553. 981:550. 94 (52)

Geochemical Prospecting for Natural Gas Field of Dissolved-in-Water Type in Japan*

by
Koji Motojima**

1. Geochemical Characteristics of Natural Gas Field of Dissolved-in-Water Type

Natural gas field of this type is the workable accumulations of natural gas consisting mainly of CH_4, dissolved in groundwater.

Static pressure of groundwater increases by 1 atm. pressure at every 10 m in depth, and 33 m*l* of CH_4 can be dissolved in 1 *l* of water at room temperature under one atm. pressure. Therefore, one volume of groundwater can dissolve 1.25 volume of CH_4 at the depth of 500 m, 2.1 volume at 1000 m and 2.7 volume at 1400 m. Therefore, this type of natural gas field of economic value is formed.

In Japan, there are many natural gas fields of this type, which are economically important. Characteristics of this type of natural gas fields can be summarized as follows:

(a) Geological horizon: Recent—Miocene. Fields of Pliocene and Pleistocene age are economically most important.

(b) Sedimentary facies: Wide varieties of sedimentary facies have been observed, but large scale fields have been mainly found in marine facies.

(c) Reservoir rocks: Loose sands and pebbles are the best rocks as gas reservoir. Gas reservoir of the Miocene age is fracture type. Gas production (Q_g, m³/day) is a function of gas-water ratio at casing head (R, Calculated from m³/k*l*) and volume of groundwater producted per day at the well (Q_w, k*l*/day), and can be expressed as $Q_g = R \times Q_w$. Since R is determined by depth, Q_g is mainly determined by Q_w. Q_w is determined by permeability of reservoir rocks.

(d) A very intimate relation has been observed between natural gas and associated water. Natural gas mainly consists of CH_4, CO_2 and N_2. When CH_4 content is high, gas-water ratio is high, in which case, contents of HCO_3^-, NH_4^+, $KMnO_4$ cons. (Cl^-, I^-, B in the case of marine facies and P in fresh water facies) in water increase. In the case of younger gas field (Recent—Upper Pleistocene), when gas-water ratio is high, CO_2 content increases and the water tends to be acidic.

(e) The genesis of this type of natural gas field can be fully explained by the process of organic carbon $\rightarrow CH_4 + CO_2$, $CO_2 \rightarrow CHO_3^-$ and organic nitrogen $\rightarrow N_2 + (NH_4^+)$.

2. Methods and Techniques of Geochemical Prospecting

2. 1 Field Survey

Geology, topography and climate of the area should be studied through literatures before commensing field survey. Geologic age, sedimentation environment, facies and fossils of and in the strata, igneous rocks, geological structure, hot and cold springs in the area should be studied before field work. The scale of survey (cost of survey, number of surveyors, number of days for survey, apparatus to be used) should be fixed by considering the above informations

*This paper is prepared for ECAFE Seminar on "Geochemical Prospecting Methods and Techniques" (Aug. 1963, Bangkok)
**Technological Department

as well as traffic situation and climate of the area. A small chemical analyses laboratory to be used as the basement should be set up in the area.

Wells, hot and cold springs in the area are utilized for measurement. If there is no such point in the area, bore holes of about 10 m depth are drilled using simple boring instrument, from which water and gas samples for chemical analyses are collected.

Aspects to be measured at each measuring point are: Location of the point, climate, environment of the point, depth and diameter of the well, materials of casing, method of making the well, age of the well, status of water shut-off, geology of the well, position of strainer, water level, method of sampling, temperatures of air and water, volumes of natural gas and water, gas-water ratio, appearance, taste and smell of water.

Methods of field analyses of groundwater are as follows:

pH and RpH—are obtained using colorimetric method.

HCO_3^-—can be measured from alkalinity of methyl-orange, and is expressed by mg/*l*.

free CO_2—can be obtained from acidity of phenolphthalein and is expressed by mg/*l*.

CO_3^{2-}—is obtained from alkalinity of phenolphthalein and expressed by mg/*l*.

total CO_2—can be obtained by calculation from the values of HCO_3^- and free CO_2 ($pH<8.3$) or of HCO_3^- and CO_3^{2-} ($pH>8.3$), and is expressed either by mg/*l* or m*l*/*l*.

