SAMPLING GEOPRESSURED FLUIDS: SOME CONTRIBUTIONS FROM THE PROPERTIES OF THE H_2O-CH_4 SYSTEM

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I. INTRODUCTION

The geopressured formations of the United States Gulf Coast are being probed for methane recovery feasibility. One of the critical variables involved is the amount of methane actually dissolved in the pore brines. Sampling and subsequent analysis of these geopressured fluids is therefore important for the economic assessment of the resource. Thus, interest in use of conventional downhole fluid samplers and, recently, in development of samplers especially designed for geopressured environments, has been stimulated.

The purpose of these tools is to obtain fluid samples at reservoir conditions and to bring them to the surface, preserving their integrity, for subsequent chemical analysis. The sampling process may be envisioned as the following simplified sequence. First the sampler is lowered along the wellbore to the reservoir depth (hereafter the bottomhole). At the bottomhole the sampler is filled with formation fluid. The valve(s) are then closed and the sampler is pulled back to the surface. There it is housed in the wellhead lubricator. A valve isolating the lubricator from the wellbore is then closed. The next stage is to dispose of the hot, high pressure fluid contained in the lubricator in order to reach the sampler. The sampler is then recovered. Finally, the fluid enclosed in the sampler is transferred to suitable containers for subsequent chemical analysis.

Pore fluids in geopressured formations are subjected to very high (up to 1400 atm ≃20000 psi) pressures, and moderately high (up to 200°C) temperatures (e.g., Dorfman and Fisher, 1979); significant amounts of methane, sodium chloride and lesser chemical species are dissolved in the formation waters. During the sampling process described above, the temperatures of the fluid in the sampler in the wellbore may depart significantly from the common bottomhole value; furthermore, the pressure of the fluid surrounding the sampler decreases with decreasing depth. Correspondingly, various effects associated with the thermodynamic properties of the fluids would be induced. These effects may include; gas exsolution, both in the sampler and in the wellbore; vertical compositional changes along the wellbore due to slippage between the gas and the liquid phase; temperature-induced pressure drops in the fluid sample; substantial changes of the differential pressure exerted on the sampler walls, which relate to possible leaks; and formation in the sampler of a solid methane hydrate.

Prediction of such effects, and estimates of their magnitudes are useful for both users and designers of downhole geopressured fluid samplers. For example, this knowledge may help interpret field results, be used in assessment of sampling conditions to avoid those that favor leakage of the sampler, and suggest safer procedure for handling the sampler in surface operations, as will be shown in this paper.

This paper is devoted to predicting and quantitatively estimating geopressured fluid behavior during sampling of reservoirs in their natural, unperturbed conditions. Both the fluid in the sampler and the wellbore fluid are considered. To that end, I have developed a simple model (an "equation of state") to estimate thermophysical properties of geopressured fluids. This model is briefly described in Section II; full details are given elsewhere (Iglesias, 1980).

In Section III the "equation of state" is applied to compute and discuss fluid properties associated with the different stages of the sampling process. Questions explored include: the probable range of CH_4 content of the samples; pressure, phase transitions, fraction of total volume corresponding to each phase, and composition of each phase present in the sample, over the expected range of temperatures; whether and under what conditions the fluid collected at wellhead in a flowing well provides a representative sample of the bottomhole fluid composition; the expected range of fluid pressures in the lubricator; and the expected range of differential stresses on the sampler. Bottomhole temperatures and pressures generally increase with depth in the geopressured formations of the Gulf Coast (e.g., Dorfman and Fisher, 1979). Thus, two well depths, representing approximatley the top and the bottom of the geopressured zone, were considered in detail to assess effects associated with depth.

Finally, results and recommendations are summarized in Section IV.

II. A SIMPLE MODEL FOR GEOPRESSURED FLUIDS

With the exception of a correction factor for methane solubility in NaCl solutions, I neglected the complications posed by the presence of dissolved solids and considered a system composed only of water and methane. This approach is appropriate for the estimative purposes of the present work.

In this model, the thermophysical properties of the water-methane mixture are formulated in terms of five main variables; namely, pressure P, absolute temperature T, molar volume v, mole fraction of methane in the system λ, and volumetric gas saturation S. The contributions of methane to the liquid- and gas-phase molar volumes are estimated from a correlation (Brelvi and O'Connell, 1972), and from the ideal gas law, respectively. The corresponding quantities for liquid water and steam are estimated from the IFC Formulation*.

