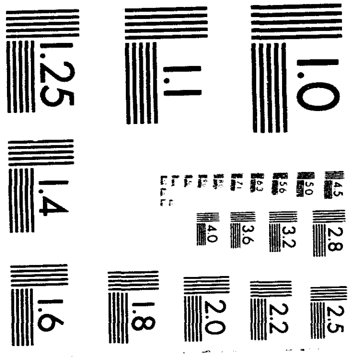
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BNL
Informal Report

A CO_2 BASED ANALYSIS OF A LIGHT-OIL STEAMFLOOD AT NPR-1, ELK HILLS, CA

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ABSTRACT

A steamdrive pilot was run on a light-oil reservoir at the Naval Petroleum Reserve No 1 (NPR1) in the Elk Hills oil field, Kern County, CA. The goal of this work was to establish a correlation between a documented growth in CO_2 concentrations found in producing wells in the pilot area to the light-oil steamflood (LOSF); then to use a thermodynamic analysis of the expended energy to come up with an energy efficiency of the steamdrive.

Introduction

The United States Department of Energy and Chevron USA Inc. are unit partners in the Naval Petroleum Reserves located in Elk Hills, California. Elk Hills is located in Kern county, approximately 25 miles southwest of Bakersfield. The reserves at Elk Hills were discovered in 1919, unitized in 1944 and after fluctuating production was opened to full production status in 1976. The current unproven reserves in the shallow oil zone (SOZ) are estimated to be 100 million bbl of oil and it is found at an average depth of 3,000 ft.

Average Reservoir Data	
Well depth, ft	2,820
Oil gravity, °API	27
Current reservoir pressure, psig	50
Reservoir temperature, °F	120
Oil viscosity at 125°F	17
Average permeability to air, md	1,000
Average porosity, %	30.6
Average oil content, bbl/acre	888
Average oil saturation, %	55

Table 1. Average Reservoir Data

The Tracer Technology Center, TTC, is a subdivision at Brookhaven National Laboratory, BNL, and has been involved with several experiments at the Elk Hills petroleum reservoir. A recent experiment involved the injection of several perfluorocarbon tracers into the SOZ at the Elk Hills field. The purpose of the tracers is to aid in the understanding and knowledge of the dispersion and extent of injected gas within the reservoir. It was during this experiment in the SOZ that certain abnormalities were noted in the gas analyses coming from observation wells. The noticed abnormality was an extremely high CO_2 mole fraction in the produced gas samples. CO_2 mole fractions up into the 90 percentiles were noted which is several times higher that what might usually be expected. Typical CO_2 concentrations in a petroleum reservoir should be less than 10%.

Scope

In August of 1992 a study was started to identify the cause of the high CO_2 fractions within the gas samples from producing wells surrounding the LOSF injection project. With the cooperation of the field operator, Bechtel Petroleum Operations Inc., gas analysis data sheets were gathered from as many surrounding wells as possible. It was felt that the CO_2 was somehow produced in conjunction with a light oil steam flood, LOSF, which began in July 1987. The reservoir sections which were focused on in the gas analysis search were 3G, 4G, 9G, and 10G. This search area covers four square miles and allows for a minimum of a one mile search radius from the expected source of CO_2. The center of the LOSF is located approximately 500 feet to the northeast of the intersection of these four sections.

Background

The LOSF is an enhanced oil recovery (EOR) technique which was used by the producers of the Elk Hills field in hopes of stimulating additional petroleum production. EOR is defined as the act of recovering oil by the injection of materials not normally present in the reservoir.[8] A steam flood is a thermal EOR process (see figure 1) which has a fairly basic intent. The intent of the steam flood, or steamdrive, at Elk Hills was to reduce the residual oil saturation, ROS, of the reservoir. The residual oil saturation of a reservoir is the point at which the saturation of oil in the reservoir cannot be reduced further by conventional production techniques. In the steamdrive process, steam vaporizes a fraction of the residual oil and transports it to the steam front where it condenses to form a distillate oil bank. This process, the vaporization and transport of the residual oil, which condenses into a miscible distillate bank, is known to reduce the steam swept pore space to an ROS as low as 5%.[1]

