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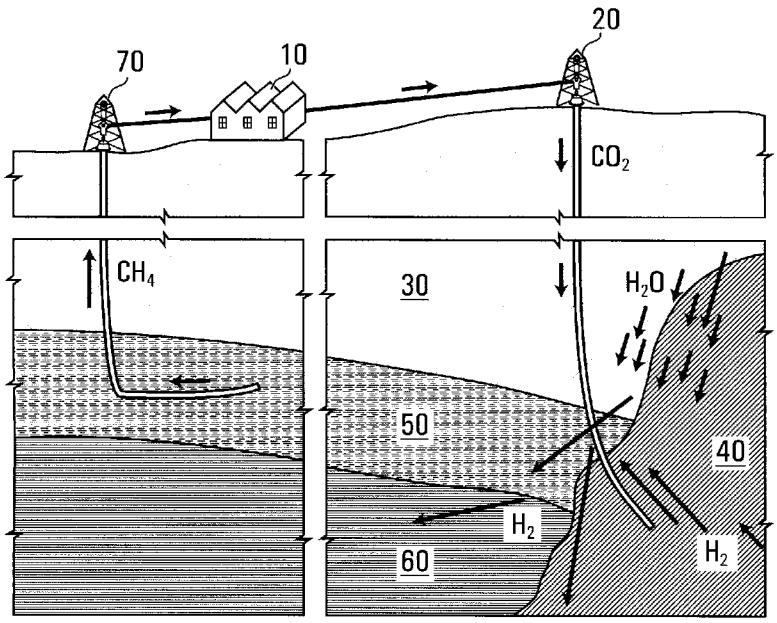

FIG. 2

(57) Abstract: The present invention is directed to a method for active sequestration of carbon dioxide by conversion to methane in a subterranean formation using microorganisms. The methane may be recovered as part of the process. In another aspect of the invention, the method is modified for producing methane in a surface reactor.

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PROCESS FOR SEQUESTERING CARBON DIOXIDE

This application claims the benefit of U.S. provisional patent application No. 60/907,829 filed on April 18, 2007.

This invention relates to a process for active sequestration of carbon dioxide by conversion to methane using microbial action in a subterranean formation.

BACKGROUND

A number of different microbial species may be found in, and can survive in, subterranean formations. Numerous microorganisms have been proposed for achieving various microbial objectives in subterranean formations, including, for example, Microbial Enhanced Oil Recovery (MEOR).

Microbial techniques often involve injection and establishment of an exogenous microbial population, which usually includes supplying the population with growth substrate and mineral nutrients. However, the growth of exogenous microorganisms is often limited by the conditions that prevail in the formation. Physical constraints may severely limit the types of microorganisms that can be injected and that will thrive in the formation. Such constraints include small and variable formation pore throat diameters; high temperatures, high salinities and pressures of fluids in the formation; and low concentrations of electron acceptors in formation water. Biological constraints may also act to limit the viability of exogenously supplied microorganisms. These include competition from indigenous reservoir microbes, the inherently adverse environment of subsurface reservoirs and the stress of changing environment from surface to reservoir. To overcome these problems, the use of

indigenous microorganisms to facilitate beneficial subsurface sediment processes, commonly indigenous anaerobic organisms, have been proposed.

Microorganisms are commonly present in sediments in subterranean formations cooler than about 80°C. With appropriate environmental conditions, indigenous bacteria and archaea can convert sedimentary organic matter (including petroleum—both crude oil and natural gas—or other fossil fuels such as coals) to methane either directly or over long geological time periods in the subsurface. Use of microorganisms for producing methane gas from hydrocarbon reserves in subterranean formations has been described elsewhere. (See for instance US 6,543,535 and WO 2005/115649.)

Subterranean formations may contain multiple, mixed consortia of microorganisms, which may include methanogens. Methanogens convert various low molecular weight compounds, including amines, alcohols, organic acids and gases into methane, CO_2 and water. Subsurface formations may also include methanotrophic archaea, which can convert methane into CO_2 and water, usually in a symbiotic partnership with sulfate-reducing organisms. Methanotrophic archaea are capable of destroying any methane produced from methanogenesis. This may occur either in proximity to or more distant from the site of methane formation. Microorganisms that reduce carbon dioxide to acetate may also exist in a subterranean formation, and may also reduce the amount of carbon dioxide available for consumption by CO_2 reducing methanogens.

Carbon dioxide reduction to methane is typically thermodynamically feasible provided the concentration of

hydrogen partial pressure remains above around 0.1 Pa. However, as the hydrogen partial pressure increases, CO_2 reduction to acetate is a greater possibility. Methane is then more likely to also be generated via acetoclastic methanogenesis. Acetoclastic methanogenesis occurs via acetoclastic methanogens, which convert acetate to carbon dioxide.

Methanogenesis is an exclusively anaerobic microbial process, and is commonly associated with biodegraded petroleum reservoirs and other deep subsurface environments. Carbon isotopically lighter methane obtained from methanogenesis is frequently found admixed with thermogenic methane (e.g., methane produced by thermal breakdown of petroleum or kerogen in source rocks).

Methanogens represent common indigenous members of the microflora of the petroleum reservoirs and other subsurface formations. The methanogens most frequently found in petroleum reservoirs described are those that reduce carbon dioxide to methane with fewer reports in the scientific literature of acetoclastic methanogens. Radiotracer and other experiments on subterranean reservoirs also suggest that carbon dioxide reduction to methane is more prevalent than acetoclastic methanogenesis. Also, high pressures in subterranean reservoirs favour net volume reducing reactions such as methanogenesis from carbon dioxide reduction.

Reducing carbon dioxide emission to the atmosphere has clear environmental and economic benefits. Various methods have been proposed to sequester carbon dioxide in subterranean formations, including in subterranean hydrate formations. Carbon dioxide has also been introduced into petroleum

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reservoirs to enhance oil recovery (see, for example, US 4,446,919).

While known methods for sequestering CO_2 may be practical in some instances, other methods may be more appropriate.

A process that utilizes natural microbiological methods of reducing carbon dioxide in subterranean formations to sequester carbon dioxide as methane may be useful. Also any methane gas produced could be recovered, and, for example, used as fuel. A closed system that recycles CO_2 emissions for production of CH_4 as fuel may also then be obtained.

SUMMARY

According to an aspect of the present invention, there is provided a method for sequestering carbon dioxide in a subterranean formation comprising: identifying a subterranean formation suitable for microbial methanogenesis; identifying an indigenous methanogenic microorganism in the subterranean formation, and/or introducing an exogenous methanogenic microoganism into the subterranean formation; introducing carbon dioxide into the subterranean formation; and promoting metabolic conversion of the carbon dioxide by the methanogenic microorganism to methane; wherein the methanogenic microorganism is hydrogen oxidizing, carbon dioxide reducing.

In one embodiment of the present invention, there is provided a method for carbon dioxide sequestration and microbial methane production in a subterranean formation wherein a natural source of hydrogen indigenously produced is available in the subterranean formation, the process comprising: (a) analyzing one or more components of the formation to determine characteristics of the formation

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environment; (b) detecting the presence of a microbial consortium comprising a CO_2-reducing methanogenic microorganism within the formation; (c) assessing whether CO_2-reducing methanogenic microorganisms in the consortium are currently active or whether exogenous microorganisms or other stimulants are needed; (d) determining whether the microbial consortium comprises a methanotrophic microorganism; (e) determining at least one characteristic of the CO_2-reducing methanogenic microorganism, and comparing the characteristic with a comparable characteristic of a known microorganism; (f) determining at least one characteristic of the methanotrophic microorganism if present, and comparing the characteristic with a comparable characteristic of a known microorganism; (g) using information obtained from steps (a) through (f) for determining an environment that promotes CO_2 sequestration and *in situ* microbial generation of methane by CO_2-reducing methanogenic microorganisms of the consortium; (h) modifying the environment to promote CO_2 sequestration and *in situ* microbial generation of methane by the CO_2-reducing methanogenic microorganisms of the consortium; and (i) introducing carbon dioxide into the formation before, after or during any one of steps (a) to (f). Carbon dioxide may be introduced into the formation at any step in the method. The hydrogen produced may be by decomposition of water, and the formation may be modified to promote natural hydrogen generation. The method may comprise in step (g), if methanotrophic microorganisms are present, determining an ecological environment that inhibits or retards *in situ* microbial degradation of methane by methanotrophic microorganisms of the consortium. Step (h) may then comprise modifying the environment to inhibit or retard *in situ* microbial methane degradation.

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In another embodiment of the invention, there is provided a method for producing methane using methanogenic microorganisms comprising introducing methanogenic microorganisms into a surface reactor containing a hydrogen generating rock media; introducing carbon dioxide into the surface reactor; promoting generation of hydrogen from the rock media in the surface reactor; introducing additional hydrogen from a subterranean formation or other natural or industrial source into the surface reactor, as is required; and promoting metabolic conversion of the carbon dioxide by the methanogenic microorganisms to methane. The methane can be optionally recovered. In a further embodiment, the hydrogen generating rock media contains mined aggregate from kimberlite or another rock that is capable of generating hydrogen.

BRIEF DESCRIPTION OF FIGURES

Figure 1 illustrates competing methanogenic and methanotrophic pathways.

Figure 2 is a schematic representation of one embodiment of the present invention.

Figures 3A to 3E are schematic representations of a kimberlite pipe with an injection/production well for use in accordance with embodiments of the present invention. In Figures 3A to 3C, a single injection/production well embodiment is shown. In Figures 3D and 3E, an invention embodiment using a first injection well for injection CO_2 and a second production well for producing methane is shown.

Figure 4A displays the cumulative carbon dioxide injected and cumulative carbon dioxide produced during a simulation of a continuous process embodiment of the present invention.

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Cumulative production volumes of methane and hydrogen from the reservoir are also plotted. Figure 4B displays the carbon dioxide injection and gas component production rates of Figure 4A.

Figure 5 displays the carbon dioxide mole fraction in the gas phase in a fracture after 10 years of carbon dioxide injection according to a simulation of a process embodiment of the present invention. The mole fraction of methane in the fractures is also shown.

Figure 6A displays the cumulative carbon dioxide injected, produced, methane produced and hydrogen produced versus time for a simulation of a process embodiment of the present invention. Figure 6B shows the carbon dioxide injection rates and gas production rates of Figure 6A.

Figure 7 displays the mole fraction of carbon dioxide and methane in a fracture after 35 years of carbon dioxide injection according to a simulation of one embodiment of the present invention.

Figure 8A displays the cumulative carbon dioxide injected, produced, methane produced and hydrogen produced versus time for a simulation of a process embodiment of the present invention. Figure 8B shows the carbon dioxide injection rates and gas production rates of Figure 8A.

DESCRIPTION

The term "microorganisms" as used throughout this application is intended to include bacteria and archaea, their enzymes, and other products, as well as relevant eukarya. It will be understood that bacteria and archaea are representative of microorganisms in general that are

involved in methane production and destruction in the subsurface under anoxic conditions.

The process of this invention may be used to stimulate and sustain the activity of a mixture of different microorganisms in a subterranean formation to convert carbon dioxide to methane, which may under appropriate conditions be produced to surface. Species of methanogens that metabolize carbon dioxide and hydrogen into methane and water are referred to in this application as "CO_2 reducing" or "hydrogen oxidizing" or sometimes simply as "methanogens". Figure 1 illustrates this metabolism, together with some of the potentially competing processes that oxidize methane or compete with methanogens for electron donors. Competing processes, among others, include acetate and hydrogen oxidation by sulphate reducing bacteria and methane oxidation by methanotrophic archaea. An aspect of the present invention is to promote methanogenesis while inhibiting competing processes.

Hydrogen for metabolism of CO_2 to CH_4 by methanogens may be introduced into a subterranean formation directly from the surface, generated *in situ* by microbial action on introduced or indigenous organic matter, or the hydrogen may have been generated in the subsurface formation itself and thus it may be indigenous. Indigenous sources of hydrogen include, for example, hydrogen generated by thermal decomposition of organic matter deep in a sedimentary basin, from radiolytic decomposition of water or from water-mineral reactions. Hydrogen may be generated in one site in the formation that is different from the site of active methanogenesis, for example.

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Other environmental conditions may also promote or inhibit metabolism. In one aspect of the present invention, microbiological and geological environments have been identified that promote, or that can be modified to promote, CO_2 metabolism to CH_4 for active sequestration of carbon dioxide. In the present context "active" sequestration is distinguished from non-active or passive sequestration, in which chemical conversion from one chemical entity (e.g., CO_2) to another (e.g., CH_4) does not occur.

The terms "formation" and "reservoir" as used throughout this specification and claims is not intended to be limited to any particular kind of formation or reservoir. The invention includes within its scope any reservoir or formation suitable for use in the methods of the invention. That is, sedimentary rocks, fractured igneous or metamorphic rocks, sandstone, oil shale deposits, newly worked and abandoned coal seams, coal bed methane reservoirs, tight shale gas reservoirs, tar sands and other suitable fossil fuel deposits may be used. The formations can also be an unconsolidated sediment package, such as might be found associated with hydrogen generating igneous rock packages and sediments just below the seafloor. The term "fossil fuels" is used in the present application in a broad sense to include, without limitation, solid carbonaceous deposits such as kerogen, peat, lignite, and coal; liquid carbonaceous deposits such as oil; gaseous hydrocarbons; and highly viscous carbonaceous deposits such as bitumen and tar. Petroleum reservoirs may also be suitable.

Suitable formations may be determined, and environmental conditions modified using procedures described in more detail below.

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Formation Analysis

One or more samples of fluids (e.g., waters, oils if present, gases) and rocks may be analyzed in a formation.

Collecting Samples

Samples can be obtained by sampling procedures that are known to those skilled in the art. For instance, a fluid (e.g., water, gas) sample may be retrieved from the formation through a perforation in a well casing or from an open-hole test. The fluid can be sampled either downhole with, for example, a wireline formation fluid tester or fluid sampler; or at the surface wellhead using a subsurface test, such as a drill stem test, a production test, or normal production.

A rock sample may also be useful for evaluation of the formation environment. Rock samples can be retrieved from, for instance, drill cores, cuttings, produced sediments and/or outcrop sites or rock data can be secured by interpretation of well logs or other techniques.

Environmental and Sample Analysis

Analysis of a formation's environment can provide important information in determining suitable *in situ* environmental conditions for microbial activity and suitable microbial growth stimulants or inhibitors, if required. This analysis may include determining temperature and pressure of the formation, which can be obtained in any suitable manner known to the skilled person.

A geochemical analysis can be made of one or more fluids of the formation, such as formation water and gases, and/or one or more solids of the formation, which analyses are familiar

to those skilled in the art. Preferably, the analysis is made of fluid and/or rock samples obtained from the formation. The fluid analysis can include measurement of state values (for example, temperature and pressure) as well as a geochemical analysis of the formation water. This may include one or more of an assay for dissolved gases; identification of major anions and cations; determining pH; determining oxidation potential (Eh); and detecting chloride, sulphate, phosphate, nitrate, iron, ammonium ion, salinity, selenium, molybdenum, magnesium, calcium, cobalt, copper, nickel, silicon and other trace metals and metalloids.

Rock analysis may include mineralogical, chemical, isotopic and facies descriptions as well as measurements of formation properties, such as porosity, permeability, capillary pressure, and wettability. Analysis of the solid matrix of the rocks in a reservoir may include optical analysis, x ray diffraction, Mossbauer spectroscopy(to determine the nature of iron present) and/or chemical analysis to determine the mineralogy and elemental composition of the rock in the formation. Iron content and valence state may be determined in this manner. Magnetic properties of the rock may also be determined.

