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CORROSION PROTECTION FOR WELLS

Filed May 14, 1965

TX 166/250

FIG. 5

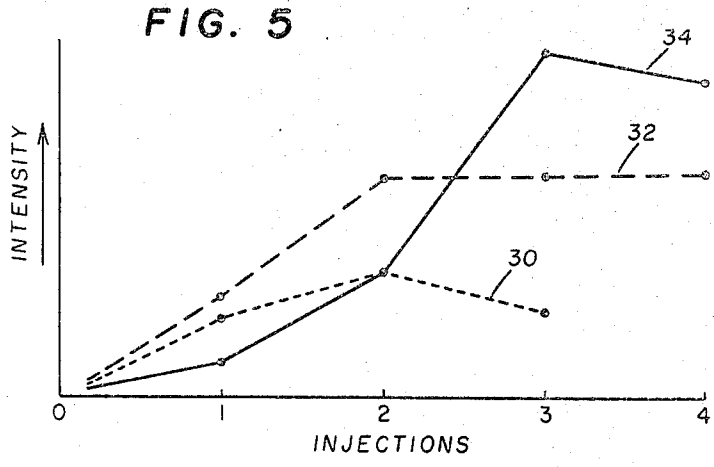


FIG. 1

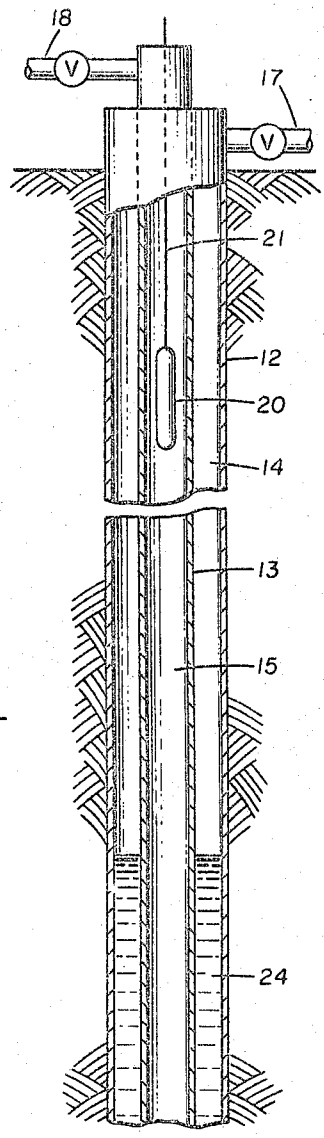
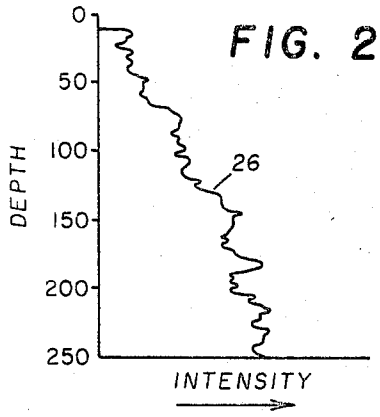


FIG. 2



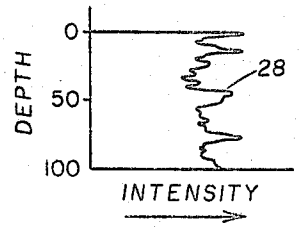
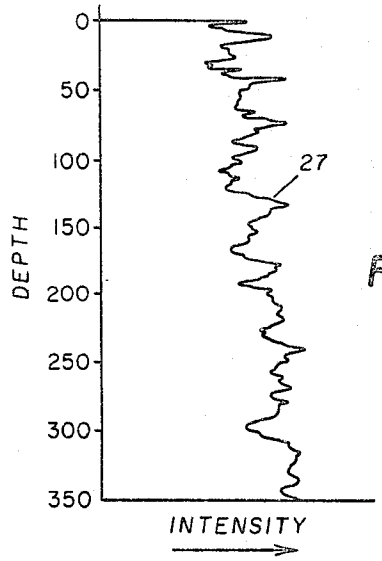


