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CALCITE INHIBITION FIELD TRIALS AT THE MINDANAO GEOTHERMAL PRODUCTION FIELD (MGPF), PHILIPPINES

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ABSTRACT

Wells APO-1D and SP-4D at the Mindanao Geothermal Production Field (MGPF) experience calcite deposition causing output declines of 0.6 MWe/month and a need for annual workovers. An attempt to inhibit calcite deposition at APO-1D by injection of a 10% solution Nalco 9354 inhibitor at 10 L/hr using relatively large diameter (ID of 2.4 cm and OD of 3.4 cm) carbon steel sucker rods to a depth of 950 meters was not successful. The sucker rods experienced corrosion and plugging of the injection nozzle and rods with debris and boiled inhibitor deposits. The relatively large diameter sucker rods may have reduced the output of the well. FT-IR spectra of the Nalco 9354 inhibitor and boiled deposits demonstrate that the inhibitor did not undergo any degradation at temperatures up to 240°C. Na-benzoate was successfully used as a proxy tracer to determine on-line concentrations of the inhibitor and for water flow measurements. The WATCH program successfully calculated the saturation index Q/K_{CaCO3}.

A simpler, smaller diameter and lower cost delivery system using 0.635 cm OD SS316 capillary tubing and a teflon protected stinger in the wellhead was successfully installed and operated in well SP-4D. An inhibitor concentration of 5 ppm Nalco 9354 in the total mass flow of the well fully inhibits calcite formation. Due to the presence of a wellbore obstruction, the SP-4D well is now operated at reduced flow conditions to maintain the flash point at shallow depth where inhibition can be performed. Even at reduced flows it is more economical to operate this well continuosly with inhibition than to perform annual scale cleanouts.

1. INTRODUCTION

Wells APO-1D and SP-4D located at the Mindanao geothermal production field (MGPF) are experiencing active calcite deposition close to their flash point. Output declined by about 50% after only 4 months of production, and the wells became non-commercial in another 3 months. Initial output declines of APO-1D and SP-4D were at 0.6 MWe/month in 1997 and at 0.4 MWe/month in 1998. To rehabilitate APO-1D , a work-over and acidizing operation costing US$345,000 was undertaken in March 1998. Another work over was carried out in May 1999 at a cost of US$125,000. SP-4D was similarly worked-over in February 1998 and May 1999 at an average cost of US$123,000. Even with work-overs, the well's output steadily declined and continuosly reduced generation earnings. In contrast, the cost of a calcite inhibition system with one year supply of chemicals would be from US$70,000–US$100,000, with maintenance of stable output and earnings. Thus, a successful calcite inhibition program is more cost effective in the long term. These figures still do not include lost revenue opportunity of about US$6,000 per day for the 6 MWe well during WO or acidizing operations.

One proven method of preventing calcite deposition in geothermal wells is through the installation of a calcite inhibition system (Benoit, 1990 and 1999; Lovekin, 1990). This technology has been applied commercially since 1988 in the USA, New Zealand and Japan.

2. ANTI-SCALANT CHEMICAL (INHIBITOR)

Nalco 9354 is an aqueous solution of an acrylate polymer known to have scale inhibition and dispersant properties for geothermal application. Nalco 9354 is a clear to pale yellow liquid with a density of 1.2-1.32 g/ml, pH of 5.4-8.0 and a viscosity of 51 cps. Nalco 9354 was chosen from a group of commercial scale inhibitors for having near neutral pH, highest inhibition efficiency and a proven track record for geothermal calcite inhibition control (Benoit, pers com 1999).

Screening tests using the NACE calcium carbonate method was conducted for various commercial inhibitors with results shown in Table 1. This standard test is designed to measure the inhibition efficiency using a synthetic brine with high scaling potential (Ca levels of 2,000 ppm saturated with CO_2) under static conditions at 71°C for 24 hours. Nalco 9354 showed the highest inhibition efficiency at 10 ppm concentration in the mixture. This test suggests that the polyacrylates have a higher % inhibition than the other polycarboxylic acids at 10 ppm. Since, the MGPF reservoir brine has much lower TDS and Ca scaling tendency than the synthetic brine, optimum dosage is expected to be much lower than 10 ppm to fully inhibit down hole scaling.