Methane solubility is computed from an empirical correlation (Haas, 1978), which assumes that steam exists in the gas phase at its saturated pressure and defines the methane partial pressure as the difference between P and the saturation pressure of pure steam.

III. RESULTS AND DISCUSSION

i) Bottomhole Compositions

The geopressured brines of the Gulf Coast are believed to be saturated with dissolved methane. Methane solubilities in water and in NaCl solutions depend on temperature and pressure. Thus, given the ranges of pressures and temperatures found in the geopressured formations, the probable range of methane content in bottomhole fluid samples can be estimated from known solubilities, as follows.

Bubble-point curves for the water-methane system were computed from Haas' correlation. These results are shown in Figure 1. The shaded area represents, roughly, the P, T ranges spanned by the fluids of the Gulf Coast (e.g., Dorfman and Fisher, 1979 and references therein). Assuming that in the unperturbed reservoir the pore water is saturated with methane, CH_4-H_2O ratios can be estimated from Figure 1 for given pressures and temperatures. Multiplying these results by the factor f_{NaCL}, which has been plotted in Figure 2 as a function of the NaCl content, corrects these solubilities for salinity (Haas, 1978).

From Figure 1, the maximum methane solubility in the shaded area (for zero NaCl) is about 14,400 ppm at 1400 atm (this pressure corresponds approximately to the bottom of the geopressured zone). This solubility may decrease to about 5000 ppm, corresponding to $f_{NaCl} \cong 0.35$ for 250,000 ppm of NaCl (Figure 2). Taking 700 atm (corresponding to about 3000 m, the top of the geopressured zone, if the lithostatic pressure gradient is adopted), the minimum methane solutibility is about 4000 ppm for zero NaCl

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*International Formulation Committee, 1967, "A Formulation of the Thermodynamic Properties of Ordinary Water Substance," IFC Secretariat, Verein Deutscher Ingenieure, Dusseldorf, Prinz-Georg-Strasse 77/79.

(Figure 1) which converts to about 1400 ppm for 250,000 ppm of NaCl.

Two cases were considered in detail: a deep well (Z_B = 6000 m) representing an approximate upper limit to the pressures expected, and a "shallow" (Z_B = 3600 m) well sunk to near to the top of the geopressured formations. The corresponding bottomhole pressures were estimated from the lithostatic gradient. Bottomhole temperatures were then picked from Figure 1, and methane solubilities in pure water computed from inversion of $P(\lambda,T)$ as defined by Haas. These results are presented in Table 1.

ii) Wellhead

It is appropriate to consider here the question of whether and under what conditions does the fluid collected at wellhead from a flowing well provide a representative sample of the bottomhole fluid composition.

Since until the present time no geopressured reservoir has been under significant production, the scope of this paper is limited to unperturbed reservoirs. In these conditions the pore fluids are believed to consist of a single, liquid phase saturated with methane. Wellbores penetrating geopressured reservoirs are filled with formation fluid due to the high pore pressures. Along the wellbore pressure decreases with decreasing depth causing gas (mostly methane but also some steam) exsolution. Buoyancy then tends to separate the gas bubbles from the parent liquid. This effect may cause the fluid composition at wellhead to differ significantly from the bottomhole composition.

To estimate the wellhead overall composition, slippage between the gas and the liquid phase must be considered. The typical slippage length, ΔZ, at wellhead can be derived from Z_B and the ratio of the bubble-liquid relative velocity, v_r to the flow velocity v_f,

$$\Delta z = z_B \, (v_r/v_f)$$

The extremely high bottomhole pressures imply near sonic flow velocities when friction losses are considered (C. Miller, private communication). Sound velocities may range from approximately 1000 m s^{-1} to perhaps 100 m s^{-1}, depending on gas saturation; a typical value for v_r is 0.5 m s^{-1} (e.g., Haberman and Morton, 1953). Thus ΔZ may range up to a few hundred meters for geopressured wells. One can therefore neglect slippage and take $\lambda_w = \lambda_B$ in these fast flowing wells. In this argument, small bubble regime has been tacitly assumed for the wellbore flow. Due to the relatively small temperature gradients and high pressures involved, this is a very reasonable assumption; this assumption is supported by the small gas saturations found later in this paper.