FIG. 4

FIG. 3



ALLAN D. SHELL
INVENTOR

BY Williams D. Jackson
ATTORNEY

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CORROSION PROTECTION FOR WELLS

Allan D. Shell, Midland, Tex., assignor to Mobil Oil Corporation, a corporation of New York

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ABSTRACT OF THE DISCLOSURE

This specification describes a procedure for providing corrosion protection for wells. A corrosion inhibitor liquid is injected into the annulus defined by the well casing and tubing at a rate sufficient to form a unitary slug within the annulus. As the slug travels through the annulus it leaves a protective film on the exterior surface of the tubing and the interior surface of the casing. In one embodiment the inhibitor liquid includes a tracer material. After injection of the inhibitor, a detector is passed through the tubing to determine the extent of coverage.

This invention relates to the provision of protective films of treating agents on well conduits and more particularly to the provision of protective films which will prevent or mitigate the corrosion of such conduits.

Wells such as those used for the production of oil or gas normally contain metal conduits such as tubing and casing which provide passages extending from subterranean locations to the surface. One or more of these passages in a particular well may contain fluids which are highly corrosive to the steel conduits. For example, in the general area of the Permian Basin's Northern Shelf area, wells typically are completed utilizing at least one casing or "oil string" and an internal tubing string through which the wells are produced. Internal casing corrosion has been a persistent problem in this area since its development. The absence of corrosion on the outside of the tubing through which the subterranean fluids are produced and which is consequently relatively warm suggests that a condensating mechanism on the cool casing surfaces in the presence of carbon dioxide and hydrogen sulfide is responsible for the corrosion. Since corrosion results in early casing failures, thus necessitating extensive workovers, numerous programs have been developed to provide corrosion protection for the internal casing surfaces. In most cases, the ultimate goal in these programs is the provision of a protective corrosion inhibitor film on the internal wall of the casing.

Methods of providing these films have taken many varied forms. One common technique is to place the corrosion inhibitor at the bottom of the well by injection through either the tubing or the annulus and then allow it to be carried upwardly with the flow of produced fluids through the annulus. Another conventional practice is the injection of a corrosion inhibitor through the annulus so that the inhibitor solution will leave a film on the metal surfaces as it moves downwardly in the well. This often has proved unsuccessful because of the failure of the inhibitor solution to contact completely the casing and tubing surfaces as it moves downwardly through the annulus. In order to overcome this, operators have resorted to injecting relatively large volumes of inhibitor solutions on the premise that increasing the volume of solution injected increases the statistical probability that the entire metal surfaces will be contacted with the resultant provision of a complete protective film. While this procedure may improve coverage, it is very uneconomical since a large quantity of inhibitor is wasted. More specifically, a vastly greater volume of inhibitor is injected than is needed for the provision of a protective film over the casing and tubing surfaces.

In accordance with the instant invention, there is provided a method of achieving complete peripheral coverage of the conduit surfaces with a corrosion inhibitor without resorting to the wasteful procedure of injecting the inhibitor in a quantity greatly in excess of that actually needed. In carrying out the invention, a corrosion inhibitor liquid is injected into the annular passage defined by the well conduits to be protected at a rate sufficient to form a unitary slug that completely blocks the passage. Thus, as the slug of treating liquid moves downwardly through the passage, the wall surfaces of the conduits defining the passage are contacted throughout their perimeters so that complete peripheral film contact is provided on the walls.

In one embodiment of the invention, a treating agent including a corrosion inhibitor and a tracer material such as a radioactive substance is injected into a well passage. Subsequent to the movement of the treating agent through the passage, a detecting means which is responsive quantitatively to the presence of the tracer material is moved through a second passage which is separate but coextensive with the passage treated with the corrosion inhibitor. In this manner, the extent of coverage of the corrosion inhibitor on the wall surfaces defining the first passage may be determined without contamination of the detecting means.

For a better understanding of the invention, reference may be had to the following detailed description taken in conjunction with the accompanying drawings in which:

FIGURE 1 is a schematic illustration partly in section of a well showing a typical environment in which the instant invention may be carried out;

FIGURES 2, 3, and 4 are logs taken after injections of corrosion inhibitor solutions in accordance with the instant invention; and

FIGURE 5 is a graph illustrating the coverage obtained after successive injections of corrosion inhibitor solutions.

