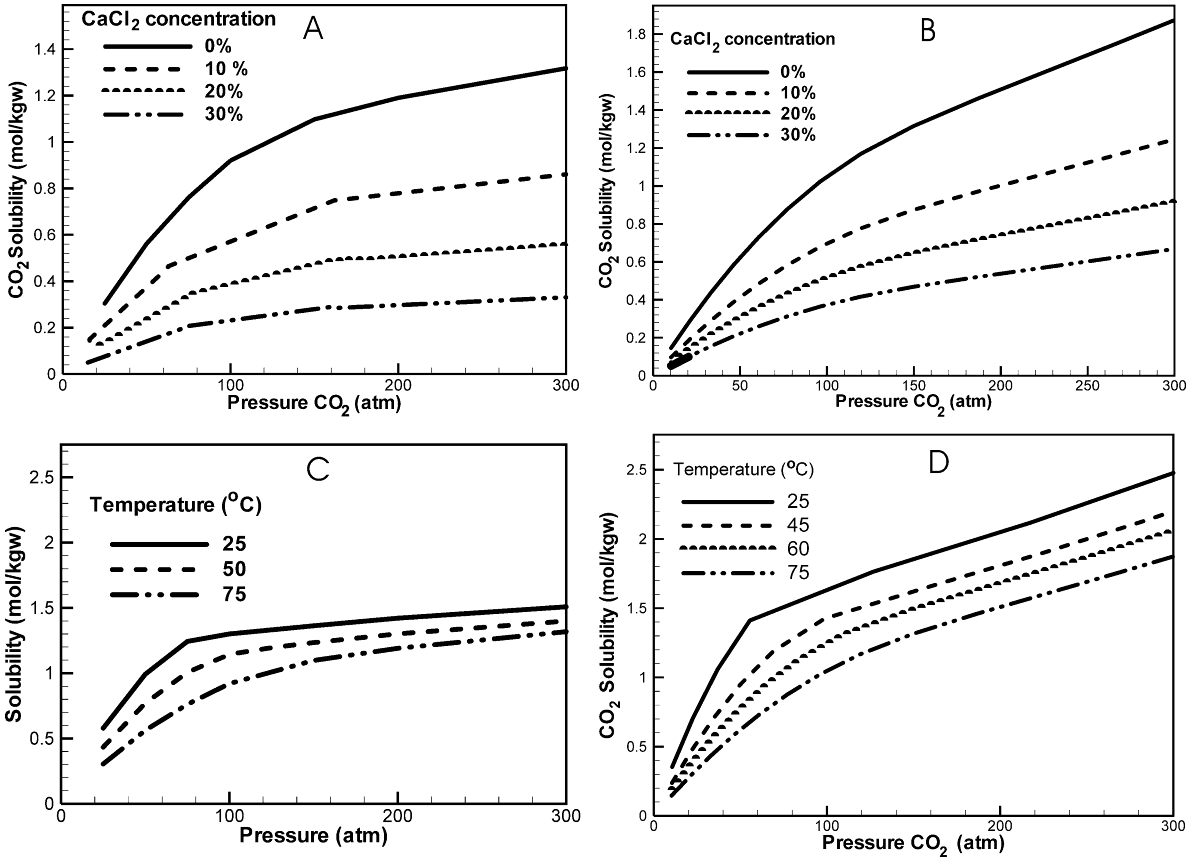

Figure 3. Solubility of CO_2 in pure water and brine as a function of pressure (A) at various concentrations (wt %) of $CaCl_2$ and 75 °C (from Prutton and Savage[121]), (B) at various concentrations (wt %) of $CaCl_2$ and 75 °C (calculated using the Geochemist's Workbench Simulation Program, GWB), (C) in pure water at various temperatures (from Wiebe and Gaddy[77,78]), and (D) in pure water at various temperatures (calculated using Ph-Redox Equilibrium Equation Program in C Language, PHREEQC).

of coalbed gas can vary from zero to >99%.[46,50,60−70] The observation that some coalbed gas can be high in CO_2 content is a particularly pertinent observation, relative to the use of coalbeds as a sequestration sink for CO_2. It clearly shows that, at least in some instances, CO_2 can safely remain in coal for geologically significant time periods. The observation also provides reason to believe that coal can be safely and effectively utilized to both store CO_2 and recover CH_4. Clayton describes the various origins of CO_2 in coal.[71] Smith et al. have used stable isotope ^{13}C measurements to show that CO_2 present in the Australian coals they studied was derived from mantle sources during igneous intrusions near the coal seam.[72]

Levine has estimated the amounts of CO_2 generated from fossil plant debris through various stages of coalification.[73] Most coals contain much less CO_2 than the theoretical amount generated during coalification. This observation implies that even though CO_2 is strongly sorbed to the coal matrix, it can nevertheless be transported away from the coal. Scott suggests that CO_2 is dissolved in water and subsequently transported away from the coal.[74] Some coal formation waters are characterized by high salinity, which can significantly impact the solubility of CO_2. Figure 3a shows the solubility of CO_2 in water, as a function of pressure, at several different salinity levels for the simplified case of $CaCl_2$ at 348 K (75 °C). These experimental measure-

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(72) Smith, J. W.; Botz, R. W.; Gould, K. W.; Hart, G.; Hunt, J. W.; Rigby, D. Outburst and Gas Drainage Investigations: Energy Research Development and Demonstration Program, Australia; Report No. EG/84/321, 1984.

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(74) Scott, A. R. Composition and Origin of Coalbed Gases from Selected Basins in the United States. In *Proceedings of the International Coalbed Methane Symposium*, Tuscaloosa, AL, May 17−21, 1993; pp 207−222.

ments show the same trend as the results of simulations performed with the Geochemist's Workbench (GWB)[75] for the same conditions as those shown in Figure 3b. CO_2 solubility decreases by a factor of 3−4 when the concentration of $CaCl_2$ increased from zero to 30%. Fugacities given using the PH−REdox Equilibrium equation program in C language (PHREEQC) and GWB were converted to pressures, according to Duan et al.[76]

The dissolution of CO_2 in coal formation waters is important, because it can lead to increased acidity of the water. The issue has been tackled through theoretical modeling as well as experimential techniques covering a great range of temperatures and pressures. Temperature and pressure ranges relevant to brine sequestration were covered by Wiebe and Gaddy and are summarized in Figure 3c for the case of solubility in pure water.[77,78] The solubility increases as the pressure increases. These show deviation from Henry's Law, particularly at high pressures and low temperatures. Figure 3d shows the results of modeling the same relation using PHREEQC.[79] The trends observed here are the same, with a slight shift in the magnitude toward higher solubility. An evaluation of the solubility of CO_2 in water and brine can be found in the publications of Enick and Klara.[80,81]

There are conflicting data. The observation that CO_2 is a major component of some coalbed gases indicates that CO_2 can be stored for long time periods within a coalbed and remains in coalbeds for geologically significant time periods. Scott has suggested that CO_2 can be transported away from the coalbed by becoming dissolved in water.[74] These observations have obvious implications for the long-term sequestration potential of CO_2 in coal. An open question relative to CO_2-ECBM/sequestration is "how long does CO_2 injected into a coal seam remain in the seam?" Will it remain for geologically significant time periods or will it be dissolved in formation water that re-invades the seam after CH_4 recovery and CO_2 sequestration are complete?

II. Coal and Coal Seam Properties: Evaluation, Relative to Carbon Dioxide Sequestration

Many coal properties are important for, or may be changed during, the adsorption and desorption of gases. The fact that coal is a mixture of inorganic minerals and organic material in a complex, three-dimensional network, that may change during the adsorption or desorption process, can complicate matters considerably. The ability to transport the CO_2 through the coal seam is dependent on both the permeability of the seam itself (Darcian flow) and the intrinsic permeability of the coal matrix (Fickian diffusion). Other coal properties such as rank, maceral content, and moisture content affect the capacity and rate of CO_2 up-take and CH_4 desorption. The CO_2 retention capacity of a coal is related not only to the properties of the coal itself, but also to the in situ pressure and temperature.[45,82,83] This relationship is usually expressed as the adsorption isotherm. These properties are considered individually below.

Density Measurements. Even a seemingly simple, basic property such as density can be elusive when applied to coal. The measured density is dependent not only on the goal of the measurement (bulk versus intrinsic), but often the way the measurement is conducted (in helium, N_2, CO_2, or other gas). A valid measure of the coal density is particularly important in volumetric (or manometric) isotherm measurements, because the void volume of the cell, which is needed for the calculation of the gas-phase moles, is calculated based on the coal density, usually as measured in helium. The coal surface area is important because it provides the sites for the adsorption of CO_2. The "true" surface area of coal, and how to best measure it, has been the subject of a long-running debate.[84]

Three different types of densities have been reported for coals: true density, particle density, and apparent density. These densities are usually reported on a dry-mineral-matter-free (dmmf) basis. In other words, the original density measurement is corrected for mineral matter and moisture content assuming an average mineral density.[85] Coals contain different amounts and types of mineral impurities that have relatively high density. The density of coal mineral matter as ash is typically determined experimentally.[86] Alternatively, an average ash density of 2.7 g/cm^3 can be used as a rough estimate.

True Density. True density is the weight of a unit volume of the pore-free solid coal. The ideal probe molecule for coal density measurements should not adsorb or absorb to the coal and should be able to access all of the pore volume. Note that no fluid fills the coals pores completely. As such, this phenomenon should be considered when interpreting true density measurements.

True densities of coal are typically measured by helium displacement. The experimental methods for measuring densities with helium have been described in detail.[85] Although helium is the smallest atom available and should have the greatest access to all the pore volume in coal samples, X-ray studies and other techniques have determined that a significant coal pore volume is closed to helium.[87] It has been estimated that helium can access pores with a diameter of >4.2 Å at room temperature.[88] In addition, the smaller the particle size of the coal, the more the closed pore volume is opened and made accessible to helium, resulting in an increase in the measured helium density.[89] Helium

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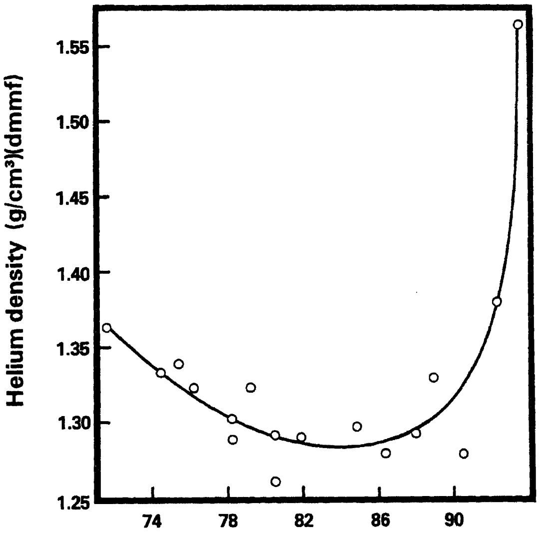

Figure 4. Variation of helium density of coals, relative to carbon content. (From Mahajan and Meyers.[96])

adsorbs on coals at room temperature. However, this amount of helium adsorption is small and does not cause significant errors in the measured densities.[85]

The helium density has been related to the chemical composition of coal. Density, when expressed on a dmmf basis, correlates to the rank and the carbon content of coal.[90−94] Generally, density decreases as carbon content increases from 69% to 80%. A shallow-depth minimum is reached near a carbon content of 84%, and then the density increases sharply at a carbon content of 90% (Figure 4).[95,96] For instance, the density minimum near a carbon content of 84% has been attributed to a change in the average number of aromatic and hydroaromatic rings in coal per C atom.[97] Neavel et al. related density and composition of coal by the following equation:[98]

$$\text{density}_{\text{HighRank}} = 0.023\text{C} + 0.0292\text{O} - 0.0261\text{H} + 0.0225\text{S} - 0.765 \quad (1)$$

Parkash suggested that Neavel's equation holds true only for high-rank coals and suggested a second equation for use with low-rank coals:[92]

$$\text{density}_{\text{LowRank}} = 3.5742 - (0.0197\text{C} + 0.0192\text{O}) - 0.0691\text{H} \quad (2)$$

where the elements are expressed as a weight percentage, on a dmmf basis. Density can also be expressed as the specific volume, otherwise known as the inverse of the density. Specific volume shows a linear dependence on the hydrogen content of the coal.[92,94]

Particle Density. Particle density is the weight of a unit volume of the solid, including pores and cracks. Particle density is usually determined by displacement of mercury. The experimental methods for measuring densities with mercury have been described in detail.[85] The entry pressure required to force mercury into a cylindrical pore is determined by the Washburn equation:[85,99]

$$P = -\left(\frac{2\gamma \cos \theta}{r}\right) \quad (3)$$

where P is the maximum pressure of mercury, r the cylindrical pore radius, γ the surface tension of mercury, and θ the contact angle between the mercury and the pore wall. To obtain a meaningful particle density of coal, it is essential to determine the minimum pressure that must be applied to the mercury to fill the interparticle void volume. Cody and Davis showed that the mercury method opened cracks that are not present in the coal but are fractures formed during sample analysis.[100]

Apparent Density. Apparent density is determined using the pycnometric method. Procedures for measuring the apparent density have been described elsewhere.[90] Most often, organic solvents are used to determine apparent density of coal. It has been reported that apparent densities usually exceed helium densities, because of the imbibition of solvents. Apparent density is dependent on particle size, range of pore diameters in the solid, molecular dimensions of the fluid, its degree of interaction with the solid (swelling and surface effects), and time allowed for penetration of the fluid.[85]

The density of coal is not unique but is dependent on the fluid used to measure it. Huang et al. compared apparent hydrogen density measurements with true helium density measurements.[95] Hydrogen, which is the smallest linear molecule, should be able to access the entire pore volume of coal. However, the hydrogen density of coal was determined to be larger than helium densities because hydrogen adsorbs and absorbs on the coal during the density measurement.[91] Toda[90] also compared density measurements of coal and found methanol apparent densities to be higher than helium true densities. Toda proposed that helium is denied access to closed pores, whereas methanol can penetrate into closed pores by imbibition. He also found that the methanol molecule has access to the same porosity as the CO_2 molecule, provided that the coal sample does not contain hydroxyl groups. The volume of micropores accessible to methanol but inaccessible to CO_2 was considered to be directly proportional to the hydroxyl group content of coal. Overall, Toda concluded that the ease of accessibility of molecules to micropores of coals decreased in the following order: methanol (CH_3OH), CO_2, and helium.[90]

Walker et al. also determined the apparent density of coals with methanol and water (with a wetting agent,

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(100) Cody, G. D.; Davis, A. *Energy Fuels* **1991**, *5*, 776−781.

Triton X-100).[93] They concluded that methanol and water could penetrate pores that are closed to helium and imbibe into the coal structure. This imbibing into the coal structure results in the swelling of coal macerals. The extent of swelling is rank-dependent and ranged from 1% to 30% for both methanol and water.

Surface Area Measurements. The concepts and measurements used to determine surface areas, and especially coal surface areas, are important for understanding the nature of the coal–CO_2 interaction. However, understanding the results of surface area determinations under conditions where the adsorbate changes the structure of the adsorbent has proved difficult. It has even been stated that surface areas of coals are meaningless and, therefore, should not be reported.[84] Marsh, however, has suggested that surface area is a function of how it is measured and how the adsorption data are interpreted.[101] He suggests that surface area should be expressed as an equivalent surface area, which he defines as a variable parameter that is dependent on the measurement technique—not an absolute value. Coal surfaces are fractals and, as such, the surface area varies with the size of the adsorbed molecule used to measure it. Larsen et al. showed that coal pores are isolated and can only be reached through the solid matrix.[102]

Coal surface area was originally measured by the adsorption of N_2 at −196 °C. Experimental methods have been described elsewhere.[85] The Brunauer–Emmett–Teller (BET) equation was generally used to determine the surface area. However, N_2 surface areas of coals (varying in the range of 1–9 m^2/g) were lower than expected. At −196 °C, micropores in coals are not completely accessible to N_2 molecules due to activated diffusion.[103,104] It was concluded that the surface area, as measured with N_2, is a measure of the macroporosity of coals.

Because of the activated diffusion or temperature effects with measuring N_2 surface area, it was realized that the surface areas of coals should be measured by the adsorption of gases at the highest possible temperature. Several different gases have been used as coal surface area determination agents. After 1965, adsorption of CO_2 at 25 °C was generally accepted as the standard method for measuring the surface area of coals.[84] It was believed that CO_2 at 25 °C was capable of filling the entire pore volume of coals.[105] Therefore, the total surface area of coals could be measured with CO_2.[106]

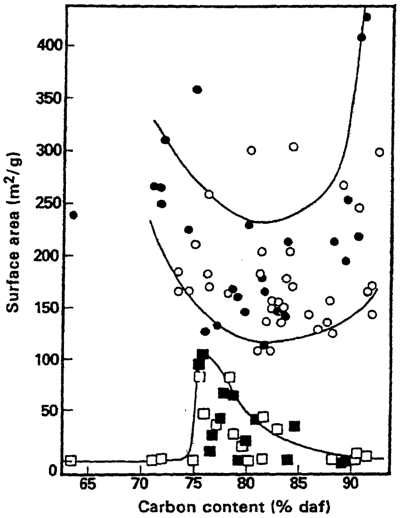

Figure 5. Variation of CO_2 and N_2 surface areas of coals, relative to carbon content (○, ●,) CO_2; (□, ■,) N_2. (From Mahajan.[173])

Mahajan reviewed the literature on CO_2 surface area measurements of coals; he explained the intricacies associated with CO_2 surface area measurement of coals and discussed the validity of surface area measurements of coals.[84] Mahajan concluded that the CO_2 surface areas of coals vary within a range of 110–425 m^2/g and that no correlation for CO_2 surface area of coals versus carbon content is evident (Figure 5). The CO_2 surface area of coals of the same carbon content can vary by as much as 275 m^2/g. It is believed that CO_2 gives higher surface area values, compared to other adsorbates, because, through imbibition, CO_2 is available to both open and closed porosity.[84] Radovic et al. recently observed activated diffusion of CO_2 in coals in the temperature range of 273–298 K (0–25 °C). Thus, these results should be considered when interpreting CO_2 surface area measurements. Marsh commented on microporosity in his review article[101] and defined ultramicroporosity as the micropore diameters in coal equal to or less than the diameter of the adsorbate molecule. The rates of adsorption in ultramicropores are temperature dependent with measurable activation energies. He postulates that the differences in adsorption of N_2 and CO_2 in coals are due to activated diffusion, not swelling.

It is well-known that CO_2 adsorption swells coal.[90,93,94,107] The total uptake of CO_2 on coal includes contributions from physical adsorption on pore walls, pore fillings, and swelling. Surface area measurements of coal conducted at 25 °C and at pressures of <1 atm are largely unaffected by swelling.[93] However, surface area measurements are likely to be affected at higher CO_2 pressures, because coals expand between 1.6% and 3.8% near 50 atm.[93] In addition to swelling at high CO_2 pressures, the organic matter in the coal matrix may be extracted by CO_2 (see the sections entitled "ES&H Aspects of Produced Water" and "Effect of CO_2 Adsorption on Organic Matter", presented later in this review). Extractions result in higher surface area and pore volume measurements.[84]

Reucroft and Patel investigated the surface area and swellability of coal using various solvents.[108] As is often seen, the surface area behavior and measurements were dependent on the probing solvent used. Water vapor exhibited typical Brunauer Type-II isotherms, indicating the existence of both micropores and mesopores. CO_2 surface areas were greater than N_2 surface areas. Because CO_2 has a solubility parameter close to that of

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the coal itself, it could induce swelling within the coal. They concluded that the use of CO_2 as a surface area sorbate actively influences the final outcome of the measurement, because of these swelling effects.

Coal surface areas have also been determined by water sorption.[93] The BET equation is used to calculate specific surface areas. Unlike CO_2, water sorbs only on hydrophilic surface sites. In the case of coal, these sites are hydroxyl and carboxyl groups. Water coverage on coal is typically less than CO_2 coverage. The fractional coverage by water is dependent on coal maceral composition and can range from 0.04 to 0.73. Small-angle X-ray scattering (SAXS) is another technique used to determine surface area of coals. An advantage of this technique is that SAXS can determine the pore size distribution and surface area of both open and closed pores in coals. SAXS surface areas generally are larger than CO_2 adsorption surface areas.[109]

Porosity Measurements. Coals are highly porous materials. Pores in coal vary in size from micrometer to angstrom dimensions. A significant proportion of their total open pore volume is located in small pores (<20 Å).[110] Coal pores are classified into four groups: macropores (>500 Å), mesopores (20–500 Å), micropores (8–20 Å), and submicropores (<8 Å).[111] Quantifying porosity in coals is essential to understanding how gases such as methane and CO_2 are stored in the coal seam. Coal porosity is quantified by determining the pore volume, surface area, and pore size distribution. Several techniques have been applied to the determination of coal porosity: gas and liquid adsorption, transmission electron microscopy (TEM), Xe NMR, and SAXS.[112–116] However, gas and liquid adsorption are the most common techniques used to measure coal porosity.

Coal porosity can be determined by gas and liquid adsorption methods, including density and surface area measurements.[85] The total open pore volume (V_p) of coal is calculated from density measurements by the following equation:

$$V_p = \frac{1}{\rho_{Hg}} - \frac{1}{\rho_{He}} \tag{4}$$

where ρ_{Hg} and ρ_{He} are the mercury and helium densities (dmmf), respectively. Porosity (φ), which is defined as the percentage of particle volume of coal accessible to helium, is calculated from the relationship

$$\phi = 100\rho_{Hg}\left(\frac{1}{\rho_{Hg}} - \frac{1}{\rho_{He}}\right) \tag{5}$$

The open pore volume of coals can also be extracted from CO_2 gas adsorption measurements on coal at 25 °C. The porosity is then calculated with the Polanyi–Dubinin (P–D), Dubinin–Radushkevich (D–R), or Dubinin-Astakhov (D–A) equations.[89,101]

Some workers have determined pore size distributions via mercury porosimetry, using the Washburn equation as previously defined.[85,99] Because of the high compressibility of coal, a maximum pressure of 69 MPa (680.97 atm) is generally used.[117] The mercury porosimetry method should be used with caution, because of the formation of fractures during the measurement process.[100] Pore size distributions are also determined by N_2 adsorption on coals at 77 K (−196 °C).[86] There is some uncertainty regarding the use of the adsorption or desorption branch of the N_2 adsorption isotherm for calculating pore size distribution. Cranston and Inkley addressed this uncertainty and found little variation in the pore size distribution between the adsorption and desorption branches of the N_2 isotherm for a wide variety of solids.[118]

Gan et al. studied the nature of coal porosity using techniques such as gas adsorption, helium and mercury displacement, and mercury porosimetry.[86] They determined total pore volume from helium and mercury densities, pore surface areas from adsorption of N_2 at 77 K (−196 °C) and CO_2 at 298 K (25 °C), macropore size distribution from mercury porosimetry, and pore size distribution from N_2 isotherms at 77 K (−196 °C). From these measurements, Gan et al. classified pore volume accordingly:

(1) total open pore volume for pores accessible to helium ($V_P = V_1 + V_2 + V_3$), as estimated from helium and mercury densities;

(2) pore volume for pore diameters of >300 Å (V_1), as estimated from mercury porosimetry;

(3) pore volume for pore diameters between 300 and 12 Å (V_2), as estimated from N_2 adsorption; and

(4) pore volume for pore diameters of <12 Å (V_3), where $V_3 = V_P - (V_1 + V_2)$.

Gan et al. found that all coals exhibit molecular sieve properties.[86] Using Gan's classification, Parkash and Chakrabartty found that 70% of the total pore volume consists of pores with diameters of <120 Å from the 11 sub-bituminous coal samples they studied.[117] They concluded that almost all the surface area in coals is located in the micropores.

The porosity of coals can also be measured by TEM. Harris and Yust studied high-volatile bituminous coal samples consisting almost exclusively of exinite and inertinite using TEM.[119] They observed two types of porosity in the samples that they studied. The first type consists of mesopores and macropores in the exinite portion of the coal sample; the second type consists of mesopores in the inertinite portion of the coal.

Xe NMR spectroscopy has also been used to characterize porosity in coal. Wernett and co-workers determined the micropore diameter of Illinois No. 6 coal samples by Xe NMR.[102,115] They found an average micropore diameter of 5.2 Å.[120] Using Xe NMR of the Argonne Premium Coals, Tsiao and Botto also estimated

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the average size of coal pores that had diameters of <20 Å.[116] They found two pore structures of similar size (ca. 6.0 Å diameter) that had different chemical compositions. These were tentatively assigned to aromatic and aliphatic regions of the coal.

SAXS[120] and SANS with contrast matching[122] have been used to characterize porosity. It is believed that both techniques provide a complete description of porosity, because they are sensitive to both closed and open pores.

Much effort has been put forth in understanding coal porosity. Bond first proposed that coal is porous with slitlike pores interconnected by narrow capillary constrictions.[123] Although Bond's proposal is the dominant theory of coal porosity, Larsen and Wernett recently challenged this viewpoint, stating that, although coals are porous materials, the pores are not open to the external surface.[124] According to Larsen's theory, molecules can reach the pores only by diffusion through the solid coal, not through an interconnected pore network.[124] Hall et al. also provides support for Larsen's conclusion in their porosity study of high-rank coals (Pocahontas and Upper Freeport) with SANS.[122] They concluded that these coals do not contain microporosity in their structure and do not have a connected pore network. Interestingly, these coals produce gas, although these authors claim they do not contain microporosity. In contrast to Larsen's view, Walker and Mahajan provide evidence of an interconnected micropore network in coals and discuss examples that would be difficult to explain if coal pores were not open to the external surface.[84,125,126] As these studies have proven, coal is a complex material with a complex porous structure that is difficult to classify. Regardless of the mechanism by which gases are transported through the organic matrix of the coal, the microporosity of coal is the dominant factor in the gas adsorption process.[127]

Diffusion, Permeability, and Transport. The terminology of CBM production, which is largely used to describe CO_2 sequestration, uses the term "permeability" in two different but related senses. In one sense, the term is used to describe the migration of gas through the organic matrix of the coal. By analogy, this would be similar to diffusion of a gas in porous polymers. In this case, the permeability might be more descriptively termed an intrinsic permeability that is dependent on the nature of the organic matter itself. In the second sense, permeability is used to describe the transport of gases through the coal seam via the network of fractures (natural or induced). In this case, it might be more descriptively termed coalbed or seam permeability. Both processes are important for the overall production or storage of gas but the rate laws that govern the two processes are different.

The transport mechanism by which gases are transferred to or conducted from the wellbore is composed of two basic steps. In the case of CBM production, the methane must diffuse from an adsorption site to the cleats and then be transported through the fracture system to the wellbore. The process is reversed for the case of CO_2 sequestration. When the rate of gas desorption (via diffusion) from the matrix is higher than the flow rate in the face cleats, then gas production is both flow limited and pressure-driven. Thus, it can be modeled with Darcy's Law, which describes gas flow through a complex (though homogeneous) permeable solid. However, if the diffusion rate is slower than the flow rate in the cleats, gas production is diffusion-limited and driven strictly by concentration and is usually modeled as Fickian, although Knudsen flow has also been used (see the subsection entitled "Diffusion", presented later in this review). Cervik was the first to report that CH_4 flow through coalbeds was a combination of Darcian and Fickian transport.[128,129]

Cleats. Most gases and water move through the coal seam via the cleat system.[94,130,131] The cleat system in a coal seam is composed of closely spaced fractures that formed during coalification. These fractures are commonly referred to as face and butt cleats. Face cleats are more prominent than butt cleats. The spacing of the face cleats can range from one tenth of an inch to several inches. Face cleats are relatively planar and continuous analogous to systematic joints.[132] Butt cleats, on the other hand, are usually perpendicular to the face cleat. However, these cleats have a tendency to be discontinuous and nonplanar cross joints. Butt cleats commonly terminate against face cleats. The permeabilities of typical coalbeds range from 0.1 to 100 mD; most commonly, the permeability ranges between 1 and 10 mD.

Much of this "seam" permeability is due to the cleat system, although the presence of larger scale discontinuities such as fractures, joints, and faults can also make a significant contribution. Factors affecting cleat gas transport of desorbed gas are the total number and apertures of the cleats and their connectivity. The removal of moisture has a tendency to shrink a coal's structure, causing cracking and fracturing, especially in low-rank coals, thus enhancing the cleat system.[46] Coalbed seam permeability is greatly influenced by cleat spacing and effective stress.[133] Cleat spacing is related to rank, petrographic composition, mineral matter content, bed thickness, and tectonic history.[134]

Diffusion. The diffusion step is usually considered to be Fickian in nature. Coalbed gases are thought to penetrate through apertures as small as 4−5 Å.[135] Methane diffuses readily, compared to higher hydro-

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carbons, which diffuse more slowly, demonstrating a size dependency and possibly molecular sieving activity. Diffusion also seems to be an activated process in which a molecule must overcome a minimum activation energy to diffuse through the pore aperture. Thus, migration occurs more readily at higher temperature.

Nandi and Walker studied the diffusion of N_2 and CO_2 in coal.[105] They found that the activation energy for the diffusion of N_2 was higher than for CO_2. It was stated that the minimum dimension for the pores is ~4 Å. Also, it was found that diffusion into and out of the coal is controlled by the same mechanism, demonstrating a fundamental physical interaction between coal and gas. The energies of activation for diffusion were less for anthracite than for bituminous coal. This suggests that bituminous coal may have a smaller pore size or there is less physical interaction in the anthracite.[105]

Thimons and Kissell attempted to study CH_4 diffusion through coal, citing previous studies where Knudsen diffusion was observed.[136] Knudsen diffusion occurs in capillaries when the diameter of the pore being traversed is less than the mean free path of the CH_4 molecule (~500 Å). Knudsen flow occurs only in gas phases through porous media, and in some cases, surface flow may add to any Knudsen flow present. Molecular sieve effects were observed in all of the coals studied, especially in Pittsburgh coal, and saturation of the coal with water decreased the permeability.[136]

Dual Porosity. Coal seams are characterized by dual porosity: they contain both a micropore or a primary porosity, and a macropore, or a secondary, fracture porosity system.[137] Warren and Root[138] introduced the dual porosity concept when they studied naturally fractured reservoirs. The primary porosity was defined as intergranular and controlled by deposition and lithification.

The secondary porosity was considered foramenular, controlled by fractures, fissures, and jointing. They represented the reservoir as a set of building blocks (parallelepiped), where the blocks represented the matrix, and the spacing between fractures. It was assumed that the flow in the fractures was unsteady state, whereas flow in the matrix was quasi-steady-state.[139,140]

The micropore system in the coal has the same role as the matrix porosity in the conventional dual-porosity reservoir. The micropores have a large storage capacity but contribute little to the long-distance transport of reservoir fluids. The macropore system of a coal seam represents the volume occupied by the natural fracture system (cleats). The primary porosity in coal seams and in conventional reservoirs have similar roles. However, there are differences: due to the size of micropores in coals, the gas exists in the adsorbed state, whereas in conventional dual porosity reservoirs, gas is in the free state. Consequently, the gases stored in these two media obey different laws.[141]

Permeability. Puri and Seidle recently reviewed coal permeability measurements made prior to the 1990s.[142] Puri and Seidle measured the permeability of coal under coal seam conditions, relative to CBM production.[142] They found that, as the reservoir pressure was depleted during well startup, permeability decreased by a factor of 5. After this initial pressure reduction, permeability then remained constant over the life of the well for CBM production. To avoid the initial reduction in permeability during well startup, they suggested using ECBM recovery techniques based on CO_2 and N_2 injection. In this technique, reservoir pressure depletion is usually not required. As such, the reservoir pressure is maintained and permeability does not decrease. They developed the following conclusions from these studies:

(1) permeability measurements have a tendency to be highly sensitive to hydrostatic confining pressure;

(2) increasing the confining pressure can cause the permeability to decrease by as much as 3 orders of magnitude;

(3) permeability usually declines exponentially with increasing stress; and

(4) repeated coal permeability measurements as a function of stress showed permeability to be dependent on the stress history and to decrease with repeated tests.

Puri and Seidle noted that these permeability measurements may not be related to in situ conditions found in coal seams, because of the variety of experimental conditions chosen for the aforementioned studies.

Kuuskraa believes that the measured decrease in permeability observed by Puri and Seidle[142] is either a unique situation for a highly stress-sensitive coal or a laboratory-based artifact.[143] Permeability reductions due to pressure reduction (e.g., compressibility) are much less. Kuuskraa has observed that the increases in coal permeability due to desorption counteracts the loss in coal permeability due to compressibility.

Harpalani and Zhao investigated coal permeability in relation to CH_4 gas desorption from coal seams.[144] Their results suggest that, upon reduction of gas pressure without desorption of CH_4, the permeability of coal decreases. After the pressure falls beyond the point where adsorbed methane desorbs, however, the permeability of coal to methane increased dramatically (Figure 6). According to their research, the increase in permeability of coal below the desorption pressure is due to shrinkage of the coal matrix. The blocks of coal between the fractures shrank inward due to desorption of methane, thus enlarging the fracture width and resulting in higher permeability (Figure 7).[145] These results suggest that the permeability of CBM reservoirs might increase significantly over the production life of the well. Harpalani and Chen also investigated the volumetric change of the coal matrix upon desorption of CH_4 and its relationship to cleat porosity and permeability.[131] They

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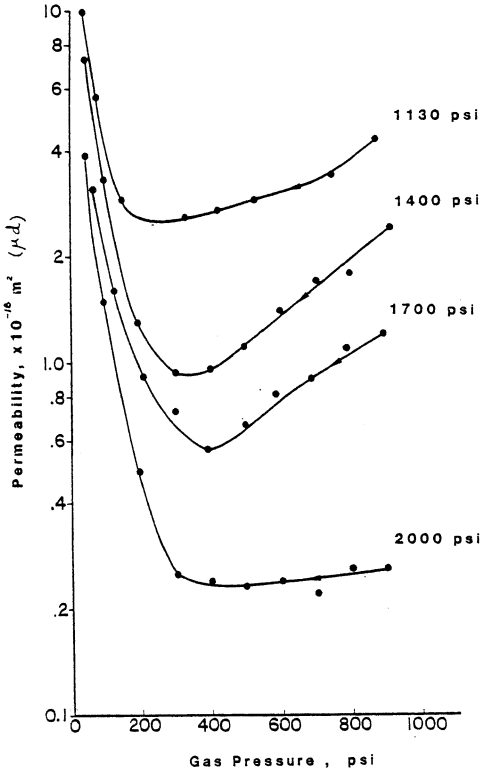

Figure 6. Variation in permeability of coal with decreasing gas pressure at four different hydrostatic stress levels. (From Harpalani and Zhao.[144])

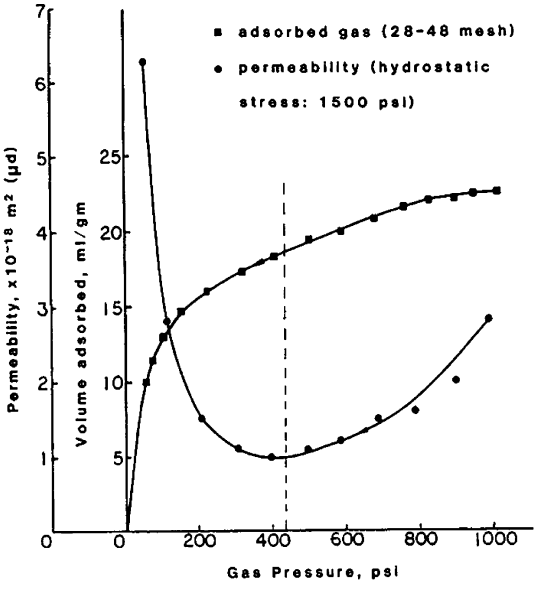

Figure 7. Variation in absorbed gas volume and permeability of coal to CH_4, relative to increasing gas pressure. Sample from the Piceance basin. (From Harpalani and Schraufnagel.[145])

found that the coal matrix volume decreased as CH_4 pressure decreased. As a result, the cleat porosity increases by 80% and the permeability increases by 60%.

Recently, Massarotto et al. began investigating the nature of coal permeability with respect to CO_2 sequestration.[146] In their preliminary studies, they examined the in situ coal permeability during CO_2 injection. Over the next few years, they hope to characterize the competitive adsorption and desorption process for CO_2 and CH_4, resolve the opposing forces of net stress and matrix shrinkage on permeability, and determine the permeability of CH_4 and CO_2 in coal under in situ conditions.

Transport. A two-stage process characterizes the transport of gas through a coal seam. With the onset of pressure reduction due to water removal, gas is desorbed through micropore walls and migrates through a system of interconnected micropores in the coal matrix until it reaches the cleat system. Once in the cleat system, the gas moves along with brine toward production wells.[147] The coal matrix can be referred to as a primary porosity system where the permeability to gas is negligible and the diffusion is the dominant form of transport. Three diffusion flow mechanisms may act individually or simultaneously in this pore system: (i) bulk flow, with dominant molecule-molecule interaction, (ii) Knudsen flow, with dominant molecule-surface interaction and (iii) two-dimensional surface diffusion of the adsorbed gas layer.[148] Nevertheless, the matrix gas flow obeys Ficks's law of diffusion, regardless of the dominant flow mechanism.

The secondary porosity system in a coal seam has unique features. There are two distinct fracture networks—the face and the butt cleats—and they act as both a sink for the solid matrix and a conduit to the production well.[149] The flow of gas in the cleat system is generally a laminar process and is governed by Darcy's law.

Both transport models occur in any individual coal seam. However, depending on the coal rank, depth, and fracture density, gas production may be influenced more or less by the diffusion process or by the laminar flow process.[150]

Gentzis[151] proposed a conceptual model for CBM production. In this model, diffusion controls the transport processes in the earliest stages as the pressure in the areas closest to the wellbore decrease. Because, in this case, most of the gas being produced is in close proximity to the wellbore, the rate of diffusion of the gas through the organic matrix is slow, compared to the rate at which it can be transported though the short distance to the wellbore. As the drawdown radius increases, the rate at which the gas can be transported through the increasingly large distances becomes more and more important and the rate of gas flow will move from a diffusion-controlled process to one controlled by Darcy flow.

Gas production from a deep coal seam requires an initial pressure reduction within the seam.[46] Typically, this is accomplished via the removal of water trapped

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in the cleat system. As the seam pressure is decreased via water removal, the gas confining pressure in the pores is decreased from the original reservoir pressure until a critical pressure is reached where the seam's CH_4 loading corresponds to the saturation pressure which causes a reduction in the pore pressure. After the pore pressure is reduced, the gas may flow from the matrix surface into the cleat system. From there, it travels readily to the wellbore.

Rank, Macerals, and Mineral Matter. *Rank.* Coals are often classified according to their rank, or thermal maturity. The three main classifications of coal rank from low-rank to high-rank are lignite, bituminous, and anthracite. Carbon content is often used as a measure of rank. As the carbon content of the coal increases, rank increases. Studies have shown that permeability and porosity are related to rank. Typically, high-rank coals have low permeability. Although it is not fully understood what role coal rank has in gas sorption, different coal ranks have different adsorption capacities. Coal rank affects and influences the properties of the coalbed reservoirs. For most commercial CBM projects, coals of middle rank provide optimum gas content and permeability. Porosity generally has a tendency to decrease as coal rank increases. King and Wilkins found that the total porosity of the coal structure decreases from 20% at a carbon content of 82% to 3% at a carbon content of 89%.[152] Conversely, Senel et al. characterized 12 Turkish coals with carbon contents varying from 61% to 84% and found no trend between porosity and coal rank.[109] Menon, Kyotani, and co-workers also found no consistent trends between porosity and coal rank.[153]

Gan et al. characterized coals ranging from lignite to anthracite and related porosity to coal rank. They found that, in lower-rank coals (carbon content of <75%), porosity is primarily due to macropores. In medium-rank coals (carbon content of 76%−84%), porosity is due to micropores and mesopores. For high-rank coals (carbon content of >84%), microporosity dominates.[86] Hall et al. studied the porosity of high-, middle-, and low-rank coals with contrast-matching small-angle neutron scattering (CM-SANS). They observed that the porosity decreased as rank increased. In addition, they determined that coal porosity was preserved by the presence of water.[122]

Sorbate accessibility to the coal matrix decreases as rank increases. Also, gas sorption in coal involves competition for sites available for sorption; low-rank coals have a greater affinity for sorption of water than for methane.[135] Rank is also an important factor in matrix diffusion of CO_2. Coals that are near full bituminization require higher activation energies than do anthracites for desorption of sorbates to occur.