LOSF Process

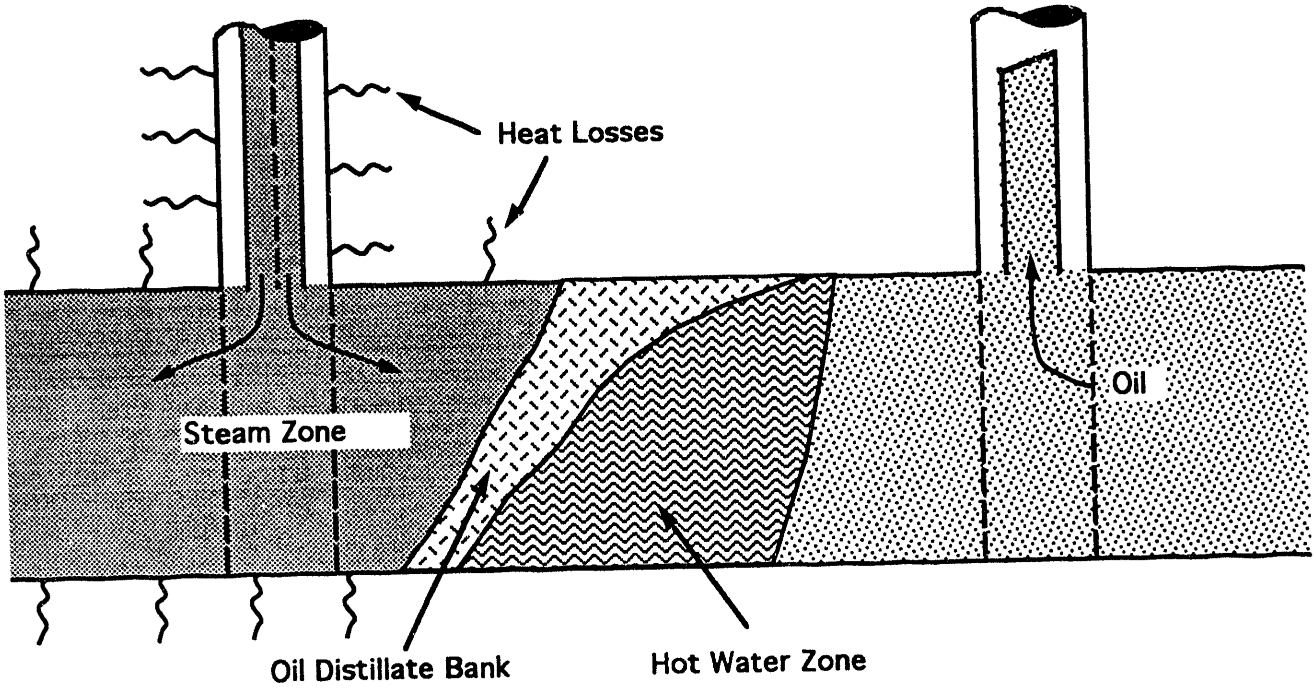

Figure 1. Schematic of the light-oil steam flood.

Analysis Preparation

As part of keeping track of the progress of the steamdrive, Bechtel Petroleum Inc. would periodically sample gas produced from the wells surrounding the steam injection area. More than a thousand gas analysis data sheets from over a hundred sampling and production wells were received by BNL from Bechtel Petroleum. Each analysis was entered into a computer data base. The date, well, plot and major chemical composition mole fractions were noted for each analysis. Each analysis sheet was individually checked for validity. When deciding whether or not an analysis was valid, one must look at all of the parameters and keep in mind what is being sampled. If certain mole fractions were abnormally high, or unreasonable, the analysis was removed from the data set. An example of this would be an analysis showing approximately 20% oxygen and 70% nitrogen. This would indicate that the sample contained mostly air and that there was a flaw in the sampling or analysis technique. Another example of a bad sample would be one in which the fraction of propane was much higher than that of methane. As a general rule, methane should be the largest mole fraction in a gas sample obtained from a hydrocarbon reservoir. If this is not the case, it is highly probable that something has gone awry with the sampling or analysis process.

Analysis

The goal of examining the gas analyses was to determine if there was a correlation between the sampling wells containing a high CO_2 concentration and the location of the LOSF. This was accomplished by individually examining and generating scatter charts plotting CO_2 concentrations with respect to elapsed days from the start of the LOSF. Unfortunately, not all of the wells were periodically analyzed after the start of the LOSF, but there were a sufficient number that had comprehensive analyses that it was felt a reasonable conclusion could be drawn from the available data.

It was noted from the plots of CO_2 concentration as a function of time that there did appear to be a correlation between the area affected by the LOSF and the increase in CO_2 concentration in the surrounding wells. Wells which were closest to the LOSF injection, and those which are believed to have reservoir conductivity with the LOSF injection wells showed a definite and systematic increase in CO2 concentrations from a pre LOSF level to an equilibrium level at some time after the start of the LOSF. This equilibrium CO_2 concentration will be identified as $C(\infty)$.

It was observed that the $C(\infty)$ for each well was not a constant value. Each well was individually examined and a value of $C(\infty)$ was obtained by averaging the CO_2 concentration levels over a period of time where it appeared that the CO_2 had reached an equilibrium value. The $C(\infty)$ for some of the wells with sparse gas analyses were derived if data was available during the approximate elapsed time at which the other wells appeared to be reaching an equilibrium concentration. Once all of the $C(\infty)$ were found, the results were used to generate a subsurface isopleth map of CO_2 concentrations over the four square mile study area (see figure 2). An isopleth map is a map showing lines of constant CO_2 concentration with respect to well position within the reservoir. The isopleth was then examined with the current geological mapping of faults in the region (see figure 3). The isopleth generated from the collected data appeared to correlate with the geology in that wells with the high CO_2 concentrations followed the major faulting system, allowing conductivity with the steam injection wells.

