

1

3,111,178

GAS DRILLING METHOD

Byron E. Marsh, Brookfield, Jack E. Haughm, Park Forest, and Richard J. Michelini, Aurora, Ill., assignors, by mesne assignments, to Armour and Company, Chicago, Ill., a corporation of Delaware

No Drawing. Filed Dec. 31, 1958, Ser. No. 784,089

4 Claims. (Cl. 175-69)

This invention relates to a method for drilling wells wherein a gas such as compressed air is circulated through the bore hole to remove water and cuttings therefrom, and more specifically, to a gas drilling method wherein a lifting agent is injected into the gas column to form an aerated column for the lifting of water and cuttings and the reduction of operating gas pressure.

It is well-known that a major problem in the air or gas drilling of wells lies in the presence of moisture in the formation and the influx of water into the bore hole. Ordinarily, when water bearing formations are encountered, the rate of bit penetration is substantially retarded and there is a danger that the cuttings will ball and bridge near the bit. Unless some means is employed to disperse and lift such cuttings, drill pipe torque and hydrostatic pressure will progressively increase and the cuttings will tend to cling to and jam the pipe.

An object of the present invention is to overcome the aforementioned problems attending water infiltration of a bore hole in a gas drilling operation by introducing into the descending gas column a surface active flotation and dispersing agent which not only has exceptional foaming and surface tension reducing properties to facilitate the lifting of cuttings and formation water but which also inhibits corrosion of the metal parts in contact with the air-water mixture.

One aspect of the invention lies in the discovery that water-soluble quaternary ammonium salts are corrosion-inhibiting flotation agents which, when mixed with formation water in a bore hole or with water added to the hole, form an aerated column for lifting water and cuttings while at the same time retarding corrosion of the metal parts in contact with the formation water and aerated solution. Preferably, the quaternary ammonium salt, or a mixture of such salts, has at least one alkyl chain ranging in length from between 8 to 18 carbon atoms. The alkyl radical may comprise octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, octadecenyl and octadecadienyl groups and, in any given foaming agent a number of such groups of different carbon chain lengths will ordinarily be present. Alkyl trimethyl ammonium nitrite and alkyl trimethyl ammonium chloride have been found particularly effective, although other quaternary ammonium salts such as diisobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride, alkyl methyl polyethoxy ammonium chloride, and N-methyl N-tallow morpholinium chloride have also been found suitable for this purpose. All of such quaternary ammonium salts are water soluble and are cationic in character. When agitated with water, they foam profusely, as indicated in the table of Example III. Such a foam is relatively stable and, when formed in a well bore, reduces hydrostatic pressure and aids in the lifting of water which has entered the hole from the adjacent formation. The aerated column also acts to disperse cuttings and permits them to be raised to the surface through the annulus between the drill pipe and the side of the bore hole, at lower pressures than would otherwise be possible.

2

For injection into a drill pipe, the quaternary ammonium salt should first be dissolved either in water or in a water-miscible solvent. Isopropanol and hexylene glycol have been found particularly effective although other suitable solvents might also be used. The salt solution is then injected, with or without additional water, directly into the descending gas column in the drill pipe to form a foam with the formation water in the bore hole. The injection of additional water is ordinarily necessary only where the amount of formation water, when mixed with the dissolved chemical and air, is insufficient for effective dispersion of cuttings and reduction of pressure build-up.

Excellent drilling rates have been maintained through water-bearing formations where the concentration of the injected salt in the formation water falls within the general range of .04 to 0.2 percent. Concentrations less than .04% appear to result in inadequate foaming action and water removal while concentrations greater than 0.2% tend to produce "heading"—that is, excessive foaming resulting in erratic discharges of rich foam and wide fluctuations in line pressure. The most effective results have been obtained where the quaternary ammonium salt concentration at the formation water level fall within the preferred range of .06 to 0.1%. Such concentrations may be approximated by varying the amounts of injected salt solution in accordance with the amounts of water discharged from the blow line. For instance, where operation is continuous and the rate of water discharge is uniformly about 50 barrels (2100 gallons) per hour, the injection of 4.2 gallons per hour of a 40% solution of the quaternary salt should maintain a salt concentration in the formation water of approximately .08%.