Associative equilibria, which have been used to explain differences in coal swelling in the presence of different solvents, are also highly rank-dependent.[154] Differences in extraction yields suggest that molecular interactions leading to strong associative bonding in coal are a function of coal rank.

A decrease in CH_4 capacity as the moisture content in the coal increased has been reported for the Bowen basin coals of Eastern Australia. Lower-rank moist coals showed a lower methane adsorption capacity. As the carbon content of coals increased, the CH_4 retention capacities increased linearly.[24]

Macerals. Coal is composed of macerals (which constitute the organic portion) and minerals (which are the inorganic portion). The maceral portion is further subdivided into three main petrographic groups: inertinite, liptinite, and vitrinite. The inertinite, liptinite, and vitrinite composition and ratios to each other may be different in coals of the same rank. Coals are characterized by rank and type, and maceral composition is a type parameter. There are hundreds of maceral names found in the literature. Almost all maceral names are subclasses of the inertinite, liptinite, and vitrinite groups. Because most coals contain 50%−80% vitrinite, the gross properties of coal reflect the properties of vitrinite.[94]

Vitrinite-rich coals are generally open and unmineralized, thereby favoring high permeability. Variations in adsorption capacity are related to porosity in that vitrinite-rich coals are more highly microporous than inertinite-rich coals.[26] Bustin and Clarkson also found similar relationships between maceral composition and porosity.[127,155] They found that the micropore capacities generally increase with total vitrinite content and decrease with increasing inertinite content. The increase in micropore capacity with vitrinite content is due to an increase in the number of micropores.[127,155] Crosdale[26] and Lamberson[156] have shown that CH_4 and CO_2 gas adsorption capacity is generally higher for vitrinite-rich coals than for inertinite-rich coals. Harris and Yust studied bituminous coal samples with TEM and related the petrographic composition to pore size and porosity.[119] They found the vitrinite portion to be mainly composed of micropores and mesopores, the inertinite portion to be composed of mesopores, and the liptinite portion to be composed of macropores. Their research further concluded that the inertinite portion was the most porous maceral group, whereas the liptinite portion was the least porous.

It was generally accepted that the ability of coals to store gas is a function of their rank and that storage capacity increases as the coal rank increases. These relationships are not in concert with all the observed facts.[157,158] The relationship between CH_4 capacity of coal and carbon content for a group of dry coals is shown in Figure 8.[51,159] Bustin and Clarkson investigated the CH_4 storage capacity of a wide variety of coals from Canada, Australia, and the United States and concluded that there was "no or little correlation between coal rank and methane adsorption capacity (as commonly assumed), although in particular basins there are general trends with rank and composition."[25]

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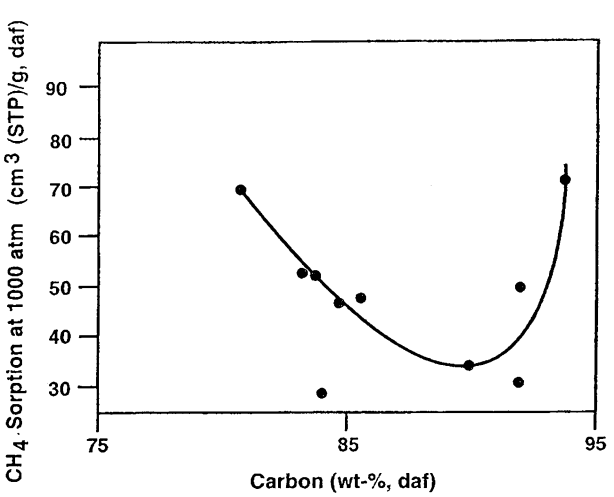

Figure 8. Changes in methane accessibility in dry coal, as a function of coal rank. (Data from Levine.[159] Adapted from Moffat and Weale.[51])

The petrographic composition of coal can have an effect upon its capacity to adsorb gases. Laboratory studies of the sorption capacity of vitrinite have shown that it has the highest capacity of the three major maceral groups for CO_2. Thomas and Damberger demonstrated that vitrain bands within coals over a wide range of ranks had CO_2 accessible surface areas that averaged 60 m^2/g larger than whole coals of the same rank.[160] Similar measurements obtained on a single sample of fusain showed the CO_2 surface area to be only 35 m^2/g, whereas vitrain bands of coal of the same rank had a CO_2 surface area of 220 m^2/g. These CO_2 surface areas are thought to correspond approximately to the ability of coal to imbibe CO_2. Bustin and Clarkson showed that "for suites of isorank coals there are poor (Permian Bulli and Wongawilli seams, Australia) to good (Gates Formation coal seams, Lower Cretaceous, Canada) positive correlations between vitrinite content and methane adsorption capacity."[25] Furthermore, they observed that the rate of CH_4 desorption among these above-mentioned coals is correlative to total gas content ($r = 0.79$); however, there was no correlation with rank or any compositional parameter.

Vitrinite-rich coals also have a tendency to desorb gas more slowly, possibly due to their porous microstructure.[26] However, maceral composition, in and of itself, is not the critical factor governing sorption processes. Rather, it is the influence that rank and maceral composition have upon the coal pore structure that controls the gas sorption. The adsorption capacity is related to the micropore development.[26]

Mineral Matter. Mineral matter seems to have little effect on the CH_4 sorption capacity of coal. It serves as an inert diluent. Plots of mineral matter content as a function of CH_4 gas yield extrapolate to zero at 100% mineral matter.[161] Mineral matter has little capacity to sorb CH_4 onto its surface. The presence of mineral matter in coal takes up space that would otherwise be filled with organic matter, thus reducing the surface area and sorption capacity.[46] The methane gas content of coals with low amounts of mineral matter is higher than similar coals with more mineral matter.[26] In stark contrast to the CH_4 results, Karacan and co-workers, using X-ray tomography, showed that clays and inertinites are the main storage reservoirs for CO_2 in Pittsburgh seam coal.[162,163]

Karacan and Mitchell have studied the behavior of different coal microlithotypes in a 2.5-cm-diameter Pittsburgh coal sample when exposed to CO_2, while under a constant confining pressure of 1.36 MPa (13.42 atm) during gas uptake.[163] The coal was exposed to CO_2 at three different pressures: 1.7, 3.06, and 4.4 MPa (16.78, 30.2, and 43.42 atm). The CO_2 storage process was observed using both qualitative and quantitative X-ray computerized tomography (CT) scanning. The core was examined petrographically after exposure to CO_2 to identify those microlithotypes showing different adsorption behavior. Results showed that different microlithotypes react differently when exposed to high-pressure CO_2, displaying different adsorption and rate properties. Vitrinite was shown to be a swelling maceral under CO_2 adsorption conditions. Clay and inertinite have the highest CO_2 adsorption rate, whereas the gas adsorption rates of vitrinite and liptinite were comparably low.

In another investigation using a confined high-volatile bituminous Pittsburgh seam coal, Karacan pressurized a 2.5-cm-diameter core that was 2.5 cm long with CO_2 at 298 K (25 °C) at various pressures and various confining pressures.[162] Changes in the sorbed gas concentration in the coal and matrix properties were simultaneously investigated, using dual-energy X-ray computed tomography. Application of this technique allowed measurement of the amount of gas sorbed in various microlithotypes, while observing changes in the coal matrix and estimation of the kinetics of the complex heterogeneous processes. Different parts of the coal reacted differently. Vitrinite, liptinite, and clarite swelled as a result of imbibition of CO_2. Clay and inertinite were compressed. Vitrinite swelled and, after reaching a maximum, expelled some CO_2. This was called "breathing" and is thought to be the result of rearrangement of the macromolecular structure. The highest amount of CO_2 was stored in inertinite and clay regions, which imbibed 0.08 g CO_2 per gram of coal. Vitrinite adsorbed 0.06 g CO_2 per gram of coal. Clay-rich sections were compressed to compensate for the swelling in vitrinite regions. In vitrinite, liptinite, and clarite regions of the coal, the amount of gas adsorption increased substantially, followed by a falloff where some of the sorbed gas is expelled due to rearrangement of the macromolecular network to a structure that has decreased gas solubility.

Gas Adsorption/Desorption. The gas-retention capacity of a candidate coal seam can be estimated using direct methods that measure the volume of gas released from a coal sample into a sealed desorption canister (gas-in-place), or by indirect methods based on the adsorption/desorption isotherms obtained in the laboratory. A review of the techniques for the estimation of the gas-in-place is readily available.[164] The CO_2 adsorp-

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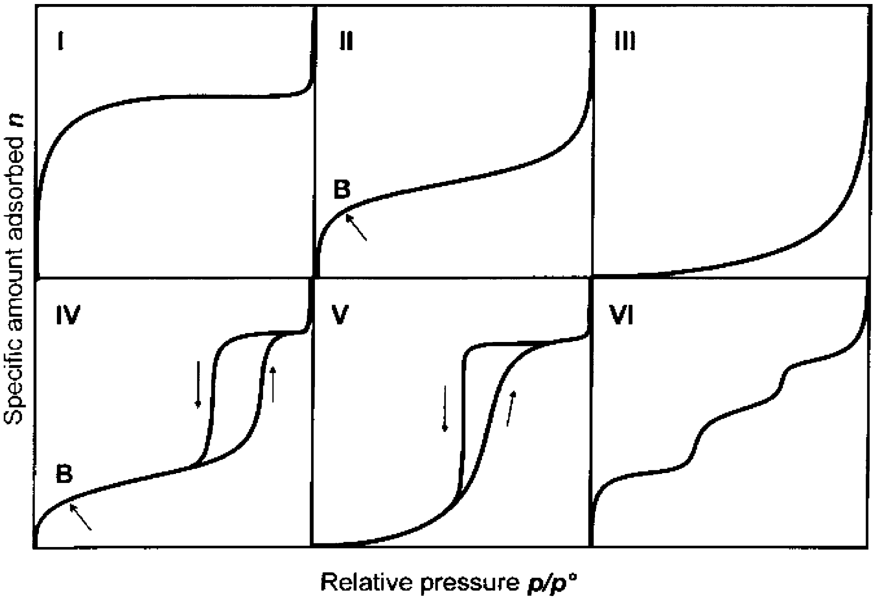

Figure 9. The six types of adsorption isotherms. (From Sing et al.[306]) The two lines in plots IV and V are hysteresis loops.

tion or storage capacity of a coal seam is generally estimated indirectly from the adsorption isotherm data.

Adsorption Isotherms. Adsorption isotherms can be obtained by one of the commonly used methods including gravimetric,[165] manometric (volumetric),[166,167] and chromatographic[168] methods. In the gravimetric technique, the adsorption isotherms are constructed by measuring the weight change using a microbalance after accounting for the sample buoyancy. In the manometric technique, the adsorption isotherms are obtained by calculating the adsorbed amount of gas from the real gas equation, which accounts for the compressibility factor of the gas (z), at each equilibrium pressure. In the chromatographic method, the adsorption isotherm can be obtained from the gas breakthrough curve. The accuracy of each method is dependent on the careful design of the measurement apparatus and careful control of the experimental conditions.

The quantity of gas that is taken up by a solid sample is dependent on the mass of the sample, temperature, pressure, and the nature of both the solid and the gas.[169] Adsorption for a given gas adsorbed on a particular solid can be represented by an adsorption isotherm, which is a plot of the amount adsorbed as a function of pressure at constant temperature. The shape of adsorption isotherms can provide information on the adsorption process, the porosity, and the surface area of the adsorbent. According to the International Union of Pure and Applied Chemistry (IUPAC) classification,[111] there are six different adsorption isotherms that describe the majority of the cases of physical adsorption (Figure 9).[169] The Type I isotherm is produced when a monolayer of adsorbate molecules is adsorbed on a nonporous solid, or when the adsorption is dominated by a micropore filling process. This type of isotherm is often referenced as the Langmuir-type isotherm. Type II is an S-shaped isotherm that is displayed by nonporous or macroporous adsorbents. This isotherm is characterized by an inflection point, which represents the completion of the monolayer and the beginning of the formation of the multilayer. The Type III adsorption isotherm is typical of a nonporous or macroporous adsorbent and is observed for weak adsorbent−adsorbate interactions. The Type IV isotherm, which is similar to the Type II isotherm, is typical for a mesoporous adsorbent. Unlike the other types, it contains a hysteresis loop which is associated with capillary condensation. The Type V isotherm is typical for a nonporous or macroporous adsorbent. It is observed in cases where the adsorbent−adsorbate interaction is weak and is similar to the Type III isotherm. The final isotherm shown is Type VI, a stepped isotherm. This type is rare and it is included in this classification for completeness. The adsorption isotherms for CO_2 and methane on coal are often interpreted as Type I isotherms.

Adsorption Phenomena. When a solid is exposed to a gas or vapor, gas may be adsorbed by the solid adsorbent. Adsorption is a complex physicochemical process, and different expressions are used to describe it. For instance, although the term “adsorption” is used to imply the condensation of gases on free surfaces, the term “absorption” (or “imbibition”) is used to delineate the penetration of the molecules of gas into the mass of the absorbing solid. Similarly, the term “sorption” is used to emphasize the adsorption on a surface. Absorption involves penetration into the lattice of the solid, and/or capillary condensation within the pores.[106] The IUPAC definition is generally accepted for the ‘adsorption’ as the enrichment of one or more components in an interfacial layer.[169] The situation with coals is complicated by the fact that coals are capable of adsorption, followed by absorption, followed by structural rearrangement (relaxation of the macromolecular network) that effect both adsorption and absorption.[170]

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Thus sorption measurements may have a strong temporal component.

Adsorption is generally classified as chemical adsorption (chemisorption) and physical adsorption (physisorption). In chemisorption, the adsorbate is bound to the solid surface by a direct chemical bond. The energy generated is of the same order of magnitude as the heat of reaction, which is 15−100 kcal/mol (62.76−418.4 kJ/mol).[171] The surface coverage in chemisorption is a monolayer. In physisorption, adsorption occurs mainly via van der Waals and electrostatic forces between the adsorbate molecules and the atoms composing the adsorbent surface. Because there is no chemical bond between the adsorbate molecules and the solid surface, physical adsorption is a reversible process. Physical adsorption is exothermic and the energy involved is not much larger than the energy of condensation of the adsorbate, in the range of 2−10 kcal/mol (8.37−41.84 kJ/mol).[171] It is most likely that the adsorption occurs as a monolayer at low pressures and as multilayers at relatively higher pressures, depending on the type of adsorbent and the adsorbate investigated.

The atmospheric boiling point of a compound is thought to be a good relative measure of the sorption strength of a compound on coal.[172] The stronger adsorbing compounds have higher boiling points. Thus, it is possible to estimate the relative adsorption strength of components in a gaseous mixture by comparing their boiling points.[13]

Adsorption is the chief gas storage mechanism in coal seams. Gases are stored in coal by three mechanisms: (1) physically adsorbed compounds on the internal surfaces of the coal, (2) compounds absorbed within the molecular structure, and (3) compounds absorbed within the pores.[158] CH_4 is primarily stored on the coal surface as an adsorbed layer. Gas molecules can be held via weak intermolecular van der Waals interactions between the coal and gas (see previous discussion in this subsection) or retained as trapped molecules within the molecular sieve like pore structure of the coal.

Many theoretical models have been and continue to be developed to physically interpret the adsorption isotherm data. The adsorption isotherms are described using many mathematical formulations, some of which are based on a simplified approach to the physical phenomenon of adsorption. Other mathematical models are purely empirical and are intended to correlate the experimental data using simple equations with two or three empirical parameters.[174] However, empirical equations that do not relate to physical factors lack a practical significance, because they do not allow extrapolation beyond the range of variables for which the parameters have been determined.[175]

The Langmuir monolayer adsorption model, which is the simplest isotherm model, is derived theoretically from both kinetic and statistical mechanical points of view.[176] The mechanism described in the Langmuir model is the adsorption of adsorbate molecules on a fixed number of well-defined localized sites, each of which can hold only one adsorbate molecule. All sites are energetically equivalent and there is no interaction between adsorbate molecules adsorbed on neighboring sites. The Langmuir equation is typically expressed as

$$n = \frac{n_0 bP}{1 + bP} \tag{6}$$

where n_0 is the maximum number of sites available for the adsorbing molecules (adsorption capacity) and b is the equilibrium constant, which describes the partitioning of the adsorbate molecules between the adsorption sites and the free, unassociated state.

Introduction of the BET multilayer adsorption model in 1938[177] extended the Langmuir model. The BET model assumes that, in addition to the assumptions made in the Langmuir model, each adsorbate molecule in the first layer serves as an adsorption site for an adsorbate molecule into the second layer, the second layer for the third layer, and so on. The heat of adsorption of the second and subsequent layers is assumed to be equal to the heat of condensation of the adsorbate and is different from the heat of the adsorption of the first layer.[178] The general BET equation has the form

$$n = \frac{n_0 C(P/P_0)}{(1 - (P/P_0))[1 + (C - 1)(P/P_0)]} \tag{7}$$

where n_0 is the maximum number of sites available for the adsorbing molecules (monolayer adsorption capacity), C is a constant related to heat of adsorption, P is the pressure, and P_0 is the saturation pressure of the adsorbate at adsorption temperature.

The Langmuir and BET theories are generally applied to the adsorption on a single flat surface or on a pore surface when the radii of the pores are large. However, this application is not appropriate for microporous adsorbents for which the pore sizes are only a few molecules wide. [179,180] Adsorption potentials associated with dispersion forces are strongly enhanced in micropores due to overlap of the adsorption force fields from the opposite pore walls. Therefore, the adsorption mechanism in a microporous adsorbent can be better explained by a pore filling mechanism rather than by a surface coverage process. Polanyi[181] defined the adsorption potential of an adsorbate molecule within the attractive force field of an adsorbent as the work required to bring an adsorbate molecule from the gas phase to the adsorption space within the adsorption forces (see discussion in the subsection entitled “Surface Area Measurements”, presented earlier in this review).

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The physical adsorption of gases or vapors by microporous solids can be described well by Dubinin's pore filling theory.[182] The most common Dubinin-Astakhov (D−A) equation is given by

$$n = n_0 e^{-[D \ln(P_0/P)]^j} \tag{8}$$

where n is the moles of gas adsorbed, n_0 is the pore volume of the adsorbent, D is the Dubinin constant (defined as $D = RT/\beta E$, where R is the gas constant, T is the temperature (in Kelvin), β is the affinity coefficient, and E is the characteristic heat of adsorption), P and P_0 are as defined previously, and j is the structural heterogeneity parameter. A special form of the D−A equation is the Dubinin−Radushkovich (D−R) equation, in which $j = 2$.

Although the Langmuir monolayer and the Dubinin pore-filling models provide different adsorption capacities, there is good correlation between the two models. Toda and Toyoda[183] applied the Langmuir and Polanyi−Dubinin (P−D) equations to the isotherms of CO_2 adsorption on coals at 298 K (25 °C). They found a linear relationship between the monolayer adsorption capacity (the Langmuir constant, b) and the micropore volume (the inverse of the Dubinin constant, $1/D$). Their results showed that the monolayer adsorption capacity was smaller than the micropore capacity, by ~60%.

Adsorption Isotherms of Gases on Coals. Adsorption of CO_2 on coals has been studied extensively since the early 1900s.[184] However, many of these studies have been performed at lower pressures (usually below atmospheric) and often extremely low temperatures (−78 °C), to estimate the surface area[86,104,185] and micropore structure[186−189] of the coal. Although these low-pressure data have provided information that is relevant to today's sequestration projects, they do not properly represent the in situ conditions of high-pressure and elevated-temperature encountered in deep, unmineable coal seams. High-pressure, high-temperature CO_2 adsorption data on coal are limited. Predicting high-pressure CO_2 isotherms from low-pressure data is not yet possible, because coal does not seem to behave as a rigid solid under these conditions. To our knowledge, only one group has attempted to account for both CO_2 solubility in the coal matrix (absorption) and coal swelling in a quantitative model.[190,191] They obtained good agreement with low-pressure work; however, if their model is correct, the additional constant(s) needed to predict high-pressure behavior cannot be easily obtained at lower pressures.

Reservoir simulations of primary and enhanced CH_4 production require mathematical models that describe binary adsorption behavior of CO_2 and CH_4. Because other gases are present in the coal system, ternary and higher gas adsorption isotherms are needed. Clarkson and Bustin note that the composition of adsorbate gas significantly affects the total and single component adsorbed gas volumes in coal systems.[192,193] Multicomponent desorption isotherms determined using realistic initial reservoir gas compositions are required for accurate predictions of adsorbed gas content during production.[192,193]

Development of an understanding of the adsorption properties of CH_4 and CO_2 is vital for the optimum development of techniques to recover CH_4 while sequestering CO_2.[192,194] Detailed knowledge of the adsorption isotherms of CH_4 and CO_2 is required input for CH_4 production simulations. This information is needed to estimate the coal seam CO_2 storage capacity and the overall economics of the process for a given coal seam, as well as operating conditions that will ultimately be used. Thus, accurate measurement and modeling of the adsorption process is required for economic predictions of CH_4 recovery. Over the years, the ability of many models to predict the experimentally determined isotherms have been evaluated. These include the BET, Langmuir, extended Langmuir, D−R, and D−A models. These models have been applied alone and in combination with ideal adsorbed solution (IAS) theory for CO_2.[192] Other models that are based on simplified local density and models that are based on two-dimensional analogues of activity coefficients, as well as others, have also been evaluated.[192,194] Clarkson and Bustin recently demonstrated that the IAS theory and the extended Langmuir model differ significantly in their ability to predict the behavior of binary gas mixtures. According to Clarkson and Bustin, "comparison of model predictions to experimental data demonstrates that the IAS theory, in conjunction with D−A single component isotherm are [sic] more accurate for the prediction of mixed gas desorption isotherms collected in this study than the extended Langmuir. IAS predictions, however, are strongly dependent upon choice of the pure gas isotherm equation."[192]

Extensive literature is available on the physical adsorption of gases and vapors on microporous adsorbents, especially for activated carbons. Martin-Martinez et al.[195] combined the use of preadsorbed *n*-nonane with CO_2 adsorption at 273 K (0 °C) to interpret the adsorption mechanism of CO_2 in narrow micropores of a series of carbons prepared from anthracite by thermal activation in a CO_2 atmosphere. The mechanism of adsorption

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was dependent on the shape and size of the pores. In narrow micropores of molecular dimensions, CO_2 was probably adsorbed by micropore filling in a fashion similar to that proposed for the adsorption of N_2 at 77 K (−196 °C). With increasing extent of thermal activation, the micropores widened and the adsorption of CO_2 in micropores larger than two molecular dimensions probably occurred by surface coverage.

The CH_4 and CO_2 adsorption capacity of coal is a direct function of both the temperature and pressure of the coal. Increasing pressure results in increased storage, whereas increased temperature results in decreased storage.[196−198] Hall et al.[199] initially found that, at pressures above 1400 psi (95.26 atm), adsorption of CO_2 rises rapidly to almost 2.5 times more than that adsorbed at lower pressures. More recently, Gasem[200] recalculated the extent of adsorption using the Span and Wagner equation for the compressibility factor of CO_2 and did not see the same sudden increase. Reeves has noted that, "contrary to popular wisdom, CO_2 sorption on coal does not appear to exhibit abnormal behavior at high pressures, as sometimes attributed to multilayer sorption or other phenomena. Langmuir-type sorption models should therefore be sufficient to emulate this process."[19,201] On the other hand, Krooss et al.[202] recently measured the adsorption isotherms of CO_2 and CH_4 on dried and moisture-equilibrated coals. Although the CH_4 adsorption isotherms were Langmuir-like, the CO_2 isotherms displayed unusual behavior at pressures of ∼14 MPa (138.17 atm). Because the high-pressure adsorption data is limited for CO_2, further work is needed to understand these findings.

Clarkson et al.[203] investigated the application of the monolayer (Langmuir), multilayer (BET), and the adsorption potential (D−R or D−A) theories to high-temperature, high-pressure (up to 10 MPa (98.69 atm)) methane adsorption isotherm data and low-pressure CO_2 isotherm data, to determine which model best represented the experimental data. Clarkson et al. also gave a brief summary of the application of these equations.[203] They found that the three-parameter D−A equation yielded the best fit to the high-pressure methane isotherm data. It was concluded that the Langmuir theory assumption that the adsorption surface is energetically homogeneous is not strictly true for coal. They also concluded that, although the adsorption potential theory applies to the low-pressure CO_2 isotherm, the high-pressure CO_2 isotherms needed further testing.[13]

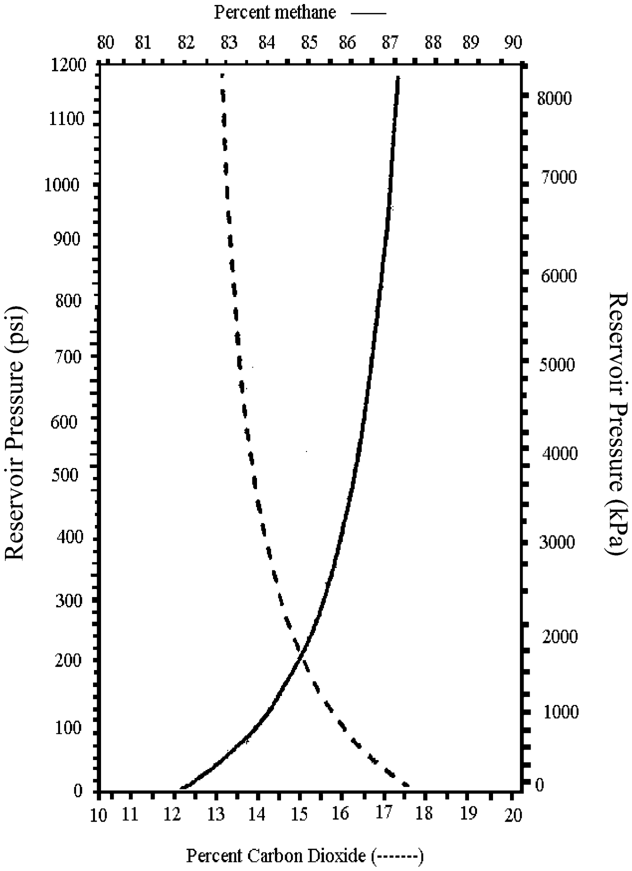

Figure 10. Changes in gas composition with decreasing pressure. The composition of the coalbed gases changes with decreasing reservoir pressure. These curves are estimated from desorption data. (From Scott.[74])

During CO_2/N_2-ECBM recovery, the compositions of coalbed gases change as the reservoir depressurizes (Figure 10).[74,204] The degree of variance is dependent on the CH_4, CO_2, and N_2 desorption isotherms for the coal in the reservoir. Scott has noted that "the amount of each gas in the free gas phase is not proportional to the amount of the same gas component sorbed onto the coal surface" (Figure 11).[74,204] CO_2, ethane, and higher hydrocarbons are held in the coal by stronger intermolecular forces than those holding CH_4 and N_2. The sorption isotherms for CH_4, CO_2, and N_2 on coal are shown in Figure 12.[157] As pressure increases, the amount of each gas sorbed on the coal increases. At any one pressure, more CO_2 is adsorbed by the coal than CH_4 and N_2 and more CH_4 is adsorbed than N_2. The hydrocarbons are held onto the coal by van der Waals forces, which are a function of molecular volume. Because the higher hydrocarbons are larger than CH_4, the intermolecular forces that are developed between a coal and these molecules are greater than those between coal and CH_4.

DeGance et al.[205] investigated the high-pressure pure and multicomponent adsorption isotherms for methane, nitrogen, and CO_2 on a wet coal sample. They applied

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(196) Meissner, F. F. *Hydrocarbon Source Rocks of the Greater Rocky Mountain Region*; Woodward, J., Meissner, F. F., Clayton, J. L., Eds.; Rocky Mountain Association of Geologists: Denver, CO, 1984; pp 401−431.

(197) Wyman, R. E. *AAPG Mem.* **1984**, *38*, 173−187.

(198) Joubert, J. I.; Grein, C. T.; Bienstock, D. *Fuel* **1974**, *53*, 186−190.

(199) Hall, F. E.; Zhou, C.; Gasem, K. A. M. Adsorption of Pure Methane, Nitrogen, and Carbon Dioxide and Their Binary Mixtures on Wet Fruitland Coal. In *Proceedings of the Eastern Regional Conference & Exhibition of the Society of Petroleum Engineers*, Charleston, WV, November 8−10, 1994, SPE Paper No. 29194, pp 329−344.

(200) Gasem, K. A. M. Adsorption of CO_2 on Coal at High Pressures, personal communication, 2003.

(201) Reeves, S. The Coal-Seq. Project. *Greenhouse Issues*, **2002**, (59). (Available via the Internet at http://www.ieagreen.org.uk/march59.htm#coalseq.)

(202) Krooss, B. M.; van Bergen, F.; Gensterblum, Y.; Siemons, N.; Pagnier, H. J. M.; David, P. *Int. J. Coal Geol.* **2002**, *51*, 69−92.

(203) Clarkson, C. R.; Bustin, R. M.; Levy, J. H. *Carbon* **1997**, *35*, 1689−1705.

(204) Arri, L. E.; Yee, D.; Morgan, W. D.; Jeansonne, M. W. Modeling Coalbed Methane Production with Binary Gas Sorption. In *Proceedings of the Rocky Mountain Regional Meeting of the Society of Petroleum Engineers*, Casper, WY, May 18−21, 1992; SPE Paper No. 24363, pp 459−472.

(205) DeGance, A. E.; Morgan, W. D.; Yee, D. *Fluid Phase Equilib.* **1993**, *82*, 215−224.

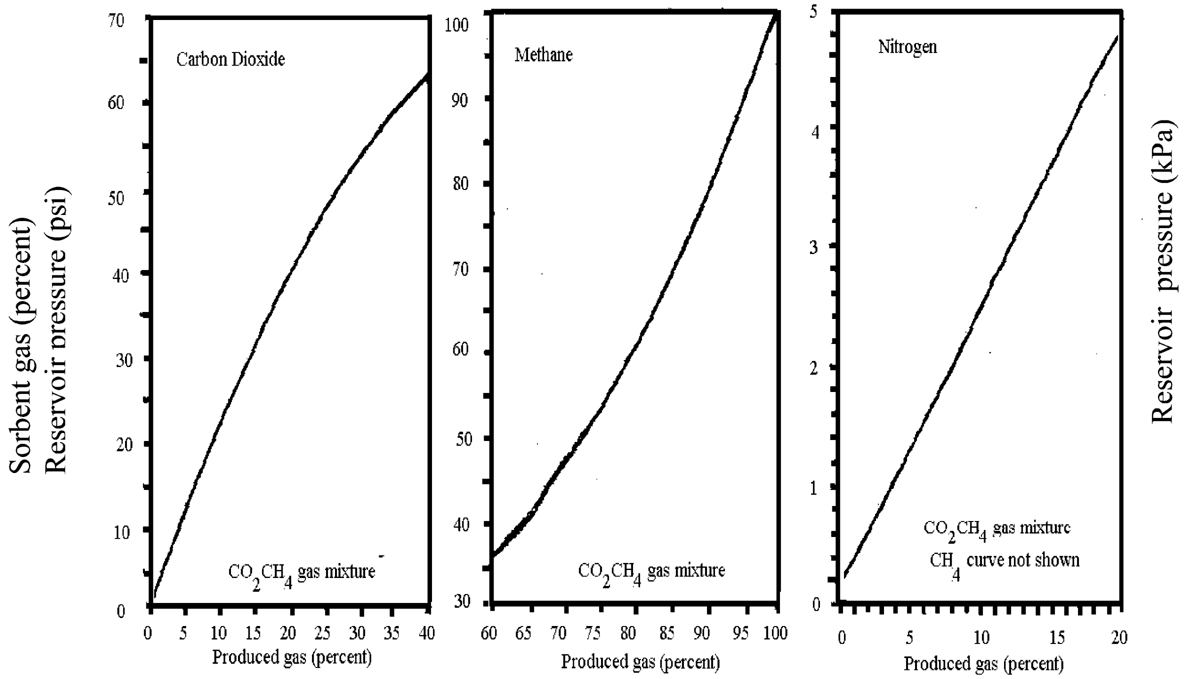

Figure 11. Sorbed and produced gas fraction for CO_2, CH_4, and N_2. The quantity of a gas component occurring in a produced coalbed gas is disproportional to the amount of the component sorbed on the coal surface. CO_2 is strongly sorbed to the coal surface, whereas CH_4 and N_2 are less strongly sorbed. (From Scott.[74])

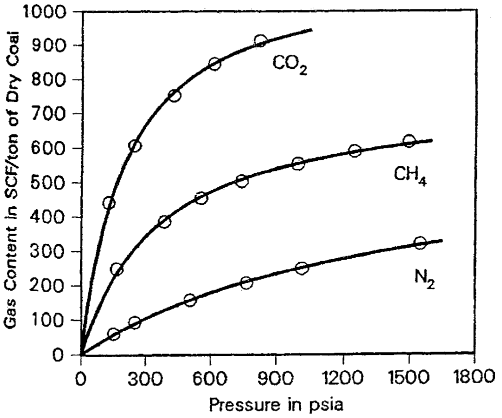

Figure 12. Sorption of different pure gases on coal. Solid curves are the best-fit Langmuir isotherms. Sorption data are for a Fruitland coal sample from the San Juan basin. All data are the absolute sorption measured at 115 °F and at moistures exceeding the equilibrium moisture content. Modified from SPE 24363. (See Yee et al.[157])

a two-dimensional virial equation of state, the IAS theory, and the Langmuir equation to the multicomponent systems. They concluded that, although the EOS approach has difficulty matching the experimental data on wet coal substrates, the simplicity of the virial equation of state (eq 9), derived originally by Haydel and Kobayashi,[206] could be used in modeling efforts:

$$\frac{A\pi}{RT} = \sum_i \omega_i + \sum_i \sum_j \boldsymbol{b}_{ij}\omega_i\omega_j + \sum_i \sum_j \sum_k \boldsymbol{c}_{ijk}\omega_i\omega_j\omega_k + ... \qquad (9)$$

where A is the surface area per mass of adsorbent, π is the spreading pressure, R is the gas constant, T is the temperature, $\omega_{i,j,\mathrm{or}k}$ denotes the number of moles of component i, j, or k adsorbed per mass of adsorbent, and $\boldsymbol{b}$ and $\boldsymbol{c}$ are virial coefficients.

A few investigators have reported on the adsorption isotherms of binary and ternary gas mixtures. The gases of most interest are mixtures of CO_2, CH_4, and N_2. Stevenson et al. studied the adsorption properties of CO_2, CH_4, and N_2 at 30 °C on dry Westcliff Bulli coals at pressures as high as 5.2 MPa (51.32 atm).[207] Arri et al. studied several binary gas mixtures, including CH_4/N_2 and CH_4/CO_2 adsorption isotherms at 46 °C and multiple pressures on moist coal. They showed that the gases compete for adsorption sites and, thus, are not independent of each other.[208] Greaves et al. studied CH_4/CO_2 adsorption/desorption isotherms at 23 °C on dry Sewickly seam coal and observed hysteresis in the isotherms (see later discussion).[209] They observed the impact of hysteresis on predicting adsorbed phase compositions.[209] Harpalani and Pariti investigated the $CH_4/CO_2/N_2$ ternary gas adsorption/desorption at 44 °C on moisture equilibrated coal.[210] The extended Langmuir isotherm gave a reasonable fit for all of the data obtained by Arri et al.[208] and Harpalani and Pariti.[210]

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(206) Haydel, J. J.; Kobayashi, R. *Ind. Eng. Chem. Fundam.* **1967**, *6*, 546−554.

(207) Stevenson, M. D.; Pinczewski, W. V.; Somers, M. L.; Bagio, S. E. Adsorption/Desorption of Multicomponent Gas Mixtures at In-Seam Conditions. In *Proceedings of the Society of Petroleum Engineers Asia−Pacific Conference*, Perth, Western Australia, November 4−7, 1991, SPE Paper No. 23026.

(208) Arri, L. E.; Yee, D.; Morgan, W. D.; Jeansonne, M. W. Modeling Coalbed Methane Production with Binary Gas Sorption. In *Proceedings of the Society of Petroleum Engineers Rocky Mountain Regional Meeting*, Casper, WY, May 18−21, 1992; SPE Paper No. 24363, pp 459−472.

(209) Greaves, K. H.; Owen, L. B.; McLennan, J. D.; Olszewski, A. Multi-component Gas Adsorption−Desorption Behavior of Coal. In *Proceedings of the International Coalbed Methane Symposium*, University of Alabama, Tuscaloosa, AL, May 17−21, 1993, Paper No. 9353, pp 197−205.

(210) Harpalani, S.; Pariti, U. M. Study of Coal Sorption Isotherms Using A Multicomponent Gas Mixture. In *Proceedings of the International Coalbed Methane Symposium*, University of Alabama, Tuscaloosa, AL, May 17−21, 1993; Paper No. 9356, pp 151−160.

Chaback et al.[211] measured the sorption isotherms of N_2, methane, and CO_2 on wet bituminous coals under in situ conditions, at a temperature of 46 °C and pressure up to 11 MPa (108.58 atm), and obtained results similar to those obtained earlier by Arri et al., as shown in Figure 12. They concluded that the Langmuir equation, in both its simple form for single gases and its extended form for multiple gases, was satisfactory for representing the adsorption isotherm data of the pure components and for the mixtures of gases, respectively. The ratio of the adsorption capacity of CO_2:CH_4:N_2 was found to be 4:2:1. (See subsections entitled "CO_2-ECBM," "Burlington Resources, Allison Unit CO_2-ECBM Pilot", and "Estimated Amounts of CH_4 in Coal", presented later in this review.)

The adsorption/desorption isotherms have been studied extensively for methane[24−26] and other gases such as ethane,[166] hydrogen, [82,212] and their binary mixtures at elevated-temperatures and pressures. However, until recently, there have been few studies of CO_2 isotherms under in-seam conditions. This void is being filled because of the interest in both ECBM and CO_2 sequestration.[127,213−215] Clarkson and Bustin studied the low- and high-pressure adsorption isotherms of CO_2 and CH_4 on four dried bituminous coals of the Cretaceous Gates Formation at 30 °C and up to 5 MPa (49.35 atm).[127] They concluded that the CO_2 isotherms had a slight inflection at high pressure, possibly as a result of multilayer adsorption and that the isotherm data fit the D−A equation.

Effect of Water on the CO_2 and CH_4 Adsorption Capacity and Selectivity. Water is associated with coal in several different forms. In addition to the water that floods the cleat system of deep coal seams, water is also associated with the organic and inorganic phases of the coal. The water associated with the inorganic phases is principally water of hydration. This "inorganic" water is expected to have a negligible role in the coal-swelling process. A large body of information is available regarding the nature of the water associated with the organic matrix of the coal. Work using differential scanning calorimetry and proton NMR indicates that water is held within the organic matrix primarily in two forms: a tightly bound unfreezable form and a bulk freezable form.[216] These two states are not discrete but do exist as a continuous distribution between bound and free water.

