



CO₂ SEQUESTRATION IN COAL SEAMS WITH CO₂-ENHANCED GAS RECOVERY AND IN SITU FIRE-FREE GASIFICATION OF COAL

Hitoshi KOIDE, Waseda University

1.CO₂ SEQUESTRATION IN COAL SEAMS AND METHANE RECOVERY

In Japan, there remain 18.2 billion tons of possible coal reserves in technologically minable coal seams, while only one underground coal mine " Kushiro Mine" is still in operation. Most of coal seams cannot be commercially mined by conventional underground mining practices at the present and foreseeable economical and social circumstances in Japan. However, some R&D activities began to develop new type of " coal mines" without underground works (Figure 1). In once abandoned Akabira mine, power generation test of micro gas turbine is carried out using coal mine gas emitted from the old pit mouths and the combustion exhaust gas is injected into another old pit in order to improve recovery of coal mine gas and sequestration of exhausted CO₂ into old coal mine [1].

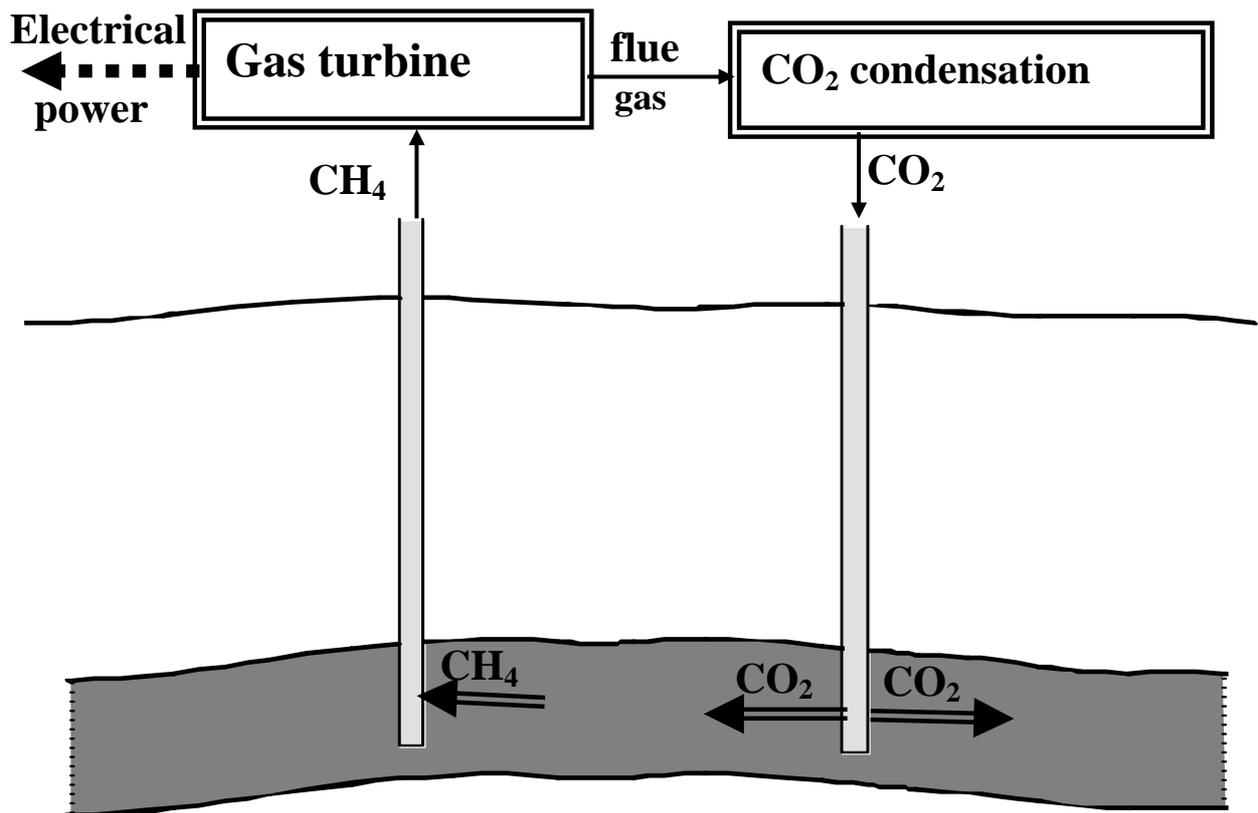


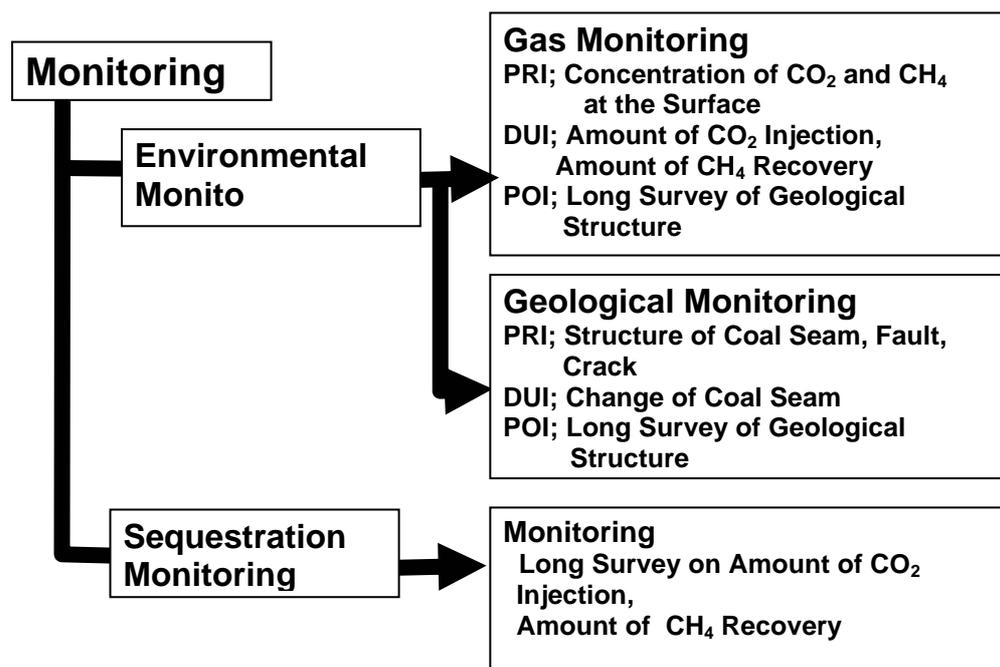
Figure 1: CO₂ emission-free closed-circuit system of electric power generation by CO₂-ECGR (enhanced coal seam gas recovery)

and Energy (ANRE) in the Ministry of Economy, Trade and Industry (METI) launched a new research and development project “ CO₂ sequestration in coal seams” (Fig.2). METI provided 246 million yen for the first year of the first phase of new national project. Kansai Environmental Engineering Center Co., Ltd.(KANSO) and JCOAL are main players of the R&D project including preliminary field tests on CO₂ sequestration in coal seams and coal seam gas recovery in a coal mine and on CO₂- ECGR in deep virgin coal seams. Research Institute of Innovative Technology for the Earth (RITE), Non Profit Organization (NPO) Think-tank Kyoto Institute of Natural History, Hokkaido University, Akita University, Kyoto University and Waseda University contribute to the fundamental researches of the national project. Kansai Electric Power Co. Inc., Mitsubishi Heavy Industries,Ltd. etc are also among the R&D team. The fundamental researches include studies on CO₂-CH₄ replacement mechanism, CO₂ behavior simulation, the optimum condition for CO₂ sequestration, CO₂ adsorption mechanism and CO₂ seepage behavior in coal seams. The development of CO₂ injection-CH₄ recovery technology, suitable CO₂ capture technology from flue gas, system analysis for operation, and investigation of CO₂ sequestration capacity in inland and offshore coal seams in and around Japan are also among main subjects of

the R&D project.

