Removal of Water Blocks from Gas-producing Formations†

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ABSTRACT

A method was developed by the Bureau of Mines in the laboratory and in the field to relieve capillary water blocks in gas wells. Impaired gas permeability was improved by this inexpensive chemical treatment which lowers the surface tension of the water held in the capillaries of the formation. Effectiveness of the alcohol-surfactant treatment was tested with a variety of chemicals and with sandstone cores cut from rocks having relatively low permeability. Field tests on 20 gas-producing and storage wells demonstrated the effectiveness and limitations of the method. The productive capacity of some wells was doubled by the treatment.

The final test was evaluated by the neutron logging technique for measuring changes in apparent liquid saturation. Maximum apparent liquid saturation was reduced by 52 percent; gas production rate increased from 2.3 to 3.5 MMcf/D (million cubic feet per day).

INTRODUCTION

Recent emphasis by petroleum industry and Government research on production stimulation methods led to the development of a chemical treatment to improve the deliverability of gas wells. This report on a part of the petroleum engineering research describes the work completed by the Bureau of Mines on a study of the effects of water intrusion into capillaries in low-permeability reservoir rocks and the development of an effective method for removing the water blocks. Laboratory and field investigations show that formation damage frequently occurs when water invades low-permeability rocks.

After testing 51 sandstone and dolomite cores in the laboratory, it was determined that water would block core samples in the permeability ranges from 0.2 to at least 526 md and that cores in the lower permeability ranges were more readily blocked. In the initial test, cores were blocked with water. In later tests, cores were blocked with kerosine and diesel oil or with a water-kerosine or water-diesel oil combination. In some tests water alone would not block the core, but with the addition of kerosine or diesel oil a block was formed. A variety of surfactants was tested in the laboratory to remove water or water-oil blocks from cores having permeability usually less than 100 md.

Twenty gas-producing and storage wells were treated for the removal of water blocks. The alcohol-surfactant treating fluids applied in the field previously were studied in laboratory core tests. The treatments in most wells were designed to relieve the apparent water-blocked condition by contacting an approximate 1-ft section of the formation affected around the well bore.

During initial field tests, the treating fluids were displaced into the affected formation by pipeline gas. Later, in lieu of high-pressure natural gas, or when gas was not available, carbon dioxide was used as the liquid-displacing medium because of its general availability and ease of handling. These tests demonstrated the effectiveness of the alcohol-surfactant method in relieving water-blocked conditions as shown by the increases in the rates of gas production from the wells tested. Results of this study extended the laboratory work reported by other investigators. In addition, results from laboratory tests were applied in the field.

Water blocks have been discussed in the literature,[7,8,13,16,17]‡ where results of laboratory and field research have been published and specific causes of formation damage have been described.[9,10] Usually, water blocks are formed in low-permeability reservoirs during completion and workover operations. These restrictions can be caused by the accidental or intentional intrusion of water while balancing the reservoir pressure with water to permit workovers. Other causes may be from the intrusion of liquids used in drilling muds, cement, mud-weighting materials, brine, fresh water, acid, and some hydraulic fracturing fluids. Some formation damage almost always occurs when tight formations are exposed to water, regardless of the length of exposure and preventive measures applied.

A basic laboratory study by Yuster and Sonney[17] concluded that water blocks were formed by the establishment of a condition known as the Jamin action.[11] From tests on water-filled cores, they found that when air pressure was increased sufficiently at the inlet side it was almost impossible to force in more air. The process was observed through a microscope showing air bubbles occupying some of the pores. When pressure was applied, these bubbles were distorted in attempting to pass through the constrictions. The distortions required considerable force and, if a breakdown pressure was not exceeded, the bubbles remained in place hampering the movement of fluids through the sand. In effect, the water held in place in the sand pores by high surface tension results in capillary pressures too high to be overcome by existing reservoir energy. Calhoun[3] defines surface tension as the force in dynes acting perpendicular to a line of 1 cm length and for a distance of 1 cm in order to produce the new unit area of surface.

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†Presented at the spring meeting of the Eastern District, API Division of Production, April 1965.

‡See references at the end of the paper.

This phenomenon does not exist unless two immiscible fluid phases are present; the removal of one of the phases should eliminate the plug or block. The recommendation by Yuster and Sonney for removing a water block, based on the results from laboratory experiments, was to inject into the producing formation a treating fluid consisting of a surface-tension-reducing additive and a solubilizing agent to absorb the water. Liquids used with success were acetone and a 9-to-1 mixture of acetone and diethyl ether. They concluded that in this system the capillary forces would be decreased and that gas pressure in the reservoir would expel the water. The forces which express the molecular action between the various solid, liquid, and gas phases in a reservoir, according to Calhoun,[3] are called capillary forces.

The Bureau of Mines reported[1,15] the results of laboratory and field tests which opened the way for development of a practical and economic method for removing water blocks. The recent study resulted in an inexpensive alcohol-surfactant method to improve gas-well deliverability.

WATER-BLOCK MECHANISM

Laboratory and field investigations show that formation damage can occur when water invades low-permeability reservoir rocks. Producing zones in some wells are more vulnerable to water damage than those in other wells, and the effects from water intrusion may not be readily apparent in some wells. However, as the unaffected productive zones become pressure depleted, the water-blocked zones having flow capacities restricted by water do not contribute normal volumes of fluid. Thus the well deliverability is significantly and sometimes permanently reduced.

Formation damage that reduces permeability around the well bore results from many causes. Usually it is difficult to determine the specific cause or combination of conditions that decrease deliverability from a gas well. The formation around each well bore that fails to retain original permeability presents an individual problem. A careful study of well-completion data and performance records helps to determine whether or not a well is water-blocked.

The method described here is based on the physical and chemical properties of alcohol and detergents. Alcohol, the principal constituent of the treatment, serves as a liquid drying agent, a mild surfactant, and as a carrying agent for the detergent. The detergent, commonly referred to as a surfactant, is a surface-active agent.

A primary function of the surfactant, in addition to the cleaning or detergency feature, is to make the water more mobile. This is accomplished by the inherent ability of surfactants to reduce the surface tension of water. The normal surface tension of water, 72 dynes/cm, can be reduced to 30 dynes/cm or less by adding a detergent in concentrations as low as 0.01 weight-percent active ingredient. It was shown previously[6] that the myriad surfactants available for testing in commercial applications represent a wide variety of chemical compositions and properties. Table 1 contains data relating to the surface tension, type, active ingredient, and manufacturer of various surfactants. Relatively complete data on surfactant properties are found in a report by Dunning and Johansen.[5]

Johansen, Dunning, and Beaty[14] report that detergents (surfactants) are divided into three types: cationic, anionic, and nonionic, according to their ionization products. If the oil-soluble part of the molecule forms a positive ion, the detergent is classed as cationic; when the oil-soluble ions are negatively charged by gaining electrons, the detergent is anionic. Amphoteric detergents contain cationic and anionic groups and are either cationic or anionic under acidic or basic conditions, respectively. True amphoterism occurs in a system when the right amount of acid is added to balance the cationic and anionic properties. At this point a zwitterion is formed that is both positive and negative at the same time. Those detergents that do not ionize but owe their solubility in water to the polar group in the hydrophilic (water-loving) side chain are classed as nonionic. Built detergents commonly contain inorganic substances such as carbonates, borax, and polyphosphates, which enhance the effectiveness of the detergent.

During the annual injection cycles in gas-storage operations, the formation around the well bore filters from the gas a mixture of dust, scale, compressor oil, and other finely divided particles. This potential plugging material is not always removed from the sand face by blowing. Consequently, it is important to include a surfactant in the treating fluids to clean the sand face. In discussing detergency, Dunning, Hsiao, and Johansen[4] show that the problem of petroleum displacement from oil-wet surfaces is similar to that of cleaning soiled fabrics. A dirty cloth is one in which the fibers are generally wet with grease, and the problem of cleaning is to displace the grease by an aqueous phase. Water alone may not displace the grease (compressor oil), but a good detergent solution will do so by changing the contact angle at the water-oil-solid junction from 0 deg in the oil and 180 deg in the water to 180 deg in the oil and 0 deg in the water. According to Calhoun[2] in discussing the condition of liquid held in a capillary, the angle that the liquid surface makes with the solid surface is called the contact angle. Since surface tension acts in the surface of the liquid, it acts at the contact angle to the solid surface.