To investigate the differential stresses exerted on the sampler at surface level, estimates of wellhead pressures and temperatures are needed. For simplicity I considered steady-state, fast flowing wells for the two well depth cases described above.

Neglecting drawdown and friction effects associated with finite flow velocity, the wellhead pressure P_W was approximated as the bottomhole pressure minus the hydrostatic head. The assumed steady-state flow conditions imply wellhead temperatures T_W not far from T_B. Thus, for convenience I assumed a linear temperature profile for the wellbore, with T_W ranging from T_B to (T_B -50°C). These temperatures result in small gas saturations in the well, which are negligible in terms of mass. Neglecting the contributions of the gas phase and of the small amounts of dissolved methane to the total density, I approximated $\rho_1 \cong \rho_1^L(P,T)$. Results so computed for the two well depths considered are shown in Table 1. Note the small differences in P_W arising from the temperature dependence of the density.

From P_W, T_W, and λ_W, which completely specify the thermodynamic state of the system, other wellhead variables of interest such as S, x, y and r were computed using the "equation of state." The corresponding results are summarized in Table 1.

In addition to yielding the wellhead conditions sought, these results provide semiquantitative information of interest for planning actual production. This information can be summarized as follows: if at bottomhole conditions the brine is saturated with methane, gas will first evolve within the wellbore early in the production history, but the concomitant drawdown will eventually result in phase separation within the formation. The volume fraction corresponding to the gas phase anywhere along the wellbore is small, most likely less than about 4%. Therefore, the flow is expected to be in the small bubble regime. A substantial fraction of the total methane remains in solution at wellhead: about 50% if thermal losses along the wellbore are significant, and substantially more otherwise for the cases considered (Table 1). However, the computed values of r_W are upper limits because the actual wellhead pressures will be smaller than shown in Table 1 due to neglected friction losses and drawdown, and consequently there will be greater methane exsolution. Note that these results apply to the early stages of production; i.e., before a gas phase develops in the reservoir. After separation of the fluid in the reservoir slippage may become non-negligible.

iii) Sampler

This subsection focuses on thermodynamic changes (pressures, phase transitions, etc.) taking place in the fluid sample over the expected range of temperatures.

Neglecting leaks and thermal expansion effects, the sampler can be regarded as a closed, isochoric system. On this basis, fluid variables of interest were computed as functions of temperature as the fluid is cooled from T_B to 25°C. The necessary initial conditions (P_B, T_B, λ_B) were taken from Table 1.

Gaseous methane and steam evolve in the process. The corresponding gas saturation values range from zero at bottomhole temperatures to less than 10% at 25°C, and increase (i.e., correlate, via the multiple correlation linking depths, temperatures and pressures of geopressured fluids) with well depth (Figure 3). Methane is computed (Figure 4) to constitute in excess of 98 mole % of the gas phase over the range of temperatures considered; however, our model probably underestimates the gas phase steam mole fraction. The fraction of total methane remaining in solution correlates negatively with well depth; r decreases as cooling proceeds, until a minimum, whose position is insensitive to well depth, is reached near T = 50°C (Figure 4). The minimum value of r ranges upward of 20% indicating that considerable methane exsolution will take place upon depressurization for sample transfer, even at near ambient temperatures.

As expected, the sampler's fluid pressure correlates with well depth. Cooling effectively decreases the sampler's fluid pressures from bottomhole values of up to about 1400 atm at 200°C to a maximum value of about 300 atm at 25°C, where calculations were terminated (Figure 3). These results imply that formation of a methane hydrate, that takes place at pressures in excess of 463 atm at 25°C (Kobayashi and Katz, 1949), will not constitute a problem if the sampler is cooled to that temperature. However, the possibility of methane hydrate formation in and near transfer valves exists because of possible local overcooling due to depressurization, if transfer is attempted at near ambient temperatures. This problem should be easily controllable by use of local heating (e.g., electric wires) of the affected zone.