3. APO-1D FIELD TRIAL

Well APO-1D has a reservoir fluid entry temperature of about 240°C, a down hole maximum pressure of 6 MPag and 80-100 ppm Ca in the pre-flash brine. Initial WATCH calculations for the APO-1D fluids show a $Q/K_{CaCO3} > 4$ indicative of the high deposition potential of the fluids. However, during deposition the $Q/K_{CaCO3} \cong 1$ showing the equilibrium of the fluid with the forming deposit (Fig. 1). It is expected that with chemical inhibition, the fluids will maintain the high Q/K_{CaCO3} values in the absence of deposition.

The deposition rate of APO-1D was modeled using the SOLVEQ/CHILLER software (Spycher and Reed, 1990). The results for the baseline samples in 1996 suggest an average volume of scale deposited 8.70 E-04 cm^3/kg solution. This translates to a scale volume of 0.135m^3/month. If we consider 150 meters length of scale which reduces the effective open hole section of the production casing to less than 3 inches at the center, the estimated total volume of deposit will be 1.026 m^3. Then it will take about 7.6 months to choke the well to non-commercial levels. This model matches the reduction in output experienced by the well in 1997.

The injection system is composed of about 8 meter lengths hollow mild steel sucker rods with OD of 3.4 cm and ID of 2.4 cm joined to reach a depth of 951 meters. At the bottom of the sucker rods is the chemical injection head with a non return valve (NRV) and nozzle assembly with six 1/8 inch ports. The injection set-up is shown in Fig. 2. The NRV serves two functions: 1) to prevent the entry of geothermal gases into the hollow tubing during run-in and, 2) maintaining high pressure inside the tubing to prevent boiling of the inhibitor during injection. The injection system is pressurized to prevent boiling which can result in crystallization or polymerization of the inhibitor. Also, a two phase flow would result in higher pressures and lowering of pump flow rates. Expected Pinj at various well bore conditions are given in Table 2.

Field testing in August 1988 of a 10% Nalco 9354 solution was at an initial dosage flow rate of 10L/hr, resulting in a 5±1 ppm concentration in the total mass flow (50-60 kg/s). This resulted in a residence time of about 48 hours in the tubing. The 5 ppm concentration was maintained during the test. Physical and chemical monitoring data during inhibition are shown in Fig. 3.

The actual injection pressures were always much higher than predicted. These very high pressures were undesirable because they are already at the maximum limit of the pump capability and could result in mechanical failure. These high injection pressures were postulated to be due to: either 1) partial blockage of nozzle ports with debris from dilution water and/or crystallized inhibitor, or 2) NRV is stuck in partially closed position. The chemical feed solution in the tubing was replaced by plain water in preparation for surface discharging the whole contents of the sucker rod to jar any loose debris in the nozzle. However, only 380 liters of water was injected to replace the total volume of 480 liters. Thus, during discharge, the remaining 100 liters of the 125,000 ppm inhibitor solution was boiled off and crystallized. Pull-out and inspection showed that the bottom joint had 7 meters of deposit. The deposit was estimated to be about 3 kgs, which can be accounted for by the remaining inhibitor during discharge of sucker rods. The 125,000 ppm inhibitor solution could produce about 10 kgs of deposit. However, the nozzle assembly was free from inhibitor deposits but blocked by rock chips too big to pass the nozzle ports.. This may have been introduced in the tubing during lay-down on the ground prior to installation.

The remaining 119 joints were free of deposit but reeked of a smelly sulfurous odor which grew stronger nearer the bottom. This was attributed to the presence of 8000 ppm S, which is a catalyst during the manufacturing process (Benoit, pers com.).