With reference to FIGURE 1, there is shown a typical well installation which includes a casing string **12** disposed in a borehole and an inner string of production tubing **13** which is suspended within the casing in a manner well known in the art. Casing **12** and tubing **13** define an annular passage **14** which as shown in coextensive with the production passage **15** defined by tubing **13**. The upper end of annulus **14** is closed by suitable closure means (not shown) and the casing is provided with a valved flow line **17** at a point below the closure means. The upper end of tubing **13** also is closed and is provided with a valved flow line **18**.

There also is shown in FIGURE 1 a detecting means **20** such as a radioactivity-responsive logging tool for use in carrying out one embodiment of the invention. The logging tool is supported in the tubing **13** by a wire line **21** or other supporting means which extends to the exterior of the tubing string through a suitable stuffing box (not shown) at the upper end thereof. The wire line **21** is attached to a suitable reel (not shown) for movement of the logging tool through the tubing string.

It will be understood that FIGURE 1 is diagrammatic only and is not intended to show all the details of a typical well installation. For example, the well normally would include one or more outer casing strings. These casing strings, as well as the casing **12** shown, normally would be cemented to the surrounding earth formations. Also, the tubing string might be provided with a pump at the lower end thereof and a packer at a position above the pump. The packer would function to seal off the annular space between the tubing string and the casing in a manner well understood in the art.

In most cases, the well will contain a column of liquid as designated by reference numeral **24** in FIGURE 1. The upper interval of the annulus **14** above the liquid level

contains gas and, of course, is void of such a liquid column. It will be understood from the following disclosure that the hereinafter described slug of corrosion inhibitor liquid is formed within this upper interval. Where liquid is present within the well, the section to be treated in accordance with the invention is above the liquid column and the invention will result in little, if any, inhibitor placement within the section of the annulus covered by the liquid **24**. In some cases, of course, the corrosion inhibitor slug may lose its integrity before reaching the top of the column of liquid.

In carrying out the invention, a liquid corrosion inhibitor solution is injected through flow line **17** into the annular passage **14** between the casing **12** and tubing **13** at a sufficiently rapid rate such that within the interval above the liquid **24** it forms a slug which completely blocks the annulus and travels downwardly therethrough as a unitary body. The unitary slug cannot avoid contacting the entire periphery of the tubing and the casing, and thus complete peripheral contact by the inhibitor film is obtained on the casing and tubing surfaces traversed by the slug above the level of the liquid **24** in the well.

In the embodiment of the invention in which the inhibitor solution contains a radioactive tracer material, the radioactivity detector **20** is moved through the passage **15** defined by the tubing string subsequent to the injection of the inhibitor solution. This logging tool generates a signal indicative of the intensity of the radioactivity in the adjacent annular passage. This signal is measured and recorded by a suitable recording means (not shown) at the surface. This record provides a reliable indication of the inhibitor coverage on the walls of the tubing and casing strings.

The movement of the logging tool through a passage which is coextensive with, but separate from, the passage treated by the corrosion inhibitor is advantageous in that this procedure prevents contamination of the logging tool with the tracing material. This prevents false measurements due to such contamination and insures that an accurate indication of inhibitor coverage is obtained at all levels within the well.

The treating liquid must be injected into the annulus **14** at a rate sufficient to form at some level within the well a unitary slug which completely blocks the annulus. Since a significant portion of casing failures due to corrosion occur near the surface of the well, the corrosion inhibitor preferably will be injected at a rate sufficient to form the unitary slug at a level adjacent the point of injection.

It will be understood that the volume of inhibitor solution and the injection rate necessary for the formation of the unitary slug will vary somewhat with the characteristics of the treating liquid and the well involved and that it is impossible to set forth definite parameters of injection conditions for all possible situations. In most instances, it will be most expeditious to inject the corrosion inhibitor in a petroleum oil solution. This normally will be crude oil from the field in which the treatment is applied. The following examples of specific applications of the instant invention utilizing an inhibitor crude oil solution are given in order to enable those skilled in the art to better understand the invention and to develop some parameters for the successful practice of the invention.