Some water-blocked formations include an oil phase either as formation fluid or as oil introduced during hydraulic fracturing. Oil-water blocks are most difficult to correct and require special treatment. Johansen and Dunning[13] show that a system in which the reservoir rock is preferentially water-wet normally allows more efficient flow of water, and that forcing water through an oil-wet capillary requires extra pressure. The presence of even small amounts of asphaltic material in some crude petroleums appears to cause the system to be preferentially oil-wet. Complete removal of the asphaltic materials by propane precipitation is required to change the wetting tendency of oil, indicating that the

Table 1

Surfactants* Tested and Others with Low Surface-tension Values†

Trade Name	Manufacturer	Type	Active Ingredient, Percent	Surface Tension, Dynes/Cm
Surfactants Tested				
Armac CD-50	Armour Industrial Chemical Co.	Cationic	50	29.2
Armomist	do	do	40	35.8
Arquad T-2C-50	do	do	75	27.8
Foamitron	Champion Chemical Co.	Nonionic	100	—
HOWCO suds	Halliburton Co.	do	65	36.8
Hyamine 1622	Rohm & Haas Co.	Cationic	100	32.2
Igepal CO-710	General Aniline & Film Corp.	Nonionic	99	32.0
O.K. Liquid	Procter & Gamble Co.	Nonionic and anionic.	50	31.9
Santomerse KDT	Monsanto Chemical Co.	Nonionic	100	27.7
Tergitol D-TMN	Union Carbide Chemical Co.	do	90	25.5
Triton X-45	Rohm & Haas Co.	do	100	28.9
Triton X-100	do	do	100	31.4
Other Surfactants with Low Surface-tension Value [5]				
Aerosol 1-B	American Cyanamid Co.	Cationic	100	26.3
Aliquat 4	General Mills, Inc.	do	50	27.1
Igepal CO-430	General Aniline & Film Corp.	Nonionic	99	28.6
NNO	Atlas Powder Co.	do	100	25.7
OPE-3	Rohm & Haas Co.	do	100	28.6
Solar F-183	Swift & Co.	do	100	31.8
Span 20	Atlas Powder Co.	do	100	25.9
Surfonic N-40	Jefferson Chemical Co.	do	100	32.1
Synthetics C-69	Hercules Powder Co.	do	100	29.2
Triton X-114	Rohm & Haas Co.	do	100	29.6
Victawet 12	Victor Chemical Works	do	100	27.0

*Reference to specific brands is made for identification only, and does not imply endorsement by the Bureau of Mines.

†Surface-tension values at 25 C were determined by the du Nouy ring method for solutions of a concentration of 1.0 percent by weight or 10,000 ppm.

substances in crude oil, which are responsible for the wetting characteristics, are closely associated with the asphalt fraction. An oil-water block in which the oil phase is asphaltic would not be expected to be removed by an alcohol-surfactant treatment.

It has been shown that the alcohol-surfactant treatment developed during this study restores the permeability of the productive formation to gas by removing water from the capillary pores of the formation in the vicinity of the well bore. The surfactant decreases the surface tension of the water causing a decrease in capillary pressure which allows the water to be more easily displaced by injected gas. The alcohol acts as a drying agent; thus, the combination of surfactant and dessicant forced into the formation by a gas at high pressure is very effective for removing a water block in the immediate vicinity of the well bore.

LABORATORY EXPERIMENTS

Procedure

Samples of outcrop formation and petroleum reservoirs were collected, and cylindrical cores cut parallel to the bedding planes were dressed to about 2 cm in diameter and 3 cm in length. The cores were dried in an oven for about 3 hours at 200 F previous to measuring the before-blocking permeability. If the measured permeability of the core sample was greater than 100 md, generally the sample was discarded.

Each of the core samples referred to in Table 2 was inserted in a holder, and the permeability to gas was measured by flowing dry nitrogen through the system at about 80 psig. After the permeability was reduced by injecting a blocking liquid the permeability to nitrogen was again determined. The treating fluid was then injected and the after-treatment permeability was measured. Conventional gas-permeability equipment was used for this investigation. About 2 to 3 pore volumes of blocking liquids, listed in Table 2, were forced into each core by nitrogen pressure until flow diminished and a block occurred. The blocked core was then allowed to come to equilibrium under pressure in the injection system for 3 to 36 hours. An attempt was made to remove the block by injecting into it either a previously mixed solution or hot nitrogen. After 10 cu ft of the gas passed through the core the after-treatment permeability was measured.

Results

Laboratory test results on 51 cores are listed in Table 2. The tests indicate that permeability (k) was appreciably reduced by water and oil-water intrusion. Cores with permeability greater than about 100 md, tested but not listed in Table 2, were not affected by similar liquid intrusion. Before-blocking permeability (k_{bb}) ranged from 0.1 to 94.0 md, excluding 2 high-permeability cores. Reduction in the after-blocking permeability

$(k_{a\,b})$ ranged from 0.0 to 49.0 md. After-treatment permeability $(k_{a\,t})$ was increased from 0.1 to 81.0 md. The ratio $k_{a\,b}/k_{b\,b}$, shown in the next-to-last column in Table 2, represents the percent of before-blocking permeability that remained after the core was blocked. The ratio $k_{a\,t}/k_{b\,b}$ indicates the percent recovery from the before-blocking permeability following the treatment.

Cores 1 to 16 were treated with a mixture of methanol and a variety of surfactants. The average before-blocking and after-treatment permeabilities were 67 and 52 md, respectively. The average recovery ratio of permeability of the damaged cores shown in the last column in Table 2 was 78 percent.

Cores 17 to 20 were treated with a water-surfactant mixture to compare results with those treated with the alcohol-surfactant mixture. The average recovery ratio $(k_{a\,t}/k_{b\,b})$ of damaged permeability for these cores was 59 percent. Core 21 was treated with methanol, and a recovery ratio of 40 percent of the damaged permeability was effected.

Water-damaged cores, numbered 22 to 24 in Table 2, were treated with isopropanol. The recovery ratio of permeability of these cores was 80 percent, indicating that under laboratory conditions the alcohol portion of the treatment effects much of the removal of the water blockage.

Results of laboratory tests on cores 25 to 28 show that dimethoxypropane is effective in correcting water-blocked reservoir conditions around gas wells. However, the high cost of the liquid may prohibit its use in this application. Dimethoxypropane acts as an effective drying agent by chemically reacting with water to form acetone and methanol, which in turn are miscible with water in all proportions. Average recovery ratio of permeability in these cores was 66 percent, which compares very well with the alcohol-surfactant treatment. Approximately 5.8 parts by weight of 2,2-dimethoxypropane react with 1 part of water under slightly acidic conditions, as shown by the equation:

$$\textit{2,2-dimethoxypropane} + \textit{water} \rightarrow \textit{acetone} + \textit{methyl alcohol}$$

or:

$$\textit{104 parts} + \textit{18 parts} \rightarrow \textit{58 parts} + \textit{64 parts}$$

Comparative tests were made on cores 29 and 30 of varied permeability to determine the vaporization effect of large volumes of dry nitrogen flowing through the cores at room temperature. Although a 78-percent recovery ratio of damaged permeability was effected, it was shown that the volume of gas required to remove the water block effectively prohibits the use of this method of removal.

