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**SOLVENT EXTRACTION OF METHANE FROM
SIMULATED GEOPRESSURED-GEOTHERMAL FLUIDS:
SUB-PILOT TEST RESULTS**

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ABSTRACT

The extraction of methane dissolved in 15 wt% sodium chloride solution at 150°C and 1000 psi has been demonstrated using n-hexadecane as the solvent in a sub-pilot scale extraction column operated in a continuous, countercurrent flow mode. Greater than 90% recovery of methane was obtained with solvent/brine mass flow ratios in the range of .040 - .045. The height of an ideal stage in this experimental Elgin-type spray column is estimated to be 1.5 ft. Application of this process on actual geopressured fluids is technically feasible, and when combined with direct drive injection disposal is economically attractive. Design and operation of a methane saturated-brine supply system to provide simulated geopressured fluid continuously at 150°C and 1000 psi are also described.

INTRODUCTION

Assessment of the technical feasibility of methods for recovery of methane (CH_4) from geopressured-geothermal fluids at elevated temperatures and pressures is discussed in earlier reports.⁽¹⁻³⁾ The value of such methods becomes evident when we consider the enormous amount of fluids that are produced from geopressured reservoirs and the concomitant disposal requirements. The presently accepted method for disposal is by subsurface injection into unconnected high capacity aquifers. The spent fluids can be injected by retaining sufficient pressure on the fluid to permit direct drive, or by use of mechanical pumps. However, there are drawbacks to each technique. Maintenance of fluid pressure for direct injection (the current practice at geopressured test wells) results in loss of CH_4 still dissolved at that pressure. Since the solubility of CH_4 in water is not

linear with pressure, an appreciable fraction ($\sim 25\%$) of CH_4 is still dissolved at injection pressures of say 1000 psi, which is less than 1/10 of the pressure in typical geopressured reservoirs. Solubility dependence with pressure is shown in Figure 1. If the fluid is completely depressurized to release all the dissolved CH_4 , then mechanical pumps are needed to inject the fluid. However, pump operational and maintenance costs nearly exceed the value of the increment of CH_4 that is recovered by depressurizing from the pressure needed for direct injection drive. Hence, neither of these options is satisfactory.

We have proposed retaining the direct pressure drive option, but with high pressure recovery of CH_4 .⁽¹⁾ The most promising of several suggested methods is solvent extraction. We have shown that this option is economically superior to depressurization and mechanical pumping even with utilization of a portion of the hydraulic energy potential.^(2,3) Although solvent extraction is widely used throughout the chemical processing industry, and as envisioned for geopressured fluid applications seemingly straight-forward, there are a number of critical technical issues and concerns which we felt could only be addressed by experimentation and testing. We made solubility measurements to verify the suitability of two solvents.⁽²⁾ We also constructed a sub-pilot sized extraction tower and a simulated geopressured fluid feed system for test purposes. The main objectives were to identify major problem areas and to acquire some basic process data for detailed analysis.

Figure 1. Solubility of Methane in Water and Aqueous NaCl at Elevated Pressures.

SOLVENT SELECTION AND SOLUBILITY

The required solvent properties are both general and specific. In general high solute capacity, low vapor pressure, good chemical and thermal stability, and, of course high selectivity are desired. To extract CH_4 from geopressured fluids, all of the above must be met. In addition the solvent must be exceedingly insoluble in brine, and as the extract not pose any problems in CH_4 desorption. Since the value of CH_4 contained in the fluid at injection pressures of 1000 psi is probably less than 5¢/bbl (< 10 scf/bbl @ \$5/Mcf), it is evident that processing costs must be held to a minimum. N-hexadecane ($\text{C}_{16} \text{H}_{34}$), a high-boiling, paraffinic hydrocarbon should be an ideal solvent ^(1,2) and hence was selected for test purposes. Its solubility in 15 wt% aqueous NaCl at 150°C was measured and found to be < 1 ppm with or without the presence of CH_4 up to a partial pressure of 450 psia. ⁽²⁾ The solubility of No. 2 Diesel fuel, a potential low cost solvent, was also determined, and based solely on solubility considerations, it would be an acceptable solvent. ⁽²⁾ Diesel fuel is, therefore, a good candidate for future process evaluation tests.