Cl^-—is obtained by Mohr's method and expressed by mg/*l*.

Redox potential—is obtained using portable pH meter and expressed by mV.

NH_4^+—is measured using Nessler reagent and expressed by mg/*l*.

Fe^{2+}, Fe^{3+}—is measured by either thiocyanate or α—α' dipyridyl methods and expressed by mg/*l*.

P—is measured using molybdenium blue and expressed by mg/*l*.

SO_4^{2-}—is measured through nephelometry using barium sulphate and expressed by mg/*l*.

dissolved O_2—is measured from the value of O_2 absorbed in pyrogallolic alkali, after driving out CH_4+N_2+Ar from water using CO_2 bubble, and expressed by m*l*/*l*.

dissolved CH_4+N_2+Ar—is obtained from the value of residual gas described above, and expressed by m*l*/*l*.

dissolved CH_4—is driven out by air from water and measured by optical interferometry and expressed by m*l*/*l*.

Chemical components to be analysed at the basement are as follows:

Ca^{2+}, Mg^{2+}—is measured through titration using E.D.T.A. and expressed by mg/*l*.

$KMnO_4$ cons.—is obtained through back titration and expressed by mg/*l*.

NH_4^+—is absorbed in H_2SO_4 through air distillation and measured using Nessler reagent and expressed by mg/*l*.

CH_4, CO_2, O_2 and residual gas ($=N_2+Ar$)—are measured by Orsat method and expressed by vol. %.

The following chemical components are usually analysed at the chemical laboratory on return to institute.

CH_4, C_2, C_3, CO_2, N_2, H_2, Ar, He in gas—are measured using gas-chromatographic or mass-spectrometric methods and expressed by vol. %.

Na^+, K^+—are measured using a flame-photometer and expressed mg/*l*.

I^-, Br^-, B, Mn^{2+}, Si, T.S.M.—are obtained by wet chemical analyses.

2. 2 Survey by Drilling

Since interstitial water in mudstone near a gas reservoir of the younger strata generally has similar chemical composition as reservoir fluid, gas potentiality (≒ gas-water ratio) of the reservoir can be estimated from systematic chemical analyses of the interstitial water of the mudstones.

Intervals between the points of core sampling are determined to be from 5 to 50 m, in accordance with the geological condition of the hole. Methods of measurement are as follows:

Specific gravity—is measured using weighing bottle as pycnometer.

Water content—is obtained from dry loss at 105 °C, and expressed either by vol. % or wt. %.

Cl^-—is obtained using Mohr's method from centrifugally separated liquid from the sample crushed in distilled water, and expressed by mg/l after multiplying with the next factor R.

Dilution ratio (R)—is obtained from the equation $R = (a+b)/b$, where a is volume of H_2O added to the core sample and b is volume of interstitial water in the sample.

Ph, HCO_3^-, $KMnO_4$ cons., SO_4^{2-}, NO_2^-—are obtained by the similar way as above.

In some cases, mother rocks of the gas are examined through the measurements of contents of organic C and hydrocarbon in the mudstones. Characteristics of the sedimentary basin of the area are also considered in some cases on the standpoint of economic geology, from the date of inorganic components of the rocks in the area.

2. 3 Interpretation of Results

It is most important to interpret the results of chemical analyses in connection with the genesis of the gas field. Since ground-fluids have general geochemical characteristics as tabulated below according to the status of natural gas accumulation, gas potentiality can be judged from the table. Therefore, it can be predicted that the groundwater contains high amount of methane gas, if the strata of the surveyed area are younger than Pliocene and marine origin, and groundwater shows high content of Cl^-, HCO_3^-, I^-, NH_4^+, organic C.

