Sept. 25, 1956 G. H. ROHRBACK ET AL 2,764,465

PREVENTION OF OIL WELL CASING CORROSION

Filed April 29, 1953 2 Sheets-Sheet 1

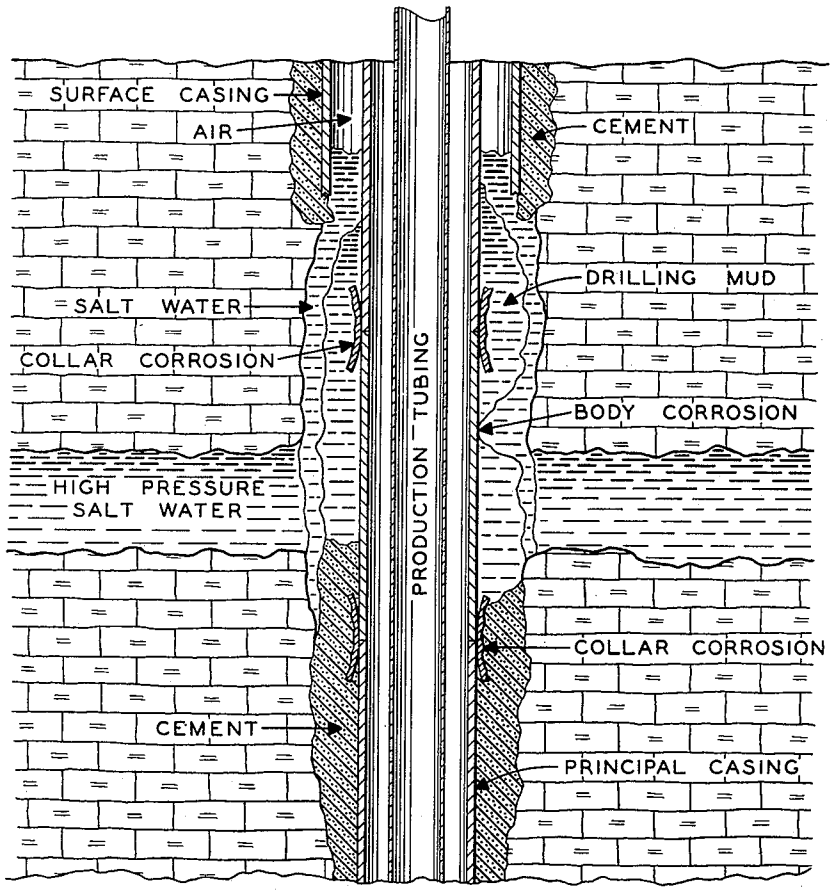


FIG. 1

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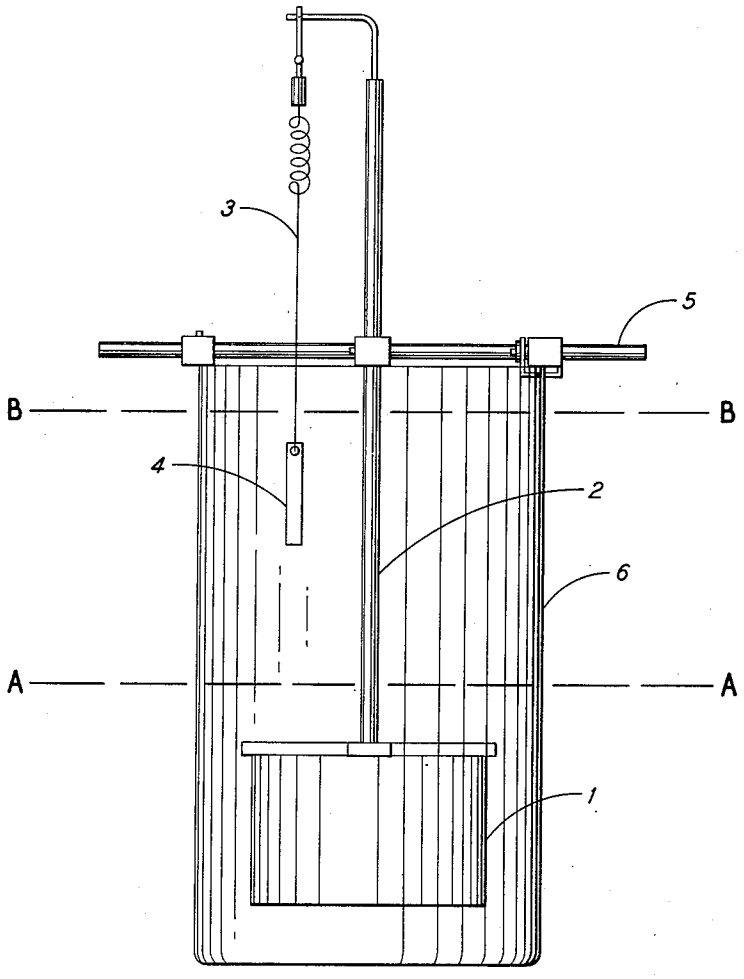