Petrologic analysis of the deposit from the sucker rod joint show it is mainly composed (80%) of the chemical inhibitor as confirmed by the FT-IR spectra shown in Fig. 4. The clay minerals (10%) are likely impurities from the make-up water for dilution and the 5% corrosion products are from reaction of the oxygenated water with the carbon steel tubing. Comparative analysis of the FT-IR spectra of the original chemical inhibitor and the dried deposit show no substantive difference (Fig. 4). This also shows that the chemical inhibitor has not undergone any chemical or thermal degradation at temperatures close to 240°C.

Water flow monitoring using Na-benzoate as a tracer was conducted on the two-phase discharge line on a weekly basis to assess the status of the inhibition program. Water flow is a good measure of the well's output since 80% of the total mass flow is water. In the month long test (Aug.24-Sept 25, 1998), there was no decline in water flow and well head pressure. However, installation of the sucker rods inside the well reduced output from 6.2 to 5.1 MWe. This reduction in output is mainly due to: 1) decrease in production area and 2) resistance to two-phase flow. This reduction was confirmed by the increase in output back to 6.2 MWe upon removal of the sucker rods .

The inhibitor is expected to maintain the high drive potential of the fluid for deposition, but prevent actual lost of Ca as a deposit. WATCH simulation studies during the inhibition show high Q/K_{CaCO3} >4 at the flash point temperature of 235°C confirming 100% inhibition. Similarly reservoir Ca levels were maintained at stable levels of 80 ppm.

4. SP-4D FIELD TRIALS

SP-4D undergoes active calcite deposition close to its flash point at ~790 mMD at FBD. In 1998 deposition depth was at 619-814 mMD as tagged with 6 ¼ inches (15.875 cm) drill pipe. Similarly, a 6 inch (15.24 cm) sinker bar tagged blockage at 735 mMD and a 3 inch (7.62 cm) go-devil at 795 mMD. The well was worked over in February 1998 to remove the calcite blockage and recover its output. The well was put on line with a commercial output of 6 MWe in March 1998. Calcite deposition recurred at a slower rate of 0.41 MWe/month and another work-over was undertaken in April 1999. However, the blockage in 1999 was tagged at deeper levels of 794.5 –854.5 mMD in the 7 5/8 inch liner indicative of a deeper flash point depth under the operating conditions in 1998.

The deposition rate of SP-4D was also modeled using the SOLVEQ/CHILLER software (Spycher and Reed, 1990). The results for the baseline samples in 1996 suggest an average volume of scale deposited of 4.08E-04 cm^3/kg solution. This translates to a monthly deposition rate of 0.0634 m^3/month. During the work-over the volume of the scale blocking the well was estimated to have a total volume of about 0.68 m^3. Re-calculation suggest that it will take about 10.7 months to deposit this scale inside the well. This model roughly matches the reduction in output experienced by the well in 1997 prior to its work-over in early 1998. The repeated occurrence of calcite deposition and declining output after each work-over (Fig.5) prompted the installation of a calcite inhibition system. This time sucker rods were no longer considered.

The injection system chosen for SP-4D is a ¼ inch OD (0.25 inch) capillary tubing weighted down with sinker bars (~70 kgs) and dispersion head at the bottom run to a depth of 815 mMD (Fig. 6). The capillary tubing is protected by a stinger near the well head. To protect the tubing from rubbing against the stinger and the lubricator assembly, braided teflon was introduced in the surface pack-off and the bottom of the stinger. The weight of the sinker bars was calculated considering the drag force and the flow of the well at the target injection depth. This injection set-up was installed in well SP-4D after its work-over in May 1999.

The flash point depth of the well changes with variable operating well head pressures from simulations using HOLA and WELLSIM (Table 3). Under full bore conditions (low OWHP) the flash point depth is at 940mMD, while under throttled conditions (higher OWHP) it ranges from 500-809 mMD. Since the available capillary tubing was of limited length (1100m) and an unidentified obstruction occurs at 825mMD, it was decided to operate the well under throttled conditions. The injection setting depth was limited to 815mMD, to minimize risk of tubing breakage due to the obstruction. The well was put on-line under choked conditions (OWHP~13 kscg) producing about 3.0 MWe for the inhibition trial. The SP-4D energy generation comparison (Table 4) clearly show that with calcite inhibition higher revenue will be realized even under choked conditions.