The moisture content of coal has a significant role in the methane sorption capacity of the coal, as illustrated in Figure 13. Clearly, as the methane pressure increases, the methane capacity increases. Coal has a significantly greater CH_4 sorption capacity on a dry basis than on a moisture-containing basis.[198] Many low-rank coals have a strong preference for water over CH_4. Thus, when the CH_4 sorption capacity is measured on a dry basis, it can be very different from the results obtained when the coal is water-saturated.[198] The moisture content of coal will also affect the amount of CO_2 that the coal can imbibe.[192] Levine has also stated that the ability of coals to sorb small molecules such as CH_4 and CO_2 is a function of the amount of trapped compounds present as occluded material. The presence of trapped compounds in the coal matrix adversely affects the capacity of the coal to store gases by "plugging" the micropore structure in the coal.[217]

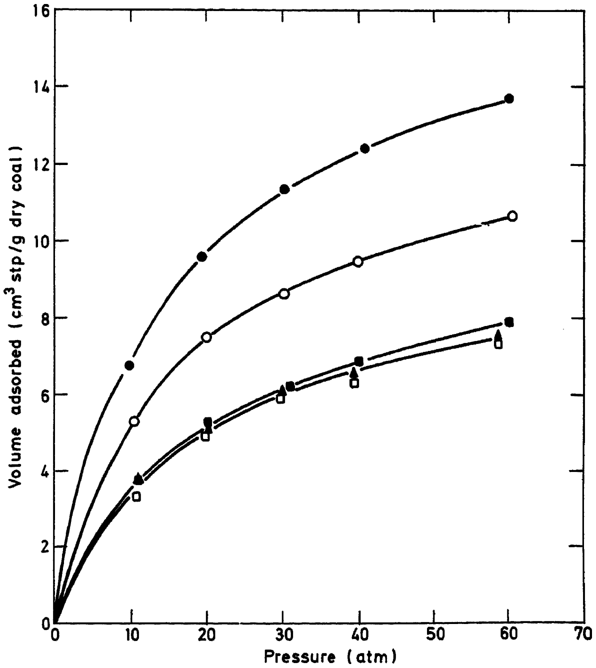

Figure 13. Methane adsorption isotherms for Illinois No. 6 coal at 30 °C. Moisture content: (●) 0%, (○) 5%−44%, (■) 10%−70%, and (□) 14%−28%. (From Joubert et al.[198])

Two of the most important factors controlling the amount of CH_4 stored in coal are the confining pressure and the surface area of the internal micropore system within the coal. Under favorable temperature and pressure ranges, per unit volume, coal seams can contain up to 5 times the amount of CH_4 as a conventional gas reservoir of similar volume.[151]

The sorption of methane on coal and the effects of temperature, moisture content, and particle size on the sorption capacity have been investigated by several researchers, and good reviews are available in the literature.[24−26] The methane adsorption capacity has been shown to decrease with increasing temperature and moisture content.[198,218] Joubert and others studied the effect of moisture on the sorption isotherm of methane on bituminous coal at 30 °C and at pressures up to 900 psi (61.24 atm).[218] For all coals studied, the amount of adsorbed methane decreased with moisture content up to a critical value that was characteristic of the coal type. Moisture in excess of the critical value had no additional effect on the methane sorption. Methane adsorption in the presence of a moisture

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(211) Chaback, J. J.; Morgan, W. D.; Yee, D. *Fluid Phase Equilib.* **1996**, *117*, 289−296.

(212) Saunders, J. T.; Tsai, G. M. C.; Yang, R. T. *Fuel* **1985**, *64*, 621−626.

(213) Nodzenski, A. *Fuel* **1998**, *77*, 1243−1246.

(214) Clarkson, C. R. The Effect of Coal Composition, Moisture Content, and Pore Volume Distribution Upon Single and Binary Gas Equilibrium and Nonequilibrium Absorption: Implications for Gas Content Determination, Ph.D. Dissertation, 1998.

(215) Al-hawaree, M. Geomechanics of CO_2 Sequestration in Coalbed Methane Reservoirs. M.S. Dissertation. University of Alberta, Canada, 1999.

(216) Suuberg, E. M.; Otake, Y.; Yun, Y.; Deevil, S. C. *Energy Fuels* **1993**, *7*, 384−392.

(217) Levine, J. R. The Impact of Oil Formed During Coalification on Generation and Storage of Natural Gas. In *Proceedings of the Coalbed Methane Symposium*, 1991; pp 307−315.

(218) Joubert, J. I.; Grein, C. T.; Bienstock, D. *Fuel* **1973**, *52*, 185.

content m less than the critical moisture content m_c is represented by an empirical equation that was developed by Ettinger et al:[219]

$$\frac{n_d}{n_w} = C_0 m + 1 \qquad (10)$$

where n_d and n_w are the amount of methane adsorbed on the dry and moist coal, respectively, and C_0 is obtained from a plot of n_d/n_w versus m. C_0 has been reported as 0.27 by Joubert et al.,[198] 0.39 by Levy et al.,[24] and 0.31 by Ettinger et al.[219] None of the authors found any further reduction in methane adsorption capacity when the moisture content was increased higher than the critical value m_c.

Coal Shrinkage/Swelling. The interpretation of surface area, porosity, permeability, and adsorption data usually do not take into account the fact that the coal matrix is not a rigid solid. Coal is a polymer-like network that is often affected by the gas or solvent with which it is in contact. The coal matrix shrinks as water and hydrocarbons are desorbed and swells as certain gases are adsorbed onto its surface. Deevi and Suuberg[220] conducted drying studies on U.S. western lignites and brown coals. Moisture adsorption and desorption isotherms showed some irreversibility. Re-swelling of previously dried samples showed that samples regained only 80% of the original wet volume. In no case did a sample recover its initial volume. It was hypothesized that the 20% loss in volume was due to the internal collapse of relatively large voids of ~70 Å that could no longer hold moisture. Thus, the drying of coal alters the coal structure irreversibly. Shrinkage was examined in macroscopic coal samples and found to be prevalent among the lignites as expected. Initial shrinkage was rapid and large. Initial shrinkage, in turn, imposed stress upon the coal creating fissures and cracks. It was also found that shrinkage was not equal in all directions and, thus, displayed anisotropy. However, no clear relation was seen between the orientation of the coal, its bedding plane, and shrinkage, although it was noted that cracks developed along bedding planes prior to cracks across bedding planes. Deevi and Suuberg interpreted this behavior of low-rank coals upon water loss, in terms of colloidal gel behavior.[220] The gels do not develop zero porosity after shrinking.

Reucroft and Patel investigated the gas-induced swelling of coal using a dilatometer.[221] The initial evacuation of the sample chamber induced some shrinkage in the coal sample. The amount of shrinkage correlated with the amount of moisture originally in the coal. The coal with the highest moisture content exhibited the greatest shrinkage.

In 1955, Moffat and Weale performed a classic investigation of the sorption characteristics of methane on 10 different coals.[51] The sorption isotherms generated using finely ground coal and lump coal (1.25 cm) gave the same isotherms and took approximately the same time to achieve equilibrium. They also investigated the changes in coal dimensions during CH_4 sorption and found that the expansion was not isotropic; measurements were made both parallel and perpendicular to the bedding plane and were combined to give a bulk expansion. The CH_4 adsorption isotherms for coal H, a vitrain, are given in Figure 14. Two types of isotherms, the total sorption isotherm (V_T, denoted by the upper curve) and the apparent sorption isotherm (V_S^a, denoted by the lower curve) are presented as explained in the figure caption. The bulk expansion (total expansion in all directions) observed for three coals at various CH_4 pressures is shown in Figure 15. As seen in Figure 15, some coals do not return to their original dimensions after release of CH_4 pressure. Expansion was greater perpendicular rather than parallel to the bedding plane.

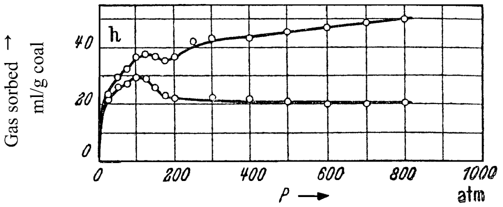

Figure 14. Two types of adsorption isotherms for Vitrain H were measured.[51] The total sorption (V_T) is given by the upper line, and the lower line is the apparent sorption (V_s^a). Both are presented in the figure. The total sorption ν_T (given in terms of milliliters at normal temperature and pressure (ntp) per gram of coal) is the methane sorbed by the lump volume of the coal V'_{coal}, and includes the methane which is simply compressed in the pore space. It is calculated from the expression $\nu_T = [V_p - (\rho_g/\rho_o)(V_{system} - V'_{coal})]/(\text{mass of coal})$, where ρ_g denotes the methane density at 25 °C and equilibrium pressure, and ρ_o is the methane density at ntp. The apparent sorption ν_s^a (given in terms of milliliters (ntp) per gram of coal) is calculated from the volume of the coal substance V_{coal} determined in helium, so that the porosities of the coal are regarded as part of the free space of the sorption apparatus, and $\nu_s^a = [V_p - (\rho_g/\rho_o)(V_{system} - V_{coal})]/(\text{mass of coal})$.

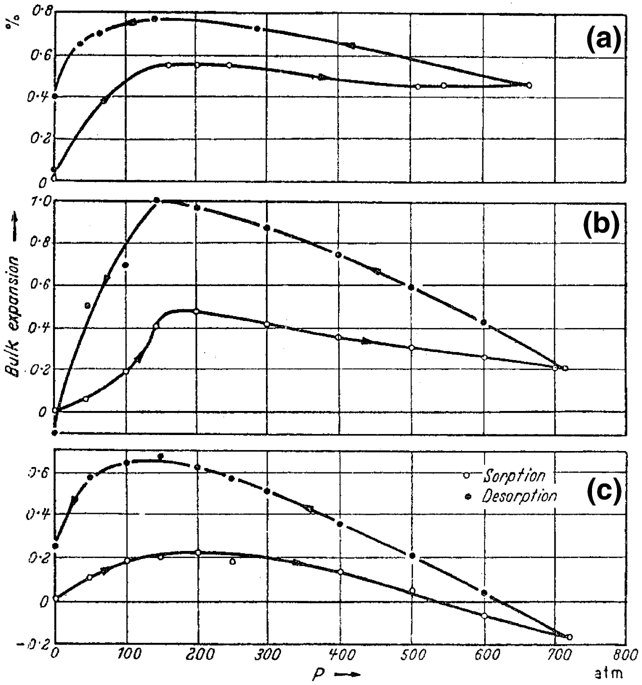

Figure 15. Bulk expansion as a function of gas pressure: (A) coal D, (B) coal G, and (C) coal H. (From Moffat and Weale.[51])

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[219] Ettinger, I. L.; Dmitriev, A. M.; Shaupakhina, E. S. *Systemic Handbook for the Determination of the Methane Content of Coal Seams from the Seam Pressure of the Gas and the Methane Capacity of Coal*; U. S. Bureau of Mines Translation No. 1505/National Coal Board Translation A 1606SEH, 1958.

[220] Deevi, S. C.; Suuberg, E. M. *Fuel* **1987**, *66*, 454–460.

[221] Reucroft, P. J.; Patel, H. *Fuel* **1986**, *65*, 816–820.

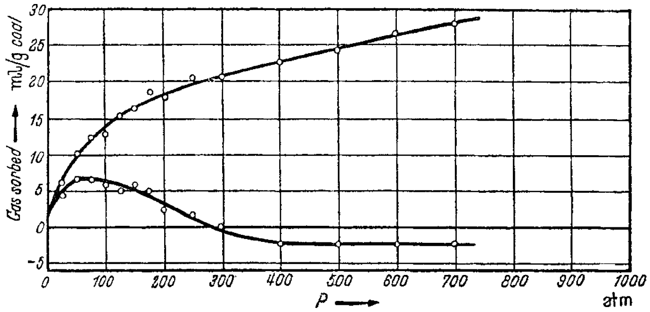

Figure 16. Isotherm for coal H (embedded in Wood's Metal). (From Moffat and Weale.[51]) The top isotherm is the sorption isotherm, and the bottom isotherm is the apparent isotherm calculated as described in the caption for Figure 14.

They also performed an interesting experiment where they confined a piece of coal in Wood's Metal and repeated the CH_4 sorption isotherm measurement. Specifically, a cylinder of vitrain was encased in molten Wood's Metal and the CH_4 isotherms were measured again. When subjected to the confining presence of the metal, the isotherms were different. The sorption was significantly reduced by the metal and the shape of the isotherm was altered, as can be observed by comparison of isotherms measured for coal H in Figure 14 and again for coal H in Wood's Metal shown in Figure 16.[51]

Walker et al. measured the extent of swelling of coals and macerals in CO_2.[222] They observed a measurable expansion at ambient temperatures that was a function of the CO_2 pressure. Increasing the pressure to 3.4 MPa (33.55 atm) produced a significant expansion of the coals. Moreover, the rates of expansion were higher for experiments that were performed at the higher pressure, compared to those at ambient pressure. For a lignite sample, equilibrium expansion was almost instantaneous. It was also noted that the swelling of coals exposed to elevated pressures of CO_2 was not fully reversible. Cycling between high and low pressures increased the residual expansion of the coal matrix. This behavior was attributed to the uptake of the CO_2 in the micropores. They also reported a residual, strongly bound CO_2 even after "full" desorption. The CO_2 described as strongly bound by Walker et al. may not be strongly bound but may be diffusionally trapped.

The adsorption and desorption of gases is expected to affect the cleat width and coalbed permeability. During the recovery of coalbed hydrocarbon gases, the coal matrix shrinks. Using a pressurized triaxial cell to independently control the applied stress and applied pressure, Harpalani and Schraufnagel[145] observed a volumetric shrinkage of 0.4% when the gas pressure fell from 6.9 MPa (68.1 atm) to approximately atmospheric pressure. The authors suggested that higher flow rates might be expected in the coal seam as a result of the enlarged cleat structure.

More recently, Seidle and Huitt conducted experiments to measure the shrinkage under in situ coalbed temperatures and pressures.[223] In their experiments, matrix shrinkage was observed to correlate with both the composition and pressure of the gas. However, shrinkage did not correlate with the total decrease in pressure; rather, the pressure had to fall below a certain crucial pressure before shrinkage occurred. Below this crucial pressure, desorption led to matrix shrinkage and permeability increases. The volume of the coal matrix decreased by 0.5% during desorption cycles. The change in permeability was dependent on the composition of the gas and was larger for CO_2 than for methane.

St. George and Barakat[224] conducted a study of the change in the stress associated with gas desorption from a coal seam. Desorption and subsequent shrinkage of the seam had an effect on permeability and the strength of the strata. Matrix shrinkage predominantly resulted from gas desorption from the coal. Methane desorption in particular increased the stress within the coal. Stress increased by a factor of 2.5 times more than what was expected from the incremental relief of gas pressure.

Inferred Molecular-Scale CO_2−Coal Interaction Mechanisms: Disparate Results and Alternate Points of View. Surprisingly, no literature could be found that addresses, generally, molecular-scale CO_2−coal interaction mechanisms that are relevant to coal seam CO_2 sequestration or ECBM production. Consequently, such mechanisms must be inferred from the molecular-scale interaction of CO_2 with substances other than coal. Otherwise, such mechanisms must be inferred from results such as those related to the sorption of CO_2 on coal (including coal "surface areas" based on CO_2 sorption) and the swelling of coal by CO_2.

CO_2 is potentially capable of undergoing many different types of noncovalent interactions with coal. Such interactions fall in the broad categories of acid−base interactions, dipole−quadrupole interactions, and van der Waals or London dispersion force interactions. Special types of acid−base interactions are electron donor−acceptor interactions (including, perhaps, "π-bonding") and hydrogen bonding.

With respect to acid−base character, CO_2 and coal are similar to each other, in the respect that both CO_2 and coal are more acidic than basic. A difference between the acid−base character of the two is that all of the acidity of CO_2 is Lewis acidity, whereas the acidity of coal is primarily Brönsted acidity.

Scales of CO_2 Interaction. Table 4 lists experimental hard and soft acid/base (HSAB) parameters for CO_2 and other molecules.[225] Such parameters serve as scales of interaction for CO_2.

In Table 4, I represents the ionization potential, A represents the electron affinity, and χ and η are Pearson's "absolute electronegativity" and "absolute hardness," respectively.[225] The latter two parameters are defined by the equations $\chi = (I + A)/2 = -\mu$ (where μ is electronic chemical potential) and $\eta = (I - A)/2$. According to Pearson's HSAB principles, hardness and softness are closely related to polarizability. Soft acids and bases have a relatively high degree of polarizability, whereas hard acids and bases do not. Soft molecules can easily change both their number of electrons and their charge distributions, whereas hard acids and bases must rely

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[222] Walker, P. L., Jr.; Verma, S. K.; Rivera-Utrilla, J.; Khan, R. *Fuel* **1988**, *67*, 719−726.

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[225] Pearson, R. G. *J. Org. Chem.* **1989**, *54*, 1423−1430.

Table 4. Experimental Hard and Soft Acid/Base (HSAB) Parameters for CO_2 and Other Molecules (eV)[a]

molecule	I[b]	A[b]	P	B
SF_6	15.4	0.5	8.0	7.4
O_3	12.8	2.1	7.5	5.4
SO_3	12.7	1.7	7.2	5.5
Cl_2	11.6	2.4	7.0	4.6
H_2	15.4	−2.0	6.7	8.7
SO_2	12.3	1.1	6.7	5.6
N_2	15.58	−2.2	6.70	8.9
Br_2	10.56	2.6	6.6	4.0
C_2N_2	13.37	−0.58	6.40	6.98
O_2	12.2	0.4	6.3	5.9
BF_3	15.8	−3.5	6.2	9.7
CO	14.0	−1.8	6.1	7.9
I_2	9.4	2.6	6.0	3.4
BCl_3	11.60	0.33	5.97	5.64
CCl_4	11.5	~0.8[c]	5.9	5.6
HNO_3	11.03	0.57	5.80	5.23
CH_3NO_2	11.13	0.45	5.79	5.34
PF_3	12.3	−1.0	5.7	6.7
HCN	13.6	−2.3	5.7	8.0
PBr_3	9.9	1.6	5.6	4.2
S_2	9.36	1.66	5.51	3.85
$C_6H_5NO_2$	9.9	1.1	5.5	4.4
PCl_3	10.3	0.8	5.5	4.7
acrylonitrile	10.91	−0.21	5.35	5.56
CS_2	10.08	0.62	5.35	5.56
C_2H_2	10.0	0.6	5.3	4.7
HI	10.5	0.0	5.3	5.3
CO_2	13.8	−3.8	5.0	8.8
HF	16.0	−6.0	5.0	11.0
CH_2O	10.9	−0.9	5.0	5.9
CH_3I	9.5	0.2	4.9	4.7
CH_3Br	10.6	~−1.0	4.8	5.8
SiH_4	11.7	−2.0	4.8	6.8
HCl	12.7	−3.3	4.7	8.0
CH_3CN	12.2	−2.8	4.7	7.5
HCO_2CH_3	11.0	−1.8	4.6	6.4
CH_3CHO	10.2	−1.2	4.5	5.7
C_2H_4	10.5	−1.8	4.4	6.2
C_5H_6N	9.3	−0.6	4.4	5.0
butadiene	9.1	−0.6	4.3	4.9
H_2S	10.5	−2.1	4.2	6.2
$HCONH_2$	10.2	−2.0	4.1	6.1
styrene	8.47	−0.25	4.11	4.88
CH_3COCH_3	9.7	−1.5	4.1	5.6
C_6H_6	9.3	−1.2	4.1	5.3
toluene	8.8	−1.1	3.9	5.0
CH_3Cl	11.2	−3.7	3.8	7.5
p-xylene	8.4	−1.1	3.7	4.8
1,3,5-trimethylbenzene	8.40	−1.03	3.69	4.72
cyclohexene	8.9	−2.1	3.4	5.5
DMF	9.1	−2.4	3.4	5.8
CH_3F	12.5	−6.2	3.2	9.4
H_2O	12.6	−6.4	3.1	9.5
$(CH_3)_3As$	8.7	−2.7	3.0	5.7
$(CH_3)_3P$	8.6	−3.1	2.8	5.9
c-C_3H_6	10.5	−5.0	2.8	7.8
$(CH_3)_2S$	8.7	−3.3	2.7	6.0
NH_3	10.7	−5.6	2.6	8.2
CH_4	12.7	−7.8	2.5	10.3
$C(CH_3)_4$	10.4	−6.1	2.2	8.8
$(CH_2)_2O$	10.0	−6.0	2.0	8.0
CH_3NH_2	9.0	−5.3	1.9	7.2
$(CH_3)_3N$	7.8	−4.8	1.5	6.3

[a] From ref 225. [b] For sources, see ref 260 cited in Pearson.[225]

on existing charges and dipoles as sources of ionic bonding. Generally, hard acids prefer to coordinate to hard bases, and soft acids prefer to coordinate to soft bases. In Table 4, all of the molecules are arranged in the order of descending absolute electronegativity; accordingly, the strongest Lewis acids are at the top of the table, and the strongest Lewis bases are at the bottom. In comparison with other molecules, CO_2 has an intermediate absolute electronegativity and is a relatively hard molecule. For example, based on the principle that acids and bases of similar hardness have a tendency to coordinate with each other, CO_2 should have a greater tendency to accept pairs of electrons from H_2O, NH_3, and $(CH_3)_2O$ (forming electron donor−acceptor complexes in the process) than from pyridine and $(CH_3)_3N$, which is the strongest Lewis base listed in Table 4. Similarly, according to HSAB principles, N_2 and H_2 are more likely than Lewis acids such as I_2 and SO_3 to accept pairs of electrons from CO_2.

Complexation of the CO_2 Molecule with Electron Donors. In principle, the relative importance and strength of CO_2−coal interactions can be inferred from the extent to which CO_2 bends during its complexation with various donors in coal. Such a change in the geometry of the CO_2 molecule has been observed[226] and calculated[227] (Hartree−Fock self-consistent field method, 3-21G* basic set) for CO_2 dissolved in electron-donor solvents, and more extreme cases of bending of the CO_2 molecule as a result of electron donation have been reported for the formation of transition-metal complexes of CO_2.[228−230] For the latter case, Leitner[228] explained that the binding of a transition metal to the C atom of CO_2 results in the net transfer of electron density from the metal to the lowest unoccupied molecular orbital (LUMO) of the ligand. Since the LUMO of CO_2 is an antibonding orbital, such electron transfer should result in a weakened C−O interaction, and according to Walsh's rules,[231] a bent CO_2 molecule similar to a bent CO_2 radical anion[232] is expected. It is important to note that the change in the geometry of the CO_2 molecule resulting from the donation of electrons to the CO_2 LUMO seems to result in an increase in the basicity of the complexed CO_2. Evidence for this lies in the fact that the electron donation results in the CO_2 molecule bending away from the electron donor.[228] This phenomenon is attributable to electron−electron repulsion and the consequent redistribution of electron density to the O atoms of the complexed CO_2 molecule.

Dobrowolski and Jamróz[226] concluded that the splitting of the bending−vibration band of CO_2 dissolved in various electron-donating solvents is caused by the donation of electrons from the solvent to the (electron-deficient) C atom of CO_2. Such interaction results in the formation of what is referred to as an "electron donor−acceptor complex" (i.e., an "EDA complex"). In a follow-up study, Jamróz et al.[227] used an ab initio method to calculate the strength of the bond formed between the electrons of a wide variety of Lewis bases and the C atom of CO_2. Such calculations reflect that, relative to pure CO_2, the formation of CO_2−EDA complexes results in a decrease in the equilibrium O−C−O angle of CO_2, which, in turn, results in an increase in the binding energy between a given electron donor and CO_2.

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Possible Types of Interactions between CO_2 and Anthracites (Dispersion Force Interactions, π-Bonding, etc.). The mechanism(s) by which CO_2 interacts with anthracites is (are) inherently different from those by which CO_2 interacts with lower-rank coals. The reason for this is that anthracites have little intrinsic acid−base functionality. Instead, they are probably primarily associated by London dispersion interactions ("stacking interactions") between polynuclear aromatic systems.[233] Accordingly, anthracites, unlike hydrogen-bonded coals, do not swell in strong bases such as pyridine.[234,235] Yet, CO_2 uptake shows a maximum on anthracites.[86] One possible explanation of these phenomena is that CO_2 sorbs extensively on anthracites by means of London dispersion forces. However, bonding between the extensive π-electron system of anthracites and the (electron-deficient) C atom of CO_2 (π-bonding) cannot be ruled out. A model for such an interaction has been presented by Jamróz et al.,[227] who calculated a binding energy between $CH_2{=}CH_2$ and CO_2 of −1.61 and −1.98 kcal/mol (−6.78 and −8.28 kJ/mol, respectively) for the perpendicular and parallel orientation, respectively, of the ethylene molecule to the plane of the slightly bent CO_2 molecule. Finally, the possibility of significant interactions between the π-electrons of anthracites and the quadrupole moment of CO_2 cannot be disregarded.

Note that whereas the primary CO_2−anthracite interactions may be dispersion force interactions and/or π-bonding, such interactions are not limited to anthracites. They, undoubtedly, may also occur in lower-ranking coals, albeit to a lesser extent than that in anthracites.

Summary and Conclusions. Inferred CO_2−coal interaction mechanisms are dependent on coal rank. For anthracites, the main interaction mechanisms are likely to be London dispersion force interactions, π-bonding, and, possibly, dipole−quadrupole interactions. These types of interactions undoubtedly also occur in lower-ranking coals, but to a lesser extent than that in anthracites. Because lower-ranking coals are enriched with acid−base functionality, including appreciable amounts of hydrogen bonding, it is inferred that the main type of interaction between such coals and CO_2 is acid−base interaction.

EDA interactions seem to transform the ordinary (linear) CO_2 molecule into an appreciably more interactive molecule. Mechanistically, this seems to result from various degrees of electron donation to the CO_2 LUMO[228] and to corresponding degrees of bending of the CO_2 molecule.[227] There is a consequent increase in the CO_2-electron donor binding energy and a redistribution of electron density to the O atoms of the complexed CO_2. That is, the formation of an EDA complex of CO_2 presumably results in an increase in the basicity of CO_2.

Although the CO_2 molecule in an EDA complex may form hydrogen bonds with *unassociated* hydrogen bond donors (e.g., OH and COOH groups), its ability to break *existing* hydrogen bonds in coal is not known, because there are no known accounts in the literature of the calculation or measurement of hydrogen bond energies for CO_2 after it has interacted with coal. Nevertheless, spectrometric methods for characterizing hydrogen bonding in coal have been well-established[236−239] and, accordingly, should be applied to the investigation of CO_2−coal interactions.

Based on HSAB principles,[240] some of the best electron donors in coal for the (hard) CO_2 molecule are ether groups and water molecules, both of which are hard. As indicated previously, the formation of EDA complexes between CO_2 and ether groups or water molecules in coal would increase the propensity of the complexed CO_2 to form hydrogen bonds, at least with unassociated hydrogen-bond donor groups in the coal. However, CO_2−ether group interactions, unlike CO_2−H_2O interactions, could conceivably result in the dissolution of CO_2 in coal and the subsequent swelling of coal without the occurrence of hydrogen bonding. On the other hand, CO_2−H_2O complexation with subsequent hydrogen bonding between the complexed CO_2 and coal could also result in the penetration of CO_2 into coal, followed by coal swelling. In addition, CO_2−H_2O complexes, unlike CO_2−ether group complexes, could have a relatively high degree of mobility in coal; they would be free to move around in coal until they find suitable sites with which to bind.

According to Table 4, organic molecules that contain C=O groups are relatively soft. Nevertheless, the (hard) CO_2 molecule is known to accept electrons from C=O groups in polymers,[241,242] and the extent of such interactions increases with the concentration of carbonyl groups in the polymers. Similar results are expected for the interaction of CO_2 with C=O groups in coal (e.g., those in carboxylic acid moieties), although such an interaction is expected to be weaker than CO_2−ether group interactions and CO_2−H_2O interactions.

Thermochemical Reactions. The CO_2 molecule is not very reactive at normal temperatures. Its thermodynamic stability has been summarized by Freund and Roberts.[243] The high thermodynamic stability of CO_2 greatly limits the number of reactions involving its conversion to other molecules via the breaking of its (strong) C=O double bonds. However, CO_2 is hydrated under mild conditions and subsequently reacts with water to form low concentrations of carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}) ions.

Comprehensive thermochemical studies of the interactions of acids and bases with coal were conducted by Jones[244] on high- and low-mineral-matter bituminous coal samples and high- and low-mineral-matter anthracite. The thermochemical data were supplemented with zeta potentials, showing that coals behave similar to Brönsted−Lowry acids (i.e., donate protons and become negatively charged) when dispersed in basic liquids, and

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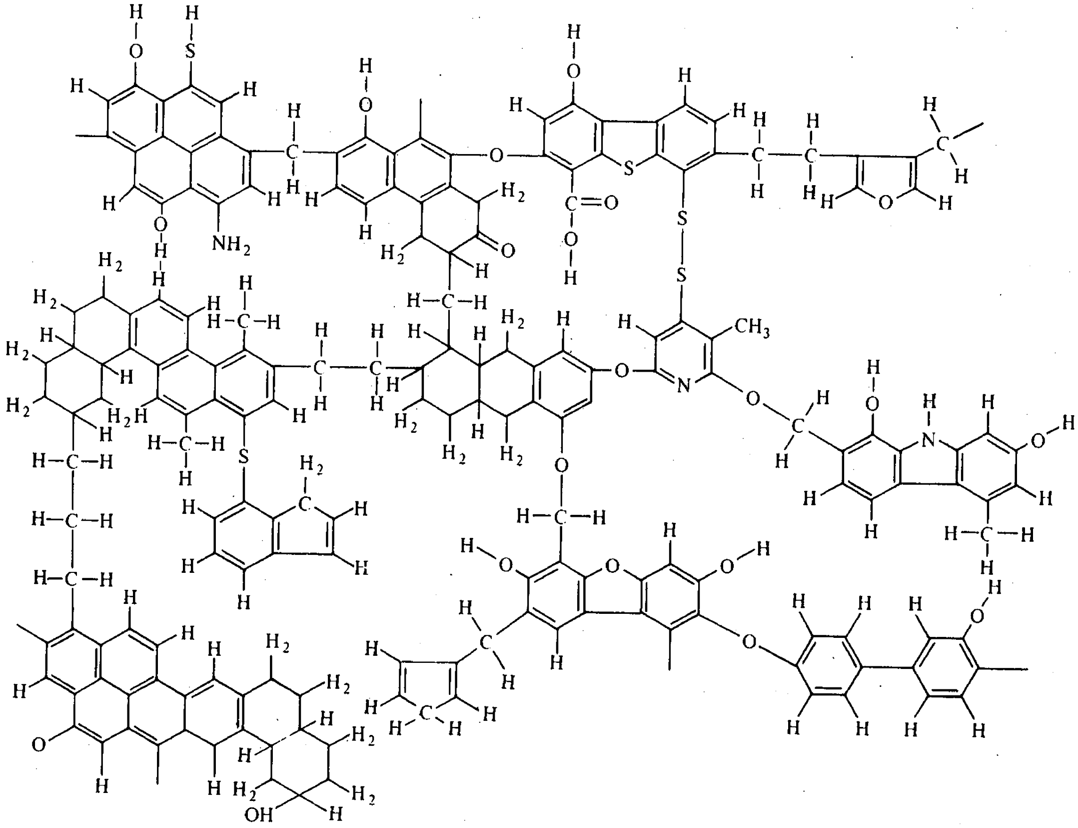

Figure 17. Proposed model structure for the coal macromolecule. (From Essenhigh.[437])

behave as bases (i.e, accept protons and become positively charged) when dispersed in Brönsted–Lowry acids. Morever, Jones[244] found that, when dispersed in amphoteric liquids such as water and aliphatic alcohols, most of the low- and high-mineral-matter coals he studied were predominantly acidic (i.e., they had a tendency to donate protons and, consequently, became negatively charged). The only exception to this was a high-pyrite-content bituminous coal sample which, presumably due to the extreme oxidative weathering of its pyrite, had a high mineral acid content. This mineral acid dissolved in water and aliphatic alcohols and protonated the coal, rendering it positively charged. If CO_2 were injected into coal seams that contained bulk water, the CO_2 could then become hydrated and form carbonic acid, which, in turn, could donate protons, or hydrogen bond to electron-donating N and O sites in the coal.

The basicity of the CO_2–EDA complexes stems from their donation of lone pairs of electrons from the O atoms in CO_2. Sato et al.[245] showed that the specific hydrogen bonding between the O atoms in CO_2 and water molecules makes CO_2 more soluble in water than CO, even though CO_2 is larger than CO and does not have a net dipole moment. The (Lewis) acidity of CO_2 is due to the fact that its C atom is somewhat electrophilic.

In addition to the amphoteric character of coal, the acidity of CO_2, the basicity of CO_2–EDA complexes, and the presence of several different types of acidic and basic sites in coal add to the complexity of the surface chemical interactions of CO_2 with coal during sequestration. This acid–base heterogeneity of coal is shown in Figure 17, which depicts several different types of Lewis and Brönsted–Lowry acid–base sites associated with O, N, and S atoms.

Several different studies directly or indirectly related to the thermochemistry of CO_2–coal interactions have been conducted. In addition to CO_2, such studies have been made with various other acidic, basic, and amphoteric molecules, which either serve as models for CO_2 (e.g., ketones) or whose interactions with coal are based on the same principles as CO_2–coal interactions. Surprisingly, a relatively small number of these studies have involved the use of calorimetry to determine the heats of interaction of CO_2 or CO_2 analogues with coal *directly*. The majority of the studies made thus far have involved the calculation of "isosteric heats" of interaction from sorption isotherms (an *indirect* way to obtain heats of interaction). Although isotherm heats are useful for establishing trends for the interaction of CO_2 with coals for studies conducted by a given research group, it is difficult to compare "isosteric heats" collected by one research group with those collected by another group. Indeed, it is necessary to judge each set of "isosteric heats" published in the literature on its own merits. The reason for such difficulties is that a relatively wide variety of methods and equations have been used to determine "isosteric heats." Some research groups base "isosteric heats" of interaction on the Clausius–Clapeyron equation,[246] whereas others base this parameter

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on a van't Hoff equation[247,248] or derive their own equation.[213,249]

It should be noted that the ΔH value in the Clausius–Clapeyron equation is the heat of condensation of the gaseous sorbate. Hence, utilization of the Clausius–Clapeyron equation to calculate "isosteric heats of sorption" in those cases in which the sorption site density on the sorbent is too low to enable the sorbate molecules to be in intimate contact with each other is not valid. In such a case, all conventional sorption isotherm models should break down. Furthermore, in those cases in which isosteric Clausius–Clapeyron heats of sorption deviate considerably from the heat of condensation of the sorbate, one is forced to consider whether the heat of condensation of the sorbate has been significantly altered, somehow, by sorbate–coal interactions.

One should not expect "isosteric heats" obtained from sorption isotherm data to agree closely with the heats of sorption obtained calorimetrically, unless one is convinced that the sorption mechanism is the same in both cases and that the proper sorption isotherm model was used to calculate the isosteric heats. However, note that calorimeters have the advantage of being able to measure heats of sorption (i.e., *adsorption* and/or *absorption*) accurately, regardless of the packing density of the sorbate,[250] even when the sorbate molecules are not in intimate contact with each other.

Most of the ΔH data reported in the literature for the interaction of CO_2 and CO_2 analogues with coal are expressed in terms of energy per unit mass of coal or energy per unit of coal surface area. A relatively small amount of ΔH data is expressed in terms of energy per mole of sorbate ("*molar* heats of interaction"). These molar heats are more useful than the former, because they enable the assessment of the strength of the interaction of CO_2 (and its acid–base analogues) with coal and, thus, allow one to predict how well a given coal will retain the sequestered CO_2. On the other hand, both sorption isotherm experiments and calorimetry experiments have potential pros and cons, with respect to the determination of accurate *molar* heats of sorption. A benefit for sorption isotherm experiments is that the determination of the number of moles of sorbate sorbed is reasonably accurate. A drawback, as already indicated, is the potential uncertainty in the magnitude of the calculated "isosteric heats." For calorimetry, particularly flow calorimetry, which is the calorimetric method that is most amenable to the study of gas sorption, a positive aspect is that *total* heats of interaction can be determined quite accurately. Another negative is that calorimetric thermograms for CO_2 sorption (sequestration), and even CH_4 desorption (production), have a tendency to be complex signals. Therefore, for greatest accuracy, the signals must be resolved mathematically;[251] however, the literature suggests that very few calorimetrists studying coal seam CO_2 sequestration and/or the concomitant production of CH_4 mathematically resolve their signals. Another negative for calorimetry is that the accurate determination of the number of moles of sorbate sorbed during calorimetry is arduous and requires the synchronization of the signal from the sorbate detector, e.g., an infrared or ultraviolet spectrometer with the heat signal from the calorimeter and an accurate accounting of the sorbate retention time.

Ozdemir et al.[252] calculated molar isosteric heats of CO_2 sorption based on application of the Clausius–Clapeyron equation to sorption isotherm data they obtained on two Argonne Premium Coals—Illinois No. 6 and Upper Freeport. Using the isotherm data without the volumetric correction that they later applied,[190,191] they obtained ΔH values of -14.6 ± 0.8 kJ/mol and -23.8 ± 2 kJ/mol for the Illinois No. 6 and Upper Freeport coal, respectively. Using a flow calorimeter to quantify the heat and a nondispersive CO_2 analyzer to quantify the number of moles sorbed on the coal, Jones[251] obtained virtually the same heat of interaction (−23.3 kJ/mol) as Ozdemir et al. on a predried Argonne Premium Upper Freeport Coal sample. Glass and Larsen[253] obtained an isosteric heat of -27.6 ± 0.8 kJ/mol for the interaction of CO_2 with an original sample of Argonne Premium Illinois No. 6 Coal, based on their application of a van't Hoff equation to inverse gas chromatographic (IGC) data. Although they reported an isosteric heat of adsorption that is almost twice that reported by Ozdemir et al.,[190] the two laboratory results agree well, after the volumetric effects are taken into account.[191] In the most-recent work, Ozdemir et al. reported a heat of adsorption of 26.1 kJ/mol, regardless of rank, for the entire series of Argonne Premium Coals. The observed rank independence seems to exclude significant CO_2–heteroatom interactions. For the Illinois No. 6 coal, a value of 26.6 kJ/mol was obtained, which compares favorably to Glass and Larsen's value of 27.6 kJ/mol. They attribute the slightly lower value to the difference in technique. The IGC experiment, which is performed under conditions approaching infinite dilution, have a tendency to favor stronger adsorption sites, whereas the isotherm heats were obtained at ~37% coverage.[191] The methods used by Glass and Larsen seemed to produce reasonable trends for the 16 basic and amphoteric molecules they interacted with the Illinois No. 6 sample.

A very important finding by Glass and Larsen[247] that is relevant to coal seam CO_2 sequestration is that CO_2 interacts preferentially with the organic component of the coal. Specifically, they obtained almost the same value for the isosteric heat for the interactions of CO_2 with an original sample of the coal (-27.6 ± 0.8 kJ/mol), a sample that had been washed with citric acid to remove mineral carbonates (-26.8 ± 0.8 kJ/mol), and a sample that had been demineralized with HF–HCl (-24.3 ± 0.8 kJ/mol). They suggested that the preferential interaction of CO_2 with the organic component of Illinois No. 6 coal may be related to Drago's concept

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that "like" acids and bases form the "most effective" acid−base complexes.

Huang et al.[254] investigated the thermodynamics of gas "adsorption" on eight Argonne Premium Coals and one Utah hvB coal by gas chromatography. They used three different types of gas probes: the carbon oxides CO_2 and CO; the hydrocarbons CH_4, C_2H_6, C_3H_8, and C_3H_6; and the elementary gases argon, N_2, and O_2. Huang et al. used the same van't Hoff equation that Glass and Larsen[253] used, which enables one to calculate "heats of adsorption" from plots of ln K_p against $1/T$ (where K_p is the Langmuir coefficient of gas adsorption) or, based on the assumption that K_p is directly proportional to the retention volume V_R, from plots of ln V_R against $1/T$ (which is the approach that was taken by Glass and Larsen). For the hydrocarbon gases, the heats of adsorption obtained by Huang et al., using this approach, were, similar to the "nonspecific isosteric heats" of Glass and Larsen, in their own words, "higher...than they should be." These researchers attempted to explain this apparent anomaly on the basis of similarities in the structures of the hydrocarbon gas molecules and the coal structures.

As previously mentioned, Chikatamarla and Crosdale[255] recognized that the proper interpretation of isosteric heats should be dependent on the type of sorption isotherm used. Accordingly, they calculated isosteric heats for the interaction of CH_4 based on two different sorption isotherms: the Langmuir isotherm model for monolayer coverage, and the BET model for multilayer coverage for numerous dry Australian coals ranging in rank from high-volatile bituminous to anthracite. Their isosteric heats based on the Langmuir isotherm model were extremely small and corresponded with sorption data that were independent of the degree of surface coverage. Hence, they concluded that the Langmuir model does not adequately describe the adsorption of methane on dry coals. On the other hand, the (molar) isosteric heats of CH_4 sorption that they calculated from the BET model seem to be quite reasonable. They are similar in value to the heat of condensation of methane (−8.8 kJ/mol) and correspond with sorption data that are dependent on the degree of surface coverage.

Glass and Stevenson[248] calculated isosteric heats for the sorption of CH_4 and other hydrocarbons, both saturated and unsaturated, on Argonne Premium Wyodak sub-bituminous coal. They used the same inverse gas chromatography (IGC) procedures and the same van't Hoff equation used by Glass and Larsen[247] to obtain such data. The calculated isosteric heats obtained by Glass and Stevenson are reasonable. Their values for methane and other saturated hydrocarbons are similar to the heats of condensation of such molecules. This suggests that monolayer coverage of the Wyodak coal by such molecules, as specified by the Langmuir isotherm model, is reasonable.

