TERRESTRIAL SEQUESTRATION OF CO_2: AN ASSESSMENT OF RESEARCH NEEDS

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1. INTRODUCTION

National and international concern is rising about the possible effects of greenhouse gases on the climate. Currently, the burning of fossil fuels provides about 85% of the world's energy. In the United States, approximately 90% of anthropogenic greenhouse gas emissions are due to energy production, most of which result from burning fossil fuels. Although the development of more efficient and alternative energy systems will lead to reduced greenhouse gas emissions, it is

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inevitable that the burning of fossil fuels will continue to provide a considerable proportion of the nation's energy well into the next century. With that in mind, one strategy for reducing greenhouse gas emissions into the atmosphere is to capture carbon dioxide from the products of fossil fuel burning and sequester it below the earth's surface, either on land or in the oceans. The period of geological sequestration should be for a minimum of 50–100 years, and 1000 years would be better.

This paper addresses geoscience issues associated with terrestrial sequestration of carbon dioxide. The primary venues being considered for terrestrial sequestration are active or depleted oil and gas reservoirs, deep saline aquifers, and underground coal beds. Creation of large underground cavities is another possibility, but this solution is thought to be prohibitively expensive. The technology exists for removing carbon dioxide from flue gases and injecting it into the earth. In the petroleum industry, for example, CO_2 is regularly injected into reservoirs for enhanced oil recovery and used for hydraulic fracture. In Norway, CO_2 has been injected into saline aquifers for disposal, and natural gas is regularly stored underground.

Although the considerable experience of the oil industry in CO_2 injection and gas storage is relevant, issues arise in long-term sequestration that are different from those associated with energy extraction or seasonal storage. Examples include the following questions:

- Did production of hydrocarbon reservoirs degrade the properties that made the reservoirs desirable?
- How will CO_2 interact chemically and mechanically with fluids present in the reservoirs (brine, oil)?
- Under what conditions will CO_2 displace existing fluids?
- How will CO_2 react with existing rock?
- Can rock–fluid–CO_2 -interactions be assessed at the temperatures and time scales (hundreds to thousands of years) of interest?

Other issues common to both hydrocarbon retrieval and CO_2 sequestration concern uncertainties about the response of geological reservoirs over long time periods in complicated mechanical, hydrological, and chemical environments. For example, what rock types and material properties (permeability, porosity, connectivity, and current level of saturation) make a good reservoir? Can reservoir properties be identified remotely by geophysical techniques such as seismic, electromagnetic, or others? Can these techniques identify rapid-flow pathways that could compromise the integrity of the reservoir or make effective utilization of pore space difficult? Although the oil industry has considerable experience with hydrocarbon reservoirs, much less is known about the geologic, thermal, and fluid properties of deep aquifers.

There is little question that terrestrial sequestration of CO_2 is possible. But determining whether it is an effective strategy to reduce greenhouse gases in the atmosphere will require careful consideration of economic issues, including the cost of removing and collecting gases from fuel byproducts, transportation of the gas to sequestration sites, and compression for injection. Furthermore, the efficiency of injection and the safety and integrity of containment will depend largely on the scientific understanding of the hydrological, mechanical, and chemical behavior of the reservoir.

We begin with a brief review of major characteristics of reservoir structures and lithologies as a guide to reservoir selection for CO_2 disposal. The remainder of the chapter focuses on existing experience and uncertainties in reservoir characterization and response to CO_2 injection and long-term containment of sequestration sites. The associated sections are organized according to the disciplinary points of view of geochemistry, geomechanics, geohydrology, and geophysics—although an effective debate on questions of interest would require interaction among them. Within each disciplinary division, the sections address concerns relating to reservoir characterization, changes during injection, and long-term containment and integrity.

1.1. Geologic Setting of Reservoirs

Oil and gas reservoirs and aquifers share some common geometric elements. Generally, both are tabular bodies in which the fluid flow is constrained by upper and lower less-permeable lithologies. Typically, such barriers are presumed to be formed by shale. Faults may cut both reservoirs and aquifers with variable and often unpredictable effects on fluid flow. Aquifers typically have large lateral extents; hydrocarbon reservoirs tend to be restricted. Lateral, low-permeability barriers may be caused by facies changes or by faults that inhibit flow across them. The latter is illustrated by the southern boundary of the Anadarko Basin, Oklahoma, where the fault contact places sedimentary against crystalline rocks and acts as a seal to fluid migration (Al-Shaieb *et al.*, 1994). Hydrocarbon reservoirs vary from a few meters to thousands of meters thick and range in aerial extent from a few kilometers to over 100 square kilometers. Small reservoirs may contain only one producing well, but large fields may contain hundreds of wells.

Although reservoirs can be classified according to whether the fluid-trapping mechanism is structural or stratigraphic (Fig. 1), they are more commonly distinguished by dominant lithology: clastics and carbonates (Tables 1 and 2). Fractured reservoirs are generally treated as a third class (Nelson, 1985; Roehl and Choquette, 1985; Coalson *et al.*, 1989).

Clastic reservoirs are found in sandstones, siltstones, and shales, often with interlayered sequences of each, such as in the Powder River Basin, Wyoming (Surdam, 1997). The sandstones and siltstones generally have a granular, quartz framework that may be poorly consolidated or cemented by quartz, clays, or

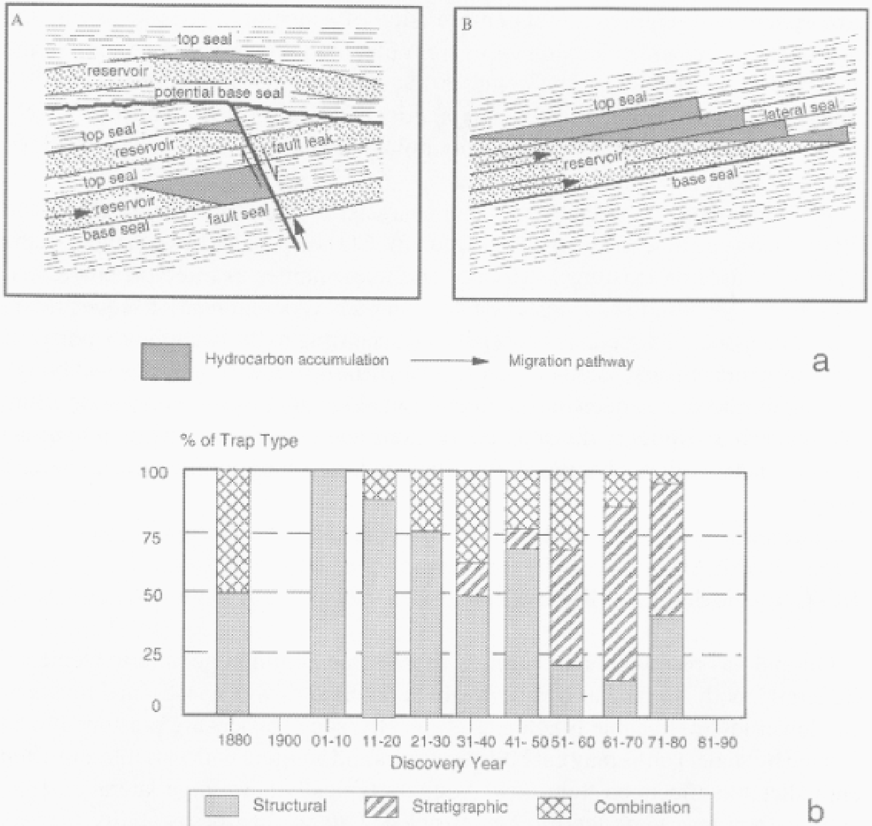

FIG. 1. (a) Major elements of (A) structural and (B) stratigraphic traps (from Biddle and Wielchowsky, 1994). (b) Relative distribution of structural, stratigraphic, and combination petroleum fields for the Rocky Mountain region through 1980. The 155 fields are for sandstone reservoirs that produced more than ten million barrel equivalents of petroleum. The change in relative percentage with time reflects a shift from surface structure recognition to the development of new seismic techniques for subsurface exploration (from Coalson *et al.*, 1989).

carbonates. Porosities and permeabilities are determined to a large degree by the depositional environment and, thus, tend to be relatively homogeneous over wide areas, at least compared to other environments. This element of predictability has made them attractive for hydrocarbon production and for water aquifers. Porosity and permeability, however, vary widely from reservoir to reservoir. For example, within the Rocky Mountain region the Muddy "J" Sandstone in the Denver Basin, Colorado, has porosities from 8 to 12% and permeabilities from 0.05 to 0.005 md, while the Muddy Sandstone in the Bell Creek Field, Montana, has porosities from 6 to 26% and permeabilities from 0.1 to 13,000 md (Coalson *et al.*, 1989).

TABLE I CHARACTERISTICS OF SELECTED CLASTIC RESERVOIRS

Field	Location	Producing horizon	Nature of trap	Average depth (m)	Thickness (m)	Areal extent (sq. km)	Porosity (%) (avg.—max.)	Permeability (md) (avg.—max.)	Fractures
Bell Creek	Powder River Basin, Montana	Muddy Sandstone	Stratigraphic	1372	7	29.2	28–36	2250–13,000	Associated with vertical faults
Hawk Point	Powder River Basin, Wyoming	Minnelusa "B" Sandstone	Stratigraphic	3459	9	2	13–18	30–144	Negligible
Lexington	Anadarko Basin, Kansas	Morrow "A" Sandstone	Stratigraphic	1683	3–12	4	15–27	275–2000	Limited, healed vertical
Luckey Ditch	Southern Moxa Arch, Wyoming/Utah	Dakota Sandstone	Structural/ stratigraphic	4420	3–11	51.8	14–23	60–713	Insignificant
Painter Reservoir	Thrust Belt, Wyoming	Nugget Sandstone	Structural: thrust belt	2950	255–285	9	12–21	9–1450	Abundant vertical, open or gouge filled
Rangely	Piceance Basin, Colorado	Weber Sandstone	Structural	981	84	77	12–25	2–250	Extensive; provide permeability
Spindle	Denver Basin, Colorado	Terry Sandstone member, Pierre Shale	Stratigraphic	370	6	256	14–19	2–17	Insignificant
Wattenberg	Denver Basin, Colorado	Muddy "J" Sandstone	Stratigraphic	2316	6	2535	8–12	0.005–0.05	Insignificant
Weld Draw	Powder River Basin, Wyoming	Teapot Sandstone member, Mesaverde Fm.	Stratigraphic	2067	5	453	14–20	4–17	Insignificant
West Lindrith	San Juan Basin, New Mexico	Dakota Sandstone	Stratigraphic	2225	12	25.2	8–18	0.05–2.5	Assisted permeability some members

Note: Data selected and compiled by J. M. Logan from Coalson *et al.* (1989) and Nelson (1994).

TABLE II CHARACTERISTICS OF SELECTED CARBONATE RESERVOIRS

Field	Location	Producing horizon	Lithology	Nature of trap	Average depth (m)	Thickness (m)	Areal extent (sq. km)	Porosity (%) (avg.—max.)	Permeability (md) (avg.—max.)	Fractures
Belle River Mills (converted to gas storage, 1965)	Michigan Basin, Michigan	Guelph Formation	Dolomite	Stratigraphic	762	131	1	10–30	8–1000	Non-tectonic
Chatom	Gulf of Mexico coastal plain, Arkansas	Smackover Formation	Dolomite	Stratigraphic; structural	4900	0–9	13	25–35	63–200	Minor, generally calcite healed
Fairway	Texas	James Reef Formation	Limestone	Stratigraphic; structural	2900	30	115	11 avg.	3–27	Sparse
Little Knife	Williston Basin, North Dakota	Mission Canyon Formation	Dolomite; calcitic dolomite	Stratigraphic; structural	3000	7–33	96	14–27	30–167	Common; widely spaced; vertical hairline
Mt. Everette; South Reeding	Anadarko Basin, Oklahoma	Hunton group	Limestone; dolomite	Stratigraphic	2401	15	5	8–20	93–560	Locally important; high angle, open or calcite filled
North Bridgeport	Illinois Basin, Illinois	St. Genevieve Formation	Limestone; dolomite	Stratigraphic; structural	490	5–12	4.4	20–40	240–9500	Moderate in dolomite; few in limestone
Puckett	Central Basin Platform, Texas	Ellenburger Formation	Dolomite	Structural	4115	0.3–45	68	3–12	30–169	Tectonic and solution collapse
Seminole Southeast	Permian Basin Texas	Strawn Formation	Limestone	Stratigraphic	3292	4	6	13–18	29–80	Vertical; hairline to solution enlarged
Sunniland	South Florida Basin, Florida	Sunniland Formation	Limestone; dolomite	Stratigraphic; structural	3540		9	18–30	65–1000	Negligible
West Cat Canyon	Santa Maria Valley, California	Monterey Formation	Dolomite; siltstones; shales	Structural	1190	175	10	12 avg	186 avg.	Numerous

Note: Data selected and compiled by J. M. Logan from Roehl and Choquette (1985) and Nelson (1994).

Carbonate reservoirs include those that are primarily composed of dolomite such as the Williston, North Dakota, and the Central Basin Platform of Texas; dolomite and limestone such as the Anadarko Basin; chalks such as in the North Sea; and limestone reefs such as those found in the Michigan Basin (Roehl and Choquette, 1985). In contrast to clastics, the properties of carbonate reservoirs more often reflect facies variations and early diagenetic changes. Because the latter are often spatially and temporally variable, reservoir properties are relatively heterogeneous. Although carbonate reservoirs often have high porosity, the permeability can be low and, even more importantly, often unpredictable within a given formation. Approximately 60% of the recoverable oil in the world resides in carbonates (Oil and Gas Journal, 1983).

Fractured reservoirs occur in all types of lithologies: limestone in Kirkuk, Iraq (one of the largest fields in the world), schist in the Wilmington Field of California, Devonian shale in a gas-producing reservoir in the Big Sandy Field in Kentucky and West Virginia, sandstones in California, and granite in Kansas (Nelson, 1985). In some fields, fractures enhance the permeability but in others, they provide the essential porosity and permeability. For example, in the Big Sandy Field, the shales have low to negligible intrinsic porosity and permeability, and the fractures provide all transport avenues. On the other hand, in the Sprayberry Field of Texas, the reservoir siltstone has an average porosity of 8% and a permeability of 0.29 to 0.50 md, but abundant fractures increase the total permeability to 16 md or higher (Hubbert and Willis, 1955). The disadvantage of fractured reservoirs is the low storage capacity of the fracture-bounded blocks and the low recovery of fluids from them. Commonly, fractures cause the flow to be strongly anisotropic because of either their preferred orientation or their response to the *in situ* stress field. Frequently, the presence and importance of fractures to reservoir development are discovered only indirectly by significant discrepancies between the results of pressure-decay tests in exploratory wells and predictions by means of single- and double-porosity theoretical models.

Most reservoirs do not consist of a single complex but are made up of several isolated compartments. The existence of these compartments for millions of years indicates a measure of stability to tectonic and diagenetic processes. Some reservoir compartments retain extreme over- or underpressure (Fig. 2, see color insert). This suggests very low permeability of their bounding seals and a number of pressure-controlling processes, including compaction, volume-increasing organic and inorganic reactions and phase transitions, and thermal expansion. Some compartments are extremely large (basin scale) and therefore represent great holding capacity (Ortoleva, 1994a, 1998, and Ortoleva *et al.*, 1995). Underpressured compartments appear to be particularly attractive for the purposes of CO_2 sequestration. Breaching of their seals would tend to draw in fluids from the environment rather than expel them.

1.2. Differentiating Characteristics of Coal Reservoirs

Another possible subsurface candidate for the sequestration of CO_2 is an underground coal deposit. As in other reservoirs, gas is stored in pores and fractures and is dissolved in formation water. However, in coal beds, most of the methane, other light hydrocarbons, and carbon dioxide are primarily held in the adsorbed state on the internal surface of the coal micropores (Bell and Rakop, 1986), most probably as a monolayer. These micropores constitute a large surface area on the order of 1 million sq. ft/lbm (205 m^2/t; McElhiney *et al.*, 1989) that enables a much greater amount of methane (or CO_2) to be stored than can be accommodated in the compressed state or dissolved in formation water. For example, Bell and Rakop (1986) observed that the Mary Lee coal group in the Black Warrior Basin in Alabama had an average gas content of 400 scf/ton (11.3 m^3/t) at pressures just less than hydrostatic pressure. The equivalent amount of compressed gas would require a coal porosity of 66%. Therefore, coal beds can store three to seven times the amount of methane that can be held in conventional reservoirs at conventional depths and pressures (McElhiney *et al.*, 1989). Redistribution, drainage, and recharge of methane in coal are controlled by ubiquitous fracture systems referred to as cleats. The cleat-transport properties are determined not only by *in situ* stress states, but also by considerable shrinkage of coal following the release of methane.

Research into the adsorption/desorption of methane, CO_2 and other gases has been performed by several researchers (Anderson *et al.*, 1966; McCulloch *et al.*, 1975, Lee, 1982; Ruppel *et al.*, 1974; Bell and Rakop, 1986; McElhiney *et al*, 1989). The amount of gas content of a coal bed (which conversely may be the amount of gas that can be readsorbed after dewatering and methane release) will depend on moisture content, thermal maturity (rank), coal quality, and reservoir pressures (Ayers and Kelso, 1989). Kim (1977) showed that the quantity of adsorbed methane and the density of coal grew with increasing coal rank, i.e., from high-volatile bituminous to anthracite. The gas content of coal also varies with regional formation pressure (McElhiney *et al.*, 1989), pressure-gradient, inorganic (ash) content, moisture content (Joubert *et al.*, 1973; Yalcin and Durucan, 1991), temperature, and the wettability of coal (Bell and Rakop, 1986).

2. Geohydrology

2.1. Introduction and Experience in CO_2 Enhanced Oil Recovery

Primary aspects of CO_2 sequestration in geologic formations include the geohydrologic characterization, injection behavior, and long-term containment of supercritical CO_2 for storage in aquifers and reservoirs. A supercritical fluid has some of the properties of a liquid (e.g., density) and a gas (e.g., low viscosity), and is

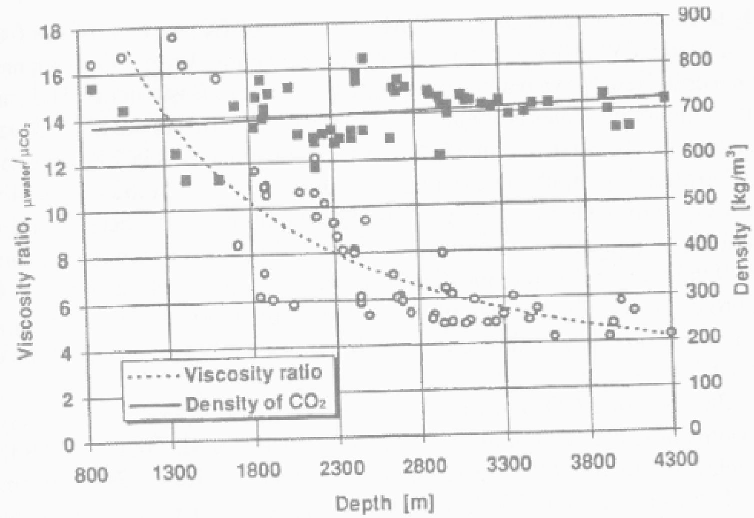

FIG. 3. Viscosity and density ratios between water and CO_2 for 63 different North Sea formations, illustrating the low viscosity of supercritical CO_2 and higher density (from Lindeberg and van der Meer, 1996).

not miscible with water. Therefore, the properties of supercritical CO_2, including density, viscosity and miscibility, have a profound effect on its behavior in candidate aquifers saturated with water and in oil and gas reservoirs containing water as well as other fluids. For example, the supercritical CO_2 phase injected in an aquifer below approximately 800 m will exist as a separate phase that is less dense than water and will rise from an injection point and gravity segregate along the top of the aquifer (Fig. 3).

The following deliberations focus on the geohydrologic characterization, injection behavior, and long-term containment of supercritical CO_2 for storage in aquifers and reservoirs. The section will emphasize the physics of fluid flow in heterogeneous formations. Important ties of geohydrologic processes to the geochemical (e.g., formation of carbonate minerals) or geomechanical (e.g., fracturing) behaviors of the systems will be discussed later. In addition to process-based research in geochemistry, geomechanics, and the physics of flow, site-specific data from reservoirs or aquifers will be required to flesh out numerous important issues concerning CO_2 sequestration. Thus, case studies will be an important element of future research.

Early industrial practices for sequestering CO_2 in geological formations are based on many years of proven experience injecting supercritical CO_2 for enhanced oil recovery (EOR) (Orr and Taber, 1984; Blunt *et al.*, 1993). As of January 1998, about 179,000 barrels/day (28,460 m^3/day) of oil were recovered using CO_2 injection in about 66 projects (Moritis and Guntis, 1998). Typically, it takes 4–10 MCF of CO_2 to recover a barrel of oil (17 Mcf = 1 ton of CO_2). Most of the CO_2 is being injected in West Texas, where several large pipelines bring CO_2 from natural occurrences in New Mexico and Colorado to the Permian Basin fields. The current capacity of major pipelines is about 1.25 Bcf/day (35.4 Mm^3) or about 20,000 tons/day of carbon—about 0.6% of the U.S. daily carbon emissions in 1990 due to fossil fuel burning. By replacing existing CO_2 injections, which are essentially all natural CO_2, with CO_2 now being emitted to the atmosphere there would be a measurable but modest effect on overall CO_2 emissions. Since some production of CO_2 with the oil is inevitable, most projects reinject significant quantities of CO_2 over a project's life. The fraction of CO_2 retained in an oil field after a project is complete can vary considerably, but it is certainly a significant portion of the CO_2 purchased for injection.

The efficiency of a CO_2 enhanced oil-recovery flood depends strongly on the equilibrium phase behavior of mixtures of CO_2 with the oil (Blunt *et al.*, 1993; Orr *et al.*, 1995). When the CO_2 is dense enough, it is a solvent for some hydrocarbons in the oil. As the injected CO_2 flows through the reservoir rock, components in the oil are extracted into the CO_2, and some of the CO_2 dissolves in the oil and water that is inevitably present. If the pressure is high enough, the partitioning of hydrocarbons into the CO_2—coupled to the flow at different velocities of CO_2-rich and oil-rich phases—can create mixtures that pass close to the critical locus for the CO_2/hydrocarbon mixtures. Mathematical analysis (similar to that applied in chromatography theory) has proved that essentially 100% of the oil present in a one-dimensional porous medium can be displaced (in the absence of dispersive mixing) if the pressure exceeds the so-called "minimum miscibility pressure" (MMP), which depends on the composition of the oil and the temperature (Orr *et al.*, 1995; Wang and Orr, 1998). The MMP is the pressure at which CO_2 readily dissolves in the oil and the interfacial tension between oil and CO_2 becomes small. Real displacements always include some dispersion, but even then, it is theoretically possible to displace more than 90% of the oil in the zone swept by CO_2 if the pressure exceeds the MMP (Fig. 4). Efficiencies in the field are significantly lower, especially when a reservoir has strong heterogeneities or is heavily fractured. When paths of high permeability or fractured rock connect injectors and producers, significant channeling and cycling of CO_2 from injection to production wells may occur (Tchelepi and Orr, 1994). This leads to an undesirable, early breakthrough of injected CO_2 and large amounts of unwanted CO_2 production.

Injection of CO_2 for enhanced oil recovery is equally applicable in sandstone and in carbonate reservoirs. A primary consideration is whether the reservoir is deep enough so the pressure is above the MMP for the oil at the reservoir temperature. (Of course, this is not an issue for CO_2 sequestration.) If the pressure has been lowered in the reservoir (e.g., by depletion), it may be possible to raise the pressure again by water injection, for example, as long as there is not a large gas cap or aquifer. CO_2 is attractive for injection into relatively low-permeability reservoirs because the low CO_2 viscosity allows pumping at a greater volumetric rate than water. In order for the use of CO_2 for EOR to be economic, the reservoir must be large enough to justify the cost of pipeline, injection well, and CO_2 separation facilities.