SIMULATED GEOPRESSURED FLUID SUPPLY SYSTEM

A system was constructed to continuously supply CH_4 saturated NaCl solutions for the solvent extraction runs. The system is capable of supplying fluid at temperatures and pressures of 150°C and 1500 psi at a rate of 1 liter/min. The main components and process flowstreams are shown in Figure 2.

Figure 2. Flow and Instrument Diagram of Experimental Solvent Extraction Apparatus.

Brine makeup

Brine of any desired concentration is prepared in a plastic lined mixing drum. The fluid is transferred into two 316-type stainless steel tanks, each with a nominal capacity of 55 gallons. The brine is then deaerated with a liquid ring vacuum pump. Removal of air is necessary not only to simulate geopressured fluids, but also to greatly reduce fluid corrosivity. Once the air is removed, a slight positive pressure of CH_4 of ~ 4 psig is maintained in the vapor space above the liquid to prevent air influx and to provide a net positive head to the feed pump.

Brine pressurizing pump

A BIF model 1742 duplex proportioning pump with a maximum capacity of 16.6 gph (1.05 l/min) raises the pressure of the brine from the supply tanks to the desired test pressure (set by a CH_4 pressure regulator) and ensures a known constant flow rate through the system. The wetted portions of this pump are either Carpenter 20 stainless steel or Hypalon. Adjacent features are a suction filter, an accumulator to dampen out discharge pulsations, a relief valve to limit discharge pressure to the maximum allowable working pressure (MAWP) of 2000 psig, and a valve to short circuit the discharge back to the suction if required.

Brine pre-heater

After the brine is pressurized, it passes through coiled tubing which is submerged in a heated bath to raise the brine temperature from ambient to approximately 140°C . This bath consists of a 35 inch long cylindrical vessel made from 10-inch pipe. A 12-KW immersion heating element is attached to the bottom and centered in the pipe. Approximately 15 feet of tubing, in hair-pin turns, occupies the annular space between the heater and the vessel wall. The vessel is filled with Dowtherm A heat transfer fluid (Dow Chemical Company) which has a normal boiling point temperature of 257.1°C . The

bath operates below this temperature and is also vented so that pressure cannot rise above atmospheric pressure. Power to the heater is regulated by a temperature controller which senses either the temperature of the brine as it exits the bath or the Dowtherm A temperature. Inconel 600 tubing is used throughout to contain hot pressurized brine.

Methane saturator

From the pre-heater, the brine flows into the top of a vessel through a set of atomizing nozzles, and exits into a pressurized methane atmosphere to saturate the brine with the gas. The saturating pressure exceeds the experimental pressure by the amount of pressure drop required to drive the brine through the remainder of the equipment. A liquid level is maintained in the lower third of the vessel and is indicated by a reflex-type sight glass. The level is manually controlled to maintain constant brine flow rate to the experiment. The saturator vessel was fabricated from 8" schedule 140 pipe, 4 feet long with flanged end closures. The material is carbon steel with a 1 to 2 mil coating of electroless nickel.

Brine post-heater

Above $\sim 95^{\circ}\text{C}$ CH_4 solubility in brine increases with temperature. By raising the temperature without changing CH_4 partial pressure, we can undersaturate the brine prior to onset of further pressure drop. Although this goal was not fully realized, the purpose of the post-heater, then, was to prevent free gas formation; otherwise interpretation of extraction column performance would become excessively complicated. The construction of the post-heater is similar to that of the pre-heater. It is fabricated from 6-inch pipe approximately 20 inches long and has a 2-KW immersion heater. The total length of tubing that contacts the Dowtherm A heat transfer fluid is approximately 8 feet. Like the pre-heater, the vessel has a controlled vent to the atmosphere to preclude any possible pressure rise. Power to the heater is controlled by sensing the exiting brine temperature.