Ozdemir, Schroeder, and Morsi[246,252,256] used an approach similar to that of Chikatamarla and Crosdale[255] to determine the isosteric heats of sorption for coals. Specifically, Ozdemir et al.[252,256] tested and, to account for the swelling of coal by CO_2, modified several different sorption isotherm models, including the Langmuir model, the BET model, and various pore-volume-filling models (e.g., the D−A model). This approach enabled them to calculate what seem to be reasonable molar heats of sorption.

Jagiello et al.[249] obtained isosteric heats for the sorption of CO_2 and CH_4 on coal from a derived equation that interrelated pressure, the amount of gas sorbed, and temperature. Moreover, their equation enabled them to determine the total work that can be performed by a gas while being liberated from a coalbed (i.e., the "outburst ability" of a gas) at a given temperature and pressure, as well as the decrease in coal temperature during desorption. Their heats for the sorption of CO_2 on three different Polish coals of unknown rank decreased from approximately −36 kJ/mol for low surface coverage to approximately −10 kJ/mol for high surface coverage. This is a reasonable trend because, intuitively, one would expect the CO_2 to sorb onto the more strongly acidic sites on the coal surface first, and then to sorb onto more weakly acidic sites. Their "isosteric sorption heats" for CH_4 were between −20.7 and −23.3 kJ/mol. Such heats are unexpectedly high, because they are 2−3 times the heat of condensation of CH_4.

Using basically the same *derived* equations that he and some of his co-workers used previously,[249] Nodzenski[213] calculated "isosteric heats" for the sorption of CH_4 and CO_2 on four different Polish anthracites at pressures up to 6 MPa (59.2 atm). Generally, the ΔH values that he calculated for CH_4 sorption are unexpectedly large (between −20.1 and −54.3 kJ/mol, which is 2−6 times the heat of condensation of CH_4). In addition, for two of the four anthracites, his isosteric heats of CH_4 sorption were quite similar to those for CO_2 sorption. He offered no explanation for such similarities; perhaps the similarity is due to the fact that anthracites have relatively high carbon contents and relatively low levels of (chemically reactive) acid−base sites, so that the heats of sorption of both CH_4 and CO_2 on the two anthracites under consideration primarily reflect dispersion force interactions.

Starzewski and Grillet[257] used a flow microcalorimeter to determine the enthalpies of CO_2 sorption on a sub-bituminous coal, two different high-volatile bituminous coals, and an anthracite at 30 °C. Using three different schemes for the CO_2 sorption experiments, they obtained ΔH values in the range of −39 to −47 kJ/mol for the sub-bituminous coal (8.2% moisture), −42 to −65 kJ/mol for the two bituminous coals (1.4% moisture each), and −47 to −48 kJ/mol for the anthracite (1.0% moisture). Such heats seem to be reasonable; however, without more information, including the method that was used to determine the number of moles of CO_2 sorbed, it is difficult to characterize the magnitudes of such heats further. It is also difficult to conclude whether it is reasonable for the molar heats for the bituminous coals to be larger than those for the sub-bituminous coal. However, on the surface, such a trend seems counterintuitive.

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Jones[251] used a flow microcalorimeter and nondispersive infrared CO_2 and CH_4 analyzers to calculate molar heats of sorption and desorption related to the sequestration of CO_2 by coal seams and the concomitant production of CH_4 therefrom. He obtained such ΔH values for three different Argonne Premium Coal samples: Upper Freeport bituminous coal, Wyodak subbituminous coal, and Beulah-Zap lignite. These data were collected under two different sets of conditions: (1) after the as-received moisture of the coals had been removed, and (2) while dehydration of the coals was still in progress, up to a final extent of dehydration (determined hygrometrically) of 73%−78%. Condition 1 data were collected for the bituminous coal, whereas Condition 1 and Condition 2 data were obtained for the sub-bituminous coal and the lignite. Relative to the predried condition, methane production during CO_2 sorption for the sub-bituminous coal under Condition 2 was accompanied by increased molar heats of CO_2 sorption and increased molar heats of CH_4 desorption. Such results suggest that the presence of moisture in the coal during CO_2-ECBM/sequestration affects both the adsorption of CO_2 and the desorption of CH_4.

In the aforementioned study, Jones observed that methane production levels were enhanced whenever the molar heat of CO_2 sequestration was more negative than a certain value, which was within the range of −36 to −52 kJ/mol. Note that such ΔH values are similar to those determined calorimetrically by Starzewski and Grillet for the sorption of CO_2 on a low-moisture sub-bituminous coal.[257] Moreover, he observed evidence that a fraction of the sequestered CO_2 was irreversibly sorbed when the sub-bituminous coal and the lignite were extensively dehydrated. Such observations may be related to the following phenomena: (i) water sorbed at relatively high surface concentrations can hinder the transport of gases through coal via swelling and decreased permeability effects,[145] especially when the surface coverage of the water is at least a monolayer; and (ii) water sorbed at less-than-monolayer coverages can be beneficial, because it can enhance CO_2 retention by catalyzing the chemisorption of CO_2 at dehydrated coal surface sites (e.g., such water can promote the reaction of proton-donating coal sites with CO_2 to form bicarbonated coal). Initially, CO_2 injected into coals whose water surface coverage is at least a monolayer is believed to bond mainly to the sorbed water. As more and more coal surface sites become dehydrated, the CO_2 is more free to interact directly (either physically or chemically) with acid−base sites on the coal surface. Because lower-rank coals have a tendency to have significant levels of carboxylic acids,[258] and because carboxylic acids are more strongly acidic than water, one would expect the molar heat of CO_2 sorption to be larger for extensively dehydrated low-rank coals than for the as-received (high-moisture) coals.

Possible insight into the previously described phenomena can be found in a paper published by Nishino,[259] who compared the sorption of water vapor with that of CO_2 on 20 different demineralized coals, whose carboxyl group content ranged from 0.04×10^{-3} to 2.40×10^{-3} equiv/g-coal. This worker concluded that the carboxylic acid functional groups of coals may be considered to be the preferential sites for CO_2 (and H_2O) sorption, when compared with hydroxyl groups (e.g., the −OH groups of phenols), even when the −COOH groups are fewer in number than the −OH groups.

III. How CBM Recovery and CO_2-ECBM Recovery Are Performed

In reservoir engineering terms, coalbeds are naturally fractured, low-pressure, water-saturated reservoirs, where most of the gas is retained in the micropore structure of the coal by physical adsorption. A reservoir is that portion of the coal seam that contains gas and water as a connected system. Thus, coal serves as a reservoir and a source rock, containing relatively pure methane. Compared to conventional gas reservoirs, coal reservoirs have low effective porosity and high compressibility and are dominated by gas adsorption.

Gas stored by sorption in the coal matrix accounts for ~95%−98% of the gas in the coal seam.[260,261] The remaining gas is stored in the natural fractures, or cleats, either free or dissolved in water. Consequently, the gas produced from the cleat system can be described by Darcy's Law. Darcy's Law is used in reservoirs with a simultaneous flow of more than one fluid by considering the effective permeability of each flowing phase, which is a function of saturation. Thus, relative permeability curves are used to define the effective permeability of a flowing phase at a specific saturation. Most of the gas flows by diffusing through the coal matrix into the cleat system, which is then produced through desorption from the cleat surfaces. Thus, gas that is produced from coal is the result of desorption and diffusion. In the desorption transport process, CH_4 molecules exit the micropore surfaces of the coal matrix and enter the cleat system. The relationship between the adsorbed gas concentration and the coal matrix and the free gas in the cleats is described in an adsorption isotherm. The diffusion process represents the flow of gas from an area of high concentration to an area of low concentration. The diffusion process in the matrix is described by Fick's Law. In practice, the diffusion coefficient is related to a sorption constant by the cleat spacing. The dual transport mechanism of CH_4 in matrix and cleats determines the primary behavior of gas production in coals.

Physical adsorption can be reversed by reducing the partial pressure of adsorbed species. In the field, this translates to a reduction in the hydrostatic pressure of the system through dewatering.[262] This is the first stage of primary depletion, when water, or water and some gas, is produced. In this stage, gas and water flow at relatively constant rates until a pseudo-steady state is attained. At the end of this stage, the well reaches its minimum bottom-hole pressure. A second stage begins at the pseudo-steady state and is characterized by a decline in gas production and a declining water rate. In this stage, the relative permeability to water de-

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creases, the relative permeability to gas increases, and changes in gas desorption rate are observed. Outer boundary effects become significant at the end of this stage. A third stage starts when the gas rate has peaked and water production is negligible. A mild gas production decline is observed and is continued for years, and negligible changes in relative permeabilities are observed. This final stage represents most of the economic life of a coal well.[263] These three stages of primary coal gas depletion can be observed in Figure 1.

On the basis of this short description of the primary gas production from coals, two parameters are determined to have an important role in evaluating a CBM prospect: the total gas-in-place and the reservoir gas deliverability. The total gas involves data obtained from a variety of sources such as well logs, core testing, and well/production testing. Two methods to determine gas-in-place are available: volumetric and material balance.

The volumetric method is the summation of the gas stored through adsorption in the matrix and the free gas in the cleat system:

$$\text{total gas-in-place} = \text{free gas} + \text{adsorbed gas} \quad (11)$$

The free gas can be expressed as

$$\text{free gas} = \frac{Ah\phi_{\mathrm{f}}(1 - \mathrm{S}_{\mathrm{wfi}})}{B_{\mathrm{gi}}}$$

where h is the thickness (in meters), A the drainage area (in square meters), ϕ_{f} the interconnected fracture porosity (fraction), B_{gi} the gas formation volume factor, and S_{wfi} the interconnected fracture water saturation (fraction).

The adsorbed gas is calculated using the following equation:

$$\text{adsorbed gas} = Ahr_{\mathrm{c}}C_i(1 - f_{\mathrm{a}} - f_{\mathrm{m}}) \quad (12)$$

where r_{c} is the bulk coal density (given in units of g/cm^3), C_i the gas content (m^3/ton), f_{a} the average weight fraction of ash (fraction), and f_{m} the average weight fraction of moisture (fraction).

Geologic evaluations and conventional logarithmic analysis are needed to determine the thickness, density, continuity, coal seam extent, coal characteristics, fractures, and faults. Well testing is needed to calculate the drainage area and permeability of the cleat system.

For reservoirs where the volumetric method cannot be applied, King[264] developed a material balance method for coal seams and shales by adding terms to account for the sorption mechanism in these media. The generalized equation assumes an equilibrium between the free and adsorbed gas phases. The method is a modified p/z^* method and can be applied to analyze nonvolumetric behavior of a coal seam.[265] For the successful application of this method, reliable production, pressure, and pressure−volume−temperature (PVT) data are needed. Using this method, future gas and water production can also be predicted.

Gas deliverability of a coal reservoir represents the ability of the reservoir to produce gas through a well, or a system of wells. Theoretical description of coal well deliverability is complicated by two-phase flow considerations. Wells produce significant quantities of water at the early stage, and after the drainage area of the coal well has been dewatered, water production becomes negligible. Most of the productive life of the well, which spans 10 to 20 years, can be conceptualized as a dry gas well producing minimal amounts of water. Because the gas is stored by sorption in the coal, a low bottom-hole pressure is required to recover a large amount of the original gas-in-place. A real gas pseudo-pressure is required to treat such cases rigorously. Seidle[263] developed equations for gas flow in a dewatered coalbed, based on the pseudo-pressure method. Seidle's equation can be used to construct gas deliverability curves for a coal well. The deliverability equation is dependent on gas pseudo-pressure, effective gas permeability, well radius, reservoir drainage radius, skin factor, reservoir height, and a non-Darcy flow constant. It was observed that two types of factors control well productivity: factors related the physical properties of the reservoir and project development factors.[265]

The physical reservoir properties are related to the spacing and continuity of the cleat system, the amount of gas stored, relative permeability characteristics, and desorption isotherms. The continuity of the fracture system is quantified by permeability, which, in turn, is dependent on reservoir pressure. The interactions between gas, water, and coal are quantified by relative permeability and capillary pressure curves. The tendency of the coal matrix to release stored gas is quantified by the diffusion coefficient and desorption isotherms.[265]

The project development factors that control well productivity are well stimulation, well type, and well spacing. Most coal wells are stimulated to obtain economic rates of gas production. Well stimulation can be defined as a set of practices necessary to improve the flow of fluids around the wellbore. In coal seams, the most common practices are "cavity completions" and hydraulic fracturing. The cavity completion is an open-hole enlargement procedure, which increases well productivity by increasing the wellbore radius. Hydraulic fracturing is used to produce fractures in the coal seam that can modify the flow in the wellbore from radial to linear. Coal wells can be drilled vertically, horizontally, or parallel to the bedding plane. The advantage of slanted or horizontal wells is that a larger portion of the reservoir can be contacted. In naturally fractured reservoirs, such as coal seams, horizontal wells can intersect the fractures and drain them more effectively.

Numerous technological advances that have been noted previously, such as horizontal drilling capabilities[266,267] and hydraulic fracturing methods,[13,15,268−277]

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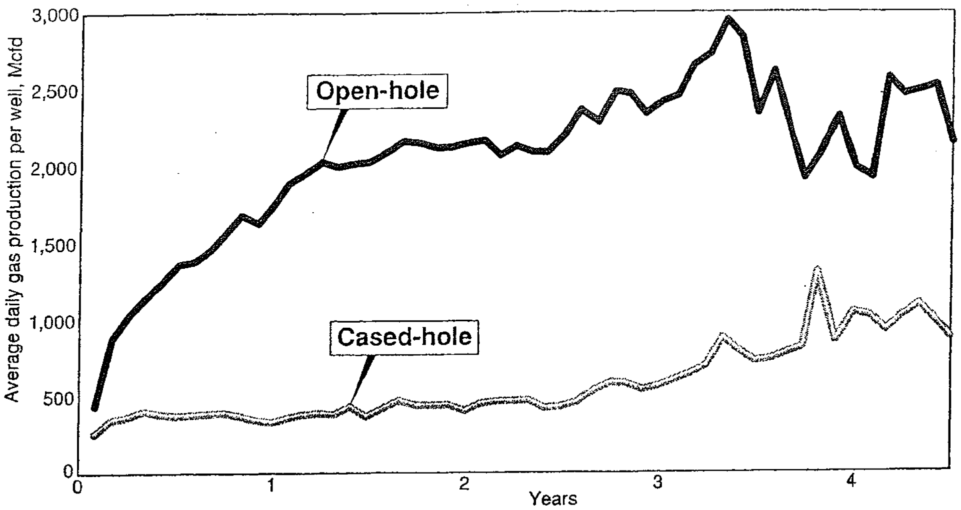

Figure 18. Average well performance in the Utah Fairway. (From Stevens et al.[284])

have significantly improved CBM production, so that ~50% of the CBM in place could be recovered. These advances are responsible for improving conventional CBM pressure depletion wells, in many cases, to profitable production wells and also for developing technology vital to successful ECBM, CO_2-ECBM, and CO_2-ECBM/sequestration operations. McDaniel[278] traced the historical application of hydraulic fracturing in two major U.S. commercial CBM producing areas: the Black Warrior basin and the San Juan basin.

Well spacing and well patterns have an important role in production optimization. Most commonly, five-spot patterns of different area/spacing (40, 160, 320 acres) are used, depending on reservoir conditions. The degree of well interference, which is related to well spacing, also has an important role in economic gas recovery. The degree of well interference is affected by permeability and well stimulation. In addition to the factors discussed previously, compressibility effects, initial gas saturation, and hydrodynamic influences (such as water influx from aquifers) can influence CBM well productivity.[279−281] Thus, geologic evaluations are important for determination of the continuity of coal fracture system and faulting.[282,283] A communication between coal seams and groundwater sources can make it difficult to dewater the reservoir and reduce reservoir pressure.

It has been clearly shown in the San Juan basin that open-hole cavitated wells significantly outproduce wells that have been conventionally cased and fractured completions, as shown in Figure 18.[284] Dynamic open-hole cavitation is accomplished by injecting water/air mixtures into the coal seam multiple times, followed by rapid depressurization. This process encourages sloughing of the coal into the wellbore, resulting in an increased diameter wellbore by several feet.

Hydraulic stimulation increases the degasification rate of coalbeds. The flow rate of gas in a coalbed is a function of permeability and pressure of the seam. Increased methane desorption rates can be achieved by increasing the coalbed permeability. This, in turn, is accomplished by increasing the surface areas that are available for more rapid degasification. Hydraulic fracturing of coal seams in the eastern United States result in 5-fold to 20-fold increases in gas production rates. A complete description of how this is accomplished may be found elsewhere.[268]

Advances in reservoir simulation contributed to the development of CBM production. Dual-porosity compositional simulators can provide accurate production estimates and can be used to assess the influence of

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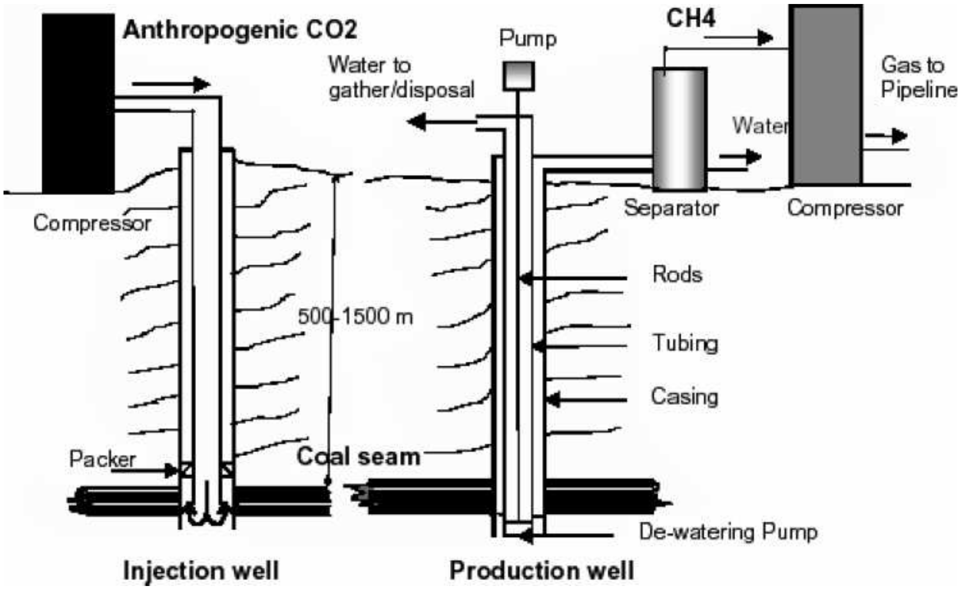

Figure 19. Surface and subsurface equipment for CO_2 injection and CH_4/H_2O production and well configuration. (From Hamelinck et al.[21] Also available via the Internet at http://www.chem.uu.nl/nws/www/publica/e2001-07.pdf.)

reservoir and project development parameters on production.[265,285] However, despite all the advances in geologic evaluation, reservoir characterization, simulation, and well development, the primary field recoveries reported are low, and a large fraction of the gas remains in the reservoir. The gas that remains in the reservoir after primary production can be partially recovered, using advanced recovery techniques, which are discussed below.

Primary CBM recovery is begun by identifying a coal seam that has sufficiently high CH_4 content to make it economically worthwhile to recover. Initially, the reservoir is drilled vertically, possibly horizontally, and sometimes fractured. The CH_4 present in the coal diffuses from an area of higher pressure within the coal to an area of low pressure at the bore holes. The seam is allowed to naturally depressurize with time. The rate of diffusion of CH_4 from coal can be increased by pumping water out of the seam. The formation pressure declines as gas is produced. This method produces large amounts of formation water for disposal.[151] Dewatering the coal causes the coal structure to collapse and shrink, changing the chemical and physical properties of the coal.[286] Removing moisture from high-rank coals and the changes associated with it seem to be reversible.[287,288] However, the changes associated with a loss of moisture from low-rank coals are irreversible, because collapse of the molecular structure results in the formation of new intermolecular interactions in the macromolecular network. Low-rank coals shrink and visibly crack when dewatered. The primary production of CH_4 results in the recovery of 20%−60% of the CH_4 in the coal.[289,290]

The remaining CH_4 is recovered by drilling additional wells—at least an injection well and one recovery well. Typically, there are multiple recovery wells and one injection well that are arranged in a five-spot pattern, although other well patterns, such as a three- or a seven-spot pattern could also be applied.[21] A schematic diagram of the CO_2-ECBM process, showing both the surface and subsurface facilities, is shown in Figure 19. CO_2 is injected into the injection well and methane, water, and coal fines (and sometimes oil) are recovered from the recovery well. This technique increases the production of methane per unit time by reducing the partial pressure of CH_4 in the coal and by CO_2 displacement of CH_4 from sorption sites within the coal.

CH_4 production occurs by displacement chromatography during CO_2-ECBM/sequestration. CH_4 is desorbed from the coal matrix and CH_4 production increases. CH_4 production, as a function of time, for several production scenarios is depicted in Figure 1.[13,151] Note that ECBM recovery has been performed using N_2, or combustion gases, as well as CO_2. The CH_4 is recovered by displacement, desorption, or inert gas stripping. For CO_2, the mechanism is primarily the desorption of CH_4. As the production data in Figure 1 indicates, more CH_4 is recovered from a given coal seam using CO_2-ECBM recovery techniques than simple primary recovery, and that production occurs over a shorter time. When BP−Amoco used a mixture of CO_2 and N_2 as the injection gas, little CO_2 was detected in the production well after 18 months, whereas N_2 ap-

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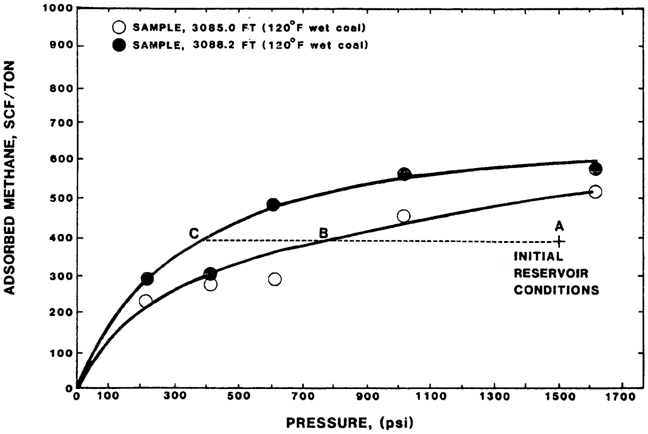

Figure 20. Adsorption isotherm for the Fruitland Formation Coal-Glover No. 1 well. (From Jones et al.[294])

peared at the production wells within weeks.[291] Gunter et al. mentioned the possibility of injecting combustion gases from an electric power generating plant directly into a coalbed and speculated that any SO_x or NO_x in the flue gas would not find its way to the production well.[292] In fact, Conoco and Bugas performed a similar experiment with diesel engine combustion gases injected into a coalbed.[293] Gunter et al. also speculated, in the case of sequestration of raw combustion gases into a barren coal seam, that it may be possible to produce a stream of N_2 at the production well.[292]

Use of Adsorption/Desorption Isotherms in CH_4 Production. The primary recovery of CH_4 from coals is dependent on several factors, such as desorption pressure, static coalbed pressure, temperature, nature of the desorption isotherm, seam thickness, absolute permeability, directional permeability, relative permeability, porosity, diffusion, capillary pressure, irreducible water saturation, and pore compressibility. When ECBM recovery is performed, the nature of the mixed gas adsorption/desorption isotherms are also critically important.[196] Undersaturation of coal, with respect to methane, under initial reservoir conditions, has major implications, with respect to well design and production operations, as well as reservoir planning.[294]

The methane adsorption isotherm controls the onset of CH_4 evolution, as shown in Figure 20. The initial reservoir pressure in the coal seam in the vicinity of the Glover No. 1 well in the Fruitland Formation (point A) was ~1500 psi (102.07 atm). According to the isotherm, no CH_4 will be desorbed from the coal until the reservoir pressure decreases below 750 psi (51.03 atm). No gas is desorbed between point A and B (see Figure 20). When the seam pressure decreases as a result of a hole being drilled into the seam, the reservoir pressure decreases until it corresponds to the saturation pressure. At this point, CH_4 may begin to desorb from the coal. Furthermore, if the coal seam is thick and has high permeability, a higher capacity pump will be needed to pump water at a high enough rate to reduce the downhole pressure sufficiently to begin methane production. Another possibility is to drill multiple holes into the seam and pump each one sufficiently to reduce the pressure to the point of CH_4 desorption. According to isotherm B (see Figure 20), after the pressure has been reduced to 400 psi (27.22 atm), ~300 scf/ton (8.49 m^3/ton) of gas is still adsorbed. (Note: scf denotes standard cubic feet.) Only 80 scf/ton (2.265 m^3/ton) of gas will be desorbed by reducing the reservoir pressure by 1000 psi (68.04 atm). Reducing the reservoir pressure to 50 psi (3.40 atm) will allow another 300 scf/ton (8.49 m^3/ton) to be produced.

When attempting to produce CH_4 from low-permeability coalbeds, long, high-conductivity fractures are needed. Such fractures can be provided by drilling laterally into the seam to result in commercially acceptable CH_4 production rates.[294,295] If the CH_4 desorption rate from the coal matrix and diffusion through the butt cleats is higher than the flow rate in the face cleats, then CH_4 production is "flow-limited" and is driven by pressure and can be modeled by Darcy's Law. On the other hand, if the CH_4 diffusion rate from the coal matrix and into the butt cleats is slower than the rate in the face cleats, then CH_4 production can be modeled by Fick's Law and is "diffusion-limited" and concentration-driven.[151] Cervik[128,129] first showed that CH_4 flow through coalbeds was a combination of Darcy and Fickian transport.

The sorption isotherm of a coal is the amount of gas that can be stored in a coal at a particular temperature, as a function of reservoir pressure. It is the maximum amount of gas a coal can sorb, and if the coal is fully saturated, it is also the maximum possible amount of gas-in-place. The sorption isotherm is a laboratory measurement that is made on a representative specimen of the coal seam to ascertain the gas storage capacity, as a function of pressure at a constant temperature. The term "isotherm" results from the constant temperature aspect of the measurement. A recent manuscript by Mavor et al. describes the procedures for performing the measurements and methods to interpret the experimentally derived data to estimate the gaseous storage capacity and diffusion coefficients of the coal matrix.[296] The sorption isotherm can be used to determine if a coal is saturated or undersaturated, with respect to a gas. Information in the isotherm can be used to provide an estimate of methane recovery. Figure 21 shows an idealized gas sorption isotherm for two coals: one saturated with CH_4 and the other undersaturated. This figure shows the relationship between gas content and reservoir pressure.[46] When the information present in the adsorption isotherm is combined with the CH_4 content of the seam, one can make estimates of the CH_4 production potential of the seam. Coal A (see Figure 21) contains ~18.2 cm^3/g (18.2 m^3/ton) of CH_4 at a seam

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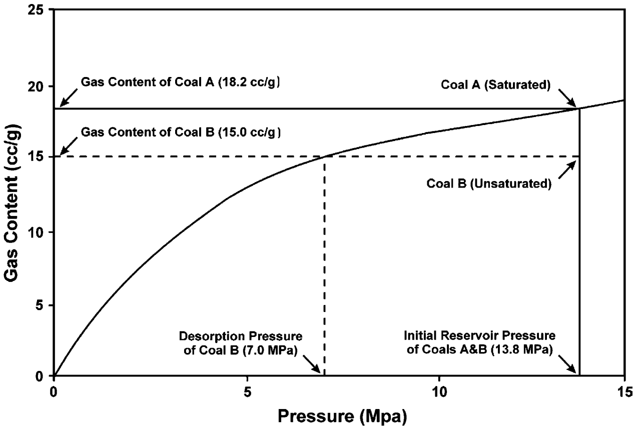

Figure 21. Idealized coalbed gas sorption isotherm showing relation between reservoir pressure and gas content for a (A) saturated and (B) undersaturated coal. Heavy solid line indicates the maximum amount of gas that can be stored at given reservoir pressure. (From Rice et al.[46])

pressure of 13.8 MPa (136.2 atm). Thus, it is saturated with CH_4 and will begin to desorb CH_4 immediately. Coal B is undersaturated, with respect to CH_4, containing 15.0 cm^3/g (15 m^3/ton), at a seam pressure of 13.8 MPa (136.2 atm). Consequently, the seam must be depressurized to ~7.0 MPa (69.08 atm) before coal B will begin to desorb CH_4.[46]

Lee compared the field desorption results from 10 San Juan basin wells with results from the isotherms obtained in the laboratory and found that, in 8 of the 10 instances, the field results were considerably lower than the equilibrium value obtained from the laboratory measurements.[297] This disparity could be the result of hysteresis effects that cause the adsorption and desorption isotherms of CH_4 on coal to be slightly different. The desorption isotherms have a tendency to be more nonlinear. This effect translates into requiring the coalbed to be drawn down to pressures lower than those expected to achieve the same level of CH_4 release.[298]

Enhanced Coalbed Methane (ECBM) Production. *Process Definition.* ECBM may consist of various gas recovery processes (gas drive, huff and puff, well stimulation) and could cover many recovery agents (N_2, CO_2, flue gas, compressor gas, and other industrial off-gases). This notion should not restrict ECBM to a particular phase in the reservoir production recovery sequence, such as primary, secondary, or tertiary.[299] Numerous patents documenting ECBM have been issued.[14,15,300−305,307−309] Most of these patents focus on N_2 or CO_2 injection. Thus, the two principal and best-documented ECBM processes are N_2 injection and CO_2 injection. A combination of both methods is also listed as being possibly useful for achieving optimal economical recovery of CBM and/or economics.

N_2-ECBM. N_2-ECBM was initiated in the early 1990s as an alternate method of primary CBM recovery. In conventional primary recovery, the loss of reservoir pressure reduces the available energy until fluids stop flowing into the wellbore, resulting in low CH_4 recoveries. Laboratory research has shown that CH_4 sorbed on coal was stripped by N_2 without reducing the system pressure.[310] Moreover, with the energy supplied by N_2 injection, the reservoir pressure could be maintained or increased while concomitantly desorbing CH_4 from the coal matrix and allowing it to diffuse through the cleat network system. With this method, up to 90% of CH_4 contained in the matrix can be recovered from homogeneous coal reservoirs.[299]

The first N_2-ECBM field test in a CBM reservoir was conducted by BP−Amoco in 1993.[284] The test pattern was a five-spot arrangement with four N_2 injection wells and a central producer. The test was conducted in the northwestern part of the San Juan basin, and the test was successful. The production well was producing 200−250 million cubic feet of gas per day (MMCFD) ($5.66 \times 10^6 - 7.08 \times 10^6$ m^3/day) before N_2 injection; however, approximately a month after injection, production climbed to 1400 MMCFD (39.64×10^6 m^3/day) and remained near that level for most of the year-long test. It was calculated that the average gas production increased 5-fold.[311] Encouraged by this first N_2 injection pilot success, BP−Amoco and Meridian undertook a four-well CO_2 flood pilot in late 1993; however, performance results have not been released.[284]

CO_2-ECBM. Laboratory isotherm measurements demonstrate that medium- to high-rank coal can adsorb approximately twice as much CO_2 by volume as methane.[310] The common assumption is that, for higher-rank coals, the ECBM process stores 2 moles of CO_2 for every mole of CH_4 desorbed. Stanton et al.[34] determined that some low-rank coals may adsorb as much as 10 moles of CO_2 for every mole of CH_4. Field applications and laboratory experiments showed that this ratio could be even larger at depths greater than ~800 m, where the gaseous CO_2 changes to supercritical CO_2.[199] The depth interval for CO_2-ECBM is expected to be the same as that for CBM production (1000−5000 ft (304.8−1524 m)); however, the production increase due to CO_2 injection requires more time to develop than when N_2 injection is used. This is due to the sorption of CO_2 near the well. The sorbed CO_2−CH_4 front is expected to grow

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elliptically out from the injection wells, because of coal anisotropy. After a sufficient volume of CH_4 has been displaced for gas drive to become effective, the CH_4 productivity increases. When CO_2 breaks through in the production well, the project would then be terminated. Therefore, CO_2-ECBM is potentially capable of providing storage for anthropogenic CO_2, as well as improving the production of CBM.[289] (Also, see subsections entitled "Adsorption Isotherms of Gases on Coals," "CO_2-ECBM," "Burlington Resources, Allison Unit CO_2-ECBM Pilot", and "Estimated Amounts of CH_4 in Coal" in this review.)

Flue Gas ECBM. This is an alternative approach that can be considered to be a combined N_2-CO_2 injection. For N_2 injection, early N_2 breakthrough at the production wells results in additional operational costs to separate N_2 from CH_4 before sale. According to Gale and Freund,[289] combining CO_2 and N_2 injection may improve the economics, because the appearance of N_2 will be retarded, compared to N_2 injection alone, and the total CH_4 production will be increased by the addition of CO_2. To date, however, there is only a small amount of research in regard to the injection of flue gas into geological formations. The Alberta Research Council has now performed a single-well micropilot test with flue gas injection, the results of which are now being evaluated.[312]

Injection Well Characterization (Injection Methodology, Well Completions, Well Testing). Characterization of injection wells used for ECBM or sequestration is crucial to the development of an understanding of reservoir response, and for managing the reservoir for maximum CH_4 production or CO_2 sequestration.[313] The experience gained from CO_2 injection for EOR shows that a reservoir pilot injectivity test is one of the most reliable predictors of field performance. The test provides a direct measurement of reservoir injectivity for at least one well. However, the results from a single injector must be treated with caution, because they provide only indirect information about full field performance. Injectivity can vary considerably for different wells in the same field and for the same well, given different operating conditions.[314] For interpretation of ECBM recovery pilots, the injectors are tested before the start of the injection and during the injection. Some well-testing methods for injectors are briefly discussed below.

Step Rate Tests. Step rate tests are conducted to determine fracture parting pressure in injection wells.[315] A step rate test is simple, inexpensive, and fast. Fluid is injected at a series of increasing rates, with each rate lasting the same amount of time. In low-permeability formations such as coals, each injection rate should last at least an hour. As few as four rates are used, but normally six or seven rates are preferred. The analysis consists of plotting injection pressure at the end of each rate versus injection time. The plot should have two straight-line segments. The break in the line indicates the formation fracture pressure.

Seidle et al.[313] addressed the step rate tests conducted in the injectors of a N_2-ECBM field test to determine the fracture parting pressure. Beginning with a N_2 injection rate of 400 MCFD (11.3×10^6 m^3/day), the rate was stepped up by 400 MCFD (11.3×10^6 m^3/day) every 2 h up to a maximum injection rate. The maximum injection rate in the first well was 3.2 MMCFD (90.61×10^6 m^3/day) at a calculated bottom-hole pressure of 1660 psia (112.95 atm). Throughout both tests, operational constraints made it difficult to maintain constant injection rates, reducing confidence in the data. The high-rate data are especially suspect. One of the key features of these tests is their sensitivity to rate variations and, consequently, every effort should be made to maintain stable rates within each given step. Interpretation of both these tests was difficult due to their unorthodox behavior. Because no clear fracture parting pressure was apparent from either of the step rate test plots, pressure gradients associated with the maximum injection rates were calculated and compared with fracture gradients for this coal deposit obtained from stimulations performed on several wells in the test unit. The maximum pressure gradient for the first well step rate test was the same as that observed in the fracture stimulation, whereas the maximum gradient observed in the second well test was only 90% of that observed during the fracture stimulation. These gradients were associated with only the highest injection rates. Pressure gradients corresponding to normal field injection conditions were substantially lower than the fracture parting gradients. It was concluded that, during normal operations, N_2 injection would not part the formation.

Injection/Falloff (IF) Tests. An injection/falloff (IF) test measures the pressure decline after the closure of an injection. It is conceptually identical to a pressure build-up test. The IF test interpretation is difficult if the injected fluid is different from the original reservoir fluid.[316] The IF test has become the most common test for estimating reservoir properties of CBM and other low-permeability reservoirs. IF tests are used to estimate permeabilities of wells that do not flow naturally, such as CBM wells. Other useful information extracted from an IF test are wellbore condition and average reservoir pressure.[313,317] Wellbore condition is quantified in the petroleum literature as damage or improvement in the operating (producing or injecting) wells. The most common method represents the wellbore condition by a steady-state pressure decrease at the wellface, in addition to the normal transient pressure in the reservoir. This additional pressure decrease is called the "skin effect" and the degree of damage (or improvement) is

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called the “skin factor.”[315] An excellent testing procedure for IF tests in coal seams, including the test tools and the interpretation procedure, is given by Badri and Clare.[318]

Hall Plots. Hall plots have been used in waterflooding of conventional oil reservoirs to detect, among other things, changes in wellbore condition. Hall’s technique for analyzing injection wells assumes a series of steady-state injection conditions. Based on an integral form of Darcy’s Law, a Hall plot is a graph of a summation approximation to a pressure integral versus cumulative injected water. Following the method of Hall for water injection wells as described by Earlougher,[315] it is possible to derive an equation for a Hall plot that is associated with a CO_2 or N_2 injector.[313] Essentially, an integral over time of the pressure-squared form of Darcy’s Law for gas flow can be used to construct Hall plots for the injectors.

Gas Injection and Injectivity. Injection wells for CO_2-ECBM are similar to those used in EOR operations. Stainless-steel or fiberglass tubulars, which are corrosion-resistant, can be used but are not necessarily needed, provided that the CO_2 has been dehydrated. Injection wells are completed by setting the surface casing to a specified depth of ~350 ft (106.68 m). The well then is drilled in the coal formation and the production casing is then cemented across the coal zones and perforated. Acidization and hydraulic stimulation are generally avoided, to reduce the risk of connecting to natural conduits that could channel injected CO_2 outside of the targeted coal reservoir.[290,313] The wellhead injection system should be capable of handling a working pressure of at least 2000 psi (136.1 atm).

To quantify the injectivity of ECBM injection wells, an injectivity coefficient (J) can be calculated[317] as

$$J = \frac{Q_{\mathrm{inj}}}{k_{\mathrm{g}}h(m(P_{\mathrm{inj}}) - m(P_{\mathrm{avg}}))} \tag{13}$$

Here, J is the injectivity index (in units of MCFD cP/(mD ft psi^2)), Q_{inj} is the gas injection rate (in MCFD), k_{g} is the effective permeability to gas (in mD), h is the thickness of the coal seam (in feet), $m(P_{\mathrm{inj}})$ denotes the real gas pseudo-pressure (in psi^2/cp; P_{inj} is the bottom-hole injection pressure (the pressure at shut-in)), and $m(P_{\mathrm{avg}})$ is the average reservoir pressure from well testing calculations. The injectivity coefficient is used to estimate the CO_2 injection pressure and flow rates in an injection well. These calculations also can be used to size compressors for ECBM and sequestration projects.

The injectivity of CO_2 is dependent on coal permeability and reservoir pressure. Several experimental studies investigating the effects of stress on coal permeability have been reported in the literature,[319] and that research has indicated that coal permeability declines exponentially with depth.[133,320,321] CO_2 sorption on coal causes the matrix to swell, decreasing cleat width and, consequently, permeability. Conversely, the injection of CO_2 increases the reservoir pressure, decreasing the confining pressure on the cleats, thereby increasing permeability. The maximum injection rate is then the product of two competing terms. Maximum injection pressure increases as the square of depth, whereas permeability declines exponentially. As depth increases, the gas injection rate at first increases, then reaches a maximum value, and finally declines as the exponential term dominates.[321]

Reservoir Screening Criteria for ECBM with CO_2 Sequestration. Some geological settings are inappropriate for coal seam sequestration. Generally, a thick, deep coal seam that contains significant quantities of CH_4, that has good porosity and permeability and a continuous capping seal with minimal folding and faulting located in a tectonically stable area is desirable. Areas of significant folding and faulting pose the possibility of CO_2 and/or CH_4 being released to the surface in large quantities along open fractures. The seam should be laterally continuous and vertically isolated. The coal seam should be overlain by a laterally extensive aquitard (such as shale) or an aquiclude (such as an anhydride or salt layer), so that CO_2-laden waters that originate in the coal seam cannot migrate to overlaying formations that are shallower (of less pressure) and eventually to the surface. A permeability of at least 1−5 mD as a lower bound is needed to permit water to freely flow through the coalbed.[18]

Reservoir screening criteria are needed to locate areas favorable for successful application of CO_2-ECBM. Stevens et al.[290] developed preliminary criteria, similar to those established for EOR injection-based processes, such as waterflood, miscible, and steamflood operations. Some of those criteria were expanded and refined, based on the results of reservoir simulations. Experience with EOR suggests that screening criteria will continue to evolve for some time. These initial criteria are as follows:

(a) Homogeneous, isolated reservoir: The coal reservoir(s) should be laterally continuous and vertically isolated from other coal seams. This will help containment of the CO_2 injectant within the reservoir and lead to efficient lateral sweep through the reservoir. Ideally, the coal seam should be encased in impermeable rock, such as shale.