FIG. 2

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PREVENTION OF OIL WELL CASING CORROSION

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7 Claims. (Cl. 166—1)

This invention relates to a method for inhibiting the corrosion of oil well casings.

Although relatively little attention has been given to corrosion failure of oil well casings in the literature, the problem is rather wide-spread. A number of theories have been proposed to account for casing corrosion and some attempts to control it have been made on the basis of the theories. Among the theories heretofore advanced to explain casing corrosion have been suggestions that the corrosion was due to bacterial action; due to electric currents flowing through the casing; due to localized corrosion at metal flaws; due to particular compositions of formation water; due to corrosion by self-potential currents, and due to interzonal migration of salt water. So far as is known, no successful method of controlling casing corrosion has been developed on the basis of any of these theories. Meantime, casing failure due to corrosion continues to be a serious problem in many oil fields. Repair of casing failure is difficult at best and if the failure escapes detection for an appreciable period of time, the well ceases to produce and production may not be resumed, even though the casing be repaired, necessitating abandonment of the well.

Thirty instances of casing failure due to corrosion in a California field were carefully studied. The average time of failure was about five years, but failures occurred at times ranging from less than one year to about sixteen years from completion of the well. These failures occurred in the body of the casing resident in the salt water zone above the cemented zone or at casing collars. Corrosion of the casing in all instances was highly localized and from an overall study of the circumstances attending these casing failures it was concluded that the corrosion was electrochemical in character and due to differential oxygen availability at different points along the exterior surface of the casing.

As a result of differences in oxygen availability at two points along the casing, a cell is established in which the reaction at the anode is

$$Fe \rightarrow Fe^{++} + 2e$$

and the reaction at the cathode is

$$\tfrac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^-$$

The portion of the casing constituting the anode is subjected to highly localized attack and the iron dissolves away, causing casing failure in this area.

The difference in oxygen availability at two points along the exterior of the casing which gives rise to the electrochemical attack on the casing may be either a difference in the concentration of oxygen actually physically present at the two points, or it may be a difference in chemical availability or recativity at two points, though the physical concentration is essentially the same at these points. Differences in pH of the fluids in contact with two points of the casing give rise to differences in chemical availability of the oxygen at those points, the availability being greater at the point of higher pH.

Figures 1 and 2 of the appended drawings are referred to hereinafter to describe the invention in detail. Figure 1 of the drawings is a diagrammatic illustration of a section of the well casing and formation. Figure 2 of the drawings is a diagrammatic illustration of laboratory equipment employed in exploring the mechanism of casing corrosion and evaluating means for controlling it.

The situation frequently existing in a well when serious corrosion of the body of the casing is encountered will be better understood by reference to Fig. 1 of the appended drawings, which is a diagrammatic illustration of a section of the casing and the formation. The portion of the casing in contact with formation water of relatively low pH is the area at which rapid corrosive attack upon the body of the casing occurs.