Once the $C(\infty)$ for each well was determined, then the time needed for the CO_2 concentration to go from the pre-LOSF level to the $C(\infty)$ level was derived. Since it has been observed that chemical reactions, such as decomposition reactions, are

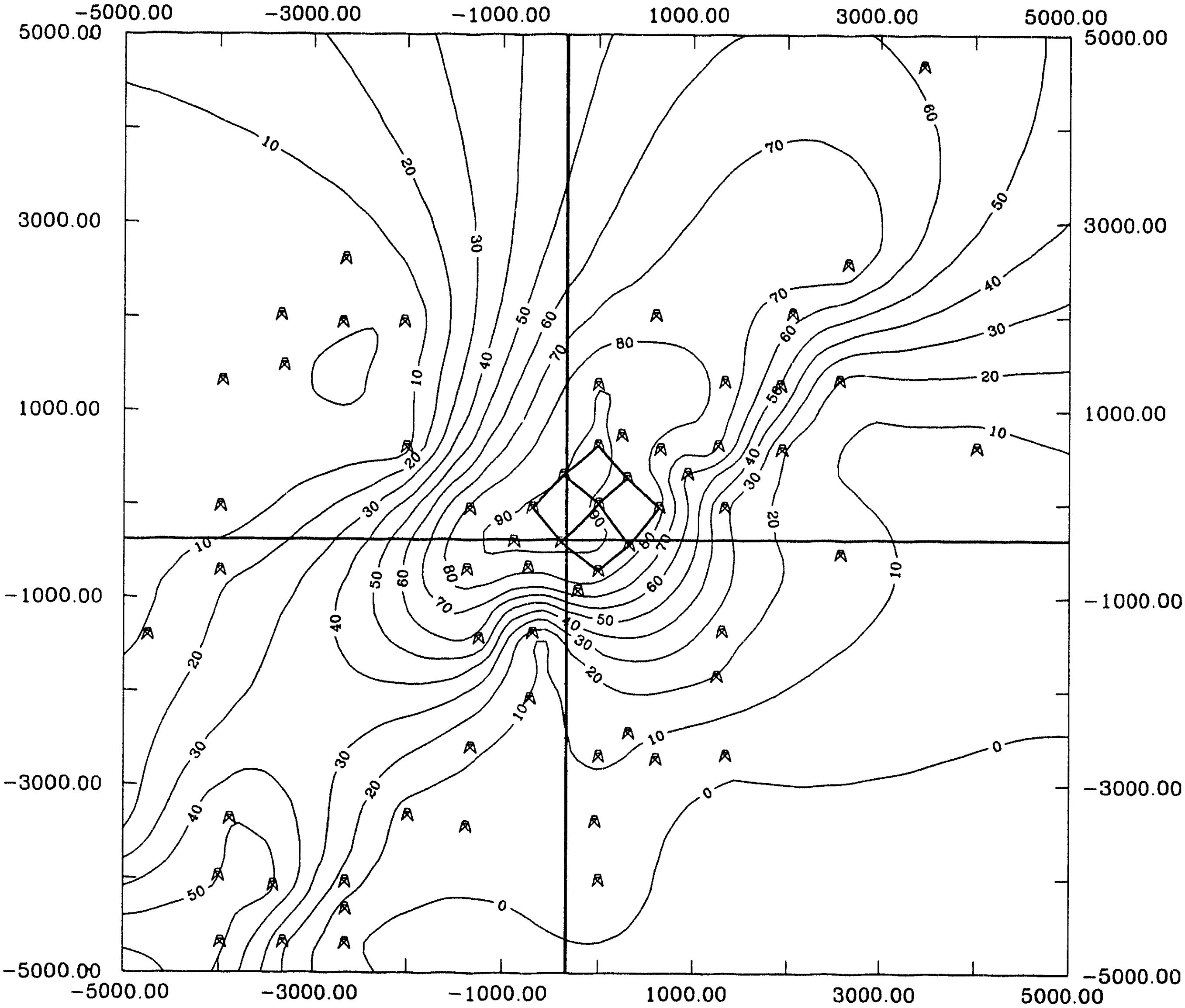

Figure 2. An isopleth map relating equilibrium CO_2 levels with the location of the well. The injection pattern in the middle of the map is made up of four separate five spots; there is a steam injector in the middle of each five spot. The units on the outside of the map represent feet away from the center of the injection pattern. The units on the isopleths are percent concentration of CO_2.