Gas-Liquid separator

A separator was added to remove free gas after the above and other measures were unsuccessful in eliminating two-phase flow to the extraction column. Undersaturation by post-heating and elimination of all flow restrictions and hence pressure drop in the fluid were not sufficient. We surmised that minute gas bubbles were generated from surface bound gas released upon coalescence of the brine droplets in the CH_4 saturator vessel. The need for a separator became obvious. It consisted of a piece of 2" x 24" Monel 400, schedule 80 pipe mounted horizontally. The liquid exit was located at the pipe axis and provided single phase flow to the extraction column. The vapor space in the upper half of the separator was bled continuously through a pressure let-down valve. There was no significant pressure drop across the separator.

SOLVENT EXTRACTION SYSTEM

Extraction column

The pressure vessel is a 6-feet long piece of 3" schedule 160, Monel 400 pipe with weld-neck flanges on both ends. The internal apparatus results in an Elgin-type spray column configuration with a 1 5/8" dia. x 68" max. length working volume. Brine feed enters an overflow weir at the top of the column and exits from the bottom. The bottom section gradually expands to 2 1/2" dia. to accommodate the centered solvent distribution head with enough annular flow area to maintain constant brine velocity. Spent brine is cooled to below 100°C in a tube and shell heat exchanger before it exits through a throttling valve and is discarded. Small valve adjustments are periodically made to maintain a set liquid level in the CH_4 saturator vessel which, as previously described, receives a constant rate of brine flow from the feed pump. An accumulator is included in the system in order to dampen any pressure excursions.

Solvent loop and desorber

Solvent is pumped into the column at a constant rate and engages the brine as fine droplets produced by a distributor. A perforated plate-type distributor was initially tried, but instead of discrete droplets, produced globules of solvent that grew on the faceplate until broken loose by bouyant forces. A new distributor was fabricated from a bundle of 20 stainless steel capillary tubes spaced uniformly across the flow cross-sectional area of the column. Tube diameter was 6 mils (.15 mm) initially, but was later changed to 15 mils (.38 mm) for reasons described below. Maximum size of the solvent (hexadecane) droplets is ~ 5 mm in brine at room temperature and pressure. We have no bubble size observations at actual test conditions. Discrete bubbles rise up through the continuous brine phase at an estimated slip velocity of 4-5 cm/s absorbing methane from the brine. The drops coalesce at the brine-solvent interface which is maintained above the brine inlet weir. The extract exits through a flow and pressure throttling valve and sprays into an atmospheric chamber that is fabricated out of a 12"-long piece of 6" diameter glass pipe and stainless steel end plates. A mesh-type demister is also included. Desorbed CH_4 is separated from the liquid solvent and vented. The solvent passes from this chamber (essentially zero hold-up time) into a 2" diameter x 12"-long glass cylinder where a liquid level can be observed and maintained by adjustment of the throttling valve. By this technique, we are able to maintain the level of the interface within the extraction column provided that solvent losses are minimal and the column runs full. Both of these provisos are met under normal operating conditions. From the glass cylinder, solvent enters the circulating pump intake to complete the closed cycle. The cylinder is volumetrically calibrated to permit flow measurement checks of solvent flowing out of the extraction column or solvent drawn by the circulating pump. A 10- μm membrane filter is located between the solvent pump and column to prevent particles from blocking the distributor capillary tubes. An accumulator is located between the filter and pump to dampen flow pulsations.