In Fig. 1 of the drawing it will be noted that the annular space above the cemented zone between the casing and the formation is filled with drilling mud. Pursuant to a fairly common practice, the lower part of this annular space may be filled with an aqueous polyphosphate solution and the upper part of it with mud. The annular space below the cemented zone and between the casing and the formation (not shown) is filled with drilling mud. When a well has been drilled to the desired depth and is ready for completion, the casing is full of drilling mud. Cementing of the casing is commonly accomplished by forcing a cement slurry (optionally preceded by an aqueous solution of a polyphosphate) downwardly through the casing, causing the mud contained in the casing to flow around the lower circumference of the casing and upwardly through the annulus between the outer casing wall and the formation when the desired amount of cement slurry has been introduced into the casing, the cement is forced into position between the outer casing of the drilling wall and the formation by pushing it down the casing with additional mud. When the cement is in place it is allowed to set and that portion of the annulus between the outer casing wall and the formation is filled with drilling mud which was pushed ahead of the cement slurry.

During the drilling of a well the drilling mud is continually circulating and continually in contact with air. The mud which normally comes to final rest in the annulus between the casing and the formation has a very substantial oxygen content. The pyrowash solution (sodium polyphosphate), if one is used, likewise normally has a substantial oxygen content when it is introduced into the well.

The oygen which is introduced into the annulus between the casing and the formation in solution *m*, absorbed in or entrained in the fluids which become finally resident in that annular space, is the oxidizing agent which makes possible the electrochemical corrosion of the casing.

Casing corrosion can be substantially completely controlled by eliminating elemental oxygen from the fluids which are introduced into the annular space between the casing and the formation during the completion of a well.

Laboratory studies of the nature of casing corrosion and of compositions and methods for controlling it were made in the apparatus diagrammatically illustrated in Fig. 2 of the drawings.

In the drawing container 6 is a glass jar having about 4 gallons' capacity. Electrode 1 was made up of three short sections of concentric pipe welded together. The weld areas were covered with a plastic paint to eliminate undesirable galvanic couples from these areas. The total area of this electrode was about 330 square inches. Electrode 4 is a small strip of iron having a surface area of approximately 2 square inches. Electrode 1 is welded to iron rod 2 which is attached to adjustable support 5 so that the position of electrode 1 in the jar can be ad-

justed at will. Electrode 4 is connected to rod 2 by wire 3. In making the experimental tests two fluids were introduced into jar 6. The fluids differed from each other in both pH and density. In each test, jar 6 was filled with the denser of the two fluids employed to level AA and then the less dense of the two fluids was introduced into jar 6, filling the jar to about level BB. Electrode 1 was positioned in the jar so that it was entirely surrounded by the fluid of higher pH. Electrode 4 was positioned in the jar so that it was entirely surrounded by the fluid of lower pH. The electrodes were then left in these relative positions for a period ordinarily of 14 days, at the end of which electrode 4 was removed and weighed to determine its loss of weight. In order to determine the weight loss of electrode 4 due to electrochemical action alone, a second small iron strip approximately identical with electrode 4 in size and shape was suspended from the wall of the jar in the same fluid which surrounded electrode 4. At the end of the test period the weight loss of electrode 4 and the weight loss of the second metal strip were determined and the difference between these two losses was the loss of weight of electrode 4 due to electrochemical action. Results of a series of experiments are set forth in the table below. The muds employed in the tests were typical commercial drilling muds. The formation water was a typical aqueous effluent from a California well and the pyrofluid was an aqueous solution of tetrasodium pyrophosphate such as is commonly employed for washing the mud cake prior to introduction of the cement and which is commonly left in the annulus between the outer casing wall and the formation when the well is completed. The effect of various additives on the weight loss due to electrochemical corrosion is shown in the table.