Samples of, for example, rock and water obtained from different parts of a formation can also be incubated under laboratory conditions to determine the potential for hydrogen generation and/or active methanogenesis. This may include incubation at a range of temperatures and pressures to assess activity under *in situ* conditions.

Geochemical analysis may also be used to identify known by-products of indigenous microbial activity. The

identification of such markers can be used as a first step in determining the presence of active anaerobic microbial consortia.

For example, the presence of methane, CO_2, microbial RNA, DNA, enzymes, and carboxylic acids can be indicative of microbial activity. Also, methane relatively depleted in the carbon 13 isotope is frequently found where natural methanogenesis has occurred.

Where hydrocarbons are also found associated with a reservoir, anaerobic hydrocarbon degradation metabolites, such as alkyl and aryl substituted succinates, naphthoic acids and/or reduced naphthoic acids (particularly 2-naphthoic acids or reduced 2-naphthoic acids) and demethylated hopanoid compounds, indicate that anaerobic degradation of organic matter is taking place. The presence of these compounds is also indicative of anaerobic degradation conditions that may be appropriate for methanogenesis.

Compounds which are indicative of active methanogenesis under indigenous conditions are archaeols (which are lipid molecules characteristic of archaea) characteristic of methanogens. Specific phospholipids and other polar lipids and microbial nucleic acids characteristic of methanogenic archaea can also be used to positively identify reservoirs with active methanogenic processes.

In addition, methanogens contain novel co-factors such as F_{430}, a nickel porphyrin associated with methyl coenzyme M reductase. A similar, but distinct nickel porphyrin with a higher molecular weight is associated with anaerobic methane oxidizing archaea. Analysis of these co-factors can provide

information on the relative prevalence and location of methanogens and methane-oxidizing archaea.

Hydrogen generating subterranean environments can also be identified by formation analysis. Hydrogen rich gases may be associated with several subsurface settings including sedimentary rocks, and evaporites. More commonly hydrogen rich gases are found associated with rocks rich in ferrous iron such as rocks in oceanic rift zones, ophiolites, dunites, serpentinised rocks and weathered basic and ultrabasic rocks in general. Hydrogen may be produced by reaction of water and ferrous iron containing minerals at temperatures low enough to permit subsurface microbial life. Active microbial populations are often also associated with subterranean hydrogen generating environments.

The inventors have observed that in some large accumulations of microbially produced gas significant quantities of hydrogen are found having a hydrogen isotopic signature of -700 to -800 per mil. VSMOW. This signature is typical of hydrogen produced by reactions of minerals, such as olivine, with water. The inventors have concluded that abiotically generated hydrogen gas can be used by methanogens, in addition to biologically produced hydrogen gas, to reduce carbon dioxide to methane. Detection of hydrogen with a characteristic isotopic signature may be used to identify reservoirs suitable for reactive sequestration of carbon dioxide. Without limitation, suitable subterranean formations may include basic and ultrabasic rocks, such as dunites, serpentinites and kimberlites, and other rocks containing minerals, such as serpentine, magnetite or olivine and other mafic minerals.

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Analysis of the reservoir geological environment may be carried out using geophysical and geological mapping procedures known to a person skilled in the art. In this manner, relative volumes and spatial arrangements of solid and fluid zones may be identified as suitable for practising the methods of the invention.

Information obtained from the above analyses may be used to identify reservoirs that contain suitable organisms and environments for carbon dioxide sequestration.

Microbial Analysis

Methanogenic and methanotrophic archaea are often found in the same subterranean formations. Knowing the distribution, abundance and activity of these archaea is an element of predicting the net rate of carbon dioxide conversion and methane production, and for taking steps to modify the environment to promote methanogenesis over methanotrophy.

Collecting Indigenous Microorganisms

Microbial populations in deep subsurface environments are typically present at very low abundance and are on the order of five to six orders of magnitude less abundant than in near-surface sediments (ca. 10^3 to 10^4 cells per cubic centimetre in the deep subsurface). To minimize misidentification of contaminant organisms as indigenous, stringent contamination control measures should be adopted. Treatment of all reagents and materials, except amplification primers, with UV and enzymatic treatment with DNase I is recommended when nucleic acid based analyses are conducted. It is also recommended that samples for nucleic acid analysis be frozen immediately or fixed by addition of, for example, filtered 50% ethanol immediately upon sampling.

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It is advisable that subsamples be taken from the centre of whole cores under sterile conditions to minimize contamination from the exterior of the core, which may be contaminated during drilling. Formation water and/or drill cutting samples may also be analyzed for the presence of active microorganisms if conditions are maintained to inhibit exogenous contaminant organisms while promoting those adapted to *in situ* conditions. Samples for cultivation based studies may be stored either chilled or at close to *in situ* temperatures to reduce the growth of contaminating microorganisms during storage and transport.

Microorganisms in water samples may be concentrated by, for example, filtration and/or centrifugation before the analysis is performed. This may facilitate detection. The indigenous microbe population will typically occupy a very small fraction of a sample's volume. A typical formation water may contain less than 0.025 mg of microorganisms per liter.

Incubation of samples in microcosms that replicate as much as possible *in situ* conditions to identify factors that promote or inhibit particular metabolic processes may also be used.

Conventional microbial detection techniques, which are familiar to those skilled in the art, may be used to detect microorganisms in a sample.

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Characterizing Indigenous Microorganisms

Characteristics of a microorganism or consortium of microorganisms may be determined by, for example: biochemical methods, physiological methods, biogeochemical process measurements, optical methods, and/or genetic methods. The degree of similarity between determined characteristics of sampled microorganisms and characteristics of microorganisms with known properties can be used to establish identity of the sampled microoganisms and/or infer the physiology, metabolic functions, and ecological traits of the sampled microorganisms. Characterizations and comparisons may be done using techniques well established in the field of microbial ecology.

The following is a list of non-limiting examples of characterizations and comparisons that may be used:

(a) Enrichment culture techniques may be used to obtain isolates of microorganisms from which biochemical, morphological, physiological, ecological and genetic traits may be determined and compared against traits of known microorganisms.

(b) Determination of the phospholipid fatty acid composition (PLFA) of the sampled indigenous microorganisms may be obtained and compared to PLFA distributions of known microorganisms.

(c) Determination of isoprenoid glyceryl ether distributions characteristic of methanogenic and other archaea may be obtained and compared to isoprenoid glyceryl ether distributions of known microorganisms.

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(d) Compound-specific (carbon, hydrogen) isotope analysis may be performed to identify organisms utilizing methane.

(e) Nickel porphyrins may be identified to detect and distinguish between methanogenic and methane-oxidizing archaea.

(f) Genetic characterization methods may be performed on sampled indigenous microorganisms and the results compared to known microorganisms.

For genetic characterization, 16S rRNA genes and genes encoding the alpha subunit of methyl coenzyme M reductase can in principle be used to detect methanogenic archaea. But, homologues of methyl coenzyme M reductase are also found in anaerobic methane oxidizing archaea. Also, 16S ribosomal RNA sequences of methane oxidizing archaea have been identified in biodegraded petroleum reservoirs and similar organisms have been found in gas seeps near mid oceanic ridges. Care must therefore be taken if a genetic characterisation is to be made based on 16S rRNA genes and genes encoding the alpha subunit of methyl coenzyme M reductase so that methanogenic microorganisms are not confused with methanotrophic microorganisms.

Genetic characterization of indigenous microorganisms may be performed by using any one of a number of methods known to a person skilled in the art. The following are two non-limiting examples of methods that may be used in determining the presence, identity and/or abundance of methanogenic and methanotrophic archaea:

1. Sequence identification. Sequences of genetic fragments from sampled microorganisms may be determined.

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These gene fragments include but are not restricted to: 16S rRNA genes; and genes encoding the alpha subunit of methylcoenzyme M reductase (*mcrA*) from methanogenic and methane-oxidizing archaea. These sequences may then be compared against nucleic acid sequences from microorganisms with known metabolic capabilities. Sequences from known microorganisms may be obtained from, for example, the Ribosomal Database Project, Michigan State University, East Lansing (rdp.cme.msu.edu); the Genbank database at the National Center for Biotechnology Information located in the National Library of Medicine (Building 38A Room 8N805), Bethesda, Md. 20894, U.S.A. (www.ncbi.nlm.nih.gov); the EMBL nucleotide sequence database available through European Bioinformatics Institute (www.ebi.ac.uk/embl/) ; or Greengenes (greengenes.lbl.gov/). This information may be used to establish the phylogenetic identity with nearest known relatives using established techniques. Sequences recovered from relevant subsurface environments can be compared with, for example, the GenBank and EMBL databases using the BLAST and FASTA algorithms for instance, to identify their closest relatives. Any one or more of the available databases could be used to obtain information about the identity of the organisms present in the formations. Nearest neighbour sequences and sequences from the relevant formations may be aligned with the ARB database using the ARB software (www.arb-home.de/). Phylogenetic trees may then be constructed in ARB to obtain a final phylogenetic designation for the sequences recovered.

2. Quantitative analysis using real-time polymerase chain reaction (PCR) techniques of target genes characteristic of particular organisms or processes that can be controlled to promote carbon dioxide conversion to methane. Specific primers can also be designed and used to

distinguish and quantify key variants of *mcrA* involved in methanogenesis and methane-oxidation. For example, oligonucleotides designed to hybridize to the 16S rRNA genes of microorganisms and target genes indicative of processes such as methane generation and methane oxidation may be used in PCR-based methods.

Oligonucleotide probes labelled with radioactive phosphorus, biotin, fluorescent dyes, enzymes and other suitable tags may also be used, although they will likely lack the sensitivity required for analysis of subsurface samples unless linked to amplification techniques. Suitable amplification techniques may comprise catalysed reporter deposition-fluorescence *in situ* hybridization (e.g., the CARD-FISH method), polymerase chain reaction, or culture-based enrichment or analysis of microcosms. Oligonucleotide primers targeting regions that are conserved in methanogen *mcrA* genes and distinct in methane-oxidizer *mcrA* genes can be used to distinguish between the two types of organisms. Broad specificity *mcrA* primers could be used followed by cloning and sequencing of the *mcrA* genes sampled in order to determine their provenance.

Environmental Modification

Following one or more of the above described determinations, an ecological environment that promotes activity that will sequester carbon dioxide and promote its conversion to methane may be determined. Using information obtained about the formation and indigenous microorganisms, the environmental conditions in a formation can be modified to promote microbial conversion of carbon dioxide to methane, which may include inhibiting microbial degradation of methane.

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The activity of microorganisms in the subsurface may be altered by:

1) Modifying the microbial ecology. This may involve, adding, subtracting and/or maintaining components required for microbial growth and/or activity. These components may be determined by, for example, laboratory and/or *in situ* pilot studies.

- and/or -

2) Modifying the formation environment. This may involve controlling and/or maintaining the subsurface environment, including, for example, chemistry (including salinity, pH, etc.), temperature, and pressure.

One or more of the environmental conditions may require adjustment or maintenance within specific ranges to initiate or sustain carbon dioxide sequestration and conversion to methane.

Modification of parameters may include addition of one or more stimulants and/or inhibitors; and/or a change of one or more environmental factors. The particular modifier or modifiers suitable for a particular environment will depend on the microbial consortium to be modified and the formation environmental conditions.

Modifying Microbial Ecology

To accelerate methane production, the activity of methanogenic archaea may be accelerated, and/or the activity of methanotrophic archaea reduced. Carbon dioxide reducing methanogenic archaea include *Methanobacteriales*, *Methanomicrobiales*, *Methanococcales*, *Methanosarcinales* and relativesand *Methanopyrales*. Obligately acetoclastic

methanogens from the *Methanosarcinales* however will be unsuitable for carbon dioxide reduction.

Organisms that may result in lower methane yields, such as anaerobic methane oxidizing archaea, may also be present in the formation. Three major known groups of methane-oxidizing archaea exist, and are referred to in the literature as ANME-1, ANME-2 and ANME-3. The methane-oxidizing archaea are related to but distinct from methanogenic archaea. Other microorganisms may also be present in a formation, such as, sulfate-reducing archaea and bacteria, nitrate/nitrite-reducing bacteria and iron-reducing bacteria, which will all compete more effectively for hydrogen than methanogens in the presence of their preferred electron acceptors. The activity of such organisms can be controlled to promote methanogenesis.

Understanding the subsurface ecology allows one skilled in the art to deduce likely additives that can stimulate subsurface activity. Suitable additives (in an appropriate form for distribution throughout the formation) may include one or more of, but not limited to:

(a) Nutrients containing nitrogen and phosphorus. These may be added by liquid or gaseous injection, for example, to quickly disperse through gas caps facilitating nutrient supply very quickly over large areas of the formation. Care must be taken in adding nutrients to minimize or avoid accelerating competing processes such as nitrate or sulphate reduction. This may be done by selecting suitable forms of the nutrients, or by independently blocking these reactions. Non-limiting examples of phosphorous and nitrogen nutrients that may be used to promote methanogenesis include: ammonium phosphate;

potassium ammonium phosphate; Na_2HPO_4, K_2HPO_4 and NH_4Cl, which may be added via water injection or ammonia gas (NH_3), for example; and volatile phosphorus compounds (e.g., PH_3, and CH_3-PH_2) though these may be toxic at high concentrations or decompose during injection. Phosphates may precipitate chemically in formations and therefore less reactive forms of phosphorus such as polyphosphate and phosphorus pentoxide may be more appropriate additives. Nitrogen can also be added in the form of urea. Of the microorganisms typically present in a formation, methanogens exclusively use ammonium ion as a nitrogen source or are dinitrogen fixers. (Mean concentrations of ammonium ion naturally occurring in subsurface formations range from a few ppm up to around 500 ppm, but are typically around a few tens of ppm. In contrast in near surface anoxic environments (e.g. landfills) concentrations of ammonium ion range up to over 1000 ppm.) While $NaNO_3$, KNO_3 and NH_4NO_3 can accelerate the syntrophic components of methanogenic consortia, they should in most instances be avoided as addition of nitrate may stimulate nitrate reducing bacteria that may be present in the formation, which can repress methanogenesis by more effective competition for electron donors. If nitrate is added, the activity of nitrate reducing bacteria could be independently blocked, by addition of chlorate, for example.

(b) Vitamins: non-limiting examples may include folic acid, ascorbic acid, riboflavin and Vitamin B12.

(c) Trace elements: non-limiting examples may include B, Zn, Cu, Co, Mg, Mn, Fe, Mo, W, Ni, and Se. These elements could be added as water soluble salts, for example.

(d) Buffers for environmental control of pH, for example.

(e) Aqueous solutions of different salinities and/or pH values than present in the formation, or aqueous solutions containing complexing agents. Suitable complexing agents may include organic acids, such as oxalate, citrate, EDTA or other multi dentate ligand organic compounds, such as hydroxylated acids. These agents may facilitate mineral dissolution and release of natural nutrients including, but not limited to, nickel, cobalt, nitrogen, potassium, ammonium or phosphate ion from dissolution of feldspars, clays or other silicates and carbonates. Indeed, the supply of nutrients from mineral dissolution in reservoirs or reservoir encasing shales may be the rate-limiting step for many microbial processes in the subsurface. Mineral dissolution and release of nutrients may also be facilitated by fresh, low salinity aqueous solutions, or acidic or basic aqueous solutions depending on the mineralogy of the rock. Most phosphorus in many subsurface petroleum and other reservoirs and reservoir encasing sediments is in feldspars; thus, for example, it has been suggested that natural feldspar dissolution in some oil reservoirs is related to biodegradation of the associated oils. In general, phosphorus contents of oils are low (approximately 1 ppm or much less); whereas, phosphorus contents of sandstone reservoirs or reservoirs encasing shales are much higher (up to 1000 ppm or more of oxide equivalents).