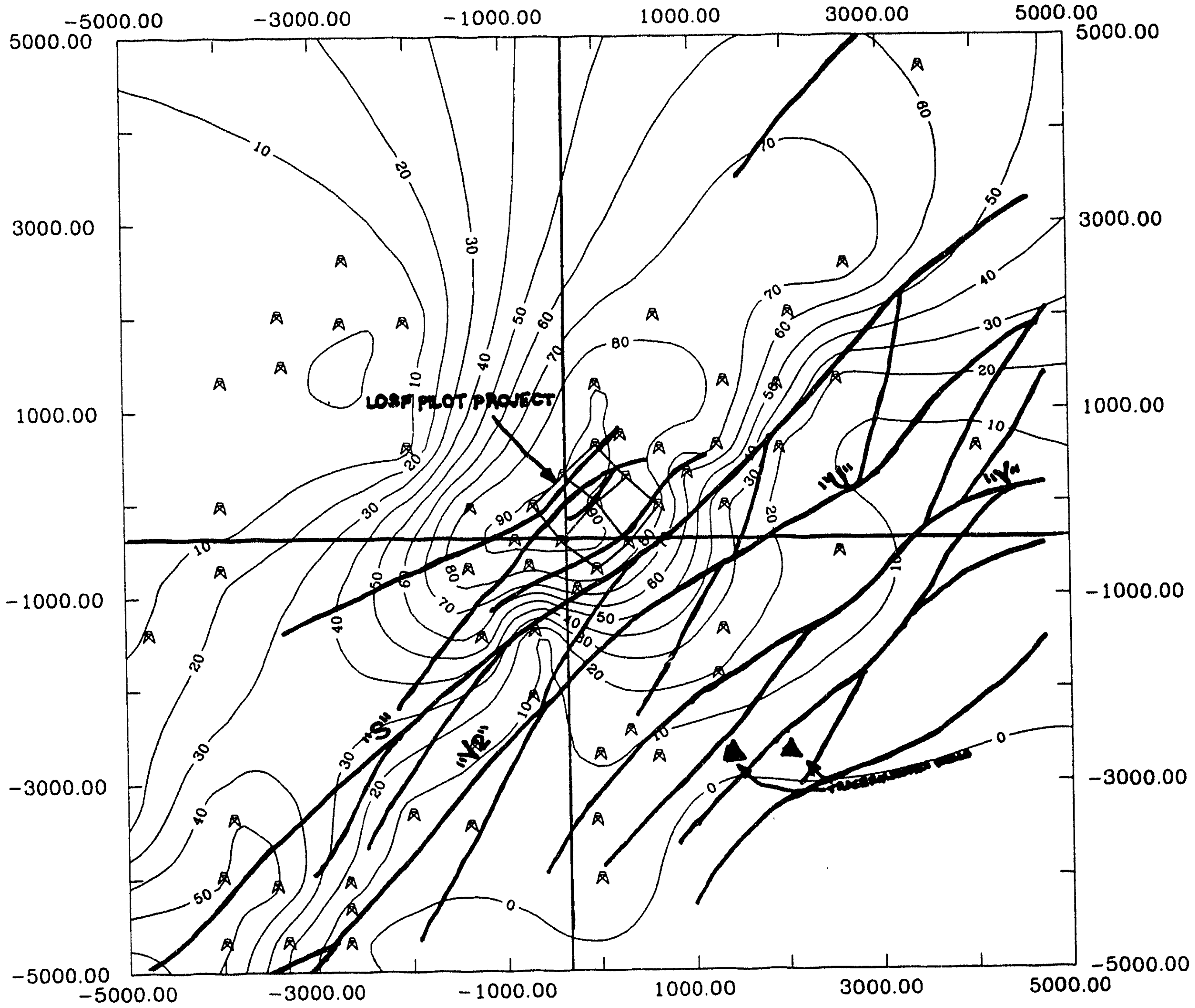

Figure 3. The CO_2 equilibrium concentration isopleth map integrated with the localized reservoir faulting system.

frequently governed by an exponential type growth, and since the plots appeared to follow an exponential growth, best fit exponential curves of this form were derived:

$$C(t)=C(\infty)(1-\exp[a]\exp[-t/\tau]) \quad (1)$$

Figure 4 displays the exponential growth curve along with a description of the $C(\infty)$ data points. In this equation, $C(t)$ is the concentration of CO_2 with respect to time, a is the y-axis intercept of equation 2, described below, and τ is the the reciprocal of the slope of equation 2 and the negative of τ can also be thought of as the growth rate of, or the time needed to form the CO_2. To obtain these values, a graph of the equation below needs to be formed:

$$\ln[1-C(t)/C(\infty)]=-t \quad (2)$$

Substituting the calculated value of $C(\infty)$ and the experimental data for $C(t)$ and t, and plotting the left side of equation 2 on the y-axis and the right side on the x-axis, a straight line can be fit through the points obtained. It is from this straight line that the values for a, and τ are obtained. Figure 5 displays an example of this plotting technique.

Now we have curve fits for the data at each well from the initiation of the LOSF up until the end of the time where the equilibrium concentration was achieved. What appears to be happening in the reservoir is a chemical reaction between the hot injected steam and the reservoir rock.

$$x\,MCO_3 + y\,SIO_2 + z\,H_2O \rightarrow x\,MO\cdot y\,SIO_2\cdot z\,H_2O + xCO_2 \quad (3)$$