A 5% solution of Nalco 9354 was injected at flows of 14-17 L/hr to achieve a dosage concentration of 5 ppm in total mass flow. The actual concentration of the prepared diluted Nalco 9354 solution can be determined by the Hyamine method, a simple turbidity test for long chain hydrocarbons. The injection flow rate can then be adjusted to achieve the desired on-line dosage based from the following equation:

$$C_{inj}*F_{inj} = C_{line}F_{line} \quad (1)$$

where C_{inj} is the actual concentration of the injectate inhibitor solution in ppm, F_{inj} is the dosage flow rate in kg/s, C_{line} is the on line dosage concentration in ppm which we try to maintain at 5 ppm, and F_{line} is the total mass flow (TMF) of the well in kg/s. The density of the injectate solution is also taken to be able to convert the F_{inj} which is measured in liters/s into mass rate (kg/s). The TMF can be calculated from bore output measurements or tracer flow test data.

The actual residence time of the inhibitor ranges from 45 minutes to 1.5 hours in the 1100 m (including the spooled portion at the surface) capillary tubing (ID=0.180 inch) at flows of 20-14 liters/hour. This was established from tracer injection using Na-benzoate. Injection pressures were stable at values ranging from 200-240 psig. These injection pressure are just slightly above the OWHP of 185 psig.

The on-line concentration of the inhibitor (polyacrylate) in the two-phase discharge cannot be determined by the Hyamine method. Interference of other brine components (e.g. silica) which precipitate out with the polymer occur at pH 7 producing much higher apparent inhibitor on-line concentration. Other analytical methods based on the properties of hydrocarbons or the polyacrylates should be investigated by the chemical companies.

In the absence of a direct on-line analysis of the inhibitor, another tracer was injected to evaluate the injection set-up. Na-benzoate is the tracer routinely used by PNOC-EDC for water flow measurements. The concentration of Na-benzoate can be determined by UV-VIS spectrophotometry by reading the absorbance at λ=230 nm. A known concentration of Na-benzoate was mixed with the inhibitor solution and injected using the calcite inhibition set-up. Water samples were then collected after 45 minutes in the two-phase line and analyzed for the concentration of Na-benzoate. The breakthrough curve obtained from the Na-benzoate analysis is shown in Fig. 7. The results confirm the integrity of the injection set-up, expected residence time in the tubing and constant dosing flow rate.

Physical and chemical monitoring of the progress of the inhibition trial in SP-4D is shown in Fig. 8. The results show that the on-line inhibitor concentration was maintained at desired 5 ppm level. Water flow monitoring using Na-benzoate show an average stable value of 31 kg/s. The power output of the well was maintained at 3.0 MWe. Modeling of the reservoir chemistry flashed at 235°C inside the well show $Q/K_{CaCO3} > 2$, suggestive of the absence of deposition and success of the inhibition (Fig. 9).

5. CONCLUSIONS AND RECCOMMENDATIONS

Field trial of the chemical inhibitor Nalco 9354 at wells APO-1D and SP-4D proved its anti-scalant properties against calcite deposition. Nalco 9354 has near neutral pH, making it less corrosive and easier to handle. However, an on-line monitoring analysis of the inhibitor concentration in the line discharge is still not available. Deposit forming components of the brine (e.g. silica) interfere with the existing Hyamine or turbidity test for the polymer.

The downhole injection system still remains as the more difficult component of the inhibition technology. Attempts to use big diameter (ID of 2.4 cm) sucker rods for the delivery system failed. Sucker rods are not suitable injection system for calcite inhibition which requires low flows. The simple system of hanging a ¼ inch capillary tubing weighted down by sinker bars and a dispersion head, with a protective stinger near the well head proved more successful and easier to install. The correct sinker bar weight which will withstand well flows without breaking the tubing can be calculated based on drag force and the fluid counter flow inside the well. The small diameter capillary tubing is preferred over the sucker rods due to ease of injection and absence of output reduction.