It has been observed that microbial activity in deep subsurface reservoir environments is often phosphorus, potassium or nitrogen limited. This could be addressed by adding nutrients or aqueous solutions, as described above.

Natural and/or artificial electron acceptors, such as SO_4^{2-}, NO_3^{2-}, Fe^{3+}, humic acid, mineral oxides, quinone compounds, CO_2, O_2, and combinations thereof may stimulate microbial

activity. With the exception of CO_2, however, these chemical entities will generally be detrimental to methane generation. These electron acceptors will generally stimulate organisms that will outcompete methanogens for electron donors. These entities should therefore generally be avoided in the methods of the invention, or the activity of the competitive microorganisms suppressed.

For example, injection of solutions containing sodium molybdate (or other hexavalent cation) may be used to inhibit sulphate-reducing bacteria and sodium chlorate solutions may be used to inhibit nitrate reducing bacteria. Methane-oxidizing archaea are unlikely to be active at the site of methanogenesis, but if they are present in other regions of the formation, they may be inhibited. The fact that these groups of archaea are likely to be spatially separated is important since the known inhibitors of anaerobic methane oxidation (e.g. bromoethane sulfonic acid) also inhibit methanogens. Thus, spatially targeted inhibition may be used to stop any methanotrophic activity near production zones. In addition methane-oxidizing archaea often exist in close association with sulphate-reducing bacteria that consume the products of anaerobic methane oxidation driving methane oxidation to completion. Anaerobic methane oxidation may therefore be inhibited with inhibitors of sulphate reduction such as sodium molybdate. Other means of inhibiting competing processes may also be used.

Additives, such as those described above, may be selected to specifically promote carbon dioxide sequestration using what is known about the microbial ecology. For example, it may be determined that cobalt or nickel stimulates growth of the closest-matching known methanogenic microorganisms to

indigenous microorganisms identified in the formation using techniques described herein. Assessment of the formation may determine that cobalt or nickel is only present in the formation in limited concentrations in a labile accessible form. Addition of these limiting components in an accessible soluble form may then stimulate the indigenous methanogens of the formation.

Suitable stimulants can be tested and optimized using indigenous microorganisms in laboratory microcosms, cultures or *in situ* pilot sites to determine their effectiveness at promoting rapid methanogenesis. However, stimulants that increase the rate of activity of methanotrophic or nitrate, iron or sulphate reducing microorganisms that may suppress methanogenesis by competition for common electron donors may be avoided, or their activity independently blocked, for example.

Indigenous microbial consortia can be grown in nutrients using a range of nutrient media, with varying pH, salinity, trace metals, using methods known to the skilled person, and to find those conditions which support high rates of methanogenesis and/or low rates of methane degradation. These microcosm and culture studies will typically involve several cycles of stimulant additives and stimulant combinations as well as varied environmental conditions (e.g., salinity, temperature, pH).

It will be apparent to a person skilled in the art that the indigenous microorganisms found in a given formation and environmental conditions of the formation will most likely be unique to the formation. It will also be apparent to the skilled person that conditions for promoting growth of indigenous microorganisms may therefore vary from one

subsurface formation to another, and most importantly, may vary from one location in the reservoir to another. Conditions favourable for microorganism growth in one part of the formation may not be optimum in another part of the reservoir formation. In addition it may be necessary to inhibit methane-oxidizing archaea that are present in locations that are removed from the site of methane generation to minimise loss of methane in instances where methane is to be recovered.

This invention is not limited to use of indigenous microorganisms. Exogenous microorganisms can also be injected into the reservoir formation, although promoting indigenous methanogens is generally preferred. Formations most favourable for sequestration of carbon dioxide include those that are currently microbially active.

In one invention embodiment, exogenous microorganisms suitable for growing in the subterranean formation are introduced into the formation by known techniques before, during, or after practicing the process of this invention.

Modifying Formation Conditions

The present invention can be practised in any formation that is suitable for microbial life or that can be modified to be suitable for microbial life. In general, this means a formation having: formation fluids with a temperature less than about 125°C; a pressure less than about 10,000 psig (6895 kPa); a subsurface pH between about 3 to about 12 and a salt concentration less than about 300,000 parts per million. When the formation has a pH greater than 10, usually the addition of a buffer may be needed to decrease the pH to about 10. Higher salinity environments may slow the rates of methanogenesis. Reservoirs cooler than about

80°C or which can be cooled to below about 80°C are good candidates for the methods of the invention. In these circumstances exogenous methanogenic consortia could readily be introduced. Indigenous organisms are not likely to be active in formations hotter than about 80°C or where geochemical and geological data indicate that the reservoir has ever been heated to more than about 80°C, inactivating the indigenous microorganisms.

In the case of igneous rock reservoirs such as fractured kimberlites, while the rocks have experienced very high temperatures during emplacement of the kimberlites (>800°C), most reservoirs will have been colonized by microorganisms after cooling and weathering of the rock body in near surface depths(<3km). Innoculation may occur by near surface organisms migrating into the subsurface or most likely by invasion of organisms from already methanogen infected subsurface environments which naturally contain methanogens. Thus, in the case of the Western Canada kimberlite fields in the Buffalo Head Hills area, infection of kimberlites by methanogenic organisms might have occurred as the kimberlites intrude petroleum reservoirs containing biodegrading petroleum where appropriate carbon dioxide reducing methanogens are present.

Environmental conditions in subterranean formations may not be conducive to thriving populations of the appropriate indigenous microorganisms. The appropriate microorganisms may need to be stimulated to be more active. This stimulation may be achieved by modifying one or more parameters of the formation environment. Parameters of the formation environment may be determined according to methods described above.

The environment may also be altered to slow the rate of methane degradation. Changes that increase the rate of methanogenesis may be selected to simultaneously decrease the rate of methane degradation.

The environmental conditions for promoting growth of a microbial consortium in a formation will necessarily involve many factors including, without limiting the scope of this invention, the following:

(a) temperature, pH, Eh, mineralogy, and salinity of the formation;

(b) concentrations of gases (e.g., CO_2, H_2), organic acids, nutrients, vitamins, trace elements, and toxic substances (e.g., to suppress the activity of competing microorganisms) in the formation;

(c) availability of electron acceptors (high levels will suppress methane generation) and donors; and/or

(d) existence, maintenance or creation of interfaces between different microbial populations, and/or microbial methanogenesis zones.

Modifying formation conditions to increase the concentration of hydrogen gas may include not only introducing exogenous hydrogen gas, but also by facilitating release of H_2 gas. For example, hydrogen may naturally diffuse from one site in the formation to the site of active methanogenesis, and/or its movement could be facilitated by mechanical means, such as by drilling or fracturing formation rock and adjusting pressure regimes by injection or pumping fluids to facilitate fluid flow from one region to another. Because the temperature at which some H_2 is generated geochemically may be too high to support active methanogens, methanogenic

activity may need to be stimulated in adjacent lower-temperature regions to which the hydrogen has diffused and/or been transported. In general, however, water-mineral reactions *in situ* may generate sufficient quantities of hydrogen to maintain methanogenesis within the temperature range at which microbial life can be sustained in the subsurface (e.g., at temperatures predominantly below 80°C).

The rate of production of hydrogen within the igneous rock body is important to the conversion of carbon dioxide to methane microbiologically where *in situ* produced hydrogen is to be used in the method of the invention. While large volumes of reactive Fe^{++} bearing minerals and permeability related to fractures or included sedimentary rock fragments are important for *in situ* hydrogen production and fluid mobility allowing hydrogen and carbon dioxide flow, it is possible to create a local environment having more *in situ* hydrogen by using carbon dioxide as a sweep gas to sweep hydrogen generated from part of a rock body to the microbial reaction zone elsewhere. Deep injection of carbon dioxide into the kimberlite or other igneous rock body means that carbon dioxide may act as a sweep gas, flushing hydrogen up to a microbial reaction zone where modifiers such as ammonium phosphate, for example, have been injected to support high rates of microbial activity and enable methane to be produced efficiently.

Interfaces between microbial populations and/or methanogenic zones may be selected and/or modified in a number of different ways. Microorganisms in subterranean formations tend to be most active at environmental boundaries such as between fermentation zones and methanogenesis zones. Thus, configurations for the process of the invention may be selected to optimise the surface area of an interface

between a zone where carbon dioxide is injected and a zone where hydrogen is being generated or introduced, through, for example, diffusion or advection from elsewhere in the reservoir, or as an exogenous gas. Increasing the number of such boundaries, which serve as environmental interfaces, may increase microorganism activity in a formation.

There are a number of other methods that could be used to modify environmental interfaces. US 6,543,535 claims one method for increasing the number of environmental interfaces is to modify water flood injection rates. The number of reservoir boundaries could also be increased by, for example, alternating or varying the injection of modifiers into the formation to in effect create moving environmental fronts. Also, small-scale environmental interfaces could be formed by, for example, forming emulsions in the formation or by changing the chemistry of any clay minerals present using techniques known to the skilled person. Reservoirs could also be selected where there already exist natural interfaces between hydrogen charged waters and carbon dioxide rich waters produced either naturally over geological time or by anthropogenic activity. This would require knowledge of the reservoir, such as, for example, its geometry, porosity and permeability variations, and the connectivity of different parts of the reservoir to one another.

Selecting and Modifying Kimberlite Containing Formations

According to one aspect of this invention, a method is provided that sequesters carbon dioxide in reservoirs that contain hydrogen by reaction and conversion to methane, a useful fuel. Kimberlite "pipes" or intrusions are fractured igneous rocks that are hydrogen generating and may therefore

be used for sequestration of carbon dioxide in accordance with a method of the present invention. These kimberlite pipes contain ultramafic rocks that can be hydrated to form hydrous silicates (serpentine) and hydroxides as follows:

$$Fe_2SiO_4 + 5\ Mg_2SiO_4 + 9\ H_2O \rightarrow 3Mg_3Si_2O_5(OH)_4 + Mg(OH)_2 + 2Fe(OH)_2$$

Free hydrogen is then formed by oxidation of Fe_{2+} to magnetite (Fe_3O_4):

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2$$

Thus, the matrix and fracture network in a kimberlite pipe can have dissolved hydrogen concentrations up to the mM range and free hydrogen gas levels to nearly 60 mol% of the gas phase in the rock system. The hydrogen can support a population of H_2-utilizing microbes including sulphate reducers and most importantly, methanogens.

Kimberlites are intrusive igneous rocks that tend to form bodies of rock several hundred meters across and typically half a kilometre to several kilometres deep. Kimberlites often contain serpentine and clay minerals when weathered, and may have locally low matrix permeabilities which would necessitate hydraulic fracturing and fracture propping of the rocks to allow flow of nutrients or gases in and out of the formations. However, when kimberlites form, high temperature (> 1200°C) CO_2 rich lavas are emplaced in shallow environments(<3 km) and the local rocks are subjected to high temperatures (>400°C) and when the encountered host rocks contain water, explosive boiling can occur with emplacement and mixing of host rocks into the kimberlitic matrix. This may lead, for example to sandstone or other permeable lithologies being admixed in the kimberlites as

xenoliths or inclusions with local enhancement of the reservoir properties of porosity and permeability.

Despite the high temperature emplacements, the host rocks are frequently relatively unaltered in that there is little cementation of the included sediments which can thus maintain porosity and permeability and can thus maintain reservoir flow properties. The location of kimberlites in sandstone rich environments may be a favourable target environment for sequestration according to a method of the present invention. Such occurrences are common in Western Canada, for example in the Buffalo Head Hills area where Lower Cretaceous sandstones of petroleum reservoir quality are intruded by Upper Cretaceous kimberlite intrusions with much brecciation (breaking of host rock and kimberlites into a fractured mixture of rock types) and inclusion of host rock in the kimberlite. As these kimberlites are close to producing oil reservoirs in the Peace River and Athabasca oil sands where thermal recovery operations tend to generate large quantities of carbon dioxide usually associated with steam generation, this is one example of a setting in which the invention may be practised. The occurrences of sandstones having serpentine-containing kimberlites may be easily detected by geophysical tools such as magnetometry and by borehole geophysical logs.

The mineralogy of kimberlites can be quite varied; however, careful injection and circulation of CO_2-bearing water may enhance the alteration of olivines such as forsterite or fayalite ($Fe\text{-}MgSiO_4$) to serpentine to produce H_2 for methanogenesis while promoting carbon dioxide precipitation as magnesite, Fe precipitation as magnetite and excess Ca precipitation as calcite, all of which are more dense minerals than possible clay mineral alteration products.

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Moreover, kimberlites containing lesser amounts of diopside may be of benefit because the alteration of diopside consumes hydrogen. These can be recognised by mineralogical analysis using techniques such as x-ray diffraction or petrographic microscopy.

The skilled person will appreciate that carbon dioxide precipitation as magnesite or calcite provides an added means of sequestering additional carbon dioxide in a method of the present invention. Kimberlite deposits in a formation, including deep subsurface environments, can then be selected to further maximize carbon dioxide sequestration in addition to carbon dioxide sequestration by methanogenic bacteria.

Magnetite (Fe_3O_4) formation is favoured in low SO_4 waters typically found in kimberlites if HCO_3- is present in the water as it would be for this carbon dioxide injection process. While this reaction consumes some H+, magnetite is a very dense mineral that would create pore space improving reservoir permeability to enable fluid circulation.

Injection of CO_2-rich waters into kimberlites which are not in contact with fresh meteoric water may cause precipitation of carbonate minerals, usually as calcite, until calcium from the alteration of diopside ($CaMgSi_2O_6$) and olivine ($CaSiO_4$) is consumed. CO_2-rich water may then be mixed with H_2-rich kimberlite waters to form methane microbially.

Maintaining the pH above 10 in some reservoir zones may encourage magnetite precipitation instead of hematite. As both magnetite and hematite are very dense minerals, this may minimize pore space loss. The SO_4 content of injected waters should be minimized to limit sulphide precipitation and Fe trapping in hematite rather than magnetite and also

not to inhibit methanogenesis in that part of the formation. In other zones where microbial activity requires lower pH, then pH modification by, for example, acid injection may be required, including by, for example, inorganic (e.g. hydrochloric acid) or organic acid (e.g. acetic or citric acid) injection.

The porosity and permeability of kimberlites is higher near the surface where the rock is weathered as compared to lower at depths where there is no alteration. Also, very dense minerals (spinel or olivine) are being converted into a less dense hydrated mineral when serpentine is produced, resulting in a loss of porosity. The reservoirs are typically fractured with sand or ceramic propped fractures on a regular basis to maintain hydraulic connection in the reservoir.