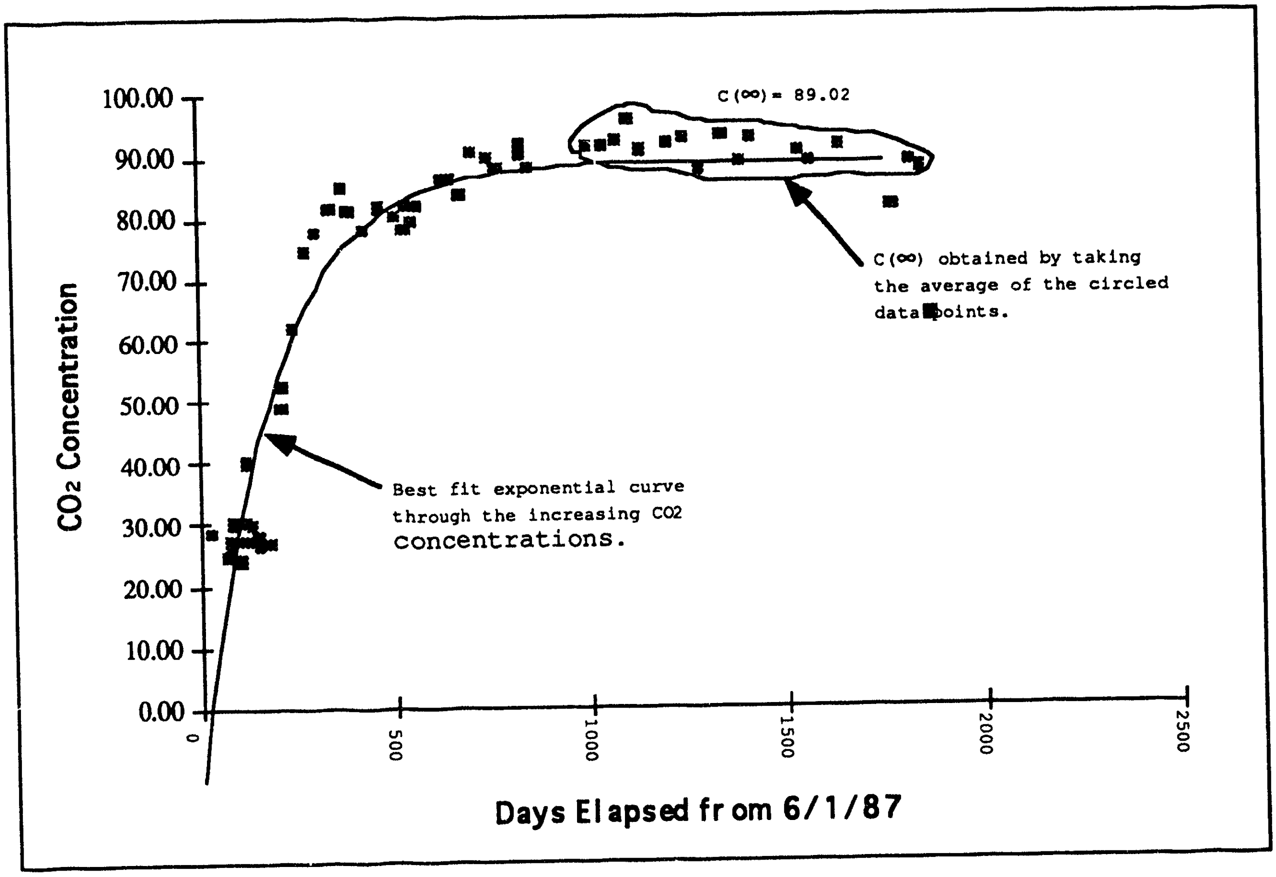

Figure 4. A sample scatter chart of CO_2 concentrations with respect to time for one of the wells in the analysis area. Well 18-3G.