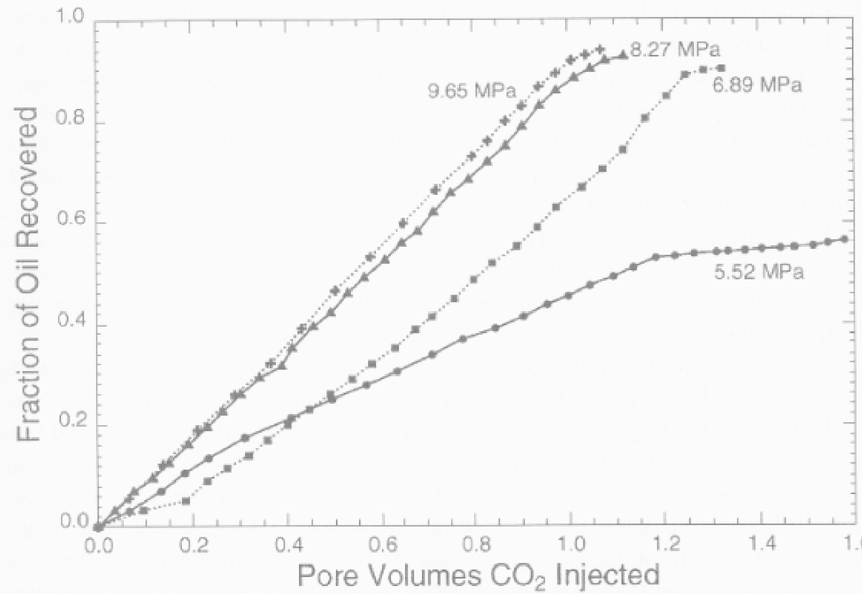

FIG. 4. Recovery of oil by CO_2 injection in an ideal flow setting. Displacement efficiency increases with displacement pressure when a Permian Basin crude oil is displaced by CO_2 in a nearly one-dimensional flow setting (a long tube packed with small glass beads). More than 90% of the oil is displaced by the CO_2 when the pressure exceeds about 7 MPa, the MMP for this oil at the displacement temperature of 32°C (from Orr *et al.*, 1983).

2.2. Reservoir Identification and Characterization

Injection of CO_2 for storage in reservoirs or aquifers is not inherently different from water (secondary recovery) or EOR injection in oil reservoirs. Primary flow characterization issues include preinjection fluid pressure and composition as well as thickness and permeability that determine the rate of injection, pressure buildup at the injection well, and changes in the stress field. Equally important are porosity and reservoir/aquifer volume, permeability heterogeneity affecting what fraction of the aquifer can be reached by injected CO_2 and how far the injected CO_2 propagates, and the location and character of faults and fracture systems. Although existing methods can be used to investigate many of these site-characterization questions, the currently achievable resolution appears to be inadequate.

The characterization problem will differ with reservoir and aquifer type. Oil and gas reservoirs will be much better characterized than aquifers. Reservoirs have a record of production history, well tests, and seismic and other geophysical data, as well as many existing holes that can be used for additional characterization activities. On the other hand, aquifers can provide significantly more space for storage. A potential optimal solution is a well-characterized reservoir overlying a large aquifer. Characterization information from the reservoir could be projected into the surrounding (underlying) aquifer. Since reservoirs have already demonstrated long-term integrity, the underlying aquifers should also have this property.

One of the most important geohydrologic issues is the identification of candidate subsurface reservoirs and aquifers. What characteristics, especially geological characteristics, define the best candidates for CO_2 storage? Is it, for example, depth, lithology, or proximity to CO_2 generators? A detailed answer to this question depends on the research outlined in this paper, especially in geochemistry and geomechanics, but there are two clear factors: depth and the nature of the pressure confinement. The deeper the reservoir or aquifer, the higher the pressure and the larger the mass of CO_2 stored per unit volume (at the cost of the compression of CO_2, which will generate more CO_2 if fossil fuel is used to drive the compression). Whatever the depth, underpressurized reservoirs and aquifers provide additional incremental storage capacity for injected fluids. Underpressures can be statically maintained by seals (Demming, 1994; Bradley and Powley, 1994; Ortoleva *et al.*, 1995; see Section 4: Geomechanics), transient dynamic hydrologic processes (Bredehoeft and Hanshaw, 1968; Neuzil, 1995), or simply topographically driven flow systems (Toth, 1962; Neuzil, 1995). Distinguishing among these possibilities will be important for assessing long-term confinement.

2.3. Injection

Geohydrologic issues associated with CO_2 injection start at the wellhead and then move with the injected fluid as it migrates into the aquifer or reservoir until it finds a storage place in the pore space as a separate fluid, dissolved in water, or until it is converted into a mineral. Two fundamental questions must be answered: (1) How far does the CO_2 travel? and (2) What happens to it when it gets there, particularly when viewed on the scale of hundreds of years?

Whichever form—fluid, dissolved, or precipitate—storage will take place in the primary, intergranular porosity, i.e., the spaces between the grains. The numerical value of the primary porosity represents the proportion of a volume occupied by this space. It can vary from a small percentage in deeply buried and diagenetically altered sandstone to almost 50% in shallow, unconsolidated sand. The porosity is determined by the depositional environment (e.g., as it affects sorting) and subsequent diagenesis and compaction, as described further in the Geochemistry and Geomechanics sections of this chapter. The organization of the pore space also determines the permeability, which controls the movement of fluids. Primary porosity is usually viewed as a tortuous network of larger pore bodies connected by narrower pore throats (Fig. 5, see color insert). Most of the storage volume is in the pore bodies. Pore throats play the major role in permeability since they determine pore-space connectivity.

Diagenetic precipitation or solution of minerals in the pore space has, more or less, a linear effect on storage (e.g., volume of rock dissolved or precipitated equals volume of storage gained or lost, respectively). However, the precipitation or solution of minerals in the pore throats results in strongly nonlinear changes of permeability. Both precipitation and solution are possible in the presence of dissolved CO_2, depending on the chemistry and minerals present.

A major geohydrologic issue is the natural spatial variability or heterogeneity of permeability, porosity, and other rock properties (Gelhar, 1993; Dagan and Neuman, 1997). In homogeneous rock (e.g., Berea sandstone), permeability ranges over two orders of magnitude, while seven orders of magnitude is not uncommon in typical heterogeneous sandstones (Fig. 6, see color insert). Carbonates show more spatial variation of properties, and fractured systems are often even more heterogeneous. Because of the depositional, diagenetic, and stress history, natural heterogeneity is usually geometrically organized, such as in layers, and can be described using geostatistical and geological models. With geometrically organized heterogeneities, zones of flow and high permeability create preferential flow paths or channels if the heterogeneities are sufficiently correlated in layers or other structures. As a result, not all portions of an aquifer or reservoir are accessible to injected fluids, which can diminish the volume of CO_2 that can be stored.

Permeability and porosity will change with time and space as a consequence of CO_2 injection and storage (or prior oil or gas production), for both geochemical and geomechanical reasons. Usually, the result will be a reduction of permeability and porosity, making transport and storage of CO_2 more difficult. Because of the presence of different minerals on the pore scale and because of larger scale heterogeneities on the aquifer/reservoir scale, precipitation and dissolution may occur simultaneously in adjacent portions of the pore space or aquifer/reservoir.

Injection of CO_2 into reservoirs or aquifers presents several special flow problems, many of which have already been addressed by the community using CO_2 for EOR. Because CO_2 has relatively low viscosity (a few hundredths of a centipoise) no matter what the injection conditions, hydrodynamically unstable displacement will occur. In a homogeneous porous medium, displacement of a viscous fluid by a less viscous one leads to "viscous fingering" in which fingers of low viscosity fluid penetrate the high viscosity fluid rather than displacing it uniformly (Homsy, 1987; Fig. 7, see color insert). It is now known, however, that in many if not most oil reservoirs and aquifers, the distribution of permeability dominates the formation of viscous fingers (Tchelepi *et al.*, 1993; Tchelepi and Orr, 1994). The low viscosity CO_2 easily finds the preferential flow paths. In effect, the permeability distribution creates the paths in which fingers develop. This situation is often called "channeling." Thus, permeability heterogeneity can reduce substantially the fraction of a reservoir or aquifer that can be swept by the injected CO_2 in a reasonable time (Fig. 8). In an EOR application, adequate characterization of the spatial distribution of permeability within an oil reservoir is important to predicting CO_2 flood performance or sweep efficiency. CO_2 is usually lighter than oil and always less dense than water, so gravity segregation of the injected CO_2 also contributes to reduced sweep efficiency (Tchelepi and Orr, 1994).

In a water-filled aquifer, supercritical CO_2 will be displacing an immiscible water phase. Even in the absence of viscosity or gravity effects, displacement will be inefficient because of capillary effects caused by the relatively high interfacial tension between CO_2 and water. The water usually is more wetting, and the CO_2 displacement will prefer larger pore spaces. This is the same space preferred by single-phase viscous flow and by viscous fingers of CO_2 displacing water. Capillarity amplifies the effects of heterogeneity, with CO_2 bypassing large volumes of tighter rock, further reducing sweep efficiency.

Viscous, gravity, and capillary forces act together in a heterogeneous rock to create channels of preferred flow in higher-permeability materials with large bypassed zones in between. Since the objective is to sequester CO_2 rather than use it to drive oil, sweep efficiency may not be an important issue: it matters less where the CO_2 goes as long as there is sufficient volume available at reasonable injection pressure and the CO_2 stays in the reservoir or aquifer. If fluid is not being withdrawn from the aquifer (to create volume, for example), then cycling of CO_2 through high-permeability flow paths is less important. As discussed later, it only appears to be an issue when chemistry is considered and may even be advantageous for delivering large amounts of CO_2 far from the well.

Transport of CO_2 along the preferred flow paths will be relatively quick, especially when the paths are composed of open fractures, with a much slower transfer of CO_2 from these paths to the surrounding bypassed zones. If the material around the preferred flow paths is composed of much finer pores, supercritical CO_2 will have difficulty penetrating the tighter porous rock matrix where storage will take place, especially because capillary forces may limit penetration. If the CO_2 is dissolved in the aqueous phase it will enter the surrounding rock by diffusion (if the permeability contrast is not large) and by cross-flow. In any event, the time scales for chemical reactions will be completely different in the fast paths and the bypassed zones because the supply of reactants will be controlled by different processes. The large-scale kinetics of interaction between the fast paths and bypassed zones will be determined by their contrasting properties, configuration, and relative size and frequency. Only in this sense does it appear that the details of heterogeneity and preferred flow become important. Ideally, the chemistry might be arranged such that precipitation of carbonates occurs in the bypassed zones, while transport is maintained or even enhanced by dissolution along the preferred flow paths.

Fractured porous rock represents a special case of heterogeneity, with an interaction potential between matrix rock and fractures depending on the size distributions of the matrix blocks and fracture apertures, and the fracture connectivity. Storage in the fractures themselves is often negligible. The conceptual view of this process requires the consideration of large rock volumes in order to invoke continuum concepts like porosity. In the standard "double porosity" model of naturally fractured systems, all large-scale flow is assumed to take place in the fracture network, while the matrix blocks provide the storage. Communication between the two is due to local cross-flow, caused by pressure gradients between the isolated matrix blocks and the surrounding fractures or, in the case of dissolved CO_2, by diffusion. The next most sophisticated model assumes that there is also some net flow through the matrix blocks. This "double permeability model" is appropriate when the permeability contrast between matrix and fractures is small. These multiple porosity models fail, however, when the number density of fractures drops and the continuum hypothesis is no longer valid. Discrete fracture models are then used if the geometry of the fracture network is represented explicitly. The difficulty with this approach lies in determining the location, connectivity, and properties of the fractures that are parallel characterization issues in geomechanics and geophysics. Natural fracture porosity could move significant amounts of CO_2 from an injection site to storage locations in matrix blocks far away. Single-phase flow in fractured systems is not well understood if alterations of fracture geometry and connectivity by stress or chemistry are considered, and much less is known about multiphase flow in fractures, such as would occur with supercritical CO_2 displacing water.

CO_2 could also be injected into shallower aquifers and reservoirs (Fig. 9, see color insert). Depending on the salinity, significant amounts of CO_2 can be dissolved in water—enough to increase its density by as much as several percent (Bachu *et al.*, 1996). However, viscosity would effectively be unchanged. One major disadvantage of this option is the much larger volumes of fluid that would need to be injected to store the same amount of CO_2. Following injection in an aquifer, the pore space would continue to be saturated with water. The resulting single fluid phase flow would be determined by the permeability of the aquifer and the composition, temperature, and pressure of the water as it affects viscosity and density. There would be no viscous fingering. Preferred flow paths and bypassed zones would still be issues, but would be determined by the permeability heterogeneity with no contributions from viscous fingering or capillarity. Density gradients would continue to be significant and produce a tendency for water to segregate by gravity along the bottom of the aquifer. If the bottom were sloped, then a dense plume of CO_2-saturated water would tend to move deeper into the subsurface. This same principle is used to support one of the ocean-disposal options for CO_2, and could limit the need for an overlying seal in aquifers.

Mathematical modeling of CO_2 injection performance for all kinds of reservoirs (including coal) must consider cross-coupling of geochemistry, geomechanics, flow, and transport—this will be referred to as RTM (reaction, transport, mechanics) modeling. Over the last 30 years, considerable effort has been expended to build and improve flow and transport models of oil recovery CO_2 flood performance at the reservoir scale. Although these models often ignore chemistry and mechanics, many issues of these models also apply to the CO_2 storage problem. This experience suggests three essential components for accurate field-scale predictions for CO_2 storage in aquifers and reservoirs:

1. Accurate representation of capillary pressure behavior and phase equilibria of CO_2/hydrocarbon/water systems with an equation of state to determine local displacement efficiency
2. Accurate description of the spatial distribution of permeability (which strongly influences the fraction of the reservoir or aquifer swept). The difficulty in acquiring detailed reservoir description data is often the limiting factor in reservoir EOR performance predictions. Careful use of geostatistical descriptions can help but cannot eliminate problems because of sparse sampling of reservoir properties.
3. Flow simulations performed on a computational grid fine enough to resolve heterogeneities and any gravity segregation that occur. The computational costs associated with very fine grids have induced considerable research on ways to compute average properties that can be used on a coarser grid, with limited success for multiphase flow.

The foregoing components should be part of an RTM modeling approach simulating the movement of CO_2 away from the injection points to storage locations, where mineral trapping might occur. Coupled modeling also creates the opportunity to address related questions:

- How do the natural aquifer/reservoir heterogeneities influence the location and nature of mineral trapping?
- Do the mineral-trapping reactions plug the preferred flow paths, especially fractures?
- Or, as plugging occurs, does CO_2 injection drive the formation pressure to the threshold for fracturing?

2.4. Long-Term Containment, Monitoring, and Integrity of Seals

Gravity segregation will bring supercritical CO_2 upward until it meets a seal at the top of the aquifer or reservoir. Not much is known about the long-term integrity of seals, even in oil and gas reservoirs. In general, seals have much lower strength than the rock they overlie, and it is not clear how they will react to the changing stress and chemical conditions that follow CO_2 injection (see Geochemistry and Geomechanics sections). By definition, no seal is perfect; they all leak. It is only a matter of time. Trapped oil and gas reserves prove that the time can

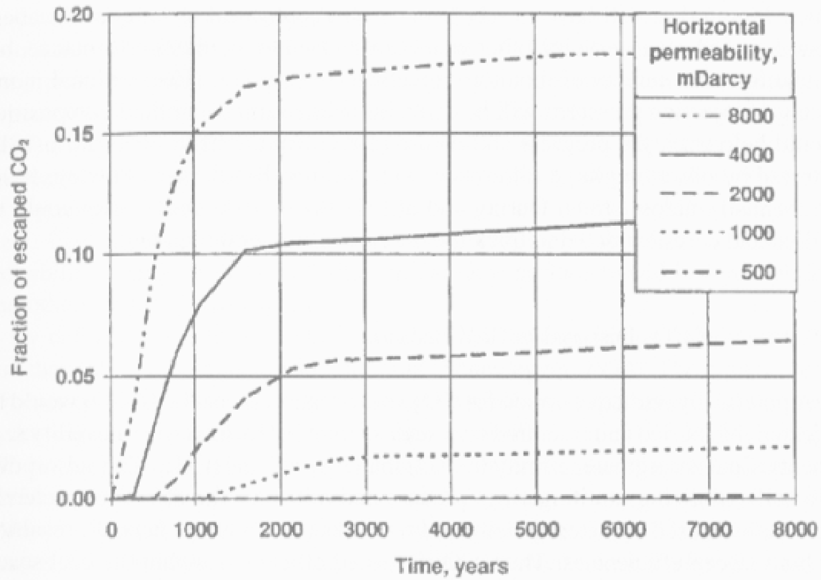

FIG. 10. Simulated CO_2 escape curves from a large but finite, horizontal, homogeneous aquifer. The boundary is 8000 m from the injection well. The CO_2 accumulates under the seal and slowly migrates under gravity toward the boundary, where it escapes. The rate of escape depends strongly on the horizontal permeability. There is no fingering in this simulation (from Lindeberg and van der Meer, 1996).

be very long indeed, but the many dry reservoirs that leaked off long before they were drilled demonstrate that leakage is the rule. Slow leakage of CO_2 to adjacent, overlying formations may be of no consequence, particularly if those formations are other deep saline aquifers. Slow leakage that returns CO_2 to the atmosphere is unacceptable because it defeats the purpose of disposal. Catastrophic leakage is unacceptable. What is needed is systematic investigations of what constitutes a good seal ("trap"), on one hand, and seal failure modes, on the other, over the time scales of interest for CO_2 sequestration (Fig. 10). The Geochemistry and Geomechanics sections review these issues. However, one aspect that those sections do not treat is sealing mechanisms. A pressure seal blocks all pore fluid movements over "substantial intervals of geologic time" (Neuzil, 1995). A capillary seal functions by a wetting fluid preferentially occupying the fine-grained pore space of the seal (e.g., shale), thus preventing the movement of a nonwetting fluid (Revil *et al.*, 1998). Of importance is the absence of methods for evaluating the sealing potential of aquifers (for example, significant under- or overpressures or anomalous water chemistry). This raises additional characterization issues for aquifers and reiterates the need for site-specific data and case studies.

Monitoring of injection and long-term integrity will involve a combination of monitoring wells completed in the storage reservoir or aquifer and in overlying units. Monitoring will have to rely heavily on geophysical techniques. In abandoned oil and gas reservoirs, other wells can be used to monitor performance, but in aquifers, the number of monitoring wells will be limited. Conventional monitoring of injection pressures will be essential, while samples of fluid composition would help track the progress and nature of the displacement. Seals are usually inferred by observing large differences in pressures (Bradley and Powley, 1994) or chemistry across strata. During and after injection, additional holes could be drilled and cores extracted to track the progress of mineral trapping.

2.5. Issues of CO_2 Disposal in Coal Beds

A potentially attractive option for CO_2 sequestration is coal beds. CO_2 would be injected into buried and fractured coal seams, bounded by lower-permeability sediments. Coal has a greater affinity for CO_2 than for methane (CH_4). This adsorption is a self-stabilizing (antifingering) process and mitigates the effects of preferred flow paths caused by heterogeneity and fractures (called cleats in coal), resulting in high sweep efficiencies. Thus, CO_2 is stored efficiently within the coal seam, with breakthrough occurring only after filling most of this storage. Since storage is likely to take place at depths shallower than those for supercritical CO_2 injection, it is important that the probability for release to the surface be low. Therefore, a critical element is the integrity of the confining beds bounding the coal seam. In spite of some apparent advantages, CO_2 sequestration in coal beds entails several major uncertainties. These include the fundamentals of desorption and adsorption processes (CH_4 vs CO_2), wettability, moisture content, temperature, the geometry and characteristics of the fracture network, the flow through the network, and the effects of changing stress on all of these.

Desorption of the gas from the coal is controlled by the hydrostatic head of the aquifer (McElhiney *et al.*, 1989), but also appears to vary nonlinearly with pressure. By dewatering the coal seams, the pressure is reduced and methane is desorbed from the coal. After desorption, the methane diffuses through the coal into the cleat system and flows to the production well. For example, Bumb and McKee (1988) found that a 70% reduction in external pressures was required before 25% of the absorbed methane was released from the Mary Lee coal group in the Warrior Basin, Alabama.

If coal-bed methane reservoirs have been reflooded with water after production, it becomes important to understand the effect of coal wettability to CO_2 and other reservoir fluids on coal-seam permeability and relative permeability. Satisfactory history matches for water and gas flow in coal-reservoir simulations appear to suggest that it is acceptable to treat coal as water-wet. However, on the field scale, a coal seam is made up of coal interbedded with shale and other impurities that may mask the true wettability properties of the coal. On the laboratory scale, a coal sample will consist of a heterogeneous mixture of organic and inorganic (i.e., mineral matter) components. The organic components of coal are generally expected to be more hydrophobic than the mineral matter components (Nelson, 1989). Additionally, the distribution of minerals in a cleat is important in terms of the wettability of the cleat surfaces. If the flow paths through the cleat cross over the carbonate minerals, these sites in the cleat would be hydrophilic (i.e., water-wet). Coal cleats with some mineralization would probably have a composite wettability, implying that some sites on the cleat surface would be hydrophobic and others would be hydrophilic.

By definition, the wetting phase consists of a fluid making a contact angle of less than 90° with a solid and another fluid (Scheidegger, 1974). The organic components of coal include varying amounts of paraffinic, naphthenic, and aromatic hydrocarbons. The contact angle of water on paraffin in air is 112–114° (Adam, 1964), i.e., the paraffin is hydrophobic and the water is nonwetting. Measurements of the contact angle of water on coal in air have yielded values ranging from 30° (Arnold and Aplan, 1989) to 132° (Surinova and Polushkin, 1987), and the water ranges from wetting to nonwetting. Therefore, it is uncertain what inferences can be drawn about the wettability of coal surfaces from measurements of air–water–coal contact angles and whether these wettability data can be extrapolated to reservoir conditions where the coal would not have been altered by aerial oxidation and where the second fluid is methane rather than air. Aerial oxidation would increase the overall wettability of the coal surface (Nelson, 1989). Given the present state of knowledge, the wide range of contact angle values reported for water on coal in air are caused by variations in (1) oxygen functionality of the organic component of the coal surface, (2) the mineral matter content of the coal surface, (3) impurities, (4) porosity, and (5) surface roughness (Arnold and Aplan, 1989). Conclusions about the wettability of coal surfaces from air–water–coal contact angle measurements may be misleading, unless both the physical and chemical composition of the coal surface and the experimental conditions under which the measurements were made are known.

Critical elements for coal-bed sequestration will be the understanding of ubiquitous cleat systems in coal and the integrity of the confining beds bounding the coal seam. Cleats are naturally occurring fractures that provide the permeability necessary for fluid (i.e., gas and water) flow. As in other reservoirs (see the Geomechanics section), the geometry and distribution of void spaces in the cleat system will control the overall permeability of coal. Complications may arise from changes in reservoir permeability over time as injection of gas occurs and the coal begins to swell (Harpalani and Zhao, 1989). During methane production, losses of volatiles caused by desorption (Briggs and Sinha, 1933; Moffat and Weale, 1955) results in volumetric shrinkage of the coal matrix and a possible increase in fracture apertures. Conversely, during gas or CO_2 injection, the net confining pressure within the reservoir system will decrease to alter the geometrical properties of the cleat network. Knowledge of the impact that the change in net stress has on cleat permeability is essential for accurate simulations of CO_2 injection potential of coal reservoirs. The role of fractures and the dependence of cleat permeability on stress have been treated more prominently in coal-bed analyses than in oil and gas reservoir simulations. Several of these aspects will be discussed later in detail from the viewpoint of geomechanics.

The importance of cleats suggests the need for research on remote characterization concerning cleats and cleat systems. Pyrak-Nolte *et al.* (1997) and Montemagno and Pyrak-Nolte (1999) used x-ray computerized tomographic (CT) imaging to obtain quantitative aperture data for three-dimensional interconnected fracture networks in coal. This work revealed that the aperture distribution of the networks was spatially anisotropic and dependent on the number and geometry of the individual fractures. Void area in the individual fractures ranged between 45 and 58%, while total volumetric porosity of the samples was on the order of 0.1%. A three-dimensional, autocorrelation analysis on the fracture network and a two-dimensional analysis on the individual fractures found that the apertures were correlated over distances of 10 to 20 mm in the direction of flow. Further research is needed to determine how the aperture distribution and connectivity of the fracture network (and thus, the relative permeability) in coal is affected by gas adsorption, which produces swelling in coal. In addition, research is needed to determine how laboratory results can be used on the field scale if apertures are only correlated over 10 to 20 mm.