Results obtained from drying cores 31 to 35 with warm nitrogen are tabulated in Table 2. A recovery ratio of 89 percent of the damaged permeability resulted from drying these cores with warm nitrogen. Conceivably, this method could be applied effectively to shallow, low-pressure, water-blocked wells where reservoir temperatures are low. Either nitrogen or natural gas preheated in the range of 180 to 200 F and injected through small-diameter tubing or a siphon should permit enough heat transfer to a producing formation to relieve a water-blocked condition. Water-damaged wells producing gas at reservoir temperatures above 200 F probably would not be corrected by injecting a heated gas.

Cores 36 to 51 were blocked with either diesel oil, kerosine, brine, or distilled water, or by a combination of fluids capable of producing an emulsion-type block. In addition, a test procedure for evaluating water-oil block removal was established for testing cores 36 to 46 with results listed in Table 2. The laboratory procedure developed for these tests was to measure the permeability of each core with nitrogen gas before a water-oil block was induced, again after the blocked condition was induced, and finally, after treating the core with approximately 10 pore volumes of methanol. The purpose of this series of tests was to obtain information on water-oil blocks caused by hydraulic-fracturing treatments where diesel oil, kerosine, or condensate was used as the fracturing fluid.

Tests on core samples 36 and 37 used diesel oil as the blocking agent. Only partial blocks were obtained in attempts to damage these cores. Several attempts were made to block core 38. It was saturated with distilled water and permeability measurements were taken before and after the blocking attempts, which were 51 and 45 md, respectively. Diesel oil was then injected to determine what effect, if any, it would have on the water block. A permeability measurement indicated the after-blocking permeability was reduced to 42 md. The core was then soaked in diesel oil for 3 days in an attempt to further block the core. Results of the permeability measurements before and after this attempt were unchanged. The last attempt to block the core was made with a two-phase liquid system composed of distilled water and diesel oil. This injection reduced the permeability of the core to zero. After treating the core with methanol, permeability was restored to 42 md.

Distilled water and diesel oil were used as the agents to water-oil block cores 39, 44, and 46. A total block was achieved in these attempts except for the test on core 46. Distilled water and kerosine were used as the agents to water-oil block cores 40, 41, and 43. Again, a total block was achieved in these attempts except for the test on core 43. Distilled water and black condensate were used to water-oil block core 42, with only a partial block obtained. Permeability was reduced from 40.0 to 24.0 md after blocking. The methanol treatment used to remove the distilled water-condensate block was not successful. Possibly some asphaltic material was precipitated from the black condensate. A comparison of ratios in the last two columns in Table 2 shows that no improvement in the permeability of this core was effected by the treatment.

Although it is premature to draw conclusions from one test, it is reasonable to assume that blocks formed by precipitating asphaltic material, paraffin, or any

Table 2

Water Block Removal from Cores with Selected Agents (1 weight-percent active ingredient)

Core	Blocking Liquid	Surfactant[a]	Desiccant	Permeability to Nitrogen, Md: $k_{b\,b}$, Before Blocking	$k_{a\,b}$, After Blocking	$k_{a\,t}$, After Treatment	$k_{a\,b}/k_{b\,b}$, Percent	$k_{a\,t}/k_{b\,b}$, Percent
1	Distilled water	Triton X-100	Methanol	70.0	15.0	51.0	21.0	73.0
2	do	do	do	72.0	27.0	61.0	38.0	85.0
3	do	do	do	60.0	10.0	40.0	17.0	67.0
4	do	do	do	90.0	21.0	66.0	23.0	73.0
5	do	Triton X-45	do	64.0	9.0	44.0	14.0	69.0
6	do	Arquod T-2C-50	do	68.0	12.0	44.0	18.0	65.0
7	do	do	do	48.0	13.0	44.0	27.0	92.0
8	do	Santomerse KDT	do	80.0	20.0	55.0	25.0	69.0
9	do	Igepal CO-710	do	54.0	9.0	33.0	17.0	61.0
10	do	Tergitol D-TMN	do	63.0	6.0	45.0	10.0	71.0
11	do	Hyamine 1622	do	89.0	42.0	69.0	47.0	78.0
12	do	Arquad T-2C-50	do	94.0	38.0	81.0	40.0	86.0
13	do	Triton X-100	do	69.0	42.0	71.0	61.0	103.0
13	do	do	do	71.0	3.0	73.0	4.0	103.0
14	do	Arquad T-2C-50	do	61.0	40.0	47.0	66.0	77.0
15	do	HOWCO suds	do	76.0	49.0	59.0	64.0	78.0
16	do	Armomist	do	3.0	1.0	3.0	33.0	100.0
17	do	Arquad T-2C-50[b]	—	86.0	23.0	54.0	27.0	63.0
18	do	do[b]	—	78.0	5.0	24.0	6.0	31.0
19	do	HOWCO suds[b]	—	41.0	10.0	30.0	24.0	73.0
20	do	Armac CO-50[b]	—	75.0	27.0	51.0	36.0	68.0
21	do	None	Methanol	52.0	19.0	21.0	37.0	40.0
22	do	do	Isopropanol	74.0	17.0	56.0	23.0	76.0
23	do	do	do	48.0	13.0	35.0	27.0	73.0
24	do	do	do	70.0	39.0	64.0	56.0	91.0
25	do	do	Dimethoxypropane	47.0	9.0	21.0	19.0	45.0
26	do	do	do	110.0	0.0	85.0	0.0	77.0
27	do	do	do	83.0	23.0	54.0	28.0	65.0
28	do	do	do	85.0	26.0	65.0	31.0	76.0
29	do	do	N_2, 200 scf	526.0	140.0	378.0	27.0	72.0
30	do	do	N_2, at 200 F	58.0	41.0	48.0	71.0	83.0
31	do	do	N_2, at 72 F	88.0	29.0	78.0	33.0	89.0
32	do	do	N_2, at 200 F	76.0	31.0	73.0	41.0	96.0
33	do	do	N_2, at 200 F	73.0	32.0	68.0	44.0	93.0
34	do	do	N_2, at 200 F	75.0	15.0	58.0	20.0	77.0
35	do	do	N_2, at 200 F	67.0	25.0	61.0	37.0	91.0
36	Diesel oil	None	Methanol	58.0	34.0	51.0	59	88.0
37	do	do	do	46.0	26.0	42.0	57	91.0
38	Distilled water	do	do	51.0	45.0	—	—	—
38	Diesel oil	do	do	—	42.0	—	—	—
38	do[c]	do	do	—	42.0	—	—	—
38	Distilled water[d]	do	do	—	0.0	42.0	0.0	82.0
39	do[d]	do	do	52.0	0.0	48.0	0.0	92.0
40	do[e]	do	do	27.0	0.0	26.0	0.0	96.0
41	do[e]	do	do	12.0	0.0	10.0	0.0	83.0
42	do[f]	do	do	40.0	24.0	24.0	60.0	60.0
43	do[e]	do	do	36.0	7.0	32.0	19.0	89.0
44	do[d]	do	do	20.0	0.0	17.0	0.0	85.0
45	Diesel oil	do	do	23.0	17.0	—	—	—
45	Distilled water[d]	do	do	—	0.0	16.0	0.0	70.0
46	do[d]	do	do	14.0	8.0	13.0	57.0	93.0
47	10 pct NaCl brine	Triton X-100	do	0.1	0.8[g]	1.0[g,h]	—	—
48	do	do	do	0.5	0.8[g]	1.0[g,b]	—	—
49	Distilled water	do	do	0.2	0.1	0.1[g] 2.0[h]	—	—
50	As received	do	Isopropanol	0.5	—	0.1[g] 1.0[b]	—	—
51	do	None	do	0.1	—	0.1[g] 0.3[h]	—	—

[a] See Table 1 for full data on surfactants.
[b] Surfactant in distilled water.
[c] Soaked in diesel oil 8 days.
[d] Distilled water and diesel oil.
[e] Distilled water and kerosine.
[f] Distilled water and condensate.
[g] Oil-in-water emulsion recovered.
[h] Permeability after drying at 212 F for 18 hours in oven.

solid material not soluble or dispersible in methanol will require more compatible chemical treatments.