An important aspect of the present method lies in the fact that the injection of a solution of the aforementioned ammonium salt not only overcomes the problems of water encroachment by producing an aerated discharge column for the lifting of water and cuttings, thereby implementing the penetration of a rotary bit, but also reduces or inhibits the corrosive action of the air-water mixture on the metallic equipment employed to penetrate the formation and to circulate the fluid. Furthermore, the effectiveness of the quaternary ammonium compounds as corrosion inhibitors is not significantly affected by the salts usually present in formation water and in natural brines.

In addition, the natural salt content of formation water does not appreciably affect the foaming properties of the quaternary ammonium salt solution. As indicated by the test results of Example VI, the foaming action of the agent is observed to be even greater in a brine solution than in plain water while the stability of the resulting foam is only slightly reduced.

This invention can be further illustrated by the following specific examples:

Example I

In a well drilling operation in Oldham County in the Panhandle of Texas, alkyl trimethyl ammonium nitrite solution of 40% concentration in isopropanol was introduced into the bore hole to assist in the removal of water and cuttings.

After a temporary shutdown in the air drilling procedure, it was found that several hundred feet of water had collected in the bore hole. Normally, high volumes of air are blown through the drill pipe requiring about five hours before the well is dry enough to proceed with air drilling. Instead, two quarts of the quaternary ammonium salt solution were introduced directly into the drill pipe

and about two gallons were injected with ten barrels of water into the air stream. About five minutes after injection had begun, a very rich foam emerged from the exhaust line. After ten minutes of foam discharge, practically all of the water had been removed from the hole. The entire drying operation required a total time of about forty-five minutes.

Later, when the drill pipe was pulled to change bits, it was noted that there was about 1,000 feet of water in the hole. Injection of the foaming agent along with air and water was begun. Initial injection rates were four gallons of the ammonium salt solution and five barrels of water per hour; estimated water output was ten to twenty barrels per hour. With this rate, the foam was too rich and there was a tendency for the well to "head," that is, the mist flow would either stop completely or slow-down, the pressure would build-up, then extremely high flow rates of the rich foam would begin again. These cycles would take about thirty minutes. Consequently, the injection rates were cut to two gallons of foamer and two barrels of water per hour. The water output appeared to be about the same as before. This rate of injection was more satisfactory, and the heading tendency was practically eliminated. However, pressures were still higher than anticipated. The rates were gradually decreased until about five pints of foamer and two barrels of water per hour were being injected. Water output rate was estimated to be twenty to twenty-five barrels per hour. At this rate, the foam was still quite rich.

The water input rate was increased to about five barrels per hour and the foamer to about three gallons per hour. Output was twenty-five to thirty barrels of water per hour. A gradual pressure decrease was noted which stabilized at 350 pounds per square inch (p.s.i.). (Previous pressures had been 500 p.s.i.) The output was in the form of a fine mist with a small stream of frothy water at the bottom of the line. Further experimentation resulted in the final rate of 1.9 gallons of foamer and five barrels of water injected, and an output of about thirty barrels (1,260 gallons) of water to maintain an ammonium salt concentration in the bore hole of approximately .06%.

Example II

Alkyl trimethyl ammonium nitrite of the character set forth in Example I was also used in air drilling operations in a well located in Logan County in Northwest Arkansas. Injection was begun when water was encountered in shales at a depth below 350 feet. The initial injection rate was three quarts of the 40% quaternary salt solution in a period of forty minutes. Pressure started to build-up to about 150 p.s.i., and no water was being blown out the exhaust line. The chemical injection pump was shut off for about one and one-half hours. After about thirty minutes following injection shut down, some water was exhausted and as time passed increasingly larger amounts of water came out in the form of a thick froth. When the chemical pump had been off for about one and one-half hours, the well appeared to have cleaned up. Injection was begun again at a rate of not more than one pint of foamer per hour. For about an hour, the chemical pump was operated intermittently because of pressure build-ups each time injection occurred. Finally the pump was left on and pressure continued up to about 150 p.s.i., at which time several large "slugs" of water blew out. The pressure then dropped back to about 100 to 130 p.s.i.