3. Geochemistry

3.1. Introduction

A useful way of identifying key issues in connection with CO_2 sequestration is to begin by considering the simple model problem of injecting CO_2 into a closed mineral/fluid system and to ask how well can we predict its subsequent evolution. Initial conditions need to be specified and a minimum characterization at $t = 0$ will involve pressure, temperature, fluid fraction and solute chemistry, and mineral fractions including their spatial distribution. The ability to calculate the state of the system at long times requires thermodynamic data, and for this there exist a number of software packages (e.g., EQ3/6 maintained by Lawrence Livermore National Laboratory) believed to be quite adequate for present purposes. Although the final state of the system can in many cases be calculated with reasonable confidence, predicting the path and rate by which the system evolves to this final state is extremely problematic. The main source of uncertainty derives from our inability

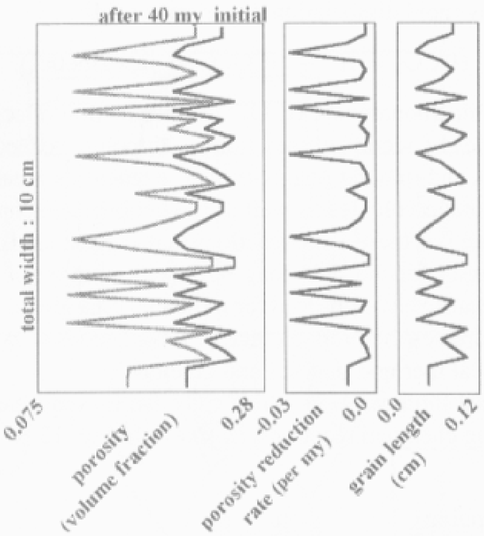

Fig. 11. Enhanced heterogeneity resulting from coupled pressure-solution and diffusive mass transfer. Initial heterogeneity is due to differing quartz volume mass transfer. Changes in heterogeneity are caused by varying rates of pressure-solution associated with grain sizes and porosity. In carbonate systems similar processes can occur three to five orders of magnitude faster due to greater kinetic reaction rates of carbonate minerals (modified from Park and Ortoleva, 1999).

to realistically specify the kinetics of the various homogeneous and heterogeneous reactions that take place (Fig. 11).

Uncertainties in the rates of reactions expected to take place following CO_2 injection severely limit our present ability to predict the ultimate storage capacity and storage integrity of natural reservoirs associated with trapping injected CO_2 by the precipitation of carbonate phases. Several potentially important trapping mechanisms are discussed, and some indication is given as to whether the key reactions are expected to be fast or slow. However, quantitative statements regarding the effectiveness of any given trapping mechanism requires realistic kinetic information, but such information is not currently available for anything but the very simplest of situations.

Beginning with a simplified approach that focuses on geochemical reactions, we can examine elements of the sequestration problem by following the evolution of CO_2 upon injection into the subsurface and resulting physical displacement of the existing pore fluids. Figure 12 shows that CO_2 injection initiates a complex network of reactions that involve aqueous solutions and host rock minerals. First, CO_2 transfers across the gas–water interface to become an aqueous ion by the reaction

$$CO_2(g) + H_2O = H_2CO_3 \text{ (slow kinetics).} \quad (1)$$

This is followed by rapid dissociation of carbonic acid

$$H_2CO_3 = H^+ + HCO_3^- \text{(very fast kinetics).} \tag{2}$$

The formation of bicarbonate ion, HCO_3^-, and production of acidity by release of H^+ leads to a series of secondary reactions with complex feedbacks that buffer solution properties and mineral reactivity. These reactions greatly complicate estimates of CO_2 storage volumes as well as the geophysical characteristics of the host rock. However, it is these same reactions that suggest land disposal may have an enormous capacity for the safe, long-term sequestration of CO_2 by the same mechanisms that nature has employed for millennia on a global scale. The following discussion addresses the probable fate of this aqueous CO_2 from the point of view of geochemical thermodynamics and kinetics.

There are at least three ways in which CO_2 can be sequestered in subsurface processes involving chemical reactions, as shown in Fig. 12.

3.2. Aqueous Trapping

In the first mechanism, pore fluids can accumulate dissolved CO_2 by Rxn (1) and (2) through "aqueous trapping." The pressure (P), temperature (T), and salinity (TDS as total dissolved solids) conditions of most subsurface disposal environments limit CO_2 accumulation by thermodynamic constraints that are well understood in comparison with other uncertainties. Although solubilities are maximized in formation waters with low salinities, generally speaking, pore fluids can hold only a small percentage of HCO_3^- regardless of TDS or the PCO_2 at injection (Bachu *et al.*, 1996). Thus, the capacity of subsurface fluids to capture CO_2 by aqueous trapping is relatively small.

3.3. Mineral Trapping

In a second type of trapping, dissolved CO_2 reacts with divalent cations to form carbonate mineral precipitates. This "mineral trapping" mechanism offers the greatest potential for increasing CO_2 sequestration capacities while also rendering CO_2 immobile for longer time scales (Perkins and Gunter, 1996). Overall reaction stoichiometries for the most common minerals show that carbonate precipitation consumes bicarbonate ion while producing acidity by the reactions

$$HCO_3^- + Ca^{2+} = CaCO_3 + H^+ \quad \text{calcite (fast kinetics),} \tag{3a}$$

$$HCO_3^- + Mg^{2+} = MgCO_3 + H^+ \quad \text{magnesite (fast kinetics), and} \tag{3b}$$

$$HCO_3^- + Fe^{2+} = FeCO_3 + H^+ \quad \text{siderite (fast kinetics).} \tag{3c}$$

Rates of these reactions are known to be relatively fast but have a complex dependence on reactant concentrations, in situ pH, temperature, and salinity (e.g.,

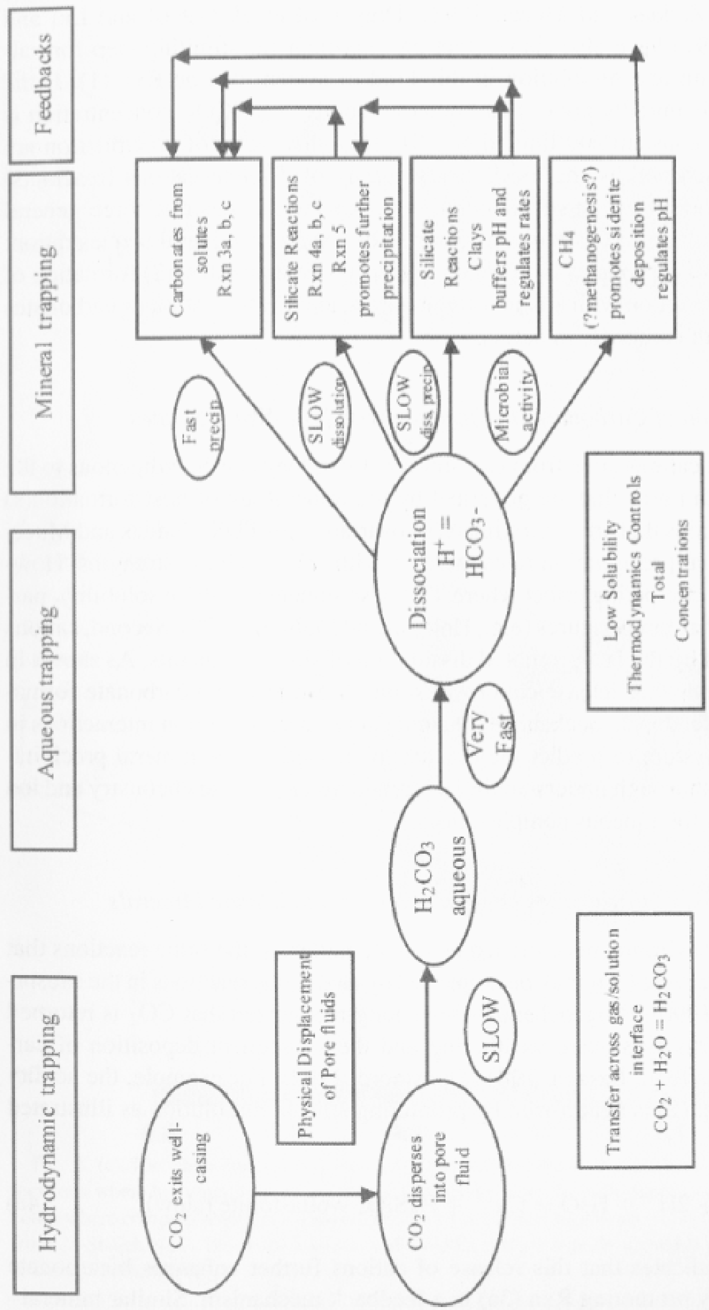

FIG. 12. CO_2 terrestrial sequestration-chemical processes and reservoirs (Dove, unpublished).

Morse, 1983; Zuddas and Mucci, 1998). Dreybrodt *et al.* (1996) and Liu and Dreybrodt (1997) have also shown that an important rate-limiting step for calcite precipitation and dissolution in this kind of system can be Rxn (1). If the host reservoir is initially poor in carbonate minerals, the HCO_3^- concentration is approximately constant and limited by CO_2 solubility; rates of precipitation are primarily constrained by the much larger supply of divalent cations (reactants) and consumption of protons (products). A closer look shows that three general scenarios affect these constraints to control the extent of mineral sequestration: (1) Formation of carbonates by reaction with pore-water solutes, (2) formation of carbonates by reaction with siliciclastic minerals, and (3) formation of carbonates by reaction with carbonate minerals.

3.3.1. Formation of Carbonates by Reaction with Pore-Water Solutes

The reactant cations arise from two sources. First, they can be indigenous to the pore fluids with ratios that are governed by the mineralogy of host formation(s) and concentrations that are approximately covariant with TDS. Zuddas and Mucci (1998) show that precipitation rates increase with solution ionic strengths. However, there is a competing effect where TDS also enhances calcite solubility, particularly at higher temperatures (e.g., Holland and Malinin, 1979). Second, cations can be released by the H^+-promoted dissolution of silicate minerals. As shown in Fig. 11, reactions that release cations to solution can promote carbonate formation through a feedback mechanism. Quantifying mineral–solution interactions in this dynamic system to predict the conditions that maximize mineral precipitation requires a thorough understanding of carbonate-electrolyte chemistry and ion pairing models for aqueous complexation.

3.3.2. Formation of Carbonates by Reaction with Siliciclastic Minerals

In geologic environments enriched in silicate minerals, the same reactions that nature uses to recycle CO_2 may be employed by analogous reactions in the subsurface (Siefritz, 1990). Biogeochemists have long recognized that CO_2 is returned to the solid earth by silicate weathering and the subsequent deposition of carbonate minerals (e.g., Lasaga, 1981; Dunsmore, 1992). For example, the acidity produced in Eq. (2) is neutralized by promoting silicate dissolution as illustrated by the reaction

$$CaSiO_3 + 2H^+ + H_2O = Ca^{2+} + H_4SiO_4 \text{ wollastonite (slow).} \qquad (4a)$$

Figure 12 indicates that this release of cations further enhances bicarbonate consumption by promoting Rxn (3a) in a feedback mechanism. Similar mineral–water reactions favor additional formation of magnesium and iron carbonates by

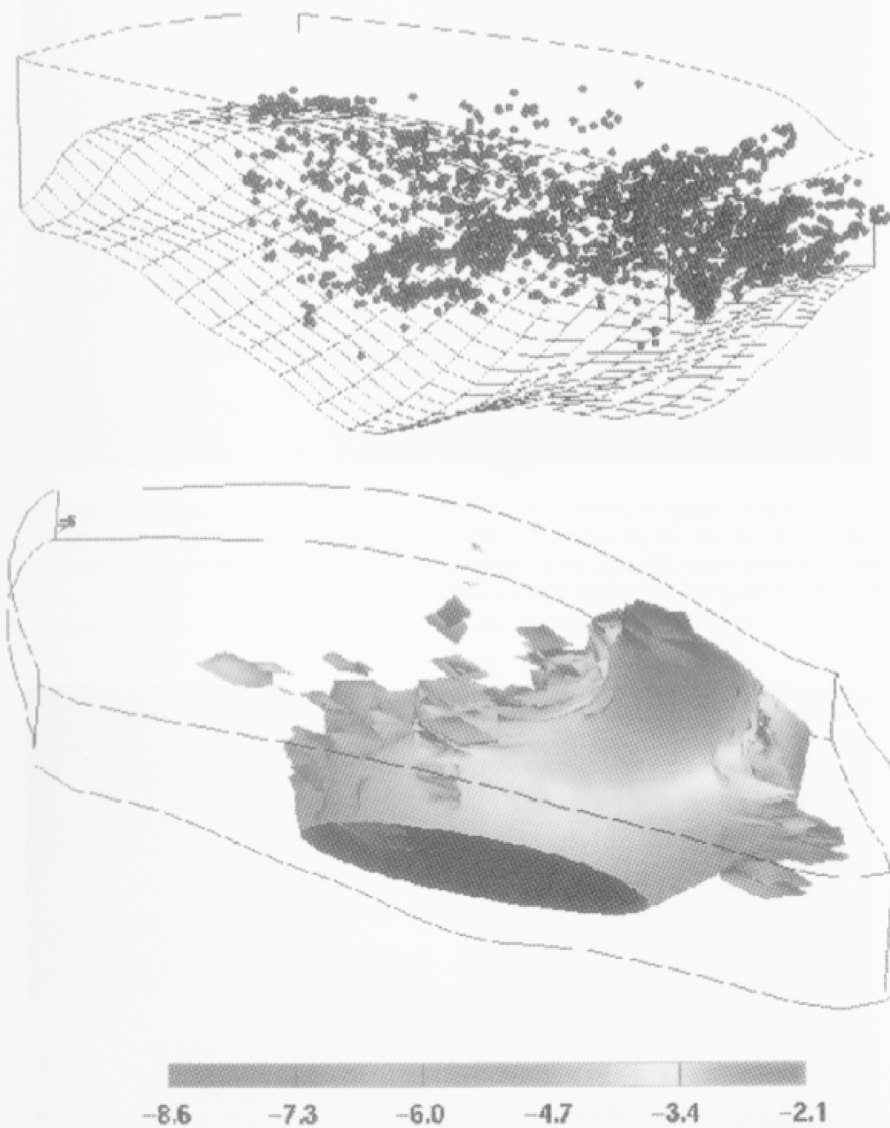

FIG. 2. (a) The three-dimensional view of the Anadarko Basin is seen from the south showing locations where high-quality pressure data are available. Note the high density of data in the deeper zones where compartmentation is generally believed to be most significant (from Ortoleva, 1998; data from Al-Shaieb *et al.*, 1994). (b) Isosurface of 100 kPa overpressure developed from data of frame (a) (from Ortoleva, 1998).

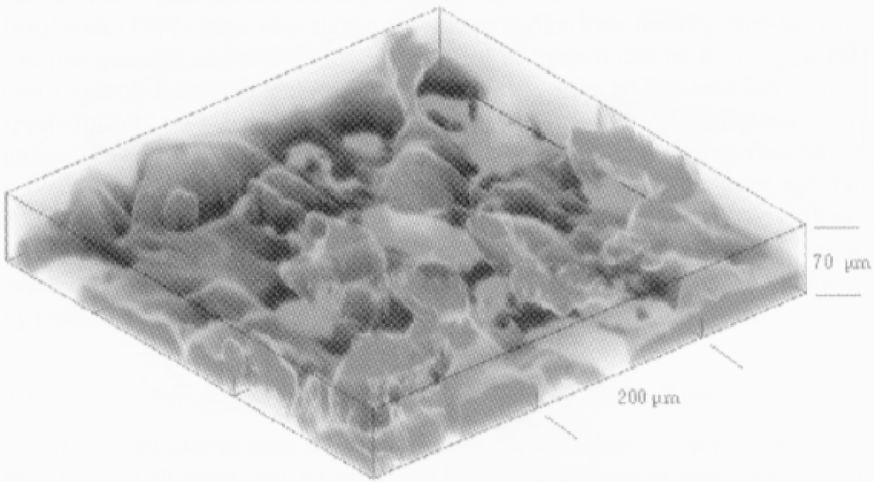

FIG. 5. High-resolution 3D image of pore space in Berea sandstone obtained with Laser Scanning Confocal Microscopy. The pore phase and solid grains are opaque and translucent, respectively. The data illustrate a complex fine-structure including conspicuously thin pore necks and throats connecting the larger (nodal) pore bodies (from Fredrich, 1999).

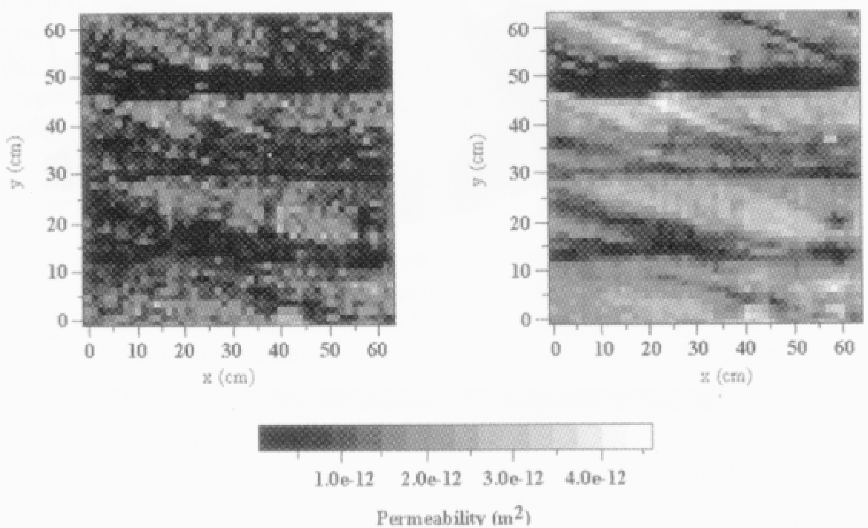

FIG. 6. Not only does permeability heterogeneity vary from rock to rock, it is also a function of the scale of measurement or simulation. Above are two permeability maps, each based on 2,500 individual measurements on one face of a meter-sized block of Massilon sandstone (from V. Tidwell and J. Wilson, personal communication, 1999). The sampling device used for the measurement on the right (b) integrates over a volume 64 times larger than the device used for measurements on the left (a). Note the distinct smoothing.

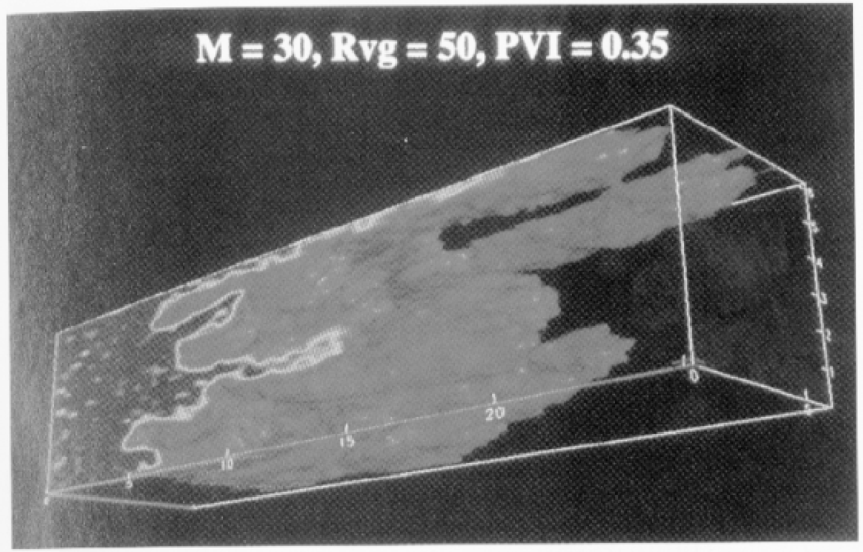

FIG. 7. A three-dimensional view of particle tracking simulations of viscous fingering and gravity segregation in a three-dimensional, homogeneous porous medium (from Tchelepi and Orr, 1994). A CO_2-like low viscosity fluid displaces another fluid 30 times more viscous from left to right. Viscous fingers move rapidly through the zone of low density, low viscosity fluid that forms at the top of the porous medium. Viscous fingers also form lower in the porous medium, but the gravity-dominated preferential flow that occurs at the top of the medium carries more of the low viscosity fluid.

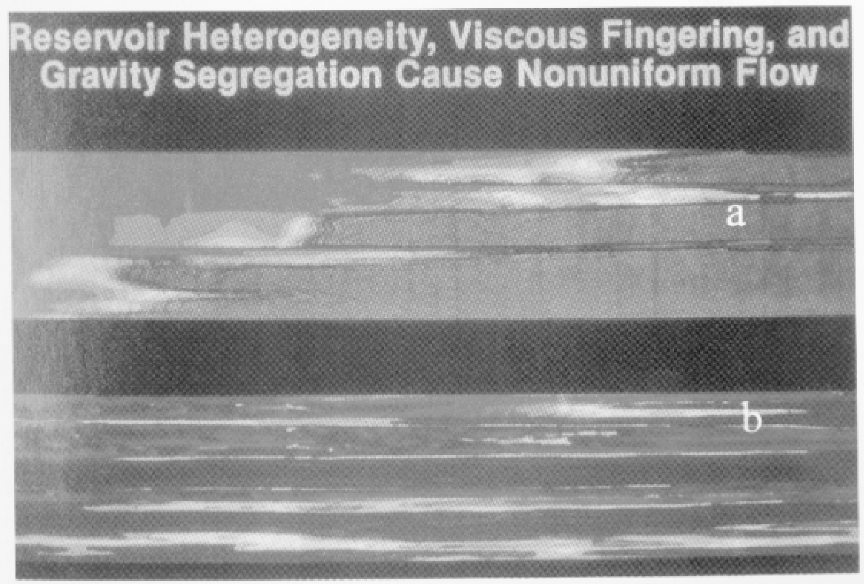

FIG. 8. Calculated flow behavior for injection of CO_2 into a heterogeneous oil reservoir resulting in viscous fingering under the combined effects of gravity and heterogeneity. The lower panel (b) shows the spatial distribution of permeability in the two-dimensional cross-section. The upper panel (a) shows the portion of the reservoir invaded by CO_2. The low-viscosity CO_2 invades the higher permeability zones preferentially, and gravity forces cause the lower-density CO_2 to invade the upper zone as well. Similar behavior will occur in aquifers (K. K. Pande, personal communication).

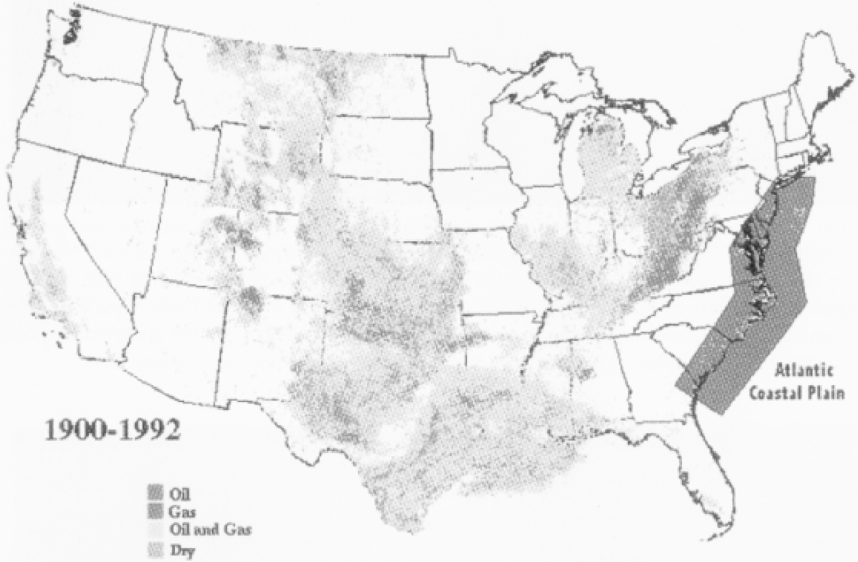

FIG. 9. Map of petroleum wells drilled in the U.S. (lower 48 states) from 1900 to 1992, illustrating the sedimentary basins located over vast portions of the U.S. that could be used for deep injection of supercritical CO_2. Productive gas wells indicate a formation capable of storing natural gas, and thus also capable of storing CO_2. Dry wells, especially dry wells close to productive gas wells, indicate that although the geologic interpretation suggests gas storage, natural gas either never developed or it escaped during the formation's history. It may not be possible to successfully sequester CO_2 in these areas. The blue region shown on the east coast indicates the clastic portion of Atlantic coastal plain aquifers that might be used for shallow injection of dissolved CO_2 (from Gautier *et al.*, 1996, modified by J. L. Wilson, 1999).

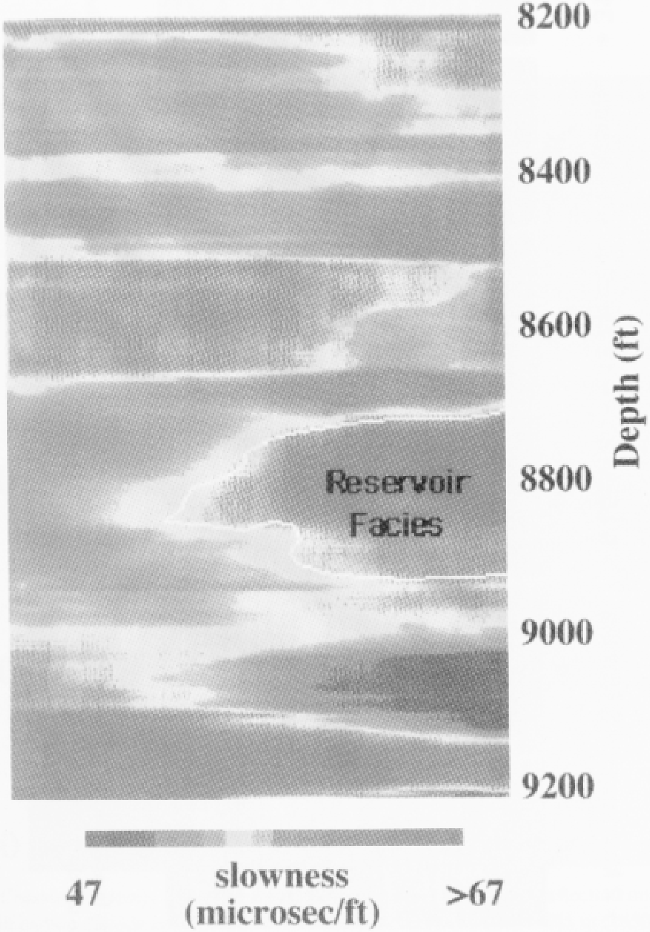

FIG. 39. High-resolution image produced with crosswell seismic tomography (from Langan *et al.*, 1997). The tomogram delineates an oval-shaped low-velocity zone representing a high porosity reservoir facies anomaly. The anomaly can be seen at a depth of approximately 2785–2660 m (8700–8950 ft) in the right hand side of the image. Crosswell methods are potentially capable of producing these high-resolution images in 2D. Research is needed to extend this capability to three dimensions.