The following tests were carried out in the Seminole-San Andres Field, Tex. In each test the outer diameter of the tubing and the inner diameter of the casing, respectively, were 2.875 inches and 6.456 inches and the interval to be treated extended from the surface to the liquid level in the well at a depth of about 4,500 feet. The tests were carried out in each instance with the injection of one and one-half barrels of inhibitor crude oil solution which included five millicuries of radioactivity provided by iodine 131 in alcohol. The crude oil used was from the Seminole-San Andres Field. This oil had a gravity of 32.1 degrees API and a viscosity of 12 centipoises at 60° F. without the addition of the corrosion inhibitor. With the corrosion inhibitor added in an amount of two gallons per barrel of inhibitor-oil solution, the treating liquid solution was found to have a viscosity of nine centipoises at 60° F. and an API gravity of 31.9.

In one test the corrosion inhibitor-oil solution was injected into the annulus of a well at a rate equivalent to a velocity of 30 feet per minute based upon the area of the annulus cross section. After allowing sufficient time for the injected corrosion inhibitor solution to fall through the annulus, a radioactive logging tool was moved through the tubing in order to monitor the radioactivity intensity in the annulus. The log obtained by this procedure is illustrated in FIGURE 2 wherein curve **26** shows intensity in counts per second of gamma activity plotted on the horizontal axis against depth in feet on the vertical axis. As shown by the log, the intensity was relatively low in the upper portion of the annulus and increased until it reached a fairly constant value at about 180 to 200 feet. This log indicates that the injection rate equivalent to a velocity of 30 feet per minute did not result in a unitary slug of treating liquid at the point of injection, but that such a slug was formed at a depth of about 180 to 200 feet.

In another test, the above-described inhibitor-oil solution was modified by the addition of a standard frac gel (available from Cardinal Products, Inc., Dallas, Tex. as "LJ–4") in an amount of one gallon per barrel of inhibitor-oil solution. The gelled solution had a high viscosity in excess of 6,000 centipoises. In this test, the inhibitor solution again was injected into the annulus of a well at a rate equivalent to a velocity of 30 feet per minute based upon the cross-sectional area of the annulus. After the injected slug fell through the annulus, the radioactive logging tool was moved through the tubing string as in the previous test. The log obtained in this case is shown in FIGURE 3 with curve **27** being a plot of gamma activity in counts per second as the horizontal ordinate and depth in feet as the vertical ordinate. In this case, it should be noted that the intensity at the top of the hole was relatively high and that there was relatively little increase in intensity with depth. This indicates that the coverage at the top of the hole was relatively constant and that the solution was injected at a rate equal to or greater than the free-fall velocity of the solution in the annulus. In other words, the solution was injected at a rate sufficient to form a unitary slug at a point adjacent the point of injection, thus providing for complete peripheral contact of the contact surface from this point downwardly through the portion of the annulus traversed by the slug.

Another test was carried out in order to determine the injection rate necessary to achieve the formation of a unitary slug at the top of the hole, and thus coverages from the top of the hole downwardly, utilizing the inhibitor-oil solution without the addition of frac gel. This of course is preferred since the elimination of the frac gel reduces the expenses involved in the treatment. In this case, the inhibitor-oil solution described above was injected into the annulus at a rate equivalent to a velocity of 60 feet per minute based upon the area of the annulus cross section. The resultant log shown in FIGURE 4 in which curve **28** is a plot of intensity versus depth in feet obtained in the same manner as previously described. As can be seen from FIGURE 4, the intensity at the top of the hole was relatively high and maintained a fairly constant value with depth. As in the case of the log illustrated in FIGURE 3, this indicates that a unitary slug of inhibitor-oil solution was formed at the top of the hole and that complete peripheral coverage was obtained from this point downwardly.