Monitoring technology for CO₂ sequestration in coal seams (Figure 3), environmental impact assessment, safety assessment and public outreach are emphasized in the geologically unstable Japanese archipelago.

Figure 3 MONITORING FOR CO₂ SEQUESTRATION IN COAL SEAMS (KANSO, 2002)



PRI: Monitoring before CO₂ injection,
 DUI: Monitoring during CO₂ injection,
 POI: Monitoring after CO₂ injection.

2.SUPERCritical CO₂-ECGR AND MICROBIAL GASIFICATION OF COAL

The Ariake Coalfield is the offshore extension of the old Miike Coal Mine that was the largest coal

mine in Japan with the maximum annual coal output of 6.57 million tons in 1970 but closed in 1997. Offshore extensions of main four coal seams in the old Miike Mine become deeper in the westward-dipping Paleogene Miike Coal Bearing Formation in the Ariake Coalfield. Measured adsorption capacity of the Miike coal is 72.3 kg-CO₂/ton-coal on an average. Total CO₂ sequestration capacity in the submarine Ariake coal seams is about 32 million tons-CO₂.

CO₂ is highly soluble in water under high pressure. CO₂ sequestration is also possible in dissolved state in groundwater in pores of underground rocks. Paleogene rocks in the Ariake coalfield are abundant in sandstone of average porosity 7.04%. Average geothermal gradient is 3.2°C/100m. Pore fluid pressure and temperature can be estimated from the depth. CO₂ solubility is estimated from fluid pressure and temperature. The Miike Coal Measure can sequester 104 million tons of CO₂ and upper Paleogene sandstone of the Yotsuyama Formation can sequester 174 million tons of CO₂ in dissolved state in groundwater. The Paleogene formations in the Ariake coalfield are covered by Quaternary impermeable clay layers. Therefore, coal seams and Paleogene sandstone in the submarine Ariake Coalfield can accommodate total 300 million tons of CO₂ in dissolved state in groundwater.

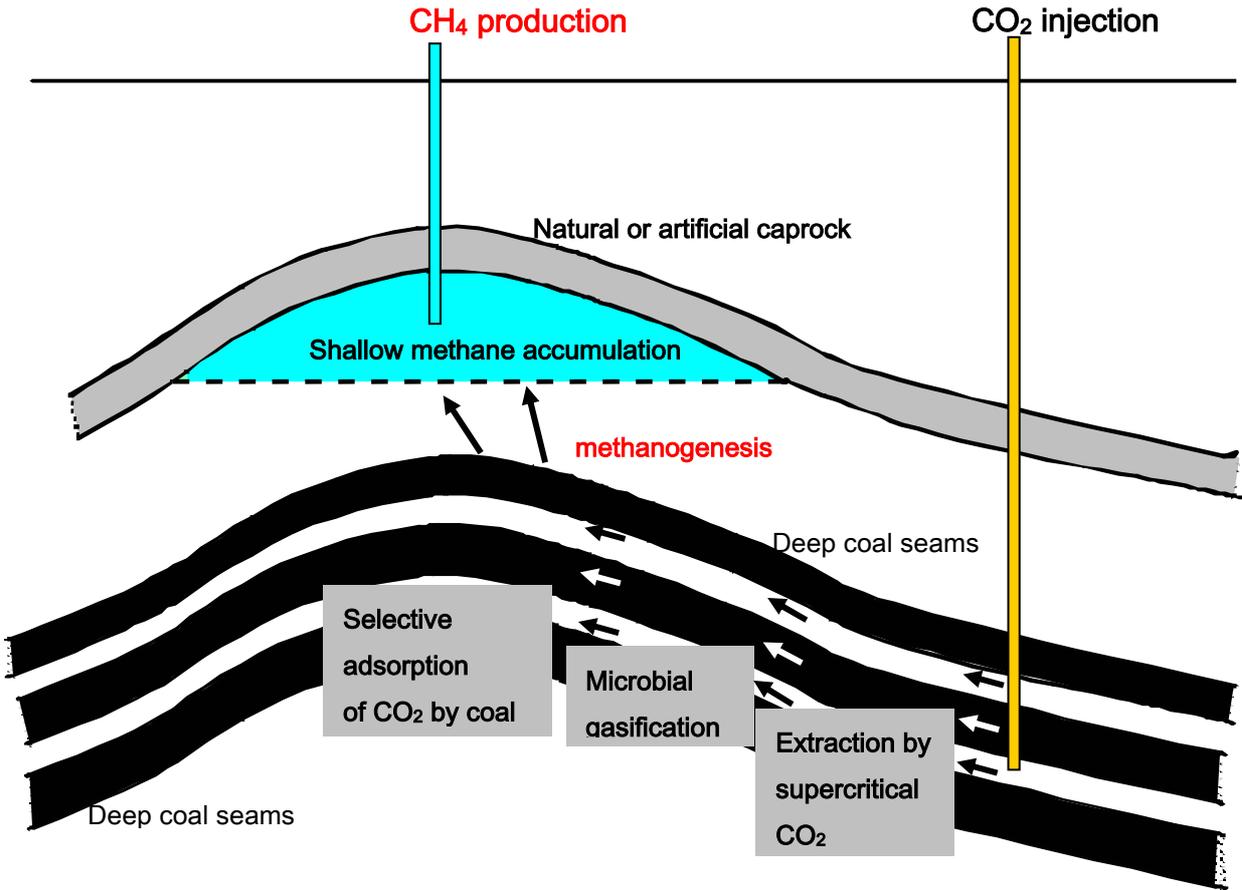


Figure 4: Supercritical CO₂-enhanced coal seam gas recovery (ECGR) and in situ fire-free microbial gasification of coal

The Miike coal contains only 6 m³-methane/ton-coals on an average [5]. Coal seam methane is too poor to realize closed-circuit power generation in the Ariake-Miike Coalfield. However, almost pure CO₂ can extract efficiently volatile components of coal as a supercritical fluid at high pressure. The critical pressure of CO₂ is 7.39 MPa. The critical temperature of CO₂ is 31.1°C. Almost pure CO₂ (99.9%) is extracted from the flue gas using monoethanolamine (MEA) or improved solvent KS-1[6]. Injected pure CO₂ behaves readily as a supercritical fluid around injection wells in deep coal seams (Fig.4). Pressured CO₂ dissolve in groundwater around supercritical fluid zone. Microbial gasification is ready in the mixture of coal, CO₂, water and extracted carbon compounds. Finally, selective adsorption of CO₂ and desorption of methane in coal enrich the hydrocarbon gas mixture (Figure 4). In the laboratory, 35 to 50% of coal can be converted to methane using genetically adapted bacterial cultures, which is equivalent to 534 to 763 m³/ton [7]. Supercritical CO₂-enhanced coal seam gas recovery (ECGR) and in situ fire-free microbial gasification of coal can produce sufficient amount of methane for the CO₂ emission-free closed-circuit power plant and new type of “ coal mine” without underground works even in gas-poor coalfields.