The drilling muds and the pyrowash solutions employed in the experiments reported in the table were prepared in a manner corresponding to their preparation for field use and contained very substantial proportions of dissolved and adsorbed elemental oxygen. The formation water used in the tests was essentially free of oxygen as it is in the formation. The mud employed in Test No. 12 was deliverately prepared by mixing the dry solid with freshly distilled water in the absence of air. The only oxygen contained in this mud was that which was adsorbed on the surface of the solid mud particles prior to their dispersion in water.

The data in the above table was obtained employing pairs of fluids, mud and formation water, having high pH differences. Commercial drilling muds ordinarily will have pH values lying in the range from about 8.5 to 12. The corrosive attacks of the character illustrated in the table occur wherever there is a pH differential between the two fluids and the rate of that attack is greater when the pH difference of the two fluids is greater. From the results shown in the table it is clear that corrosive attack is substantially completely eliminated by the addition of either ferrous chloride or stannous chloride to the high pH fluid, which in practical effect means the addition of these materials to the mud and to the pyrowash solution if such a solution is used in completing the well. Similar tests establish that the addition of numerous other reducing agents to the drilling mud or pyrowash solution in a quantity sufficient to react completely with the dissolved and elemental oxygen contained in these materials also substantially completely eliminates casing corrosion. Other effective reducing agents are the alkali metal sulfides, pyrogallol, dihydroxybenzenes, polyphenols, sulfur dioxide, sodium thiosulfate, and ammonium sulfide. In general, the addition of any reducing agent capable of reacting with elemental oxygen at room temperature or slightly higher temperatures can be added to the fluids which become resident in the annular space between the casing and the formation during the completion of a well, and the addition of such a reducing agent will substantially completely inhibit the corrosion of the casing.

It is the absence of elemental oxygen in the fluid resident between the casing and the formation that is necessary if corrosion is to be eliminated. The absence of oxygen in these fluids can be assured not only by chemical means such as the use of the reducing agents above described, but it can also be realized by physical methods such as stripping the fluids with a material such as nitrogen, normally gaseous hydrocarbons, or steam, to remove dissolved and adsorbed elemental oxygen from these fluids. A very marked reduction in the amount of oxygen contained in these fluids and, therefore, in the casing corrosion which can be anticipated is obtained simply by mixing the fluids in a closed vessel preferably under an inert atmosphere such as an atmosphere of nitrogen or flue gas. If the fluids (mud or pyro solution) are prepared in this manner, very little air is dissolved in

TABLE I

Weight loss in corrosion cells for different combinations of treated and untreated fluids

Test No.	Electrode 1			Electrode 4			Measured Weight Loss from Electrode 4 Due to Current (Milligrams)
	Fluid	Treatment	pH	Fluid	Treatment	pH	
1	Mud	None	12.0	Formation Water	None	7.1	120
2	do	Quebracho	12.3	do	do	7.3	139
3	do	Sodium Chromate	12.3	do	do	7.2	132
4	do	$SnCl_2$	12.2	do	do	7.1	5
5	do	$FeCl_2$	12.1	do	do	7.1	0
6	Pyro	None	12.3	Mud	do	8.5	968
7	do	do	12.2	do	Sodium Chromate	8.4	522
8*	Mud	do	8.5	Pyro	$SnCl_2$	12.1	0
9	Formation Water	do	7.1	do	$SnCl_2$	12.2	0
10	Mud	$SnCl_2$	12.2	do	$SnCl_2$	12.2	0
11	do	Stripped	12.1	Formation Water	None	7.2	27
12	do	No exposure	12.0	do	do	7.2	31

2. Mud contained quebracho—0.42 percent.
3. Mud contained sodium chromate—0.02 percent.
4. Mud contained $SnCl_2$—0.15 percent, Pyro—0.5 percent, and quebracho—0.5 percent.
5. Mud contained $FeCl_2$—0.5 percent, Pyro—0.5 percent, and quebracho—0.5 percent.
7. Mud contained sodium chromate—0.02 percent.
8. Pyro contained $SnCl_2$—0.15 percent, and quebracho—0.5 percent.
9. Pyro contained $SnCl_2$—0.15 percent, and quebracho—0.5 percent.
10. Both mud and pyro contained $SnCl_2$—0.15 percent, and quebracho—0.05 percent.
11. Mud stripped with gaseous hydrocarbons.
12. Mud was mixed with freshly distilled water in absence of air.