Monitoring the Process

Continuing assessment of the microbial and formation environment in subsurface or surface reactors may be conducted, and modified appropriately. The formation conditions and the microbial dynamics (ecology) may be monitored throughout the process of the invention. This monitoring can be performed in any suitable manner, including the formation and microbial analyses described above. Normally fluid (for example, gas and/or water) samples are obtained from the formation through one or more wells in communication with the formation. The samples can be analyzed for hydrogen, carbon dioxide and methane concentrations and carbon (methane, CO2) and hydrogen (methane, hydrogen) isotopic compositions as well as to determine the concentration and type of microorganisms in the fluid and the concentration of modifiers and microbial

products in the fluid. Other geochemical analyses may also be performed to assess the effectiveness of any microbial and/or formation modifications made and to confirm compatibility of any modifiers added with the microbial and formation ecology. If based on this monitoring the modifier effects in the formation are outside desired ranges, then appropriate adjustments can be made.

Introduction of Modifiers

The invention is not limited to any particular process of introducing a material into the formation. For example, if the modifier is an added agent, the agent could be added to any suitable carrier including, for example, an aqueous solution, gas (such as CO_2), solvent or polymer injected into the formation by any appropriate procedure. The implementation of the present invention will often involve adding a stimulant package of modifiers by waterflood injection. However, addition of water is not necessary to practice the process.

In one embodiment, microbial stimulants or reservoir treatments are added to the carrier and injected into the formation through one or more injection wells and pumped to flow toward one or more production wells.

The amount of carrier introduced into the formation and the concentration of modifier contained in the carrier will depend upon the results desired. The person skilled in the art will be able to determine appropriate amounts and concentrations.

Multiple modifiers can be injected into the formation together or in separate injection steps. For example, a slug or bank of water carrying one modifier may be followed

by a second slug or bank of water carrying a second modifier. Another example includes alternately injecting a slug or bank of water carrying one modifier followed by a gas injection step carrying a second modifier. Other examples include injection of stimulants at one location to enhance methanogenesis, and/or injection of inhibitors at a different location to inhibit detrimental processes such as methane oxidation or hydrogen consumption.

Injection of a gas below the reactive zone may facilitate circulation of waters and nutrients to the microorganisms and may also allow for injection of volatile microbially accessible nutrients such as phosphines or ammonia which would disperse rapidly in any gas phase in the reservoir environment. This may be accomplished by having one or more injector wells below the reaction zone.

Carbon Dioxide Introduction

Carbon dioxide may be introduced into the formation using means known to the person skilled in the art, and including means described above for adding a modifier to the formation. For example, it may be introduced as a pure stream of gas, or as supercritical carbon dioxide or as a carbon dioxide rich gas such as a flue gas containing enhanced levels of carbon dioxide. This may be done physically by using one or more wells that penetrate the formation.

Carbon dioxide may be introduced into the formation before, after or at the same time modifications are being made to the microbial or formation ecology. Modifications may be made to enhance dissolution of injected carbon dioxide, such as by modifying formation pH and/or salinity using means

known to the skilled person, including means described herein.

Methane Recovery

Methane produced as a result of carbon dioxide sequestration can be recovered by any suitable means known to one skilled in the art.

In one embodiment of the present invention, one or more modifications are made to the microbial and/or formation ecology, carbon dioxide is injected, and then the formation is partially or wholly sealed for a sufficient period of time to allow carbon dioxide sequestration, and methane generation. Methane is then subsequently recovered. In another invention embodiment, methane is continuously recovered while modification of the environment and/or carbon dioxide injection is occurring.

Methane may accumulate in a gas zone or gas cap. This gas could be withdrawn through, for example, a conventional gas production well that communicates with the gas zone or gas cap. An effective seal or cap rock may be desirable to build up a free gas phase. However, gas production rates according to the processes of the invention will be high compared to geological gas production rates such that economic concentrations of methane can accumulate even in the absence of high quality seals that would be needed to maintain a gas accumulation over long geological timescales. An effective seal could be made by means known to a skilled person, including, without limitation, by creation of an artificial impermeable layer *in situ* (such as, for example, by injection of a polymer) or by modification of the formation environment (such as, for example, by modifying clay mineral formations to cause expansion/contraction).

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Methane may also accumulate in a free-gas phase overlying a water saturated zone or as an enhanced methane concentration within a water saturated zone in the formation. Methane could then be produced, for example, as a product entrained in produced water. In still other formations, methane may be produced through different zones of wells previously used for other purposes. To enhance microbial gas release it may be beneficial to drop the overall formation pressure by, for example, water production.

Gas flushing or sparging of reactive zones of a formation by injecting gas from a well or by producing gas in a reservoir layer below the zone to be flushed could also be employed to recover methane. For instance, a gas phase (e.g., carbon dioxide, nitrogen or mixtures of methane, carbon dioxide or nitrogen) could be injected below a methane producing zone in a formation. Simple partitioning would occur to permit methane removal in a free gas phase or gas flushing could be used to move hydrogen from one part of the formation to a site of microbial carbon dioxide conversion.

In one embodiment, a layered reservoir bioreactor is created in the formation. This serves the purpose of generation of a gas sweep *in situ* by the methanogenic degradation of, for example, organic matter injected into the formation. Reactive zones may be vertically segmented and the formation environments controlled in the following manner, for example:

(a) Organic substrates are introduced deep into the formation.

(b) Carbon dioxide to be converted to methane is injected into a hydrogen rich reservoir zone.

(c) Degradation of reactive organic substrates to free gas (e.g., methane, carbon dioxide) in a second zone in the formation is promoted by environmental modification, and wherein the second zone is lower than the first zone compared to the Earth's surface.

(d) Free gas from the lower (second) zone buoyantly moves up through the layered bioreactor, carrying hydrogen to the first microbial reaction zone and partitioning any free methane and/or methane in solution into the moving gas phase to be carried to a production well for recovery.

Gas produced from introduced organic waste in the deeper zone may increase formation pressure, improve fluid or gas recovery, including by producing gas bubbles which may aid in movement of fluid through the reservoir zones transporting hydrogen, nutrients and methane.

Care must be taken when adding organic matter that methanogen activity is not adversely affected due to the composition of the added matter.

Organic matter containing fluids include, without limitation, sewage waste, waste waters (e.g. liquid waste), biomass, industrial chemical wastes and farm wastes, among others and synthetic mixtures of reactive organic matter and water. Organic matter may also be introduced for purposes other than for the production of gases. Organic matter containing fluids may accelerate methanogenesis, including by providing beneficial microorganisms and nutrients to methanogenic archaea. Organic matter degrading microorganisms can also be introduced into the formation. Injection of organic matter-degrading microorganisms can be facilitated by injection of reactive liquid organic matter into or below gas accumulation zones or into or below

previously used fluid production wells, for example. Organic matter containing fluids could be injected as part of a pressure maintenance program into microbially active formations or into sterile formations needing inoculation with microorganisms, for instance.

To accelerate degradation of reactive organic matter nutrients such as ammonium ion and phosphate may be added. However, in doing so care must be taken to minimize interference with carbon dioxide sequestration.

An exemplary embodiment of the invention is shown in Figure 2. Figure 2 illustrates a combination of a vertical, inclined or horizontal production well and a vertical, or inclined injector well. A power plant (10) is shown, which generates a carbon dioxide rich effluent gas stream. This gas stream flows to an injector well (20) that injects the CO_2 gas plus any microbial or formation modifying agents (including water, organic wastes) into a geological formation, such as, for example, a fractured ultrabasic rock formation, which is actively generating hydrogen gas by mineral-water reactions.

Figure 2 shows a subterranean environment having four formations (30, 40, 50 and 60). Formation (30) may be an overburden comprising sedimentary rocks, for example. Formation (40) may be a kimberlite or other igneous rock containing olivine or serpentine, for example. Formation (50) may be a porous and permeable sandstone at the base of the sedimentary package, for example, and overlying a basement package of igneous and metamorphic rocks (60), for instance. In Figure 2, CO_2 gas injection is taking place into both the fractured kimberlite formation (40) and the more permeable sandstone

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formation (50). The injected carbon dioxide is microbially reduced to methane with hydrogen generated in the kimberlite.

Because of the greater water solubility of carbon dioxide, pressure conditions in the reservoir may be adjusted to maximise carbon dioxide concentration in formation waters while allowing produced methane to flow to the production well.

Production well (70) may be used to produce any gases or gas saturated waters to surface. Some fraction of the produced methane may be used as fuel. Carbon dioxide may be separated from recovered gases for reinjection into the injector well (20), recycling it.

Ground water (H_2O) flows into the formation. Moving and stationary groundwater reacts with ferrous iron or other minerals in the kimberlite formation (40) and basement rock formation (60) to make hydrogen which then reacts with the injected carbon dioxide mediated by the methanogens to make methane in the kimberlite formation (40), sandstone formation (50) and basement formation (60). In Figure 2, methane is recovered by the production well from the most permeable lithologies, separated at surface and transported to the power plant. Effluent from the powerplant may be recycled appropriately and produced waters which may be rich in divalent cations or unused nutrients may be modified and reinjected into the subterranean environment to promote further CO_2 sequestration as carbonates as well as methanogenesis.

As the subsurface microbes increase the conversion of carbon dioxide in the pores to methane, the methane concentration (not shown) increases in the fluid phases (water and gas).

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Eventually the methane concentration may exceed the saturation level in the fluids and form bubbles of methane. The generated methane can migrate to the top of the formation to add to any existing gas cap that is under production well (70); flow as dissolved gas in water produced at the production well (70); flow as a separate gas phase along with produced water; and/or if oil was originally present in the reservoir, methane may flow as gas dissolved in oil recovered in production well (70). Methane may then be recovered at production well (70) using means known to a person skilled in the art.

The carbon dioxide gas may be injected into one part of the formation, for example, in a hydrogen rich lower portion of the kimberlite (40), and the produced gas is produced from another part of the system, for example, in the upper portion of the kimberlite (40) in a continuous process. The natural density stratification can be used to separate the carbon dioxide and the methane. The production well (70) is used to produce methane.

An optional first step of the process might be to hydraulically fracture the formation to increase the fracture density in the formation to enhance carbon dioxide injection into and gas production from the formation. The carbon dioxide may be a component of the fracturing fluids and may be in liquid carbon dioxide or aqueous solution form. If gas hydrate formation is an issue, hydrate inhibitors can be added to the injection stream provided that the impact on the methanogenic process is minimal or none. Typically these would not be needed.

In a further embodiment, a cyclical method to produce hydrogen gas may be employed. As shown in Figures 3A to 3C,

carbon dioxide may be injected through an injection/production well (100) into the fracture/matrix system of a kimberlite pipe (140) until a target pressure is achieved or a target volume of carbon dioxide is injected into the formation. The rock matrix is porous and has the ability to store gas or liquid. Fractures in the formation enable transport of gas within the formation. The injection/production well may be of any configuration including vertical, deviated, horizontal, extended reach, multilateral, etc.

Once the target CO_2 is injected or target pressure is reached, the well may be shut in for a soak period and the rock system and injected gas allowed to mix and react under microbial action to produce methane. However, it is not a requirement of the method that the well be shut in for methane to be produced. Methane can be produced in some wells without a shut in period as will be apparent to the skilled person. After sufficient methane volume has accumulated in the formation and/or the shut in period has passed, the injection/production well may then be converted to a production well. Gases produced from the rock may be pipelined away to market. Gas production can be permitted to continue from the rock system until the methane content is below a specified limit, for example 50% of produced gas by volume and cannot function as a typical fuel gas. Gas production may also be stopped at any stage of the process and the well converted to an injection well and the above process repeated. That is, carbon dioxide is again injected into the formation and the optional shut in and recovery cycle may be repeated.

In an alternative embodiment shown in Figure 3D and 3E, carbon dioxide is injected into a formation (140) through a

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well (100) and starts to fill the pore space in the formation. A production well (110) is located at some distance away and operated at a pressure different from the injection well to allow for a specified residence time for the injected carbon dioxide in the formation as it moves from the injection well to the production well. The pressure difference can be established by someone skilled in basic reservoir engineering. As the carbon dioxide moves through the fractures (140) and porous matrix it is converted to methane and ultimately the moving gas composition changes, via microbial carbon dioxide reduction to methane using indigenous and/or added hydrogen, from one rich in carbon dioxide to one rich in methane as it flows from the injection well to the production well. One benefit from this process is that as the carbon dioxide is injected into the formation, excess unreacted indigenous hydrogen gas in the formation is displaced towards the production well and unreacted portions of the hydrogen can also be produced from the formation as part of the production gas stream. This produced hydrogen has uses as fuel or chemical feedstock. Alternatively, it can be further reacted on surface with carbon dioxide to produce methane.

Example 1

Data from a dual-permeability (i.e. a reservoir with permeability in both matrix porosity and in fractures as well) simulation model of a continuous process carried out in fractured kimberlite rock reservoir is shown in Figures 4 and 5. In this simulation, the average spacing between the fractures is 5 meters. Matrix porosities range from 13-25% but with abundant sandstone inclusions could be higher. In this simulation a matrix porosity of 20% is used and matrix permeability is several millidarcies (mD), respectively,

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which are typical of those found in fractured rock systems. The porosity of the fractures is 0.02(2%) and the permeability is taken to be 10,000 mD. The initial temperature and pressure of the formation is 24 degrees Celsius and about 2900 kPa, respectively. In the matrix, the initial water saturation is 0.45 (45%) whereas it is 0.10 (10%) in the fracture.

The simulation consists of a gas-water system so there is no oil phase present. The gas composition at initial conditions is 100% hydrogen gas, both within the matrix and the fracture system and the simulation model also encompasses formations that contain some methane. Hydrogen gas is allowed to leak into the reservoir section of the model from the bottom of the reservoir to represent the capability of the reservoir rock to generate hydrogen gas from its entire volume.

The properties of carbon dioxide, hydrogen, methane, and water including molecular weight, critical pressure and temperature, heat capacity correlations, and viscosity correlations have been taken from standard, publicly available databases. Standard diffusion and dispersion coefficients have been used although most of the transport results from bulk fluid flow due to pressure differences in the reservoir rather than diffusive and dispersive transport. In the matrix, a standard set of gas-liquid relative permeability curves have been used. In the fractures, stick curves (straight-line relative permeability curves) have been as is standard in modelling flow in fractures. In the simulation, methane-producing microbes are also present within the rock system. The injected and produced volumes reported in the Figures are at 1 atmosphere

pressure and 15.5 degrees Celsius(This we term standard conditions).

A good tool for modelling reservoir scale microbial processes is a reactive reservoir simulator such as the commercially-available reservoir simulation software package STARS™ by Computer Modelling Group Inc. This system permits the reaction and interconversion of many components in an environment which allows for effective simulation of advection and diffusion of the typical fluids found in a petroleum reservoir including solid, oil, water and gas phases. Reactive reservoir simulators have been in use for decades and are an accepted means of simulating and designing reservoir processes that involve mass, heat and fluid transport along with chemical reactions and phase transitions. Microorganisms are included in the reaction scheme acting as catalysts for the conversion of carbon dioxide and hydrogen to methane. Separate reactions and kinetic schemes are used to provide hydrogen from rock alteration. The basic reaction system can be modified to reflect particular formation conditions as will be understood by the skilled person.

In this simulation, 16,000 m^3/day (283 mcf/day) carbon dioxide (at standard conditions, 1 atmosphere and 15.5 degrees Celsius) is injected into the formation through a lower well for 35 years. Simultaneously, the upper production well is opened and gas flows from the system. In this example, the constraints on the production well are maximum flow rate of gas from the production well of 12,000 m^3/day (212 mcf/day-thousand cubic feet/day) gas (at standard conditions) and minimum bottom hole pressure of 500 kPa (meaning the production well is shut in if the pressure drops below 500 kPa). The pressure of the production well

can be altered to control the accumulation of gas in the system. Where the process is operated in shallow formations, or where an effective cap rock is absent, the pressure regimes in injection and production wells can be managed to maintain an effective "cap rock" integrity.