It was demonstrated in six cores that more severe blockage was effected by two-phase systems using oil and distilled water than in single-phase systems using either distilled water or oil. Only a partial block was obtained by forcing diesel oil through core 45. A total block was obtained by injecting a mixture of diesel oil and water into the core. In addition, injections with diesel oil and water formed total blocks in cores 38, 39, and 44. Similarly, kerosine and water caused total blocks in cores 40 and 41.

Further laboratory tests were made with extremely tight sandstone cores, 47 through 51, from the Morrow sand in a gas well in Beaver County, Okla. This well produced gas at an average rate of 4 MMcf/D after fracturing. For no apparent reason, other development wells in the area did not respond favorably to hydraulic-fracturing treatments with brine. Laboratory experiments were performed to demonstrate the possible effects fresh water and brine may have on the flow characteristics of Morrow sand cores from this well. The cores were subjected, as received, to water-block and water-block removal tests. During the water-blocking operation, an oil and water emulsion was flushed from the cores. After standing for a few days the emulsion separated into clear condensate and water. These gas-sand cores appeared to contain more than average oil saturation. An analysis showed that the sand contained some water-sensitive clays. Results of saturating the alcohol with calcium chloride to minimize clay swelling, and results of other means to remove oil-water blocking from these tight cores are included in Table 2. Tests on the Morrow sand cores indicate that reduction in permeability resulted from clay swelling and from water-oil blocking.

Cores 47 and 48 were subjected to a blocking fluid consisting of a 10-percent NaCl solution with permeability measured before and after fluid injection. Attempts were made by injecting NaCl solution, to establish water-blocked conditions in the cores having before-blocking permeability of 0.1 and 0.5 md, respectively. An oil-in-water emulsion was flushed from the cores by the injected NaCl solution; this improved the permeability. Further treating with a 1-percent solution of surfactant in methanol increased the after-treatment permeability of the cores to 1.0 md.

Core 49 was blocked by injecting distilled water into the sample. During this operation an oil-in-water emulsion was removed from the core and the permeability measured after blocking, as compared to the value before blocking, decreased from 0.2 to 0.1 md. The permeability measured after the alcohol-surfactant treatment did not show an improvement over the blocked permeability. This was attributed to the combined effects of the emulsion and the swelling of clay particles in the presence of distilled water. Drying of the core in an oven at about 212 F for about 18 hours resulted in increasing gas permeability from 0.1 to 2.0 md, possibly effected by the evaporation of water and consequent dehydration of clay particles in the sample.

After a 1-percent solution of surfactant in isopropanol was injected into core 50, gas permeability decreased from 0.5 to 0.1 md. An oil-in-water emulsion was removed from the core by the treating fluid. Again, either the clay swelled in the presence of alcohol, or some emulsified materials remained to plug the core. The permeability of this core increased from 0.1 to 1.0 md after drying at 212 F for about 18 hours in an oven.

Isopropanol was injected into core 51 and some oil-in-water emulsion was removed. No significant change was measured in the permeability before and after treatment. This condition probably resulted either from clay swelling in the presence of alcohol or from some of the emulsion remaining in the core. The permeability of this core increased from 0.1 to 0.3 md after drying at 212 F for about 18 hours in an oven.

FIELD APPLICATIONS

The alcohol-surfactant method developed in the laboratory for removing water blocks was applied to 14 gas-storage wells and 6 natural-gas wells in fields throughout the United States. Each well was treated with a mixture of alcohol and a surfactant. The individual well treatment was designed to remove the blockage caused by the invading water and to penetrate and treat the affected producing formations to a predetermined radial distance around the well bore. Natural gas and carbon dioxide were used successfully in displacing the treating liquid from the well bore into the formation. The neutron log was a valuable formation-evaluation tool in determining differences in liquid saturation in the formation before and after treatment. Results of treatments presented in Table 3 range from no improvement to complete restoration of original productive capacity of individual test wells.

Procedure

Water blocks in gas wells are difficult to recognize. However, careful study of well logs, potential tests, completion data, production records, workover briefs of well servicing and production-stimulation treatments, and other available data on the well usually reveal adequate information to assist in determining if the formation is or is not water-blocked. For example, it may be known that part of the water pumped into a well to stop the flow of gas was not recovered and gas production was impaired. After the workover, blowing the well would not draw the water from the low-permeability formation and improve deliverability. Then a treatment may be designed and recommended to relieve the water-blocked condition. The task of appraising the condition of the well and designing a stimulation treatment can be facilitated when accurate well records are available. The following procedure is discussed to assist in applying the alcohol-surfactant treatment in a water-blocked well.

Table 3

Results of Alcohol-surfactant Treatments to Remove Water Blocks from Gas Wells

Company and Test Well	County and State	Storage or Production	Formation: Sand	Formation: Depth, Ft	Formation: Thickness, Ft	Treatment: Methanol, Gal	Treatment: Surfactant[a] Name	Treatment: Gal	Open-flow Production, MMcf/D: Before	Open-flow Production, MMcf/D: After	Open-flow Production, MMcf/D: Improvement	Increase, Percent
Sylvanian Corp.:												
Well 1	Steuben, N. Y.	Storage	Oriskany	3,918	17	70	Arquad T-2C-50	1	11.0	12.4	1.4	13
Well 2	do	do	do	3,850	13	70	do	1	2.2[b]	1.9[b]	—	—
Well 3	do	do	do	3,793	13	70	do	1	8.2	11.3	3.1	38
Consolidated Gas Supply Corp. and Texas Eastern Transmission Co.:												
Well 4	Westmoreland, Pa	do	Fifth	2,036	79	40	do	1	8.5	14.3	6.1	72
Well 5	do	do	do	2,227	41	80	do	2	5.6	10.2	4.6	82
Well 6	do	do	do	2,393	30	100	do	2	0.9	0.7	—	—
Well 6, retreatment	do	do	do	2,393	30	85	do	3	1.0	1.8	0.8	80
Well 7	do	do	do	2,392	10	100	do	2	1.9	1.6	—	—
Well 7, retreatment	do	do	do	2,392	10	100	Triton X-100	2	2.1	4.2	2.1	100
Well 8	do	do	do	2,272	9	100	Arquad T-2C-50	1	4.5	4.4	—	—
Well 8, retreatment	do	do	do	2,272	9	105	do	3	7.1	7.1	0.0	—
Phillips Petroleum Co.:												
Well 9	Pecos, Texas	Production	Devonian dolomite.	11,760	175	825	OK Liquid	20	2.8[c]	3.1[c]	0.3	11
Well 9, retreatment 1	do	do	do	11,760	175	1,000	None	—	2.1[c]	3.7[c]	1.6	76
Well 9, retreatment 2	do	do	do	11,760	175	2,000	OK Liquid	20	3.7[c]	4.0[c]	0.3	8
Well 10	do	do	Ellenburger	14,295	667	2,000[d]	Foamitron	20	1.5[c]	1.8[c]	0.3	20
Consolidated Gas Supply Corp.:												
Well 11	Lewis, W. Va.	Storage	Gantz	1,880	20	110	Arquad T-2C-50	2	10.7	8.4[e] 10.0[f]	—	—
Well 12	do	do	do	1,662	28	110	do	2	10.8	12.6[e]	—	—
Well 13	do	do	do	2,080	17	110	do	2	4.8	3.3[e] 4.0[f]	—	—
Well 14	do	do	do	2,195	20	110	do	2	6.2	3.2[e]	—	—
Equitable Gas Co.:												
Well 15	Wetzel, W. Va.	do	Keener	2,025	27	74	Aliquat 4	2	1.1	No Change	—	—
Well 16	do	do	do	2,030	14	77	do	2	3.1	No Change	—	—
Cities Service Gas Co.:												
Well 17	Johnson, Kan.	Production	Bartlesville.	644	19	230	Triton X-100	7	Nil	0.025	0.025	—
Continental Oil Co.:												
Well 18	Live Oak, Texas	do	Wilcox	8,585	5	1,000	HOWCO suds	5	(g)	(g)	—	—
Pan American Petroleum Corp.:												
Well 19	Palo Pinto, Texas	do	Big Saline "D"	4,661	9	324	do	5	(g)	(g)	—	—
The Pure Oil Co.:												
Well 20	San Juan, Utah	do	Hermosa	3,428	218	600[d]	do	10	2.3[c]	3.5[c]	1.2	52

[a]See Table 1 for full data on surfactants.
[b]Injectivity test by Barton gage.
[c]Single-point, back-pressure test.
[d]Isopropanol.
[e]After 10-min blowdown.
[f]After 30-min blowdown.
[g]Water in well bore.