3.BIOGEOCHEMICAL CARBON CYCLE IN TERTIARY SEDIMENTARY BASINS

In Japan, Paleogene sedimentary formations often contain bituminous coal seams but Neogene sedimentary basins contain only lignite, peat, coaly materials or other fossil organic matter. However, lignite, peat, coaly materials and fossil organic materials in black shale can be sources of biogenic methane. Sedimentary basins often contain abundant organic materials. Subsurface microbes combined with effects of compaction, tectonic load and geothermal heat decompose buried organic materials and produce abundant natural gas. Methane-rich gas dissolved saline groundwater and adsorbed in coal seams suggests active methanogenesis in sedimentary basins.

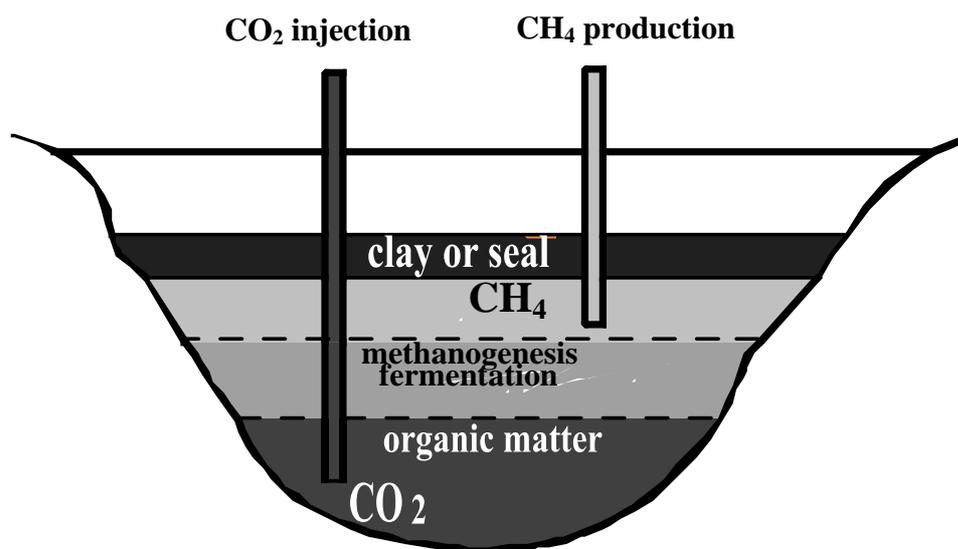


Figure 5: Microbial carbon recycling in a sedimentary basin

Chemolithotrophic microbes can fix CO₂ into organic acids. Eventually methanogens reduce CO₂ into methane. Coal seams, coaly matters or tuffaceous layers adsorb CO₂ to prevent migration. Saline aquifers in deep

sedimentary basins dissolve CO₂ to prevent leakage. Injection of CO₂ into deep coal seams or saline aquifers induces entrapment of CO₂ and exsolution of methane as methane is ready to migrate upward than CO₂. Counter extraction of methane from shallower formations prevents emanation of methane into the atmosphere and supplies a low-carbon fuel (Figure 5). Methanogenesis will restore biogenic gas in the sedimentary basin.

Nakai [8] made carbon isotope measurements on several dissolved natural gas deposits in Japan and found that carbon in CH₄ has isotopic values ranging from -65.5 to -74.8 per mil deviated from P.D.B. standard, while carbon in CO₂ has isotopic values from +2.0 to -12.2 per mil. He concluded that an isotopic equilibrium between CH₄ and coexisting methane indicates that bacterial processes formed these aquifers saturated with methane. Extremely light isotopic compositions of carbon in CH₄ suggest that methanogens formed some of dissolved methane deposits in Japan. Anaerobic chemoautotrophic methanogens belong to Archaea that are similar to early microorganisms that evolved in anoxic harsh environments on the primitive Earth. Methanogens have wide diversity. Many of them can survive in extreme environments such as high temperature, high pressure and high salinity. Most of methanogens form CH₄ from CO₂ and H₂ and gain energy.



Thus, bacterial methanogenesis is made without help of sun light. Methanogens are blamed for greenhouse gas emission as they produce methane in bowels of cows and termites and in rice paddy, as they are abundant in such anoxic habitats. Anaerobic microorganisms are abundant and active even in deep aquifers. Accumulations of methane-rich natural gas of bacterial origin have been found in many sedimentary basins in the world [9]. Stevens and McKinley [10] found that methanogens are active in aquifers deeper than 1000m in the Columbia River Basalt Group, U.S.A. Bacterially formed methane are formed even in the depth of 4,500m in the Po basin, Italy [11].

If CO₂ is injected into aquifers and dissolved in groundwater in which methanogens are active, methanogens reduce CO₂ into CH₄ as long as H₂ is available. Methane is less soluble in water and lighter than CO₂. Therefore, methane tends to be separated from water and migrate upward. If there exist no traps, methane is emitted finally into the air to accelerate global warming. Methane is much more efficient greenhouse gas than CO₂. However, if the aquifer has geological trapping structure, methane tends to accumulate at the top of reservoir under cap rock and may revive natural gas deposits (Fig.6). Chemotrophic methanogenesis is usually much slower than photosynthesis. However, appreciable amounts of biogenic methane probably form during tens or hundreds of years of CO₂ storage in aquifers at adequate conditions.

Deep aquifers are usually at high temperature, at high pressure and often at high salinity. Some kinds of methanogens, belonging to Archaea, are active at extreme conditions such as high pressure, high