iv) Differential Pressure

In this section we consider the differential pressure on the sampler, which is defined as

$$P = P\text{ (sampler fluid)} - P\text{ (surrounding fluid)}.$$

As shown above, the internal pressure of the sampler is controlled by the temperature, sample volume and composition being constant. On the other hand, the wellbore fluid pressure is mainly controlled by the hydrostatic head. The typical time taken to bring the sampler back to the surface (a few hours) considerably exceeds the thermal equilibration time between the fluid contained in the metallic sampler and the surrounding fluid. Thus, in the journey to the surface the fluid sample temperature follows the temperature profile of the well. Therefore, the internal and external pressures along the wellbore must be compared at the wellbore temperature.

Assuming, for the sake of the argument, approximately linear profiles for P and T, the wellbore pressure at a given depth is proportional to the corresponding temperature. This linear relationship, if superimposed on the P-T diagrams of Figures 3 or 7, would appear as straight lines (one for each well depth) running between (P_B, T_B) and (P_w, T_w), the points corresponding to bottomhole and wellhead conditions respectively. For given bottomhole conditions these straight lines would pivot around (P_B, T_B) if P_w or T_w are varied. As discussed, P_w is determined mainly by the hydrostatic head. Therefore T_w is the main variable controlling the slope of the straight lines representing the wellbore fluid pressure in the P-T diagram. The slope decreases with decreasing values of T_w. At a given temperature the difference between the curve representing the fluid sample pressure and the straight line representing the wellbore fluid pressure for each well depth is ΔP, the differential pressure. For T_w sufficiently large, the straight line lies below the fluid sample pressure, and ΔP is positive. But decreasing T_w causes the straight line to pivot around (P_B, T_B) towards high pressures, and eventually ΔP becomes negative in the wellbore. In actual wells the relationship between wellbore fluid and temperature generally shows some curvature. But the argument made above still applies qualitatively. Thus, in "hot" ("cold") wells, ΔP tends to be positive (negative).

At wellhead, the sampler is enclosed in the lubricator. The fluid in the lubricator is isolated from the wellbore fluid by means of valves. In this condition the fluid in the lubricator is at constant volume and composition, neglecting leaks and thermal expansion. Thus, the lubricator fluid pressure is controlled by the temperature, given the initial values of the composition λ_w, pressure P_w and temperature T_w.

Using λ_w, P_w, and T_w from Table 1 as initial conditions, I computed temperature dependent lubricator fluid quantities from the "equation of state", at constant molar volume v and composition λ, for both well depths considered. Two curves resulted for each quantity (Figures 5 through 7) because for each well, two different wellhead conditions (i.e., λ_w, P_w, T_w) were considered. Results closely resemble those obtained for the sampler.

In Figure 7 the fluid sample pressures are compared with the pressures of the surrounding fluid in the lubricator at the common equilibrium temperatures. This Figure indicates that in the lubricator ΔP may be positive or negative. This comparison is valid for cases in which the wellhead parameters during sampling are comparable to the wellhead parameters of fast flowing wells, as defined above. Negative values of ΔP are favored when $(T_B - T_w)$ ~several tens of degrees C.

These results are useful to assess the performance of certain samplers in which the valves are kept closed by the combined pressures of a spring and of the internal (or external) fluid. Since the pressure exerted by the springs is negligible with respect to the fluid pressures involved, these samplers will leak when ΔP is negative (positive).

v) Sampler Recovery

High (up to about 840 atm) internal pressures are expected for the lubricator at steady state wellhead temperatures. Even higher internal pressures, up to essentially P_B, are also indicated for the sampler. These high pressures are accompanied by high temperatures in a saline ambient which may include sulfur (and other) compounds, resulting in especially favorable conditions for micro-crack development that may result in catastrophic material failures. Hot, high pressure leaks through joints and valves constitute another unpleasant possibility. These circumstances bear not only on the material aspects of sampling geopressued fluids, but also on the risk level faced by the crew in charge of sampler recovery.