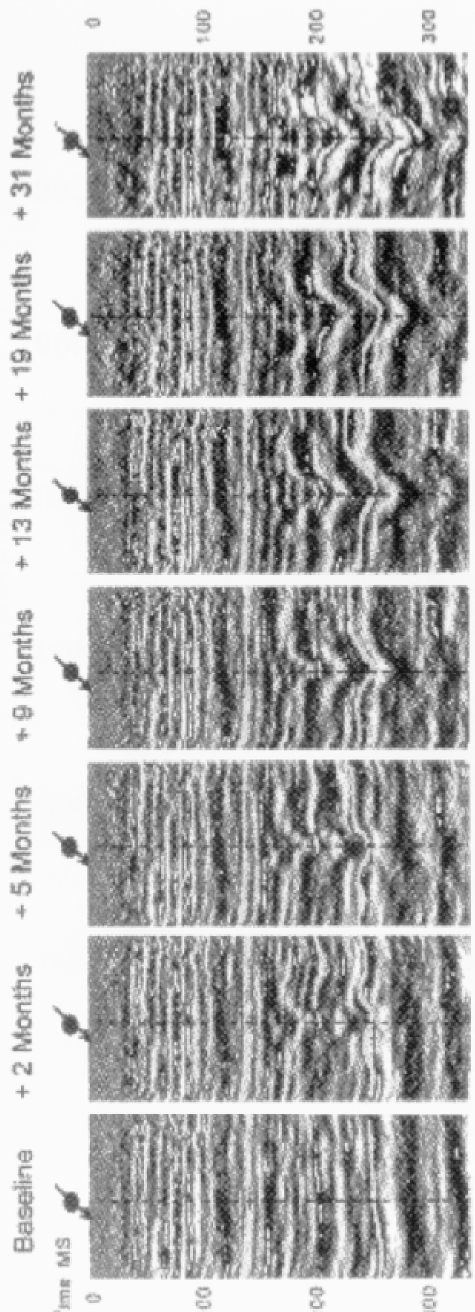

FIG. 40. Vertical sections from 3D surface seismic monitoring of steam injection. The yellow lines delineate the top and bottom of the steam injection interval. While the data do not change above the injection interval, the sag below is caused by the steam (from Jenkins *et al.*, 1997).

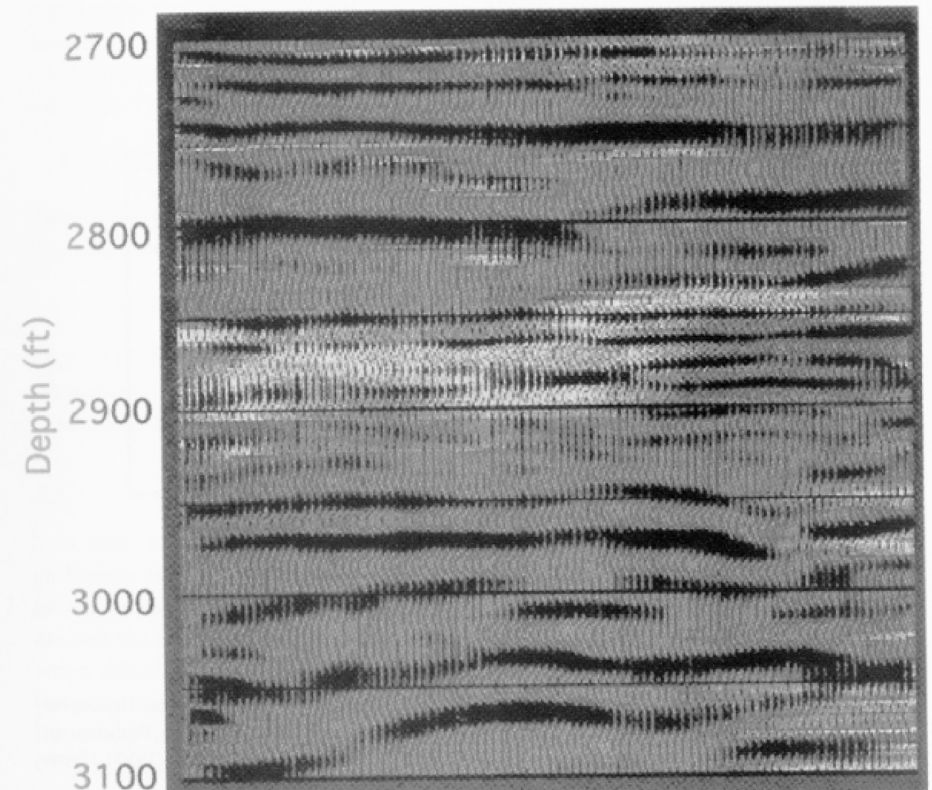

FIG. 41. Crosswell velocity difference tomogram overlaying a crosswell reflection image. The zone flooded with carbon dioxide is delineated by the yellow–red colors at 880–895 m (2850–2900 ft) that indicate a velocity decrease of about 5–10%; blue indicates no change in velocity (from Lazaratos and Marion, 1997).

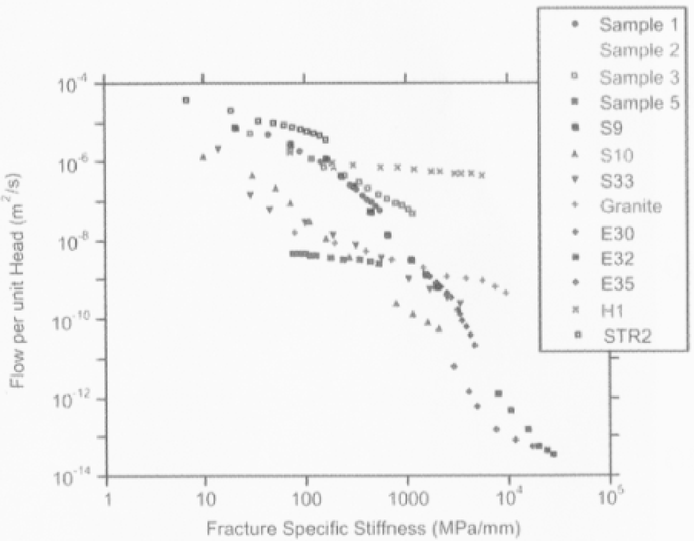

FIG. 42. Observed interrelationship between fluid flow and fracture-specific stiffness for 10 samples each containing a single fracture. The data for 13 samples have been obtained from Witherspoon *et al.* (1980), Raven and Gale (1985), Gale (1985), Gale (1987), and Pyrak-Nolte *et al.* (1987). (From Pyrak-Nolte and Morris, 2000.)

the respective reactions

$$Mg_2SiO_4 + 4H^+ = 2Mg^{2+} + H_4SiO_4 \quad \text{forsterite (slow) and} \tag{4b}$$

$$Fe_2SiO_4 + 4H^+ = 2Fe^{2+}H_4SiO_4 \quad \text{fayalite (slow).} \tag{4c}$$

Gunter *et al.* (1993) concluded that the calcium and magnesium (or other divalent) bearing silicate minerals have the greatest potential for enhancing CO_2 disposal capacities because they also act as enormous proton sinks during dissolution. Building on these simple examples, we can see that dissolution of the aluminosilicates also promotes precipitation of carbonate mineral as well as formation of clay minerals. For example, anorthite dissolution follows the stoichiometry

$$CaAl_2Si_2O_8(\text{anor}) + 2H^+H_2O = Ca^{2+}Al_2Si_2O_5(OH)_2\,(\text{kaol})\ (\text{slow}). \tag{4d}$$

More generally, an overall reaction shows that feldspar dissolution can lead to CO_2 trapping as a variety of carbonate minerals

$$\text{Feldspars} + \text{Clays} + CO_2 = \text{Kaol} + \text{Calcite} + \text{Siderite} + \text{Quartz} \tag{5}$$

Siefritz (1990) and Fyfe *et al.* (1996a and b) have further noted that the exothermic properties of these mineral reactions also provide an energy bonus of 24 kCal per mole of feldspar dissolved that could potentially be recovered to offset costs.

3.3.3. Formation of Carbonates by Reaction with Carbonate Minerals

A third environment that modifies the extent of CO_2 by sequestration is the carbonate-rich environment. Mineral trapping in this system is not generally promoted because the decreased pH associated with H^+ release by dissociation increases the solubility of carbonate minerals, whereupon they quickly dissolve. In some situations, this could be potentially hazardous to the reservoir host or seal integrity. Bergman and Winter (1995) have noted that reaction of acidic fluids with limestone or dolomitic formations can overpressure the formation through rapid CO_2 release. Note that carbonate minerals can, however, be precipitated when other minerals can act as rapid proton sinks to buffer H^+ production (Hitchon, 1996). The literature suggests considerable uncertainty in our ability to predict the behavior of carbonate-hosted, subsurface systems.

3.4. Microbial Trapping

Several studies have suggested that microbial trapping may offer a third mechanism for sequestering CO_2 (e.g., Fyfe *et al.*, 1996a; Ferris *et al.*, 1994). Because most of these studies have focused on promoting biomineralization by mechanisms that depend upon photosynthesis by direct or indirect mechanisms, it is unlikely they can promote CO_2 sequestration by terrestrial disposal. We could also consider that microbial conversion of CO_2 to methane via the simplified reaction

$$2H_2 + CO_2 = CH_4 + ? \tag{6}$$

may enhance CO_2 capacities. This reaction has been documented in deep sediments (Kieft and Phelps, 1997) and deep aquifers of the Columbia River Basalts (Stevens and McKinley, 1995). However, the volume increase associated with methane production would decrease reservoir capacity, and work by Anderson *et al.* (1998) indicates CO_2 consumption by reaction with hydrogen is unlikely. Perhaps more likely is a secondary role of microbes in CO_2 sequestration by promoting feedback on the trapping mechanisms proposed earlier. Metabolic activities can promote silicate dissolution and therefore, secondary precipitation of carbonate minerals, particularly siderite (e.g., Brown *et al.*, 1994). The possibility of harnessing microbes to promote CO_2 sequestration is intriguing.

The foregoing summary suggests that the ideal chemical trapping mechanisms are characterized by their abilities to enlarge reservoir capacities and transfer CO_2 into an unreactive form through fast kinetics. While the long-term capacity of mineral traps is enormous, the kinetics of the reactions required to form these minerals is problematic. Hence, research should focus on the rates and mechanisms of chemical reactions that improve our ability to (1) make quantitative model predictions of how a system responds to CO_2 injection, (2) identify the "bottlenecks" that occur along the path from transferring supercritical CO_2 across the gas–water interface to the final sink as carbonate minerals, (3) investigate means of "widening" the bottlenecks, and (4) determine the long-term capacity of system for sequestering CO_2 by mineral trapping. Another possible limit on rates of silicate reactions is the precipitation of SiO_2 as a secondary product. The importance of understanding clay mineral formation should not be overlooked. These fine-grained constituents have enormous capacity for buffering mineral–water chemistry as well as affecting hydrodynamic properties by modifying formation permeability. Because CO_2 injected from a fossil fuel burning facility likely will contain trace gases, research may also be needed to determine the potential for gaseous contaminants to interact with mineral surfaces within the formation. Passivation by surface sorption and isolation of reactant sites from the fluid environment could greatly inhibit rates of mineral dissolution and precipitation. The feasibility of microbial trapping also should be investigated. Microbial processes are intertwined with the systems approach described above, but subsurface microbial studies are only beginning to document these unique ecosystems.

Up to this point, we have dealt only with the very oversimplified situation of a spatially uniform (on scales larger than mineral grains) closed system. But even in this idealized limit, we would argue that the present capability to specify the time evolution of the system is seriously compromised for lack of reaction kinetic information. It is important to keep in mind that the sort of kinetic information needed is in the form of continuum-scale constitutive equations which, especially in cases of heterogeneous reactions, can involve complex averages over a variety of atomic scale processes. A full characterization and understanding of the reaction kinetics relevant to CO_2 sequestration in geological environments will require an extensive program of laboratory experimentation, along with carefully chosen field measurements to validate the upscaling of the laboratory behavior to the time and length scales of interest.

The next level of complexity that one might consider is that of spatially nonuniform open systems or potentially open systems. A potentially open system is one that is initially enclosed by a "seal" that effectively isolates it from the surroundings, but with time could become open because of mechanical or chemical breaching of the seal. In order to deal with open or potentially open systems, a number of additional constitutive equations need to be specified. Of special interest are the relationships of permeability to fluid content and mineral texture, and those relating rheology to fluid content, mineral fractions, and their texture.

3.5. Role of Coupled Processes and RTM Instability

As suggested in Fig. 13, there are many factors and processes operating naturally or during injection that are strongly coupled. Thus, simulation of the development of repositories over long time periods or their response to injection must be based on multiprocess models that account for all cross-coupling relations in the network of reaction, transport, and mechanical (RTM) processes. Furthermore,

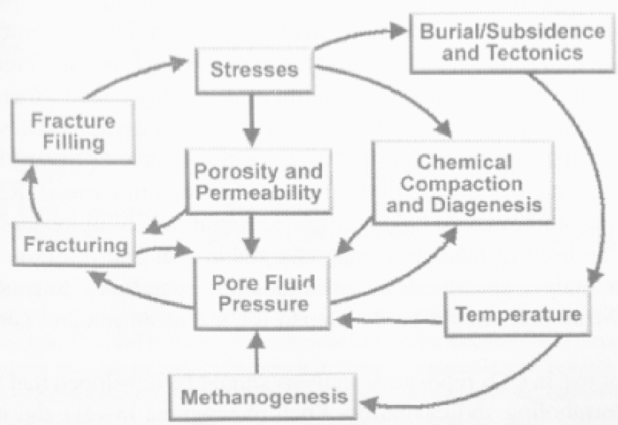

FIG. 13. Schematic of parameters and complex feedback between coupled reaction, transport, and mechanical *in situ* processes (Ortoleva, unpublished).

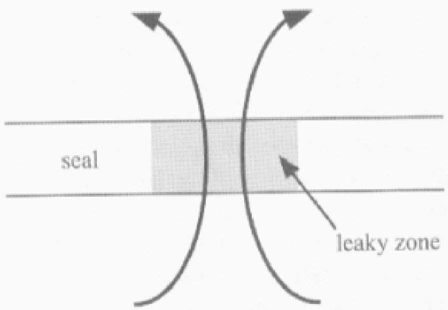

FIG. 14. Schematic view of flow self-focusing leading to a reaction-induced breaching of a seal (Ortoleva, unpublished).

these RTM simulators must be three-dimensional so that all geometric effects are accounted for (i.e., CO_2 waste fluids must be contained in all directions to ensure their sequestration from the accessible environment).

Flow self-focusing is an example of the strong effect of coupled processes that cannot be understood in terms of independent ones. (See Ortoleva, 1994b, for a review of this and other geochemical strong-coupling phenomena.) As shown schematically in Fig. 14, a slightly leaky region in a seal focuses fluid escape through it. If the fluids retained by the seal dissolve one or more minerals within the seal and thereby increase its permeability, then the escaping fluid will enhance the permeability in the leaky zone. Consequently, it will concentrate further flow there, and an efficient fluid escape pathway develops. This process illustrates the notion of geochemical seal stability: flow self-focusing can make a seal unstable with respect to fluid escape even if the minerals in the seal could not be appreciably affected when these fluids uniformly enter the seal (i.e., in an overall mass balance sense) in contrast to the destabilizing, strongly focused flow dynamic. Similarly, a front of injection-induced alteration can become unstable to fingering when that alteration increases permeability. In three spatial dimensions, these flow self-focusing phenomena are enhanced over those in two dimensions. These examples illustrate that reliable simulation of CO_2 repository behavior during injection or long afterwards requires the use of fully coupled, three-dimensional RTM models. Such modeling studies could help identify potential instability phenomena. They should also be used to tabulate chemically stable seal and reservoir lithologies as well as to analyze specific demonstration sites. Such three-dimensional, fully coupled RTM models should be developed for use as an integral part of a CO_2 repository.

Models for use in CO_2 repository analysis should be developed that account for effects of wormholing and cavitation. Such phenomena involve the interplay of free flow and Darcy flow zones, coupled to geochemical reactions. An attractive

approach seems to be the use of Brinkman's equation (Liu *et al.*, 1997). This model should be generalized for the multiphase regime.

3.6. Textural Models and RTM Dynamics

CO_2-induced clay dewatering could decrease rock strength, while CO_2-induced precipitation could increase it. Even small changes in grain geometry induced by CO_2 could alter the integrity of grain–grain contacts, and thereby affect rock strength, sound speed, and other properties.

The dynamics of the repository system depend on the distribution of rock mechanical and transport properties as well as mineralogy. In order to predict reservoir response, a complete set of texture geometric variables must be identified, and the laws for their evolution must be set forth (Fig. 15). The importance of these parameters and the interrelationship among texture parameters; porosity, permeability, capillarity, etc., are discussed in further detail in related sections.

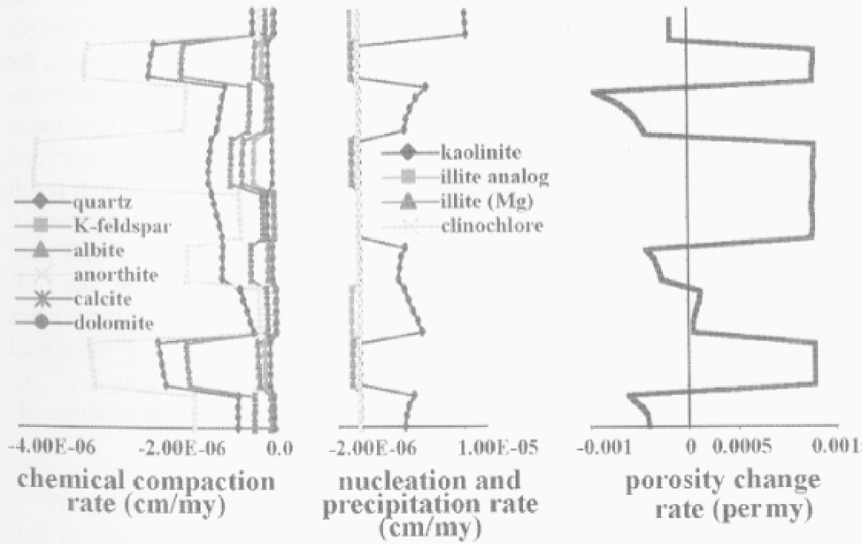

FIG. 15. Calculated reaction rates of minerals and porosity change rates for a system consisting of 10 minerals and 9 sedimentary layers. Water saturated with calcite and quartz are injected from below at a rate of 1 m/year. Coupled to water–rock chemical interaction mechanisms, advective and diffusive flow and complex mineralogy and texture result in complex mineralization patterns with potentially major effects on permeabilities and fluid pathways. In similar open systems, carbonate minerals, with higher rates than the silicates, are often the most mobile components (modified from Park and Ortoleva, 1999).

3.7. Nucleation and Ostwald Processes

A central theme in the subsurface CO_2 repository strategy is the formation of CO_2-bearing mineralization. Key geochemical processes that are poorly accounted for in most models are nucleation and Ostwald ripening and step-rule processes (Ortoleva, 1994b). Models should account for the resulting geometry of the new minerals, the mineral surfaces on which their nucleation is promoted, and the effect of Ostwald ripening. The practical challenge of embedding Ostwald ripening (and hence, the particle-size distribution) in three-dimensional RTM models should be addressed. The competition between various polymorphs (i.e., Ostwald step-rule phenomena) should also be considered (Ortoleva, 1994b; Fig. 16).

4. Geomechanics

4.1. Introduction

The assessment of reservoir storage capacities and the efficient injection and sequestration of CO_2 are directly linked to modeling geologic systems. Credible geomechanical models require the formulation of realistic constitutive models, the site-specific identification and measurement of rock properties, and the determination of boundary conditions (Fig. 17). Boundary conditions include not only the *in situ* stress states, but also the location and properties of faults bounding reservoirs or compartments within reservoirs. Uncertainties and the need for research result from the heterogeneity of geologic systems emphasized previously, the presence of fracture networks, and changes in rock properties and stress state with pore pressure, fluid content, and time during and after oil or gas production, and CO_2 injection. Some of these attributes and the extent to which reservoir characteristics change with time ultimately require that geomechanics analyses are integrated into systems analyses in order to account for the interaction or "coupling" between diverse processes referred to as RTM (reaction, transport, and mechanical) processes.

4.2. Reservoir Characterization

4.2.1. Faults as Seals or Conduits to Fluid Flow

The effects of faults on fluid-flow ranges from prevention (barrier) through little or none to enhancement (conduit). The reasons for these differences are not presently apparent, although research on the structure of fault zones has suggested some relevant factors.

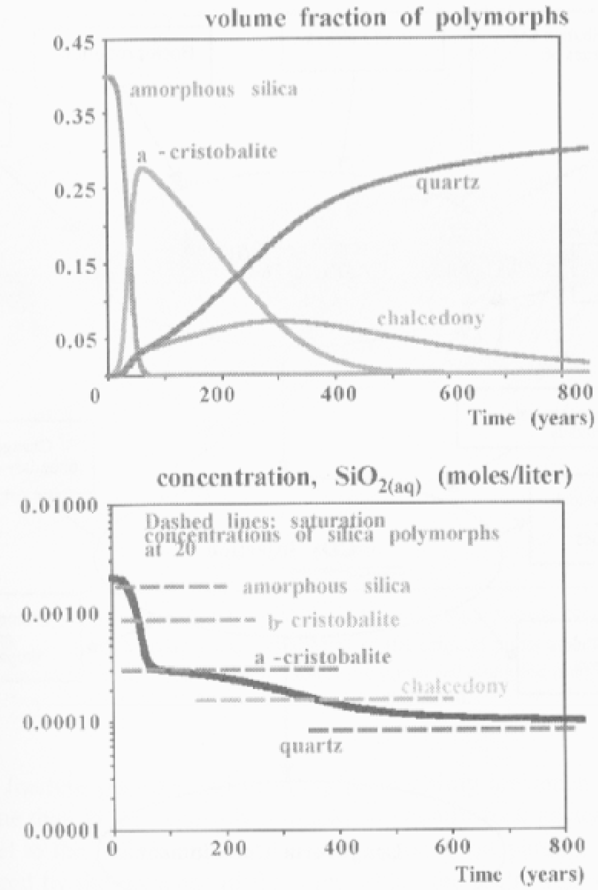

Fig. 16. Simulation showing nucleation and competitive growth (step-rule) among various silica polymorphs under room-temperature conditions. Changing physical and chemical conditions of sediments can invoke similar reaction mechanisms in carbonate systems, with the potential of large amounts of carbonates precipitating out from water (modified from Ozkan and Ortoleva, 1999).