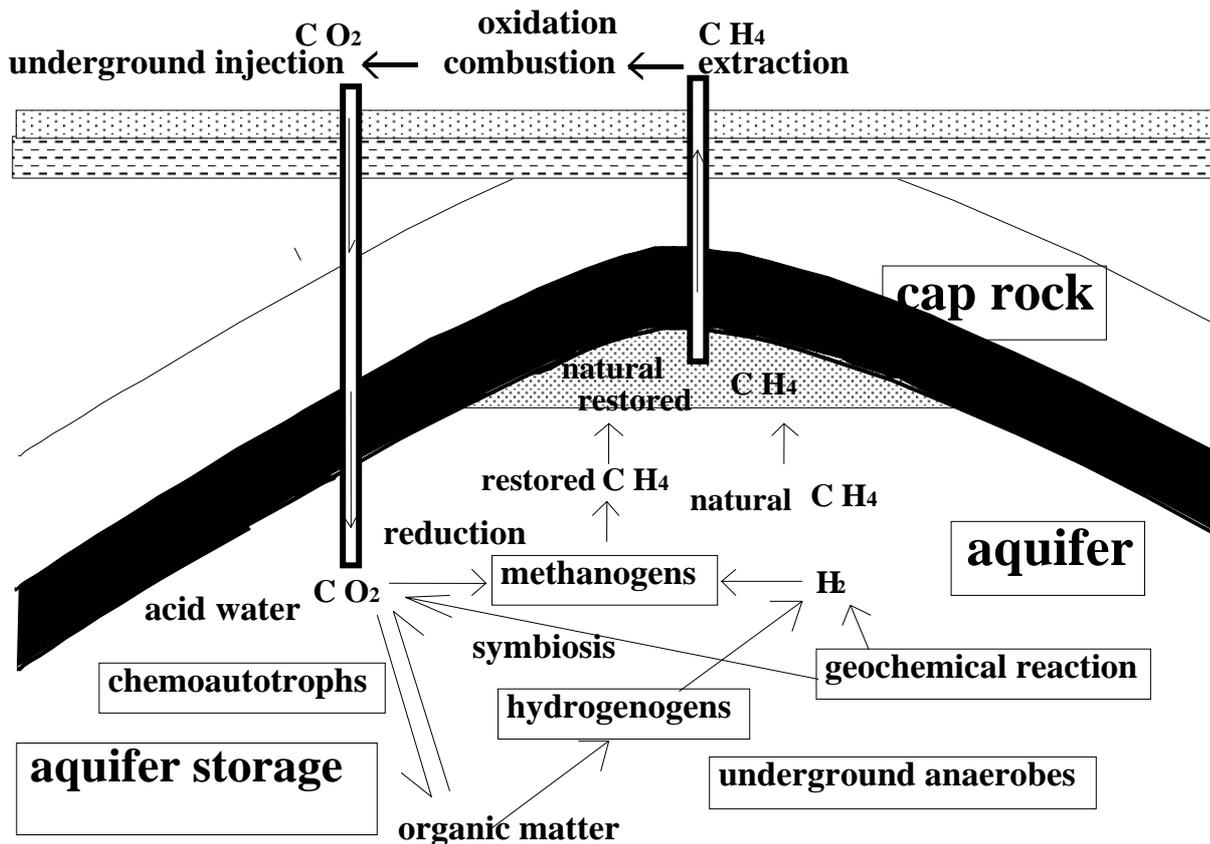


Figure6: Microbial restoration of methane deposits in CO₂ aquifer storage

temperature and high salinity. As metabolism is faster at higher temperature, warm aquifers are favorable for fast methane production unless temperature is too high. Thermophilic methanogens such as *Methanobacterium thermoautotrophicum* and *Methanococcus jannaschii* are possibly suitable for fast brew of methane. Extensive search for favorable species is needed as methanogens have wide diversity.

Hydrogen H₂ supply into CO₂-dissolved groundwater is key to biogenic restoring of methane deposits, because hydrogen is energy source for methanogenesis. Stevens and McKinley [10] pointed out that basalt - water reaction supplies hydrogen to induce active methanogenesis in deep basalt aquifers. Hydrogen is supplied by deep water-rock interaction in active geothermal regions. Anaerobic hydrogenogens produce H₂ from organic matter. Symbiosis of methanogens and hydrogenogens is favorable for active production of methane, as hydrogenogens are active when methanogens consume H₂ for methanogenesis. Adequate set of methanogens and hydrogenogens should be searched to form suitable ecosystem for methanogenesis in aquifers. As many sandy aquifers are not rich in organic matter, organic materials should be enhanced for active fermentation by alternate injection of CO₂ and organic fluid waste or solution of organic matter that is otherwise to emit CO₂ and/or CH₄ finally into the air. Elimination or reduction of sulfate is important as sulfate reducers prevent methanogenesis [12]. The coordinated ecosystem may efficiently rejuvenate methane

deposits during CO₂ aquifer storage.

Chemoautotrophs fix CO₂ into organic matter without help of sun light. A mixotrophic bacterium, a kind of *Pseudomonas* which was separated from an oil spill at Sagara oil field, Japan, converts CO₂ into medium-chain alkane and alkene anaerobically in the presence of H₂ [13,14]. This finding suggest possibility of bacterial oil production in addition to chemoautotrophic fixation of CO₂ during aquifer storage of CO₂ .

Underground biogeochemical carbon recycling makes zero-emission closed-circuit power and heat generation possible, while coal seams and saline aquifers are capacious enough to accommodate large volume of CO₂ from fossil fuel and refuse-derived fuel (RDF). Tertiary sedimentary basins are suitable as CO₂ storages, hydrocarbon gas reservoirs and possible CO₂- CH₄ converter. For an example, around Lake Biwa, Shiga Prefecture, Southwest Japan, methane gas has been used for source of energy in domestic usages since more than one hundred years ago. The methane gases are impregnated in sedimentary layers under high pressure in subsurface reducing environment. The methanogens are strong candidate to generate methane from carbonic materials and carbon dioxide in anoxic sediments. An underground closed-circuit “ methane factory” is proposed to process waste gas of a bio-power plant in the bottom of sedimentary basin where the CO₂-rich waste gas and organic materials are converted into CH₄- rich biogenic gas. Preliminary survey of the southwest part of Kanto sedimentary basin, too, revealed that late Pliocene- early Pleistocene saline sandstone aquifer can store about two billion tons of CO₂ in the dissolved state. The southwest Kanto aquifer is covered by

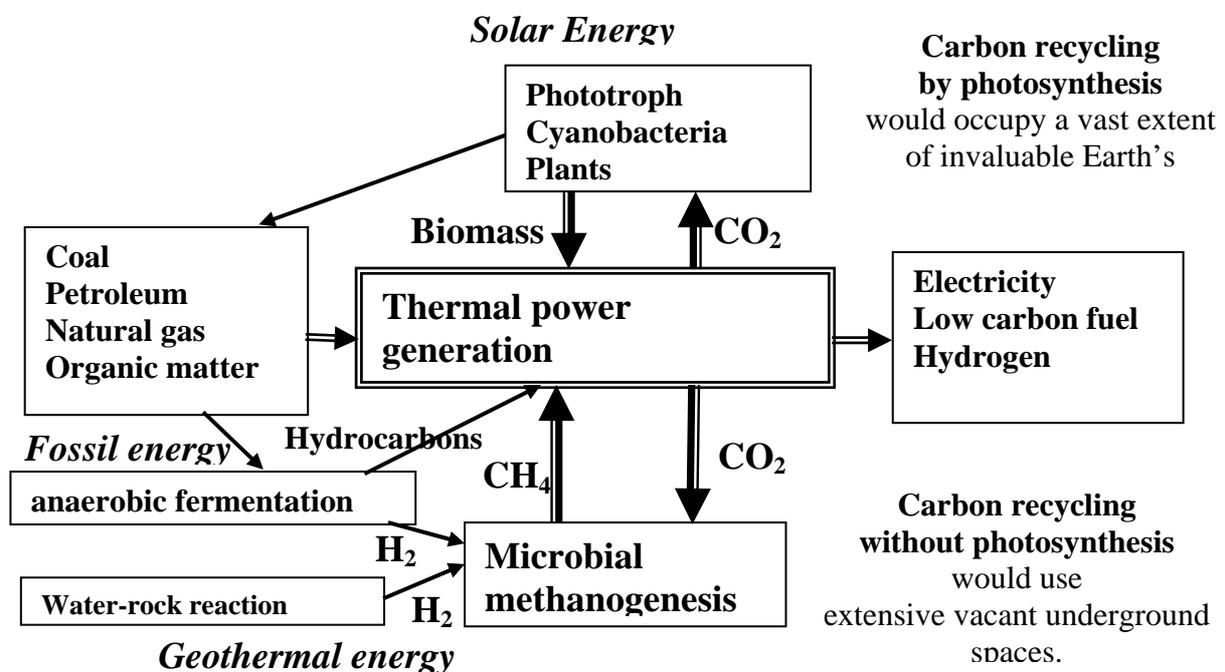


Figure 7: Underground anaerobic microbial carbon recycling

mudstone layers and close to major CO₂ sources in the Yokohama area.