SAMPLING AND CH₄ DETERMINATION

Samples of the aqueous brine phase in and out of the column, and of the extract are collected in stainless steel cylinders at operating temperature and pressure. Prior to drawing the samples, the bottles and connecting lines are evacuated to the main block valves on the system tubing. Forty cc brine "in", 150 cc brine "out", and 2 cc extract (solvent out) samples are collected. The mass of the sample is determined gravimetrically. Samples are cooled to room temperature and opened into calibrated volumes. Total pressure (less than 1 atmosphere) is read on a Wallace and Tiernan absolute pressure gauge after 30 minutes of equilibration time. Ideal gas laws are assumed to be valid at these pressures and temperatures for calculating the amount of CH₄ originally dissolved in the liquid samples. The spent brine sample is also processed and analyzed to determine solvent loss by dissolution and entrainment. Total solvent (C₁₆H₃₄) content is determined by direct extraction into methylene chloride followed by gas chromatographic analysis for C₁₆H₃₄. To obtain the dissolved C₁₆H₃₄ fraction, the spent brine sample is transferred into a separatory funnel to allow physical separation of entrained hexadecane before contact with methylene chloride.

INSTRUMENTATION AND CONTROLS

Pressure Gauges were located at various critical points in the system. Diaphragm gauge isolaters were used for brine service. A more precise Bourdon-tube (Heise) gauge was used on the extraction column. Transducers were also installed at critical locations and their readings recorded.

Temperature Bi-metallic thermometers coupled to dial readouts were used for rough indicators. Thermocouples with digital readouts provided precise temperature readings. Temperature data was also recorded.

Pressure control A closed loop, pressure feedback system was used to control extraction column pressure, but the system was too sluggish because of insufficient proportional gain and/or large reset time. It was evident from operating experience that manual control using the pressure regulator supplying CH_4 to the saturator was adequate. The system could be easily pressure stabilized and maintained manually, probably because of the large gas volume in the saturator vessel and the high dissolved gas content.

Temperature control

Temperature control was accomplished with a closed loop, feedback control system. Temperature of the brine exiting the heat exchangers was the control variable. Signal from the controller regulates power to the Dowtherm A bath heaters. External clamp-on heaters on the CH_4 saturator vessel and heating tapes on the separator and extraction column were also similarly controlled. Because of the large thermal mass of the system, temperature control was easily accomplished. The system was, of course, insulated.

Solvent-Aqueous interface control

A system was installed to control the solvent-aqueous interface level in the extraction column by maintaining a constant solvent level in a glass accumulator located in the ambient pressure portion of the solvent circulating loop. A capacitance-type level detector was used with the control signal for manipulation of the valve controlling extract flow from the column. In some of the ensuing runs, however, the flow coefficient of the valve was too large for the lowest solvent flow rates. Again we relied on manual control without sacrificing process stability.

Flow control

Brine and solvent flow rates are preset and maintained by the positive displacement feed pumps. Liquid level in the saturator vessel is controlled manually as previously

described to limit accumulation or depletion of fluid in the system. Instantaneous flow rates are determined by volumetric measurements whenever a sample set is collected.

Corrosion

The potential for failure of stainless steel from exposure to chlorides at elevated temperatures is reported in the literature. This failure mode, known as stress-corrosion cracking, can occur without a generalized attack or lessening of wall thickness. Materials that resist effectively are nickel base alloys such as the Hastelloys, the Inconels and the Monels. Ordinary carbon steel will also not fail in this manner but will, of course, corrode over its entire exposed surface. To fabricate the entire system from a nickel base alloy that would - a) not corrode generally, and b) have no tendency towards stress-corrosion cracking, was judged to be impractical. At any price, the selection of valves, fittings, vessels and other components required is ordinarily not available. Based on certain guidelines and material availability/costs, the system was constructed with the following materials:

- 1) Stainless steel fittings and valves were used very conservatively within their pressure ratings.
- 2) For pressurized brine service, Inconel 600 tubing was used throughout, since this is the item most subject to potential failure. Not only is its wall stress the greatest but it is also subject to localized stress where it is distorted by the ferrules used in the compression type fittings.
- 3) Carbon steel was used for the methane saturator vessel. To retard corrosion of this component, it was given a 1 to 2 mil coating of electroless nickel. This coating was applied more to protect the brine from contamination than as a

safety measure. At a stated MAWP of 2500 psig, the vessel has a corrosion allowance of 0.063 inch. The corrosion rate of carbon steel in deaerated brine at 150°C should not exceed 20 mils per year.