The geometry of individual faults is complex in both strike and dip directions, but studies have established a general cross-sectional geometry that appears to characterize many faults. The nominal fault zone width—or that which is often mapped as the "fault"—is a damage zone where the fracture density is significantly higher than the surrounding country rock (Fig. 18). Within the damage zone is fault rock or gouge, a region of fine-grained material much narrower than the damage zone and often only 5–10% of that width (Fig. 19). The fault rock has been deformed by a variety of mechanisms depending upon the pressure and temperature regimes. These range from mechanical comminution and "smearing"

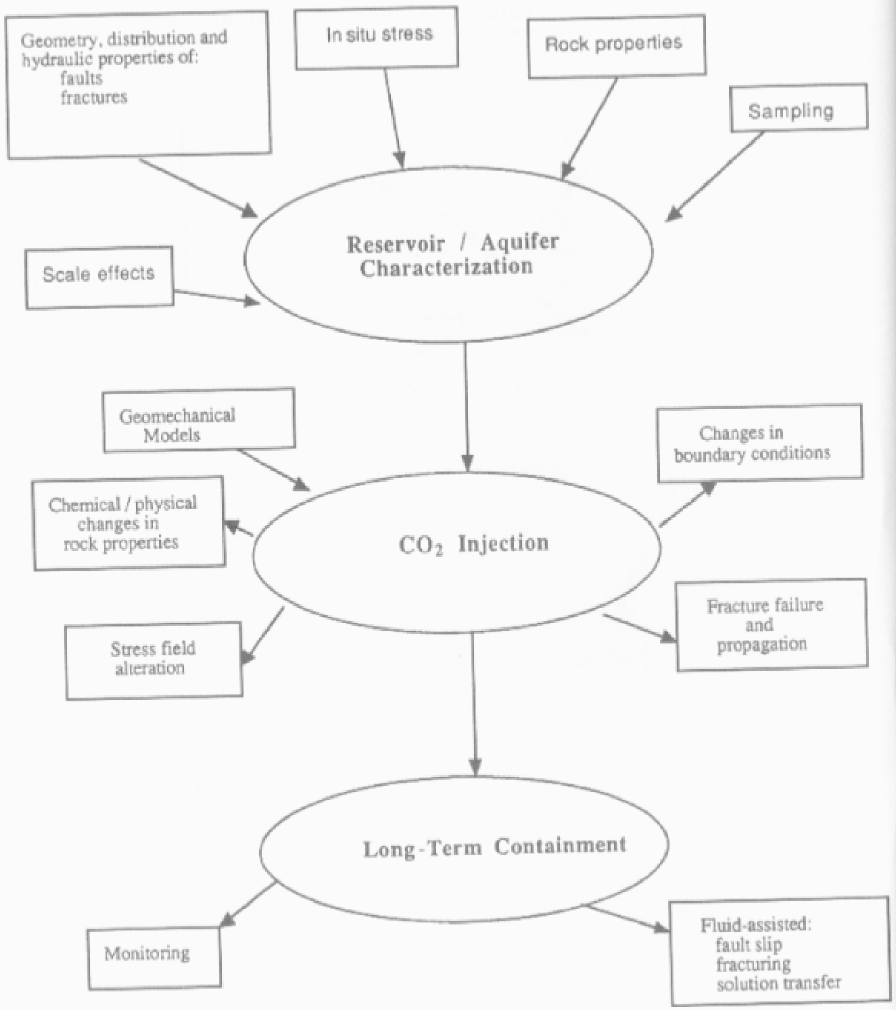

FIG. 17. Geomechanics considerations of CO_2 sequestration from reservoir characterization through long-term containment (Logan, unpublished).

of more ductile material such as some shales (Weber *et al.*, 1978) at lower temperatures and pressures, through dislocation glide, creep, and recrystallization, to solution transport at higher temperatures and pressures. Typically, deformation is not homogeneous, but is localized along fractures that evolve with increasing shear strain. The result is a grain-size reduction and heterogeneous porosity and permeability (Logan *et al.*, 1992).

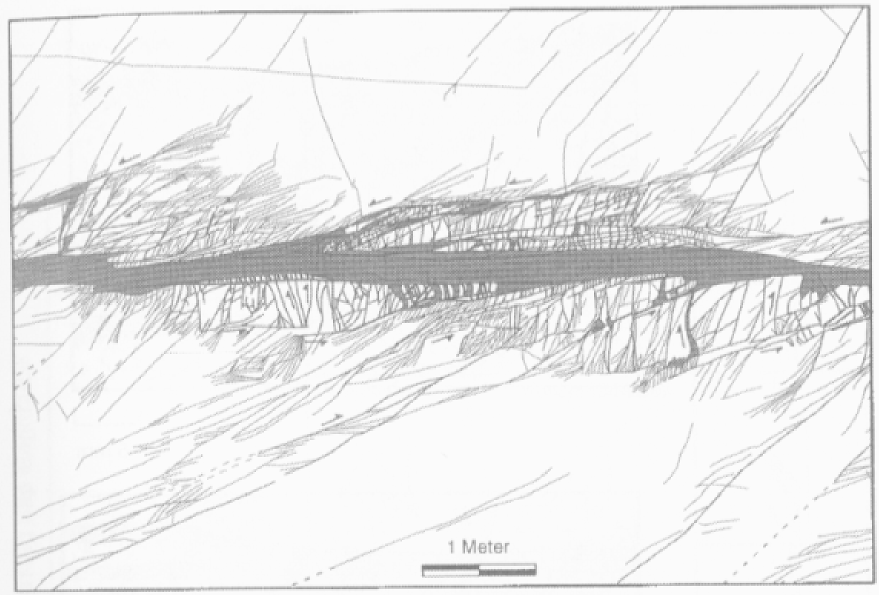

FIG. 18. Section of medium-scale fault in the Valley of Fire State Park, Nevada. Note well developed fracture network and through-going gouge zone. Most of the original joints and sheared joints are obliterated by fault slip; however, some sheared joints are preserved along the margins of the central damaged core (from Taylor *et al.*, 1997, and Myers and Aydin, 2000).

Because fracture porosity and resulting permeability are much higher in the damage zone than in the relatively unfractured country rock adjacent to it, fluid flow parallel to the fault is enhanced in this region. Flow parallel to the fault is also enhanced by the presence of fractures within the fault rock, which tend to align parallel or subparallel to the displacement vector of the fault. Transverse to the fault rock, flow is restricted by a decrease in grain size and a corresponding increase in the tortuosity of the migration path. Additionally, few major fractures cut across the fault rock. Consequently, any fault rock is potentially a barrier to fluid flow. This restricted flow may produce significantly higher values of pore pressure within the fault rocks than in the adjacent country rock. There is little evidence, however, that faults are absolute seals to fluid flow. Some leakage is expected (Surdam, 1997), but the rates are largely unknown.

Research is needed to better understand the origin of faults to predict their location, structure, extent, recurrence (or periodicity) of motion on them, and hydromechanical properties. Current hypotheses can be grouped into three categories: (1) fault formation along planes of critical shear stress, (2) faulting by cooperative deformation and growth of en echelon fractures and fracture clusters (Fig. 20),

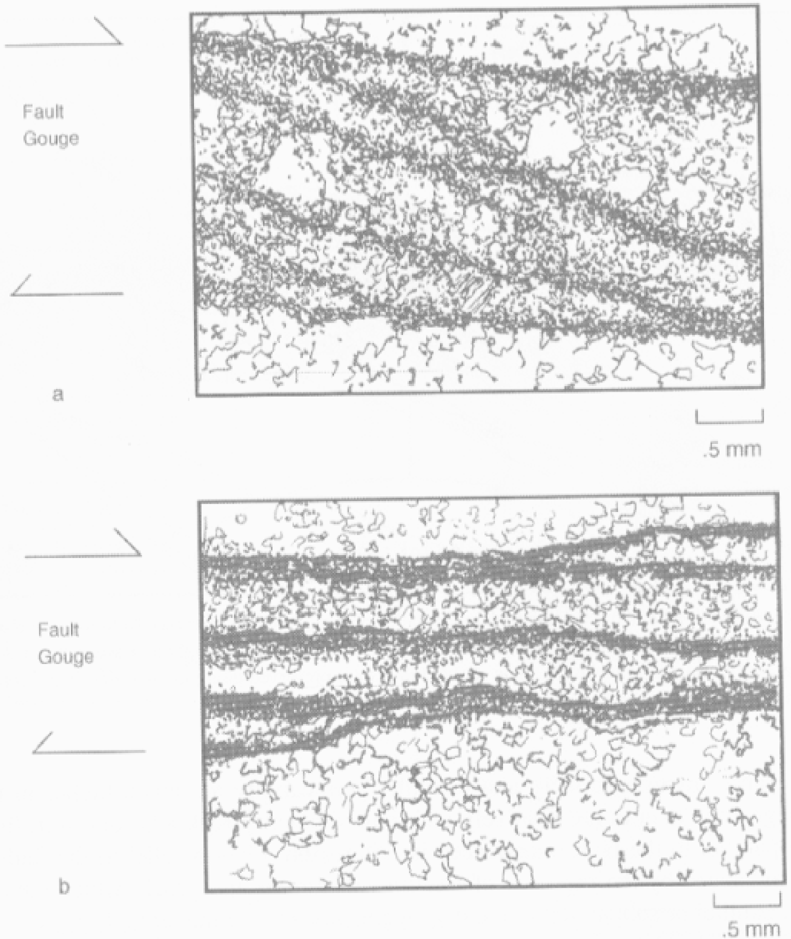

FIG. 19. Sketches of fault gouge produced in laboratory experiments in quartz sandstone showing fabric evolution. (a) Shear strain is relatively low, about 4. (b) Shear strain is about 14. The darker patterns are regions of finely comminuted grains, generally less than one micron in diameter produced by localized shear within overall gouge proper. These are boundaries of low permeability separating less deformed areas where the grains are coarser. The result is inhibited fluid flow normal to the shear direction. Sense of shear is indicated at the boundary of the gouge and country rock (Logan, unpublished).

and (3) faulting as localized shear resulting from material instabilities (Fig. 21). The second and third hypotheses offer mechanistic interpretations of rock failure and are supported by field observations and laboratory measurements (Thomas and Pollard, 1993; Taylor *et al.*, 1997; Myers and Aydin (in press); Moore and Lockner, 1995; Antonellini *et al.*, 1994; Ord *et al.*, 1991; Rudnicki and Rice, 1975; Olsson,

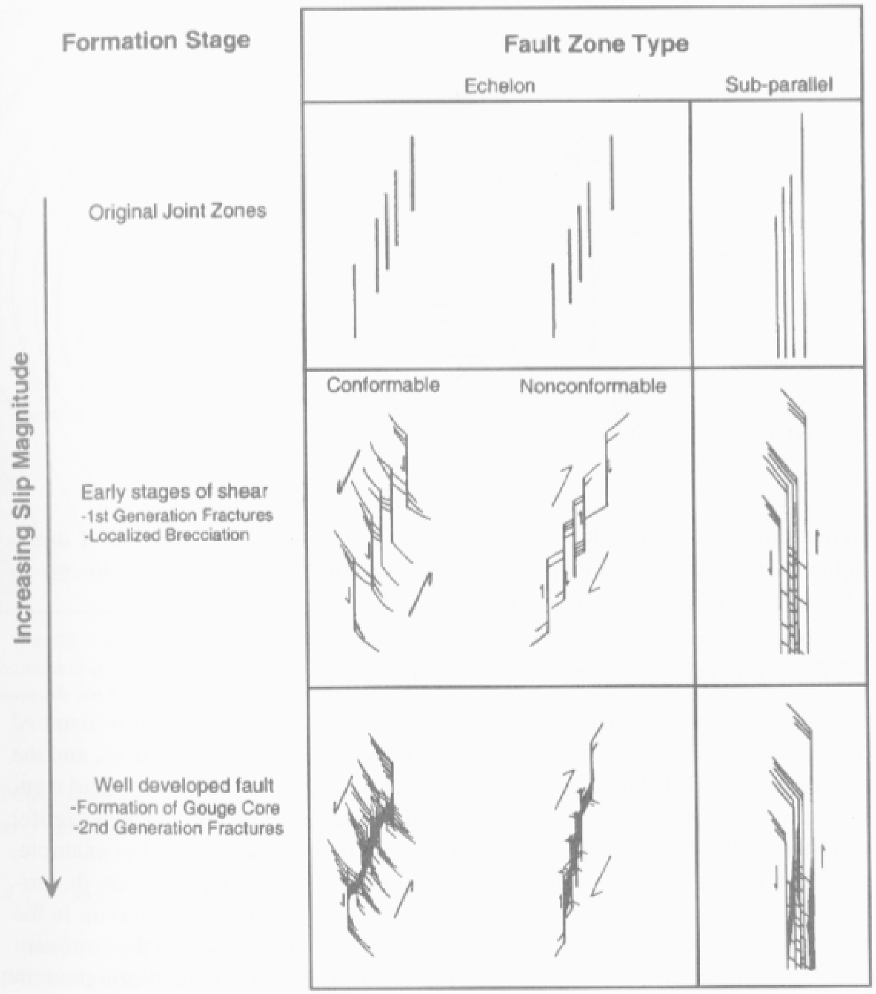

FIG. 20. Fault development by cooperative fracture growth: schematic illustration of three fault types and their major evolutionary stages (from Taylor *et al.*, 1997, and Myers and Aydin, 2000).

1998). Application and extension of these theories require an understanding of the development of fracture clusters (Taylor *et al.*, 1997) and of the evolution of the constitutive parameters of rocks (Holcomb, 1992; Olsson, 1998). Research on faulting is especially important in porous rocks (which are typical of reservoirs) and must encompass not only the initial formation of faults, but also criteria for extension and changes in structure and hydromechanical properties. Research into faulting and its relation to fluid flow has been hampered because of difficulties in

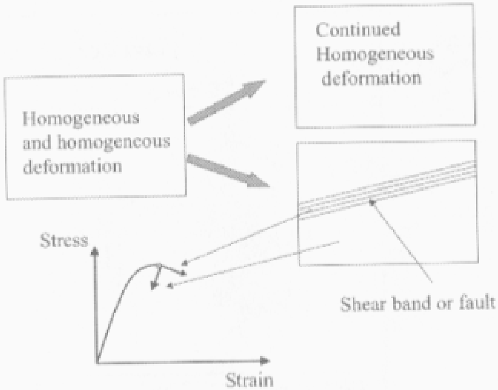

FIG. 21. Schematic illustration of fault formation (shear localization) as a bifurcation from homogeneous deformation (Rudnicki and Rice, 1975).

characterizing the three-dimensional structure of faults and a shortage of three-dimensional (as opposed to planar or axisymmetric) laboratory experiments to constrain realistic constitutive models.

4.2.2. *In Situ Stress State and Measurement of In Situ Stresses*

Rock behavior is determined by the effective *in situ* stress. Often, it is assumed that the total *in situ* stress state is the same as the lithostatic state of stress, and the pore pressure is distributed uniformly. Structural geologic evidence and field measurements indicate that reservoir stresses often are far more complicated (Teufel and Farrell, 1990; Warpinski and Teufel, 1992; Lorenz *et al.*, 1995). For example, Teufel and Farrell (1990) showed that a domal structure strongly affects the orientation of the maximum horizontal principal stress in the Ekofisk reservoir in the North Sea (Fig. 22). Similarly, Lorenz *et al.* (1995) have documented the dominant influence of basin-margin structures on the *in situ* stress distribution throughout in the Green River Basin, Wyoming. Knowledge of the tectonic history of such areas coupled with the pore fluid and compaction histories of the strata are essential for anticipating sources of stress-field perturbations and for interpreting and generalizing local *in situ* stress measurements by means of numerical modeling. Some knowledge of the *in situ* stress history over geologic times also is indispensable to characterizing fracture systems.

The importance of *in situ* stresses for reservoir characterization and monitoring mandates further research on methods of measuring *in situ* stresses and stress changes with time (Warpinski *et al.*, 1993; Amadei and Stephansson, 1997), especially at great depth as well as in anisotropic, fractured, and poorly consolidated strata. *In situ* stress states may be particularly complex in depleted reservoirs

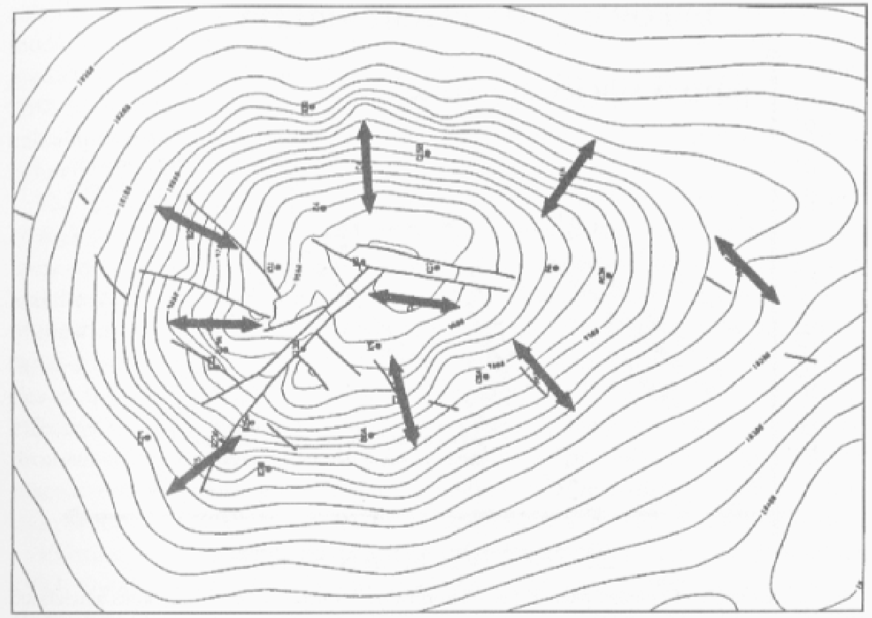

FIG. 22. Structure contour map for the top of the Ekofisk formation showing azimuth of the maximum horizontal stress. The crest of the domal structure is at a depth of approximately 2.9 km, and contour intervals are 15.2 m (from Teufel and Farrell, 1990).

being considered for CO_2 sequestration because of past anelastic deformations and heterogeneous pore pressure caused by patchy distribution of residual fluid.

4.2.3. *Rock Properties*

Earlier hydrologic discussions focused on the importance of rock porosity and permeability to fluid transport in reservoirs, but reservoir flow was assumed to be largely independent of many other physical rock properties and the influence of *in situ* stress state (Fig. 23). The hydrologic perspective in this chapter also stressed the use of continuum-type simulations, coupled with geostatistical approaches, to address reservoir heterogeneities. The discussion below encompasses some of the same issues, but with added attention to the effects of stress and the coupling of processes. This discussion also identifies difficulties in the complete constitutive characterization of rocks, which include the connection of grain-scale rock attributes and macroscopic response. Subsequent geophysical considerations will return to the topic of rock properties once more within the context of remote geophysical characterization of CO_2 sequestration sites and monitoring of injection processes, fluid distribution, and long-term site integrity.

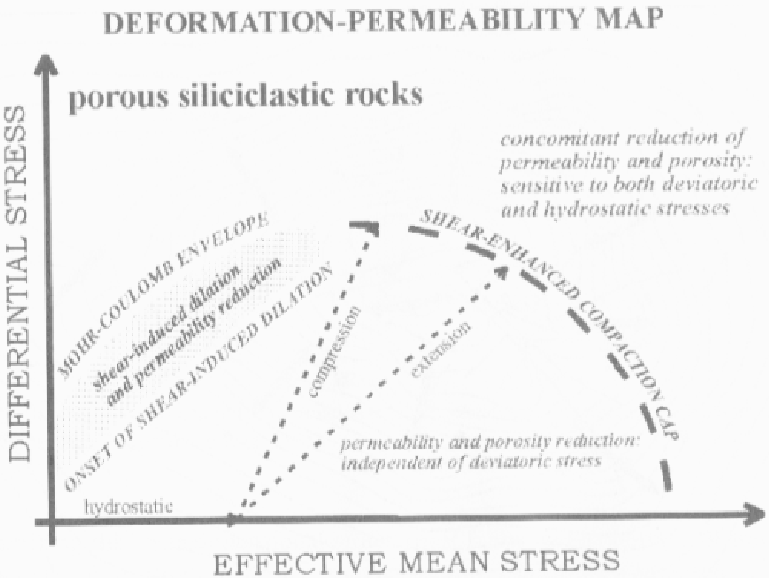

FIG. 23. Example of coupled phenomena—deformation-permeability map for porous siliciclastic rocks showing interrelationship between stress state, stress path, porosity reduction, and reduction in matrix rock permeability. The shaded area represents the brittle regime. The dashed lines with arrows represent load paths in conventional triaxial (axisymmetric) compression and extension (from Zhu and Wong, 1997, modified by Zhu, 1999).

Reliable reservoir characterizations require constitutive models, measurements of the associated material properties, and a description of the spatial heterogeneity of rock properties, including the properties of matrix rock, fractures, and faults on all scales. Often, predictions are based on an idealization of reservoir rocks as linearly elastic continua, with elastic and failure properties determined from laboratory tests. More realistic phenomenological models should incorporate inelastic deformation, dilatancy or compaction, stress-dependent and, in some cases, anisotropic porosity structure and permeability, etc. In addition to phenomenological models, models based on microscale mechanisms have been successful in qualitative and quantitative interpretations of geomechanical rock-mass behavior at high homologous temperatures. Insufficient field data and computational limitations, however, have left much uncertainty about the level of detail needed for adequate reservoir descriptions (such as the need to include inelastic behavior and the properties of natural fractures in analyses).

In the majority of reservoir studies, analyses are restricted to two-dimensional idealizations. Simulations of a diatomite reservoir (Fredrich *et al.*, 1998; Hilbert *et al.*, 1999) may provide the first large-scale example to assess important differences in rock and well bore response between two- and three-dimensional calculations. Another example using a relatively complex elastic-plastic material model resulted in subsidence predictions above a diatomite oil field that underpredicted the magnitudes of vertical and horizontal surface displacement by some 25% (deRouffignac *et al.*, 1995). The discrepancy between measurements and calculations was tentatively attributed to the omission of time-dependent material behavior (creep).

The foregoing discussion implies that constitutive modeling, the determination of rock properties, and numerical or analytical solutions of boundary-value problems are inextricably linked. Consequently, a full understanding of rock behavior and the identification of dominant parameters require parallel research in all three of these areas. In particular, research is needed on (1) rock properties under fully three-dimensional stress states, (2) the influence of stress path on inelastic properties such as pore collapse as well as directional permeability, (3) the validity of the effective stress principle under large pore-pressure changes, (4) physical and hydromechanical properties of shales and the influence of clays, (5) microscopic and macroscopic processes governing rock behavior and the evolution of the constitutive properties, and (6) the connection between static and dynamic rock properties.

Existing experimental and computational evidence (Blair *et al.*, 1993; Winkler, 1983; Dvorkin *et al.*, 1991; Bruno, 1994; Zang and Wong, 1995) provides details about how macroscopic rock behavior and changes in rock response are directly related to grain-scale properties including elastic properties of grains and intergranular cements, grain anisotropy, grain size, and grain strength. They are also related to the fine-structure of the rock fabric (including pore and crack porosity, pore shape in terms of aspect ratio, and intergranular distribution of cementing materials (Fig. 24). It is logical to assume that the storage capacity, transport properties, and reactivity of reservoirs will be affected by the local distribution of matrix rock permeability. This, in turn, is a function of the shape, distribution, connectivity, and surface area of pore spaces and how these attributes change with stress and rock-fluid interactions. Grain shape, grain-size distribution, and surface roughness (surface area) will likely influence the local reactivity—both within individual pores and in the connection between pore spaces. Experiments and computations have demonstrated that aperture distribution in discrete, rough-walled fractures (Brown, 1987) can lead to flow channeling (Fig. 25). It is possible that heterogeneity in grain, cement, and porosity-fine structure could result in channel flow in matrix rock as well. At a minimum, anisotropy in the fine structure caused by stress or deposition is expected to alter both the local and the macroscopic permeability of reservoir rocks (Bruno, 1994).