Figure 4A displays the cumulative carbon dioxide injected and cumulative carbon dioxide produced during the continuous (simultaneous carbon dioxide into lower injection well and gas production from the top well) process. Cumulative production volumes of methane and hydrogen from the reservoir are also plotted. Figure 4B displays the carbon dioxide injection and gas component production rates. The results show that after 35 years of injection, roughly 72% of the injected carbon dioxide remains in the reservoir and is not produced back to surface. The results also show that initially hydrogen gas is displaced from the reservoir as carbon dioxide is injected into it. Gradually carbon dioxide is converted to methane in the formation and after about ten years of hydrogen production, the reservoir starts to produce some unreacted carbon dioxide and biogenerated methane. The methane production rate grows to over 130 mcf/day and then declines nearly linearly as the process continues. As the methane production rate declines the carbon dioxide production rate grows. This suggests that the process may be terminated at some point where the methane rate is no longer economic and the carbon dioxide content in the produced gases is too large. Produced carbon dioxide can be separated and reinjected. This simulation of this embodiment of the process demonstrates that significant volumes of carbon dioxide can be sequestered in a reservoir for long time periods, gradually being converted to methane and that significant volumes of methane can be generated and produced. In practice, the volume of injected and produced

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gases can be measured by standard gas volumetric rate measurement equipment.

Figure 5 displays locations of the injector (lower well) and producer (upper well) and the carbon dioxide mole fraction in the gas phase in the fractures after 10 years of carbon dioxide injection. The mole fraction of methane in the fractures is also shown. The results of the simulation show that the carbon dioxide, being denser than the hydrogen and methane tends to move to the lower parts of the reservoir. The biogenerated methane exists as a bank ahead of the carbon dioxide bank. This is because methane is generated in parts of the reservoir where both hydrogen and carbon dioxide are present the generated methane tends to sit on top of the heavier carbon dioxide and below the lighter hydrogen.

Example 2

In this example, the same formation model was used as in Example 1 above. Data from this simulation model of a cyclic process carried out in fractured kimberlite rock reservoir is shown in Figures 6A, 6B and 7.

In this example, carbon dioxide is injected at 16,000 m^3/day (283 mcf/day) (at standard conditions) into the reservoir for a period of about ten years. After ten years of injection, the well is shut in (no injection or production) for a period of two years. After this soak period is done, the well is converted to production and gas is produced. In this example, the production well has two constraints: 1. a maximum gas rate equal to 12,000 m3/day (212 mcf/day) gas and 2. a minimum bottom hole pressure equal to 500 kPa. If the production well pressure drops below 500 kPa, then the well is shut in. In this example, the well is produced for

23 years. In an alternate embodiment, the well could be shut in earlier and converted back to injection to sequester and convert additional carbon dioxide gas.

Figure 6A displays the cumulative carbon dioxide injected, produced, methane produced and hydrogen produced versus time. The volumes are all at standard conditions. Figure 6B shows the carbon dioxide injection rates and gas production rates. The results show that no carbon dioxide is produced during the 35 year life of the process. That is, all of the injected carbon dioxide is sequestered and some fraction of it is converted to methane within the reservoir. The production rate of methane climbs after gas production starts and reaches over 100 mcf/day after 18 years of gas production. Thus long term sequestration of carbon dioxide is demonstrated as is economic recovery of methane.

Figure 7 displays the mole fraction of carbon dioxide and methane in the fractures after 35 years. The results show that the amount of carbon dioxide in the reservoir has nearly been depleted. This suggests that a second cycle of carbon dioxide should be started. The results also show that the gas mixture gravity segregates so the carbon dioxide sits at the bottom of the system, the methane next, and the hydrogen at the top.

Example 3

The results from Examples 1 and 2 suggest that the well placement design could be altered so that the carbon dioxide is introduced at the top of the formation and methane is produced from the bottom. This would promote a high degree of mixing of carbon dioxide and hydrogen which may raise the methane yield. Figures 8A and 8B displays the results of a

simulation according to the method described in Examples 1 and 2 above of an embodiment where the carbon dioxide injection well is placed at the top of the formation. Carbon dioxide is injected into the formation for ten years. Then, after a 2 year soak period, gas is produced from a well located near the base of the reservoir system. The resulting methane production rate is higher than those in Examples 1 and 2 showing that improvements can be made by altering the well placement. During production, hydrogen gas is also produced. Within the 35 years of the process simulated, no carbon dioxide is produced from the reservoir so it is completely sequestered.

Example 4

The injection and circulation of CO_2-bearing water may enhance the alteration of olivines such as forsterite or fayalite (Fe or Mg-SiO4) to serpentine. Serpentine may then be reacted to produce H_2 for methanogenesis. Mg precipitation as magnesite, Fe precipitation as magnetite and excess Ca precipitation as calcite are promoted, all of which are more dense minerals than possible clay minerals and tend to better maintain some minimal permeability and porosity in the rock.

The amount of water injected during an embodiment of the process can be an important factor in controlling, not only microbial activity as determined by nutrient injection, but also the rate and nature of the alteration of the rock matrix. Thus, for example, Table 1 shows water:rock ratios that achieve a rock porosity, favourable to the injection and sequestration of carbon dioxide. Excess Mg is converted to magnesite ($MgCO_3$) at water:rock ratios of 0.1 to 0.5 with minor brucite ($Mg(OH)_2$) formation if serpentine saturation is

reached maintaining maximum levels of secondary sequestration of carbon dioxide as carbonates. Table 1 assumes typical rock compositions for a kimberlite. This range of water:rock ratios is equivalent to 5 to 25 pore volumes for a 5% porosity rock (case 2 below) and 0.5 to 2.3 pore volumes for a 30% porosity rock (case 1 below).

At water:rock ratios greater than 1, serpentine and hydrogen production may stop, suggesting that careful monitoring of injection rates and water chemistry may help to optimize these reactions (Sader et al. 2007; Low-temperature serpentinization processes and kimberlite groundwater signatures in the Kirkland Lake and Lake Timiskiming kimberlite fields,Ontario, Canada: implications for diamond exploration Jamil A. Sader, Matthew I. Leybourne, M. Beth McClenaghan & Stewart M. Hamilton.Geochemistry: Exploration, Environment, Analysis, Vol. 7 2007, pp. 3-21). The pore volume and rock volume are determined from the density, pore space and mass of rock which can be determined from core analysis or well logging.

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Table 1

	pore space [frac]	**rock volume** [frac]	**m^3 rock/1000 kg rock**	**m^3 pore volume**	**water density (kg/m^3)**
Case 1	0.3	0.7	0.510	0.219	1000
Case 2	0.05	0.95	0.376	0.020	1000
For 0.3 pore space (Case 1):					
rock (kg)	water (kg)	w/r	number of pore volumes		
1000	1	0.001	0.00		
1000	10	0.01	0.05		
1000	100	0.1	0.46	optimal	
1000	500	0.5	2.29	optimal	
1000	100000	100	457.33		
For 0.5 pore space (Case 2)					
rock (kg)	water (kg)	w/r	number of pore volumes		
1000	1	0.001	0.051		
1000	10	0.01	0.505		
1000	100	0.1	5.054	optimal	
1000	500	0.5	25.270	optimal	
1000	100000	100	5054.000		

[frac]=percentage porosity; w/r= weight of rock/weight of water

Surface Processing Options

While microbial conversion of carbon dioxide to methane has thus far been described as being carried out *in situ* in the subsurface, it is also possible to use "surface reactors" to convert carbon dioxide to methane using the same rock formations and fluid injection schemes but in surface contained reactors. One skilled in the art would understand the surface reactors that may be used in this aspect of the present invention. For example, the surface reactors may be clay lined pits with a clay seal or a surface tank, pressure or reactor vessel. Piping into and out of the surface reactors permits the injection of nutrients, carbon dioxide

and water, internal production of hydrogen in the reactor and conversion of carbon dioxide to methane and also collection of produced gases and produced waters. Mined rock aggregates or mine tailings can also be used to fill the containers. The containers may be sealed so that they become anaerobic. Rock aggregate can be selected such that microorganisms would be naturally present in the rock aggregate and thus introduced into the surface reactor, but microorganisms could also be separately introduced into the surface reactor.

In one embodiment, methanogenic cultures are added to the surface reactors. CO_2 is flowed through the reactors, and the methanogens convert the CO_2 to CH_4, which may then be recovered from the reactor. Various additives may be added to reactors to promote hydrogen production and the conversion of CO_2 into methane. In one embodiment, mineral rich solutions such as tailings of mine operations, mined kimberlite or other reactive rock, or a combination thereof, may be added to the surface reactor. In another embodiment, igneous rock mine tailings are added to the reactor.

In this aspect of the invention, the surface reactor should be filled to contain a hydrogen generating rock media to provide a source of hydrogen for the methanogenic microorganisms to use in converting the added carbon dioxide to methane. The method then further comprises promoting the generation of hydrogen from the hydrogen generating rock media using methods described herein and known to the skilled person. In a further embodiment, additional hydrogen rich gas for the process may be obtained from a surface source (e.g., a natural or industrial source) or from a subterranean formation as described above and

injected into the surface reactor. Reactors could be operated in batch, semi-batch or continuous modes.

The skilled person will appreciate that the *in situ* microbial methanogenesis described herein could also be practised in conjunction with the above ground aspect of the invention.

Although the foregoing invention has been described in some detail by way of illustration and example for purposes of clarity of understanding, it is readily apparent to those of ordinary skill in the art in light of the teachings of this invention that certain changes and modifications may be made thereto without departing from the spirit or scope of the appended claims.

The citation of any publication, patent or patent application is for its disclosure prior to the filing date and should not be construed as an admission that the present invention is not entitled to antedate such publication, patent or patent application by virtue of prior invention.

It must be noted that as used in the specification and the appended claims, the singular forms of "a", "an" and "the" include plural reference unless the context clearly indicates otherwise.

Unless defined otherwise all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill and the art to which this invention belongs.

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CLAIMS:

1. A method for sequestering carbon dioxide in a subterranean formation comprising:

identifying a subterranean formation suitable for microbial methanogenesis;

identifying an indigenous methanogenic microorganism in the subterranean formation, and/or introducing an exogenous methanogenic microoganism into the subterranean formation;

introducing carbon dioxide into the subterranean formation; and

promoting metabolic conversion of the carbon dioxide by the methanogenic microorganism to methane;

wherein the methanogenic microorganism is hydrogen oxidizing, carbon dioxide reducing.

2. The method according to claim 1 further comprising recovering methane.

3. The method according to claim 1 or 2, wherein the methanogenic microorganism is indigenous to the subterranean formation.

4. The method according to any one of claims 1 to 3, wherein the methanogenic microorganism is a member of the *Methanobacteriales*, *Methanomicrobiales*, *Methanococcales*, *Methanosarcinales* or *Methanopyrales*.

5. The method according to any one of claims 1 to 4, wherein a natural source of hydrogen indigenously produced is available in the subterranean formation.

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6. The method according to any one of claims 1 to 5, wherein the subterranean formation contains a basic or ultrabasic rock.

7. The method of claim 6 wherein the ultrabasic rock comprises kimberlites.

8. The method according to any one of claims 1 to 7, further comprising fracturing the subterranean formation to maintain or improve permeability and porosity.

9. The method according to any one of claims 1 to 8, wherein metabolic conversion of carbon dioxide to methane is promoted by addition of one or more nutrients, vitamins, trace elements, buffers, organic acids, an aqueous solution to adjust salinity and/or pH, and complexing agents.

10. The method according to claim 9, wherein an aqueous solution is added to adjust pH to between about 3 and about 12.

11. The method according to claim 9 or 10, wherein phosphorous, nitrogen and/or potassium are added.

12. The method according to any one of claims 9 to 11, wherein cobalt and/or nickel are added.

13. The method according to any one of claims 1 to 12, wherein temperature of the formation is adjusted to less than about 125°C.

14. The method according to any one of claims 1 to 13, wherein pressure of the formation is adjusted to less than about 10,000 psig.

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15. The method according to any one of claims 1 to 14, wherein salt concentration in the formation is adjusted to less than about 300,000 parts per million (ppm).

16 The method according to claim 1, further comprising selecting the subterranean formation such that carbon dioxide may also be sequestered as magnesite and/or calcite.

17. A method for carbon dioxide sequestration and microbial methane production in a subterranean formation wherein a natural source of hydrogen indigenously produced is available in the subterranean formation, the process comprising:

(a) analyzing one or more components of the formation to determine characteristics of the formation environment;

(b) detecting the presence of a microbial consortium comprising a CO_2-reducing methanogenic microorganism within the formation;

(c) assessing whether CO_2-reducing methanogenic microorganisms in the consortium are currently active or whether exogenous microorganisms or other stimulants are needed;

(d) determining whether the microbial consortium comprises a methanotrophic microorganism;

(e) determining at least one characteristic of the CO_2-reducing methanogenic microorganism, and comparing the characteristic with a comparable characteristic of a known microorganism;

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(f) determining at least one characteristic of the methanotrophic microorganism if present, and comparing the characteristic with a comparable characteristic of a known microorganism;

(g) using information obtained from steps (a) through (f) to determine an environment that promotes CO_2 sequestration and *in situ* microbial generation of methane by CO_2-reducing methanogenic microorganisms of the consortium;

(h) modifying the environment to promote CO_2 sequestration and *in situ* microbial generation of methane by the CO_2-reducing methanogenic microorganisms of the consortium; and

(i) introducing carbon dioxide into the formation before, after or during any one of steps (a) to (f).

18. The method according to claim 17, wherein the hydrogen is produced by decomposition of water.

19. The method according to claim 18, wherein the formation environment is modified to promote natural hydrogen generation.

20. The method according to any one of claims 17 to 19, wherein step (g) comprises, if methanotrophic microorganisms are present, determining an ecological environment that inhibits or retards *in situ* microbial degradation of methane by methanotrophic microorganisms of the consortium.

21. The method according to claim 20, wherein step (h) comprises modifying the environment to inhibit or retard *in situ* microbial consumption of hydrogen by organisms other than methanogens.

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22. The method according to any one of claims 17 to 21, wherein the CO_2-reducing methanogenic microorganism is a member of the *Methanobacteriales*, *Methanomicrobiales*, *Methanococcales*, *Methanosarcinales* or *Methanopyrales*.

23. The method according to any one of claims 17 to 22, wherein phosphorous, nitrogen, potassium, nickel and/or cobalt are added.

24. The method according to any one of claims 17 to 23, wherein an aqueous solution is added to adjust pH to between about 3 and about 12; temperature of the formation is adjusted to less than about 125°C; pressure of the formation is adjusted to less than about 10,000 psig; and salt concentration in the formation is adjusted to less than about 300,000 ppm.

25. The method according to any one of claims 17 to 24, wherein methane is recovered.

26. The method according to claim 25, wherein methane recovered is used to fuel a process in which carbon dioxide is produced, and produced carbon dioxide is then recycled to the formation.

27. A method for producing methane using methanogenic microorganisms comprising:

introducing methanogenic microorganisms into a surface reactor containing hydrogen generating rock media;

introducing carbon dioxide into the surface reactor;

promoting generation of hydrogen from the rock media in the reactor;

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introducing additional hydrogen from a subterranean formation or other natural or industrial source into the surface reactor as required; and

promoting metabolic conversion of the carbon dioxide by the methanogenic microorganisms to methane.