The calcite inhibition program was monitored from physical output data using on line tracer techniques (e.g. Na-Benzoate for water flow) and chemical analysis (e.g. Q/K_{CaCO3}). These techniques were invaluable in gauging the success of the inhibition. Similarly, modeling of flash point depths and temperature of the well were undertaken with HOLA and WELLSIM to evaluate the correct injection depth at variable well condition.

PNOC-EDC will install similar calcite inhibition systems on wells experiencing recurring calcite deposition. Long term plans include the utilization of a more reliable protected tubing (e.g. armored, concentric) in the future.

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Table 1. NACE test of some commercial formulations.

Chemical Inhibitor (10 ppm)	**Active Component**	**PH (Neat)**	**% Inhibition**
1. Drew 11-598	PMA	<2.0	20.73
2. Bellasol S-20	Polyacrylate	9.0	51.60
3. Nalco 9353	Polyacrylate	3.1	71.01
4. Nalco 9354	Polyacrylate	5.4-8.0	84.48
5. Nalco 95DO-066	Polycarboxylic acid	<2.0	44.11
6. Scaletreat 5818	Polyacrylate + dispersant	6.5-9.2	51.77

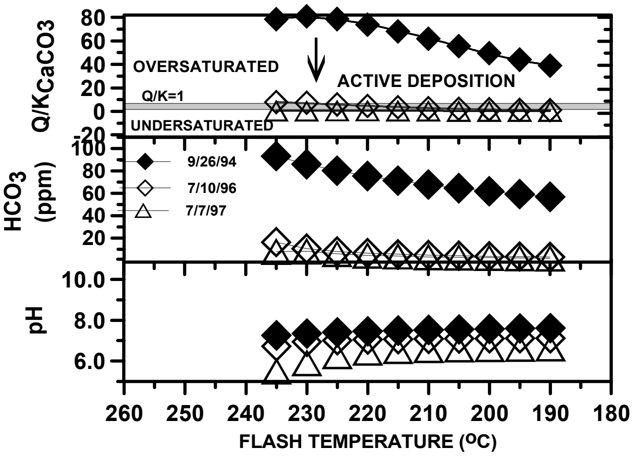

Figure 1. Boiling simulation of APO-1D reservoir fluids prior to calcite inhibition.

Table 2. Theoretical and real injection pressures (psig) during the inhibition trials. The predicted theoretical injection pressure is calculated from $P_{inj} + P_{liq} = P_{950} + P_{NRV}$.

Condition	**P_{liq}**	**P_{950}**	**P_{NRV}**	**P_{INJ}(Theo)**	**P_{INJ} (Real)**
1. cold (shut)	1340	798	1050	>508	100-600
2. heat-up	1134	747	<1050	<663	800-1000
3. discharging	1151	609	<1050	<508	100-600 (S1-3) 850-1350 (S4) 800-1000 (O)