A simple procedure, which would significantly lessen the material and personal risks concomitant with sampler recovery, is suggested by the results of this section. This procedure consists of two steps. First, the lubricator is isolated from the fluid flow by closing appropriate valves, to minimize thermal contact. Then the lubricator is externally cooled down to near ambient temperatures. The second step would substantially decrease the internal pressures of both the lubricator and the sampler (Figure 7). Thermal shocks on the sampler would be minimized this way. This procedure has the added advantage of minimizing the differential pressure felt by the sampler walls. For example, in the extreme conditions corresponding to the deep well case ΔP may reach (Figure 7) a maximum value of 554 atm, as compared to 1400 atm if no cooling were performed; the value of ΔP would be reduced to essentially the internal sampler pressure of 310 atm, at recovery, if the lubricator were brought to 25°C before pressure release.

iv) SUMMARY

A simple model for the "equation of state" of the $H_2O - CH_4$ system has been used to predict fluid behavior during sampling operations of unexploited geopressured reservoirs of the United States Gulf Coast. The main results are as follows.

The methane content of the fluid samples may vary widely, from about 1400 ppm to about 14400 pm. The former figure corresponds to hypothetical, highly saline (250,000 ppm NaCl) samples from near the top of the geopressured zone; the later figure corresponds to hypothetical, very low salinity samples from near the bottom of the geopressured zone. Sample methane content tends to increase rapidly with increasing bottomhole temperatures and pressures, and to decrease with increasing salinity.

When a geopressured well is initially tested, the overall (liquid and gas phases included) concentration of methane at wellhead differs negligibly from that of the reservoir fluid, if large flowrates (velocities $\gtrsim$ 100 m s^{-1}) occur. This provides an approximate check on results obtained with samplers.

At surface temperatures (assumed to range approximately from 25°C to nearly 200°C), and before depressurization, the fluid samples consist of a two-phase mixture (liquid and gas), but gas saturations are small ($\lesssim$ 10% by volume) and significant fractions ($\gtrsim$ 20%) of CH_4 remain in solution, indicating considerable methane exsolution upon depressurization for sample transfer. This information is useful in planning procedures and hardware for fluid sample transfer.

Cooling rapidly decreases sample pressures, e.g. from bottomhole values of up to about 1400 atm at 200°C to a maximum value of about 300 atm at 25°C. Therefore, formation of a methane hydrate, that takes place at pressures in excess of 463 atm at 25°C, is not normally expected in the sampler before transfer. However, local overcooling due to depressurization concomitant with sample transfer might cause methane hydrate formation in and near transfer valves.

The differential pressures exerted on the sampler may be positive or negative, depending on the wellbore temperature profile. Substantial temperature gradients along the wellbore ($T_B - T_w \approx$ several tens of degrees C) favor situations where the external fluid pressures exceed the internal pressure. This indicates that samplers relying on a combination of spring and internal (external) fluid pressure to keep the valve(s) closed will leak when used in "cold", non-preheated ("hot", preheated) wells.

Finally, a simple procedure to reduce personal and material risks associated with sampler recovery is suggested. It consists of externally cooling the closed lubricator containing the sampler to near ambient temperatures. This would substantially decrease the internal pressures of both the lubricator and the sampler, and also the differential pressure exerted on the sampler.

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NOMENCLATURE

Variables

f_{NaCl}: Correction factor for CH_4 solubility in NaCl solutions
n: mole number
P: pressure
$r = n_2^L/(n_2^L + n_2^G)$: fraction of total methane in the liquid phase
S: volume fraction corresponding to the gas phase
T: temperature

Table 1

Bottomhole-Wellhead Relations

Z(m)	P_B(atm)	T_B($^\circ$C)	T_W($^\circ$C)	λ_W(mole%)	λ_W(ppm)	P_W(atm)	S_W(%)	x_W(mole%)	y_W(mole%)	r_W(%)
6000	1400	200	200	1.555	14,029	846	1.64	1.19	98.19	76.0
6000	1400	200	150	1.555	14,029	834	3.53	0.72	99.44	45.9
3600	800	150	150	0.704	6,297	460	1.51	0.51	98.98	72.9
3600	800	150	100	0.704	6,297	454	2.40	0.37	99.78	52.0

NOMENCLATURE

Variables (continued)

v: molar volume
x: CH_4 mole fraction in the liquid phase
y: CH_4 mole fraction in the gas phase
z: well depth
λ: $= (n_2^L + n_2^G)/[(n_2^L + n_2^G) + (n_1^L + n_1^G)]$:
mole fraction of methane in the system