28. The method of claim 27, further comprising adding a mineral rich solution or igneous rock mine tailings to the surface reactor.

29. The method of claim 28, wherein the mineral rich solution or tailings are from a mine operation, mined kimberlite, reactive rock or a combination thereof.

30. The method of any one of claims 27 to 29, wherein the surface reactor comprises a clay lined pit.

31. The method of any one of claims 27 to 29, wherein the surface reactor comprises a surface tank.

32. The method of any one of claims 27 to 31, further comprising recovering the methane.

33. The method according to any one of claims 27 to 32, wherein the method is practised in conjunction with a method as defined in any one of claims 1 to 26.

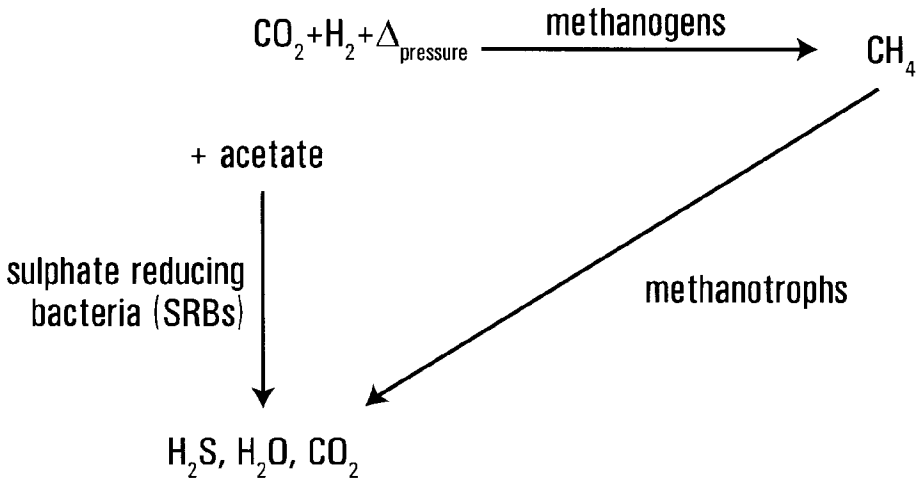
$CO_2+H_2+\Delta_{pressure}$
methanogens
CH_4
+ acetate
sulphate reducing bacteria (SRBs)
methanotrophs
H_2S, H_2O, CO_2

FIG. 1

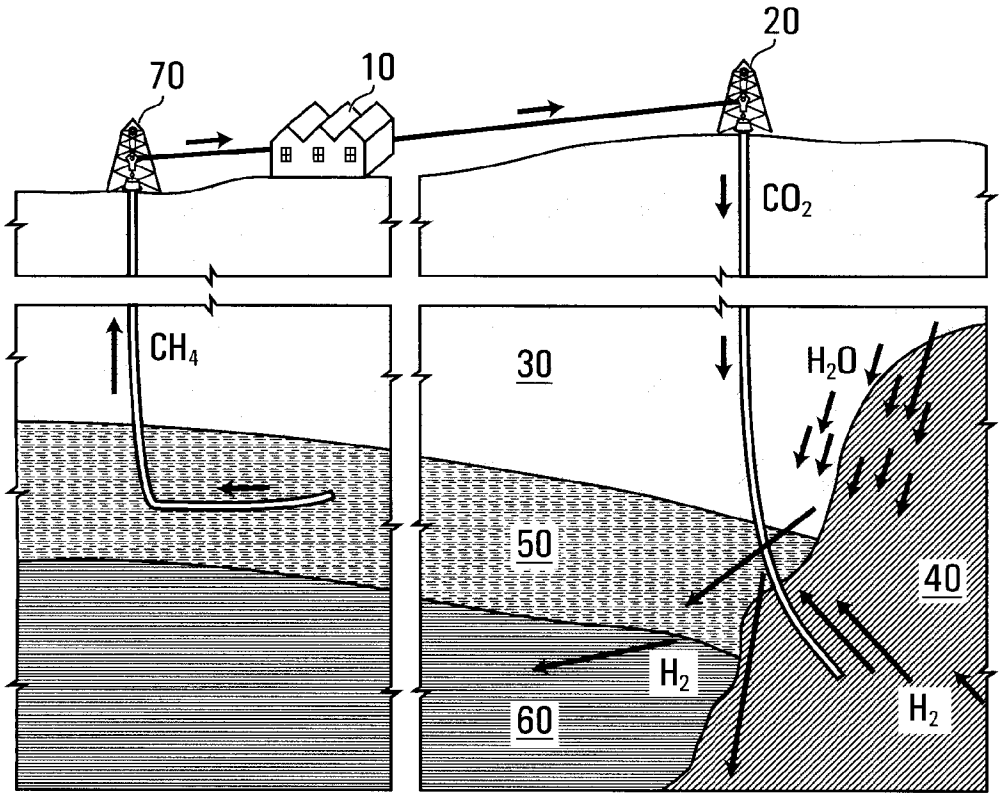
70
10
20
CO_2
CH_4
30
H_2O
50
40
H_2
60
H_2

FIG. 2

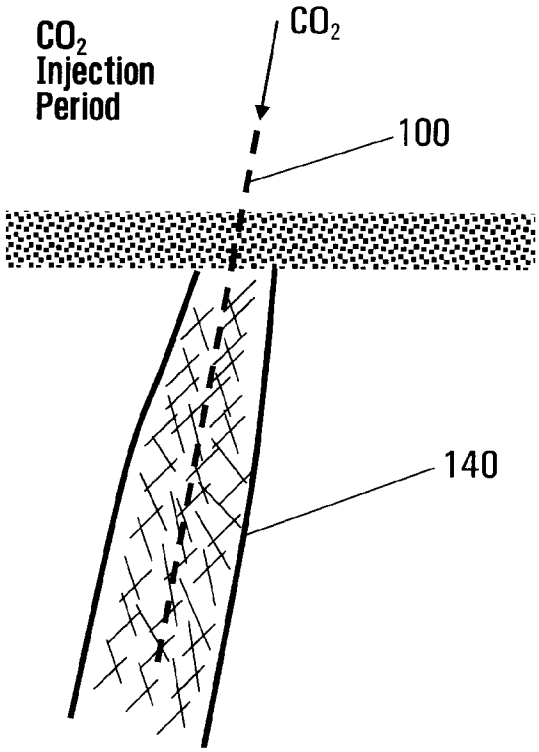

FIG. 3A

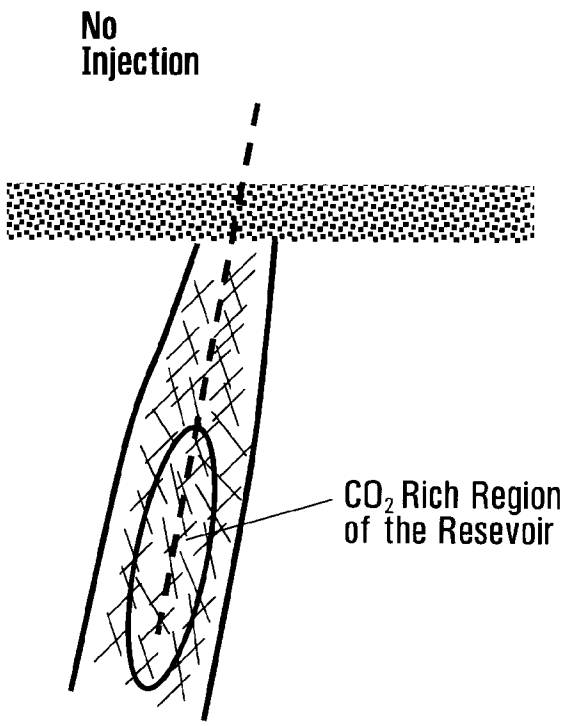

FIG. 3B

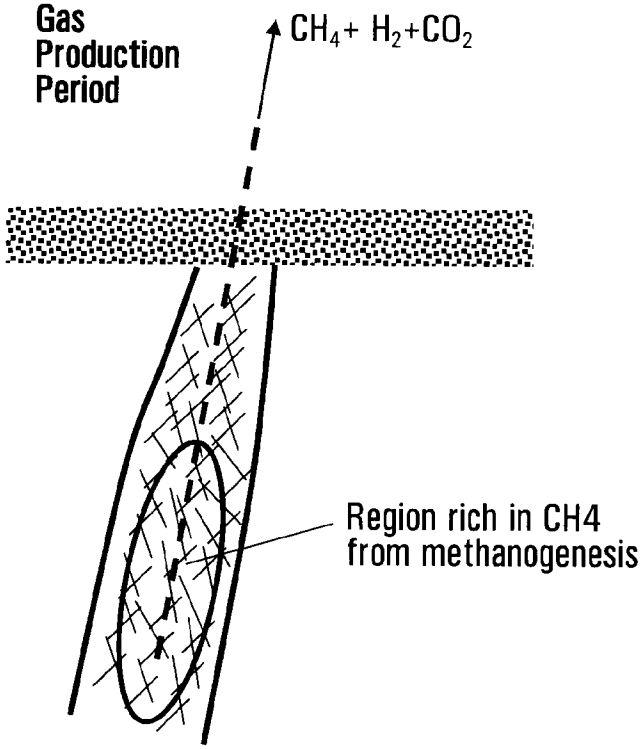

FIG. 3C

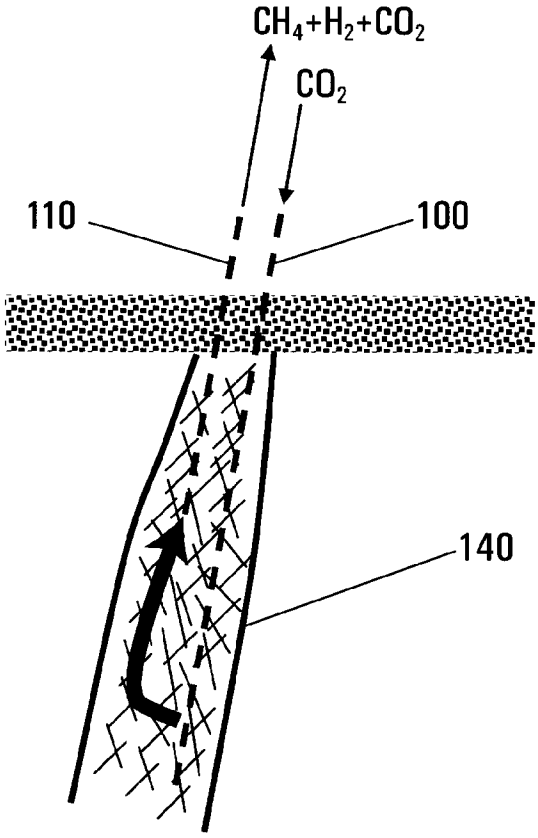

FIG. 3D

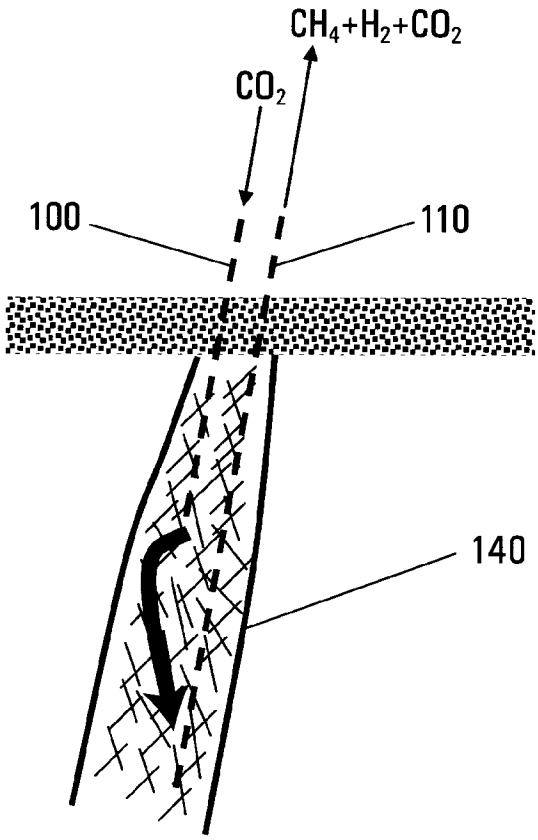

FIG. 3E

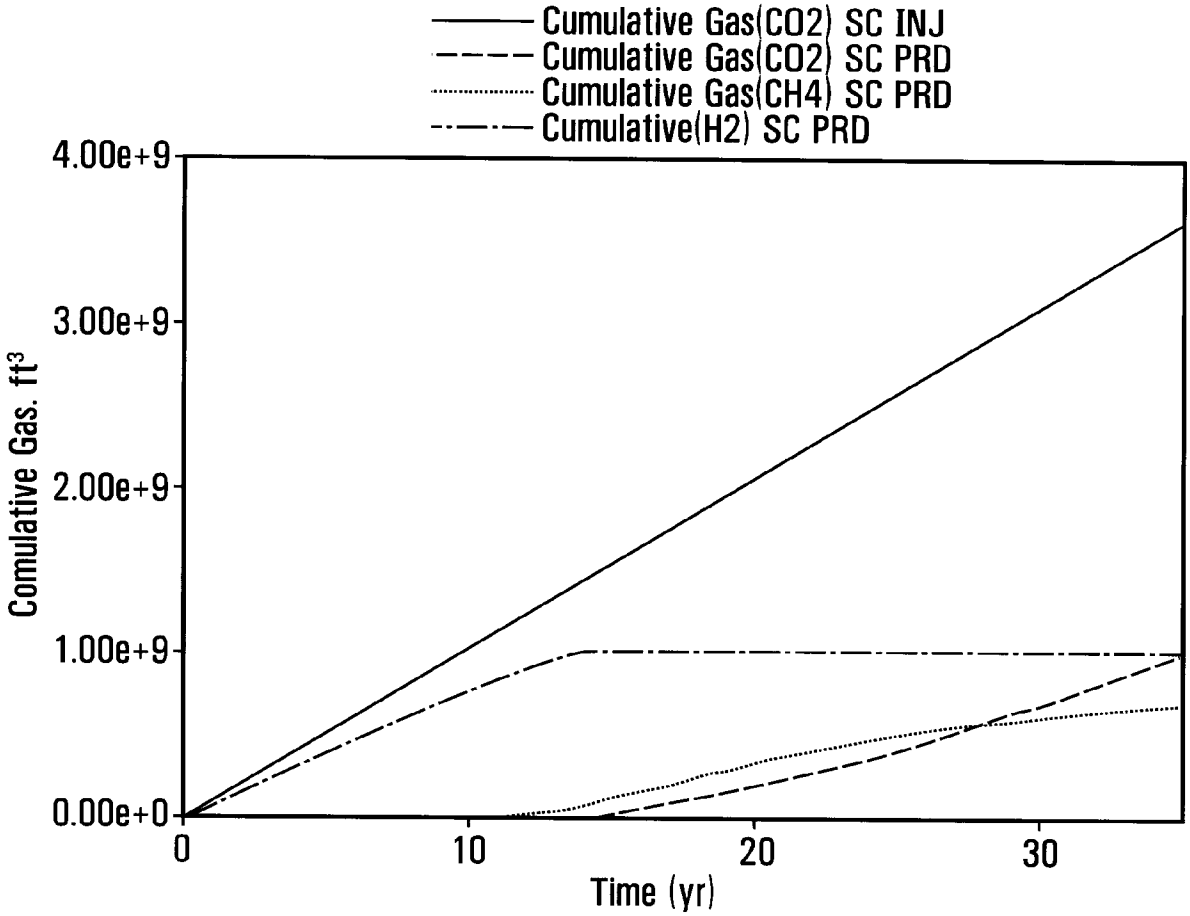
Cumulative Gas(CO2) SC INJ
Cumulative Gas(CO2) SC PRD
Cumulative Gas(CH4) SC PRD
Cumulative(H2) SC PRD
4.00e+9
3.00e+9
2.00e+9
1.00e+9
0.00e+0
Comulative Gas. ft3
0
10
20
30
Time (yr)