The corrosion inhibitor used in the above tests was a long-chained amine available from Cardinal Products, Inc. as "Nocor 224–B–1." While other corrosion inhibitors may be used in carrying out the present invention, it usually will be preferred to use film-forming long-chained amines of the type noted above.

As noted above, it usually will be preferred to inject the inhibitor in a petroleum oil solution. To summarize the results of the above tests, the inhibitor solution should be injected at a rate equivalent to a velocity of at least 30 feet per minute based on the cross-sectional area of the annulus in order to form a unitary slug within at least about the first 200 feet of the well. In most cases, however, it will be desired to obtain complete peripheral coverage from the top of the well. Therefore, in a preferred form of the invention, the inhibitor solution is injected at a rate equivalent to a velocity of at least 60 feet per minute. As indicated in the third test described above, this will result in the formation of a unitary slug at or above the point of injection.

The volume of inhibitor solution necessary for the formation and maintenance of a unitary slug will depend somewhat on the cross-sectional area and length of the passage to be treated. In most cases one-half barrel will be adequate and at least this amount should be used. However, the minimum practical amount that can be pumped by commonly available oil field equipment at the rates necessary is about one and one-half barrels, and it is preferred to inject from about one and one-half to two barrels in order to avoid having to use specially designed pumping equipment. Even for deep wells and with a generous tolerance allowance, amounts in excess of four barrels are unnecessary and should be avoided in order to prevent excessive waste of the inhibitor solution.

The logs run in the above-described tests indicate that complete peripheral contact of the tubing and casing surfaces defining the annulus is obtained after one injection of corrosion inhibitor solution. While one injection is probably adequate in many instances, it has been found that increased corrosion protection, probably due to a better oriented and more completely developed film, can be achieved by successive injections of inhibitor solution. In this regard, reference is made to FIGURE 5 which is a graph showing the relative intensities obtained after successive injections. In FIGURE 5, curves **30**, **32**, and **34** are plots of radiation intensity versus successive inhibitor injections at depths of 25 feet, 250 feet, and 2500 feet, respectively, in the well. The injections were carried out at intervals of one and one-half hours and the intensities were measured about one hour after each injection.

From FIGURE 5 it can be seen that inhibitor placement increased significantly after each of the first two runs for the 25-foot and 250-foot levels and then tended to remain relatively constant. At the 2500-foot depth, inhibitor placement increased significantly after each of the first three injections, while the fourth injection showed no increase. Values indicated for the 25-foot and 2500-foot depths for injections **3** and **4**, respectively, probably are not accurate due to inexact measurements. Intensity values for these runs probably were approximately the same as the intensity values for the preceding injections since it is unlikely that successive injections would decrease inhibitor placement. More exact measurements at the 25-foot and 2500-foot depths would be expected to produce curves similar in shape to curve **32**.

From FIGURE 5 it can be seen that although complete peripheral coverage is obtained by only one injection, increased inhibitor placesent within a relatively short time after treatment of a well results from two, and, in the case of the greater depths, three injections of inhibitor solution. Therefore, in a preferred embodiment of the invention, the inhibitor injection step is repeated at least once and preferably twice, particularly where increased initial coverage at the deeper levels is desired.

One characteristic which should be considered in successive injections is the so-called "transit inhibitor" effect, that is, the tendency of the film left on the tubing and casing walls to flow downwardly along the annular surfaces after the slug passes. This effect is evidenced by the fact that logs run at varying periods after the termination of an injection showed a tendency of the intensity curve to diminish first at upper levels and smooth out with time and to maintain intensity with depth. Since the transit effect results in a more completely developed inhibitor film, some time delay should be provided between injections. Transit inhibitor is at its greatest immediately after passage of the inhibitor slug and decreases progressively with time with the duration of the effect increasing with depth. Therefore, in order to realize at least some beenfit from this effect, there is specified in accordance with the instant invention an interval of at least one minute between successive injections. Preferably the time interval between injections should be at least about five minutes since within this time the preponderance of the transit inhibitor effect is exhausted in the upper levels of the well where treatment often is critical. Longer time intervals may be allowed, although with decreasing benefits. It is doubtful that any significant benefit derives from allowing periods of more than 20 minutes between injections when consideration is given to the increased cost of the process because of the greater labor and equipment waiting time involved. As a practical matter, therefore, the periods between successive injections should not exceed about 20 minutes.