When the condition of the sand face in a water-blocked well is in doubt, it is important that the well bore and sand face be blown clean. Potential plugging materials can be removed by cleansing the surface with a surfactant-water mixture. A low concentration of a surfactant mixed in the treating fluid will assist in relieving the complex bottom-hole condition and removing potential plugging materials, including compressor oil, silt, scale, and normal well fluids not considered in laboratory experiments. The total depth of the well and the liquid level should be measured. Neutron logs run before and after treatment, with the same instrument and calibration, will assist in determining changes in liquid levels and saturations. Liquid treating fluids should be injected in sufficient volume to fill not only the bore hole above the producing zones, but also the pore volume in the formation, to a radial distance of at least 1 ft from the sand face. Further, formations previously acidized or hydraulically fractured have extended-effective well bores which require proportionally increased volumes of treating fluids. Field applications of the method indicate that slow rates of fluid injection, less than 50 gal/min, give better fluid distribution, probably less channeling, and better results than do rapid, high-pressure treatments. These factors depend upon the size of the treatment and the time available.

The surfactant should be mixed in alcohol (methanol or isopropanol at 1 percent by volume) and pumped into the well at the same time as the displacing gas.

The alcohol-surfactant mixture can be displaced from the well bore into the reservoir by high-pressure dry gas, by liquid carbon dioxide, or by nitrogen. The injection of a displacing gas should continue until there is no doubt that the treating liquid is displaced into the formation. Usually the injection pressure decreases sharply at the time of breakthrough. After the mixture is in contact with the blocking water, the surface tension of the water is reduced and the mixed fluids can be moved by gas from the critical area around the well bore either deeper into the formation or into the well bore. A shut-in period of 12 to 24 hours should be allowed for the treating and blocking fluids to equilibriate.

When natural gas at high pressure is not available, carbon dioxide can be used to displace the treating mixture. Liquid CO_2 is readily available and easy to handle in the field. It is very soluble in most treating fluids and in water in the formation. It dissipates rapidly into the formation and assists in producing fluids into the well after the treatment. When CO_2 is used as a displacing gas it is not unusual for the shut-in wellhead pressure to decrease. In contrast to carbon dioxide, nitrogen is relatively insoluble in well fluids and is an efficient gas for displacing liquids into a reservoir. However, for field use its cost and availability are less attractive than that for carbon dioxide. Pressure-recording charts indicate that the CO_2 reverts to a gas in the tubing during the early stages of a treatment and is injected into the producing formation, carrying the treating fluid with it. Moderate pumping rates during treatment are preferred to batch treating because the misted fluid is carried to all parts of the formation invaded by the gaseous CO_2. The remainder of the CO_2 displaces the treating fluid farther into the producing formation.

The treated well should be blown to permit the ejection of the treating and blocking fluids. Often these fluids are not recovered, particularly if the fluids are displaced several feet into the reservoir. A final production test should be run to evaluate the results.

The use of the neutron log for determining liquid-filled porosity in underground formations is well-established.[1,16] The emission of neutrons from a source to bombard a formation, and the recording of the intensity of secondary gamma-ray activity caused by the neutrons afford a direct measurement of the fluid content. Hydrogen has a mass quite similar to a neutron and is most efficient in decreasing the velocity of the neutron. Therefore, the recording of activity is essentially a reproduction of hydrogen content in the formation fluids. This provides an indication of liquid-filled porosity.

Neutron logs run before and after the water-block treatment afford an indication of water saturation (with the possibility of liquid hydrocarbons) and serve to evaluate treatment effectiveness.

An evaluation of the first log permits the location of high liquid-saturated zones which, in a nonliquid hydrocarbon gas well, can be assumed to be water-blocked, or at least to have high water-saturation zones. The second log, which is run several hours after the treatment and cleanup period, indicates changes in liquid saturation. This log, in addition to production tests, gives evidence that the blocking water is either partially or totally removed from the treated zones. Through careful comparison and evaluation of the two logs (superimposing one on the other), the zones having indicated decreases in liquid saturation show a shift of the curve to the right on the second log. The lateral shift indicates a decrease in hydrogen content and thus a decrease in liquid saturation. Consequently, the use of the neutron-logging technique and a final production test help in evaluating the treating procedure by indicating zones where significant decreases in liquid saturations occur.

Results

The applicability and limitations of the alcohol-surfactant treatment for removing water blocks was demonstrated in test wells at depths ranging from 600 ft to below 14,000 ft. Maximum increase in gas-storage well deliverability resulting from a treatment was 6.1 MMcf/D. Stabilized production increase following treatments in 2 gas wells exceeded 1.0 MMcf/D with net payout periods averaging 4 months.

Tuscarora Storage — Test Wells 1 to 3

The deliverability of wells 1, 2, and 3 in the Tuscarora storage project was decreased when fresh water used to kill the wells for re-equipping operations remained in the sand at completion. After chemical treatment open-flow capacities of wells 1 and 3 were increased, while well 2 showed a slight decrease.

Well 1 was damaged when 15 bbl of water were lost in the Oriskany sand during cleanout and recompletion of the well for gas storage. Pretreatment conditioning included ½ gal of surfactant and ½ gal of methanol mixed in 25 gal water lubricated into the well to cleanse the sand face during a 1½-hour shut-in period. Gas production was increased from 11.0 to 11.9 MMcf/D following the cleaning operation.

The methanol-surfactant treatment was displaced into the formation with pipeline gas at 1,840 psi and the well was shut in for 30 hours. After treatment, the well had an open-flow rate of 12.4 MMcf/D.

Well 2 was similarly damaged when 40 bbl of water remained in the sand. The methanol-surfactant treatment was displaced into the formation with gas, and the well was shut in for 19 hours. Large pieces of very dirty sand and methanol were blown from the well following the treatment. The gas-injection rate measured with a snap-on Barton gage decreased from 2.2 to 1.9 MMcf/D.

The sand in well 3 was covered with cement while cementing casing. In addition, approximately 21 bbl of water were lost in the sand, which may have caused a water block. Before treatment, the well produced at an open-flow rate of 8.2 MMcf/D. Fine sand with a few large pieces of sand and a fine spray of water blew from the well during the open-flow test. To remove cement from the sand face, a mixture of ½ gal of surfactant, ½ gal of methanol, and 5 gal of 18-percent hydrochloric acid in 15 gal water was lubricated into the well, followed after 1½ hours by 52 gal water. After a ½-hour shut-in period the acid mixture was blown from the well, an open-flow rate of 9.0 MMcf/D was measured, and the well was shut in. Following a shut-in period of 17 hours, a methanol-surfactant treatment was lubricated into the well and displaced with pipeline gas; injection rates were checked periodically during 24 hours with a snap-on Barton gage. After treatment the well blew a salty spray and the open-flow rate was measured at 11.3 MMcf/D.