- 4) The gas-liquid separator and the solvent extraction column were fabricated out of heavy walled Monel 400 pipe. This material, an alloy of 63% nickel and 31% copper, is highly resistant to chloride attack and offers intrinsic protection from corrosion in this service.

A list of the major high pressure components and their description is given in Table 1.

Table 1. Component Listing and Pressure Ratings⁽¹⁾

ITEM	DESCRIPTION	PRESSURE RATING
Brine supply tanks	55 gal., closed, welded tank-316 SS	Full vacuum to 15 psig at 34°C-tested to 50 psig (Nor-Cal Metal Fabricators)
Methane saturator	Flanged, 8" dia. x 36" long ASME coded vessel, carbon steel	2500 psi @ 163°C (Caral, Inc.)
Methane-Brine separator	2" dia. x 24" long Monel 400, pipe caps	3000 psi @ 21°C
Solvent extraction column	Flanged, 3" dia. x 72" long vessel-Monel 400	2000 psi @ 163°C
Brine pressurizing pump	BIF model 1742 proportioning pump, 16.6 gph-Carpenter 20 SS	4000 psi @ 21°C (BIF catalog)
Solvent circulating pump	Williams model CP500D-300 injector pump, 4.6 gph-303 SS	2700 psi @ 150°C (Williams catalog)
<u>Accumulators</u>		
	Greer part no. A66702-200-1A bladder accumulator, 10 cu. in. carbon steel & 316 SS	3000 psi @ 21°C (Greer catalog)
	Greer part no. A852-200-28 bladder accumulator, 1 quart carbon steel & 316 SS	3000 psi @ 150°C (Greer catalog as modified for Viton)

Table 1. (Continued) Component Listing and Pressure Ratings

ITEM	DESCRIPTION	PRESSURE RATING
<u>Regulators</u>	Pressure regulator, 4000 psi in, 100 psi out Veriflow Corp. P/N 11500465	3000 psi @ 21°C (Veriflow catalog)
	Pressure regulator, 250 psi in., 10 psi out Matheson model no. 70 A	250 psi @ 71°C (Matheson catalog)
	Pressure regulator, 6000 psi in., 6000 psi out Circle Seal Dynareg P/N 57B1112G	6000 psi @ 21°C (Circle Seal catalog)
	Pressure regulator, 10,000 psi in, 15 to 2500 psi out Tescom model 26-1024-24-002	10,000 psi @ 74°C (Tescom catalog)
Level indicator (saturator vessel)	Reflex type sight glass Eugene Ernst part no. EEPW-15	3000 psi @ 34°C (Eugene Ernst catalog)
Temperature indicators	Thermocouple feed-throughs Conax cat. no. PG2-125-A	5000 psi @ 21°C (Conax catalog)
Pressure indicator	Pressure transducer Senso-Metrics model no. SP971C	2000 psi @ 65°C (Senso-Metrics catalog)

Table 1. (Continued) Component Listing and Pressure Ratings

ITEM	DESCRIPTION	PRESSURE RATING (Rating Source)
<u>Sample bottles</u>		
40 cc	Sample cylinder, 304L SS	
150 cc	Whitey part no. 304-HDF2-40	1800 psi @ 34°C
	Whitey part no. 304-HDF4-150	(Whitey catalog)
Brine valve	Control, 1/2 in.-316 SS	30,000 psi @ 21°C
	Cashco model 5 63S	(232°C max.)
		(Cashco catalog)
Solvent valve	Control, 1/2 in.-316 SS	5000 psi @ 21°C
	Cashco model 5 63	450°F max.)
		(Cashco catalog)

(1) The following components are either open topped or have direct atmospheric vents and therefore are not listed: 1) brine mixing tank, 2) brine pre-heater, 3) brine post-heater, 4) methane desorber, 5) solvent level glass, and 6) brine holding tank.