Super- and sub-indexes

B:	bottomhole conditions	1:	H_2O
G:	gas phase	2:	CH_4
L:	liquid phase		
W:	wellhead conditions		

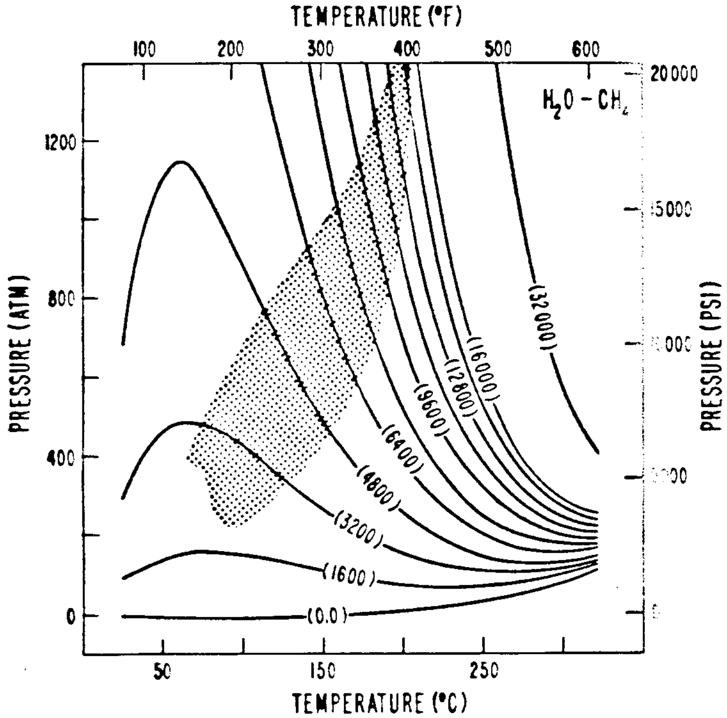

Fig. 1. Solubility curves for the H_2O-CH_4 system. (ppm) methane concentrations are indicated. The shaded area represents, approximately, the range of pressure and temperature covered by the formation fluids of the Gulf Coast in the United States.

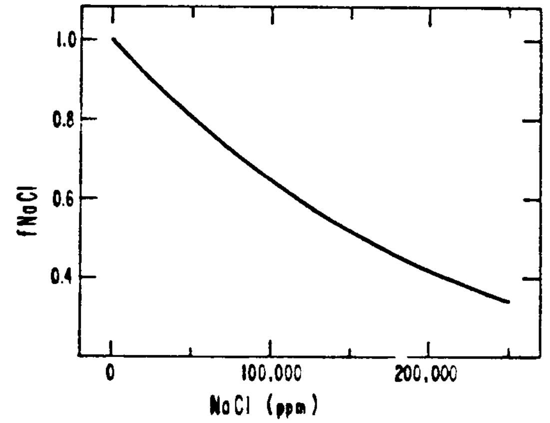

Fig. 2. Salinity correction factor. The solubilities of CH_4 in NaCl brines may be estimated by the product of f_{NaCl} times the solubility of methane in pure water at the same pressure and temperature.