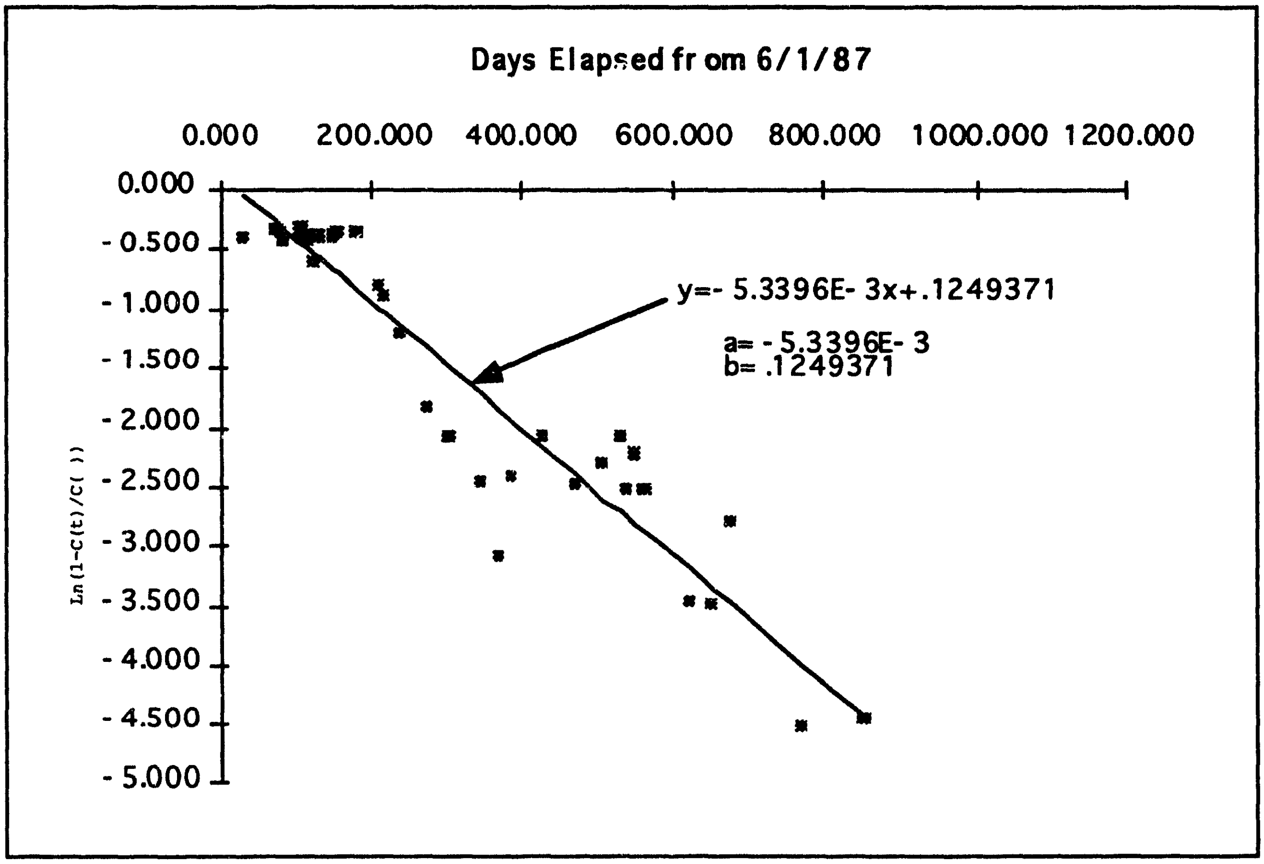

Figure 5. Curve from which a, and τ were obtained. Well 18-3G.

Well-Plot	C(∞)	t
17-3G	92.85	273.79
18-3G	89.02	187.28
18NE-3G	88.12	233.97
27-3G	76.55	316.72
28-3G	87.50	388.09
38-3G	27.85	43.17
88-4G	91.26	314.28
88NE-4G	90.15	291.37
71-9G	90.16	61.54
71NE-9G	90.74	150.98
81-9G	88.91	388.18
81NE-9G	90.85	151.13
11-10G	87.86	77.53
11NE-10G	84.86	152.38
11SW-10G	78.28	265.87

Table 2. Data for the wells with complete data sets of CO_2 concentrations. Table shows C(∞) and t for each well listed

Testing done on some well samples would seem to confirm this hypothesis of a rock-steam reaction. A carbon isotope ratio, which compares the C13/C12 ratio of the generator feedwater and the produced CO_2, was used as a test. The $\delta^{13}C$ (Chicago PDB scale) content of the CO_2 ranges from +19.70 to +21.00 with an average value of +20.27. Similarly, the The $\delta^{13}C$ content of the carbonates within three selected core samples ranges from +12.09 to +25.80 with an average value of +19.98. In contrast, the The $\delta^{13}C$ content of the bicarbonate ions in the steam generator feedwater is +8.43. The close agreement between the The $\delta^{13}C$ values for the produced CO_2 and rock samples implies that the reservoir minerals are the source of the produced CO_2.[2]

Although the temperature of the injected steam is not known, there is a temperature log available for observation well 18CW-3G. This log shows that the temperature of the steam injected sand lobes rose to values in excess of 200°F. Janjic, Briner, and Paillard conducted experiments that related the rate of thermal decomposition of several different carbonates in the presence of 27% steam. Table 3 displays their results. Although the temperatures in the table are slightly higher than those experienced in the Elk Hills reservoir, It is still reasonable to conclude that the presence of steam increases the decomposition rate of carbonates, when compared to Nitrogen. This is due to the higher heat capacity of steam, i.e. steam is able to transport more energy to the rock per volume of steam which is needed to decompose the rock.

Percent Decomposition of Calcium Carbonate (per hour)

t(°C)	100% N2	27% H2O/73% N2	Ratio
200		2	
300		2.20	
400	1	2.50	2.5
500	2	4	2
600	34	80	2.4

TABLE 3

Another piece of evidence supporting the hypothesis that the CO_2 was a result of a rock steam reaction is the comparison of the dissolved salts in the pre-steam and post-steam produced water of the LOSF (see Table 4). In the case of each carbonate, the concentration in the post-steam water is substantially greater than the pre-steam water. The increased concentration of calcium and magnesium and the increased solid content suggests that some of the alkalinic carbonates in the reservoir rock is being lost to steam injection through the proposed equation 3.