PROCESS TEST PROCEDURE

Cold, 15% by weight NaCl solutions are prepared and deaerated as previously described. Food grade salt was used.

The saturator vessel is charged with brine to the required operating level as indicated on the high pressure sight glass. The extraction column is also filled with brine and the required amount of n-hexadecane to set the interface level. In all the runs a 95% pure technical grade of n-hexadecane was used; the remaining 5% consists of mainly C_{14} - C_{18} compounds. The cost of using a purer grade is prohibitive. The entire system is brought up to operating pressure with a bottled CH_4 source (99.99% purity) which continuously provides gas on demand in the upper portion of the CH_4 saturator vessel. Power is applied to all heating elements to bring the Dowtherm A heat transfer fluid and vessels to required operating temperatures.

The brine feed and hexadecane feed pumps, pre-set for the desired flow rates, are activated. Simultaneously the extract and spent brine throttling valves are adjusted to maintain liquid levels displayed on the sight glass indicators. Fine tuning of the CH_4 pressure regulator and these two valves, becomes less frequent as the system reaches steady-state operation. Temperature controllers, once tuned for the system, need no further adjustments.

Once operating temperature is reached, the run is continued for a period of time equal to about 3-4 solvent hold-up periods in the column. Following this period of steady operation, a suite of samples is taken - brine in, brine out, and extract out - and processed as described previously. Flowrates are also measured volumetrically during each sampling period. A duplicate suite of samples is always taken and processed. A run can usually be completed in four hours, excluding preparation time and sample processing and analysis.

RESULTS

Methane-Water runs

Preliminary tests using pure water and CH_4 were conducted to check our CH_4 solubility values with literature values. These tests revealed that we were getting 2-phase flow which ultimately required the installation of a gas-liquid separator as previously discussed. We also found that the sample bottle orientation was critical. When sampling off a horizontal line, the bottle volume must be above the intake valve to preclude backflow of gas evolved with pressure and temperature drop across the sample valve.

With the necessary modifications completed, the tests showed that dissolved CH_4 concentration in water at 150°C and 1000 psig entering and exiting the extraction column (no solvent was present) ranged from 769-859 ppm $\pm 2\%$ or 6.1 - 6.8 scf/bbl (see Table 2). Experimental data of Culberson and McKetta⁽⁴⁾ at the same temperature and pressure gives 950 ppm. Based on these data, we were confident that the feed system could produce a continuous stream of water saturated or nearly saturated with CH_4 at temperatures and pressures required for the experiments.

TABLE 2. Dissolved Methane Gas Concentration in Water at $150 \pm 3^\circ\text{C}$ and 1000 ± 10 psig (without solvent circulation).

<u>Sample Point</u>	<u>ppmCH_4</u> <u>($\pm 2\%$)</u>	<u>scf/bbl</u> <u>$0^\circ\text{C}, 1 \text{ atm}$</u>
into column	829	6.54
into column	769	6.07
into column	859	6.76
into column	814	6.41
out of column	785	6.17
out of column	855	6.73

Methane-Brine-Hexadecane Runs

Phase I: The results of the initial solvent extraction experiments are qualitative only. After a large suite of runs was completed with a 34" (~ 3 ft) and a 68" (~ 6 ft) column, we discovered that the solvent distributor-circulating pump assembly was producing extremely fine solvent droplets, and/or large globules. Test performed outside the columns revealed an extremely fine drop size distribution owing to the pulsating action of the pump that imparted high instantaneous capillary velocities. The resultant hydrosol enhanced mass transfer rates at the column entrance, but reduced performance sensitivity to process variables. Furthermore, there was unacceptably large losses of solvent due to entrainment in the exit brine stream. Performance was further clouded by leaks which developed in the solvent distributor assembly.

In these initial runs at 150°C and 1000 psig total pressure, column performance in terms of CH₄ recovery varied from 60 - 90%. Because of the above problems there was no correlation with hexadecane/brine mass flow ratios which ranged from .013 to .045. The use of two column lengths 34" and 68" also did not reveal any effect on CH₄ recovery. Solvent losses were large - as much as 2500 ppm in the spent brine. Before the runs were resumed, the distributor was rebuilt with larger diameter (15 mil) capillary tubes and with welded joints. An accumulator was added to the pump output line to dampen pulsations.