Eleven hours after commencement of chemical injection the rates of discharge were consistent, pressures were as low as 90 p.s.i. and never more than 130 p.s.i., drilling rates were excellent, and the flow out of the blow line was a mist indicating all of the water was tied-up. Flow rates for this period were two to two and one-half quarts per hour of the quaternary ammonium salt solution, five and one-half barrels of injected water per hour, and an estimated water output of approximately ten to twelve barrels (420 to 504 gallons) of water per hour. The pH of the

output water was 11.5. These conditions were maintained for the remaining seven hours of observation.

Example III

The following test procedure was undertaken to evaluate the foaming characteristics of water soluble quaternary ammonium salts.

A saturated lime water solution was made. A 300 ml. portion of this solution was measured into a high speed blender and, unless specified differently in the following chart, 0.2% of the chemical to be tested was added to the portion of the lime water solution. In every case, the concentration of the quaternary ammonium salt solution before addition to the lime water was 40%, the solvent being isopropanol.

The lime water solution with foamer added was then mixed for thirty seconds and poured into a 1000 ml. graduated cylinder. The foam height was noted and the time required for 100 ml. of water to separate from the foam was recorded.

Further work was done with the alkyl trimethyl ammonium nitrite solution, changing the concentration and temperature, and adding sodium chloride to the 5% and 10% levels. While some variation in foam stability with increased temperature was detected, this variation is insignificant for the purpose of well drilling operations.

The following is a tabulation of the results of the above-described test:

Chemical	Amount of 40% Active Solution, percent	Foam Height	Time Required to Separate 100 ml. H ₂ O	Remarks
Alkyl trimethyl ammonium nitrite (alkyl groups comprising chains of 8, 10, 12, 14 and 18 carbon atoms).....	0.2	900	4'19"	32° F. 40° F. 130° F. 160° F. 5% NaCl. 10% NaCl.
Do.....	0.1	830	3'20"	
Do.....	0.2	880	5'10"	
Do.....	0.2	870	5'34"	
Do.....	0.2	960	2'45"	
Do.....	0.2	900	2'30"	
Do.....	0.2	930	3'03"	
Do.....	0.2	910	3'50"	
Alkyl trimethyl ammonium nitrite (alkyl groups comprising chains of 16 and 18 carbon atoms).....	0.2	960	4'57"	
Alkyl trimethyl ammonium chloride (alkyl groups comprising chains of 8, 10, 12, 14, 16 and 18 carbon atoms).....	0.2	970	5'30"	
Alkyl trimethyl ammonium chloride (alkyl groups comprising chains of 12, 14 and 18 carbon atoms).....	0.2	890	4'00"	
Alkyl trimethyl ammonium chloride (alkyl groups comprising chains of 16 and 18 carbon atoms).....	0.2	930	4'55"	
Do.....	0.2	1,000	5'12"	
N-alkyl N-methyl morpholinium chloride (alkyl group derived from tallow fatty acids).....	0.2	920	4'42"	
Alkyl methyl polyethoxy ammonium chloride (alkyl group derived from a cocoa fatty acid and the two polyethoxy chains have an average degree of polymerization of 15).....	0.2	600	2'3"	
Diisobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride.....	0.2	1,000	6'00"	

Example IV

To test for corrosion inhibition, cylindrical steel coupons were emersed for twenty-four hours at room temperatures in continuously aerated tap water treated with alkyl trimethyl ammonium nitrite salts in which the alkyl chain length averaged between 8 to 18 carbon atoms. The procedure consisted of a standard turbine oil test (ASTM D665-52-T) in which only water (no oil) was used and which was further modified to include continuous aera-

5

tion of the solution. 95% protection was observed in the solution having an ammonium salt concentration of .08%. Under similar conditions, but with a .04 concentration of the active ingredient, 91.5% protection was observed. The data concerning this corrosion inhibition is set forth in the following table:

Solution	Corrosion Rate in Milli-Inches/1 year
Water alone.....	81
0.08% aqueous solution of quaternary ammonium nitrite salt.....	4
0.04% aqueous solution of quaternary ammonium nitrite salt.....	7

Example V

Quaternary ammonium chloride salt solutions were tested for corrosion inhibition following the procedure set forth in Example IV. In aqueous solutions having .08% ammonium salt concentrations, the following results were obtained:

Chemical in Solution	Corrosion Rate in Milli-Inches per Year	Percent of Protection
Alkyl trimethyl ammonium chloride (alkyl groups comprising chains of 8, 10, 12, 14, 16 and 18 carbon atoms).....	67	12
Alkyl trimethyl ammonium chloride (alkyl groups comprising chains of 16 and 18 carbon atoms).....	45	41
None (tap water control).....	76.2	

Example VI

Corrosion inhibition is obtained in aerated brine solutions where, among other variables, corrosion is a function of pH. The procedure consisted of a modified turbine oil test as set forth in Example IV, the alkyl trimethyl ammonium nitrite being added to a 2.5% sodium chloride solution in which the ammonium salt concentration was .08%. Three of the four test samples contained varying amounts of calcium hydroxide to indicate the corrosion inhibition of the cylindrical steel coupons at different pH levels. Corrosion rates were calculated at the end of twenty-four hour emersion periods and are set forth in the following table:

Solution (2.5% NaCl)	pH	Corrosion Rate in Milli-Inches/1 year
Control.....	7	88
.08% quaternary ammonium salt concentration.....	7	73
Do.....	8.5	59
Do.....	11.5	15
Do.....	11.8	7
Control.....	11.8	23

6

70% protection of steel specimens was observed in 2.5% sodium chloride solution having an ammonium salt concentration of .08%, the sodium chloride solution having been previously saturated with calcium hydroxide. Further laboratory testing indicated no acceleration in the corrosion of copper or with such alloys as stainless steel, bronze or Monel.

In the well drilling method described above, either air or some other fluid such as natural gas may be used as the pressure medium. Therefore, the term "gas" as it appears herein is intended to designate any suitable gaseous pressure fluid which may be used in connection with the present method.

While in the foregoing specification various embodiments of the invention have been set forth and specified details thereof elaborated for the purpose of illustration, it will be apparent to those skilled in the art that this invention is susceptible to other embodiments and that many of these details may be varied widely without departing from the basic concept and spirit of the invention.

We claim:

1. In a well drilling method wherein gas under pressure is circulated through a bore hole for the removal of water and cuttings therefrom, the improvement comprising injecting controlled amounts of a surface-active, corrosion-inhibiting lifting agent to form an aerated column for lifting the water and cuttings from the well while at the same time inhibiting corrosion of parts in contact with the air-water mixture, in sufficient quantity to produce an aqueous blow-line effluent having a lifting agent concentration within the range of 0.04 to 0.2%, said agent comprising a water-miscible solution of an alkyl trimethyl quaternary ammonium salt having an alkyl group with a chain length within the range of 8 to 18 carbon atoms.
2. The method of claim 1 wherein said agent comprises alkyl trimethyl ammonium nitrite.
3. The method of claim 1 in which said agent comprises alkyl trimethyl ammonium chloride.
4. The method of claim 1 wherein the concentration of agent lies within the range of 0.06 to 0.1%.

References Cited in the file of this patent

UNITED STATES PATENTS

2,759,975	Chiddix et al.	Aug. 21, 1956
2,860,106	Little et al.	Nov. 11, 1958
2,866,507	Bond et al.	Dec. 30, 1958

FOREIGN PATENTS

378,318	Great Britain	Aug. 11, 1932
525,648	Canada	May 29, 1956

OTHER REFERENCES

"The Oil and Gas Journal," June 10, 1957, article "Water Still Poses Tough Problem in Drilling With Air," by A. Scovil Murray and Stan P. MacKay, pages 105-112.