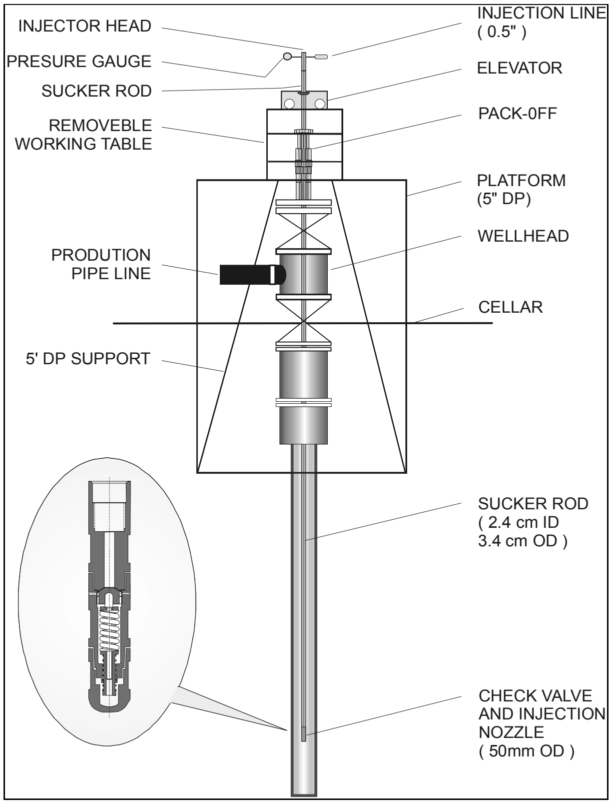

Figure 2. Final set-up of sucker rod during injection

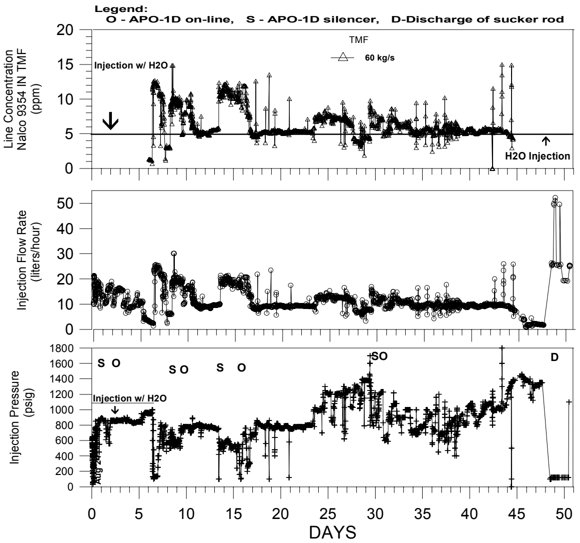

Figure 3. Physical and chemical monitoring during APO-1D calcite inhibition

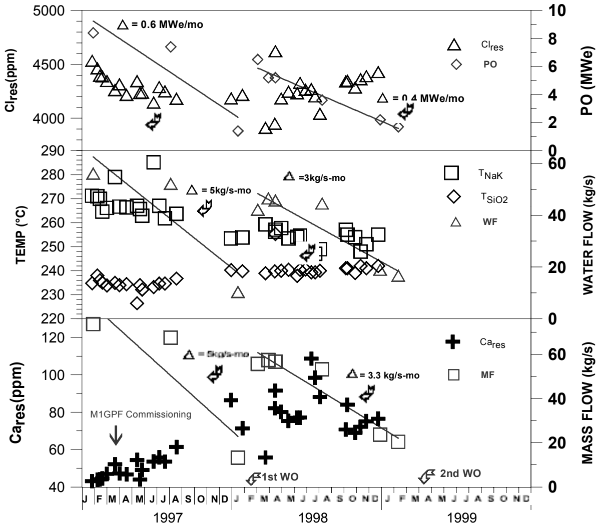

Figure 5. SP-4D physical and chemical trends with time due to calcite deposition.