Phase 2: Data acquired after completion of the distributor modifications were more reasonable and are given in Table 3. Test conditions were essentially unchanged - i.e. 150°C, 1000 psig, use of 3' and 6' column lengths, 15 wt% NaCl as the aqueous phase, 95% n-hexadecane as the solvent, constant aqueous phase flowrate of 1 liter/min, and variable solvent flowrates to give hexadecane/brine ratios from .015 - .045.

TABLE 3. Summary of Data: Countercurrent Solvent Extraction Tests at 150° C and 1000 psig.

Run no.	Column length, ft.	Flowrate, gm/min		Solvent/Brine mass flow ratio x 10 ²	Methane conc., std cc/gm			Methane recovery, % (1 - $\frac{\text{CH}_4 \text{ brine out}}{\text{CH}_4 \text{ brine in}}$) x 100
		Brine (15 wt% NaCl)	Solvent (n-hexadecane)		Brine in	Brine out	Solvent out	
1	6	1082	16.0	1.48	0.574	0.386	7.0	33
	6	1023	16.0	1.56	(a)	0.346	7.0	40
2	6	1178	48.1	4.08	0.583	0.030	13.7	95
	6	1100	48.0	4.36	(a)	0.051	13.4	91
3	6	1115	20.5	1.84	0.593	0.162	15.5	73
	6	1150	23.6	2.05	(a)	0.129	18.1	78
4	6	1137	32.6	2.87	0.596	0.254	8.6	57
	6	1126	28.3	2.51	(a)	0.280	9.1	53
5	6	1082	37.4	3.46	0.580	0.115	11.7	80
	6	1065	38.6	3.62	(a)	0.089	13.8	85
6	6	1146	25.7	2.24	0.588	0.172	17.7	71
	6	1092	25.8	2.36	(a)	0.171	17.6	71
7	3	1126	41.0	3.64	0.576	0.115	10.2	80
	3	1168	46.0	3.94	(a)	0.132	8.7	77
8	3	1166	17.6	1.51	0.597	0.344	14.5	42
	3	1154	16.3	1.41	(a)	0.351	16.7	41
9	3	1146	33.2	2.90	0.575	0.180	11.5	69
	3	1146	33.1	2.89	(a)	0.192	10.6	67

(a) only one "brine in" sample taken per run.

Expressions can be derived for multi-stagewise contact (e.g. Treybal⁽⁶⁾) relating component flows, the distribution coefficient, and number of ideal stages. For a countercurrent stagewise process in which the solvent and aqueous phases are immiscible, and the solute concentration in the incoming solvent is zero, the following expression results:

$$R = 1 - \frac{x_n}{x_f} = \frac{E^{n+1} - E}{E^{n+1} - 1} \quad (1)$$

where R = recovery

x_n = solute concentration in raffinate, nth stage

x_f = solute concentration in feed

n = no. of stages

E = extraction factor = $\frac{DS}{B}$

D = distribution coefficient

S = solvent flow rate

B = brine flow rate

Curves of this expression are plotted in Figure 3 for $n = 2$ & 4 , and for three values of the distribution coefficient. The experimental data are also plotted in the same figure. The data from the 3' column runs fit the curve representing a 2-stage countercurrent extraction with a distribution coefficient of 35. For the same distribution coefficient, the 6' column data best fit the curve for a 4-ideal stage process. Methane recovery of $> 90\%$ was achieved at $.040 - .045$ hexadecane/brine flow ratios. There are a few data points from the 6' column tests which fall well outside the theoretical curves. We have no explanation, as these data are considered equally valid.

Figure 3. Experimental Data and Theoretical Curves of Countercurrent Multi-Stage Extraction for Various Distribution Coefficients (D).