Composition of Groundwater	Natural Gas Accumulation		
	None gas Area	Poor gas Area	Rich gas Area
pH (Quaternary	≒ 7	≒ 7	< 7
pH (Tertiary			> 7
free CO_2 (Quaternary	+ (<50 mg/l)	++ (50–100 mg/l)	+++ (>100 mg/l)
HCO_3^-	+ (<100 mg/l)	++ (100–200 mg/l)	+++ (>200 mg/l)
NH_4^+	<1mg/ l	1–2 mg/l	> 2 mg/l
NO_3^-	++	+	—
SO_4^{2-}	+++	+	—
NO_2^-	—	+	—
P (fresh water sediments)	—	+	+++ (>0.3 mg/l)
$KMnO_4$ cons.	+	++	+++ (>50 mg/l)
Fe^{2+}	—∼+	+	+++
dissolved O_2	2—8 ml/l	0.0–0.2 ml/l	0.2–0.5 ml/l
dissolved N_2	14—16 ml/l	≒ 20 ml/l	1–5 ml/l
dissolved CH_4	0.0 m l/l	∼10 ml/l	> 20ml/l
dissolved Ar	+++	++	+
H_2S	—	+++	+
Cl^- (marine sediments)	< 2 g/l	2–5 g/l	> 5 g/l
I^- (marine sed.)	+	++	++++
I^-/Cl^- (marine sed.)	+	++	++++

Composition of Gas	Natural Gas Accumulation		
	None gas Area	Poor gas Area	Rich gas Area
CH_4 (vol. %)	−	+	++++ (>80%)
N_2	++++	++	+
CO_2 (Quaternary	+	++	+++++(>10%)
(Tertiary	+	+	+
N_2/Ar	+	++	+++
He/N_2	+	++	+++
H_2	?	?	?
CnHm	?	+	++

Data of chemical analyses of boring cores are useful to judge a presumed natural gas field where there is no well. When Cl^- content of interstitial water in mudstones of marine origin increases with depth and reaches more than 2–3 g/l, permeable layers nearby the mudstone will often be a payable reservoir of natural gas.

Since natural gas accumulation is dilapidated gravitationally by meteoric water, accumulations in sediments of small basin of lacustrine origin take on so-called " hammock " shape, in which gas content shows lower values at upper and lower portions.

Geochemical prospecting of natural gas field is aimed to estimate gas potential (R of $Q_g = R \times Q_w$) from the data of distribution of chemical components. Possible amount of water to be producted (Q_w), which has close relation with production of gas, is estimated from the data of electric well logging. Casing program at working gas wells can be determined on the basis of both geochemical and physical data.

Geochemical prospecting methods and techniques for dissolved-in-water type natural gas field described above are also useful for the prospecting of natural gas in oil fields, coal fields as well as related gas fields.

2.4 Examples of Geochemical Prospectings

Since 1948, Geological Survey of Japan has carried out successfully geochemical prospecting of dissolved-in-water type natural gas fields: field survey has been done at about fifty districts throughout Japan and survey by drilling at about fifteen districts.

References

1) Geology and Mineral Resources of Japan, 2nd edition, Geol. Survey of Japan, 1960

2) Kaneko, K.: Natural Gas Accumulation in Japan, Rept. Geol. Survey of Japan, No. 169, 1956 (In Japanese with English Abstract)

3) Kanehara, K., Motojima, K. & Ishiwada, Y.: Natural Gas, Asakura-shoten, Tokyo, 1958 (In Japanese)

水溶性ガス田の地化学探鉱

本島公司

要旨

1. 水溶性ガス田の地化学的性質

CH_4 は常温・1気圧下で水に約 33ml/l 溶ける。地下水では深度に対応した圧力をもつので，この数値が大きくなり，地下深部ではガス層が成立する。ガス層の層位は現世～中新世，海成層中によいガス層がみられる。ガス賦存の度合とガス付随水の性質との間には密接な関連

があり，地化学探鉱はおもにこの点を利用して実施する。

2. 地化学探鉱の方法と操作

(a) 野外調査：測点としてはなるべく地下と直結する井戸，泉，温泉などを利用する。ガスと水の分析法の概要も説明した。

(b) 試掘調査：ガス層の状況を，コアの組織的化学分析によつて判定する法について述べた。

(c) 分析結果の解釈：ガス賦存の度合を判定する表を作製した。井戸からの産ガス量は，揚水量とガス水比の積で示されるが，地化学探鉱ではガス水比の判定を行なうことをおもな目標にする。

(d) 地化学探鉱の実施例：1948年から行なわれたが，いままでに野外調査約50例と，試掘調査約15例がある。