Promising work concerning the grain-scale properties and fine structure of matrix rock should be expanded using a number of observational tools, some of which combine high resolution with the possibility of real-time measurements (e.g., Wood's metal impregnation, electron microscopy, laser-scanning confocal microscopy (Fig. 5), nuclear magnetic resonance, synchrotron radiation, and

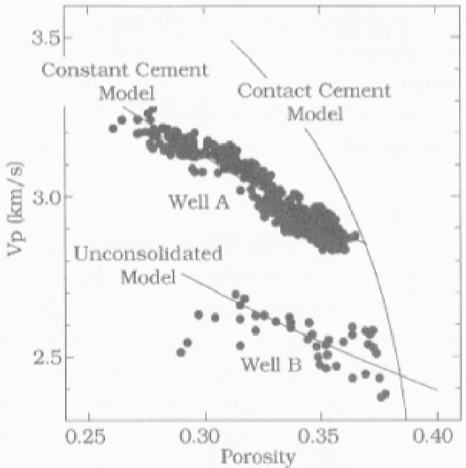

FIG. 24. Plots of P-wave velocities versus porosity demonstrate the significant effects of grain-scale properties on the bulk properties of rocks. The solid lines are theoretical curves. Their character depends on the mechanical properties of the grains and the cements and on the distribution of the intergranular cements at and away from grain contacts. Rock physics diagnostics make it possible to fine-tune velocity–porosity transforms to specific depositional environments (from The Stanford Rock Physics Laboratory, personal communication, and Avseth *et al.*, 1998).

acoustic and x-ray tomography) (Schlueter *et al.*, 1991, 1994; Fredrich *et al.*, 1995; and others). In principle, advanced algorithms for defining and representing pore geometries, and large computers, make it feasible to implement observational results in numerical simulations (O'Connor, 1996; O'Connor and Fredrich, 1999; Fredrich *et al.*, 1995; Fredrich, 1999; Lindquist *et al.*, 1996; Lindquist, 1998). Mathematical algorithm development, however, must be complemented by new experiments that measure local material properties (e.g., along grain contacts) or that derive local properties from the bulk behavior of small- or large-particle assemblages. Recent fluid-flow models at the pore scale take advantage of lattice Boltzman simulations. These and other approaches can extend and complement continuum damage models that relate bulk nonlinear rock behavior and pressure dependence to the growth and interaction of preexisting microcracks in elastic continua (Costin, 1983; Kemeny and Cook, 1991; Lockner and Madden, 1991; Rudnicki and Chau, 1996; Rudnicki *et al.*, 1996). New approaches based on grain-scale properties and matrix fine structure (texture) also promise to expand results obtained from contact analyses using highly idealized grain shapes and cement distributions (Digby, 1981; Dvorkin *et al.*, 1991, 1994; Bruno, 1994; Zang and Wong, 1995) to infer grain- and subgrain-scale micromechanical and transport processes, including preferentially aligned cement-grain bond failures, intragranular microfracturing, massive grain disaggregation, and pore collapse. Individual

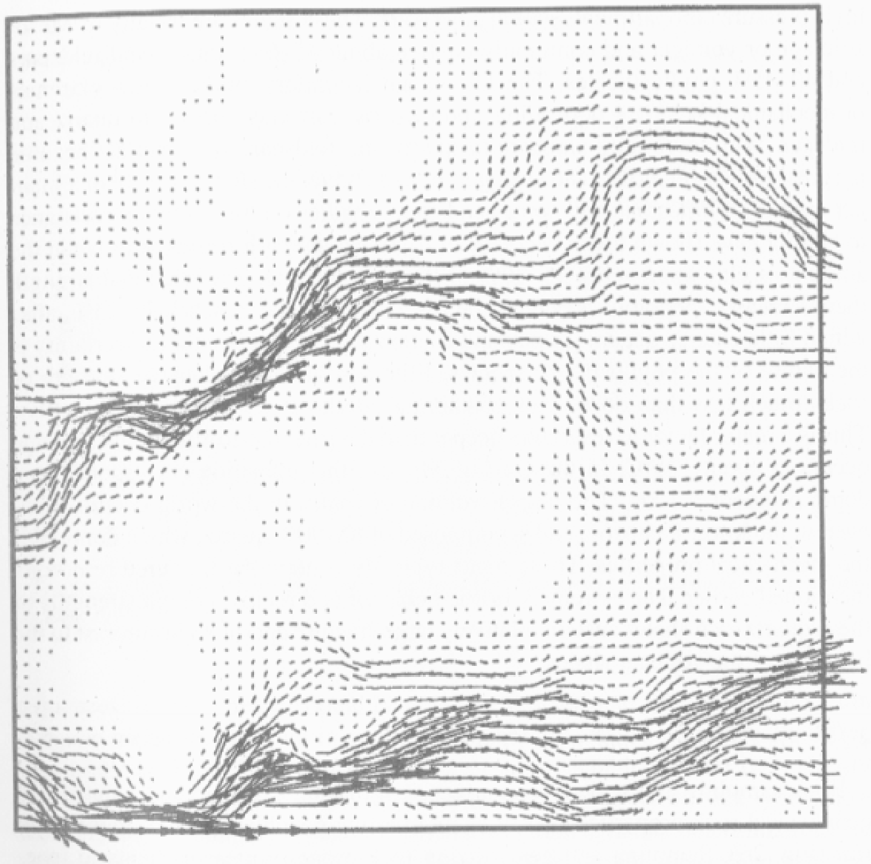

FIG. 25. Volume-flow-rate vectors demonstrating channeling in rough-walled natural fracture (from Brown, 1989).

research elements in these developments should address the influence of clays and the need to establish criteria for microfracture initiation and growth below the continuum scale (20 grain diameters?), which are influenced by local stress heterogeneity, crystal anisotropy, and local contrasts in thermomechanical material properties.

Although there are uncertainties in the properties of polymineralic rocks, such as clay- or calcite-cemented sandstones or even dolomitic limestones as reservoir materials, shales are a major area of ignorance. Except for some specialized facies, such as oil shales, little systematic research has been done on shale properties because of the sampling and preparation problems. Shales are particularly important because they frequently form reservoir boundaries or the boundaries of high-pressure compartments within reservoirs. These shales are usually of Mesozoic age or younger and commonly contain about 45–65% quartz and feldspars and 40–45% phyllosilicates. The few extant laboratory studies show extremes in mechanical behavior depending upon the ratio of clay species to quartz and feldspar. With increasing amounts of quartz and feldspar, the materials become progressively more brittle and stronger. In a dry state, the shales behave in a manner similar to limestone and some sandstone. Studies on the frictional resistance to sliding have shown that a decrease in frictional strength begins only when the amount of clay approaches 25–30% of the rock volume. The frictional strength then decreases monotonically until the percentage of clay reaches 70–75%, after which little change occurs (Logan and Rauenzahn, 1987). Another uncertainty is the nature of the phyllosilicate species. Illite and kaolinite alter the strength of rocks much less than do species containing interlayer water such as smectites. This is a major factor in reservoirs deeper than the smectite-to-illite transition that occurs at about 125°C. In the Gulf of Mexico, this transition corresponds to a depth of about 3.2 km. The largest volume of shales in the world occurs, however, in the lower Paleozoic and is composed of 85–90% quartz, which dominates the mechanical properties. These rocks typically contain the fractured reservoirs mentioned earlier. The extremely brittle behavior and relatively high strengths of these quartz-rich shales sustain relatively large fracture apertures in contrast to the behavior of the younger shales.

4.2.4. Rock Sampling and Scale Effects

Rock sampling and scale effects are critical to linking the geomechanical and geophysical rock properties as well as interpreting geophysical measurements *in situ* (Fig. 26). Sampling and generalizing rock-property measurements to inaccessible areas is a major concern in reservoir characterization. This problem is dominated by the heterogeneity intrinsic to all reservoirs, but is exacerbated by an absence of proven scaling rules for property measurements made on core material. Further difficulties arise within the time frame of sequestration because almost all laboratory measurements on core material done today fail to consider time effects. The state of knowledge of the effects of potentially chemically active pore fluids such as CO_2 on all rock types is even more limited. The presence of CO_2 may not only result in mineral deposition in pores or along fractures, but it may also alter the mechanical properties of resident minerals.

Sampling strategies and data extrapolations suffer from poor understanding about the differences between static and dynamic data on elastic properties. Most data on reservoirs come from down-hole measurements or dynamic values derived from laboratory acoustic measurements. Because most modeling assumes static behavior, some static values of elastic properties are selectively made from core material. These static data are, however, sporadic and seldom sample overlying

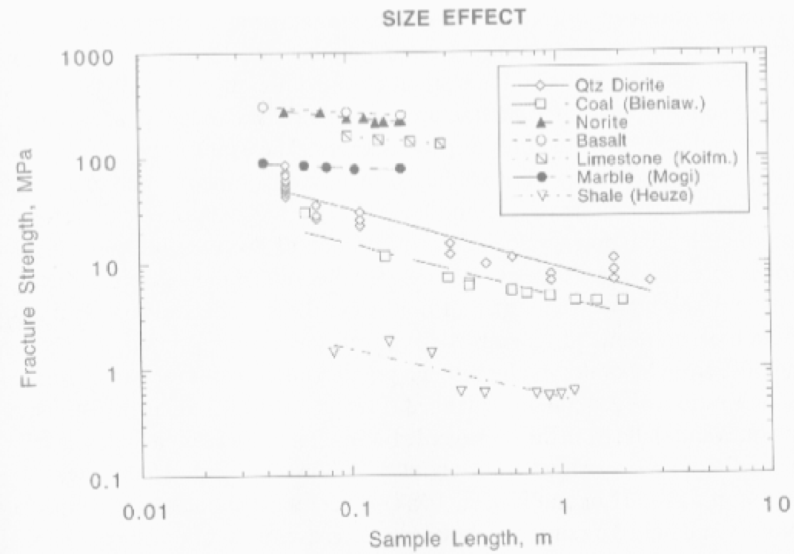

FIG. 26. Scale effects indicated by plots of the strengths of competent rock versus sample size (from Lockner, 1995).

sequences. In principle, it should be possible to determine static properties from dynamic measurements; but in practice, dynamic and static values usually differ, sometimes by large factors and often in an unpredictable fashion (e.g., Jaeger and Cook, 1979; and Yale *et al.*, 1995). Studies on a variety of rock types show static values of Young's modulus are often lower than dynamic determinations for sedimentary rocks, but they have been found to be higher for crystalline material. Quasi-static values of Poisson's ratio are frequently higher (Schatz *et al.*, 1993; and Yale *et al.*, 1995). Unfortunately, the differences are neither systematic nor consistent with the rock or investigator. This is an especially critical issue if old, abandoned reservoirs are to be considered for storage.

Down-hole logging offers an abundance of information on the reservoir and surrounding rocks, but is unable to identify inelastic properties. Given lithologic characteristics such as composition, mineral distribution, grain size, porosity distribution, and fracture frequency, it is desirable to make reliable predictions of strength and failure properties. An unrealized goal of petroleum companies has been to better constrain the inelastic properties needed for mechanical modeling of reservoirs.

Difficulties in translating down-hole logging data into laboratory data and vice versa exemplify the chronic problem of trying to characterize field properties, both elastic and inelastic, based upon laboratory measurements. This problem relates partly to the issue of laboratory sample size (i.e., scaling issues beyond the considerations of differences between the subgrain and multigrain scales). Generally, laboratory samples range up to 5 cm in diameter and 15 cm long; most laboratories use half that size for work at elevated pressures and temperatures. In selecting samples, macroscopic fractures are generally avoided; consequently, the numbers and effects of fractures are not assessed. The usual assumption, which is qualitatively supported by a few studies, is that elastic properties and rock strength decrease with increasing rock volume because of the presence of fractures, reaching asymptotic, but unknown values. The magnitude of decrease depends, however, upon the specific circumstances. A number of theoretical models (e.g., Cuisiat and Haimson, 1992) try to deal with the difficulty, but these models are largely untested.

Field measurements of igneous rocks have shown Young's modulus decreases about 30% from laboratory values in one granite, but remains the same in another; Poisson's ratio was generally unchanged (Pratt *et al.*, 1972). In an investigation of sandstones and shale from the Mesaverde Formation in the United States, decreases in Young's modulus ranged from about 5 to 30%, but little change was found for Poisson's ratio (Lin and Heuze, 1987). Theoretical modeling combined with laboratory and field data suggests, however, decreases up to one order of magnitude in Young's modulus and possible increases in Poisson's ratio (Schatz, 1995).

4.3. Joints and Fracture Networks

Joints and fracture networks may fundamentally alter the behavior of reservoir rocks, including strength, deformability, permeability, and geophysical properties (Fig. 27). These sometimes consist of regular patterns of discontinuities but more frequently are complex sets of joints, fracture clusters, and deformation bands (Friedman and Logan, 1973; Pollard and Aydin, 1988; Lorenz and Laubach, 1994; NAS/NRC, 1996; Antonellini and Pollard, 1995; Mollema and Antonellini, 1996). Because rocks *in situ* are hardly ever free from natural fractures, greater attention should be paid to the documented effects of preexisting fracture networks on reservoir performance than may be indicated by history matching and reservoir simulations without regard to fractures.

Joints and the development of fractures in CO_2 sequestration are important in evaluating not only reservoir properties but also long-term site integrity and the possibility of breaching seals, traps, or cap rocks. Primary research issues fall into three broad groups: (1) the evolution of joint systems and fracture networks including joint lengths, spacing, and joint interactions with one another and with other rock mass heterogeneities such as lenses, bedding planes, and faults (Lorenz and Laubach, 1994; and NAS/NRC, 1996), (2) the need to understand joint connectivity in fracture networks, and (3) the interaction of the mechanical behavior of joints and joint systems, fluid flow, and geochemical activity including the development and distribution of fracture fillings over time.

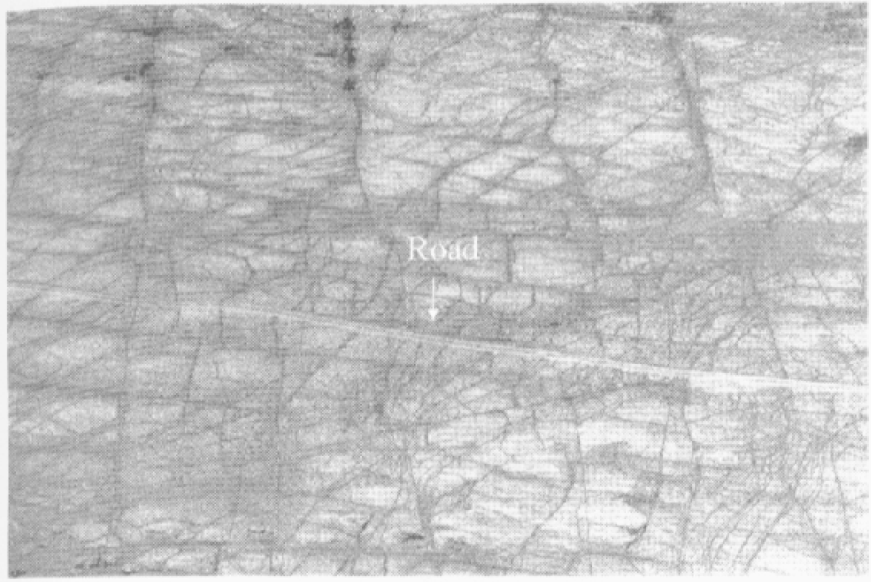

FIG. 27. Photograph of fracture network within a marine sandstone unit of the Frontier formation east of Kemmerer, Wyoming. Note road for scale (from Lorenz and Laubach, 1994, printed by permission of Gas Research Institute).

In situ principal stress directions and principal stress ratios probably are the most important parameters affecting joint orientation and the paths of growing fractures (Wu and Pollard, 1991). Great uncertainty exists concerning, for example, fracture spacing (Wu and Pollard, 1991). The influences of lithology and three-dimensional, fracture–fracture (Germanovich *et al.*, 1994) and fracture–interface interactions need clarification, especially in high-porosity, weakly consolidated rocks. Fracture interactions resulting in fracture clusters are of particular interest as major flow channels and potential precursors to faulting (Taylor *et al.*, 1997). Additional study concerning fracture development in high-porosity, weakly consolidated formations is important for hydraulic fracture design and response to fluid injection. Although joints are extensional features, generally it is unclear which and when one of several fracture growth hypotheses predominated: lithostatic stress changes, tectonic stresses, changes in pore pressure and effective stress, thermal stresses, or stresses arising from material heterogeneities dominated by differences in material properties across bedding planes.

The importance of fracture connectivity and the interdependence between fluid flow and geochemistry were subjects of earlier sections. The evaluation of fracture connectivity partly hinges on the ability to describe the geometries of fracture systems. For dense fracture systems and modest differences in fracture conductivity, some success has been achieved in statistical descriptions of fracture patterns (Long and Hestir, 1990; NAS/NRC, 1996) without regard to fracture origin and fracture interactions. Fractal rules have proven useful in the spatial extrapolation of locally observed fracture patterns (Barton and LaPointe, 1995). This approach is bound to be less successful under conditions when fluid moves through only a few channels.

Although much work is needed to characterize both the geometry and the conductivity of fracture networks, important research needs to be continued concerning fluid-flow and fluid–rock interactions in discrete fractures. The hydrological literature appears to rely primarily on the so-called cubic flow law to describe the relationship between fluid flux and mean fracture aperture. Substantial deviations have been noted between this model and experimental measurements of aperture at high stresses normal to the fracture plane (Brown, 1989; Fig. 28). Systematic studies pertaining to fluid-flow behavior at fracture intersections do not appear to exist. Research should include the effect of shear deformation on joint normal deformation and fracture permeability.

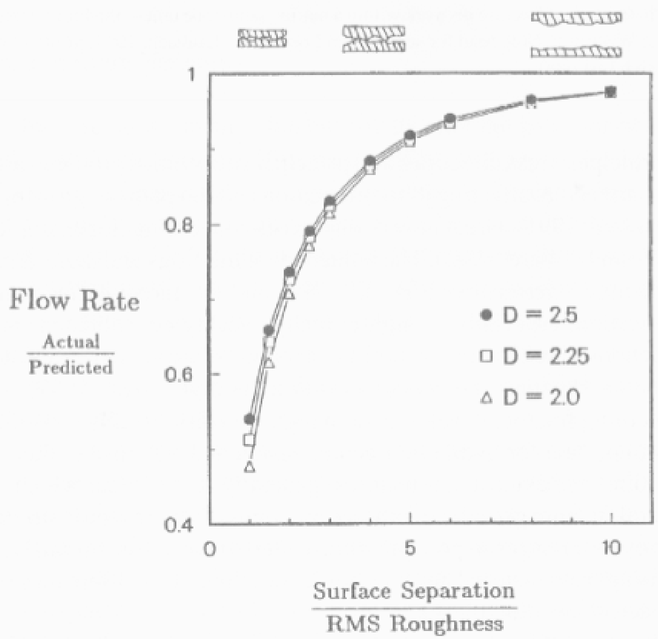

FIG. 28. Test of cubic flow law for fracture flow for fractures with different roughness characterized by fractal dimensions between 2.0 and 2.5. Significant deviation from cubic flow law occurs below abscissa values of approximately 4.1 when the fracture surfaces come into contactas shown schematically in the sketch above the plot (from Brown, 1987, modified by Brown, 1990).

4.4. Injection

Injection of any fluid (such as CO_2) into a reservoir under pressure will alter the effective stress state (Fig. 29). In addition, chemical reactions may result in spatial and temporal changes in the physical rock properties. To ensure the integrity and safety of the injection, it is necessary to evaluate whether alterations of stress will

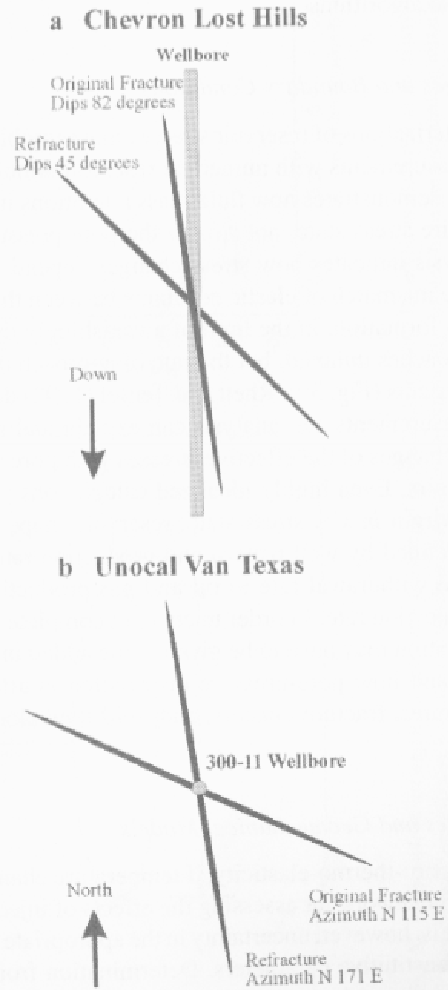

FIG. 29. Two examples of changes in *in situ* stresses due to fluid injection and production. The alteration in stress states resulted in changes in fracture orientations (azimuth and dip) between initial fracture and refracture treatments (from Wright *et al.*, 1995).

cause failure (seismic or otherwise) within the reservoir, along boundary faults, or in adjacent regions outside the reservoir. Furthermore, the alteration of stress may affect the storage capacity and hydrologic properties of the reservoir. For example, an increase in effective normal stress could substantially restrict flow along fractures that provide critical fluid pathways.

To predict the response of the reservoir to these alterations, it is necessary to adopt an appropriate theoretical framework, boundary conditions, and constitutive model to determine the relevant material properties and implement them in efficient and robust numerical algorithms.

4.4.1. Stress Changes and Boundary Conditions

Adequate characterizations of reservoir stresses must combine local, often sparse, *in situ* stress measurements with numerical reservoir simulations. An analysis by Rudnicki (1999) demonstrates how fluid mass alterations in an idealized reservoir change the entire stress state, not simply the pore pressure as is sometimes assumed. The analysis indicates how stress changes depend on the geometry of the reservoir and the mismatch of elastic constants between the reservoir material and the surrounding formation. In the limit of a vanishingly thin planar reservoir, the strain state approaches uniaxial, but the rate of approach depends on the mismatch of elastic constants (Fig. 30). Rhett and Teufel (1992) demonstrate how the combination of measurements and analysis can explain and generalize puzzling observations about changes of the effective stresses with pore pressure drawdown in several oil reservoirs. Even highly idealized calculations prove the important connection among virgin *in situ* stress state, reservoir shape, and pore pressure distribution partly defined by well pattern and production rate. The influence of fluid withdrawal and withdrawal rate in oil and gas production is analogous to CO_2 injection and injection rate. In order to conduct complete site-specific analyses, careful consideration may have to be given to the added influence of adjacent geologic structures and how pore-pressure distribution is affected by the presence of natural fractures, fracture clusters, and fluid flow along major preferred channels.

4.4.2. Rock Properties and Geomechanical Models

Poroelasticity (or poro-thermo-elasticity, if temperature changes are important) provides a minimal framework for assessing the effects of injection. Even for this idealized model there is, however, uncertainty in the appropriate values of the poro- and thermo-elastic constitutive parameters. Determination from laboratory measurements is difficult because it involves small differences in measured quantities (Warpinski and Teufel, 1992). In addition, as discussed above, issues of scaling and the effects of larger fractures make the relation of laboratory measured values to

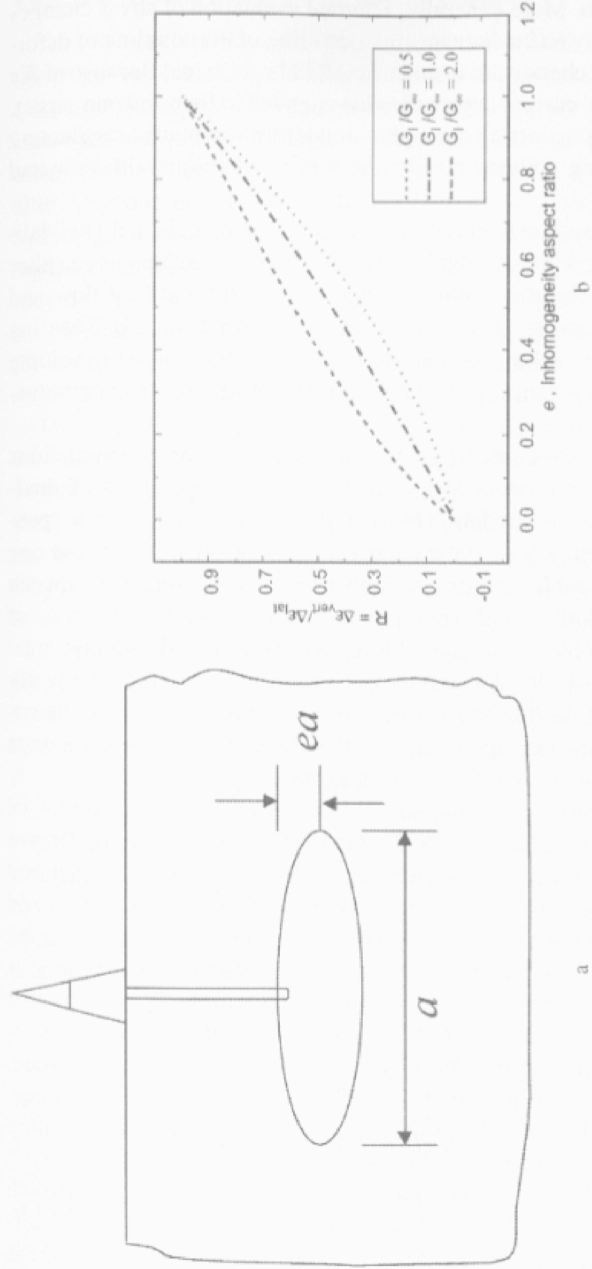

FIG. 30. (a) Sketch of the idealized geometry considered by Rudnicki (1999): Reservoir is idealized as an axisymmetric ellipsoidal inclusion with elastic properties different from the surrounding material and hydraulically isolated from the surrounding material. (b) Ratio of lateral strain increment to vertical strain increment in the inclusion due to a change of pressure as a function of the inclusion aspect ratio $e = a/c$. Results are shown for three ratios of the inclusion shear modulus to the shear modulus of the surroundings.

in situ conditions uncertain. More generally, accurate evaluation of stress changes in reservoirs is hampered by an inadequate understanding of the coupling of deformation with fluid flow and chemical reactions, i.e., RTM processes. Because of the complexity of the problem, current approaches have tended to focus on one aspect, e.g., idealizing the flow as occurring through a nondeforming matrix (neglecting deformation), or computing deformation, but neglecting coupling with flow and chemistry.