(b) Simple structure: Coals should have minimal faults and folding. Open faults and joints provide migration pathways for CO_2, whereas sealing faults compartmentalize the reservoir.

(c) Adequate permeability: Moderate cleat permeability is necessary for effective ECBM (1−5 mD). Lower permeability may be acceptable if coal has adequate injectivity and thickness.

(d) Optimal depth window: The low reservoir pressures of shallow coal limits the amount of CO_2 they can hold. The stresses of deep coals may decrease perme-

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ability below acceptable limits. This point is addressed in more detail below.

(e) Coal geometry: Few, thick coal deposits are favored over stratigraphically dispersed (multiple, thin seams) settings spread over a large interval.

(f) Gas saturation conditions: For ECBM recovery, coals saturated with CH_4 are preferred over undersaturated coals. From a sequestration viewpoint, undersaturated coal seams are still effective CO_2 disposal zones. For CO_2 sequestration, this criterion should be perhaps replaced by a hydrology constraint. Water movement through a coal deposit may displace CO_2 and transport it out of the deposit. Thus, the hydrology of candidate coals over geologic time is an important consideration for CO_2 sequestration.

(g) Lastly, caution should be exercised in selecting a coal seam for sequestration if a deeper coal seam has been mined previously or is likely to be mined. When a deeper seam has been mined, it causes formations above it to subside, resulting in development of fractures and microfractures, thus compromising the sealing potential of any cap rocks.

A geologic screening model to select sites for demonstration of sequestration technology was also developed by Pashin and co-workers.[283,322,323] They developed their criteria while conducting research on the sequestration potential of the Black Warrior CBM fairway in Alabama and the southeastern United States. The main geologic factors that are used to determine CO_2 sequestration potential include stratigraphy, structural geology, hydrogeology, and sorption capacity of coal. Other nongeologic variables that were considered include technology and infrastructure.

Stratigraphy. Coal resources in the Black Warrior basin are located in the upper Pottsville Formation (Pennsylvanian Age). Pottsville coalbeds are organized in stratigraphic clusters. The Upper Pottsville formation, which contains most of the economic coal resources in the basin, is subdivided into a series of flooding-surface-bounded depositional cycles, each with a coalbed or coal zone in the upper portion. However, the geometry of coal bodies in the Pottsville formation is variable, and well production is generally not controlled by coal thickness.

Structural Geology. Structural variables include fold geometry, fault geometry, and fracture architecture. Thin faults and folds of extensional and compressional nature are widespread in coalbeds. The openness and nature of natural fractures (cleats, joints, and shear fractures) are functions of structural geometry. The understanding of relationships among structural geometry, fracturing, and permeability is essential in characterizing the coal as a sequestration medium. An open fracture network is also important for CO_2 sequestration, because it provides access to a large volume of coal.

Hydrogeology. Hydrogeologic factors that affect CBM reservoirs include the reservoir pressure and the type of brine. Reservoir pressure is related to sorption capacity, consequently determining CO_2 sequestration potential. Vertical hydrostatic pressure gradients that are typical for geologically old basins such as the Carboniferous−Permian coal basins of North America, Europe, Asia, and Australia range from a water hydrostatic pressure of 0.43 psi/ft (0.096 atm/m) to lower values (underpressured). Brine and the contained minerals have little effect on CO_2 sequestration; however, brine poses a major administrative constraint on CO_2-ECBM/sequestration, because of the U.S. Environmental Protection Agency (EPA) Underground Injection Control (UIC) requirements.[322] All underground injection into formations with a total dissolved solids (TDS) content of <3000 mg/L is prohibited. In some cases, an aquifer exemption can be acquired for enhanced hydrocarbon recovery in those reservoirs that contain 3000−10 000 mg/L (Class II UIC requirements). Injection to dispose of material without enhanced hydrocarbon recovery (Class I UIC requirements) is only permitted in formations with TDS contents of $>10\,000$ mg/L. Thus, an aquifer exemption will be required for CO_2-ECBM/sequestration in most basins. Furthermore, the technique cannot be practiced near major recharge zones that contain waters with TDS contents of <3000 mg/L without rewriting federal regulations. Thus, coalbeds that have formation waters with a salinity of <3000 mg/L cannot be used for CO_2 -ECBM/sequestration.

Sorption Capacity and Gas Content. The sorption capacity of CO_2 in carboniferous coals is dependent on pressure and temperature.[324,325] Bituminous coal can hold at least twice as much CO_2 as methane (see discussion in the subsections entitled “Adsorption Isotherms of Gases on Coals” and “CO_2-ECBM” in this review). Consequently, an accurate determination of methane sorption capacity of a coal can be used to estimate the CO_2 sequestration capacity. In addition to temperature and pressure, the rank, grade, and maceral composition of coal can influence the sorption capacity.[25]

Field Projects in the United States. *Tiffany Unit.* This project, initiated in 1996 and located in the San Juan basin, is an ECBM recovery pilot with four N_2 injection wells surrounding a central production well in the San Juan basin.[313] Based on the success of the pilot and previous laboratory developments,[310] and after acquiring numerous patents on the process, Amoco moved forward with the first and largest full-scale N_2-ECBM commercial pilot, which is known as the Tiffany Unit. N_2 injection began in January 1998, using 10 new directional N_2 injection wells and two additional converted production wells. A portion of this field was part of a CBM reservoir characterization project in the early 1990s, which was performed by Advanced Resources

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International (ARI) and funded by the Gas Technology Institute (formerly the Gas Research Institute).[326]

Injection volumes have averaged 24−28 MMCFD (0.68×10^6−0.79×10^6 m^3/day) into the 12 wells. The total Tiffany Unit production prior to the injection of N_2 averaged ~5 MMCFD (0.14×10^6 m^3/day) from 34 wells. In early 1999, gas production peaked at 29 MMCFD (0.82×10^6 m^3/day), representing a 5-fold increase in CH_4 production. N_2 levels in the produced gas reached 16%. These results show the rapid production response and breakthrough associated with N_2-ECBM. The Tiffany Unit is being evaluated in regard to its potential for injecting a mixture of waste CO_2 and the already-generated N_2. The information collected to date from this active N_2-ECBM flood can be useful for the planning and design of a future CO_2 injection in this field.

Burlington Resources, Allison Unit CO_2-ECBM Pilot. The Allison Unit field is the home of the world's first experimental (pure) CO_2-ECBM recovery pilot.[290] The Allison Unit is located within the northern portion of the San Juan basin, in northern New Mexico, close to the border with Colorado. The San Juan basin is one of the most prolific CBM developments. In 1998, it was responsible for 75% of the total worldwide CBM production. Also, the field is well-studied and well-characterized. Prior to CO_2 injection, the Allison Unit was a mediocre performer, with gas production rates that were less than half of that of the San Juan basin Fairway wells (which average ~3 MMCFD/well (8.5×10^3 m^3/day/well)); however, it was still economically profitable. A major reason for selecting the pilot location was its proximity to a major CO_2 pipeline that crosses the basin. The pilot consists of four CO_2 injection wells and nine CH_4 production wells, drilled on a 320-acre spacing. Formerly, these nine wells had been produced using conventional pressure-depletion methods for more than five years. During 1995, Burlington Resources drilled four injection wells. Injection wells for CO_2-ECBM are similar to those used in EOR operations. In the Allison Unit, all four injection wells were completed in essentially identical fashion. After setting an $8^5/_8$ in. (21.91 cm) surface casing to a depth of ~350 ft (106.7 m), Burlington Resources drilled through the Fruitland coal formation using a $7^7/_8$ in. (20 cm) bit to a total depth of ~3300 ft (1005.8 m). The production casing ($5^1/_2$ in. (13.97 cm)) was then cemented across the Fruitland coal zones and perforated. The injection wells were not stimulated, to reduce the risk of CO_2 leakage outside of the targeted coal reservoir. The production wells at the Allison Unit field were drilled during the late 1980s, prior to any plans for ECBM application. The nine producing wells were completed using natural completion or cavitation. None of the production wells were hydraulically stimulated. However, after CO_2 injection began, several of the production wells were re-cavitated. The Allison Unit production wells typically were spudded using a $12^1/_4$ in. (31.11 cm) bit and drilled to a depth of ~250 ft (76.2 m). Surface casing ($9^5/_8$ in. (24.45 cm)) was then cemented in place. An $8^3/_4$ in. (22.23 cm) hole was drilled to just above the Fruitland coal (3000 ft (914.4 m)), and a 7 in. (17.78 cm) intermediate casing was top-set and cemented in place. Finally, a $6^1/_4$ in. (15.8 cm) hole was drilled through the Fruitland coal to a total depth of ~3200 ft (975.36 m). Either the wells were completed open-hole or a predrilled $5^1/_2$ in. (13.97 cm) liner was positioned across the coal seams.

CO_2 injection began at an initial rate of 5 MMCFD (141.5×10^3 m^3/day). Later, because of injectivity loss, injection rates were reduced to ~3 MMCFD (84.9×10^3 m^3/day).[326] During the initial six-month period of CO_2 injection, five of the production wells were temporarily shut in. It was thought that this might facilitate CO_2/CH_4 transfer in the reservoir and delay CO_2 breakthrough. However, severe water encroachment was observed during the shut-in procedure. The higher water saturation was believed to slow the desorption process and change the relative permeability curves, resulting in less gas flow.[289]

After six months, CO_2 injection was suspended to evaluate field performance, and the five shut-in wells were reopened. Injection resumed ~8 months later. Water production increased markedly at the start of CO_2 injection, demonstrating improved sweep of bypassed reservoir areas, which should lead to higher ultimate gas recovery with continued operation. The most dramatic production improvement was observed in the only well in the unit that had not been shut in and may be indicative of the best performance that could be expected from a CO_2-ECBM project. Breakthrough of CO_2 has been minimal during the life of the project, despite the injection of 57×10^6 m^3 of CO_2. After almost five years of injection, CO_2 concentrations at the production wells averaged 6%, which is only slightly greater than the initial pre-injection levels of 4%. This suggests that the physical processes of CO_2 sequestration and methane release are, indeed, happening. However, some breakthrough is likely to occur within several years. Overall, the Allison Unit CO_2-ECBM shows that CH_4 production has been enhanced by CO_2 injection. Using a CBM reservoir simulator (COMET-2), the operators estimated the ratio of CO_2/CH_4 produced to be ~2.9.[327] (See subsections entitled "Estimated Amounts of CH_4 in Coal," "Adsorption Isotherms of Gases on Coal" and "CO_2 -ECBM.") However, because of operational problems and a lack of good monitoring, the project could not show how much CO_2 could be stored in the Fruitland Formation. A research program would be needed to quantify both CO_2 sequestration capacity and ECBM performance. Consequently, a joint U.S. Department of Energy (DOE) and industry project to study the reservoir mechanisms and field performance of CO_2 sequestration in coal seams recently has been initiated.[326] The project involves laboratory and field-testing to define critical reservoir mechanisms, including multicomponent (the CO_2−methane−N_2 ternary) sorption behavior. The Allison and Tiffany Units will be the two field demonstration sites thoroughly studied by reservoir simulation to understand CO_2 sequestration and ECBM recovery performance, using both pure CO_2 and N_2, as well as CO_2/N_2 mixtures.

Future Work. The Tiffany and Allison Units will be used as a foundation for the study and understanding

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[326] Reeves, S. R. Geological Sequestration of CO_2 in Deep, Unmineable Coalbeds: An Integrated Research and Commercial-Scale Field Demonstration Project. In *Proceedings of the Annual Technical Conference and Exhibition of the Society of Petroleum Engineers*, New Orleans, LA, September 30−October 3, 2001, SPE Paper No. 71749.

[327] Schoeling, L.; McGovern, M. *World Oil* **2000**, *98*, 37−41.

of CO_2-ECBM/sequestration in coal seams. Laboratory tests for single-, binary-, and ternary-component measurements, as well as studies of the potential impact of matrix shrinkage/swelling and geochemical reactions on CO_2 injectivity, will be conducted.[328,329] A bench-top core-flooding experiment may also be performed to understand some of these issues in a controlled environment. The laboratory work will support reservoir studies, and based on the results of reservoir studies, economic optimization studies will be performed. Finally, a project-screening model will be developed.

Field Projects in Canada. *Alberta CO_2-ECBM/Sequestration Project*. The Alberta Research Council (ARC) consortium has developed a pilot site at the Fenn Big Valley, with two main objectives: (i) to reduce greenhouse gas (GHG) emissions by subsurface injection of CO_2 into deep coalbeds, and (ii) to enhance CBM recovery factors and production rates as a result of CO_2 injection.[330]

The project was divided into three phases:

(1) Proof of concept, in which an initial assessment and feasibility of injecting CO_2, CH_4, and flue gases into the coals was performed, showing that twice as much CO_2 can be injected as CH_4 can be produced from a coal seam;

(2) The design and implementation of a micropilot huff-and-puff test, using CO_2 and N_2 as injectants; and

(3) Simulation, design, and implementation of a full-scale pilot project.

Phase 1 was completed in July 1997. The operations concluded that the injection of CO_2 for ECBM was technically feasible. Phase 2 was completed in April 1999. The field test was performed in an existing well at Fenn Big Valley. The coal at the Fenn Big Valley site belongs to the Upper Manville group. The rank is high-volatile-B bituminous. The total coal seam thickness is $\sim$9 m, over two seams. The field test focuses on the upper seam. The depth of the coal seams is in the range of 1250−1300 m. Typical permeability is in the range of 1−5 mD.

The field test was designed to meet three primary goals:[331]

(1) To accurately measure data from a single well test, involving a series of CO_2 injection/soak cycles, followed by the production of CO_2 and CH_4;

(2) To match the measured data with a comprehensive coal reservoir simulation model, to obtain estimates of reservoir properties and sorption behavior; and

(3) To use calibrated simulation models to predict the behavior of a larger-scale pilot project or full-field development. Phase 2 is a preliminary and necessary step leading to the planning of a full-scale five-spot pilot test.

It was concluded that a full-scale pilot ECBM project is possible at the Fenn Big Valley location. The injection of pure CO_2 and flue gas were considered. Early results indicate that flue gas injection seems to enhance methane production to a greater degree than that which is possible with CO_2 alone, because of the different roles of the two gases while still sequestering CO_2.

Phase 3 started in October 1999, when the second well was drilled and completed at Fenn Big Valley. Core samples were collected to allow accurate determination of the gas-in-place value, gas composition, and gas storage capacity. Two micropilot tests were performed on the new well in the spring of 2000: one by injecting pure N_2, and the other by injecting the exhaust from a compressor engine that was used for underbalanced drilling (flue gas composition of 13% CO_2 and 87% N_2). The results of these micropilot tests will help in the design of the full-scale pilot, to be installed in the next phase of development (phase 3-b). In parallel with the fieldwork, geological studies were performed to evaluate the geology of other coal deposits in Alberta, such as those in the Ardley and Edmonton groups. The reservoir properties in these other areas—in particular, the natural fracture permeability—cannot be determined by the study of available geologic data. As a result, two formation evaluation wells were drilled into the Ardley and Edmonton coal seams in 2000.[332]

Field Projects in Australia. Australia has introduced an array of measures to address climate change by reducing GHG emissions. A demonstration pilot is being considered at the Dawson River Site, Southern Bowen basin in Australia, where major coalbeds and CO_2 sources are located.[333] A successful pilot could lead to an eventual installation of a commercial CO_2 ECBM/sequestration operation.[334] Three major phases are being considered:

(1) Micropilot testing (one injection/production well),

(2) Five-spot pilot testing (four injection, one production well), and

(3) Nine-spot pattern field testing (16 injection + 25 production wells).

After these three stages, sufficient information should be available to expand the project to a commercial scale.

During the first stage of the project, the selected field is studied to determine an optimum location for the pilot. This study includes both geologic and reservoir-engineering efforts to quantify the continuity, geometry, and properties of the coal seams, based on available data. An evaluation of the formation well will be performed by drilling, logging, and coring the seam to obtain data to improve the estimates of reservoir properties. Gas content, storage capacity, and other coal properties will be determined. Fall-off tests will be used to calculate flow capacity and wellbore effects. A micropilot test will be chosen on the basis of sufficient flow capacity. Stimulation was considered for the micropilot well. It is expected that the stimulated well will then begin actual production to obtain coal seam gas and

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(328) Reeves, R. A.; Kenney, C. W.; Berggren, M. H. Method to Reduce Oxidative Deterioration of Bulk Materials, U.S. Patent No. 5,-919,277, 1999.

(329) Reeves, R. A.; Kenney, C. W.; Berggren, M. H. Method to Reduce Oxidative Deterioration of Bulk Materials, U.S. Patent No. 6,-231,627, 2001.

(330) Gunter, W. CO_2 Sequestration in Deep 'Unmineable' Coal Seams. In *Proceedings of the CAPP/CERI Industry Best Practices Conference*, Calgary, Canada, April 18−19, 2000, 19 pp.

(331) Wong, S.; Gunter, B. *Greenhouse Gas R&D* **1995**, 1−4.

(332) Gunter, W. D. Alberta Field Pilot To Test CO_2 Enhanced Coalbed Methane Recovery. Available via the Internet at www.arc.ab.ca/energy/coalbed_pilot.asp, 2002.

(333) Bradshaw, B. E.; Simon, G.; Bradshaw, J.; Mackie, V. GEO-DISC Research: Carbon Dioxide Sequestration Potential of Australia's Coal Basins. In *Proceedings of the Eighteenth Annual International Pittsburgh Coal Conference*, Newcastle, NSW, Australia, December 3−7, 2001, 34 pp.

(334) Wong, S.; MacLeod, K.; Wold, M.; Gunter, W. D.; Mavor, M. J.; Gale, J. *CO_2 Enhanced Coalbed Methane Recovery Demonstration Pilot—A Case for Australia*. In *Proceedings of the International Coalbed Methane Symposium*, University of Alabama, Tuscaloosa, AL, May 14−18, 2001, pp 75−86.

water productivity information, fluid composition data, and both production and shut-in pressure data. CO_2 then will be injected, followed by a soak period, to allow the CO_2 to be sorbed into the coal. The well will be returned to production to quantify the effect of the CO_2 on the reservoir properties. The final effort during phase 1 is to evaluate all of the data and use the evaluation to predict the behavior of a phase 2 five-well pilot under both pure CO_2 injection and under a mixed CO_2-N_2 injection. The information expected to be gained from the five-spot pilot includes sweep efficiency, the increase in hydrocarbon production rates, and the optimum composition of the injected gas. These data, as well as the pressure behavior, will be matched with a comprehensive reservoir simulator. To help the simulation efforts, three pressure monitoring wells should be positioned both inside and outside the pattern, based on cleat, stress, and directional permeability data. Once matched, the calibrated simulation model will be used to predict the behavior of a large-scale project. The larger-scale project, which is installed around the existing pilot, will include 41 total wells, 16 injectors, and 25 producers. Possible well spacing scales are on the order of 80−320 acres and are dependent on the optimum size predicted using model calibrations.

The prime objective of the three-stage demonstration pilot is to collect sufficient data to evaluate the technical and economic performance of the coalbed reservoir. The timing of the demonstration is 4.3 years, and if the project were to be successful, phase 3 would become a commercial operation.

Field Projects in Poland. *Reduction of CO_2 Emissions by Means of CO_2 Storage in the Silesian Coal Basin of Poland (RECOPOL).* The RECOPOL project started in November 2001, with the intent to develop the first European field demonstration of CO_2 sequestration in coal seams. This pre-pilot field test is the first of its type outside of North America and, with the preceding research, will help in understanding the process and its potential for CO_2 reductions in Europe. A suitable site was selected for the location of the field experiment in the Silesian basin in Poland. Upper Carboniferous coals were deposited in Europe in similar settings as Upper Carboniferous coals in the United States (in Alabama and Appalachia). The site was ranked first in Europe as a potential sequestration basin,[335] because it has favorable reservoir properties (depth, permeability, gas content, etc.), an existing infrastructure (surface facilities and wells), and some other advantages (such as low cost for drilling, etc.).[336] There are two existing production wells in the field, which will help to keep the costs low. Only one new (injection) well will be drilled. Drilling and installation of the injection well has been completed. This is being followed by 18 months of injection and production. CO_2 will be supplied on-site by trucks from a local producer. An international consortium will execute the research, design, construction, and operation within the RECOPOL project. The participants are as follows: International Energy Agency (IEA)−Greenhouse Gases (GHG); Netherlands Institute for Applied Geoscience (TNO−NITG) and Delft University of Technology (both from The Netherlands); Central Mining Institute (from Poland); DBI-GUT (a gas exploration, production and consulting company) and Aachen University of Technology (both from Germany); Institute Francais du Petrol (IFP), Gaz de France, and GAZONOR (from France); the Commonwealth Scientific and Industrial Research Opportunities (CSIRO) (from Australia); the Japan Coal Energy center (JCOAL); and ARI (from the United States). In addition, an international end-user group is now being formed. The European Commission funds the RECOPOL project, and overall coordination of the project is conducted by TNO−NITG.[337]

Field Projects in The Netherlands. The Netherlands Agency for Energy and the Environment (NOVEM) financed a study to assess the technical and economic potential of combined ECBM production and injection of CO_2 in The Netherlands.[338] Part of the study was the geological evaluation of potential regions of The Netherlands on-shore, including an inventory of the (producible) gas-in-place, and an estimation of the amounts of CO_2 that can be stored in coal layers. Parameters that have been taken into consideration include the following: geology, depth, area, coal thickness, in situ gas content, and exchange ratio between CBM and CO_2. Areas selected for this study are those overlying the Carboniferous coal deposits within a depth of 2000 m. Below this depth, the permeability of the coal seams might be too low for both CBM production and CO_2 injection and the drilling costs might be too high.

Monte Carlo simulation analysis was applied in this study, to manage the uncertainties in the values of different parameters included in the equation, to calculate the producible gas-in-place and the amount of CO_2 to be stored. Uncertainty quantification of these values was then applied to economic studies. The study concluded that CO_2 sequestration, in combination with ECBM, can be economically feasible under some circumstances in The Netherlands in the short term.[339,340]

Field Projects in Japan. In 1999, Japan produced 250×10^6 tons of CO_2 (out of a total 313×10^6 tons of GHGs emitted from power plants). Under the Kyoto protocol, Japan intends to reduce GHG emission to 287×10^6 tons, representing the 1990 levels. Among CO_2 sequestration methods, CO_2 sequestration in coal seams is considered to be a viable option. Japan's CO_2 sequestration capacity in unmineable coals was estimated at 500×10^9 m^3 of CO_2. Most of this capacity is located in

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(335) Pagnier, H.; van Bergen, F. Demonstrating CO_2-ECBM: The RECOPOL Project. In *Greenhouse Issues* **2002**, (58). (Available via the Internet at http://www.ieagreen.org.uk/jan58.htm).

(336) Bossie-Codreanu, D.; Wolf, K.-H. A. A.; Bruining, H.; Krooss, B.; Busch, A. Integrated Characterization for CBM: The RECOPOL Example. In *Proceedings of the AAPG Annual Convention*, Salt Lake City, UT, May 11−14, 2003.

(337) Pagnier, H.; van Bergen, F. CO_2 Storage in Coal: the RECOPOL Project. Presented at the First International Forum on Geologic Sequestration of CO_2 in Deep, Unmineable Coalseams, "Coal-Seq I", Houston, TX, March 14−15, 2002. (Available via the Internet at http://www.coal-seq.com/Coal-Seq_I_Forum.htm.)

(338) Pagnier, H. J. M.; van Bergen, F.; van der Vate, L.; Hills, L.; Bamber, W. Inventory of the Potential of Combined Coalbed Methane Production Carbon Dioxide Disposal in the Dutch Subsurface. In *Proceedings of the 14th International Congress on the Carboniferous and Permian (ICCP)*, Calgary, Canada, April 17−21, 1999; p 109.

(339) Schreurs, H. C. E. Potential for CO_2-Sequestration and Enhanced Coalbed Methane Production in The Netherlands. In *Proceedings of the 18th Annual International Pittsburgh Coal Conference*, Newcastle, NSW, Australia, December 3−7, 2001, 13 pp.

(340) *World Energy Outlook*, 2000 Edition. International Energy Agency, Paris, France. (Available via the Internet at http://www-.worldenergyoutlook.org.)

the following coal basins: Kushiro, Ishikari, Joban, Miike, and Sakito Matsushima. Possible project sites are considered in one of these[339] basins, because of the proximity of large power plants.[341]

In May 2001, The Japan Forum on CO_2 Sequestration in Coal Seams (JCOSC) was founded, and the scope of the demonstration and industrialization of CO_2 sequestration projects was defined. The JCOSC organized a field test group, which is assessing CO_2 sequestration and CO_2 injection in coal seams and is currently drafting a field test program.[342] Starting in 2002, the Japan Ministry of Economy and Trade (METI) began a new project on CO_2 sequestration. The project term is five years and has a total budget of $27 million (U.S. dollars). The purpose of the project is the development of a cost-effective CO_2 sequestration project in coal seams and will include a research program and micropilot test.

Field Projects in China. Initial testing for CBM in China has confirmed a large resource potential for CO_2 sequestration. There are two potential settings for CO_2-ECBM/sequestration within China's Carboniferous coal deposits. The northeast China coal region is heavily industrialized with numerous coal-fired power plants that could provide CO_2 for injection. However, there is no existing gas pipeline infrastructure, and test cores drilled show low permeability (<1 mD). The Ordos basin in north-central China has superior reservoir quality, with minimal fracturing and permeabilities that are higher by 1 order of magnitude. The potential for CO_2 sequestration is $\sim$660 million tons in this basin.[18]

On March 15, 2002 in Beijing, the Canadian International Development Agency and the Chinese Ministry of Foreign Trade and Economic Cooperation (MOFTEC) signed a memorandum of understanding concerning the development of China's CO_2-ECBM sequestration project. The project's budget includes Canada's contribution of $3.1 million U.S. and China's contribution of 25 million yuan ($3 million U.S.). For three years, the project will perform up to three micropilot tests to be evaluated for selecting one suitable location and meeting the requirements for a full-scale pilot test.[343]

IV. Monitoring and Verification of Geologically Sequestered CO_2

Monitoring of geologically sequestered CO_2 will be required, to protect the environment as well as the health and safety of the public. Before geological sequestration of CO_2 becomes publicly acceptable, it must first be proven that it is safe and secure for geologically significant periods of time. The inventory of injected gas must be verified and the movement of injected gas from the injection point may be monitored. Monitoring will be required to satisfy expected regulatory demands and to reduce any uncertainties associated with the long-term safety and security of the process.[291] Results from monitoring experiments can also provide important input information to validate numerical reservoir models and confirm the chemical and physical phenomenon that is occurring in situ, by providing insight into the geophysical and geochemical interactions that are occurring between CO_2 and the geologic media. The simultaneous application and integration of results from geochemical methods (including the use of tracers, geophysical methods such as 4-D seismic, and electrical methods combined with the use of advanced geologic models, flow simulators, and forward seismic models) represent the best chance for success. These techniques produce different and unique, but complementary, information that, when integrated, begin to yield a more complete picture than that which can be obtained from any single technique.

Verification of the amount of CO_2 sequestered within a geological formation will most probably be motivated from a regulatory perspective. It is reasonable to expect that laws regulating CO_2 emissions will also require quantitative, independently verified measurement of the amount of CO_2 sequestered. It may be possible to do much of this through the use of accurate and precise flow, temperature, and pressure measurement devices. The use of such tools should at least indicate the quantity of CO_2 pumped into the coalbed or other geological formation.

Coalbed sequestration monitoring and surveillance should comprise a comprehensive approach for gathering and analyzing information obtained by repeated application of multiple methods during CO_2 sequestration and CH_4 production. Its purpose is to provide information on the movement of CO_2 throughout the coalbed and leakage of CO_2 from the coalbed into surrounding formations and, ultimately, to the surface. Quantitative information is required. CO_2 can escape as either a gas or as a solute in moving groundwater. Accurate and precise in situ pressure and temperature monitoring tools can be used to detect the loss of CO_2. A system of monitoring wells can be used to determine the gas and water composition and to identify migration pathways. Information on the amount of CO_2 stored within the coal seam, the rate of movement, and the leakage rate to the surface is needed. In addition, information on the movement and production of CH_4 is needed. The comprehensive approach is divided into multiple components: chemical tracers for direct observation of CO_2 movements, CO_2 and CH_4 soil gas fluxes, pressure and temperature monitoring, surveillance wells to monitor liquid and gas composition and migration pathways, an array of tilt meters, 4-D seismic technology and electrical methods for direct observation of gas movements within the coalbed and/or surrounding strata, and the monitoring process itself, which integrates all the information via reservoir simulation.

Some Lessons from Underground Storage of Methane. Monitoring of geologically sequestered CO_2, quantification of the amount of CO_2 sequestered within a coal seam or other geological formation, and validation

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(341) Deguchi, G. Japanese Current R&D Effort on Coal Seam Sequestration of CO_2. In Presented at the First International Forum on Geologic Sequestration of CO_2 in Deep, Unmineable Coalseams,"Coal-Seq I", Houston, TX, March 14–15, 2002. (Available via the Internet at http://www.coal-seq.com/Coal-Seq_I_Forum.htm.)

(342) JCOAL Topics No. 93 2001/06/04, JCOAL Organized Japan Forum on CO_2 Sequestration in Coal Seam (June 4, 2001). Japan Coal Energy Center. (Available via the Internet at http://www.jcoal.or.jp/jcoal/en/e_topics.nsf/7f28de9c5d8dbd3649256986002d2f7f/575cabf276ef140749256a610032c140?OpenDocument.)

(343) JCOAL Topic No. 120 2002/04/09, Chinese Coal Project Gets Canadian Aid (April 9, 2002). Japan Coal Energy Center. (Available via the Internet at http://www.jcoal.or.jp/jcoal/en/e_topics.nsf/7f28de9c5d8dbd3649256986002d2f7f/7c3ac2f9e652ff2a49256b96003da761?OpenDocument.)

that it remains in the formation will require the simultaneous application of a wide variety of techniques, including geophysical methods and the use of chemical tracers combined with reservoir simulation. In this regard, much knowledge gained from the art of monitoring underground CH_4 gas storage and EOR is transferable to monitoring the integrity of geologically sequestered CO_2. Irrespective of the care taken in selecting the most appropriate geological formation for sequestration, the second law of thermodynamics demands that all CO_2 will not remain in the formation in which it is sequestered. Entropy predicts movement to a more random order and works against any attempt to have all CO_2 remain in the coal seam. Techniques that determine when and how much CO_2 migrates from one place to another must be developed and their veracity must be proven. Tools that measure the rate of migration of CO_2 and CH_4 from one formation to another and the rate of leakage to the surface are needed. One must be able to differentiate between CO_2 leaking to the surface from an underground storage formation and natural CO_2 reaching the surface. One must be able to distinguish between CH_4 from coal reaching the surface and CH_4 produced from methanogenic bacteria in the soil. It is possible to use ^{13}C isotope ratio mass spectrometry to distinguish between these sources of gas.

Anderson and Vogh described the underground storage of CH_4 by 87 companies in the United States in 229 active reservoirs.[344−346] Most storage sites were in depleted gas fields, some in aquifers and depleted oil fields, and the fewest group of nine were in salt caverns. Thirty-seven of the companies reported some loss of CH_4. In most cases, the loss was minor, whereas, in four cases, the loss was massive and uncontrollable. Some operators reported a loss due to earthquake damage. The minor losses occurred through faulty well casings or cementing, loss to the surface, and migration to other reservoirs. Interestingly, "aquifers experienced a significantly higher incidence of serious gas loss than the other reservoir types."[345−347] Thus, experience in storing gases in geological media indicates that some instances of CO_2 leakage from coal seams might be expected. CO_2 is more viscous than CH_4 and, thus, has slightly less escapability. Furthermore, the pressure will increase in the seam after the CO_2-ECBM/sequestration, because of water recharge of the CBM reservoir. The effect of water recharge on the long-term storage stability of CO_2 in the coal seam is unknown.

Pressure Monitoring and Other Methods. Migration of CO_2 can be monitored using a variety of techniques. The simplest monitoring method is to measure the pressure. In systems where no more CO_2 is being injected, the pressure may be expected to remain constant under some circumstances unless CO_2 is leaking out or reactions that consume CO_2 are occurring. The pressure can be measured at the surface or downhole in situ. The use of surface pressure gauges suffers from uncertainties that are due to wellbore storage effects. Therefore, in situ pressure gauges are preferred. Other methods for detection of movement of stored CO_2 will include the use of tracers, isotopic ratios, geophysical methods, visual inspection (including searching for dead vegetation and bubbles in water-covered areas), and the production response of nearby wells. For example, "When our pressure is increased, does their pressure or oil and gas production go up?"[347] The use of observation wells within the geologic formation and in nearby formations will be an important monitoring tool. These wells act passively to the flow of CO_2, water, and/or oil. They can be used to acquire samples of gas, tracers, water, or oil. Observation wells are critically important to the monitoring of the fluid flow in the reservoir.

Leak Detection Using Direct CO_2 and CH_4 Soil Gas Measurements. To monitor the possible leakage of CO_2 and CH_4 to the surface, it will be necessary to determine the flux of these gases emanating from the earth above the coalbed on a seasonal basis before CO_2 is sequestered.[348] These "baseline" soil gas measurements should be made on a seasonal basis at several depths. Similarly, the isotopic composition of the CO_2 and CH_4 should be determined on a seasonal basis before and after sequestration is initiated, to identify biological flux and distinguish between natural CO_2 and CH_4 emissions from those resulting from leakage of sequestered CO_2 and thermogenic CH_4 emanating from the coalbed. Quantitative information on the CO_2 and CH_4 flux is needed to establish a mass balance. Techniques that determine the concentration of any chemical tracers that were added to the CO_2 will be important. These chemical methods will be the most important tools in our arsenal. They quantify leakage to the surface, which directly affects the environment and human health and safety.

From the standpoint of protection of public health and safety, the geophysical techniques that detect movement of CO_2 and CH_4 underground will be of less value. They are important because they will show where the CO_2 front is located within the coalbed and, thus, define bounds of the area at the surface that is most important to monitor for upward gas migration. However, the subsurface movement of CO_2 and CH_4 from one location within a coalbed to another or from the coalbed into an adjacent formation is not necessarily important from a public health and safety perspective, unless the gas makes its way to the surface. It is upward migration to the surface that is most important from an environmental safety and health (ES&H) viewpoint. Monitoring the subsurface movement of gases within the coalbed and adjacent formations will be important to optimize CH_4 recovery.

Chemical Tracers. Simply sampling the atmosphere above a sequestration reservoir and analyzing for CO_2 to determine leakage is difficult, because the background concentration of CO_2 in the atmosphere is, on average, ~360 ppm and changes seasonally. In cases where one measured an atmospheric CO_2 concentration of 1000 ± 50 ppm, an anomaly clearly has been identified. However, for a slow leak, where the atmospheric CO_2 concentration is measured at 380 ± 19 ppm, the situation is not clear. The same situation regarding

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(344) Vogh, J. W.; Thomson, J. S.; Anderson, R. P. Identification of Injected Storage Gas, Final report, February 1989−August 1990.

(345) Anderson, R. P.; Vogh, J. W. *Oil Gas J.* **1989**, *87*, 11 pp.

(346) Anderson, R. P.; Vogh, J. W. *Oil Gas J.* **1989**, *87*, 44−51.

(347) Anderson, R. P.; Vogh, J. W. *Oper. Sect. Proc.—Am. Gas Assoc.* **1988**, 526−535.

(348) Klusman, R. W. *Prepr. Pap.—Am. Chem. Soc., Fuel Chem. Div.* **2002**, *47*, 3−4.

the monitoring of CO_2 and CH_4 in the soil gas exist. If only slightly increased amounts of CO_2 or CH_4 are detected, is the formation leaking? A monitoring technique that will allow determination of a slow and/or intermittent leak of CO_2 to the surface is required. This can be done using a tracer. A tracer is an extraneous substance that is added to the CO_2. These substances can be either radioactive tracers or chemical tracers. Radioactive tracers will not be considered here, because they will probably not be initially used to monitor geologically sequestered CO_2, because of their poor public perception. Chemical tracers are nonradioactive materials that are easily detected by modern analytical methods at ultratrace levels. A problem with the use of chemical tracers is the large amount of tracer material that will be needed. The amount of tracer needed is a function of the amount of CO_2 that must be tagged, the size of the reservoir, the porosity of the reservoir, the analytical detection limits, and the molecular weight of the tracer, as well as other factors.

Experience among operators of underground CH_4 storage facilities has shown that a primary problem associated with the use of tracers is achieving their uniform distribution throughout the reservoir. For this reason, tracers should be injected as soon as CO_2 injection begins and continue to be injected for the entire life of the project.

There are several factors to consider in choosing a tracer, including the following: the stability of a compound in underground environments; its minimum detectable quantity (MDQ) and both its specificity and sensitivity to detection; very-low to zero background concentration in both the subsurface gas regime and in the surface atmosphere; freedom from background interferences within the sample; its migration rate compared to CO_2; its reaction chemistry with minerals within the various geological formations; chemical inertness; resistance to biodegradation; thermal stability; cost; availability; ES&H characteristics; and the corrosivity of the candidate tracers. The tracer must be easily handled by the field operators. Few, if any, compounds display all the optimum characteristics; therefore, application of a suite of tracers may be the best approach. Halogenated compounds have received considerable attention as tracers, because they are chemically inert, have good thermal stability, are relatively nonadsorptive, are resistant to degradation by microbes, and possess excellent detectability by gas chromatography, combined with the use of electron capture detection.

Gunter recently suggested that it may be possible to use argon as a tracer, to elucidate the subsurface movement of sequestered gas.[349] If flue gas is directly sequestered, it will contain argon, because argon is naturally present in air (at a concentration of ca. 0.93%). If these flue gases are sequestered into a coal seam, then argon could be used to trace the movement of these gases. In this case, no tracer is added. The argon is naturally present in the flue gas. Argon is a gas at room temperature and has an atmospheric boiling point of −186 °C. It is nonreactive, nonbiodegradable, noncorrosive, nonadsorptive, noncarcinogenic, and nontoxic at that level. It should move with the CO_2 front in the coal seam.[350]

Anderson and Vogh evaluated the stability and migration properties of five halogenated compounds, including sulfur hexafluoride (SF_6), dichlorodifluoromethane (CF_2Cl_2), chlorotrifluoromethane (CF_3Cl), tetrafluoromethane (CF_4), and trifluoromethane (CHF_3).[345−347,351] The stability studies were conducted in a high-pressure vessel under conditions approximating those of the storage reservoir (60 °C and 100 atm), in the presence of water and crushed Berea sandstone. The individual tracers were added to the vessel in concentrations much higher than that which would be used in normal tracer applications. Gas samples were drawn from the vessel and analyzed after 6, 11, 15, and 19 weeks. "At 131 days storage, all tracer compounds remained within 2 to 3% of their original levels and were considered to be stable at reservoir conditions."[347] The storage stabilities of these compounds, to our knowledge, have not been investigated within coal. Nevertheless, the aforementioned results are encouraging.

Understanding the migration rate of the tracer is critical to its successful application. Ideally, the migration rate of the tracer and the CO_2 through the geologic media are the same. If the tracer becomes strongly sorbed by the geologic media or is highly water soluble and stops in the water and does not migrate with the CO_2, then it becomes less useful. Unfortunately, only limited migration information on tracers is available in the literature. Partition of a tracer from the moving CO_2 phase into the geological medium such as coal is directly analogous to a frontal chromatographic system. To our knowledge, the migration of tracers in a moving CO_2 stream on coal has not been studied. Anderson and Vogh have studied the migration rates of a few halogenated tracers already mentioned on Berea sandstone enriched in clay with a high-pressure gas chromatographic system using a 2 m × 3.2 mm column packed with a 1:1 mixture of clay and Chromosorb. The column was eluted with CH_4. Pressure was maintained using a restrictor. Tracers were injected using a Valco valve that was fitted with a 0.1 mL sample loop. A thermal conductivity detector was used. Capacity factors were measured at temperatures of 0, 20, 40, and 60 °C and pressures of 50, 500, and 1500 psi (3.4, 34.02, and 102.07 atm, respectively).[347] The results are shown in Table 5. Clearly, "in a high-pressure environment, most of the tracers would migrate nearly as fast as methane."[347]

No compound has been successfully used as a tracer during CO_2-ECBM/sequestration with the express purpose of acting as a means to detect leakage of CO_2 to the surface. Coals are adsorptive, and there is concern that the coal may irreversibly sorb the compound(s) added as a tracer. Experiments that determine a potential tracer compound's sorption characteristics on coal should be performed before the compound is used

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(349) Gunter, W. D. Use of Argon to Elucidate the Subsurface Movement of Sequestered Gas, personal communication, May 1, 2002.