4.CONCLUSION

RITE and NPO Think-tank Kyoto Institute of Natural History started a R&D program on “ underground microbial CO₂ sequestration and methane factory (2002-2004)” . RITE also started another new R&D program on “ hydrate and geochemical sequestration of CO₂ in deep underground and ocean bottom environments (2002-2004)” for advanced stable carbon isolation [15, 16].

Subsurface geochemical and biogeochemical carbon recycling may realize greenhouse gas control with restoration of energy resources (Figure 7). Underground anaerobic microbial carbon recycling provides a new access to hidden another natural carbon cycle driven by geothermal energy and untapped fossil energy without solar energy. Monitoring and analysis of carbon cycle in geosphere and study of geosphere-biosphere interaction are needed for greenhouse gas mitigation and comparable solution of energy problems.

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**CO₂ SEQUESTRATION IN COAL SEAMS
WITH CO₂-ENHANCED GAS RECOVERY
AND IN SITU FIRE-FREE GASIFICATION OF COAL**

**CO₂ SEQUESTRATION EN LES FORMATIONS CHARBONNIERES
AVEC LA PRODUCTION CO₂ -AUGMENTEE DE GAZ ET
LA GAZEIFICATION SOUTERRAINE DE CHARBON SANS FLAMBER**

**Hitoshi Koide
(Waseda University, Tokyo)**

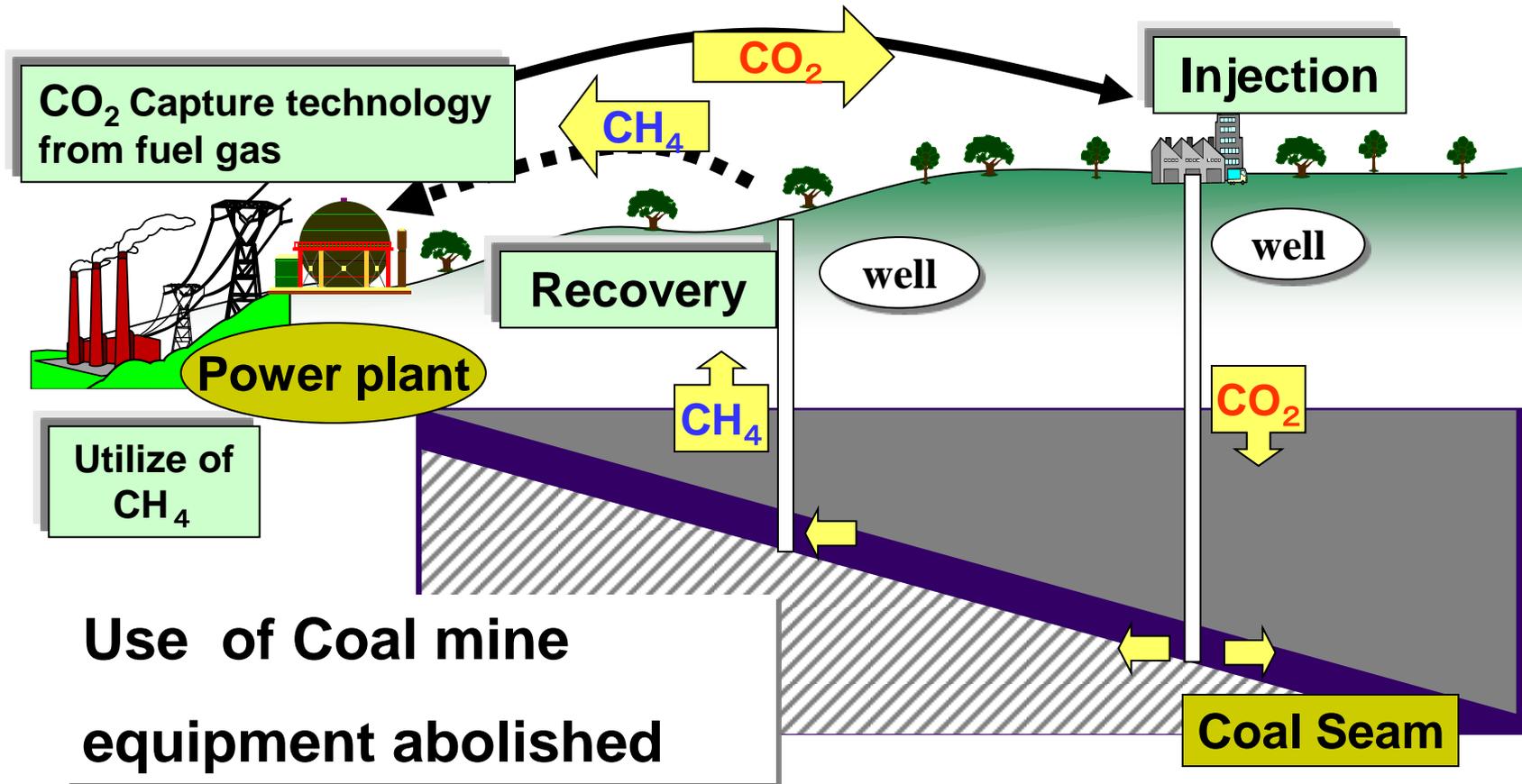
New research and development project

“CO₂ sequestration in coal seams”