Although further progress can be made using poroelastic models, field and laboratory observations suggest that relatively small effective stress changes can alter flow properties and that inelastic volume changes, coupled with fluid flow and chemical alteration, and can play a role in reservoir response (Fig. 23). Shearing can cause dilation (inelastic volume increases), and compaction (inelastic volume decreases) can be caused by shearing and/or increases in mean effective compressive stress.

According to earlier discussions on geohydrology, many current simulations of fluid flow in fractured reservoirs appear to rely on the application of dual-porosity and dual-permeability models. These models contain two separate (possibly anisotropic) overlapping porous media, one for a permeable matrix and one for fractures in an impermeable medium, and incorporate fluid exchange between the two. These models admit spatial and temporal variations in the properties of the two components. They have, however, at least two fundamental shortcomings: (1) Fracture networks are idealized as orthogonal sets of infinitely long, perfectly smooth discontinuities whose fluid-flow properties meet the conditions of the cubic flow law, and (2) the fracture apertures and, therefore, fracture conductivities are assumed to be independent of (effective) stress state.

The importance of coupled simulations was demonstrated by a model of fluid flow through a fracture network in the Frontier formation, Wyoming (Brown and Bruhn, 1997). The elastic compliance and permeability properties of fractured rock are related to fracture geometry through tensors (e.g., Oda *et al.*, 1987) and the tensors for each physical property are derived by taking a volume average of the effect of each fracture population. The volume average contains functions of the fracture orientation, (finite) fracture length, and aperture in such a way that long or wide fractures contribute relatively more than small fractures. Elasticity is implicitly coupled to fluid flow through relationships between stress state, fracture-aperture distribution, and normal and shear deformation across fractures. One important result demonstrates that frictional sliding on favorably oriented fractures may cause extreme changes in the permeability tensor of the rock mass, including both magnitude changes and rotations of the principal stress axes (Brown and Bruhn, 1997). In one case, the maximum permeability direction was determined to lie at at a 45° angle rather than parallel to the maximum principal stress direction.

4.4.3. Failure and Discrete Fracture Propagation

An issue of importance is whether injection will cause failure in any of a number of senses, including faulting as discussed previously. Experience at Rangely, Colorado (Raleigh, 1976) and elsewhere has demonstrated that fluid injection can cause seismic failure. Seismic events could damage pipelines, drill stems, and other structures associated with injection. Slip on faults, even if not seismic, could alter the properties of faults (whether barriers or conduits) and, consequently, the hydrological properties of the reservoir. Increases in pore pressure accompanying injection may cause (hydraulic) extension of fractures. In some instances, this may be desirable, but in others, fracture extension may breach seals or provide a rapid channel for fluid flow that prevents effective use of the reservoir volume for storage. Failure by shear localization, compaction, or disaggreation may have undesirable effects on the ability of the reservoir to store and contain CO_2.

The 1990s have seen great progress in the mechanics of earthquakes by using a constitutive relation for frictional slip in which the traction on the slip plane depends on the rate of slip and its history, as reflected in the current state of the sliding surface. The parameters of this relation, including a critical sliding distance, can be inferred from laboratory tests. Unfortunately, however, this critical length may be much larger *in situ* than as measured in the laboratory, and currently, there is no good means of determining values in the field (Scholz, 1990).

In practice, the possibility of seismic slip is most frequently assessed using the simple Mohr–Coulomb condition. As noted above, injection changes the entire stress state, not simply the pore pressure, and these changes must be considered in evaluating failure. The idealized analysis of Rudnicki (1999) can be used to determine whether injection causes the stress state to move toward or away from failure (Fig. 31). (Knowledge of the absolute *in situ* stress is needed to determine how far the stress state is from failure.) For example, if the reservoir strain state is uniaxial (a good approximation for a thin, tabular reservoir) and failure is assumed to be governed by a Mohr–Coulomb condition with friction angle φ, then injection at isothermal conditions will cause the stress state to move away from the failure condition if the following inequality is satisfied

$$\varsigma > \frac{2(1-\nu)\sin\varphi}{(1-2\nu)(1+\sin\varphi)}$$

Here ν is the drained Poisson's ratio and ζ is a porous media constant, equal to $1 - K/K_s'$, where K is the drained bulk modulus of the porous material, and K_s' can, in certain idealized cases, be identified with the bulk modulus of the solid constituents. Application of even this simple condition is impeded by uncertainties about the appropriate value of the porous media constant ζ and friction angle. Furthermore, temperature changes of only a few degrees can alter the conditions for

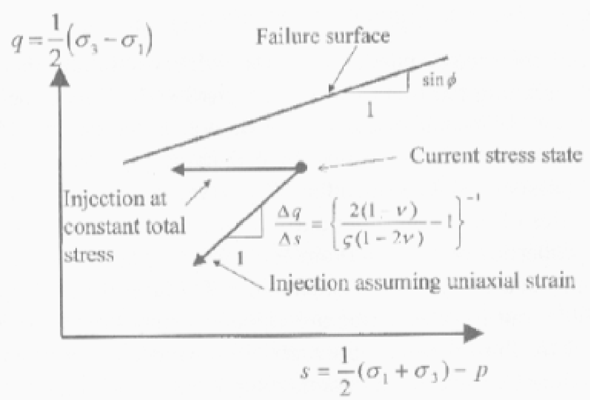

FIG. 31. Comparison of the different stress paths due to fluid injection if the total stress in the reservoir is assumed to be constant and if the reservoir is assumed to deform in uniaxial strain. The Poisson ratio of the reservoir is ν and ζ is the Biot porous media parameter (modified from Rudnicki, 9th Congr. Int. Soc. Rock Mech. Proc., 1999).

stability. Segall (1989) has used an analogous approach, based on poroelasticity, to determine stress changes outside the reservoir and the Mohr–Coulomb criterion to evaluate the potential for inducing failure (seismic slip) in regions adjacent to the reservoir. Neither approach takes into account the effect of stress alterations on boundary faults. At issue is not only whether stress alterations could cause either aseismic or seismic motions on these faults, but also whether stress alterations inducing slip could compromise the sealing ability of these faults. Despite the wide use of the Mohr–Coulomb condition, it has a number of shortcomings. It does not distinguish between rapid (seismic) and slow slip; it implicitly assumes homogeneous stress conditions, takes no account of the alteration of stress accompanying slip, and includes no means of predicting the size of an event.

The Mohr–Coulomb condition is also used to predict shear localization (fault formation), but has inadequacies in this application as well. Laboratory experiments demonstrate a clear dependence on deviatoric stress state (e.g., axisymmetric extension vs axisymmetric compression) that is absent from the criterion (Rudnicki and Olsson, 1998). Furthermore, the parameters of the relation (friction angle and cohesion) are purely phenomenological and bear little or no relation to constitutive parameters. For example, it is likely that fault formation differs in materials that compact vs those that dilate, but the Mohr–Coulomb prediction would be the same if the cohesion and friction angles were the same.

Understanding discrete fracture is a prerequisite for understanding the interaction and link-up of fractures and their behaviors at lithologic boundaries. Of particular importance for injection and containment of CO_2 are the growth and extension of fractures to form hydrological networks. Further work is needed on

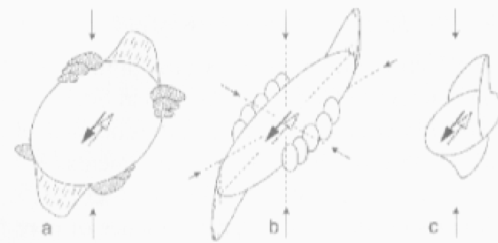

FIG. 32. Combined laboratory–field-based three-dimensional idealizations of shear fracture growth with associated development of secondary fractures [from Martel and Boger, 1998 with reference to (a) Adams and Sines, 1978, (b) Scholz, 1990), and (c) Germanovitch *et al.*, 1994].

three-dimensional effects and the effects of inelasticity and damage associated with fracture including, for example, an apparent influence of pressure and fluid diffusion in the crack-tip region.

The mechanics of discrete fracture propagation can be largely understood in terms of two-dimensional models, but three-dimensional effects are critical to fracture interactions and fluid flow (Germanovich *et al.*, 1994; Martel and Boger, 1998; Fig. 32). In particular, for a fracture with a smoothly turning edge in a linear-elastic material, the asymptotic near-tip field decomposes exactly into separate plane and anti-plane, two-dimensional problems. But in a two-dimensional model, an asperity will completely block flow, whereas in three dimensions, flow can simply go around this obstacle.

The most prevalent models of fracture are those that treat the crack-tip as a singularity of stress in an otherwise linear elastic body or cohesive zone models in which the inelasticity is confined to a line ahead of the crack. Although these models are often adequate, the inelasticity and damage near the crack-tip may dramatically alter the out-of-plane growth and interaction of cracks.

4.5. Long-Term Containment and Monitoring

It was stated earlier that analyses of geologic systems must be built on an understanding of the interdependence of processes and coupled RTM simulations. This requirement is especially important for predicting the long-term containment of CO_2 and monitoring sequestration sites. CO_2-induced geochemical processes may weaken rock strength within a reservoir compartment leading to the potential for porosity collapse, buildup of fluid pressure, and seal failure. Associated changes in rock properties and fluid distributions are likely to affect the geophysical rock properties, such as P- and S-velocities, seismic attenuation, and electrical resistivity. While credible long-term predictions require an integrated approach, they also mandate targeted research in geomechanics.

4.5.1. *Fluid-Assisted and Time-Dependent Fracturing*

Surface-chemical effects of water on crack growth may be a significant factor in the long-term containment of CO_2. (See Kirby and Scholz, 1984, for a special issue of the *Journal of Geophysical Research* on the chemical effects of water and the deformation and strengths of rocks.) Many experiments (Atkinson and Meredith, 1987) have shown that the presence of water or other pore fluids can enhance crack growth in brittle rocks. In particular, the presence of pore fluid allows slow growth of cracks at stress intensity factors below the critical value corresponding to rapid (dynamic) crack growth. Das and Scholz (1981) have attributed a variety of time-dependent earthquake phenomena to this mechanism, and there is evidence (Dieterich and Conrad, 1984; Dove, 1995) that the micromechanical mechanism of rate and state-dependent friction is related to surface-chemical effects of pore fluid. Information from laboratory experiments on environmentally assisted crack growth has been incorporated into constitutive relations and these have achieved reasonable success at describing the time-dependent deformation of bulk specimens (Costin and Mecholsky, 1983; Costin, 1987). Segall (1984) has applied a model based on relations derived from laboratory experiments to rate-dependent extensional deformation in rocks.

Despite this progress, the coupling of chemical effects of pore fluid with strength and deformation remains poorly understood and may be a significant impediment to predictions about the long-time containment of CO_2. Few, if any, observations exist on crack growth in CO_2 contaminated environments. Laboratory experiments have, for the most part, considered the time-dependent growth of macrocracks under tensile loadings and assumed that crack-tip fields can be characterized in terms of the elastic singular field. Surface chemical effects, however, may be strongly related to inelastic processes near the crack-tip. Furthermore, the long-term, time-dependent behavior of rock may be due primarily to the growth of microcracks in stress fields that are locally tensile but overall compressive. For microcracks under overall compressive loads, branching and turning complicate growth. Additional complicating factors are different responses of various constituents to pore fluid and interface effects. Laboratory experiments of crack growth rates of less than 10^{-10} m/s are impractically long, yet this rate corresponds to about 3 mm/year, which is relatively rapid over the 50–100 year intended life-time of sequestration. Thus, sound extrapolations to time scales of interest require a thorough understanding of the underlying physical mechanisms.

Subcritical crack growth is important for the long-term constitutive description of sequestration sites for evaluating the potential of macroscopic fracture development and seal degradation and for incorporating changes in (geophysical) rock properties in interpreting geophysical measurements. Important changes may also result from inter- and interagranular creep. Creep may lead to significant, possibly anisotropic, changes in rock porosity, permeability, and local rock

strength—all of which could have profound consequences for pore-pressure distribution and fluid flow, as mentioned earlier. Although studies of creep mechanisms are most readily controlled in laboratory experiments, extrapolations of laboratory data to *in situ* conditions again may entail leaps in temperature, stress, and time (strain), with attendant but unrecognized changes in the rate-controlling physical or chemical processes.

5. Geophysics

5.1. Introduction

Successful CO_2 sequestration in active or depleted oil/gas reservoirs or aquifers requires an accurate map of the hydraulic and mechanical integrity of a site. Subsurface reservoirs consist of solid, liquid, and gaseous phases that produce heterogeneity on multiple length scales and may vary temporally and spatially because of geochemical interactions and variations in stress, pressure, and temperature. The ability to detect these changes in reservoirs over time requires an understanding of the relationship among rock properties, spatial resolution, and time resolution. The rock properties most important for site selection, injection, and monitoring will dictate spatial and temporal resolution and thus the geophysical techniques used. The inversion of geophysical data maps to maps of reservoir properties will depend on the spatial and temporal resolutions achieved as well as an understanding of the relationship between geophysical information and rock properties.

With any geophysical method there is a tradeoff between the volume of rock sampled and the ability to image heterogeneity. For example, a three-dimensional seismic survey (50 Hz) can easily sample the entire volume of a reservoir 3000 m deep. However, the reservoir is sampled with a resolution of only a few tens of meters. Figure 33 indicates the tradeoff between the volume sampled and the resolution length scale for a variety of seismic methods. Laboratory measurements on cores can resolve submillimeter to millimeter features but can sample only a small fraction of the entire core volume. On the field scale, the type of seismic method used also will determine which portions of the reservoir are sampled. For example, sonic logs (10 kHz) sample the region immediately adjacent to the borehole with a submeter resolution, whereas crosswell seismic profiles (1000 Hz) sample the limited volume between wells with meter-scale resolution.

Geophysical methods have the potential to be a quantitative diagnostic tool for monitoring CO_2 sequestration, but progress is hindered by incomplete understanding of the effect of rock properties (especially porosity, permeability, saturation, geochemical alteration, and natural fractures), reservoir conditions (i.e., stress, pressure, and temperature), heterogeneities, and scaling on quantitative remote imaging. Active monitoring techniques need to be refined to quantify the changes.

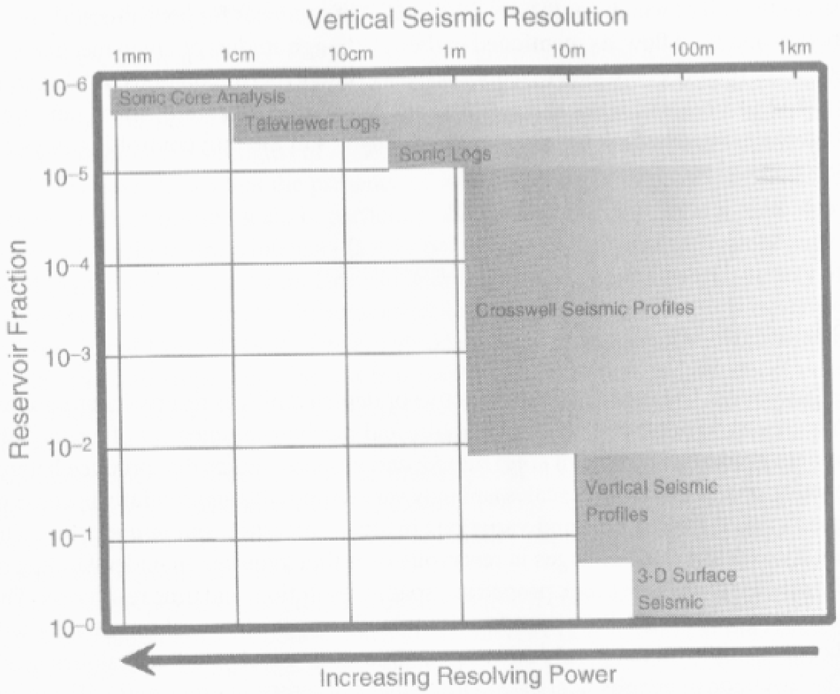

FIG. 33. Schematic of seismic resolution vs coverage as a function of seismic method (Harris, unpublished).

5.2. Rock Properties

Some of the key concerns for geophysical monitoring and interpretation involve gaps in the knowledge of the interrelationships among geophysical rock properties and geochemical, geomechanical, and flow-induced alterations. As discussed in the Geomechanics section, these gaps can be filled through an intensive program of theoretical, laboratory, field, and computational investigations at a variety of length and time scales using a combination of techniques. The geophysical characteristics of a reservoir or rock mass are strongly dependent upon the porosity and permeability characteristics of the formation. In addition, the micro-scale (pore and grain distributions, grain contacts, and cracks) and macro-scale (fractures, stratification, laminae, and other physical structures) heterogeneity in a reservoir modify the seismic, electromagnetic, and deformation responses.

Micro-scale sources of heterogeneity affect the macroscopic behavior of seismic waves propagated through rock by delaying and attenuating a wave as well as altering the frequency content of a signal. The micro-scale phenomena can be viewed in terms of discontinuity and interface phenomena, such as fractures, grain-to-grain contacts, fluid–solid interaction, and liquid–gas interaction within the pores or fractures. Nihei (1992) identified the micromechanical behavior of the grain contacts in rock as the primary source of attenuation in dry and fluid-saturated rocks. From laboratory measurements (Suarez-Rivera, 1992), a five-micron-thick coating of clay in a fracture caused significant attenuation, although the scale of the heterogeneity (clay) was 0.001 of a wavelength. The effect of non-aqueous phase liquids (NAPLs) on compressional wave propagation through soils (Geller and Myer, 1995) showed that compressional wave velocities were sensitive to increased NAPL saturation in the soil cores. However, no research has been performed to determine if the fluid–fluid interface (or front) can be resolved from seismic measurements. The ability to resolve correlated pore/grain distributions or fluid-phase distribution from seismic data is not well established.

The development of velocity and attenuation relationships from seismic and electromagnetic data is required to interpret near-surface seismic data acquired through continuous on-line seismic monitoring and to detect and identify the alteration of a rock matrix from interaction with CO_2 and other pore fluids. Fluid flow through a porous or fractured medium depends on the size and spatial distribution of the pore space and the interconnectivity of the pore space. Fundamental physicochemical changes can occur in the transport of particles or fluid chemicals through a porous medium (Imdakm and Sahimi, 1991; Fryar and Schwartz, 1994; Bertrand et al., 1994; Lappan et al., 1997). The change in pore structure occurs either from chemical interaction between the fluid and rock matrix resulting in dissolution of the solid, or from various forces that result in physical adsorption of a particle onto the rock matrix surface (i.e., precipitation).

In general, CO_2 has properties very different from those of the water and oil that remain in the reservoir. Figure 34 shows the measured compressional wave velocity of CO_2 as a function of pressure at three different temperatures (Wang and Nur, 1989). For example, at high pressures, the density of CO_2 approaches that of water, yet its bulk modulus is much lower than that of water. The seismic detectability of sequestered CO_2 depends not only on this contrast in fluid properties, but also on its saturation and the properties of the host rock and the local environmental conditions, e.g., temperature and pressure. Other changes are demonstrated (Fig. 35) by the effects of CO_2 on the seismic velocity of Beaver sandstone orginally saturated with n-hexadecane (Wang and Nur, 1989). The compressional wave velocity decreases markedly with the introduction of CO_2. The magnitude of the changes in velocity may not be this large in other rocks. Nevertheless, this example illustrates the underlying basis in rock properties for potentially monitoring a CO_2 sequestration process.

As stated in the previous sections, the presence of CO_2 may lead to significant changes in mineralogy through a complex series of reactions. Dissolution of the rock matrix may occur, increasing the size of the pores and the connectivity of the pore space. Dissolution can occur in regions with high surface energies, such

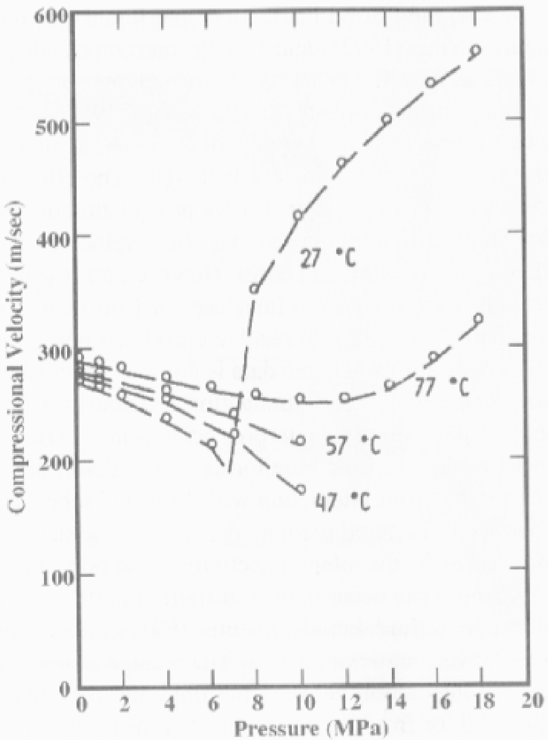

FIG. 34. Compressional wave velocity in carbon dioxide as a function of pressure at three different temperatures (from Wang and Nur, 1989).

as grain contacts under high stress. Dissolution at a grain contact reduces the mechanical stiffness of the contact by lowering the surface energy (Murphy *et al.*, 1984). A reduction in contact stiffness increases attenuation of transmitted acoustic waves (Nihei, 1992).

Precipitation or fines migration can block pore space and reduce the permeability of the rock (Gash *et al.*, 1992; Narayan *et al.*, 1997). It can also form cement at grain contacts and alter the grain-contact stiffness (Li, 1997; Li and Pyrak-Nolte, 1998). Dvorkin *et al.* (1994) found theoretically that the stiffness and amount of cement at the grain contacts controlled the elastic properties of the rock and, thus, the seismic properties.

The only laboratory investigation of the effect of sediment–pore water interaction on acoustic wave propagation was performed by Li (1997) and Li and Pyrak-Nolte (1998) on fully saturated synthetic sediments. The acoustic wave amplitude increased and decreased relative to the exchange of ions between the pore water and the sediment as indicated by electrical conductivity measurements (Fig. 36).

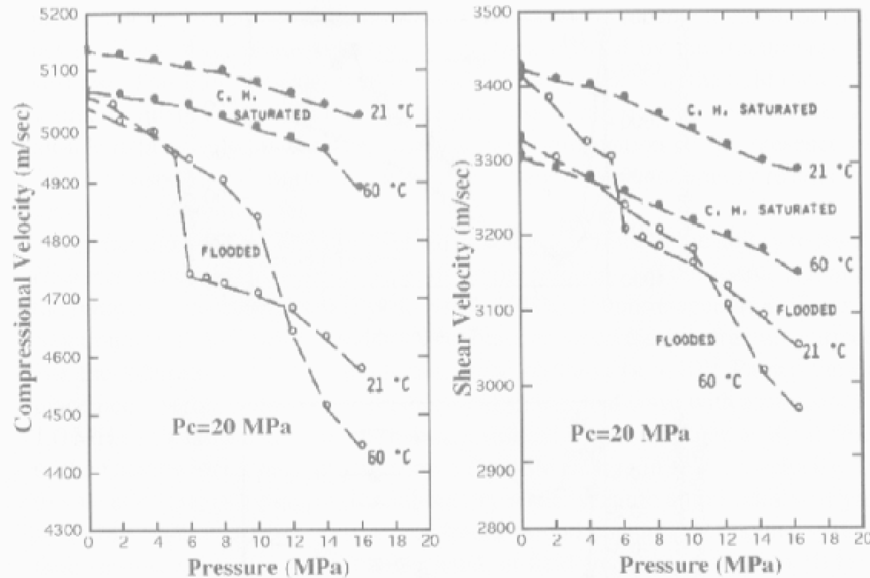

FIG. 35. Compressional wave and shear wave velocities in *n*-hexadecane-saturated and carbon dioxide-flooded Beaver Sandstone versus pore pressure (from Wang and Nur, 1989).

The lowest transmitted amplitude occurred when the ionic strength reached a minimum. Over a four-month period, the sediment sample underwent diagenesis and formed synthetic sandstone. The acoustic attenuation was observed to be sensitive to the ion exchange between the pore fluid and the sediment. However, the wave velocity was insensitive to the ion exchange, but was sensitive to compaction and cementation at the grain contacts. Microscopic investigation determined that precipitation had welded the grain contacts and reduced the porosity of the sample from 35% to 15–30%. Thus, if the geochemistry analyses demonstrate that the CO_2-related processes produce sufficient amounts of acids to significantly alter grain-to-grain contacts or fracture geometry, seismic methods have the potential to track chemically induced time-dependent changes.