COMPOSITION	PRESTEAM COMPOSITION		POSTSTEAM COMPOSITION	
	mg/l	% of solids	mg/l	% of solids
$CaCO_3$	130	<.01	560	5
$MgCO_3$	0	0	520	5
Na_2CO_3	0	0	360	3
NaCl	30,300	98	9,140	87
$CaCl_2$	2,950	9	0	0
$MgCL_2$	1,160	3	0	0

TABLE 4

Thermodynamic Economics

As a conclusion, a link has been established between the LOSF and the growth of CO_2 in the reservoir.Subsequently, an examination of the thermodynamic efficiency of the steam flood will be made. The question to be examined here is that if all of the steam was injected into the reservoir with the intent of using the thermodynamic enthalpy of the steam to help mobilize residual oil, what part of this energy went into the generation of unwanted CO_2 ? i.e., what percentage of the initial energy invested went into the making of CO_2?

First, how much steam was injected into the reservoir. From the initial LOSF design specifications it was found that steam injection was designed for 1.5 bbl/acre-ft cold water equivalent (CWE) which amounts to 220 barrel per day (BPD) per injector. Converting this to a form which is more compatible with most thermodynamic tables, a number of of 7.71×10^4 lbm of water per day per injector were injected into the reservoir.

Secondly needed is the energy which was invested into the water in order to generate steam at the reservoir pressure and temperature of 120° F and 50 psig. In examining this process, we need to take water from 60° F, warm it up to its boiling point and then vaporize all of the water into steam. It is know that substances obtain a greater percentage of latent heat in the vaporization process thus it is expected that more energy will be used to vaporize the steam than to warm it. Thermodynamics allows us to first warm our water in a constant volume process and then to vaporize it in a constant pressure process.

Since the vaporization process is the more simpler of the two, it will be dealt with first. It has been observed, in general, that the heat added to a system in a constant pressure process will be equal to the change in enthalpy on a unit mass basis.[3] Consulting the steam tables for a pressure of 65 psia, it was found that the enthalpy change, h_{fg}, between the gas and liquid phase of water was 911.9 Btu/lbm. Using equation 4:

$$Q=\dot{m}h_{fg} \tag{4}$$

a value for heat, Q, put into vaporizing 7.71×10^4 lbm/day, m, of steam was 7.03×10^7 Btu/day per injector.

The parameter which makes the calculation of energy needed to warm the water more difficult to calculate than the vaporization is that we have chosen to warm the water in a constant volume process. Values of specific heat are easily found in tables for constant pressure (c_p) processes, but are not so easily found for constant volume (c_v) processes. A relationship between c_p and c_v was found and is shown below.

$$c_p - c_v = \frac{\alpha^2 vT}{\kappa} \tag{5}$$

c_p and c_v are the specific heats of water for constant pressure and constant volume processes respectively. α is the coefficient of thermal expansion of water, v is the molal volume of water, T is the temperature, and κ is the coefficient of compressibility of water. All parameters are at reservoir pressure and temperature. The values for all of these unknowns are constants which were obtained from in various tables. $\alpha = 1027.8 \times 10^6\ K^{-1}$, v= 18.02 cc/mole, $\kappa = 63.1 \times 10^6\ atm^{-1}$, $c_p = 4.3044$ KJ/Kg•K. Substituting these values into equation 5, a value of 3.5863 KJ/Kg•K is obtained for c_v. Using this value in the relationship,

$$Q = \dot{m} c_v \Delta T \tag{6}$$

a value of 1.55×10^7 Btu/Day per injector was found for the the amount of heat needed to heat the given amount of water from 60° F to the saturation temperature of 298° F. It is noted that this is only 22.0% of the energy needed to vaporize the steam.

The total energy invested into the creation of the steam is the sum of the energy put into warming the water and the energy put into vaporizing the water. This summation is equal to 8.58×10^7 Btu/day per injector or a grand total of 3.43×10^7 Btu/day. As a check, a calculation of how many barrels of produced oil was needed to generate this quantity of energy. A formula for the calorific value of a petroleum product free of water, ash and sulphur was obtained, e.g.

$$Q_v = 51920 - 8792d^2 \tag{7}$$

Q_v is the gross calorific value (KJ/Kg), and d is the density at 15.6° C (g/cm^3).[4] Substituting a density of 0.8927 g/cc into equation 7, a value of 4.49×10^4 KJ/Kg or 6.04×10^6 Btu/bbl of crude oil was obtained. Dividing this value into the gross heat inputed into the steam generation, we get a total of 56.8 bbl/day of crude oil which must be spent to the generation of steam for injection. This is a reasonable amount of oil to invest in a steam flood.

Thirdly, we would like to examine is the amount of injected energy, in the form of steam, which went into the generation of CO_2. In order to accomplish this we need to find out how much energy is involved in the generation of CO_2 from calcium carbonate, $CaCO_3$. The chemical process which is taking place in the reservoir is assumed to be generalized by:

$$CaCO_3 \Leftrightarrow CaO + CO_2 \tag{8}$$

In order to find the enthalpy difference, we used a table of standard enthalpies of formation to find that the $\Delta H°f$ for the involved substances are as follows: $CaCO_3(s)$= 1206.92 KJ/mol, $CaO(s)$= 635.1KJ/mol, and $CO_2(g)$= 393.5 KJ/mol. Knowing that in general, we can calculate the enthalpy change for a reaction by the equation

$$\Delta H° = n \Delta H°_f(\text{products}) - m \Delta H°_f(\text{reactants}) \tag{9}$$

where *n* and *m* represent the molar fractions of a balanced chemical equation, we are able to find that the enthalpy change for this reaction is 178 KJ/mol or 42.59 Kcal/mol.