*When pyro was treated with $SnCl_2$, the cell was set up with electrode 4 in pyro solution.

them during the preparation and their capacity to cause casing corrosion is, accordingly, much reduced.

Reference is again made to Fig. 1 of the drawings, particularly to the annular space lying between the principal casing and the surface casing. Normally, this annular space contains a layer of supernatant water in contact with the mud which fills the annulus between the principal casing and the formation and this layer of supernatant water is in contact with air which fills the remainder of the annulus between the surface casing and the principal casing. When fluids substantially completely free of elemental oxygen have been introduced into the annular space between the principal casing and the formation pursuant to the invention, it is desirable to insure that these fluids remain substantially free of elemental oxygen. This condition can be insured by pouring oil into the annular space between the surface casing and the principal casing to form an oil layer on the surface of the supernatant water resident in that annular space. The oil layer prevents air from dissolving in the water and finding its way into contact with the principal casing to cause corrosion.

We claim:

1. In an oil well drilling process wherein, by the maintenance of drilling mud in substantially static condition in the annular space between the exterior of the casing and the formation, the exterior of the casing is normally placed in contact with said mud and a fluid, the oxygen availability of which is different from the oxygen availability of said mud, the improvement which comprises substantially completely eliminating elemental oxygen from said drilling mud and thereafter introducing said mud into said annular space to minimize corrosion of the exterior of said casing occasioned by said oxygen availability differential.

2. The process of claim 1 wherein elemental oxygen is eliminated from said drilling mud by treatment of said drilling mud with a reducing agent capable of reducing elemental oxygen, the amount of reducing agent employed being in stoichiometric excess over the oxygen contained in said mud.

3. The process of claim 1 wherein elemental oxygen is removed from said drilling mud by stripping said mud with gaseous hydrocarbon.

4. The process of claim 1 wherein the upper surface of the fluid contained in the annular space between the casing and the formation is covered with oil.

5. In an oil well cementing process wherein the exterior of the casing is normally positioned in contact with drilling mud in substantially static condition and a fluid, the oxygen availability of which is different from the oxygen availability of said mud by the introduction of said mud into the annular space above the cemented zone of the well and between said casing and the formation, the improvement which comprises substantially completely eliminating elemental oxygen from said drilling mud prior to introducing said mud into said annular space to minimize corrosion of the exterior of said casing occasioned by said oxygen availability differential.

6. The process of claim 5 wherein elemental oxygen is eliminated from said drilling mud by treatment of said drilling mud with a reducing agent capable of reducing elemental oxygen, the amount of reducing agent employed being in stoichiometric excess over the oxygen contained in said mud.

7. The process of claim 5 wherein elemental oxygen is removed from said drilling mud by stripping said mud with gaseous hydrocarbon.

References Cited in the file of this patent

UNITED STATES PATENTS

1,647,003	Huber	Oct. 25, 1927
2,132,586	Speller	Oct. 11, 1938
2,152,779	Wagner et al.	Apr. 4, 1939
2,241,273	Robinson et al.	May 6, 1941

OTHER REFERENCES

Protection of Oil and Gas Field Equipment Against Corrosion, by R. Van A. Mills, Dept. of the Interior, Bureau of Mines Bulletin 233, Washington Government Printing Office, 1924.

Bureau of Mines Report of Investigation No. 3719, August 1943.

World Oil, January 1950, Production Section, pages 152, 153, 154, and 157.

Bureau of Mines Bulletin 134 of 1916, pages 36–40.