Oakford Storage—Test Wells 4 to 8

Deliverability of two water-blocked gas-storage wells in the Oakford storage project was improved. For several months, each of the five wells was blown regularly with no beneficial results. Each well was subjected to one or more remedial methods to improve well performance. These production-improvement techniques required balancing the formation pressure with a column of fresh water to stop or kill the flow of gas. The loss of approximately 100 bbl of water to the formation around each well indicated that a water block may have been responsible for the decreases in deliverability of gas following the remedial treatments.

A production test before treating well 4 showed a flowing rate of 8.5 MMcf/D with a shut-in reservoir pressure of 740 psig. After treating the well by displacing the surfactant and methanol into the formation, the open flow was tested at 14.6 MMcf/D starting with 754 psig shut-in tubing pressure.

Well 5 had been opened from a recorded shut-in pressure of 530 psig and tested at 12.5 MMcf/D before a remedial treatment. After treatment, the well had an open flow of 5.0 MMcf/D at the same reservoir pressure. From a 698-psig shut-in pressure an open-flow rate of 5.6 MMcf/D was measured before the alcohol-surfactant treatment. After injection a shut-in pressure of 711 psig was recorded, and the open-flow rate increased to 10.2 MMcf/D.

Initially, wells 6, 7, and 8 showed no improvement after slug treating them with the methanol-surfactant mixture. However, after retreating wells 6 and 7 with the alcohol-surfactant mixture injected at rates of 15 to 20 gal/hour for 5 to 6 hours, the gas deliverability was improved 80 and 100 percent, respectively. The open flow from wells 6 and 7 was restored to near original conditions. No production improvement was shown on well 8 following the second water-block-removal treatment.

Puckett Field—Test Wells 9 and 10

Gas well 9 in the Puckett Field originally produced at a rate of 7 MMcf/D in the Devonian dolomite interval from 11,760 to 11,935 ft. After 2 workover operations, the well delivery to the pipeline decreased to 2.8 MMcf/D. The treating fluids were pumped into the tubing and displaced into the productive zone having a pressure of 3,175 psi with natural gas at a pressure of 3,790 psi. After treating, and while blowing the well fluids to the pit, some foam and drilling mud were removed from the well. It was placed on production at a rate of 3.1 MMcf/D.

Mud blocking was suspected, and the well was treated by dissolving 200 lb of citric acid in 133 bbl of water into which 55 gal of surfactant were mixed by circulating through the pump and auxiliary tank. This mixture was pumped into the tubing and followed by 133 bbl of water containing an additional 55 gal of surfactant. The treating liquids were displaced into the formation with high-pressure gas over a period of 4 hours. A considerable quantity of mixed foam, water, and drilling mud was unloaded when the well was blown to the pit. For 10 days following this treatment the well produced gas at rates ranging from 1.8 to 2.2 MMcf/D. At the end of 27 days, the production rate had stabilized at 2.1 MMcf/D and the well was retreated by the operator with 1,000 gal of methanol injected in 4 to 5 hours. When the well was blown, some additional drilling mud was recovered. As a result of this treatment, gas production from the well was increased to 3.7 MMcf/D. Within a few days another treatment with 2,000 gal of methanol and 20 gal surfactant effected an increase in flow to 4.0 MMcf/D.

Gas production from well 10 in the Puckett Field following completion in the Ellenburger limestone section from 14,295 to 14,962 ft decreased from 5.1 MMcf/D following a mud-acid treatment to 3.0 MMcf/D and to 1.5 MMcf/D by the end of the first year of operation. The cumulative volume of liquids produced from the well was 200 bbl of condensate with a trace of water. It was concluded that either the acid treatment had water-blocked the formation or the original drill-stem test of 5.1 MMcf/D was in error.

With a 1-million Btu gas heater connected to the tubing and two tanks containing 41 tons of liquid CO_2 connected through a charging pump and a triplex pump to the heater, the CO_2 was converted to a gas and injected at a rate of 20 gal/min into the well at a pressure of 1,600 psi and a temperature of 80 F. Simultaneously a mixture of 2 gal of surfactant in 2,000 gal of isopropanol was injected with the CO_2 at a rate of 81 gal/min. Because of the weight of the column of CO_2 in the tubing, surface pumping pressure decreased at one time to 500 psi. A total of 41 tons or 216 bbl of liquid CO_2 was pumped at a rate of 32 bbl/hour to the heater, converted to a gas and injected into the formation at an average surface pressure of 600 psi.

Following a shut-in period of 13 hours, the tubing pressure was 760 psi. Upon opening the tubing and blowing the CO_2 to the pit, only a trace of liquid was lifted. The well was shut in for 20 hours and opened to the pipeline. Spot production tests during 5 hours showed the initial production of 2.5 MMcf/D at 1,315 psi flowing tubing pressure leveled off at 1.8 MMcf/D at 1,000 psi. It was obvious from the series of spot tests that gas production from the well was not increased by the alcohol-surfactant treatment.

Kennedy-Fink Storage—Test Wells 11 to 14

Gas-storage wells 11 to 14 in the Kennedy-Fink storage field were treated by the alcohol-surfactant method to remove water blocks. During pretreatment open-flow tests, each well was cleaned with a mixture of ½ gal of surfactant and 40 gal of water to insure that a minimum of compressor oil or other foreign matter was on the sand face as potential plugging material. Open-flow tests were taken at the end of 10 min. The mixed treating liquid, 110 gal methanol and 2 gal surfactant, was lubricated into each well over periods of 2½ hours, while the well received input gas. Additional gas was injected for periods ranging from 5 to 22 hours. Approximately one half of the treating fluid was not displaced from the well bore during injection and was blown from the tubing of each well as a liquid column during the cleanup period. The final open-flow rates for wells 12 and 14 after 10 min were gaged at reduced rates of 12.6 and 3.2 MMcf/D, respectively. However, wells 11 and 13 were blown for 30 min, during which time the rates increased essentially to pretreatment values.

Decreases in gas-production rates of the wells were temporary. Subsequent tests showed the produced gas removed the alcohol and pretreatment rates were established within a few days.

Logansport Storage—Test Wells 15 and 16

Gas wells 15 and 16 in the Logansport storage were treated for water blocks while the reservoir pressure was 940 psia. A wireline measurement of well 15 indicated a total depth of 2,052 ft and the liquid top at 2,045 ft. Surveys of the formation logged sand from 2,020 to 2,052 ft with productive zones at 2,025, 2,032, and 2,037 ft. The pocket in the sand from 2,045 to 2,052 ft contained 7 ft of water. Consequently, the remaining 8 ft of open hole were filled with 8 gal of nontreating methanol to approximately the bottom of the lower pay zone. A mixture of 40 gal of methanol and 1 gal of surfactant was injected at a rate of 4.5 gal/hour with gas from the pipeline and followed within 24 hours by the injection of 34 gal of methanol and 1 gal of surfactant.

A measuring line was run in well 16 to a total depth of 2,047 ft. The sand was logged from 2,016 to 2,047 ft with pay zones at 2,017, 2,025, and 2,030 ft. The 17 ft of pocket in the sand contained 7 ft of liquid; 10 gal of nontreating methanol were required to raise the liquid level to the lower gas zone. One gallon of surfactant mixed with 40 gal of methanol was injected into the reservoir while simultaneously injecting pipeline gas at 960 psi. After the well was shut in for 24 hours, 1 gal of surfactant was mixed with 27 gal of alcohol and injected at a rate of 4 gal/hour into the producing formation.

The alcohol-surfactant treatments remained in both wells for 9 months until the end of the withdrawal cycle. Alcohol was then bailed from the well bores indicating that the treating liquid had not been adequately displaced into the formation. No change in well performance resulted from the treatments.

Craig Field—Test Well 17

Gas well 17 adjacent to the Craig storage field was selected for the next treatment. The well should have produced at an approximate rate of 225 Mcf/D at a wellhead flowing pressure of 50 psi. Reservoir pressure was 185 psig. Successive workover operations permitted more brine to invade the sand than the well was capable of expelling. The well became loaded with water, and the gas flow stopped.