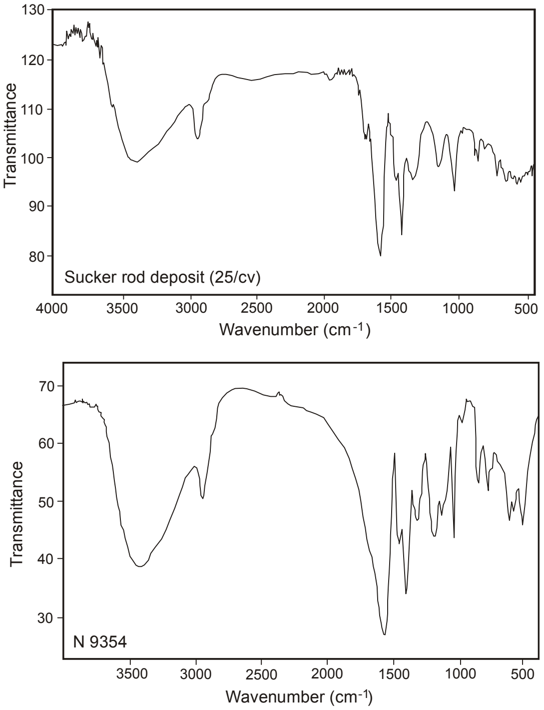

Figure 4. FT-IR spectra of sucker rod deposit and Nalco 9354

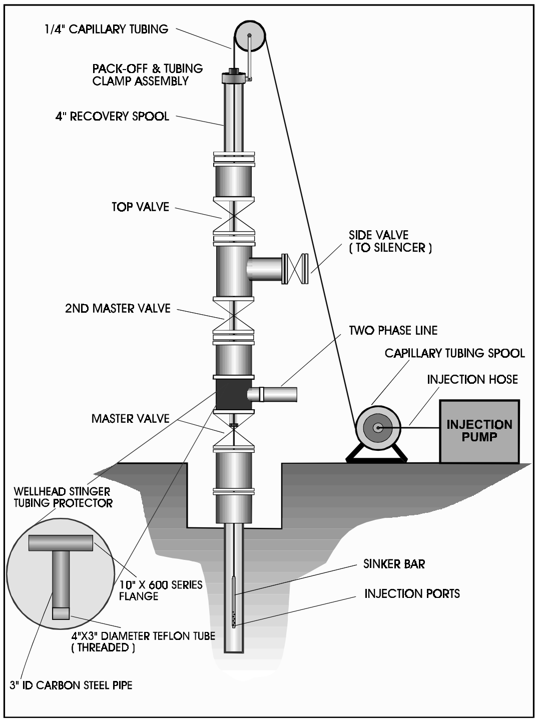

Figure 6. SP-4D final injection set-up.

Table 3. Calculated flash point parameters of SP-4D using WELLSIM.

WHP kscg	H KJ/kg	MF Kg/s	Flash Point			
			Depth		Pres MPag	Temp °C
			mMD	MVD		
PATS Survey last April 1998						
11.0	1046	57.5	800	743	3.11	236
13.4	1014	34.7	791	736	3.15	236
Bore output measurements data May 19-21, 1999						
10.0	1007	52.9	754	710	2.75	233
12.0	964	37.1	538	516	2.47	226
	1024	38.5	881	809	3.17	239
12.5	981	34.4	610	58.2	2.6	228
	1014	35.1	812	753	3.04	237
13.0	950	28.3	435	420	2.32	222
13.1	992	27.0	673	641	2.78	232
Online waterflow measurement						
13.1*	990	36.1	623	594	276	231

Table 4. SP-4D energy generation comparison with and without inhibition at throttled conditions.

	Without Inhibition			With Inhibition			With Inhibition			With Inhibition		
	MW	MWh	M$	MW	MWh	M$	MW	MWh	M$	MW	MWh	M$
June	4.7	3384	3.20	3.0	2160	2.04	2.5	1800	1.70	2.0	1440	1.36
July	4.3	3227	3.05	3.0	2232	2.11	2.5	1860	1.76	2.0	1488	1.41
August	3.0	2957	2.80	3.0	2232	2.11	2.5	1860	1.76	2.0	1488	1.41
September	3.6	2601	2.46	3.0	2160	2.04	2.5	1800	1.70	2.0	1440	1.36
October	3.3	2418	2.29	3.0	2232	2.11	2.5	1860	1.76	2.0	1488	1.41
November	2.9	2079	1.97	3.0	2160	2.04	2.5	1800	1.70	2.0	1440	1.36
December	2.5	1879	1.78	3.0	2232	2.11	2.5	1860	1.76	2.0	1488	1.41
January	2.2	1609	1.52	3.0	2232	2.11	2.5	1860	1.76	2.0	1488	1.41
February	1.8	1253	1.19	3.0	2088	1.98	2.5	1740	1.65	2.0	1392	1.32
March	1.4	1070	1.01	3.0	2232	2.11	2.5	1860	1.76	2.0	1488	1.41
April	1.1	774	0.73	3.0	2160	2.04	2.5	1800	1.70	2.0	1440	1.36
May	0.7	513	0.49	3.0	2160	2.04	2.5	1800	1.70	2.0	1440	1.36
June	0.4	252	0.24	3.0	2160	2.04	2.5	1800	1.70	2.0	1440	1.36
Total		23250.3	22.00		24120	22.82		20100	19.02		16080	15.21