METI-ANRE-KANSO-JCOAL

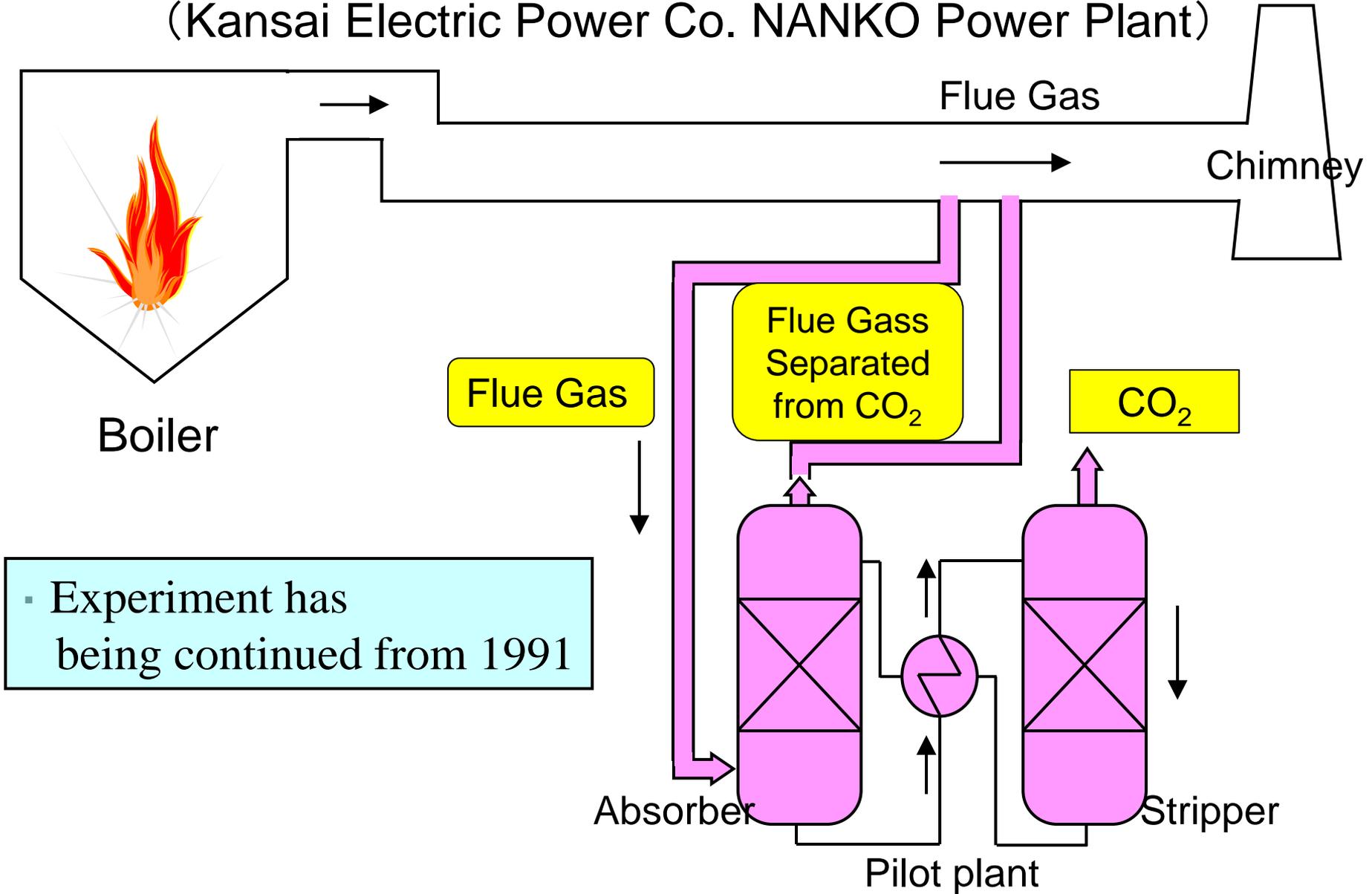
		2002	2003	2004	2005	2006
Phase I Fundamental Researches	Laboratory experiments CO ₂ - CH ₄ replacement mechanism, CO ₂ behavior simulation, Optimum Condition for CO ₂ Sequestration, and so on	■	■	■	■	■
	Examinations System analysis, Monitoring technology, and so on	■	■	■	■	■
	Preliminary field test	■	■			
Phase II Micro-pilot tests				■	■	■

Image of CO₂ Sequestration in Coal Seam



CO₂ Recovery System

(Kansai Electric Power Co. NANKO Power Plant)



Subjects in Phase I

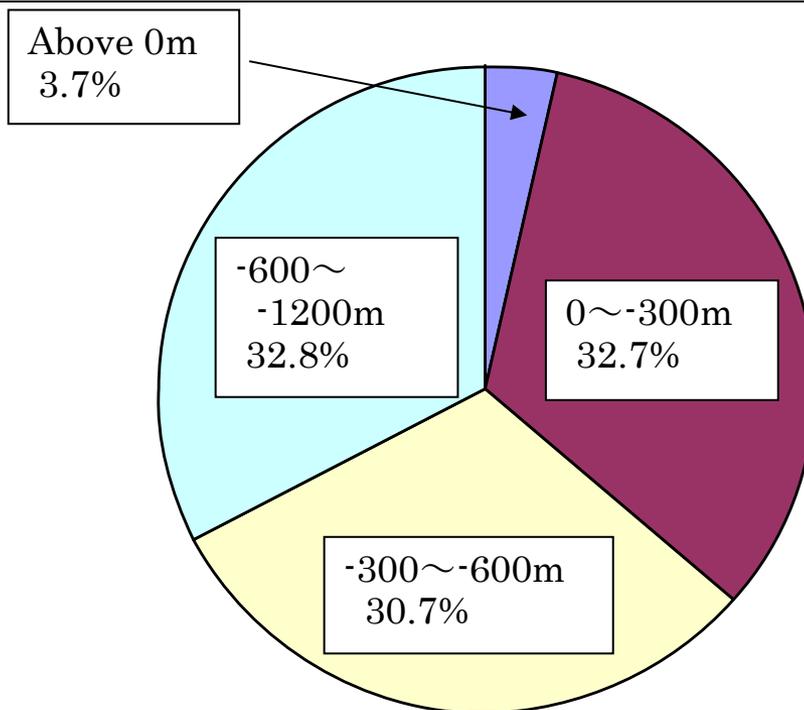
- **Understanding of CO₂-CH₄ replacement mechanism**
- **Development of CO₂ behavior simulation**
- **Interpretation of absorption properties of supercritical CO₂ in the deep coal seam**
- **Establishment of the optimum site conditions**

Subjects in Phase II

- **Micro-pilot tests will be implemented for the development of the integrated system including CO₂ sequestration in deep coal seams**
- **Recovery/utilization of coalbed methane**
- **Establishment of Total system**

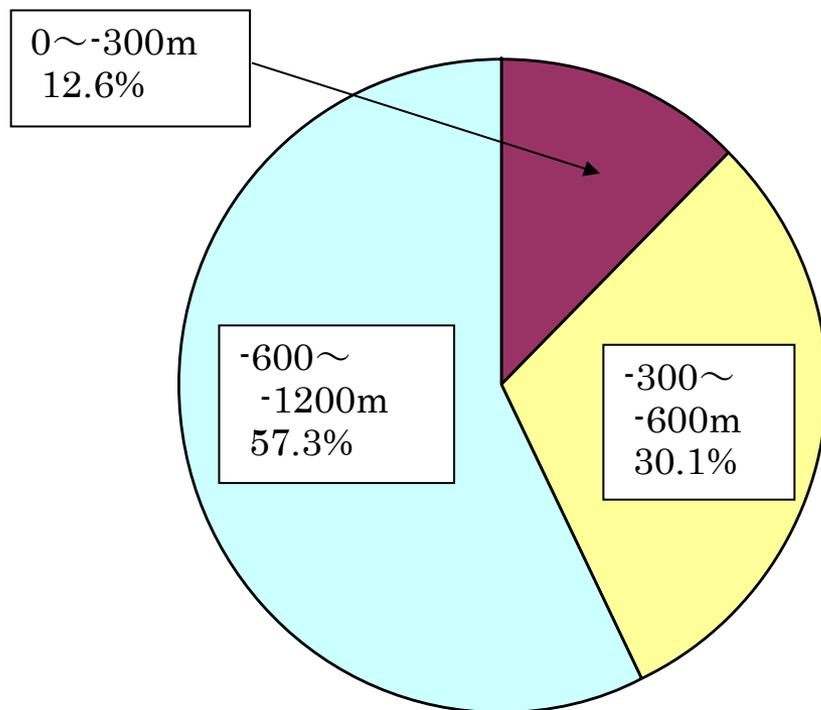


Remaining coal reserve in old coal mines
Total 18.5 Gton in Japan



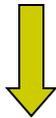


CO₂ sequestration capacity in old coal mines
Total 600 Mton

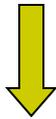


Why Monitoring?