The initial treating liquid, consisting of 2½ gal of surfactant in 55 gal of methanol, was pumped into the 2-in. tubing set on a packer at 645 ft and followed by approximately 1 Mcf of gas at 253 psi. An additional liquid treatment, consisting of 175 gal of methanol and 4½ gal of surfactant, was circulated and pumped into the well at a maximum pressure of 400 psi. The liquid treatment was followed by injecting about 8 Mcf of gas with a portable compressor. After the well was shut in for 16 hours, about 69 Mcf of gas were injected during 8 hours at an average pressure of 200 psi. After 14 hours the shut-in pressure was 136 psi. When opened, the well blew down within 5 min to a measured flow of 15 Mcf/D. Although the gas carried a strong odor of methanol, no liquid was produced. After the well was overtreated with methanol, it was allowed to feed some gas to the line and to store excess gas in a shallow observation well during succeeding months. The methanol evaporated from the formation and permitted the flow of gas to increase to 25 Mcf/D. Considering the volume of alcohol that was squeezed into the sand around the well, it is probable that most of the mobile water was carried away from the area around the well bore.

Harris-Massey Field—Test Well 18

Gas well 18 in the Harris-Massey Field was unsuccessfully treated. After field inspection, it was determined that the well produced water at an approximate rate of 100 ft fill-up per hour to a tubing height of 4,200 ft. Although the treatment had only a slight possibility for success, an attempt was made to establish contact between the treating fluid and gas in the reservoir. The bottom-hole pressure built up at a rate of 25 psi per hour to 2,190 psi—the bottom-hole pressure of adjacent wells. The bottom-hole temperature was 202 F.

The well was prepared for treatment by swabbing water from the tubing and by pressuring the tubing with gas from the pipeline at 600 psi to retard the influx of water. Then 25 bbl (4.6 tons) of liquid CO_2 were pumped into the tubing at a rate of 3 bbl/min at a pumping pressure of 1,350 psi. This was followed by a mixture of 1,000 gal of methanol and 5 gal surfactant pumped at a rate of 2 bbl/min at a maximum pumping pressure of 4,500 psi. Following a delay of about 1½ hours when the pumps became gas-locked and lost prime, the first part of the remaining 75 bbl of CO_2 was pumped at a rate of 1 bbl/min at a pressure of 4,000 psi. The pumping pressure increased to 4,500 psi for a portion of the injection. As the pumping pressure decreased, the rate of injection was increased to 1.2 bbl/min. After a shut-in period of 1½ hours the pressure was 2,400 psi. It was then flowed through a partially opened adjustable choke to the atmosphere, and after approximately ½ hour of flow the wellhead pressure had decreased to 1,000 psi. The choke opening was then increased, and the well continued to flow with the wellhead pressure decreasing to 0 psi in approximately 1 hour. No liquids were removed during this initial blowdown period. The choke opening was decreased, and after 1½ hours the wellhead pressure increased to 190 psi with a steady flow of gas being produced from the well. The choke was then completely opened, and the well began to flow slugs of gas and a treating fluid-water mixture with some black mud dispersed in the fluid. After a 14-hour cleanup period, the well was flowing slugs of gas and treating fluid-water mixture intermittently, with no mud contamination. The well was producing liquid at such a rate that a swabbing unit was engaged to swab fluid from the tubing to a depth where sufficient gas production from the formation would lift the remaining liquid and increase its productivity. However, the rate of water production exceeded the liquid-lifting capacity of the well and gas deliverability was not improved by the treatment.

Mineral Wells North Field—Test Well 19

An alcohol-surfactant treatment was applied to well 19 in the Mineral Wells North Field to relieve a water block. The initial completion in this edge well was unsuccessful from either an emulsion condition restricting permeability or a kerosine block in the formation.

From a shut-in pressure of 600 psi the well flowed gas for ¾ hour at a wellhead pressure of 375 psi. A swab was run, 2,000 ft of liquid were measured in the tubing, and 9 bbl of heavy brine were swabbed to the tank battery.

A pump truck injected 7.7 bbl or 324 gal of methanol mixed with 5 gal of surfactant at vacuum. The pumps were primed with CO_2, and 105.3 bbl of liquid CO_2 were injected through the tubing into the formation at a rate of about 1½ to 2 bbl/min. The average pumping rate during the 65 min of injection was 1⅔ bbl/min with maximum and minimum tubing pressures of 2,250 and 1,400 psi, respectively. The shut-in wellhead pressure was 1,050 psi. After a shut-in period of 2 hours, the wellhead pressure was 1,000 psi.

The wellhead shut-in pressure decreased overnight to 840 psi. The well, opened on a 16/64-in. choke setting, flowed CO_2, bottom sediment, and water for approximately 45 min with the wellhead pressure decreasing to about 250 psi. The choke was removed and the well flowed for 15 min until the wellhead pressure decreased to 0 psi.

A tubing swab contacted the top of the heavy brine at 1,100 ft from bottom. A second run with the swab removed 200 ft of liquid. The rate of gas production was not increased after swabbing, and the well was shut in. It was concluded that the low gas saturation in the Saline "D" zone around this edge well would not warrant additional stimulative treatment.

Big Indian Field—Test Well 20

An improved procedure incorporating the neutron log was used in well 20 in the Big Indian Field to determine changes in liquid saturation in the affected zones. The well was drilled to a total depth of 5,360 ft, and was completed in January 1964. Before the well was completed, drill-stem tests indicated a potential gas flow of approximately 4.9 MMcf/D. A bridge plug was set in the casing at 3,800 ft, and subsequently the casing was perforated with three 35-gram shots per foot opposite 6 zones in the Pennsylvanian Hermosa sand from 3,428 to 3,636 ft. The 6 perforated zones are at the depths indicated in Fig. 1: zone A, 3,428 to 3,440 ft; zone B, 3,476 to 3,494 ft; zone C, 3,498 to 3,502 ft; zone D, 3,546 to 3,558 ft; zone E, 3,572 to 3,582 ft; and zone F, 3,626 to 3,636 ft. Upon completion, each zone was treated and drill-stem tested separately by setting a bridge plug below the perforations and a tubing packer above the isolated zone. The five upper zones were tested as being commercially productive; however, zone F showed only a trace of gas. Zones A, D, and F were treated with a mud cleanout acid spotted opposite the perforated section and pumped into the formation at a rate of approximately 3 bbl/min at a pressure of about 3,500 psi. A production string of 2⅞-in. tubing was set on a packer at 3,405 ft with a short perforated anchor below the packer and closed on the end by a bull plug. An initial production test indicated that the well had an

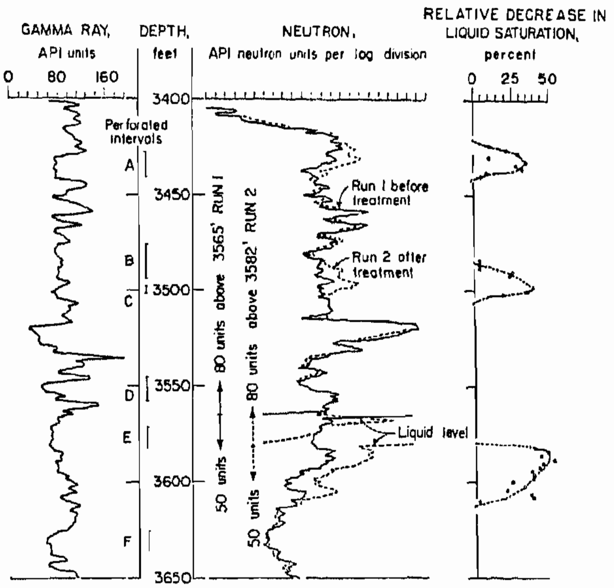

Fig. 1 — Gamma Ray and Neutron Logs of Hermosa Sand Test Well 20 Before and After Water-block Treatment and Decrease in Liquid Saturation

open-flow capacity of 2.2 MMcf/D. The difference between this potential test and the drill-stem test of 4.9 MMcf/D led to the conclusion that the productive capacity of the well had been reduced during completion operations.