(350) Gunter, B. Enhanced Coalbed Methane (ECBM) Recovery Project in Alberta, Canada. Presented at the First International Forum on Geologic Sequestration of CO_2 in Deep, Unmineable Coalseams,"Coal-Seq I", Houston, TX, March 14−15, 2002. (Available via the Internet at http://www.coal-seq.com/Coal-Seq_I_Forum.htm.)

(351) Spencer, D. F.; Tam, S. S.; Deppe, G.; Currier, R. F.; Young, J. S.; Anderson, G. K. Carbon Dioxide Separation from a High-Pressure Shifted Synthesis Gas. Presented at the 19th Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September, 2002, Paper No. 37-3.

Table 5. Capacity Factors for Tracer Compounds and Natural Gas Components[a]

	Capacity Factor											
	0 °C			20 °C			40 °C			60 °C		
compound	0.34 MPa	3.4 MPa	10.3 MPa	0.34 MPa	3.4 MPa	10.3 MPa	0.34 MPa	3.4 MPa	10.3 MPa	0.34 MPa	3.4 MPa	10.3 MPa
ethane		0.07		0.11			0.03	0.01		0.02		
propane	0.49	0.13	0.03	0.28	0.14	0.04	0.17	0.10	0.04	0.09	0.05	0.03
i-butane	2.13		0.06	1.04	0.40	0.09	0.64	0.30	0.10	0.26	0.18	0.06
n-butane	2.95	0.52	0.06	1.39	0.51	0.10	0.82	0.34	0.12	0.32	0.21	0.07
ethylene	0.19	0.06	0.01	0.25	0.08	0.02	0.09	0.06	0.03	0.04	0.04	0.02
propylene	1.79	0.39	0.08	0.88	0.43	0.11	0.38	0.28	0.09	0.19	0.18	0.06
isobutene	5.33	1.57	0.22	4.52	1.85	0.36	2.64	1.13	0.27	0.76	0.66	0.18
butene-1	4.06	1.38	0.18	3.07	1.55	0.30	2.13	0.91	0.24	0.66	.051	0.14
carbon monoxide	0	0.01	0	0	0	0	0	0	0	0	0	0
sulfur hexafluoride	0.10	0.04	0	0.08	0.04	0.02	0.05	0.02	0.03	0.03	0.02	0.01
Freon-13, $CClF_3$	0.13	0.05	0	0.10	0.04	0.02	0.07	0.05	0.02	0.04	0.03	0.02
Freon-12, CCl_2F_2	0.81	0.39	0.06	0.77	0.32	0.09	0.44	0.22	0.07	0.20	0.14	0.05
Freon-23, CHF_3	1.08	0.44	0.08	0.72	0.35	0.12	0.37	0.25	0.08	0.17	0.14	0.07
Freon-14, CF_4	0.01	0.01	0	0	0	0	0.01	0.01	0	0.01	0	0

[a] From ref 346.

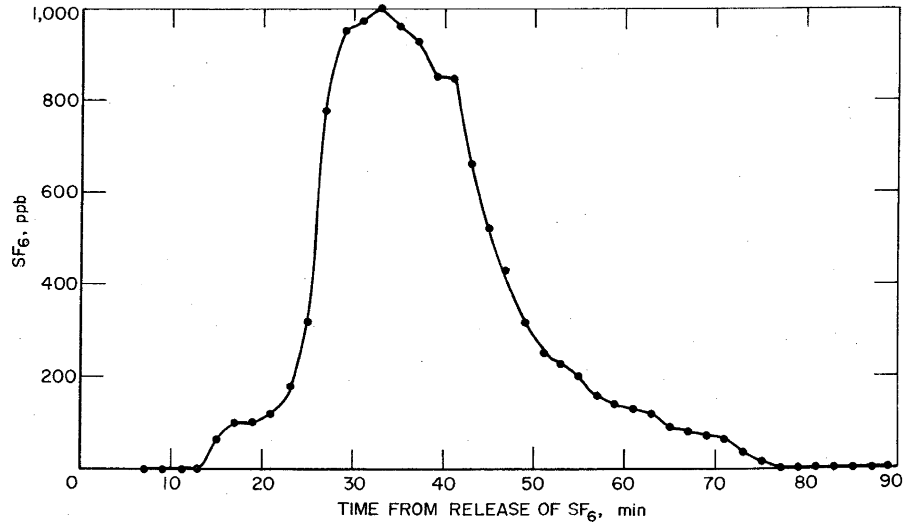

Figure 22. Sulfur hexafluoride (SF_6) concentration, as a function of time, for a case of good mixing, using SF_6 as a gaseous tracer to study ventilation systems in mines. (From Thimons et al.[352])

as a tracer. The literature indicates that this concern may not be well-founded. SF_6 has been successfully used by the U.S. Bureau of Mines (USB) as a tracer to study the ventilation patterns and systems within coal, uranium, and limestone mines.[352−355] Thimons et al. showed that it was possible to release a known amount of SF_6 into the air intake of the Safety Research Coal Mine at Bruceton, PA, and, by carefully sampling and analyzing the amount of SF_6 in the return air, they could account for all of the SF_6 released.[352,353] This observation indicates that SF_6 is not irreversibly adsorbed by coal. The quantitative data are shown in Figure 22 and Table 6. The peak in Figure 22 is actually a chromatographic peak where the coal is the stationary phase and air is the mobile phase. Note that the peak tails, but not significantly. (Tailing is indicative of sorptive processes.) The lack of significant tailing also indicates that SF_6 does not irreversibly sorb onto coal. These results are supported by other studies. "Hunt and Moore showed that SF_6 is not measurably adsorbed on reservoir sandstone. Whismore found the same for coal."[353] The aforementioned experiments and reports are not definitive proof that SF_6 will not be irreversibly adsorbed on coal when injected with CO_2 into coal. The aforementioned experiment was performed in an air stream moving through a coal mine. No such moving air stream will exist in a deep, unmineable coalbed used to sequester CO_2. However, the aforementioned results and statements are encouraging. Nevertheless, more-defini-

Table 6. Preliminary Tracer Gas Test Results from Safety Research Coal Mine[a]

test	time from release to arrival at sample point (min)	SF_6 amount (L) released	SF_6 amount (L) monitored	error (%)
19	15	10.5	10.7	2
20	14	16.1	15.9	1
21	16	1.9	1.8	5

[a] From ref 352.

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(352) Thimons, E. D.; Bielicki, R. J.; Kissel, F. N. Using Sulfur Hexafluoride as a Gaseous Tracer to Study Ventilation Systems in Mines; Report No. 7916; U.S. Department of the Interior Library, Washington, DC, 1974.

(353) Thimons, E. D.; Kissel, F. N. Tracer Gas as an Aid in Mine Ventilation Analysis; Report No. 7917; U.S. Department of the Interior Library, Washington, DC, 1974.

(354) Matta, J. E.; Maksimovic, S. D.; Kissell, F. N. Tracer Gas Method for Measuring Leakage Through Mine Stoppings; Report No. 8324; U.S. Department of the Interior Library, Washington, DC, 1978.

(355) Vinson, R. P.; Kissell, F. N. Three Coal Mine Ventilation Studies Using Sulfur Hexafluoride Tracer Gas; Report No. 8142; U.S. Department of the Interior Library, Washington, DC, 1976.

Table 7. Physical Properties of the Tracer Compounds[a]

tracer	formula	molecular weight	boiling point (K)	density of saturated liquid (kg/m^3)	solubility in water @ 25 °C (wt %)
Freon 11	CCl_3F	137.4	297.0	1476 @ 25 °C	0.11
Freon 12	CCl_2F_2	120.9	243.4	1311 @ 25 °C	0.028
Freon 13B1	$CBrF_3$	148.9	215.4	1538 @ 25 °C	0.03
Freon 114	$CClF_2^-$, $CClF_2$	170.9	277.0	783 @ 25 °C	0.013
sulfur hexafluoride	SF_6	146.1	209.7	1910 @ 223 K	0.033

[a] From ref 359.

tive experiments concerning the adsorption of tracers on coal are needed.

It has been postulated that it will not be possible to successfully apply tracers that have an atmospheric boiling point higher than CO_2, because they will be more strongly sorbed to the coal than CO_2. This postulation is not in accordance with observed facts. SF_6 has been successfully used to trace gas movements in coal mines for years.[352−355] Furthermore, during CO_2 sequestration, CO_2 will be continually injected at high pressure. Dense CO_2 is a good solvent for fluorinated compounds. The solvating power of CO_2 is a function of its density. Thus, with sequestration of CO_2 in deep, unmineable coal seams, we expect that high-pressure injection of supercritical CO_2 will be required, resulting in dense CO_2 with sufficient solvating strength to keep the tracers moving with the CO_2 through the coal. This is speculation and remains to be shown.

The gas and/or supercritical fluid chromatographic capacity factors (and, thus, migration rates) of tracers on coal in moving CO_2 have not been measured. Coal may be more adsorptive than Berea clay. However, the solvation power of high-pressure CO_2 is much greater than CH_4. As the results in Table 5 indicate, the migration of tracers is strongly related to pressure. This is the case for both CH_4 and CO_2, as well as other gases. Therefore, as CO_2 and tracer migrate from a high-pressure storage area to the surface, they will encounter areas of lower pressure and temperature. As they move toward the surface, migration of the tracers, relative to the CO_2, will slow, because as the CO_2 depressurizes, it loses its solvation power. Therefore, to maximize the probability of tracer reaching the surface with leaking CO_2, it will be prudent to use as much tracer as possible. Craig added 2500 times the minimum detectable quantity of tracer to CO_2 used in a project to compensate for losses by adsorption and other phenomenon.[356] In the experiment performed by Craig, the produced gas was sampled for tracer; thus, the samples were not diluted with gas from other sources, as would be the case when sampling surface soil gases, to search for leaks. Therefore, it may be prudent to add even more than 2500 times the minimum detectable quantity when attempting to monitor soil gases near the surface for tracer.

Craig investigated the migration and adsorption characteristics of SF_6, halocarbon-11, and CF_2Cl_2 in standard slim tube displacement tests using a 48 ft (14.63 m) long × 0.245 in. (0.622 cm) inner diameter (ID) stainless-steel tube packed with 120−200 mesh glass beads at 2200 psi (149.7 atm) and 68 °C. The injection fluid was 72 mol % CO_2, 18% sales gas, 10 mol % propane. The results indicate that the tracers migrate through the tube in tandem with the CO_2, and the produced tracer concentration was identical to the injected amount, indicating no loss through adsorption.[356]

Many chemical tracers have been used successfully in subsurface applications to monitor migration of gases. SF_6 has been used as a tracer to monitor leakage from underground reservoirs used to store CH_4 and has been detected at the surface.[357] Craig described an investigation that used halogenated compounds (SF_6, halocarbon-11, and CF_2Cl_2) to identify the source of produced CO_2 in a field-wide miscible flood EOR project in the Alvord South Field located on the northern flank of the Fort Worth basin in Wise County, TX. Results indicated “that adsorption of these tracers was insignificant and the tracer remains with the CO_2 throughout the flood process.”[356] Furthermore, when co-injected into the formation with CO_2, breakthrough of CF_2Cl_2 was coincident with CO_2 breakthrough at two production wells, lagged behind CO_2 breakthrough at another well, and led CO_2 breakthrough in another well by nine days. These results indicate that migration and adsorption of some tracers is not a problem during subsurface applications. Similarly, Carr et al. have used SF_6 and several freons to monitor chase gas solvent injection during a miscible flood at two fields in Alberta, Canada.[358,359] They concluded that SF_6 and several freons “have low adsorption on reservoir rock and partition sufficiently to solvent and gas phases in the reservoir to make excellent tracers on an interwell reservoir scale.” They also found that partitioning of the tracers into the oil phase was more pronounced for higher boiling tracers. The physical properties of some of the more common tracers are shown in Table 7. Many investigators are planning to use chemical tracers, such as SF_6[360] and perfluorocarbons,[360,361] to monitor the fate of geologically sequestered CO_2.

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(356) Craig, F. F., III. Field Use of Halogen Compounds To Trace Injected CO_2. Presented at the 60th Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, Las Vegas, NV, September 22−25, 1985, SPE Paper No. 14309, 8 pp.

(357) Araktingi, R. E.; Benefield, M. E.; Bessenyei, Z.; Coats, K. H.; Tek, M. R. *J. Pet. Technol.* **1984**, 132−140.

(358) Exposito-Caceres, J. C.; Lopez Peinado, A. J.; Carrasco Marin, F.; Rivera-Utrilla, J.; Terol, S. Extraction with Tetrahydrofuran of Coals of Different Rank. In *Proceedings of the 1986 International Congress on Renewable Energy Sources*, May 4, 1986; Volume 1, pp 699−708.

(359) Carr, L.; Wong, F.; Nagel, R.; McIntyre, F.; Rosenegger, L. *J. Can. Pet. Technol.* **1997**, *36*, 43−55.

(360) Blencoe, J. G.; Cole, D. R.; Horita, J.; Moline, G. R. Experimental Geochemical Studies Relevant to Carbon Sequestration. In *Proceedings of the First National Conference on Carbon Sequestration*, NETL Publications No. DOE/NETL-2001/1144, 2001, 14 pp. (CD-ROM.)

(361) Burrowes, G.; Gilboy, C. Investigating Sequestration Potential of Carbonate Rocks during Tertiary Recovery from a Billion Barrel Oil Field, Weyburn, Saskatchewan: The Geoscience Framework (IEA Weyburn CO_2 Monitoring and Storage Project). In *Proceedings of the First National Conference on Carbon Sequestration*, NETL Publications No. DOE/NETL-2001/1144, 2001, 20 pp. (CD-ROM.)

Blencoe et al. have described a unique approach to monitor the integrity of geologically sequestered CO_2, using the stable isotopic composition of CO_2 as the tracer.[360] By carefully defining how the various isotopes of C and O partition as a result of mineral reactions, sorption, and aqueous dissolution, it may be possible to use the CO_2 as a tracer. "As the injected CO_2 interacts with the subsurface geologic materials, its isotopic signature changes, making it a useful tracer."[360]

Geophysical Monitoring. Geophysical methods represent another major category of monitoring tools that will be applied to monitor the fate and integrity of geologically sequestered CO_2. Surveillance of the sequestered CO_2, using seismic techniques, allows the observation of moving reservoir fluids at locations distant from the bore hole. Injection of CO_2 into a geologic formation such as a coalbed affects both the bulk density of the coal and the seismic velocity of introduced waves. These phenomena combine to affect the reflected seismic wave's amplitude and travel times. By performing careful high-resolution 3-D seismic surveys before and after CO_2 injection, it is possible to obtain a time-lapsed picture of the movement of fluids in the subsurface (this type of imaging is called 4-D seismic). The added dimension is time. This technique can be applied to map the movement of CO_2 in the formation and locate the leading edge of the moving CO_2 front.

Wang and Nur measured the compressional and shear wave velocities in seven sandstones with porosities in the range of 6%−29% that were saturated with *n*-hexadecane before and after CO_2 flooding.[362] Both the experimental and theoretical results indicate that the observed decrease in compressional wave (P-wave) velocity in hydrocarbon-saturated sandstone upon CO_2 flooding may be seismically resolvable in situ. "Therefore, it is possible that seismic methods can be used in mapping and locating CO_2 zones, tracking CO_2 flood front movement, and monitoring CO_2 flooding processes in reservoirs undergoing CO_2 flooding."[362] Four-dimensional seismic surveys have been successfully used to track injection of CO_2 during enhanced oil recovery projects. Structural information derivable from high-resolution 3-D seismic surveys include location of small faults and identification of sand channels as well as shale-outs. Information on the pore fluid characteristics, porosity, and variations in permeability throughout a reservoir can be observed by seismic techniques.[363] Coal appears in some seismic surveys as a "bright spot."

Three-dimensional seismic techniques have been successfully applied to investigation of the CBM recovery process. Davis and co-workers[364,365] have used geophysical methods to define the characteristics of the Cedar Hill coalbed gas reservoir, using 3-D multicomponent seismic surveys. Coals can cause the shear wave to split into a faster S1 component and a slower S2 component. The S1 component is parallel to the open-fracture component of the coal, whereas the S2 component is perpendicular to it. Using these techniques, it is possible to determine the fracture direction. The time difference between the S1 and S2 components can provide information about the fracture density. Vertical seismic profiling can be used to predict the directional trends of open fractures within coalbeds. The P-wave component from 3-D seismic surveys can be used to detect faulting within the coalbed and surrounding strata. Furthermore, because the compressional P-wave is affected by fluids, free gas present as a result of sustained dewatering can be observed within the coalbed when the P-wave data are presented in a colorized representation. In fact, the pattern of bright spots observed by Davis suggests that free gas migrated upward along a fault and became trapped against another sealing fault. Based on this and other studies, it seems that the application of 3-D seismic and other geophysical techniques will be useful in monitoring the integrity and subsurface movement of CO_2 sequestered in coalbeds.

Davis and co-workers have applied 3-D seismic techniques to study the recovery of CBM in fractured coal seams from the Cedar Hill Field in the San Juan basin.[364,365] Davis and co-workers showed that the 3-D seismic amplitude-versus-offset (AVO) technology can be applied to characterize fractured reservoirs, to yield information concerning crack density variations. They used a 3-D multicomponent seismic survey to identify zones of large Poisson's ratio contrasts related to high crack densities in the fractured coalbed reservoir. Source−receiver azimuth sorting was used to detect the preferential direction of azimuthal anisotropy resulting from the coal's cleat system. The Poisson's ratio increases as the degree of fracturing in coal increases. Consequently, "an increase in Poisson's ratio contrasts are expected between sandstones, which separate the coal seams, and coals when the latter is considerably fractured. This increase affects the angle-dependent P-wave reflectivity for the top of the coals."[365] The authors show how this new approach can be used to reduce the economic risk as well as improve CH_4 production from fractured coalbeds.

In an earlier report, Davis and co-workers showed that multicomponent 3-D seismic techniques can be used to characterize heterogeneities in coalbeds such as isolated pressure cells, areas of greater fracture density, as well as variations in fracture directions by detailed analysis of multicomponent data and its integration with petrophysical and reservoir engineering analysis. Davis and co-workers[364,365] were able to identify strike−slip faults that compartmentalize the reservoir through interpretation of the 3-D P-wave seismic information. They further showed that there was "good agreement between stresses inferred from the structural interpretation and those indicated by the shear-wave polarizations." An example of the type of information these techniques can generate when applied to fractured coalbeds is shown in Figure 23. This is a map of the Cedar Hills Field CBM reservoir fluid pressure.[364] The authors conclude that CBM reservoirs are not as simple as once thought. Multicomponent 3-D seismic informa-

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(362) Wang, Z.; Nur, A. M. *SPE Reservoir Eng.* **1989**, 429−436.

(363) Farr, J. B. High-Resolution Seismic as a Reservoir Analysis Technique. Presented at the 53rd Annual Fall Technical Conference and Exhibition of the Society of Petroleum Engineers of AIME, Houston, TX, October 1−3, 1978, SPE Paper No. 7440, 12 pp.

(364) Shuck, E. L.; Davis, T. L.; Benson, R. D. *Geophysics* **1996**, *61*, 315−330.

(365) Ramos, A. C. B.; Davis, T. L. *Fractured Reservoirs: Characterization and Modeling Guidebook*; Hoak, T. E., Klawitter, A. L., Blomquist, P. K., Eds.; The Rocky Mountain Association of Geologists: Denver, CO, 1997; pp 165−176.

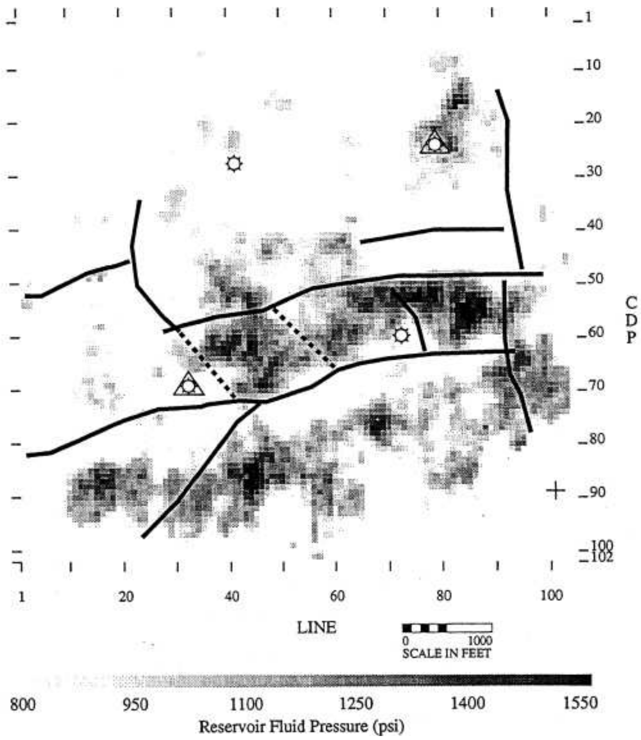

Figure 23. Reservoir fluid pressure map of lower-producing coal, computed using the relationship between the P-wave interval velocity and the confining stress. A maximum reservoir pressure of 1600 psi corresponds to a P-wave velocity of 5000 ft/s (1520 m/s), and a minimum reservoir pressure of 800 psi corresponds to a P-wave velocity of 8200 ft/s (2500 m/s). (From Shuck et al.[364])

tion is needed to perform detailed characterization of CBM reservoirs. Well locations can be made much more effective when they are selected based upon geophysical multicomponent seismic data. Thus, advanced geophysical techniques have been successfully applied to CBM recovery projects, and their application to CO_2-ECBM/sequestration should not represent significant difficulties.

Burrowes and Gilboy described several state-of-the-art geophysical monitoring techniques that are being used at the Weyburn CO_2 Monitoring and Storage Project, including multicomponent 3-D seismic surveys performed over a three-year period, using acquisition techniques to obtain both P- and S-wave information.[361] These geophysical techniques will, in turn, allow monitoring of the CO_2 flood front, as well as improving the resolution of reservoir properties, including porosity–thickness and fracture permeability.[361] These techniques are being applied to an EOR project but could be applied to situations where CO_2 is being injected into almost any geologic formation, including coal seams. In addition to the previous discussion, these investigators are also enhancing the interpretation of the 3-D seismic data through the simultaneous acquisition of 3-D vertical seismic profiles and both single-well and cross-well (horizontal to horizontal) seismic tomography.

Newmark et al. described a relatively new geophysical tool that is being developed to monitor CO_2 sequestration in geologic formations; this tool is known as electrical resistance tomography.[366] The presence of CO_2 within a layer alters its electrical resistivity. Although others have obtained high-resolution tomographs of electrical properties to monitor the subsurface movement of steam floods and water infiltration, the migration of CO_2 has not been observed by these techniques. These investigators hope to use metallic well casings as long electrodes, providing a noninvasive technique to monitor CO_2 sequestration.[366]

Westrich et al. recently described geophysical monitoring tools that they are applying to a sequestration project that is being performed at a depleted oil well in the West Pearl Queen Field in southeastern New Mexico.[367] These workers are applying remote geophysical sensing tools before, during, and after injection of CO_2. They are using surface-to-borehole surveys and surface reflection surveys to identify and possibly characterize formation changes as a consequence of CO_2 injection. The surface-to-borehole seismic approach includes a vertical seismic profile. Westrich et al. used dipole sonic logs, microseismic surveys during injection, and multilevel 3C crosswell seismic surveys.[367]

Myer recently described an apparatus for making concurrent seismic and electrical geophysical laboratory measurements on brine-saturated Berea sandstone. An apparatus for making the measurements was described in general terms and initial results were obtained while the sandstone was flushed with CO_2 under increasing pressure. The increased pressure caused the CO_2 density to vary from gaslike to liquidlike. Introduction of CO_2 into the sandstone caused the resistivity of the sample to increase significantly and there was a significant reduction in the P-wave velocity and amplitude. The goal is to apply these observations to the development of instrumentation that will permit monitoring of CO_2 sequestration.[368]

Multidimensional seismic tools are not without their limitations. A seismic survey is initially obtained before either CH_4 production from the coalbed or injection of CO_2 begins. This information is the baseline response against which later data are compared. After CH_4 production has started, and again after CO_2 injection is initiated, additional seismic surveys are obtained. The differences between the surveys represent the dynamic changes that have occurred within the coal seam. Therefore, estimation of the repeatability of the seismic measurements becomes a crucial issue. The precision of the measurements must be known. One must know the differences between seismic measurements taken over the same region where no changes in the reservoir have occurred. The fewer the differences between repeat measurements, the greater the repeatability of the measurements. The seismic differences observed in the reservoir after significant changes have occurred must be substantially greater than the seismic repeatability for the 4-D seismic method to be useful. It must be

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(366) Newmark, R. L.; Ramirez, A. L.; Daily, W. D. Monitoring Carbon Dioxide Sequestration Using Electrical Resistance Tomography (ERT): Sensitivity Studies. In *Proceedings of the First National Conference on Carbon Sequestration*, NETL Publications No. DOE/NETL-2001/1144, 2001, 18 pp. (CD-ROM.)

(367) Westrich, H.; Lorenz, J.; Cooper, S.; Colon, C. J.; Warpinski, N.; Zhang, D.; Bradley, C.; Lichtner, P.; Pawar, R.; Stubbs, B.; Grigg, R.; Svec, R.; Byrer, C. Sequestration of CO_2 in a Depleted Oil Reservoir: An Overview. In *Proceedings of the First National Conference on Carbon Sequestration*, NETL Publications No. DOE/NETL-2001/1144, May 14, 2001, 11 pp. (CD-ROM.)

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mentioned that the DOE has set the target detection limits for MMV leak detection technologies at 0.01% of the CO_2 sequestered in a reservoir per year. 4-D seismic methods are not able to meet this performance standard.

Application of these geochemical and geophysical techniques and/or simulations, to our knowledge, have not been reported in the literature, relative to CO_2-ECBM/sequestration projects. Therefore, their successful application has not been demonstrated during coal seam sequestration. Some of these techniques have been applied successfully to monitoring EOR using CO_2 injection, and to monitoring and verifying underground CH_4 storage and CBM recovery. Geophysical 3-D seismic techniques have been applied to CBM recovery; however, the 4-D seismic methodology has not. Thus, application of these techniques to monitoring and verification of CO_2 sequestration in coalbeds with concomitant recovery of CH_4 has not been demonstrated.

Seismic modeling is also a useful technique that can be applied in concert with acquisition of the seismic data. Seismic modeling can assist in approximating the magnitude of the seismic changes caused by reservoir changes. These models incorporate both rock physics and reservoir simulations to make estimates of the magnitude of seismic changes. An additional issue is whether the 4-D seismic information can be translated into changes within the coal seam. Allison et al. have developed a 3-D chemical flood simulator to model field-wide tracer flow; it involves a compositional simulator that can model transverse dispersion, areal heterogeneity, and mobile oil, and variable well production rates. The simulation considers tracer partitioning between oil and water phases and reversible adsorption. It may be possible to modify this simulator to model sequestration of CO_2 within deep, unmineable coal seams, and both depleted oil and gas fields.[369−372]

Combination of Reservoir Simulations with Information from Chemical and Geophysical Monitoring. Fanchi[373] recently evaluated the feasibility of simultaneously applying 4-D seismic and an integrated flow simulator (IFLO) to monitor CO_2 sequestered in a mature oil field. “IFLO is a pseudomiscible, multicomponent, multidimensional fluid flow simulator” that has been used to monitor the depletion of oil and gas reservoirs, water flooding of reservoirs, aquifer influx into a gas reservoir, CO_2 injection into reservoirs and other applications.[373] He concluded that IFLO can yield information that is useful in predicting reservoir geophysical characteristics. He further concluded that IFLO shows that 4-D seismic methods can be successfully applied to monitor subsurface storage of CO_2. Lastly, careful application of an integrated flow model can be used to optimize the timing of expensive 4-D seismic surveys.[374]

V. Economic Considerations of CO_2 Sequestration in Unmineable Coalbeds

Economics of CO_2 Sequestration. Geologic variables pertinent to the production and distribution of CBM were discussed in Section III. Long-term CBM markets, wellhead gas prices, pipeline, compression, and transportation costs are other direct factors important to CO_2-ECBM/sequestration economics, along with any potential “credit” for sequestering CO_2.

The economics for sequestration of anthropogenic CO_2 in unmineable coalbeds will be strongly dependent on the source of the gas and may involve capture, treatment, compression, and transportation costs prior to injection. An estimated 0.212 kWh of electric power per m^3/day of CO_2 is required for compression to 1500 psi (102.07 atm), assuming that CO_2 is captured at atmospheric pressure. Sequestration calculations are normally completed on a “CO_2 avoided” basis, where the amount of CO_2 released from the energy required for capture and treatment is calculated and subtracted from the amount of CO_2 captured.[375,376] Herzog et al.[377] completed an overview of the motivation and background for mitigation of atmospheric levels of CO_2, including many of the CO_2-related cost issues. In later reports, these issues received extensive treatment.[375−387] Although a detailed analysis of their treatments may not be appropriate here, these and other studies that relate ultimately to the cost of carbon capture will have a vital role in the overall economics of CO_2 sequestration.

Economics of CO_2 Sequestration Using CO_2 Injection. Stevens et al.[388] completed a first-order analysis for a conceptual 100-well ECBM field of 500

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Table 8. Estimated Cost Comparisons of Carbon Dioxide (CO_2) Produced from Various Sources[a]

source	comments	cost ($US/Mscf)
CO_2 wells	delivered to San Juan basin (no sequestration credit claim)	0.65
capture—hydrogen plants	delivery includes pipelines	0.50
capture—gas processing	delivered	0.68
capture—synthesis gas plants	delivered to Weyburn	0.77
capture—coal-fired power plants		
Amine—Econoamine FG		2.13
Amine—KS-1 solvent and KP-1 packing		1.00
Amine—AMP		0.33−1.33
capture—gas turbines		
Amine—Econoamine FG		2.89

[a] From ref 376.

Bcf (14.16×10^6 m^3) assumed gas reserves. The project was located in a coal seam 50 ft (15.24 m) thick at a depth of 3100 ft (944.9 m) in the San Juan basin, ~10 miles (3.05 km) from Shell's Cortez pipeline, which is the assumed CO_2 source. A 0.5 psi/ft (0.11 atm/m) reservoir pressure gradient and a temperature of 120 °F (49 °C) was assumed. Half of the injector wells were assumed to be newly drilled and located on a 320-acre spacing, and the enhanced recovery was assumed to be a conservative 25% above primary recovery. The ratio of CO_2 injection volume to the CH_4 production volume was assumed to be 2:1. Appropriate capital costs for drilling, CO_2 distribution lines, and total capital/operating costs (undiscounted) were assumed. The largest individual cost item was for the purchase of CO_2 ($0.25−$0.35 U.S./Mcf (U.S.$0.0088−$0.0124 U.S./m^3)). Based on this analysis, the incremental and undiscounted cost of CH_4 is $0.89−$1.09 U.S./Mcf ($0.0314−0.0385 U.S./$m^3$)). Section 29 tax credits would improve the economics, and potential future credits may also improve the economics.

Wong et al.[376] compared the delivered cost (including compression) of CO_2 originating from many different sources (Table 8). Table 8 also includes the estimated delivered cost for CO_2 obtained from natural reservoirs. However, CO_2 from a natural reservoir would be ineligible for sequestration credits. The more dilute the CO_2 stream, the higher the recovery costs. The flue gas stream from a coal-fired power plant contains a lower concentration of CO_2 (~13%), compared to streams from the other sources shown in Table 8, except for gas turbines (~3%). Chemical absorption using monoethanolamine (MEA) is the route used at commercial CO_2 capture facilities and it has the highest cost.[376] New amines (KS-1 and KS-2) have been developed that are less corrosive and degrade less than MEA, thus providing more-favorable economics.[382]

Table 8 shows that the CO_2 streams recoverable from hydrogen, gas processing, and synthesis gas plants can be processed and delivered at lower cost than that captured from coal-fired power plants. Such sources may be among the first sequestered. However, with improvements in solvent-based processes, researchers suggest that $1.00 U.S./Mscf ($0.0353 U.S./m^3) may be attainable for carbon capture from flue gas.[376,389] Research is progressing for CO_2 capture, and costs are expected to decrease.[376,379]

Table 9. Economics of CO_2 Storage: Moderate Gas Price with Incentives[a]

	Incentive Cases			
	$10/T CO_2		$15/T CO_2	
wellhead gas price	$3.00		$3.00	
less basin differential		($0.30)		($0.30)
less BTU adjustment @ 5%		($0.15)		($0.15)
wellhead netback	$2.55		$2.55	
less royalty/production taxes		($0.51)		($0.51)
less O&M/gas processing/SMV[b]		($0.75)		($0.75)
gross margin	$1.29		$1.29	
capital costs				
less I Wells[c]		($0.50)		($0.50)
less SMV[b]		($0.25)		($0.25)
less net CO_2 costs[d]		($0.43)		(0)
net margin	$0.11		$0.54	

[a] From ref 390. [b] SMV costs: plus 50%. [c] Capital costs = $500 000 × 16 = $8 000 000/32 Bcfg = $0.25 × 2 = $0.50/Mcfg. [d] CO_2 Costs (@ $10/T) = $25/BO × 3% = ($0.75 − $0.58)/Mcf = $0.17/Mcf × 2.5 = $0.51/(Mcf CO_2). For CO_2 costs @ $15/T, assume 0.

Kuuskraa[390] presented a conceptual economic analysis for CO_2 storage in a deep western coal basin. The basin contains an estimated 50 Tcf (1.41 Tm^3) of CBM and involves 8000 production wells at a depth of 3000 ft (914.4 m). A 100 Bcf (2.83×10^9 m^3) section with a conventional recovery of 48 Bcf (1.36×10^9 m^3) and estimated incremental recovery of 16 Bcf (0.45×10^9 m^3), because of ECBM through 16 production wells and 6 (new) injection wells, was considered. Because of the uncertainty of effects that future developments will have on costs, three cases were considered: (1) a current case, (2) a case projecting a high gas price and high efficiency, and (3) a case projecting a moderate gas price with incentives. For scenario 3, two incentive cases were examined: one assumed a cost of $10/ton for CO_2, and the other assumed a cost of $15/ton of CO_2. These incentive scenarios are summarized in Table 9. Note that an incentive of $10/ton of CO_2 shows a net margin of $0.11/Mcf ($0.0039/m^3) and an incentive of $15/ton of CO_2 shows a margin of $0.54/Mcf ($0.019/m^3). Table 10 summarizes the economic analysis of these CO_2 sequestration cases and indicates that the economics are favorable now only with an incentive of $15/ton of CO_2. The net margin of $0.11/Mcf ($0.0039/m^3) (shown in Table 9) is consistent with the statement in Table 10 that an incentive of $10/ton of CO_2 is marginal. The net

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Table 10. Economics of CO_2 in Deep Coal Seams[a]

outcome	current case	high price/high efficiency case	Modest Price w/Sequestration Incentive	
			\$10/ton CO_2	\$15/ton CO_2
economics	no	marginal	marginal	yes
CO_2 storage[b]		930 MM tons	2330 MM tons	3720 MM tons
additional natural gas		8 Tcf	16 Tcf	16 Tcf
capital investment				
Inj wells		\$1.5 billion	\$4 billion	\$4 billion
SMV			\$2 billion	\$2 billion

[a] This is a summary of the economic analysis of CO_2 sequestration in the example Western coal basin. Data taken from ref 390. [b] Using 17.2 Mcf CO_2/ton CO_2.

margin of \$0.11/Mcf (\$0.0039/m^3) is insufficient to provide an adequate return on capital, thus making the project only marginally economic.

Wong et al.[376] completed a preliminary economic analysis of a conceptual 100-well CO_2-ECBM development in the Alberta Plains with a reservoir at 4200 ft (1280.2 m) containing 30 ft (9.14 m) of coal located in two seams and using a well spacing of 320 acres in each five-spot pattern (volume of gas-in-place = 4.4 Bscf/pattern (124.6×10^6 m^3/pattern)). A 95% CO_2 stream delivered by pipeline at 2000 psig (137.1 atm) at a cost of \$1.00 U.S./Mscf (\$0.0353/m^3) was assumed. Typical new-well drilling, completion, tie-in, stimulation, and maintenance cost estimates for the region were assumed, and a 12% real rate of return was used for discount cash flow analysis. Total ECBM recovery of 72% was predicted using a commercial reservoir simulator software package to predict the performance of a five-spot pattern. The net volume ratio of CO_2 injection to CH_4 production was assumed to be 2:1. On the basis of this analysis, the supply price for CBM was \$2.89 U.S./Mscf (\$0.102/m^3). Recompletion of existing wells could reduce costs significantly. The cost of delivered CO_2 is the most significant cost factor in the analysis. Any potential “credits” for CO_2 avoided will have a significant effect on the economics.

Economic estimates of the CO_2-ECBM/sequestration process will be aided by the use of models of the process. There are many companies that sell CBM recovery models that are well-developed, are well-tested, and can be used to obtain accurate estimates of CH_4 from coalbeds.

Economics of CO_2 Sequestration Using Flue Gas Injection. Wong et al.[389] also completed a preliminary economic evaluation of a conceptual five-spot pattern, 100-well flue gas-ECBM development in the Alberta Plains region, using a commercial reservoir simulator software package. The depth, coal thickness, well spacings, gas-in-place, and other assumptions related to drilling, completion, stimulation, and well management are detailed.[376] A flue gas stream delivered to the field at 2000 psig (137.1 atm) at a cost of \$0.50 U.S./Mscf (\$0.0176/m^3) and the cost of N_2 rejection from the produced well at a cost of \$0.49 U.S./Mscf (\$0.0173/m^3) were assumed. The net ratio of flue gas injection to production of CH_4 is assumed to be 0.73:1 by volume. Assumed production is terminated when the N_2 content of the production stream exceeds 30% and a total CBM recovery of 57% is assumed. Production economics indicate that flue gas-ECBM requires a well-head supply price of \$1.58 U.S./Mscf (\$0.0558/m^3), compared to \$2.89 U.S./Mscf (\$0.102/m^3) for CO_2-ECBM. If existing wells are used or potential sequestration credits are realized, the economics are further improved.

The fact that previously noted conceptual projects for CO_2 and flue gas-ECBM/sequestration operations associated with coal basins are expected to be moderately or marginally profitable indicate that the cost of capture, separation, compressibility, and transportation of the injected gas, along with any required treatment of the product stream prior to entering the pipeline, will be major factors in the economics.

Predictive Tools for CO_2 Capture/Sequestration Decisions. Rhudy et al.[391] reported on work in progress by the U.S. Department of Energy (DOE), the Tennessee Valley Authority (TVA), the Electric Power Research Institute (EPRI), Parsons Infrastructure and Technology, the University of Tennessee, Massachusetts Institute of Technology (MIT), the IEA Greenhouse Program, and SFA Pacific to develop comparable economics for CO_2 storage and sink enhancements. They note that one of the major difficulties in evaluating CO_2 sequestration methodologies for storage in either geological or biological sinks “is obtaining consistent, transparent, accurate, and comparable economics.” The objective of their project is to evaluate, on a common basis, the economics for a wide array of CO_2 sequestration options, including geologic storage in active oil reserves, depleted oil and gas reservoirs, deep aquifers, coalbeds, oceans, and biological sinks such as forests, and croplands. Most capture-sequestration cost comparisons to date have assumed that the actual sequestration step is a small fraction of the overall costs; however, virtually no comparative economic evaluations exist.