Column end effects in the phase 2 runs are apparently not significant in terms of enhancing mass transport. A linear interpretation of the two column heights and the best number of ideal stages gives 1.5 feet as the height of an equilibrium stage equivalent to an ideal stage in countercurrent multistage process with the same feed rates. A spray tower scaled up in size should have the same performance characteristics. For example, a tower sized for 40,000 bbl/d of brine flow would have a diameter of just over 6 feet.⁽²⁾ Solvent drop size and drop slip velocity would be the same as the optimum values that result from laboratory tests. The working or contact height needs to be no greater than 6' to achieve 90% recovery. The larger diameter vessel may require axial partitions to assure constant flux over the entire cross sectional area. All in all, the design of such a hypothetical tower would be quite simple, except perhaps for the solvent distributor which must provide the optimum discrete drop size.

The distribution coefficient computed from published data of CH_4 solubility in hexadecane and aqueous NaCl ranges from 35-71, depending on which data are used for CH_4 solubility in brine. To compute CH_4 solubility in n-hexadecane, Henry's constant of 235 atm @ 150° C from Cukor & Prausnitz⁽⁷⁾ is used, assuming the value remains constant up to our experimental CH_4 pressure of 64.8 atm. This gives a CH_4 solubility in n-hexadecane of 26,700 ppm by wt at 150° C and 64.8 atm. When this value of CH_4 solubility in the organic phase is used to compute distribution coefficients (D) using three different sources of CH_4 solubility in the aqueous phase, we get: 1) $D = 71$, using O'Sullivan & Smith's⁽⁸⁾ data interpolated to the same temperature and pressure conditions, 2) $D = 65$, using CH_4 concentrations measured in the feed stream of our extraction column tests, and 3) $D = 35$, from extrapolated data of Price, et al⁽⁵⁾. As shown above, our actual column performance data agrees best

with a low distribution coefficient, even though our measured value of CH_4 concentration in the brine feed should result in a higher value. The discrepancy can be due to at least a couple of factors. The measured CH_4 concentration in brine in the test system may not be at complete equilibrium saturation conditions, and/or Henry's constant for technical grade n-hexadecane (95% purity) is significantly higher than for pure hexadecane.

Entrainment of solvent in spent brine in phase 2 operation was significantly reduced, but was still too high, ~ 300 ppm, to be acceptable from cost considerations. However, analysis of spent brine samples that were first held in separatory funnels to allow for solvent separation resulted in < 1 ppm solvent concentrations which agree with previous solubility measurements.⁽²⁾ Apparently more design considerations must be given to eliminating solvent entrainment. Advanced distributor design to preclude formation of small droplets may help, or if necessary a separate gravity settler could be installed for final solvent disengagement. The effect of drop size on extraction efficiency and solvent entrainment was unfortunately not adequately studied in these tests.

In place of hexadecane, the use of more soluble but lower cost solvents, such as No. 2 Diesel fuel, may be more practical in an actual process. The cost burden resulting from dissolved solvent losses may not be any less, but additional losses resulting from physical entrainment or process upsets would be more acceptable. Further, there could be benefits derived from fewer design constraints.

CONCLUSIONS

It has been shown that dissolved CH_4 can be effectively recovered from NaCl solutions at 150°C and 1000 psi by solvent extraction with n-hexadecane solvent. 90 + % recovery was obtained in continuous countercurrent tests using a sub-pilot scale column of the Elgin-type spray tower design. Recovery of CH_4 from the extract posed no problems. Solvent entrainment loss in the spent brine must be further reduced by such means as improved solvent distributor design or inclusion of a separate settling tank. Hexadecane solubility in the spent brine is < 1 ppm confirming previous autoclave measurements.

The column characteristics, performance, and operational stability as demonstrated in the laboratory indicate that application of such a process on actual geopressured fluids would be feasible. We believe an earlier economic analysis ⁽²⁾ of a solvent extraction process coupled with direct drive injection disposal at a geopressured well site remains valid and the application cost effective.

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