Work Project



Environmental
Assessment



Monitoring

Society Agreement Formation

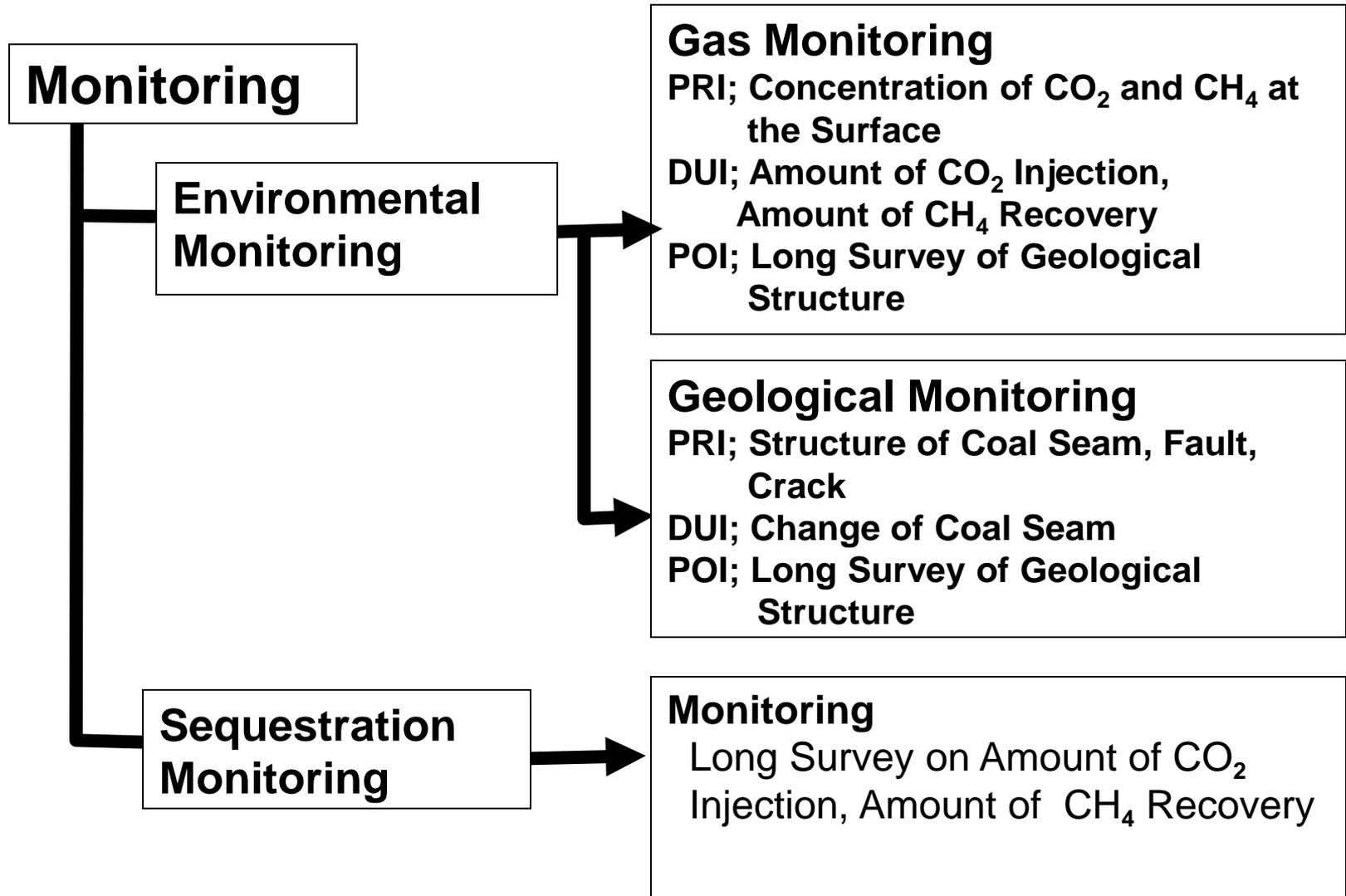
(Ground)

- Environmental Impact Assessment
- Examination of Method and Measurement item
- Communication with Public