ARI has developed a predictive coal seam sequestration simulator that is publically available at the Coal-Seq web site; this simulator predicts the cost of sequestration (in dollars per ton of CO_2 stored), the amount of CH_4 recovered, how much CO_2 can be stored, well spacing, injection rate, and other factors. These predictions are based on several input parameters, including coal rank, seam thickness, depth, temperature, and composition of the injected gas (CO_2, CO_2/N_2, flue gas, etc.). The ARI simulator is also described in the work by Taillefert and Reeves[392] (and at the following website: http://www.coal-seq.com/models.htm).

The screening criteria developed by ARI are idealistic and may not always be practical. For example, coalbeds

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(391) Rhudy, R. G.; Bock, B. R.; Nichols, D. E. CO_2 Storage and Sink Enhancements: Developing Comparable Economics. In *Proceedings of the First National Conference on Carbon Sequestration*, NETL Publications No. DOE/NETL-2001/1144, May 14, 2001, 15 pp. (CD-ROM.)

(392) Taillefert, A.; Reeves, S. Screening Model for ECBM Recovery and CO_2 Sequestration in Coal; Report, USDOE Award No. DE-FC26-0NT40924, Coal-Seq. V. 1.0, Topical Report, 7/1/02−4/31/03, 2003.

Table 11. Example Analysis: Economic Screening and Results[a]

disposal type	number of plants	CO_2 production (million tons/yr)	average cost ($/ton)	total length of pipeline (miles)
EOR fields	9	34	($30.26)	514
deep coal seams	75	330	$9.96	1580
deep saline formations	35	113	$25.64	1200

[a] From ref 396.

are not homogeneous; they often have complex geometries and occur in stratigraphic clusters, particularly where economic gas potential has been proven. This complexity has an impact on both CH_4 production and sequestration potential. Most coals in the Carboniferous Euramerican coal belt are geometrically complex and, under these screening criteria, may be eliminated. Similarly, one thick laterally continuous seam is easiest to work with; however, the reality of Carboniferous coal basins is that many beds as thin as 0.3 m are often completed for CH_4 production. These beds add significantly to both the CH_4 resource potential and the sequestration potential. More than 20 beds are sometimes completed in some CBM wells. The ability to inject CO_2 into multiple thin beds is needed.

At Battelle, Dooley et al.[393] studied the role of carbon capture and sequestration in a long-term technology strategy of atmospheric stabilization. Dooley et al.[394] also studied the role of carbon capture, sequestration, and emissions trading in achieving short-term carbon emissions reductions. These studies[393,394] indicated that economically viable carbon capture and sequestration technologies may be vital in transitioning from present energy systems designed around venting CO_2 to the atmosphere until low- or non-emitting advanced energy technologies required to stabilize the concentration of CO_2 in the atmosphere are widely deployed.

In response to the near-term need for CO_2 capture and sequestration technologies, Dahowski et al.[395] at Battelle and Mitsubishi performed work on carbon sequestration options in the United States, using the capabilities of a carbon management geographic information system (GIS). Dahowski et al. also used the carbon management GIS system as an economic tool for screening the geologic sequestration options.[396] The GIS system contains information on all fossil-fuel-fired generating capacity in the United States and Canada with a capacity rating of 100 MW or more. Data on other major stationary sources of CO_2, such as natural CO_2 storage domes, natural gas processing plants, and associated pipelines serving current or prospective EOR projects, are in the database. Data include location, operator, reservoir and oil characteristics, production, and CO_2 source. The data system also includes information on geological sinks such as deep saline aquifers and deep coal basins that have the potential for sequestering large quantities of CO_2 while simultaneously enhancing the production of CBM (Table 11). The system structure, datasets, and applications can be found in Dahowski et al.[395]

The GIS system[395,396] can perform spatial analyses and visually communicate relationships among, for example, sources of CO_2 emissions and potential geologic sites. Power plant location, type, age, ownership, environmental controls, emissions data, and proximity to geologic sinks are all in the GIS system, to help develop strategy for understanding aggregate emissions and potential liability for a single plant, company, state, or at the national level.

A customized economic screening tool is automated and permits levelized costs of CO_2 capture, transport, and disposal to be determined for each combination of plant and prospective sink, so that the optimum sequestration route for any specific stationary source or region can be found. Capture costs and performance for CO_2 capture from existing sources are modeled using Mitsubishi Heavy Industries and Kansai Electric Power Company chemical absorption processes, which are based on new amine solvents and new packings.[376,396] The value of products produced from EOR and ECBM operations and a value for carbon credits can be included in the analysis. The cost data contained within the system is based on the best available data and can be easily updated; however, the output from this economic screening tool should not be regarded as a precise measure of actual expected costs. Instead, the data provides a high-level indication of the best option for each plant and identifies the plants that may be best suited for capture and sequestration.[395,396]

A sequestration site for one plant or company may well differ from that of another, depending on factors such as plant design, generating unit, operating characteristics, location, and distance of potential sinks, as shown in Table 12. Thus, the real value of the system lies in its ability to identify the least costly sequestration pathways for analysis of carbon management as an aid to decision making. For example, note the average cost per ton comparisons for CO_2 sequestration shown in Table 12.

VI. Environmental Safety and Health (ES&H) Aspects of CO_2-ECBM/Sequestration

ES&H Aspects of CO_2. According to Bachu, "immediate safety refers to the potential for upward migration and escape into other strata during or immediately after injection", whereas ultimate safety "refers to CO_2 lateral migration in aquifers with potential for cross-formational flow, or in flow systems with a short

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(393) Dooley, J. J.; Edmonds, J. A.; Wise, M. A. *Greenhouse Gas Control Technologies*; Eliasson, B., Riemer, P., Wokaun, A., Eds.; Elsevier Science, Ltd.: Oxford, U.K., 1999; pp 857−861.

(394) Dooley, J. J.; Kim, S. H.; Runci, P. J. The Role of Carbon Capture, Sequestration and Emissions Trading in Achieving Short-term Carbon Emissions Reductions. In *Proceedings of the Fifth International Conference on Greenhouse Gas Control Technologies*, Cairns, Australia, August 13−16, 2000, pp 1127−1132.

(395) Dahowski, R.; Dooley, J.; Brown, D.; Mizoguchi, A.; Shiozaki, M. Understanding Carbon Sequestration Options in the United States: Capabilities of a Carbon Management Geographic Information System. In *Proceedings of the First National Conference on Carbon Sequestration*, NETL Publications No. DOE/NETL-2001/1144, May 14, 2001, 10 pp. (CD-ROM.)

(396) Dahowski, R. T.; Dooley, J. J.; Brown, D. R.; Stephan, A. J. Economic Screening of Geologic Sequestration Options in the United States with a Carbon Mangement Geographic Information System. In *Proceedings of the 18th Annual International Pittsburgh Coal Conference*, Newcastle, NSW, Australia, December 3, 2001, pp 1−11.

Table 12. Example Analysis: 10 Most Economically Attractive Opportunities[a]

plant	generation unit	state	sink type	sink name	distance (miles)	CO_2 emissions	cost ($/ton)
A	2	TX	CO_2 EOR − current	Anton Irish	37.4	4 247 162	−33.55
B	1	UT	CO_2 EOR − current	Rangely Weber Sand	23.3	3 662 376	−32.95
A	1	TX	CO_2 EOR − current	Anton Irish	37.4	4 613 470	−32.51
C	4	NM	CO_2 EOR − current	Greater Aneth Area	48.4	3 997 928	−28.89
D	1	WV	CBM fields	Northern Appalachian Basin	0.0	8 281 637	4.12
E	1	AR	CBM fields	Gulf Coastal Plain	0.0	6 350 662	5.41
F	3	MT	CBM fields	Powder River Basin	0.0	6 150 694	5.46
G	1	TX	CBM fields	Gulf Coastal Plain	0.0	6 166 581	5.60
H	3	PA	CBM fields	Northern Appalachian Basin	0.0	4 620 791	5.93
G	2	TX	CBM fields	Gulf Coastal Plain	0.0	6 562 411	5.94

[a] From ref 396.

residence time."[397] CO_2 is nonexplosive, nonflammable, and noncarcinogenic. It is present in humans and is a constituent of exhaled air. It is colorless, odorless, and has a gaseous density of 1.97 g/L, making it denser than air. Consequently, it accumulates at floor level and in depressions, creating an oxygen-deficient atmosphere and is an asphyxiant. This was demonstrated twice in recent years, in Cameroon, where CO_2 welled up from two different volcanic crater lakes, asphyxiating hundreds of people living nearby. This occurred on August 15, 1984 at Lake Monoun, where 37 people died, and again at nearby Lake Nyos on August 21, 1986, when more than 1700 people lost their lives.[398] Approximately 250 000 tons of CO_2 were suddenly released from the Lake Nyos crater lake.[399] In 1998, a cross-country skier in the Horseshoe Lake area near Mammoth Mountain, CA was killed by exposure to volcanic CO_2.[400] (The region has a high CO_2 flux from a large body of molten rock beneath the ski area.) This is the first known death in the United States caused by exposure to volcanic CO_2, although acute exposure to volcanic CO_2 has resulted in death in Japan, Italy, Africa, and Indonesia. A large number of dead and dying trees were observed in this same area near Mammoth Mountain in 1989; these trees were killed by CO_2 levels of >90% in the soil gases.[399,401]

CO_2 concentrations of 10% (100 000 ppm) can result in unconsciousness, followed by death from oxygen deficiency. Concentrations of 5% can result in shortness of breath and headache, whereas continuous exposure to concentrations of 1.5% CO_2 can produce physiological changes.[402] Concentrations in the atmosphere generally vary between 300 ppm and 700 ppm. Exposure to higher concentrations can produce increased respiratory rate, sleepiness, headache, dizziness, lassitude, dyspnea, and narcosis. Concentrations of >10% pose an immediate threat. The symptoms of low-level CO_2 intoxication are reversible. The Occupational Safety and Health Association (OSHA) permissible exposure limit for CO_2 is 5000 ppm (time-weighted average).[403] Acidosis occurs in humans after 1 h of exposure to atmospheric concentrations of 2.8% CO_2.[404] Messier et al. reported that the concentration of plasma calcium decreased among 7−15 humans onboard a submarine for 57 days after the first day of patrol, when the CO_2 concentration ranged from 0.8% to 1.2%, with a mean of 0.98%. The excretion of calcium and phosphorus in their urine decreased during the first three weeks, with a decrease in plasma calcium and increase in plasma phosphorus. There was a marked increase in urinary calcium excretion and a concomitant increase in the partial pressure of CO_2 (P_{CO_2}) and the HCO_3^- concentration in the blood. They hypothesize that, during prolonged exposure to low levels of CO_2 (up to 1%), the metabolism of calcium is controlled by the uptake and release of CO_2 in bones.[405] Others have made similar observations concerning CO_2 storage in bones.[406,407]

The CO_2 flux on the Earth's surface varies greatly. The rate of CO_2 outgassing in areas of volcanic activity can be quite high, even life-threatening. For example, there are surface fractures in the Earth near the Rome airport that outgas CO_2 at a rate that is sufficient to kill animals that venture nearby. In 1583, Fructuoso described the deaths of cattle, dogs, and birds in and near subterranean areas such as trenches and caves at Sao Miguel, Azores, near the Furnas volcano. He also reported that people residing in places near the volcano suffered nausea and vomiting.[408] The soil gas profiles in a park near the Furnas volcano on Sao Miguel Island in the Azores were recently measured by Baxter et al. and found to have CO_2 concentrations that ranged from background to 100%.[409] They reported that the "diffuse soil flux of CO_2 for the whole degassing area of the village was estimated at 50 T/day in 1993 and 75 T/day in 1994, with a mean flux of 15 L/m^2/h for the zone with a soil concentration of > 50%."[409] Gas measurements were made outside and inside houses near the Furnas

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volcano. A garden pit 1 m below ground level had atmospheric CO_2 concentrations of 40% on some days. Increased levels of CO_2 were found at ground level near cracks in cement floors or where waste pipes entered houses. CO_2 concentrations of 10%−30% were determined in floor cupboards and other unventilated areas within homes. Fortunately, homes on Sao Miguel Island typically did not have basements. Baxter et al. found that there was a high "risk of asphyxia in unventilated, confined spaces, such as cupboards beneath stairs, pits or other excavations below ground level." As the previous discussion shows, the natural CO_2 flux from the Earth can be sufficiently high to cause life-threatening concentrations within homes.[409] Kerrick recently reviewed the literature on CO_2 emissions from solid earth resulting from igneous and metamorphic sources that are not on or near the Earth's surface.[410]

Hydrodynamic Flow through the Coal Seam. The hydrodynamic flow through the coal seam can have safety implications. The flow of formation waters from a coal seam used for CO_2 sequestration can result in CO_2 dissolving in or reacting with the water. The CO_2 and the reaction products such as carbonic acid, bicarbonate ions, and carbonate ions can be subsequently transported from the coalbed and migrate into areas of lower pressure, where the CO_2 can be released as a gas and migrate to the surface. These species can be leached from the coal over geological time.[411] In some instances, it may be possible for artesian conditions to develop, resulting in a safety issue if the waters find their way to the surface. Injection of CO_2 into a coalbed is expected to "affect the pressure, flow regime and salinity of the formation waters." "CO_2 injection in overpressured aquifers may raise technological and safety issues."[16] Formation water that is associated with mountain building is often hot, saline, and overpressured. These qualities are not conducive to CO_2 sequestration. Geologically old Foreland basins and intracratonic basins are often underpressured and are well-suited for CO_2 sequestration.[83]

ES&H Aspects of CH_4. Leakage of CH_4 from coalbeds along faults and fractures occurs naturally and constitutes a significant source of atmospheric CH_4 on a global scale.[413,414] Clayton et al. reported CH_4 fluxes of 1000 kg/year at the surface exposure of a fault in Alabama's Black Warrior basin[413] and 13×10^6 kg/year along a creek bed in the San Juan basin.[414] Faults and fractures are significant migration routes for CH_4 resulting from the natural degassing of coalbeds. When sequestering CO_2 in coal seams, it is imperative that the injection pressure of the CO_2 does not exceed the fracture pressure of the cap rocks above the coal seam. Overpressurization would cause the cap rock to fracture and provide an escape route for the CO_2 and CH_4. CH_4 concentrations of 6000 ppm in soil at a depth of ~2 m have been reported in coal mining regions of Poland.[71] This soil CH_4 concentration was reached without the use of ECBM techniques. If CH_4 from a coalbed can reach the surface, then CO_2 can reach the surface. CH_4 is a flammable and explosive gas, whereas CO_2 is an asphyxiant. Just as CO_2-ECBM/sequestration techniques cause the production of CH_4 to occur at an increased rate (recall Figure 1), it is expected that leakage along faults, fractures, and all other migration routes will increase for CH_4 initially and later for CO_2 during CO_2-ECBM/sequestration. The ambient air concentration of CH_4 is 1700 ppb.[415]

Experience with CO_2-ECBM recovery is limited, compared with decades of experience with CBM recovery. There is much to be learned concerning ES&H aspects from CBM production that should be directly transferable. Thousands of CBM recovery wells are active in the San Juan basin in both Colorado and New Mexico, in the Powder River basin in Wyoming, in the Black Warrior basin in Alabama, and elsewhere. We suspect that some of the ES&H problems associated with CBM recovery may be amplified when CO_2-ECBM recovery techniques are applied. Well-organized citizens groups have arisen in some places, including Colorado and Wyoming, that actively oppose further CBM development in those states.

Anecdotal Information on ES&H Problems Associated with CBM. Both the ES&H aspects of CO_2-ECBM/sequestration and the public perception of ES&H aspects are important. Either would stop development of the technology that is needed to address increasing concentrations of atmospheric CO_2. With this in mind, we list some of the perceived problems associated with CBM production. The opponents of CBM development have presented a long litany of perceived ES&H problems associated with the technique. These problems are presented in newspaper accounts from places where CBM recovery is under active development. These reported problems include the following: instances of water wells going dry;[416−419] salty coalbed water disposed in streams,[416] resulting in water quality degradation[420] and the loss of farmers' ability to use it for irrigation purposes;[421] erosion and flooding problems caused by discharge of large amounts of produced water;[418] homes breaking apart;[421] water wells becoming contaminated with CH_4[416,422−424] and H_2S;[416] tap water fizzing[423] and bubbling with escaping gases; tap water

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(419) Garrett, M. Environmental Impact Fee Proposal Draws Large Crowd. *The Pueblo Chieftan*, February 21, 2002. (Newspaper article.)

(420) Trujillo, S. BLM Releases Study on Oil, Gas. *The Durango Herald*, January 13, 2001. (Newspaper article.)

(421) Johnson, C. Landowners Air Complaints Over Coalbed Drilling. *Billings Gazette*, February 14, 2002. (Newspaper article.)

(422) Trujillo, S. New Rules for Wells Aimed to Address Landowners Concerns. *The Durango Herald*, August 27, 2000. (Newspaper article.)

(423) Clarren, C. Ranchers, Developers Stand Up to Oil and Gas Industry. *The Durango Herald*, November 12, 2000. (Newspaper article.)

that can be ignited with a match;[416] rivers bubbling with escaping CH_4;[424] oily material entering water wells;[416] both CH_4 and H_2S seeping from the ground[416] and, in some cases, into homes[416,424] and streams;[416] vegetation dying because of exposure to high levels of CH_4,[424] CH_4 jets spurting above ground;[416] exploding gas wells;[423] exploding homes;[425] gas wells on fire;[426] wildfires caused by burning gas wells;[426,427] blighted landscape and a loss of pristine beauty;[419,422,423] noise problems;[420,422,423] loss of property value;[419] wells operating within 150 ft (45.72 m) of homes without the owners' permission in some states; increased traffic;[419,423] dust;[423] degraded air quality;[420] acid spills;[428,429] and production of tainted soils.[430]

It must be emphasized that the previously listed problems are described in newspapers, not peer-reviewed literature. Other explanations exist for some of these problems. The proponents of CBM production argue that some of the problems previously described are natural events that are not induced by CBM. For example, proponents claim that contamination of some water wells with CH_4 is a result of naturally gassy aquifers. Proponents state that claims associated with dead vegetation due to exposure to high CH_4 concentrations may be spurious. They note that aerial photography of those lands with dead vegetation showed that they had the same problem before CBM production began.

The exploding water well occurred in the Black Warrior basin. It lies far outside the known CH_4 drainage of any CBM wells. It is located in a horst block that has only water wells. Problems caused by CH_4 in these water wells seem to be associated with the installation of closely spaced water wells drilled into a shallow, thin, gassy coal seam that was not being used for CBM. The problem was exacerbated by a severe drought, when the wells competed for limited water. The water wells created a degasification pattern. Methane adsorption isotherms on the coal show that the gas content can be 125 Scf/t (3.54 m^3/t) at a depth of 150 ft (45.72 m).

Some of the above-mentioned ES&H problems are not clearly tied to CBM recovery or are tied to it circumstantially. Indiana University geologist Maria Mestalerz has been quoted as saying, in regard to the aforementioned discussion, "There is really no data. It's obvious that we need to look into this."[416] Yet, other experts who are boosters of the technology say that it is possible that CBM operations could cause some of the previously listed problems. Industrial representatives argue that there is no proof that CBM operations damage nearby water.[416] An Alabamian filed a lawsuit in federal court, blaming coalbed stimulation for causing long, oily strings to stream from his faucet and a strong sulfur smell to appear in his shower. As a consequence, the court ordered the Enviormental Protection Agency (EPA) to regulate the CBM stimulation process in Alabama, but only in Alabama.[424] The ES&H complaints from New Mexico and Colorado residents of the San Juan basin "have been backed by warnings from the Environmental Protection Agency in 1990, and the U.S. Geological Survey in 1992, that coalbed gas production may be polluting shallow aquifers and residential water wells."[423] However, the Colorado Oil and Gas Conservation Commission (COGCC), the New Mexico Oil and Gas Division, and the U.S. Bureau of Land Management (BLM) do not believe that there is sufficient evidence to stop gas production.[423] Brian Macke, deputy director of the COGCC, says that "there is a fairly large body of scientific data that shows there is no hydrologic connection" between coalbed water and underground aquifers.[418] Another recent report from the BLM indicates that groundwater is not significantly impacted by CBM production.[420] A county manager from Colorado has indicated that residents of Bayfield, CO "did not have a CH_4 problem until Amoco drilled 10 coalbed gas wells in the area."[423] "A lot of areas of the county have gone from no measurable CH_4 in their water wells to the saturation point."[423]

Some of the problems described previously (see prior discussion in this subsection) occurred in coal-bearing regions before any CBM recovery began. In the Powder River basin, CH_4 was known to be present near outcrops of the coal seam and was present in artesian springs. Those settlers that completed water wells into the coal seam had problems with CH_4 that was present in the water. Sparks from electric motors in the wellhouse caused explosions. The Rawhide subdivision north of Gillete, WY was constructed over a shallow seam next to the Eagle Butte mine. H_2S and CH_4 made their way into basements and came up in cracks in the streets.[57] These problems occurred before any CBM recovery was initiated.

Beckstrom and Boyer described an investigation of the causes of natural gas migration into groundwater in an area that runs along the Animas River valley near Cedar Hill, NM that reportedly had a problem with CH_4 in well water.[431] The study consisted of four water sampling and analysis projects conducted by the New Mexico Oil Conservation Division (NMOCD), and the Amoco Production Co.[431] Before the study began, a landowner reported that gas was bubbling out of his alfalfa field and from the Animas River adjacent to his field. There were additional reports of water quality deterioration that prompted the NMOCD to investigate. Public concern was sufficient to cause the NMOCD and the New Mexico Environmental Improvement Division to sponsor a "water fair" at a local school, where area residents brought in water samples for free testing.[432−434] Three possible sources of CH_4 were considered: natu-

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(424) Council, A. Methane Creates an Explosive Situation in Colorado. *The Durango Herald*, December 27, 1993. (Newspaper article.)

(425) Bowen, K. Burn Victim Wants to Stop Gas Wells. *Tuscaloosa News*, March 29, 2001. (Newspaper article.)

(426) Banks, J. Gas Well Sparks Wildfire. *The Durango Herald*, July 1, 2001. (Newspaper article.)

(427) Banks, J. Crews Confine Fire South of Durango. *The Durango Herald*, July 2, 2001. (Newspaper article.)

(428) Cewald, E. No Ill Effects Expected From Acid Spill. *Trinidad Plus*, June 5, 2001. (Newspaper article.)

(429) Garrett, M. Trinidad Acid Spill Investigated. *The Pueblo Chieftan*, June 2, 2001. (Newspaper article.)

(430) Sluis, T. BP Using Bacteria to Clean Polluted Soil. *The Durango Herald*, February 1, 2001. (Newspaper article.)

(431) Beckstrom, J. A.; Boyer, D. G. *SPE Form. Eval.* **1993**, *8*, 71−79.

(432) Health Education Division News. Santa Fe, New Mexico. New Mexico Health and Environmental Department, Office of Public Information. *HED News*, March 21, 1989.

(433) Papich, B. Seam Drilling Not Contaminating. *The Daily Times,* February 20, 1990. (Newspaper article.)

(434) Malick, A. Migrating Gas a Threat to Freshwater Aquifers. *The Durango Herald*, February 9, 1990. (Newspaper article.)

rally occurring CH_4, leaks around casings, and upward migration of gas from the Fruitland formation. Beckstrom and Boyer concluded that CH_4 was detected in solution in many water wells from the study area but it was not possible to ascertain its origin. One well contained benzene in excess of both EPA and New Mexico water quality standards. They found that CH_4 seeping from the surface has an unknown thermogenic origin, and "Fruitland coal gas can migrate vertically behind uncemented wellbores" to the surface, where it can contaminate aquifers. They concluded that "methane detected in domestic water wells near Fruitland coal development cannot be correlated directly to Fruitland coal gas development."[431]

The problems could occur because gas companies drill into a coalbed and pump out the water. This process is known as dewatering, and it reduces the water pressure in the seam. Removing water from the cleat system in the coalbed liberates CH_4 and other sorbed gas molecules and allows them to migrate up the wellbore or into other areas of lower pressure. Typically, millions of gallons of water are pumped from a coal seam, resulting in changes in undergroundwater pressure across large areas, allowing the previously sorbed gases to migrate through faults, fissures, and microfissures and conceivably into water wells, into homes, and through the Earth's surface. Old abandoned wells of various types could become conduits for gas migration to the surface.

The Need for Accurate Gas Inventorying and Accounting. Although CO_2-ECBM recovery is an attractive sequestration option in cases where sufficient CH_4 can be recovered, it is important to recognize that the entire environmental impetus for doing this is to reduce GHG emissions to the atmosphere. CH_4 is a GHG that is reported to possess 25 times more radiant force than CO_2 on a molar basis while it is in the atmosphere.[435]

For every mole of CO_2 sequestered, 0.5 mol of CH_4 is released. If 8% of this amount of CH_4 is not captured but escapes to the atmosphere by leaking from the Earth via upward gas migration from the coal seam or leaks from the production facilities, then 0.04 mol of CH_4 will be released to the atmosphere. This 0.04 mol quantity of CH_4 has a radiant force that is equal to that of the 1 mol of CO_2 that was sequestered. From a GHG/global warming perspective, more than 92% of the CH_4 liberated during CO_2-ECBM/sequestration must be captured. This is an oversimplification. As Stanton et al. have recently stated, some low-rank coals may imbibe 10 times the amount of CO_2 as CH_4 released.[34] Similarly, CH_4 does not permanently remain in the atmosphere, but rather is oxidized to CO_2 eventually. Even though the aforementioned scenario is an oversimplification, it serves to make the point that, before CO_2-ECBM/sequestration is undertaken, for the purpose of reducing GHG emissions, it will be important to conduct an inventory and accounting of the CO_2 stored in the coalbed and the amount of CH_4 that is both captured and released or escapes into the atmosphere. Not only can CH_4 leak from the deep earth to the surface over wide geographic areas during CBM production, but the CH_4 that is captured also can leak from its containment. For example, the COGCC recently awarded BP its "Environmental Protection and Cost Reduction Award" for changing leaking valves on the CBM pump's separator units and replacing 3300 controllers on 2760 wells in both Colorado and New Mexico, resulting in a reduction of CH_4 leakage of 12 000 tons per year.[422] It may be difficult to show that at least 92% of the CH_4 liberated from coal is actually captured. If 8% or more of the CH_4 released from the coal seam leaks into the air, then, according to the oversimplified scenario given previously, CO_2-ECBM/sequestration would actually contribute to the GHG emissions problems and exacerbate global warming instead of mitigating it. Therefore, a careful inventorying and accounting process must be developed that is combined with complete and constant monitoring of escaping CH_4 and CO_2 over a broad geographic region.

ES&H Aspects of Produced Water. Substantial amounts of water are produced during both conventional CBM recovery and CO_2-ECBM recovery. Coal fines are also produced. Crude oil has been reported in some CBM production wells. Crude oil is removed at the wellhead by gravity separation.[21] The produced gas and water go through a water/gas separator and the resulting gas is filtered, to remove any coal fines. Conventional glycol drying systems are used to remove any remaining water in the produced gas stream.[21,436] In most instances, the produced water cannot be disposed of directly, because it contains dissolved salts (such as NaCl and bicarbonate), other dissolved solids, and dissolved organics. The quality and quantity of water produced during CBM recovery varies from coal seam to coal seam, depending upon the geology, and associated aquifers.[48] The two most important factors associated with the quantity of water produced are the age of the seam and the depth. The permeability of deeper seams is decreased, relative to shallow seams. Less-permeable seams produce less water. Often, water production peaks in the early stages of CH_4 production and then decreases to a constant rate.

Many coalbed gas wells display a distinctive production history for both CH_4 and water, as shown in Figure 24.[438] Water production often continues throughout the entire lifetime of a CBM recovery well; however, the water production rate often declines rapidly, and, for many wells, it stops. Substantially more water is produced from a typical CBM recovery well than from a conventional natural gas well.[48] The TDS level found in water produced during CBM recovery ranges from 200 mg/L to 90 000 mg/L. Most of the dissolved solids are <30 000 mg/L.[46,280,439] The TDS level of CBM waters can be quite fresh: <2000 ppm for the Powder River basin. Produced waters generally have a pH in the range of 7−8. Typically, the water contains anions such as

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(435) Methane Emissions and Opportunities for Control. Workshop Results of Intergovernmental Panel on Climate Change, Report No. EPA/400/9-90/007, 1990.

(436) Barzandji, O. H.; Wolf, K.-H. A. A.; Bruining, J. Combination of Laboratory Experiments and Field Simulations on the Improvement of CBM Production by CO_2 Injection. In *Proceedings of the Second International Conference on Methane Mitigation*, Novosibirsk, 2000, pp 325−336.

(437) Essenhigh, R. H. *Chemistry of Coal Utilization, Second Supplementary Volume*; Elliott, M. A., Ed.; Wiley: New York, 1981; p 1184.

(438) Kuuskraa, V. A.; Brandenburg, C. F. *Oil Gas J.* **1989**, *87*, 41, 49−56.

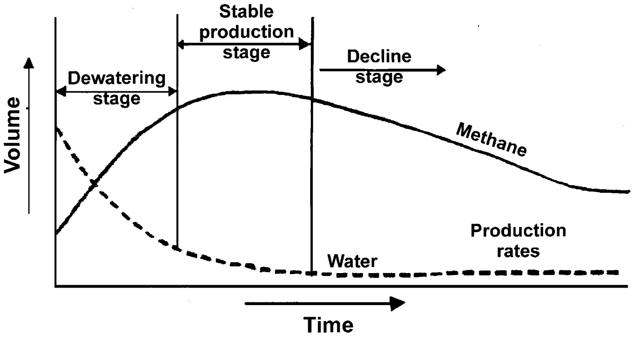

Figure 24. Generalized production history showing volumes of CH_4 and H_2O over time for a typical coalbed gas well. (From Kuuskraa and Brandenburg.[438])

CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-}, and cations such as Na^+, K^+, Ca^{2+}, Mg^{2+} in amounts that vary considerably. The TDS level and salinity are often lower in the shallower parts of a seam, because of the influence of meteoric waters. The total volume of produced water can be huge; in the Black Warrior basin, 2800 wells produced 15×10^6 m^3 of water in 1991.[46,440] Davidson et al. published a table of representative concentration values of common constituents in produced water from both CBM and conventional natural gas wells.[48] That table is reprinted as Table 13. Some produced waters from oil and gas drilling and operations can be toxic to organisms, because of osmotic imbalances and an excess or deficiency of certain common ions.[441] Produced water from the Cedar Cove Degasification Field in Alabama was not acutely toxic to either rough shiners (*Notropis baileyi*) or fathead minnows (*Pimephales promelas*), but was acutely and chronically toxic toward *Ceriodaphnia*. These effects were due, at least in part, to high concentrations of chloride.

The use of CO_2-ECBM/sequestration techniques may affect the composition of the produced waters. CO_2 is soluble in water, as shown in Figure 3A, and under conditions of elevated pressure, it forms concentrated carbonic acid solutions that are very acidic. This acidic water is expected to dissolve part of the mineral matter in the coal, react with other minerals in the coal, and result in changes in the composition in the produced water (see discussion in previous subsection entitled "Surface Area Measurements" and the upcoming subsections entitled "Effect of CO_2 Adsorption on Mineral Matter" and "Effect of CO_2 Adsorption on Organic Matter"). We expect the produced waters from CO_2-ECBM/sequestration sites to display increased amounts of calcium and magnesium, because of dissolution of the corresponding carbonate minerals from the coal. Acidic water may also affect the concentration of dissolved organics in the water. We expect that acidic aqueous solutions of carbonic acid may dissolve free organic bases in the coal, such as quinolines and other compounds. This is in contrast to typical waters from CBM recovery wells, which generally have much lower concentrations of dissolved organics than water recovered from natural gas wells.[48]

Table 13. Some Compositions for Water Produced from Coalbed Methane (CBM) and Conventional Natural Gas Extraction in the United States[a]

parameter	CBM	natural gas
pH	7.8	7
major components (mg/L)		
total dissolved solids (TDS)	4000	20000–100000
total suspended solids (TSS)		1.0
chloride (Cl^-)	2000	11000
sulfate (SO_4^{2-})	12.9	0–400
bicarbonate (HCO_3^-)	597	
carbonate (CO_3^{2-})	0.008	
fluoride (F^-)	2.6	
nitrate (NO_3^-)	3.0	
iron	10	
calcium	89	
sodium	1906	
potassium	7.5	
trace elements and hydrocarbons (μg/L)		
silver	1.1	10–70
aluminum	40	
arsenic		30
barium	2780	10–100
cadmium	5	30
chromium	3	20–230
copper	5.6	0–100
mercury	0.13	1
lithium	92	
manganese	250	
nickel	29	100
lead	55	100–170
antimony	30	70
selenium	25	60
strontium	4000	
tellurium		90
vanadium	5	
zinc	109	40–200
oil/grease		3000–25000
phenol		0–2000
benzene		1000–4000
methylbenzene (toluene)		0.2–12.3
dimethylbenzene (xylene)		500
ethylbenzene		0–300
naphthalene		30–900

[a] Data taken from ref 48.

Davidson et al. described, in detail, some scenarios for the disposal of produced water obtained from CBM recovery wells.[48] Disposal practices for water produced via CBM recovery include subsurface re-injection, discharge to surface waters, direct land application, and advanced treatment systems.[48] Many of these disposal scenarios are expected to be applicable to CO_2-ECBM/sequestration. The economics of various produced water disposal and advanced treatment scenarios are discussed in a paper by Lee-Ryan et al.[442] Advanced treatment techniques such as aeration followed by sedimentation can be used to remove some constituents of produced water. Other treatment procedures such as reverse osmosis, biological treatment, electrodialysis,

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(439) Ayers, W. B., Jr.; Kaiser, W. R.; Laubach, S. E.; Ambrose, W. A.; Baumgardner, R. W., Jr.; Scott, A. R.; Tyler, R.; Yeh, J.; Hawkins, G. J.; Swartz, T. E.; Schultz-Ela, D. D.; Zellers, S. D.; Tremain, C. M.; Whitehead, N. H., III. Geologic and Hydrologic Controls on the Occurrence and Producibility of Coalbed Methane, Fruitland Formation, San Juan Basin, Report No. GRI-91/0072, Gas Research Institute, Chicago, IL, 1991.

(440) Pashin, J. C.; Hinkle, F. Coalbed Methane in Alabama, Circular Report No. 192, Geological Survey of Alabama, 1997.

(441) Pillard, D. A.; Evans, J. M.; DuFresne, D. L. Acute Toxicity of Saline Produced Waters to Marine Organisms. In *Proceedings of the International Conference on Health, Safety & Environment*, New Orleans, LA, June 9–12, 1996; pp 675–683.

(442) Lee-Ryan, P. B.; Fillo, J. P.; Tallon, J. T.; Evans, J. M. Evaluation of Management Options for Coalbed Produced Water. In *Proceedings of the Coalbed Methane Symposium*, University of Alabama, Tuscaloosa, AL, May 13–16, 1991; pp 31–41.

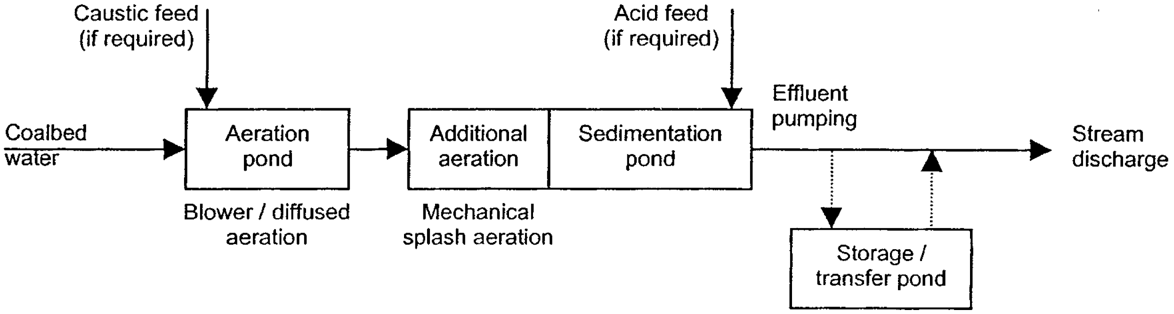

Figure 25. Aeration/sedimentation system for treating water produced during coalbed methane (CBM) recovery. (From Davidson et al.[48])

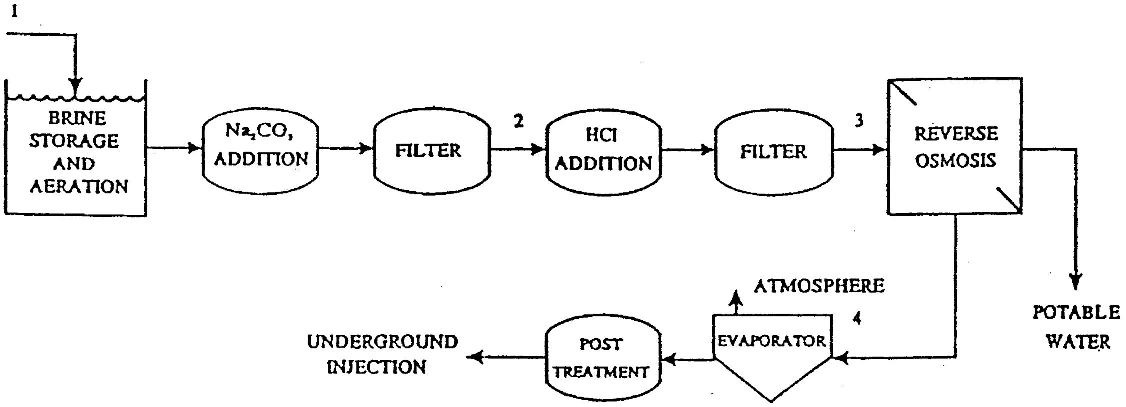

Figure 26. Schematic diagram of the brine pretreatment process (the Integrated Process for Coalbed Brine and Methane Disposal). (From Byam et al.[412])

and evaporation are all possible treatment options. Kharaka et al. described a water-treatment process for produced waters from oil production that may be applicable to waters from CBM and possibly CO_2-ECBM recovery wells.[443] Produced water from CBM recovery is usually disposed of by re-injection into another formation or surface disposal, depending upon the water quality. The water quality affects the treatment and disposal options.[48] Re-injection into depleted gas reservoirs is widely applied in the San Juan basin, whereas, in the Black Warrior basin, surface discharge is commonly used.[21,440] However, before produced water can be discharged, it must be treated. The exact treatment is dependent on the produced water quality and the pertinent environmental regulations.[21,48] An example treatment process for coalbed water is shown in Figure 25.[48] Aeration is used, followed by sedimentation, to remove iron and manganese and reduce the biological oxygen demand of produced water. Aeration oxidizes the ferrous and manganous cations. Algae that has accumulated in the ponds (see Figure 25) reduces the concentrations of dissolved organics. Unfortunately, aeration and sedimentation do not reduce the Cl^- content. It is the Cl^- content of produced water that controls the way produced water is discharged.

Aquatech Services, Inc., has developed a process to treat produced waters from CBM operations, based on reverse osmosis. The process is proprietary and is capable of treating brines of variable complexity for environmental compliance and beneficial reuse.[444] The process includes a submerged combustion evaporator and pulse combustion drying. The process has been used in a field study in the San Juan basin and in Upper Silesia, Poland at the Morcinek Mine. A block diagram of the process is given in Figure 26. The brine is collected and pumped through a filter and a softener and is then subjected to a pretreatment step, to adjust pH. After pretreatment, the brine flows to a reverse osmosis unit, where two streams are produced. One is a potable water stream, and the second is a brine stream with increased ionic concentration, relative to the original brine. The brine is then sent to a submerged combustion evaporator, where CH_4 from the coalbed is combusted to evaporate the brine to yield a concentrated brine. The overall volume of brine is reduced 97% by the process. The concentrated brine from the combustion evaporator can be further treated using a dryer where the concentrated brine is sprayed into the flame of a pulsed combustor, resulting in solid salt particles that can be delivered to a landfill or recycled for commercial use. The reverse osmosis component of the treatment process is not proprietary and is available from many vendors.

Researchers at New Mexico Tech recently described a new technology for treatment of produced water from the Fruitland coal formation using ion exchange. This water is somewhat unique in that it has a high concentration of $NaHCO_3$ (10 000 ppm), with all other components being minor. The water is treated in a bicarbonate anion exchange column, where anions other than HCO_3^- are removed and replaced with HCO_3^-. This water is then treated "in an aerated and fluidized hydrogen cation-exchange resin," that removes the Na^+ cation, releasing the H^+ cation, which reacts with the

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(443) Kharaka, Y. K.; Leong, L. Y. C.; Doran, G.; Breit, G. N. Can Produced Water be Reclaimed? Experience with Placerita Oil Field, California. Presented at the 5th International Petroleum Environmental Conference, Albuquerque, NM, October, 20–23, 1998, 26 pp.