FIG. 4A

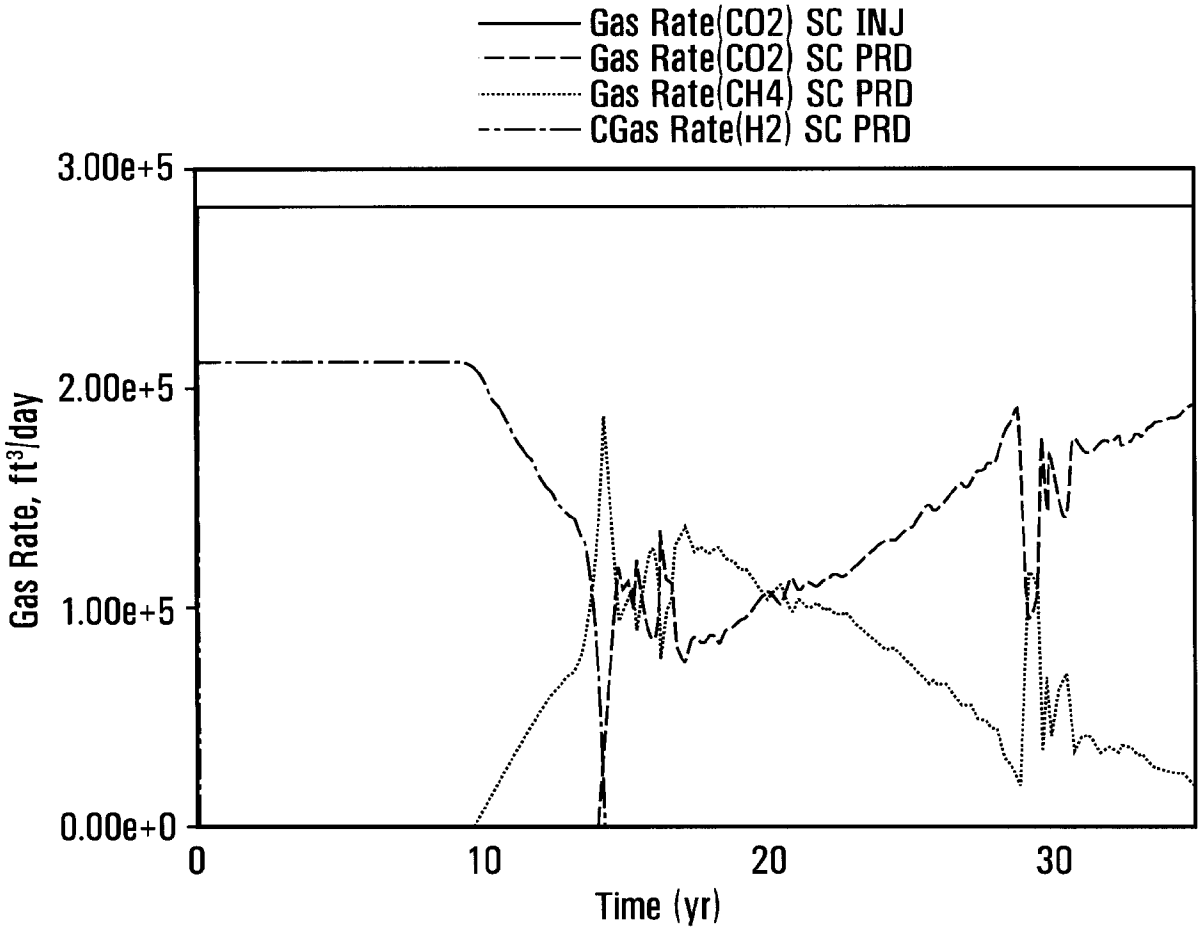
Gas Rate(CO2) SC INJ
Gas Rate(CO2) SC PRD
Gas Rate(CH4) SC PRD
CGas Rate(H2) SC PRD
3.00e+5
2.00e+5
1.00e+5
0.00e+0
Gas Rate, ft3/day
0
10
20
30
Time (yr)

FIG. 4B

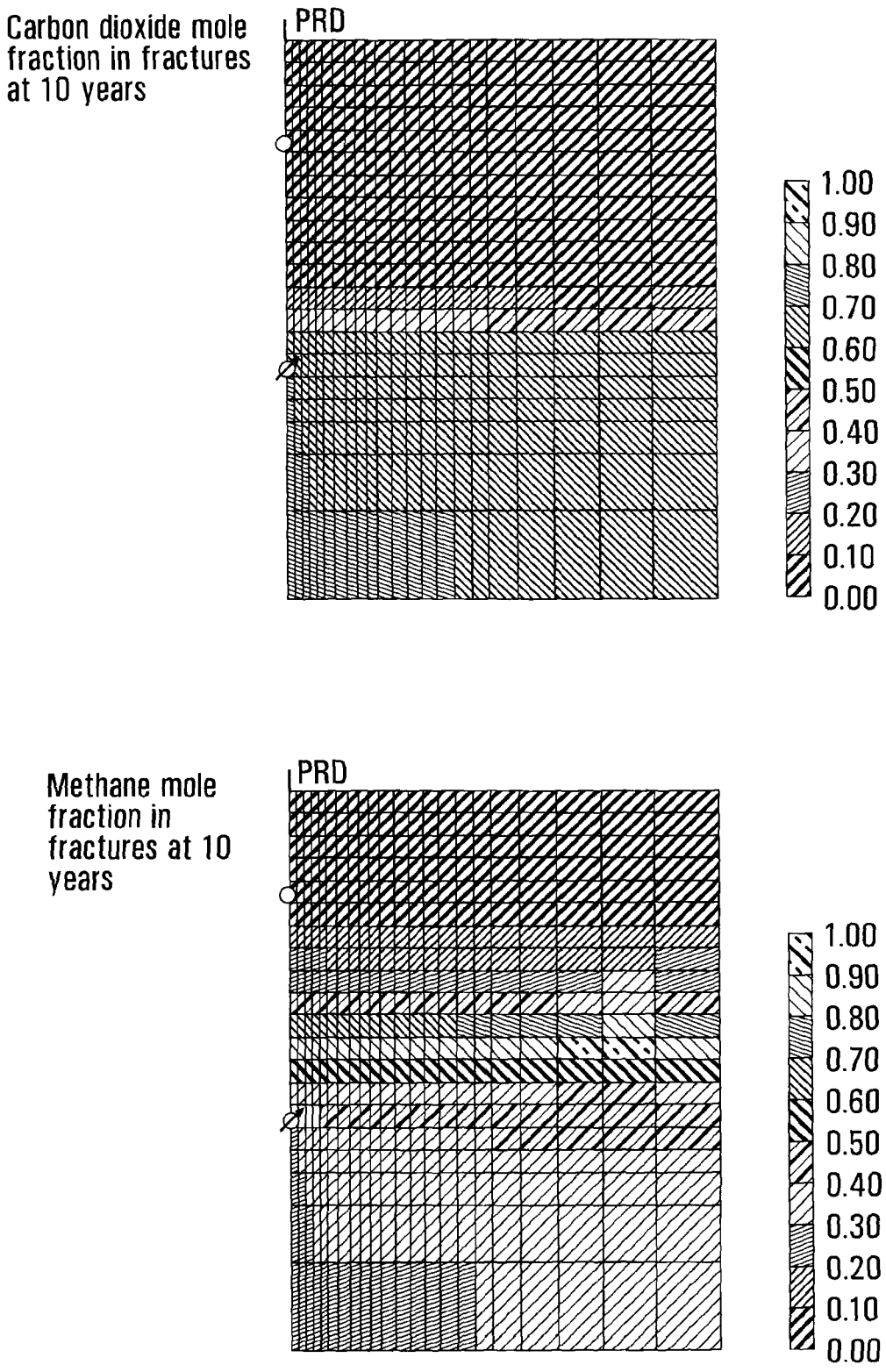
Carbon dioxide mole fraction in fractures at 10 years
PRD
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Methane mole fraction in fractures at 10 years
PRD
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00

FIG. 5

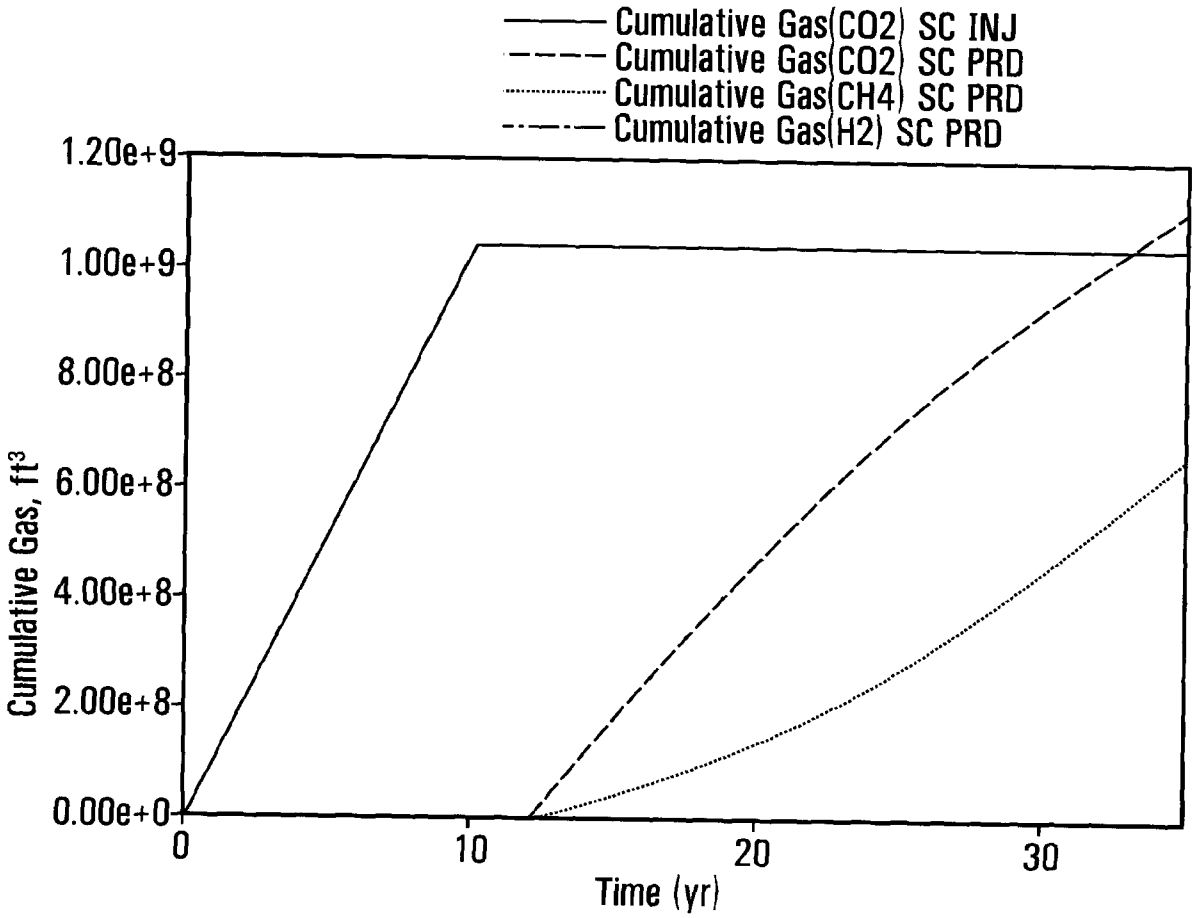
Cumulative Gas(CO2) SC INJ
Cumulative Gas(CO2) SC PRD
Cumulative Gas(CH4) SC PRD
Cumulative Gas(H2) SC PRD
1.20e+9
1.00e+9
8.00e+8
6.00e+8
4.00e+8
2.00e+8
0.00e+0
Cumulative Gas, ft3
0
10
20
30
Time (yr)

FIG. 6A

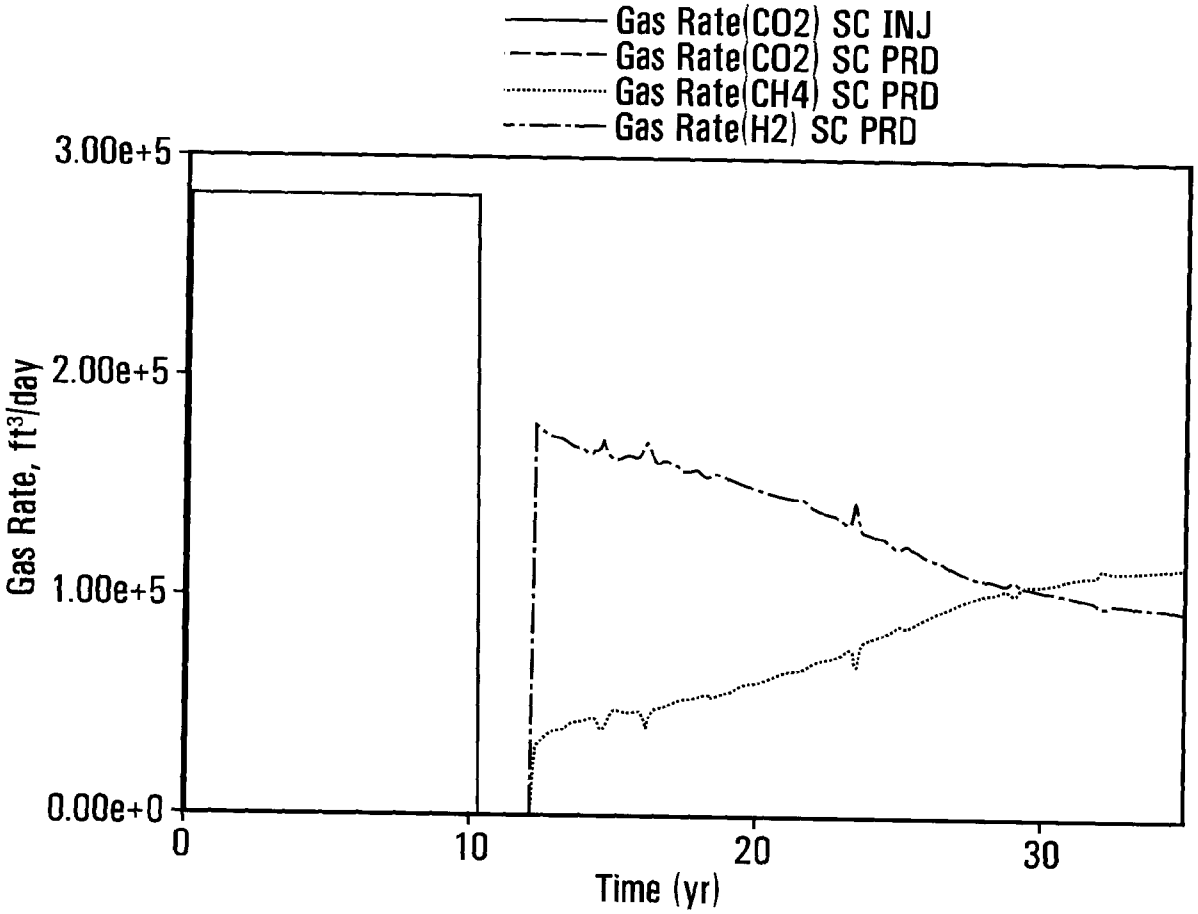
Gas Rate(CO2) SC INJ
Gas Rate(CO2) SC PRD
Gas Rate(CH4) SC PRD
Gas Rate(H2) SC PRD
3.00e+5
2.00e+5
1.00e+5
0.00e+0
Gas Rate, ft3/day
0
10
20
30
Time (yr)