To obtain the best geophysically derived maps of reservoir properties, it is important to understand how rock properties determined on the laboratory scale relate to field-scale measurements. The ability to resolve multi-scale heterogeneity depends on the type of heterogeneity present—fractures, pore/grain distributions, multiphase fluid distributions, etc. Mukerji *et al.* (1995) investigated scale-dependent velocity by comparing seismic velocities on the laboratory scale (wavelength ~0.01 cm) with the well log scale (wavelength ~0.1–1 m), and with the surface seismic scale (wavelength ~10 m). The observed scale dependence of the seismic velocity occurs because the length scale of the heterogeneity present

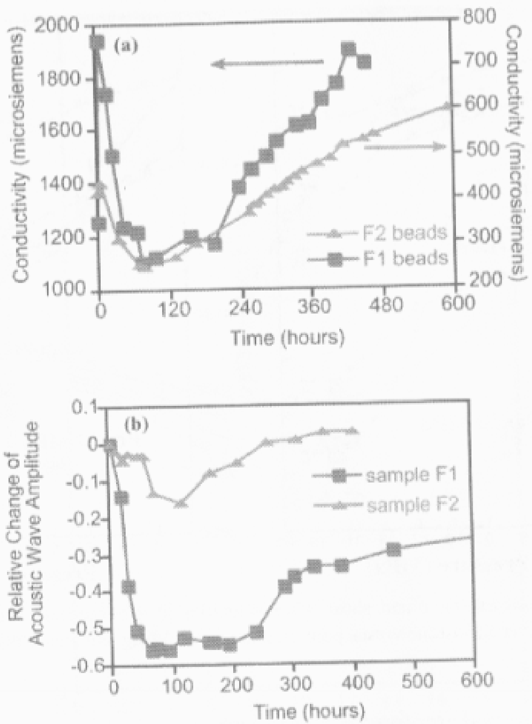

FIG. 36. (a) The electrical conductivity of the pore water and (b) the relative change in amplitude of a compressional wave as a function of time for two water-saturated synthetic sediments composed of soda-lime glassbeads. The minimum in electrical conductivity is concurrent with a minimum in compressional wave amplitude (from Li and Pyrak-Nolte, 1998).

may vary with the size of the volume of rock sampled. The seismic velocity was found to depend on spatial statistics of the petrophysical properties of the rock, the seismic wavelength, and the path length. Seismic waves would find "fast" paths of high-velocity material to propagate through the material.

Laboratory measurements of the seismic response of fractures may not be representative of the seismic response of all of the fractures observed in the field. Laboratory-scale fractures tend to have smaller apertures and possibly more contact area resulting in larger values of fracture-specific stiffness (the ratio between the stress and the magnitude of the displacement discontinuity produced by the stress). Therefore, fractures in the laboratory may exhibit less attenuation and produce fewer delays in a transmitted signal than in larger fractures in the field. However, the displacement discontinuity description (Pyrak-Nolte *et al.*, 1987, 1990a) of seismic wave propagation across a fracture contains a built-in scaling parameter in terms of a normalized frequency. Normalized frequency is the

product of the frequency of the incident signal, with the seismic impedance (product of density and phase velocity) of the rock divided by the fracture-specific stiffness. This ratio indicates which fractures can be located in the field for a given source frequency based on the specific stiffness of the fracture and whether amplitude data or velocity data will contain more information on the presence of a fracture based on the source frequency. This theory allows laboratory results to be scaled to field frequencies.

For fractures modeled as non-welded contacts, the limit of the ability to resolve fractures with field frequencies depends on the frequency of the source signal and the fracture-specific stiffness (Pyrak-Nolte, 1990a). Fracture-specific stiffness is a function of the size and distribution of contact between the two fracture surfaces. For the laboratory range of fracture-specific stiffness ($\kappa > 10^{11}$ Pa/m), the displacement discontinuity theory predicts that an incident wave with a frequency of 1.0 MHz will show a large increase in transmitted wave amplitude as the stiffness of the fracture increases, but will show very little change in seismic velocity. The theory also suggests that, on the laboratory scale, seismic amplitudes will yield more information on the presence of fractures and changes in fracture stiffness than seismic velocities. On the other hand, at field frequencies (e.g., at 10 Hz) a fracture with stiffness greater than 10^{11} Pa/m cannot be detected with either velocities or amplitudes. However, a fracture with a specific stiffness in the range of $10^5 < \kappa < 10^{11}$ Pa/m can be detected, and changes in contact stiffness could also be monitored. Other complications such as the effect of time-dependent geochemistry changes on the fractures (e.g., dissolution or rehealing) will need to be evaluated.

5.3. Characterization

Geophysical site characterization involves three tasks that range from qualitative reconnaissance through assessment to quantitative site description. The reconnaissance phase is needed to delineate the boundaries of the site, which include storage capacity, faults, etc. An assessment is also needed to determine the hydraulic integrity of the site that may be compromised by old wells, tunnels, seeps, etc. A quantitative description must set bounds on parameters such as saturation, porosity, and heterogeneity. These three characterization tasks are essential for establishing the baseline for subsequent monitoring and guidelines for site management. A variety of standard and state-of-the-art integrated geophysical techniques, including borehole and surface seismic, logs, core, potential fields, and electromagnetics, can be used with new technologies, yet to be identified, to perform these tasks.

The technologies for acquiring, processing, and interpreting seismic data are mature, but continue to evolve in their capability to image smaller and smaller

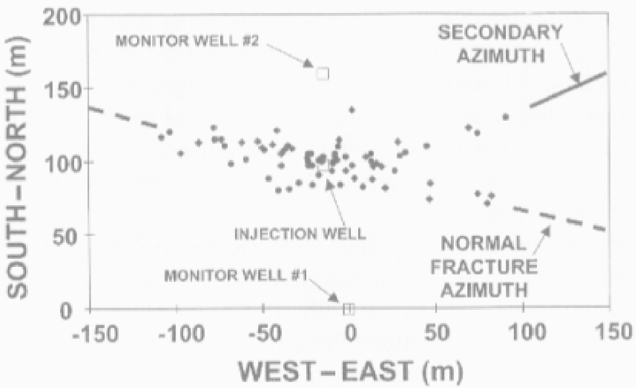

FIG. 37. Example of microseismic imaging from the GRI/DOE Multi-Site experiment (from Warpinski *et al.*, 1998).

features over larger and larger volumes. Notable improvements are occurring in the acquisition of higher frequencies and in pre-stack imaging. Stacking is the process of adding repetitive source shots to improve signal-to-noise ratios. These improved images are subsequently combined with rock physics and used as weak constraints in reservoir modeling schemes, such as geostatistics. Moreover, there is considerable research within the petroleum industry, government labs, and industry in translating these geophysical images (e.g., amplitude attributes) into more quantitative estimates of reservoir storage and flow properties, in addition to their well-established uses for structural imaging. The critical need is the development of capabilities (acquisition, processing, and interpretation) to resolve sufficient detail to ensure site integrity and efficient injection of CO_2.

Figure 37 shows an example of imaging capabilities that can be obtained with downhole arrays of seismic receivers monitoring a hydraulic fracture injection. The plot provides a plan view of the locations of numerous microseisms that were produced in the early stages of a fracture stimulation (Warpinski *et al.*, 1998) and detected from arrays in two offset monitoring wells. Of particular interest is the formation of a secondary fracture, a result that was unanticipated and not evident in any of the other fracture data. Imaging technologies such as this should help delineate the flow paths that develop during injection processes.

Figure 38 relates to drill-cuttings injection (Griffin *et al.*, 1999) monitored with downhole tiltmeters in a well offset about 43 m. As shown on the left side, the fracture creates a deformed zone that is detected by sensitive downhole-tiltmeter arrays. By matching the tilt data with an appropriate model (in this case an elliptic fracture), an integrated image of the overall size of the fracture can be estimated. This particular injection appears to be nonvertical (about 15° inclination) and of very limited height.

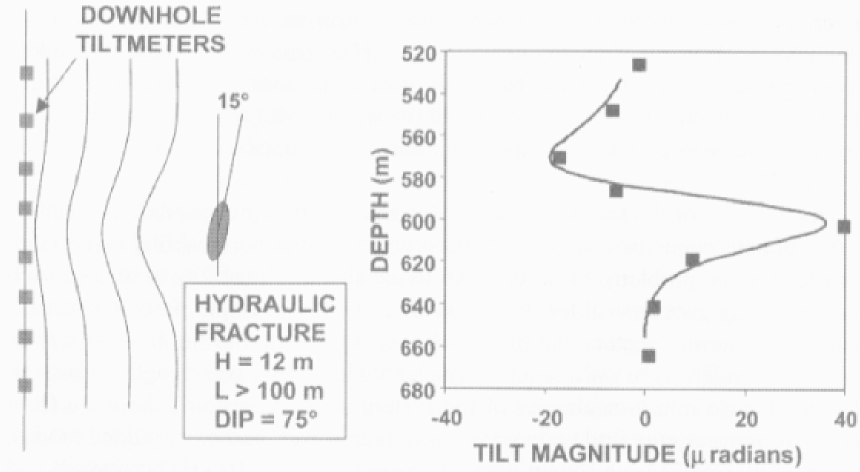

FIG. 38. Example of downhole tiltmeter imaging from the Mounds Drill Cuttings Injection Experiment (from Griffin *et al.*, 1999).

High-resolution images have been produced with crosswell seismic tomography (Langan *et al.*, 1997). The tomogram in Fig. 39 (color insert) defines an oval-shaped low-velocity zone representing an anomaly in the high-porosity reservoir facies. The anomaly is apparent at a depth of approximately 2785–2660 m (8700–89,500 ft) in the right hand side of the image. Crosswell methods are potentially capable of producing these high-resolution images in 2D. Research is needed to extend this capability to three dimensions.

To improve our ability to delineate and quantify porosity and permeability in potential CO_2 sequestration reservoirs, it is necessary to understand the effect on the mechanical-seismic response caused by (1) heterogeneity within a fracture, i.e., void space distribution, asperity heights, variation in stiffness, fluid saturation, etc.; (2) heterogeneity from multiple fractures and fracture networks, i.e., fracture orientation, number of fractures, geometrical properties of intersections, fluid saturation, etc.; and (3) other heterogeneities in porous media such as the grain contacts, fluid–grain contacts, fluid saturation, correlated grain/pore distributions, etc.

Will partial saturation of a reservoir with CO_2 be visible to geophysical techniques? If a CO_2 sequestration reservoir had a slow leak into a water or oil saturated fracture, displacement of liquid from the void space within a fracture by a gas reduces the stiffness of the fracture. The reduction in fracture stiffness delays and attenuates a wave transmitted across the fracture and enhances the reflected energy from the fracture. Seismic waves propagated along a fracture with reduced stiffness give rise to fracture-interface waves that depend on fracture-specific stiffness (Pyrak-Nolte and Cook, 1987; Pyrak-Nolte *et al.*, 1992). Thus, if during the injection process CO_2 displaces a liquid phase in a fracture, the seismic signal will be dramatically altered. This has been observed on the field scale (Majer *et al.*, 1997; Myer, 1998) in high-frequency (1–10 kHz), crosswell seismic data taken during gas injection into a water-filled fracture in limestone. Specifically, interface waves were recorded as the gas displaced the water in the fracture. Further investigation is needed to determine the minimum gas saturation that can be detected seismically.

The integrity of the site and efficiency of the injection process require identification of heterogeneities (such as fractures and thin high-permeability layers) that may lead to the problems or failures discussed above. The ability to resolve such features using geophysical techniques is an issue. For example, fractures in rock extend over tens of meters, but the "thickness" or aperture of the fracture can be as small as microns to millimeters—much smaller than a wavelength. However, the small-scale micro-mechanics of the system strongly perturbs the wave front by partitioning energy into body waves, interface waves, and other guided modes. Majer *et al.* (1997) have shown using high-frequency (1–10 kHz) crosswell and single-well survey methods that air-filled fractures with a thickness of 1 mm could be resolved using wavelengths of 0.5 to 1 m (0.001 of a wavelength) for a well separation of 50–100 m over a 20-m depth. Another research issue is the detection of fracture orientation, fracture connectivity, and other rapid flow paths.

5.4. Monitoring

Monitoring during the injection process is important to identify the location and saturation of the gas, the potential for breech, and the overall reservoir dynamics, including changes in stress states referred to earlier. These tasks require a variety of geophysical techniques: tiltmeters, seismic, electromagnetic, and various geophysical logs. Necessary research involves determining the optimum techniques for repeatability at desirable resolutions. Methodologies for quantitative comparisons of time-lapse images must be developed. Monitoring will be useful for identifying changes rather than defining static properties of fluids or flow. For example, seismic velocity is usually sensitive to the type and saturation of fluids in the pore space and to the differential pressure (pore pressure minus confining pressure), but it also varies with lithology and cementation. Therefore, estimating relative changes in saturation from time-lapse changes in seismic velocity is a better posed problem than the direct inversion of velocity for absolute fluid saturation. Many good examples (Wang and Nur, 1989) of seismic monitoring come from thermal-recovery processes (e.g., steam floods) where the change in seismic velocity caused by steam can be as large as 30%. Despite the excellent time-lapse images showing the changes from thermal-recovery processes, interpreting the images to determine saturation levels is difficult because uncertainties persist in quantifying the combined effects of steam, hot water, and oil on the rock properties.

Seismic methods have been available for monitoring petroleum recovery processes for many years, though not used routinely. Recently, the effort has focused on developing low-cost techniques for repeated use in reservoir management. An example of monitoring steam injection for enhanced oil recovery is shown in Fig. 40 (color insert) (Jenkins *et al.*, 1997). These reflection seismic images show seven time-lapse snapshots taken as steam was injected over a period of 31 months. Expansion of the steam away from the injection well is readily seen by differencing snapshots (Jenkins *et al.*, 1997). Monitoring from the surface is successful in this case largely because the change in rock properties with steam injection is large and the reservoir target is shallow. The yellow lines delineate the top and bottom of the steam injection interval. While the data do not change above the injection interval, the sag below is caused by the steam. (Jenkins *et al.*, 1997).

The potentially large contrast in the seismic properties of rocks partially saturated with CO_2 versus those saturated with water and oil suggests that both the location and the saturation of CO_2 can be monitored in a manner similar to the steam example above. However, detection of CO_2 is potentially more difficult because it depends on volumetric factors such as the thickness and lateral extent of the zone undergoing changes in saturation and the depth of the reservoir. When possible, surface seismic methods are preferred because of their large coverage and ease in deployment of instrumentation. However, in some situations, borehole methods such as vertical seismic profiles and crosswell and well logs may be required because of their capability for high resolution and ability to detect small changes in small volumes.

Recently, crosswell tomography was used to identify simultaneous *in situ* changes of saturation and pressure caused by CO_2 injection in a carbonate reservoir (Harris *et al.*, 1996a,b). More work is needed to separate these two effects in the actual time-lapse images. Shear waves are not significantly affected by fluid changes; therefore, time-lapse, S-wave images should provide a pressure map, whereas time-lapse, P-wave images sense the combined changes of pressure and saturation. Laboratory results and rock physics modeling need to calibrate and support these field observations. Moreover, laboratory data show that the magnitude of the seismic changes (2 to 20% in seismic velocity) associated with the typical west Texas CO_2 injection process varies depending on the porosity and permeability of the formations. Through monitoring, it should become possible to identify high-permeability zones by quantitatively interpreting the magnitudes of the seismic changes. Based on these crosswell results, large-scale three-dimensional, time-lapse seismic experiments are recommended.

Figure 41 (color insert) is an example of crosswell tomographic monitoring of injected CO_2 in a west Texas carbonate reservoir (Lazaratos and Marion, 1997). In this field pilot study, compressional velocity was seen to decrease by more than 1000 ft/s (305 m/s) or about 6% in a 50-ft-thick (15.2 m) zone of the reservoir. The change is easily observed with high-frequency crosswell data, but due to its depth, small volume, and small constrast, the change would be difficult to image with surface seismic. Also, the observed velocity changes in this example are due to the combined effects of an increase in pore pressure and the increase in CO_2 saturation, both associated with the injection process in oil recovery.

Geomechanics discussions alluded to the possibly significant alteration of stress state in reservoirs and the surrounding rocks by injection of high-pressure fluids or conversely, withdrawal of reservoir fluids (Warpinski and Branagan, 1989; Warpinski and Teufel, 1991; Wright *et al.*, 1995). Hydraulic fracturing and waterflooding generally result in both fracturing of the rocks and leakoff of high-pressure fluids into the reservoir. Large stress changes can occur, both locally around the injection/production well and throughout the reservoir. The magnitude of these stress changes is usually a significant fraction of the change in reservoir pressure, which typically is 10–50 MPa. These changes can be measured and modeled (although with some difficulty) by means of standard microacoustic stress testing equipment and other reservoir information. If CO_2 injection is similar to waterflooding, gas reinjection, and CO_2 flooding, the layout of the injection wells will result in a highly heterogeneous pressure surface within the reservoir, changing CO_2 solubility and fluid permeability throughout.

Monitoring the consequences of CO_2 injection would be similar to the problems of monitoring fracturing, waterflooding, subsidence, drill-cutting injections, or gas storage. Various technologies are applicable here, including microseismic monitoring of pressure-induced shear slippages in the disposal reservoir (e.g., Warpinski *et al.*, 1997), and surface and downhole tiltmeters (Wright, 1998) for detecting reservoir deformation. Tiltmeter measurements are important diagnostic tools because they yield reservoir strains (poro-thermo-elastically induced, in this case). Tiltmeters also aid in identifying fracturing, subsidence, and *in situ* stress changes. It is emphasized, however, that the foregoing diagnostic techniques have been used primarily during hydraulic fracturing and EOR operations, but have never been applied to long-term monitoring that may require new procedures and processing techniques.

5.5. Containment Integrity of CO_2

The most important consideration for ensuring the integrity of the site over extended periods of time is the frequency of the measurements. The frequency of monitoring measurements will depend on the required temporal and spatial resolution, the ability to use automatic sensing equipment, and the ability to maintain and interpret a large data set. Through time-lapse monitoring, geophysical imaging may be used to characterize the reservoir, to assess both vertical and horizontal changes, and to monitor the long-term integrity of containment. The permanent placement of geophysical sources and receivers can provide the means necessary

for cost-effective monitoring and differentiating injection-related changes from background changes. There are, nevertheless, several issues to be investigated:

- The magnitude of the seismic changes associated with CO_2 injection
- The dependence of the geophysical changes on lithology, pore structure, pressure, temperature, etc.
- The reservoir-specific issues, such as depth, heterogeneity, etc.
- The repeatability of the geophysical experiment
- The resolution required
- The experience to be gained from studying existing natural-gas storage sites

Research issues in containment related to the use of geophysical techniques include (1) quantitative definition of fast-flow paths and (2) identification of fracture formation caused by geochemical alteration or changes in local stress. Seismic methods have the potential for identifying fracture paths along which CO_2 may leak from the reservoir. Here again, the experimental, theoretical, and numerical investigations of seismic response of a fracture and fracture-specific stiffness are relevant (Pyrak-Nolte *et al.*, 1990a,b; Pyrak-Nolte and Cook, 1987; Gu *et al.*, 1996a,b). To identify fast paths in a network of fractures, the fracture stiffness for each fracture within the network could be mapped seismically. The hydraulic property of each fracture within the network would then inferred from fracture-specific stiffnesses, if the interrelationship among fracture properties is fully understood.

Fractures in rock often are highly conductive, rapid flow paths that can connect rock formations that are otherwise hydraulically isolated. Laboratory data show that the fracture-specific stiffness and volumetric flow rate of a fracture are linked (Pyrak-Nolte, 1996) through the size and spatial distribution of the apertures and contact area of the fracture. This interrelationship (Fig. 42, see color insert) between fracture-specific stiffness and fracture flow has been observed over three orders of magnitude of specific stiffness and nine orders of magnitude in flow rates for laboratory samples of granite ranging in size from 0.052 to 0.29 m (Pyrak-Nolte, 1998). However, there were two classes of behavior for the interrelationship: low data fell on a universal curve, or the flow data were independent of stiffness. Several questions remain, such as:

- Will rocks from the same tectonic setting fall on the same fracture-specific stiffness-fluid flow curve,
- Or will there be different universality classes based on rock type or stress history?
- Will repeated stress cycling alter the relationship?
- Will the relationship be scalable to the field scale?

These questions cannot be addressed without more experimental results or without experimental validation of numerical codes to simulate fluid flow and fracture deformation.

Detection of crack formation can be performed using microseismic techniques or specialized active-monitoring techniques. When a fracture forms through the linkage of microcracks, this zone of material undergoes a reduction in mechanical strength and change in volume. The reduction in mechanical strength is confined to a region much smaller than a typical seismic wavelength. Therefore, it is suggested that the weakened zone can be represented as a non-welded contact with a defined stiffness. As the stiffness of the zone decreases with increased microcrack linkage, seismic waves propagated along this zone will form guided-wave modes that are a function of the stiffness of this zone and are dispersive. Pyrak-Nolte *et al.* (1996) found that shear waves are especially sensitive to crack formation when the wave-particle motion is perpendicular to the fracture plane because these shear waves couple into interface waves propagating along a fracture. Long before catastrophic failure, when a macroscopic fracture is formed, the energy in shear wave signals shows a dramatic frequency shift. This frequency shift is a signature of the partitioning of energy out of a bulk wave and into interface waves. Because this signature is observed prior to failure, it suggests that the presence of an incipient interface wave is supported by the network of oriented, but disconnected microcracks. The change in the amplitude, velocity, and frequency content of the signals with time can indicate that failure is imminent, and CO_2 leakage may occur.

If the formation of a macroscopic fracture produces a damaged zone immediately adjacent to the fracture, the thickness or extent of this zone will have altered the seismic properties relative to the undamaged portions of the rocks and possibly the fracture itself. This is an area that needs further research to determine if the damaged zone would support guided-shear modes similar to Love waves (Nihei *et al.*, 1994), as opposed to the fracture interface waves (Pyrak-Nolte and Cook, 1987; Gu *et al.*, 1996a). The distinction between these two types of guided modes would be the polarization of the shear-wave particle motion. The ability to resolve the damaged zone from the fracture may not be possible or will depend on the spatial resolution of the probe.

6. Summary and Primary Research Needs

This paper explores the state of knowledge and uncertainties of terrestrial sequestration of CO_2 in active hydrocarbon reservoirs, depleted reservoirs, deep saline aquifers, and (to lesser extent) coal beds. Deliberations started from the premise that CO_2 disposal in geological formations is technically feasible based on (1) applicable industrial experience in hydraulic fracturing and the use of CO_2 for enhanced oil recovery, and (2) more recent experience in CO_2 disposal in saline aquifers in Norway and hydrocarbon producing regions in the Far East. It also became evident that studies of CO_2 sequestration could draw on current geoscience research in several areas such as the influence and quantification of reservoir heterogeneities on a variety of scales; low-temperature geochemistry; micromechanical processes; the evolution of fracture systems and faults; coupled processes and their numerical treatments; and geophysical measurements of rock properties and reservoir conditions.

Fundamental differences, however, exist concerning the resolution needed in reservoir characterization for oil and gas production vs long-term CO_2 disposal, reservoir response to CO_2 injection with associated hydrological, geochemical, and mechanical interactions with the host rock and its natural fluids, and long-term containment potential of the reservoir and its seals. For example, it is not possible at this time to specify the kinetics of the various homogeneous and heterogeneous reactions following CO_2 injection. Differences also were identified between oil/gas reservoirs, aquifers, and coal. Oil and gas reservoirs will be better characterized than aquifers, with recorded production histories and more existing drillholes that can be used for additional characterization activities. CO_2 injection, distribution, and containment in coal beds will be controlled by methane desorption and adsorption processes not found in oil and gas production.

Further questions concerning terrestrial CO_2 sequestration arise in predicting total storage capacities. Storage and containment evaluations are dominated by porosity and permeability distributions but also depend on the presence and contributions of natural fractures, fluid saturation, and residual fluid distribution. Additional uncertainties exist concerning the pressure limits and requirements for defined seals in saline aquifers and the origins of fracture systems in hydrocarbon reservoir rocks and coal whose contributions to fast transport and reservoir boundaries may well become important to predicting the fate of CO_2 over hundreds of years.

Special issues germane to CO_2 disposal arise in the assessment of depleted reservoirs, whose properties are known to have changed during single or repeated pore-pressure drawdown and fluid redistribution. Data about the potential effects of these changes on the integrity of the surrounding reservoir seals appear to be sparse. Other questions specific to CO_2 sequestration relate to the influence of chemical processes on reservoir flow properties and rock strength, approaches to verifying the long-term containment potential of reservoirs, and the potential need for monitoring small changes in reservoir characteristics with time (e.g., caused by slow CO_2 leakage).

In order to identify uncertainties and research needs for the terrestrial sequestration of CO_2, this study was organized around reviews from four different general perspectives: geohydrology (and reservoir engineering), geochemistry, geomechanics, and geophysics. Accordingly, some specific fundamental research areas, unique to CO_2 sequestration or common with hydrocarbon reservoir characterization and development, include the following:

- Constitutive models need to be integrated into coupled analyses, with emphasis on identifying system instabilities.
- Fundamental research needs to be coupled with studies and interpretations of natural analogues and case histories.

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