To calculate the total energy needed for the formation of the CO_2, the number of moles of CO_2 generated is needed. Using isopleth maps of thicknesses of sand layers at Elk Hills, found in the "SOZ Gas Injection Pilot Project Review and Expansion Recommendation" report, data for the thickness of each of the five sand layers were determined at each well in the pilot area. Combining all of this data together and using a three dimensional plotting program, SURFER 4.0, total subsurface volumes for each of the sand sublayers were obtained.

The volumes obtained here represent the gross sand layer thickness. The initial reservoir data indicates an oil saturation of 55%, which permits a 45% gross displaceable phase. It is this gross displaceable phase which is assumed that the CO_2 has the potential to occupy. A scaled function of CO_2 volume was defined as the ratio of the average, or $C(\infty)$, value of CO_2 concentration at each well to the highest recorded average concentration any where in the analysis area. For each individual well, this scaled CO_2 ratio was then multiplied by the thickness of each sand layer at that well to identify the true bulk volume of the sand which the CO_2 occupied. Also knowing that the average porosity of the reservoir is 30.6%, a pore volume of which the CO_2 occupies can be found by adding the porosity into the product. The total pore volume which the CO_2 occupied is 2.55×10^8 cubic feet.

Now that we have a subsurface volume occupied by the CO_2 in the gross displaceable phase, we can use the ideal gas relationship to convert the volume to standard temperature and pressure. The surface volume of the CO_2 is equal to 1.00×10^9 scf. Since it is known that one mole of gas at STP occupies 22.41 L. we can compute the number of moles of CO_2 formed in the reservoir. The number of moles of CO_2 in the displaceable phase is 1.27×10^9 moles. Multiplying the number of moles formed by the enthalpy change found in equation 9, we can find the amount of energy spent on generating the CO_2 in the reservoir in the gross displaceable phase. The energy spent is equal to 2.15×10^{11} Btu.

Along with CO_2 in the gross displaceable phase, there is CO_2 which will be dissolved in the reservoir oil. An equilibrium constant is a ratio which relates the number of moles in the vapor phase of a mixture to the number of moles in the liquid phase of a mixture. Charts relating the equilibrium constants at reservoir pressures and temperatures can be found for a number of chemical compound which can dissolve in crude oil.[5]

The equilibrium constant for CO_2 at our reservoir temperature and pressure with relation to crude oil is 25.5. Using this equilibrium constant it can be found that there is an equivalent of 3.92% of the free gas which is dissolved in the reservoir oil. Knowing that there is 1.00×10^9 cubic feet or 2.85×10^{10} L. of free gas, we can find that there is 1.12×10^9 L. of gas dissolved in the oil. Using the same methods as described for the undissolved CO_2, we can find that is takes 8.41×10^9 Btu to generate the CO_2 which is dissolved in the reservoir oil.

Adding the energy needed to generate both the free CO_2 and the the dissolved CO_2 in the reservoir, a value of 2.23×10^{11} Btu is derived. Dividing this number by the total amount of energy which was invested into the steamflood over a 1,000 day period, 3.43×10^{11} Btu, we come up with a value of 64.99%. i.e., 65% of the energy was wasted in generating CO_2 which provided no benefit to the EOR project. The 1,000 day period was used as an approximation of the number of days it took the CO_2 concentrations within the reservoir to reach an equilibrium level, based on the analysis of CO_2 concentrations at the sampling wells.

Discussion

A question which might be raised is does the CO_2 which dissolved in the reservoir oil contribute significantly to the reduction of the oil's viscosity? i.e., is there an EOR benefit to the presence of CO_2? Through examination of the equilibrium constant for CO_2 at reservoir pressure and temperature it was found that there is less than 1 ft^3/bbl of CO_2 dissolved in the oil. By examining charts relating dissolved gas with oil viscosity, it was found that such a small change in the dissolved gas would not make a substantial change in the viscosity of the oil, i.e., no benefit to EOR.

Conclusion

The purpose of the steamdrive at Elk Hills was to help reduce the residual oil saturation and recover more oil. The energy put into the steamdrive in the form of steam had to spend approximately 65% of its total potential on the generation of CO_2. This only leaves 35%, well less than half, of its potential for the initial purpose of the project. It is unknown whether the planners of the project had anticipated the formation of the CO_2 or whether they would have gone ahead with the project if this was known. A further analysis of the reservoir rock and characteristics should be performed so that producers in the future could have a better understanding of exactly what caused the formation of the CO_2, at the Elk Hills field and it consequent energy consumption so that it could be prevented in the future and therefore increase the efficiency of their steamdrives.

Acknowledgements

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