Date: May 21, 1999 Injectate (C2) = 82182.5 ppm
SP-4D (1445H) F2" = 0.0054 kg/s
WHP = 12.6 kscg BG = 2.3948 ppm

SAMPLING TIME (minutes)	SAMPLE NUMBER	Na-Bz (ppm)	F1" (kg/s)
0	1	2.3948	
45	2	16.0980	32.4
50	3	16.2172	32.1
55	4	16.2756	32.0
60	5	16.5196	31.4
65	6	16.4080	31.7
70	7	16.3788	31.7
75	8	16.6284	31.2
80	9	16.7952	30.8
85	10	16.7236	31.0
		Average =	31.6
		Std. Dev =	0.5

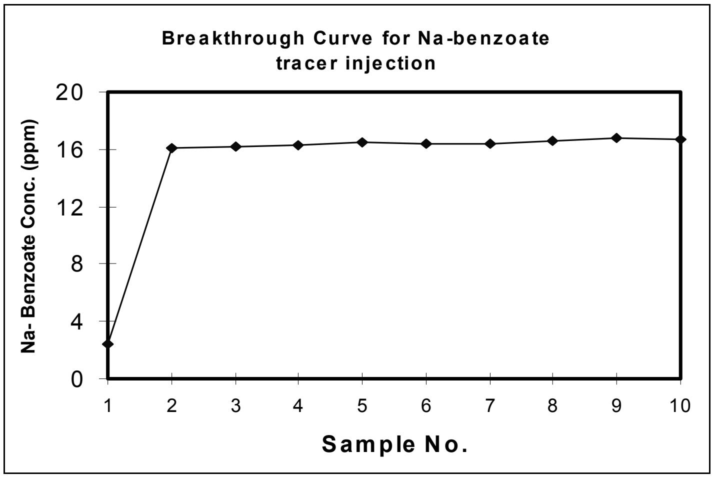

Figure 7. Water flow measurements using Na-benzoate as tracer.

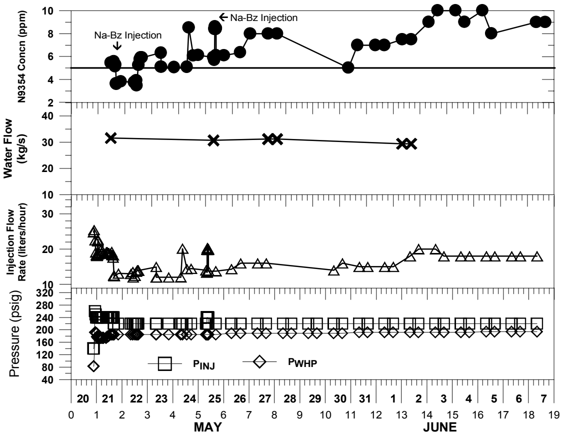

Figure 8. SP-4D physical and chemical monitoring during inhibition.

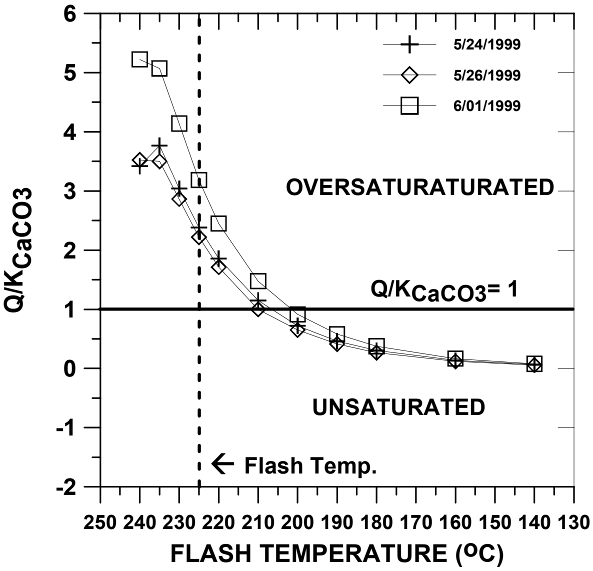

Figure 9. Calculation of Q/K_{CaCO3} of SP-4D with time during inhibition.