Having described specific embodiments of the instant invention, it will be understood that further modifications thereof may be suggested to those skilled in the art, and it is intended to cover all such modifications as fall within the scope of the appended claims.

What is claimed is:

1. In the provision of corrosion protection for a well having a first conduit disposed therein and a second conduit disposed therein interiorly of said first conduit defining with said first conduit an annulus and wherein an upper interval of said annulus is void of a column of liquid, the method comprising at a point adjacent the top of said well injecting into said annulus a corrosion inhibitor liquid at a rate sufficient to form at a level within said upper interval of said annulus a unitary slug of said liquid completely blocking said annulus whereby the wall surfaces of said conduits defining said annulus are contacted throughout their perimeters by said liquid as said slug moves downwardly through said annulus.

2. The method of claim **1** wherein said corrosion inhibitor liquid is injected at a rate sufficient to form a unitary slug of said liquid at a level adjacent the point of injection of said liquid.

3. The method of claim **2** wherein the quantity of said corrosion inhibitor liquid injected is within the range of one-half to four barrels.

4. A method of providing corrosion protection for a well having conduit means defining at least two coextending passages comprising injecting into one of said passages, in an amount sufficient to coat the walls of at least a substantial portion of said one of said passages, a treating agent including a corrosion inhibitor and a tracer material, and thereafter moving through the other of said passages detecting means responsive quantitatively to the presence of said tracer material whereby the coverage of said corrosion inhibitor on the walls of said one of said passages may be determined without contamination of said detecting means.

5. The method of claim **4** wherein said tracer material comprises a source of radioactivity and said detecting means comprises a radiation detector.

6. A method of providing corrosion protection for a well having a first conduit disposed therein and a second conduit disposed therein interiorly of said first conduit, comprising at a point adjacent the top of said well injecting into the annulus defined by said conduits at least one-half barrel of a corrosion inhibitor liquid at a rate equivalent to a velocity of at least 30 feet per minute based on the cross-sectional area of said annulus.

7. The method of claim **6** wherein the quantity of said inhibitor liquid injected is within the range of one and one-half to four barrels.

8. The method of claim 6 wherein the step of injecting said inhibitor liquid is repeated at least once after an interval of at least one minute.

9. The method of claim 6 wherein said corrosion inhibitor liquid includes a tracer material and further comprising the subsequent step of moving through said second conduit detecting means responsive quantitatively to the presence of said tracer material whereby the coverage of said corrosion inhibitor on the surfaces of said conduits defining said annulus may be determined without contamination of said detecting means.

10. The method of claim 9 wherein said tracer material comprises a source of radioactivity and said detecting means comprises a radiation detector.

11. The method of claim 6 wherein said liquid is injected at a rate equivalent to a velocity of at least 60 feet per minute based on the cross-sectional area of said annulus.

12. The method of claim 11 wherein at least one and one-half barrels of said liquid are injected.

13. The method of claim 11 wherein the step of injecting said inhibitor liquid is repeated at least once after an interval of at least five minutes.

14. The method of claim 11 wherein the step of injecting said inhibitor liquid is repeated at least twice at intervals in the range of five to twenty minutes.

15. The method of claim 11 wherein said corrosion inhibitor liquid comprises a solution of a film-forming long-chained amine in a petroleum oil and has a viscosity of nine centipoises.

References Cited

UNITED STATES PATENTS

2,357,559	9/1944	Smith	166—1
2,510,771	6/1950	Bond et al.	166—1 X
2,654,436	10/1953	Carlisle et al.	166—1
2,713,908	7/1955	Curtis	166—1 X
2,773,551	12/1956	Warden et al.	166—1 X
2,801,697	8/1957	Rohrback	166—1
2,832,414	4/1958	Battle	166—1
2,869,642	1/1959	McKay et al.	166—4

CHARLES E. O'CONNELL, *Primary Examiner.*

DAVID H. BROWN, *Examiner.*