To perform the water-block removal test, it was necessary to balance the formation pressure with salt water, and pull and reset the tubing. The well was then swabbed and flowed for a 6-hour period to insure adequate formation cleanup. The productive intervals probably were further damaged through the loss of an estimated 50 to 70 bbl of salt water during these well-servicing operations. This conclusion was substantiated by a recorded flowing pressure of 225 psi prior to servicing, as compared to 185 psi after servicing. The neutron logging tools were lubricated into the tubing and an initial neutron log was run through 380 ft of formation from 3,780 to 3,400 ft.

The treatment was designed to relieve a water-blocked condition by contacting an approximate 1-ft radius of formation around the well bore in the zones from 3,582 to 3,400 ft. The treating fluid was carbonated with 24.8 bbl of liquid CO_2 and displaced into the perforated zones with the remaining 83 bbl of liquid CO_2. Collectively, 108 bbl (20 tons) or about 344,000 scf of gaseous CO_2 were injected. Initial pumping rates were approximately 1 bbl of isopropanol with 2 bbl (0.35 ton) of CO_2 per minute, resulting in a pumping pressure of 2,150 psi at the end of the alcohol-CO_2 injection. The remaining 83 bbl (15.4 tons) of CO_2 were injected at approximately 2¼ bbl (0.4 ton) per minute to displace the alcohol-CO_2 mixture into the formation. The well was shut in about 12 hours, then opened and flowed to clean the formation before the second neutron log was run. During the cleanup period, gas production from the well was estimated to have flowed at an approximate rate of 3.5 MMcf/D through a ¾-in. choke with a flowing tubing pressure of 350 psi. Then the second neutron log was run.

A company production test, conducted after the treatment and run through a 2¼-in. orifice plate at a flowing pressure of 320 psi, indicated an immediate 52-percent increase in gas production rate from 2.3 to 3.5 MMcf/D. The effectiveness of the chemical treatment in reducing liquid saturation in the damaged zones was corroborated by the neutron logs and by the improved rate of gas production. Daily testing during a 30-day period following the treatment showed the well sustained a 33-percent average increase in the rate of gas production.

Fig. 1 shows superimposed curves of the two neutron logs and a gamma ray log through the interval of interest from 3,650 to 3,400 ft. A comparison between neutron logs shows a decrease in liquid saturation of the three most productive zones, A, B, and C. The neutron curves coincide except in zones opposite the three upper perforated zones and the zones below the liquid levels. The position of the after-treatment neutron curve appears to depart from the pretreatment curve sufficiently to indicate decreased porosity, which may be interpreted as a decrease in liquid saturation. This reduction (water-block removal) accounts for some increase in the rate of gas production. The broad variation between the two curves below the liquid level may have been caused by well-bore liquids being displaced by injecting CO_2 into the zone opposite perforations from 3,572 to 3,582 ft, by a general drying of the zone during cleanup (including some behind the casing), or by the zone being stimulated to the extent that the liquid was blown from the well.

A quantitative interpretation of these well logs shows that significant reduction in liquid saturation occurred. Maximum and minimum porosity values, determined from commercial core analyses of the sand-shale sequence from other Hermosa zone wells drilled in the vicinity of the treated well, were 35 and 1½ percent, respectively. Porosity values were determined from each neutron curve (Fig. 1) by using the service company's logarithmic porosity scaler. The dashed curve indicates the relative decreases in liquid (water) saturation following the stimulative treatment.

Porosity values before and after the chemical treatment were considered less than 100 percent liquid-filled when calculating the approximate relative changes in liquid saturation. The estimated maximum percent decrease in liquid saturation of zones A, B, and C, and the area below zone E is approximately 36, 40, and 50 percent, respectively.

PRECAUTIONARY MEASURES;

Some suggested measures for the successful application of the alcohol-surfactant treatment in removing water blocks are:

1. Do not attempt to use this treatment as a cure for

water-saturated gas sands in wells that produce at high water-to-gas ratios.

2. Review the complete history of each well to diagnose properly the causes for loss in deliverability.

3. If the sand face has been exposed to cement or mud, an acid-detergent cleanout is recommended prior to treatment.

4. Whenever possible, determine the amount and type of clay minerals in the formation that might cause swelling in the sand.

5. As a preventive measure, precondition fracturing and balancing fluids with a surfactant.

6. Determine if the permeability of the sand is within the critical range conducive to water blocking (100 md or less) prior to treatment.

7. Do not attempt to treat wells in gas-storage reservoirs when the reservoir is filled to near capacity. Under these conditions it is difficult to force the fluid back into the formation to effect contact between the treating fluids and the water-blocked zones.

8. Clean the production string and sand face with a water-surfactant mixture to prevent plugging during the treatment.

9. Treat with sufficient liquid to adequately cover the producing zone.

10. Inject liquid treatment and gas simultaneously at slow rates. Inject slightly more gas than is required to displace all of the treating fluids into the formation.

11. Treat gas wells producing from either limestone reservoirs or those containing calcareous cementing material with alcohol containing one of the nonionic surfactants to avoid possible plugging by precipitates.

12. Allow adequate time, preferably 24 hours, for reagents to react with blocking fluids.

13. Permit adequate blowing to the pit to clean the flow channels before placing the well on production.

14. Do not use alcohol on wells that contain an asphalt or paraffin base oil to avoid the possible precipitation of solids.

CONCLUSIONS

Research by the Bureau of Mines on the removal of capillary water blocks from producing formations was concluded after demonstrating in the laboratory and proving in the field the applicability and limitations of the alcohol-surfactant method. Laboratory experiments revealed that methanol assisted by a surfactant was the most satisfactory method for removing persistent water blocks from core samples. As the testing progressed, methanol was found to be an excellent mild surfactant to remove water and oil-water blocks if the blocking oil resembled kerosine or diesel oil.

During the field-test program it was shown that the productivity of some wells can be restored to their original values by this method. Liquid carbon dioxide was used as a liquid-displacing medium in lieu of natural gas. The neutron-logging technique was a useful formation-evaluation tool for indicating the changes in liquid saturation.

ACKNOWLEDGMENTS

The identification of liquid-saturated zones by use of the neutron-logging techniques and the removal of water blocks from gas wells by the alcohol-surfactant method were studied by the Bureau of Mines in cooperation with the American Gas Association.

Appreciation is expressed to the members of the AGA, NC-36 Supervising Committee, and especially to their chairman Norman M. Hulings, Jr., Vice President, Oklahoma Natural Gas Company.

The authors are indebted to the following personnel and their companies for cooperation and helpful assistance: B. F. Beeler, Carbonic Chemical Co.; Robert T. Gaut and E. W. Bond, Cities Service Gas Co.; Charles E. Brooks, Con-Gas Service Corp.; J. B. Corrin, Jr. (retired), Dick Bayne, R. S. Jefferies, and W. R. Stokes, Consolidated Gas Service Corp.; James Scott, Harry Wahl, and J. C. Shepler, Continental Oil Co.; John V. Goodman and Weldon C. Dorn, Jr., Equitable Gas Co.; W. E. Hassebroek, W. E. Hinchliffe, and Billy Bob Jones, Halliburton Co.; A. H. Youmans, Lane-Wells Co.; W. R. Clark, Natural Gas Pipeline Company of America; L. A. Hampton and Clayton Thomas, Oil Recovery Corp.; C. B. Caruthers and Robert Smith, Pan American Petroleum Corp.; R. V. Smith and Cecil R. Clement, Phillips Petroleum Co.; A. T. Sayre, E. C. Clay, P. F. Cochran, and C. E. Teackle, The Pure Oil Co.; D. T. Secor and P. H. Montgomery, Sylvania Corp.; and Tom M. Carroll, West Texas CO_2 Co.

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