(444) Brandt, H.; Tait, J. H. *Am. Oil Gas Reporter* **1992**, *9*, 3 pp.

HCO_3^- anion to ultimately yield H_2O and CO_2. The finished water can have TDS contents of 500 ppm or less.[445]

Good ES&H Practices, Relative to CBM and CO_2-ECBM/Sequestration. There are several practices that, if implemented before CO_2 sequestration in coalbeds with concomitant CH_4 recovery is initiated, may mitigate some of the perceived potential ES&H problems. Roberts described a "mineral extraction agreement" signed between a land owner and the developer that protects the land owner's interest while permitting development to proceed.[446] The agreement specifies areas of the property that can be developed and establishes requirements for the development project that minimizes the impact upon the environment. The landowner is given input into the construction and drilling operations that include approval of an annual development plan, site selection approval, and limitations on the number of workers, number of vehicles, and working hours. The agreement is reported to have minimized the impact of CBM development.[446] A second practice that may limit ES&H concerns is the establishment of a comprehensive quality assurance program for the production facilities, to ensure that they are in safe operating condition. The program consists of a monitoring and preventive approach, including facility structural inspection, water quality analysis of nearby water wells, the use of corrosion coupons and probes on metallic components of the facility exposed to CO_2 and produced liquids and gases, caliper surveys, and constant leak checking around the wellbore casing including an inspection of the cementing around the casing. The quality assurance program is reviewed and modified, as appropriate, on a regular basis.[447]

VII. An Initial Set of Working Hypotheses and Observations Concerning Some Chemical and Physical Events that Occur when CO_2 is Injected into a Coalbed

There is a fundamental lack of understanding concerning the physical, chemical, and thermodynamic phenomena that occur when CO_2 is injected into a coal seam. This lack of understanding prevents us from developing the best possible models of the process; it prevents us from making sense of operational problems that occur during production and it prevents us from taking the best possible actions to surmount operational problems. In fact, the U.S. DOE "Carbon Sequestration Technology Roadmap Pathways to Sustainable Use of Fossil Energy" identifies CO_2 flow and storage in coals as "not well defined" and describes the effects of CO_2 on coal reservoir permeability as uncertain.[2] These uncertainties and lack of understanding are barrier issues, with respect to wide scale development and implementation of sequestration of CO_2 in coal seams. When Burlington Resources performed a commercial-scale CO_2-ECBM/sequestration project in the Allison Unit in northern New Mexico, they encountered unforeseen operational problems. The initial CO_2 injection rate was ~5 MMcfd (141.6×10^3 m^3/d) but was reduced to 3 MMcfd (86.95×10^3 m^3/d), because of a loss of injectivity. "Subsequent to that, injectivity began a long period of improvement, which has continued through the last available data. These trends are consistent for all four injection wells."[448] CO_2 was injected for six months, during which time an abrupt increase in water production was immediately noticed. After six months, the injection of CO_2 was stopped. During the first six months of operations, "5 of the production wells were temporarily shut in to facilitate CO_2/CH_4 exchange in the reservoir."[326]

As a consequence of the aforementioned events, many hypotheses that describe the chemical, physical, and thermodynamic phenomena that occur when CO_2 is injected into a coal seam were formulated. These hypotheses can be used to develop models that more accurately simulate the CO_2-ECBM/sequestration process. A more complete understanding of what occurs when CO_2 is injected into a coal seam is needed to understand the causes of operational problems when they occur, and to take the most appropriate steps to resolve them. White recently has described these hypotheses in preliminary form[449] and in more-detailed form.[4]

Hypotheses and Observations. The following hypotheses and observations have been made:

(1) The glass-to-rubber transition temperature (T_g) of the coal will be dramatically reduced by imbibition of CO_2. The coal will become plasticized.[450]

(2) The cleat system within the coalbed will begin to close and become restricted, slowing Darcy flow within that area of the seam, because of swelling.

(3) There will be a substantial increase in the self-diffusivity of CO_2 in coal after it has become plasticized and is above its T_g temperature.[450,451]

(4) The diffusivity of CO_2 in coal swollen by high-pressure CO_2 can be described by free volume theory.

(5) The degree to which plasticization, swelling, increased diffusivity, reduction of the T_g value, relaxation of the macromolecular network, and depression of the softening temperature occur will be limited by the degree that the coal is free to swell.

(6) Both liquid and supercritical CO_2 moving through a coalbed will extract small molecules trapped within the macromolecular network. As the network relaxes, these molecules will be released and move with the flowing CO_2, as long as the pressure is greater than their threshold pressure.

(7) Some of the minerals commonly found in coal will dissolve in the acidic, carbonated formation water

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(445) Russell, C.; Vida, A.; Richardson, C. P. Treatment of Fruitland Coal Production Water with Ion Exchange Media. In *Proceedings of the International Unconventional Gas Symposium*, University of Alabama, Tuscaloosa, AL, May 14−20, 1995; pp 275−286.

(446) Roberts, R. D. Coalbed Methane Development: A Land Owner's Prospective. Presented at the Society of Petroleum Engineers Exploration and Production Environmental Conference, San Antonio, TX, February 26−28, 2001, SPE/EPA/DOE Paper No. 66572, 3 pp.

(447) Lee, S. L.; Aw, C. L. A Comprehensive Quality Assurance Program for Offshore Production Facilities. In *Proceedings of the International Meeting on Petroleum Engineering*, Tianjin, China, November 1−4, 1988; SPE Paper No. 17634, pp 893−901.

(448) Reeves, S. COAL-SEQ Project Update: Field Studies of ECBM Recovery/CO_2 Sequestration in Coalseams. In *Proceedings of the Greenhouse Gas Technology Conference (GHGT-6)*, Kyoto, Japan, October 1−4, 2002.

(449) White, C. M. *Prepr. Pap.*—*Am. Chem. Soc., Fuel Chem. Div.* **2003**, *48*, 114−116.

(450) Larsen, J. W. Polymeric Nature of Coals: Some Consequences and Some Unknowns. In *Proceedings of the International Conference on Coal Science*, San Francisco, CA, 2001; pp 1−18.

(451) Larsen, J. W. *Prepr. Pap.*—*Am. Chem. Soc., Fuel Chem. Div.* **2003**, *48*, 112−113.

during those times when both water and high-pressure CO_2 are present together in the coal.

(8) The calcium and magnesium content of the coal will decrease, because of (i) dissolution of carbonate minerals by carbonic acid and (ii) the fact that calcium and magnesium are being displaced from carboxylic acids in low-rank coal.

(9) The injection of dry CO_2 will dry the coal, particularly in those areas where the flow rate of CO_2 is highest.

(10) There will be a CO_2 pressure, temperature, and pH gradient across the coalbed from the injection well to the recovery well. The temperature gradient is due to Joule−Thompson cooling. When dissolved minerals and organics reach areas of the seam with lower pressure, they will precipitate, clogging the pores in the coal.

Possible Effects of CO_2 Adsorption on the Glass-to-Rubber Transition Temperature and Softening Temperature. Coals exist as either a glass or as a flexible rubber, depending on the temperature and other factors. The glassy state is characterized by brittleness and little or no large segmental molecular motion throughout the macromolecular network. Diffusion throughout the system is slow, and the diffusivity of guest molecules is highly dependent on their molecular size and, thus, their molecular weight. Individual components of the macromolecular network are held together by noncovalent interactions (such as van der Waals forces) that are of sufficient strength to prevent movement, with the exception of local vibrations and rotations.[450,451] Conversely, when in the rubbery state, sufficient thermal energy is available to surmount the noncovalent interactions. The macromolecular system then is free to move (allowing the coals to become flexible), internal molecular motion becomes liquidlike, diffusion is much more rapid, and the dependence of guest molecule diffusivities on molecular size is greatly reduced.[450,451]

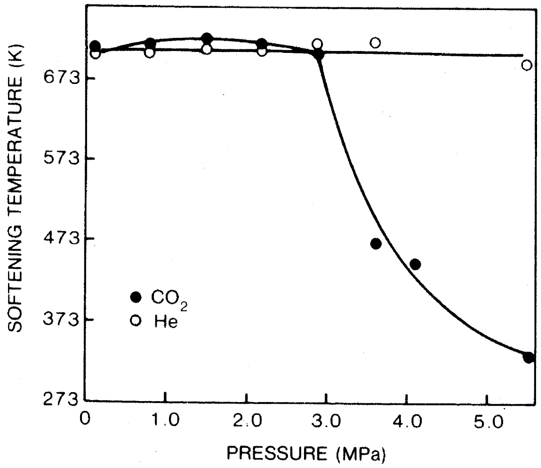

Figure 27. Depression of the softening point temperature of a coal in the presence of increasing pressures of (●) CO_2 and (○) He. (From Khan and Jenkins.[454])

Table 14. Behavior of a Bituminous Coal, a Sub-bituminous Coal, and a Lignite in CO_2 at 298 K and CO_2 Pressures of 0.5, 1.0, and 1.5 MPa[a]

CO_2 pressure (MPa)	coal swelling (vol %)	dissolved CO_2 in coal (%)
	Coal with 83.8% Carbon	
0.5	0.75	13.8
1.0	0.85	16
1.5	1.33	24
	Coal with 78.3% Carbon	
0.5	1.24	23
1.0	2.23	41
1.5	3.11	58
	Coal with 65.8% Carbon	
0.5	2.16	24
1.0	3.00	32
1.5	4.18	47

[a] Data taken from ref 170.

The temperature at which a coal is transformed from a glass to a rubber is known as the glass-to-rubber transition temperature (T_g). When coals and other macromolecular systems (such as polymers) imbibe small molecules (such as CO_2), their T_g value can be decreased (recall observation 1). The physical and chemical properties of coal change, depending on the state it is in (glass or rubber). The molecular transport dynamics of guest molecules are greatly affected. CO_2-induced depression of the glass-transition temperature and other plasticization effects have been investigated in a variety of systems.[452,453] When coal imbibes CO_2, it swells (recall observation 2). The CO_2 acts as a plasticizer, depressing the T_g value and causing a structural rearrangement of the macromolecular system. Plasticizers add free volume and molecular mobility, converting a glass into a rubber. After coal is plasticized by CO_2, it rearranges and moves to a lower energy, where it displays different adsorption properties toward CO_2. After the coal has imbibed CO_2 and swelled, the softening temperature of the coal is depressed, as shown graphically in Figure 27.[454] CO_2 reduces the T_g value by acting as a plasticizer; it dissolves in the coal, the structure rearranges and relaxes, and the softening temperature decreases. As shown in Figure 27, at low CO_2 pressures, there is little or no effect on softening temperature. However, at higher pressures (~3 MPa (29.61 atm)), the effect is dramatic. The softening temperature is decreased over 300 K (27 °C), from something greater than 673 K (400 °C) to less than 373 K (100 °C).

Hsieh and Duda[170] showed that fluids are imbibed by coal in three stages. There is a rapid surface adsorption, presumably at least in part into the pores, followed by a slow diffusion of fluid into the coal, followed by relaxation of the macromolecular network and additional diffusion of the fluid. Hsieh and Duda,[170] and Reucroft and Sethuraman,[455] showed that CO_2 dissolves in coal and is not simply adsorbed on the surface. Table 14 shows that the swelling increases as the carbon content of the coal decreases and the rank decreases. Reucroft and Sethuraman[455] also showed that swelling continues to increase with time for ~200 h as more CO_2 is imbibed into the macromolecular structure. The

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(452) Wissinger, R. G.; Paulaitis, M. E. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 2497−2510.

(453) Lee, D.; Hutchison, J. C.; Leone, A. M.; DeSimone, J. M.; Murray, R. W. *J. Am. Chem. Soc.* **2002**, *124*, 9310−9317.

(454) Khan, M. R.; Jenkins, R. G. Thermoplastic Properties of Coal at Elevated Pressures: Effects of Gas Atmospheres. In *Proceedings of the Conference on Coal Science*, Sydney, Australia, October 28, 1985.

(455) Reucroft, P. J.; Sethuraman, A. R. *Energy Fuels* **1987**, *1*, 72−75.

swelling increases as the pressure increases, and as pressure increases, the time required to reach equilibrium swelling decreases.[455]

Effect of CO_2 Adsorption on Organic Matter. When CO_2 interacts with coal, multiple processes occur. CH_4 desorption occurs simultaneously with CO_2 adsorption. CH_4 is displaced into the cleat system of the coal, where it begins to move toward an area of lower pressure (the production well). CH_4 desorption causes coal to shrink, whereas CO_2 sorption causes the coal to swell and the macromolecular structure to relax.[450] Generally, coal swelling due to CO_2 sorption is greater than shrinkage caused by CH_4 desorption (recall observation 2). The net effect is coal swelling. Weak intermolecular interactions, such as van der Waals interactions, hydrogen bonds, and charge-transfer interactions between one part of the macromolecule and another or between two macromolecules, are broken and replaced by interactions between the macromolecule and CO_2. Swelling allows the small molecules trapped within the interwoven macromolecular network to be released, so that they are free to move. Liquid and dense gaseous CO_2 are excellent solvents. As the trapped molecules are released, they become solvated and extracted by the CO_2 and migrate with CO_2 throughout the coalbed (recall hypothesis 6). The extraction process and movement of formerly trapped molecules begins with the lower-molecular-weight compounds first (see discussion in the subsection entitled "ES&H Aspects of Produced Water)." The movement of the compounds is a function of the threshold pressure of each compound. The threshold pressure of a substance was originally defined by Giddings as the lowest supercritical pressure that will cause a substance to just begin to migrate in a flowing stream of supercritical fluid.[456] Among hydrocarbons, the threshold pressure is an approximate function of their molecular weight. Generally, the amount extracted from coal is quite small (~2.5 wt % or less).

Effect on Diffusivity. The plasticization effects of CO_2 on coal (recall observation 1 and hypothesis 3) are discussed elsewhere.[450] Hypothesis 3 is an extension of one proposed by Larsen[450] to include the self-diffusion of CO_2 in plasticized coal. Mass transport through coal is a controlling function during the sequestration of CO_2. If the cleat fracture system becomes restricted, because of swelling, then Darcy flow will be restricted and transport through the coal will be primarily Fickian (recall observation 2).

A substantial increase in the molecular diffusivity of guest molecules in macromolecular systems in contact with supercritical CO_2 has been documented recently. The diffusivity of ethylbenzene in CO_2 swollen polystyrene shows a 10^6 fold increase when supercritical CO_2 is present.[457] Experimental information that defines the factors that influence and control transport properties in CO_2-swollen macromolecular systems is limited for polymeric systems and, to our knowledge, unknown for coals. Transport properties of Co(II) complexes in polymeric systems in contact with supercritical CO_2 are dependent on the degree of CO_2 swelling and the degree of plasticization.[453] These are plasticization-induced changes in the transport properties of guest molecules in the CO_2-swollen macromolecular network. We hypothesize that the substantial increases in diffusivity of guest molecules in polymeric systems applies to the self-diffusion of CO_2 in CO_2 swollen macromolecular systems such as coal. As such, we expect that the diffusion of CO_2 in coal swollen by high-pressure supercritical CO_2 will be much more rapid than in the same coal before plasticization (recall hypothesis 3).

The CO_2-swollen polymeric systems previously described were unconfined and free to swell. Similarly, the coal in the softening point depression experiment performed by Khan and Jenkins was free to swell.[454] A coal seam is a relatively fixed volume system, in which coal is confined and not free to swell. Therefore, plasticization, swelling, increased diffusivity, reduction of the T_g value, relaxation of the macromolecular network, and depression of the softening temperature will be confined and limited to the degree that the coal is free to swell. The only volume available to swell into is the cleat volume in the seam. Cleat volume is generally 0.2−2.0 vol %.[458−462] The pore volume is also available but usually amounts to <10% of the coal volume. Thus, we expect that the confined space will limit the degree that the coal can swell and, thus, will limit the increase in CO_2 diffusivity and possibly limit the other plasticization-induced changes that a coal may undergo (recall hypothesis 5).

Recent X-ray CT results published by Karacan[162] showed that the vitrinite in a 2.5-cm-diameter confined coal exposed to high-pressure CO_2 at 289 K (25 °C) first swells and then expells some CO_2. He called this process "breathing". The "breathing" process is consistent with the notion that the coal swells and the macromolecular network relaxes, rearranges, and moves to a low-energy state. The relaxed rearranged macromolecular network has a lesser ability to imbibe CO_2 and, thus, some CO_2 is expelled. Based on the limited data in the literature, we cannot be certain if coals used for CO_2 storage will ever be at temperatures above their T_g value. Nevertheless, Karacan showed that structural rearrangement caused by imbibition of CO_2 occurs within several days, even in a confined coal at 298 K (25 °C).

Lee et al.[453] showed that, in a polymeric system swollen by CO_2, the effect of CO_2 swelling on mass transport can be understood using free volume theory. They estimated the fractional free volume (FFV) of the swollen

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(456) Giddings, J. C.; Myers, M. N.; King, J. W. *J. Chromatogr. Sci.* **1969**, *7*, 276−283.

(457) Dooley, K. M.; Launey, D.; Becnel, J. M.; Caines, T. L. Measurement and Modeling of Supercritical Fluid Extraction from Polymeric Matrixes. *ACS Symp. Ser.* **1995**, *608*, 269−280.

(458) Gash, B. W. Measurement of "Rock Properties" in Coal for Coalbed Methane Production. In *Proceedings of the 66th Annual Technical Conference and Exhibition of the Society of Petroleum Engineers*, Dallas, TX, October 6−9, 1991; SPE Paper No. 22909, pp 221−230.

(459) Gash, B. W.; et al. The Effects of Cleat Orientation and Confining Pressure and Cleat Porosity, Permeability, and Relative Permeability in Coal. In *Proceedings of the SPWLA/SCA Symposium*, Oklahoma City, OK, June 15−16, 1992.

(460) Harpalani, S.; Chen, G. *Geotech. Geolog. Eng.* **1997**, *15*, 303−325.

(461) Rice, D. D.; Young, G. B. C.; Paul, G. W. In *1995 National Assessment of United States Oil and Gas Resources—Results, Methodology, and Supporting Data*; Gautier, D. L., Dolton, G. L., Takahashi, K. I., Varnes, K. L., Eds.; U.S. Geological Survey: 1995.

(462) Somerton, W. H.; Soylemezoglu, I. M.; Dudley, R. C. Effect of Stress on Permeability of Coal: Permeabilities of Three Types of Bituminous Coals under Several Stress Conditions that Simulated Possible States of Stress in Underground Environments to Depths of 2000 ft, Final Report, University of California, Berkeley, Petroleum Engineering Laboratories, 1974.

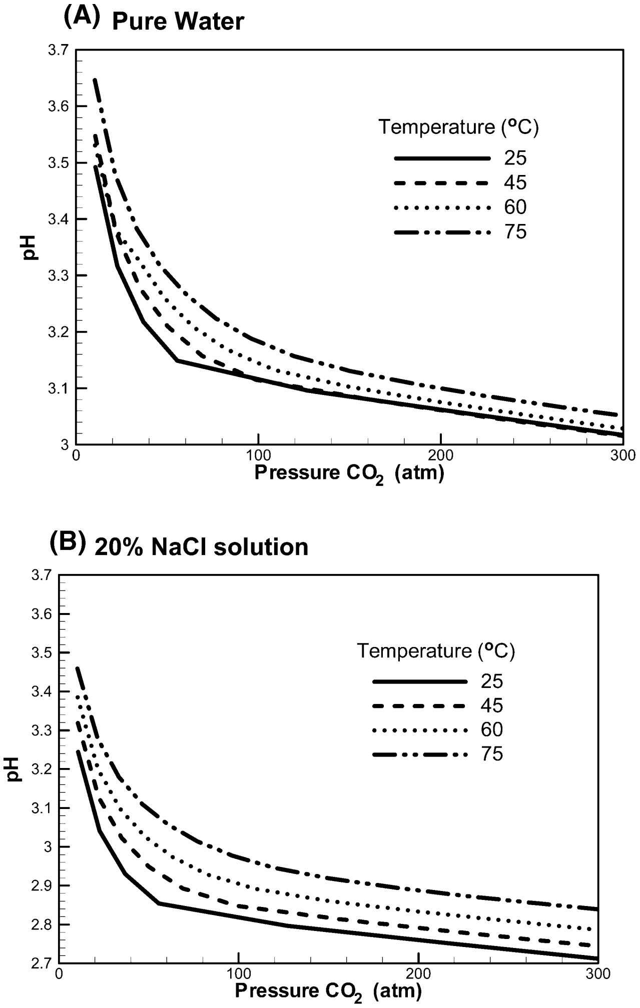

Figure 28. pH of (A) carbonated water and (B) carbonated brine (water containing 20% NaCl), as a function of pressure, at temperatures of 25, 45, 60, and 75 °C. The results in pure water were estimated using PHREEQC, whereas the brine results were estimated using GWB.

polymeric system from the following relationship:

$$\mathrm{FFV} = \frac{V_\mathrm{m} - V_\mathrm{w}}{V_\mathrm{m}} \tag{14}$$

where V_m is the molar volume of the swollen polymer ($V_\mathrm{m} = M/d$, where M and d are the molecular weight and density of the swollen polymer, respectively) and V_w is the estimated van der Waals volume. CO_2 diffusivity should decrease exponentially with the reciprocal free volume (1/FFV). As swelling increases, the free volume increases and diffusivity increases. The same theoretical approach may explain CO_2 diffusion in supercritical CO_2 swollen coals and allow estimation of the CO_2 diffusivity under a variety of conditions in swollen coal matrixes (recall hypothesis 4).

Effect of CO_2 Adsorption on Mineral Matter. When CO_2 is dissolved in water, it readily forms carbonic acid (H_2CO_3), which reduces the pH of the solution:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \tag{15}$$

The GWB simulation shown in Figure 28 shows the pH of carbonated water (Figure 28A) and brine (20% NaCl) (Figure 28B), as a function of CO_2 pressure at 298, 318, 333, and 348 K (25, 45, 60, and 75 °C). Increased acidity generally leads to a greater solubility of minerals. As the pressure increases, the pH decreases. As the temperature increases, the pH increases. High-pressure CO_2 and water can have a profound effect on the mineral matter present in coal. Many minerals present in coal are soluble in acidic aqueous solutions (recall hypothesis 7). The solubility of CO_2 in water and brine is substantial at high pressures (see Figure 3). According to the simulations that have been performed, the pH of CO_2 solutions in pure water and brine at 10.1 MPa (99.68 atm) and 318 K (45 °C) is ~3.1 in pure water and ~2.9 in brine (see Figure 28). Alkaline-earth metals are removed from the coal by treatment with acidic aqueous solutions. Calcite, dolomite, and other carbonate minerals are removed from coal at room temperature by extraction under acidic conditions with aqueous CO_2 solutions. The solubilities of some minerals common to coal in carbonated water and brine solutions at various pressures of CO_2 at 323 K (50 °C) are shown in Figure 29. The solubility of carbonate minerals in carbonated brine was estimated using GWB,[75] whereas the solubility of other coal-associated minerals and clays, in pure water, was estimated using PHREEQC.[79]

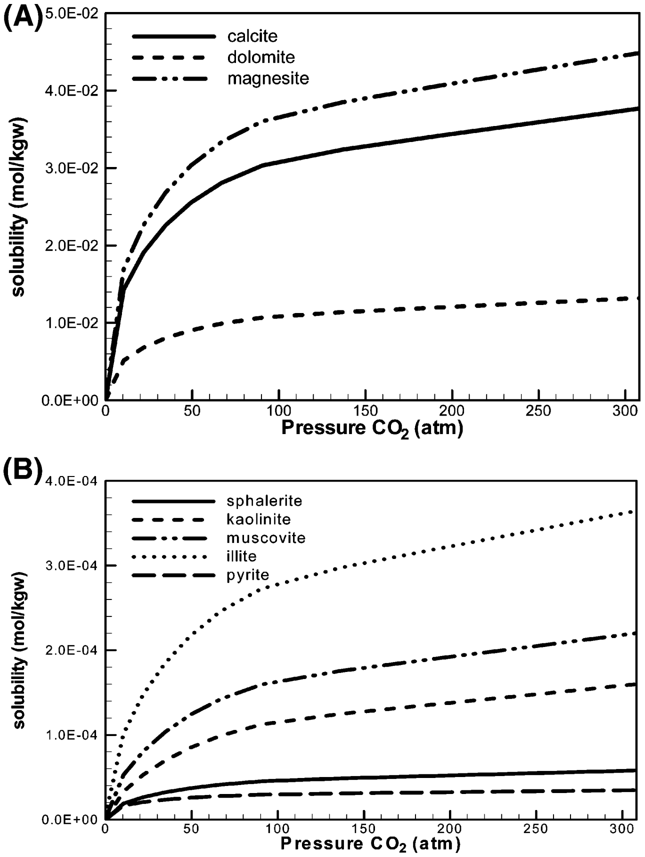

Figure 29. Solubility of calcite, dolomite, and magnesite in (A) carbonated water and (B) carbonated brine (water containing 20% NaCl), as a function of pressure at 323 K. The results in pure water were estimated using PHREEQC,[79] whereas the brine results were estimated using GWB.[75]

Hayashi et al. [463] studied the removal of calcium and magnesium from several low-rank coals by batch ex-

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(463) Hayashi, J.; Takeuchi, K.; Kusakabe, K.; Morooka, S. *Fuel* **1991**, *70*, 1181−1186.

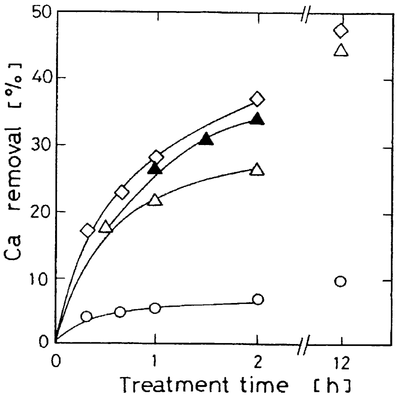

Figure 30. Removal of calcium from several low-rank coals by batch extraction with CO_2 dissolved in water at a pressure of 0.6 MPa and temperature of 298 K at various extraction times. (From Hayashi et al.[463])

traction with CO_2 dissolved in water at 600 kPa (5.92 atm) and 298 K (25 °C) at various extraction times (see Figure 30). They showed that the calcium removal yield is affected by the total calcium content of the coal and the total carboxyl content. Calcium removal is also affected by the coal:water ratio, in that calcium removal decreases as the amount of water decreases. During CO_2 sequestration in coal, it is expected that the water content of the coal will initially decrease with time. The coal will most probably be dewatered before CO_2 injection. This process will remove some of the bulk water in the cleat system. After CO_2 injection begins, we expect that the remaining water in the cleat system and the water present in the pores will be reduced. This hypothesis of reduced water content is consistent with the field results observed during the Burlington Resources commercial CO_2-ECBM/sequestration project. When CO_2 injection began, water production increased. CO_2 flow will sweep water from the formation by changing the relative permeability balance. The rate and extent of these processes are unknown. The calcium and magnesium content of the coal will be reduced when both water and CO_2 are present (recall hypothesis 8). The dissolved minerals will be transported through the coal seam and eventually recovered in the produced water when the process is taken to completion. As the water content decreases, the amount of calcium and magnesium removed will decrease. If water migrates back into the seam, then the removal of calcium and magnesium could increase. The solubility of carbonate minerals in acidic aqueous solutions requires both H_2O and CO_2.

Drying of Coal by Flowing CO_2. Iwai et al. reported the use of supercritical CO_2 to dry coal.[464] Water is removed by either dissolving in the CO_2 or by being displaced by it. Under the temperatures and pressures expected to be encountered during CO_2-ECBM/sequestration, water is only sparingly soluble in supercritical CO_2. Nevertheless, under some conditions, water is almost quantitatively removed from low-rank coals. Iwai et al. showed that the drying of ground and sieved coal (8 g, between 1000 μm and 595 μm) with CO_2 (1.5 mol/h for 20 h) at either 9.8 or 14.7 MPa (96.72 or 145.08 atm) and 313 K (40 °C) removed water (Table 15) and increased the surface area and the pore volume of the coal (not shown in Table 15). The degree of coal drying that will occur during CO_2-ECBM/sequestration is unknown; however, it will probably not be quantitative, except near the injection well (recall hypothesis 9). Water removed during the dewatering process and that removed by CO_2 can be eventually replaced by a recharge of water from the aquifers. In areas of the seam that are at pressures higher than the surrounding hydrostatic pressure, the re-invasion of water is expected to be slow.

Table 15. Results from Supercritical CO_2 Drying of Coal[464]

sample	Berau coal (g-water/g-dried coal	Taiheiyo coal (g-water/g-dried coal
supercritical drying (@ 14.7 MPa)	0.0188	0.0100
thermal drying (@ 383 K)	0.0153	0.0091
raw coal	0.2271	0.0622

Precipitation due to the Pressure Decrease. There will be both a pressure decrease and a CO_2 partial pressure (P_{CO_2}) decrease from the point of injection to the production well (recall hypothesis 10). The injected CO_2 follows the path of least resistance, moving from areas of high pressure near the injection well to those of lower pressure (toward the production well), through the areas of the coalbed that have the highest permeability. As injection continues, the areas of highest permeability initially become less permeable with time, because the swelling process begins to close the cleat system, which initially controls gas transport within the coalbed. Extracted compounds that are moving with the flowing CO_2 will begin to clog or plug the coal's pores (recall hypothesis 10).[217] The effect of this pore clogging on permeability is unknown. The back pressure increases because of closing of the cleat system caused by initial swelling. CO_2 begins to flow into other areas of the coalbed that now represent areas of higher permeability. Eventually, many areas of the cleat system become restricted. When this happens, the pressure across the coalbed increases, increasing the density and solvating power of the CO_2, which is directly related to its pressure and density. The precipitated components then begin to redissolve, according to their threshold pressure. As the redissolution process occurs, flow begins again from areas of high-pressure toward the production well. CO_2 moves through the coal as a front, probably with fingering, similar to frontal chromatography. The P_{CO_2} value will be high in areas behind the front and at the front, but low ahead of the moving CO_2 front. When dissolved carbonate minerals migrate to areas of lower P_{CO_2} value and/or decreased amounts of water, they will precipitate out of solution and initiate the clogging process.[465]

Eventually, the flowing CO_2 finds its way to the area of lowest pressure at the production well, causing the CO_2 density and solvent strength to decrease. This causes the dissolved organic molecules and minerals to precipitate again when the pressure becomes less than their threshold pressure, clogging the coal matrix adjacent to the production well. Eventually, these

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(464) Iwai, Y.; Murozono, T.; Koujina, Y.; Arai, Y.; Sakanishi, K. *J. Supercrit. Fluids* **2000**, *18*, 73–79.

(465) Pitman, J. K.; Pashin, J. C.; Hatch, J. R.; Goldhaber, M. B. *AAPG Bull.* **2003**, *87*, 713–731.

molecules will be re-extracted as the CO_2 pressure amasses behind them, redissolving them and moving them into the production well. The calcium and magnesium content of the produced water may not increase until the CO_2 front has migrated close to the production well. Minerals that contain calcium and magnesium will precipitate out of solution rapidly as the pH increases, because of the loss of CO_2 pressure at the production well, eventually forming carbonate scale in the production well, if production is taken to finality.

It is important to note that these are only initial hypotheses. Additional experimental confirmation from laboratory and field studies are still needed.

VIII. Gaps in Knowledge

There are substantial opportunities for further study. There are many unknowns and gaps in our knowledge and understanding of the CO_2-ECBM/sequestration process. The volume available for CO_2 to occupy within geological formations such as coalbeds is uncertain. There has been no investigation of the long-term stability and fate of CO_2 sequestered in coalbeds after the dewatering process stops and water re-invades the seam. Does the CO_2 dissolve in or react with the water to form H_2CO_3 and subsequently migrate out of the seam? Few data on the CH_4 content of deep, unmineable coals exist. The U.S. Bureau of Mines (USB) and National Energy Technology Laboratory (NETL) performed a study of the CH_4 content of U.S. coals; however, much of that information concerns mineable coals. The effects of SO_x, NO_x, and O_2 on the sequestration process are unknown. What type(s) of caprock are best? Are the caprocks soluble in carbonic acid solution at high pressure and elevated temperatures? What are the long-term microbial effects of CO_2 sequestered in coalbeds? Can methanogens convert the sequestered CO_2 back to CH_4? If so, how long does it take? What effect will seismic activity have on CO_2 sequestered in coalbeds? What is the most accurate model that describes the adsorption/desorption of CO_2, CH_4, O_2, SO_x, NO_x, H_2S, and NH_3 on coal? Is it the Langmuir, extended Langmuir, Dubinin−Radushkevich (D−R) and Dubinin−Astakhov (D−A), or Ideal Adsorbed Solution (IAS) theory? There are no tracers applicable for detection of CO_2 leaks to the surface that are proven to work with CO_2-ECBM/sequestration. We have little definitive information on the long-term effects of CO_2 on mineral matter in the coal. Little information on the impact of swelling on the rates of CH_4 production and CO_2 sequestration within an actual reservoir exists. The CO_2 adsorption capacities of many deep, unmineable coal seams are unknown. Improved reservoir simulation software is needed. None of the reservoir simulation software products evaluated by Wong and Gunter were capable of predicting the produced gas composition observed during the Fenn Big Valley field test.[466] An improved understanding of what happens when CO_2 is imbibed into coal, along with a much better understanding of multiple gas adsorption/desorption and diffusion, is needed. The economics of the overall process are not totally defined for many coals of interest. A proven monitoring and verification process that is cost-effective is, as yet, undefined.

Although we have brought attention to a myriad of technological, environmental, and economic questions in the previous paragraph, which require a long-term commitment to further work, this uncertainty should not overshadow the major accomplishments reviewed in this paper of an emerging, potentially viable greenhouse gas (GHG) control technology. Substantial technological progress has been achieved in the past decade, which now forms the basis for current and future field studies that will ultimately determine the fate of the methodology.

IX. Conclusions

This review documents that commercial-scale sequestration of carbon dioxide (CO_2) into deep, unmineable coal seams, with a simultaneous recovery of methane (CH_4), has been successfully practiced at Burlington Resources in New Mexico, and is planned in many other locales. The success of the Burlington Resources project in storing CO_2 in the Fruitland coalbed, along with over 30 years of commercial application of CO_2 injection into depleted petroleum reservoirs for EOR purposes, combine to indicate that sequestration of CO_2 in coal seams represents a practical and viable approach to storing CO_2 in the geosphere. This approach allows us to continue to use fossil fuels for electric power generation. CO_2-ECBM/sequestration is in the embryonic stages of development, and many important questions remain unanswered and, in some cases, unasked. Much work remains to be performed. There are potential environmental safety and health problems associated with the technology, as described in the review. Despite these potential problems, the results from Burlington Resources indicate that the storage of CO_2 in deep, unmineable coalbeds is technically feasible and can have little or no negative environmental aspects.

Acknowledgment. Thanks are given to Larry Headley (NETL) for suggesting that we prepare this review and for providing the resources and support to complete it. Our co-workers Bernie Kenney (NETL), JoAnn Yuill (NETL), Emily Brown (NETL), Karen Pietosi (NETL), and Pauletta Beehler performed the literature searches and acquired the articles for review. Rod Diehl provided valuable assistance by adding information to a bibliographic database. The authors thank Bradley Bockrath (NETL), Gary Cairns (Consol), Maurice Deul (Geologist Geochemist Consultant), Turgay Ertekin (Pennsylvania State University), Hugh D. Guthrie (NETL), Larry Headley (NETL), Scott Imbus (Chevron Texaco), Scott Klara (NETL), John Kolak (U.S. Geological Survey), John P. Kuszuba (Los Alamos National Laboratory), Vello Kuuskraa (Advanced Resources International), John W. Larsen (Pennsylvania State University), Jos G. Maas (Shell Technology), Jonathan Mathews (Pennsylvania State University), Jack Pashin (Alabama Geological Survey), Larry Pekot (Advanced Resources International), and Scott R. Reeves (Advanced Resources International) for reviewing the manuscript and providing valuable comments and thoughtful suggestions for its improvement. Fred White (NETL) performed work on the graphics, whereas Carol DeBerry (NETL) pro-

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(466) Wong, S.; Gunter, B. Testing CO_2-Enhanced Coalbed Methane Recovery. *Greenhouse Issues*, **1999**, (45). (Available via the Internet at http://www.ieagreen.org.uk/nov45.htm#ecbm.)

vided valuable assistance with the graphics and tables. Disclaimer: Reference in this report to any specific commercial product or service is to facilitate understanding and does not imply endorsement by the United States Department of Energy.

SI Metric Conversion Factors

1 acre = 4046.825 m^2
1 ac-ft = 43560 ft^3
1 ft = 0.3048 m
1 ft^3 = 0.02831628 m^3
1 psi = 6.894757 kPa
1 atm = 101.325 kPa
1 mD = 9.869×10^{-10} m^2
1 in = 2.54 cm
1 cp = 10^{-3} Pa·s
temperature(degrees F) = 1.8(temperature(degrees C)) + 32
1 Mcf = 10^3 cf = 28.31685 m^3
1 MMcf = 10^6 cf = 28316.85 m^3
ton (long) = 1016.047 kg

Acronyms and Abbreviations Used

Å = angstrom
ARC = Alberta Research Council
ARI = Advanced Research International
AVO = amplitude-versus-offset
BET = Brunauer−Emmett−Teller equation
BLM = United States Bureau of Land Management
CBM = coalbed methane recovery
COGCC = Colorado Oil and Gas Conservation Commission
CSIRO = Commonwealth Scientific and Industrial Research Organization
CT = computerized tomography
D−A = Dubinin-Astakhov equation
DBI-GUT = Central Mining Institute of Poland
DMMF = dry, mineral matter free
DOE = United States Department of Energy
D−R = Dubinin−Radushkevich equation
ECBM = enhanced coalbed methane recovery
EDA = electron donor−acceptor
EGR = enhanced gas recovery
EOR = enhanced oil recovery
EPRI = Electric Power Research Institute
EPA = United States Environmental Protection Agency
ES&H = Environmental Safety and Health
1/FFV = reciprocal fractional free volume
GHG = greenhouse gas
GSI = Geographical Information System
Gt = gigaton (1×10^9 ton)
GTI = Gas Technology Institute
GWB = Geochemist's Workbench Simulation Program
HSAB = hard and soft acid/base principles
IAS = ideal adsorbed solution theory
IEA = International Energy Agency
IEAGGRD = IEA Greenhouse Gas R&D Program
IFLO = integrated flow simulator
IFP = Institute Francais du Petrol
IPCC = Intergovernmental Panel on Climate Change
IUPAC = International Union of Pure and Applied Chemistry
JCOAL = Japan Coal Energy Center
JCOSC = Japan Forum on CO_2 Sequestration in Coal Seams
KS-1, KS-2 = sterically hindered amine-based solvents
LUMO = lowest unoccupied molecular orbital
MDQ = minimum detectable quantity
MEA = monoethanolamine
METI = Japan Ministry of Economy and Trade
MIT = Massachusetts Institute of Technology
MODFLOW = Modular Three-Dimensional Finite-Difference Groundwater Flow Model
MOFTEC = Chinese Ministry of Foreign Trade and Economic Cooperation
NCCTI = National Climate Change Technology Institute
NETL = National Energy Technology Laboratory
NMOCD = New Mexico Oil Conservation Division
NMR = nuclear magnetic resonance
NOVEM = Netherlands Agency for Energy and the Environment
OSHA = United States Occupational Safety and Health Administration
φ = porosity
P−D = Polanyi−Dubinin equation
PHREEQC = Ph-Redox Equilibrium Equation Program in C Language
R&D = research and development
RECOPOL = Reduction of CO_2 Emissions in Poland
SANS = small-angle neutron scattering
SAXS = small-angle X-ray scattering
TDS = total dissolved solids
TEM = transmission electron microscopy
T_g = glass-to-rubber transition temperature
TNO−NITG = Netherlands Institute for Applied Geoscience
TSOP = The Society for Organic Petrology
TVA = Tennessee Valley Authority
UIC = Underground Injection Control
UNFCC = United Nations Framework Convention on Climate Change
USB = United States Bureau of Mines
V_P = total open pore volume
Xe NMR = xenon nuclear magnetic resonance

EF040047W