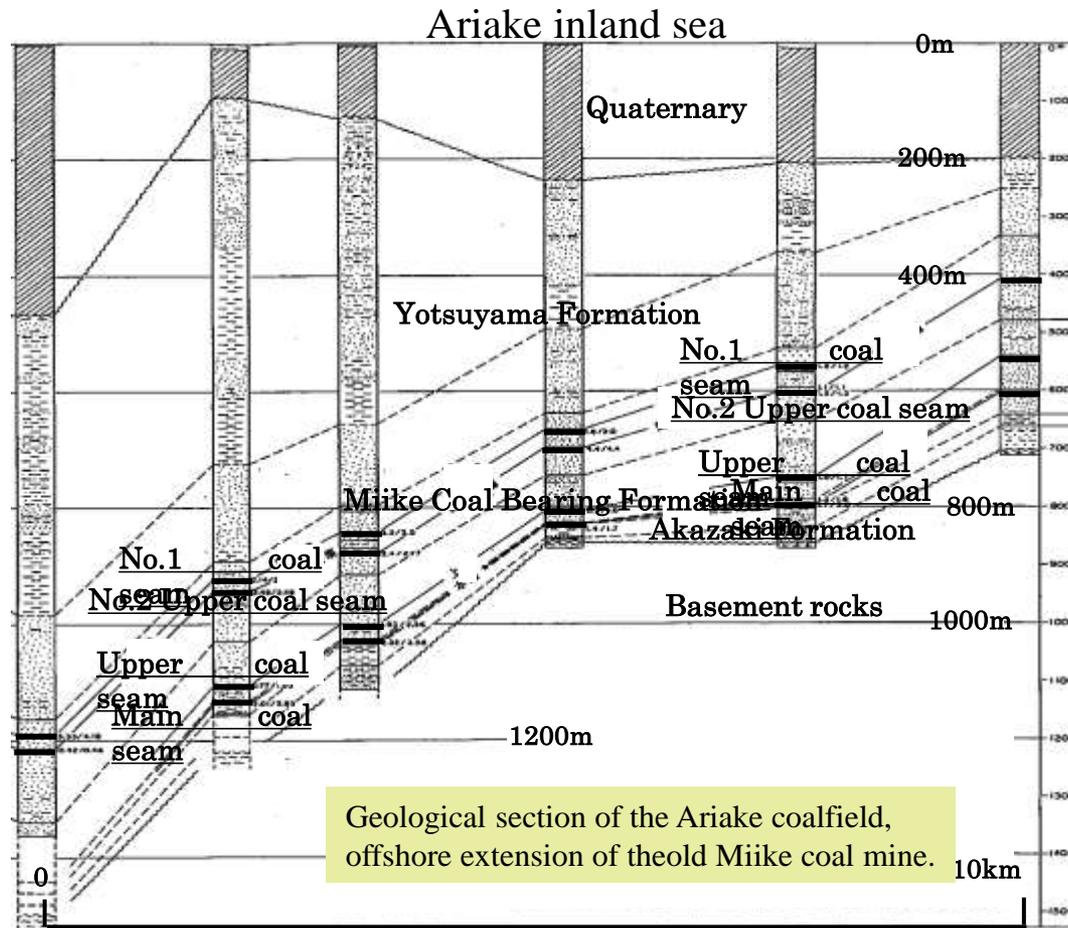
Un-sureness of Prediction

- Environmental Impact on development
- Safety Assessment

Monitoring concept for ECBMR

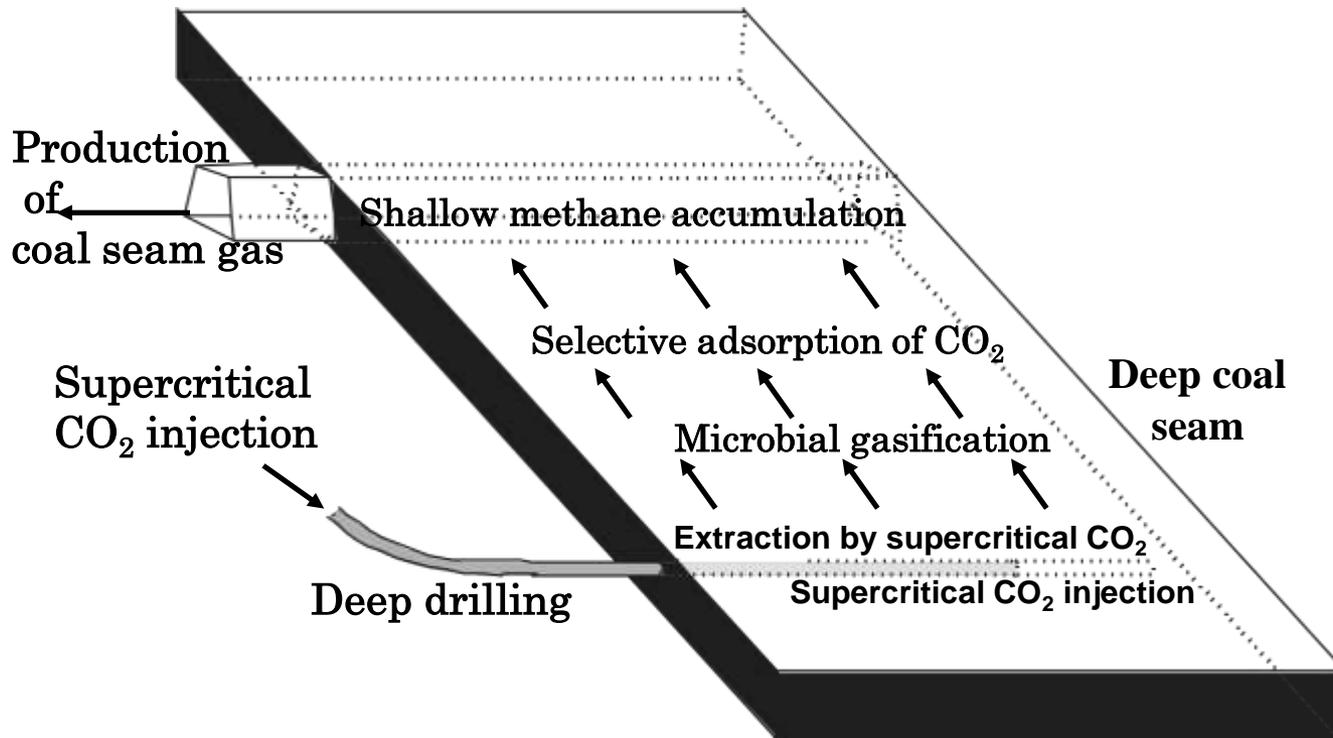


Offshore deep extension of coal seam is hopeful CO₂ sink in Japan

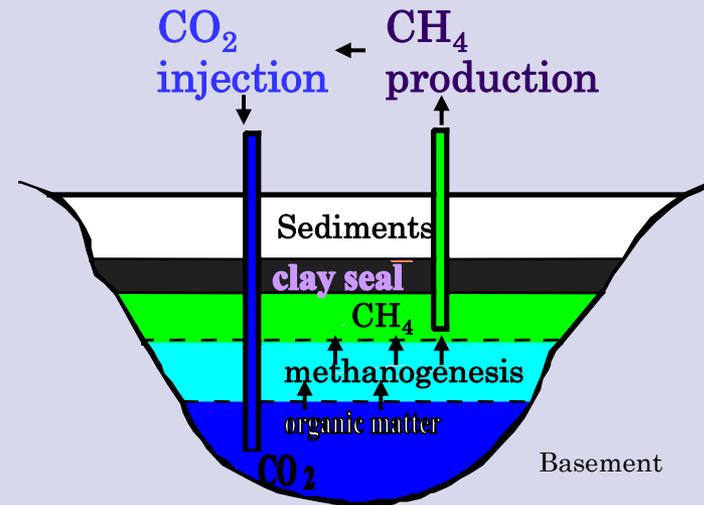
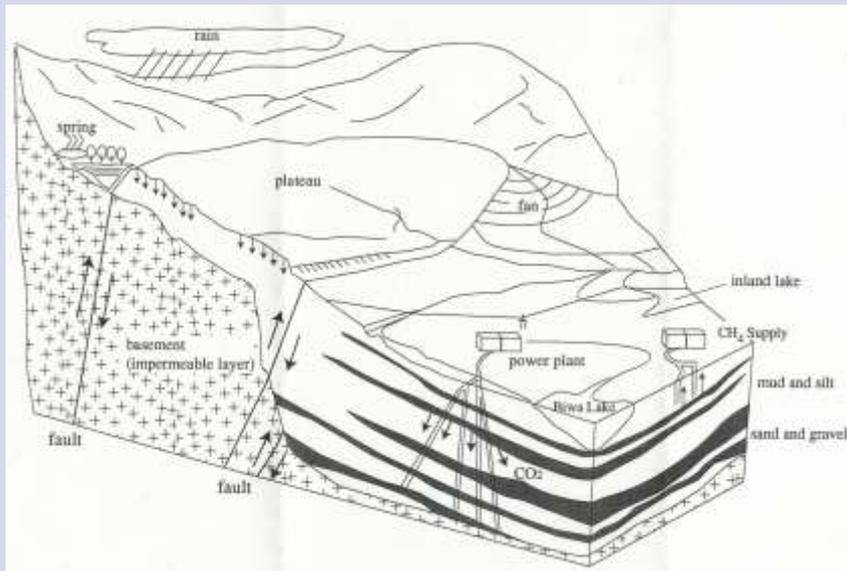


Advanced CO₂ sequestration concept

**Supercritical CO₂-enhanced coal seam gas recovery (ECGR)
and in situ fire-free microbial gasification of coal**



Microbial carbon recycling in a sedimentary basin



Underground anaerobic microbial carbon recycling