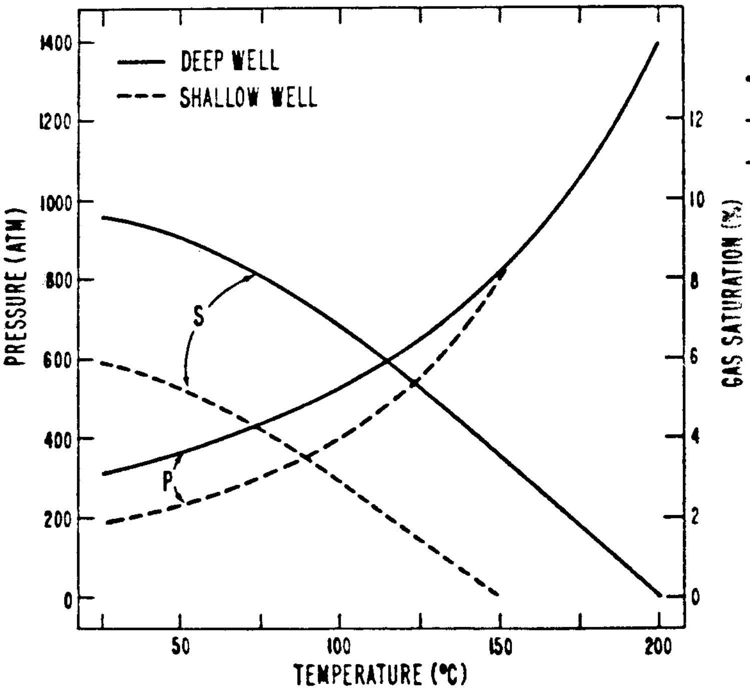

Fig. 3 Pressure and (volumetric) gas saturation responses of the sampler's fluid to cooling for two well depths: 6000 m (-) and 3600 m (---).

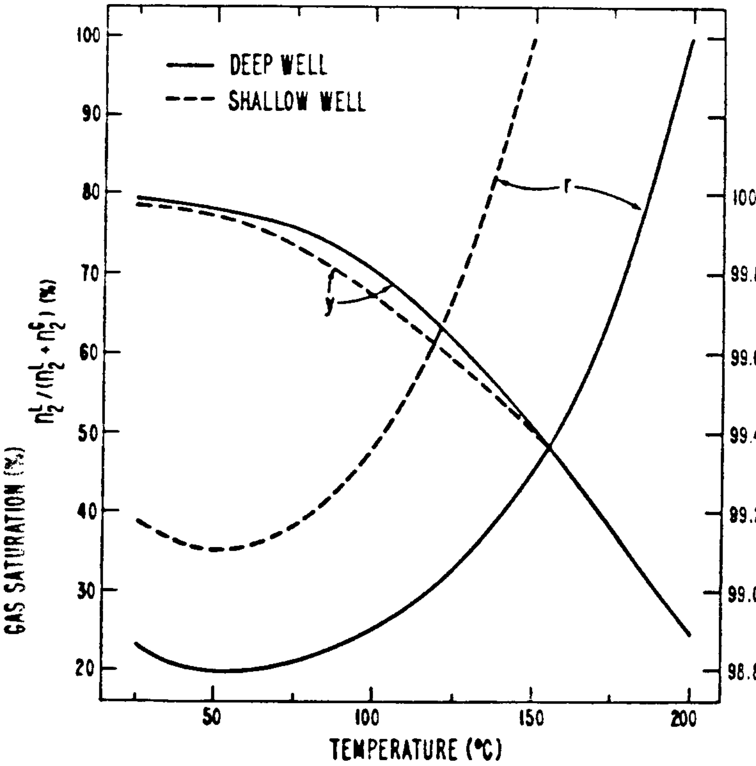

Fig. 4. Fraction of total methane in solution and gas phase methane mole fraction responses to sampler cooling for two well depths.

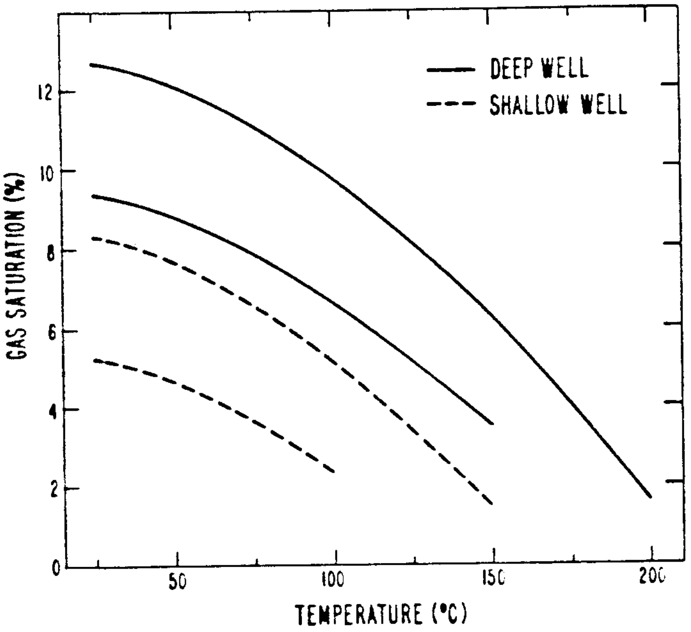

Fig. 5. Gas saturations vs. temperature for the (closed) lubricator. Two curves, corresponding to two different assumed values for the steady-state wellhead temperature, are shown for each well depth.