FIG. 6B

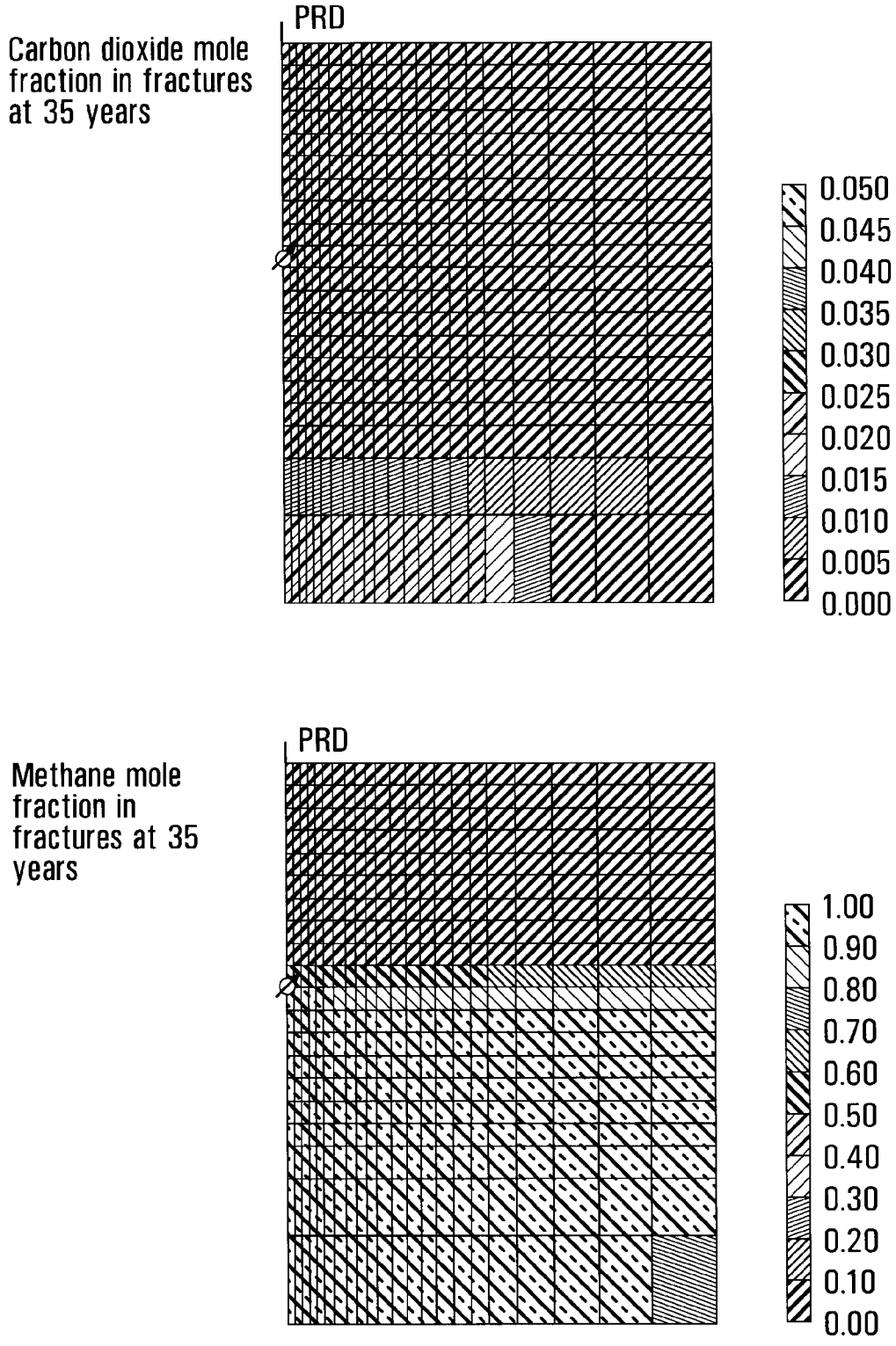
Carbon dioxide mole fraction in fractures at 35 years
PRD
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
Methane mole fraction in fractures at 35 years
PRD
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00

FIG. 7

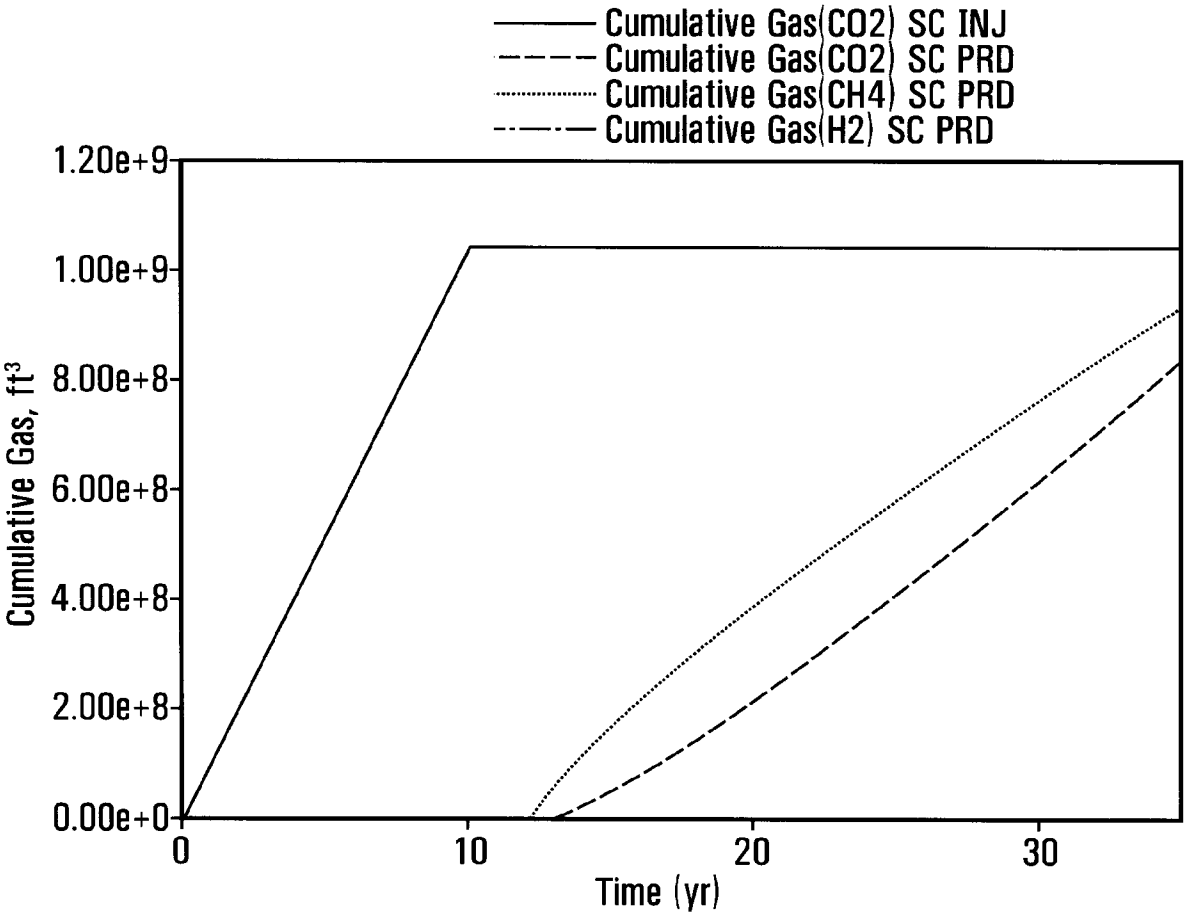
Cumulative Gas(CO2) SC INJ
Cumulative Gas(CO2) SC PRD
Cumulative Gas(CH4) SC PRD
Cumulative Gas(H2) SC PRD
1.20e+9
1.00e+9
8.00e+8
6.00e+8
4.00e+8
2.00e+8
0.00e+0
Cumulative Gas, ft3
0
10
20
30
Time (yr)

FIG. 8A

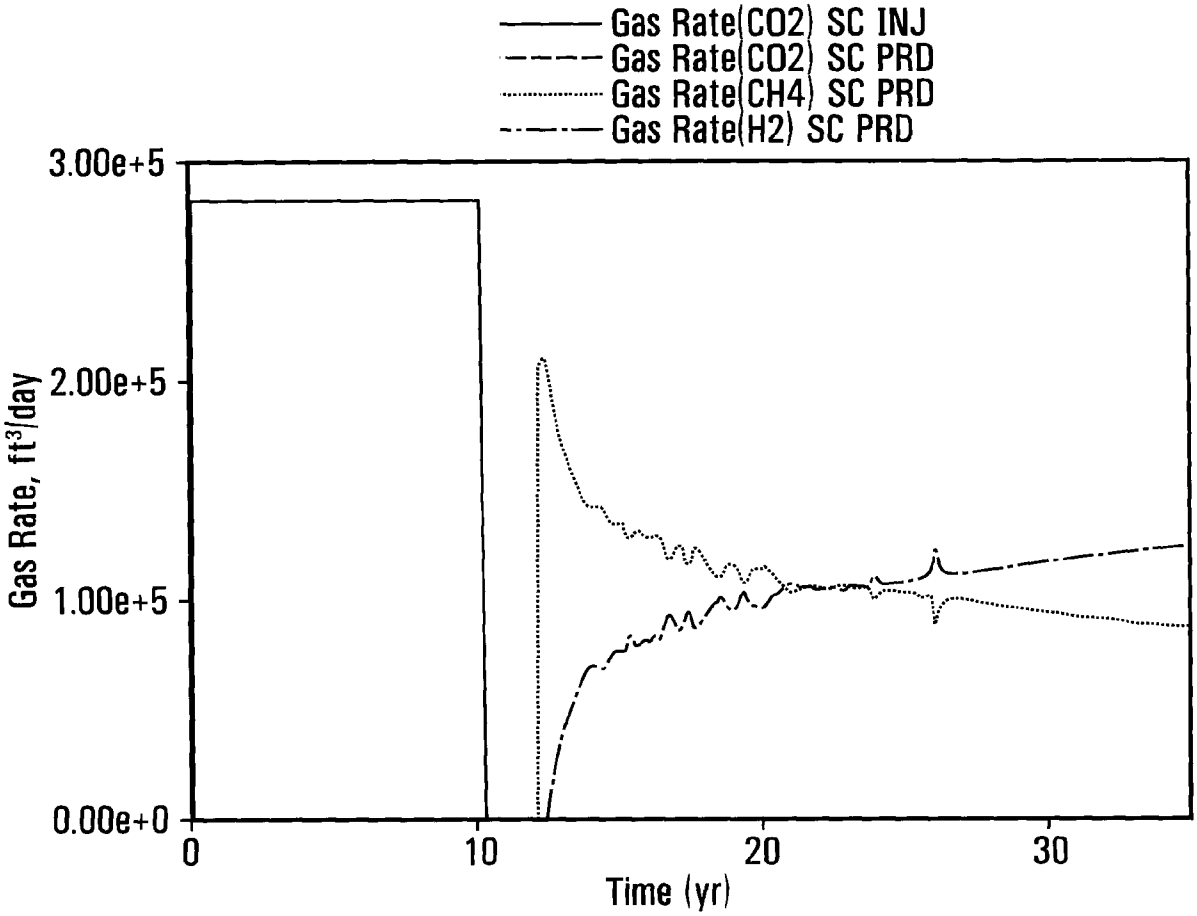
Gas Rate(CO2) SC INJ
Gas Rate(CO2) SC PRD
Gas Rate(CH4) SC PRD
Gas Rate(H2) SC PRD
3.00e+5
2.00e+5
1.00e+5
0.00e+0
Gas Rate, ft3/day
0
10
20
30
Time (yr)

FIG. 8B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2008/000717

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***C12P 5/02*** (2006.01) , ***A62D 3/02*** (2007.01) , ***B01D 53/84*** (2006.01) , ***C10L 3/00*** (2006.01) , *C12Q 1/02* (2006.01)
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C12P (2006.01) , ***A62D*** (2007.01) , ***B01D*** (2006.01) , ***C10L*** (2006.01) ,
C12Q (2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Delphion, CAPLUS, ENERGY, Scopus
Keywords: carbon dioxide, sequestering, sequestration, methane, subterranean, microorganism, microbe

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant	Relevant to claim No.
X Y	EP0963780 A1 (WILD, W.) 15 December 1999 Whole document	1 and 2 3-33
Y	WO2005/115649 A1 (LARTER, S.R. et al.) 08 December 2005 Whole document	3, 4, 6-17, 20, 22-33
Y	WO2005/115648 A1 (LARTER, S.R. et al.) 08 December 2005 Whole document	5, 17-19, 21, 27-33
Y	KOIDE, H. and YAMAZAKI, K., "Subsurface CO2 disposal with enhanced gas recovery and biogeochemical carbon recycling", ENVIRONMENTAL GEOSCIENCES, 2001, Vol. 8. No. 3, pages 218-224, ISSN: 1075-9565 Whole document	18, 26, 27 and 33
Y	DE4230644 A1 (MULLER, J.M.) 17 March 1994 Whole document	27-33

[ ] Further documents are listed in the continuation of Box

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 July 2008 (02-07-2008)	6 August 2008 (06-08-2008)

Name and mailing address of the ISA/CA	Authorized officer
Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476	Christiane Hansen 819- 934-5144

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2008/000717

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
EP 0963780A1	15-12-1999	AT 320302T	15-04-2006
		CA 2292073A1	13-06-2001
		CA 2292073C	11-12-2007
		DE 59813439D1	11-05-2006
		DK 0963780T3	10-07-2006
		EP 0963780B1	15-03-2006
		ES 2257788T3	01-08-2006
		PT 963780T	31-05-2006
		US 6664101B2	16-12-2003
		US 2003022324A1	30-01-2003
WO 2005115649A1	08-12-2005	BR PI0511635A	02-01-2008
		CA 2568574A1	08-12-2005
		CN 1988970A	27-06-2007
		EP 1776198A1	25-04-2007
		GB 0412060D0	30-06-2004
		NO 20066037B	26-02-2007
		US 2007251146A1	01-11-2007
WO 2005115648A1	08-12-2005	BR PI0511636A	02-01-2008
		CA 2569954A1	08-12-2005
		CN 1988971A	27-06-2007
		EP 1765529A1	28-03-2007
		GB 0412059D0	30-06-2004
		NO 20066038B	26-02-2007
		US 2007298479A1	27-12-2007
DE 4230644A1	17-03-1994	DE 4230644C2	19-09-1996