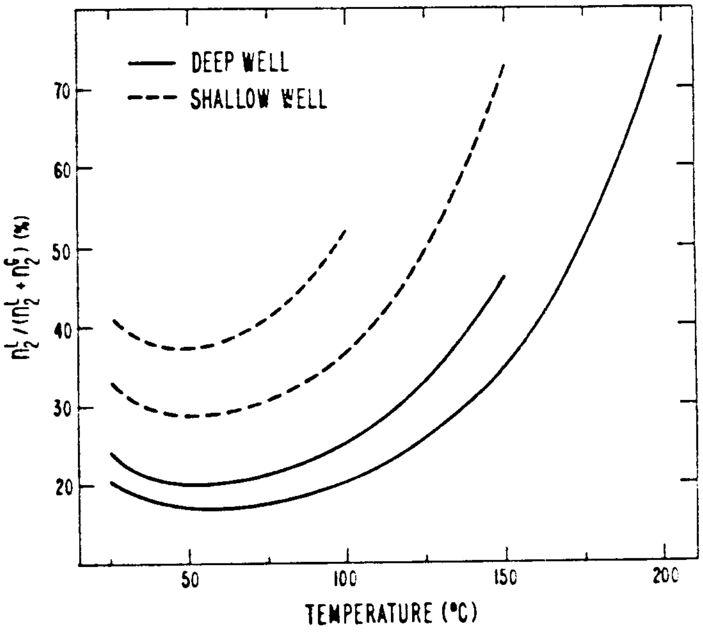

Fig. 6. Fraction of total methane in solution vs. temperature for the (closed) lubricator. Two curves, corresponding to two different assumed values for the steady-state wellhead temperature, are shown for each well depth.

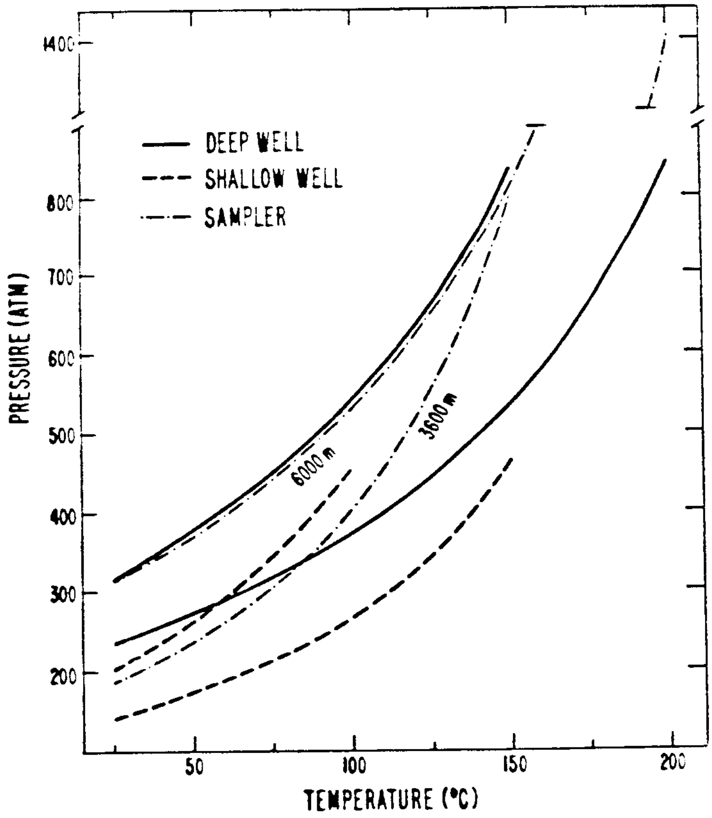

Fig. 7. Fluid pressure vs. temperature for the (closed) lubricator. Two curves, corresponding to two different assumed values for the steady-state wellhead temperature, are shown for each well depth. For comparison, the P-T curves corresponding to the sampler fluid for each well depth are also shown.