

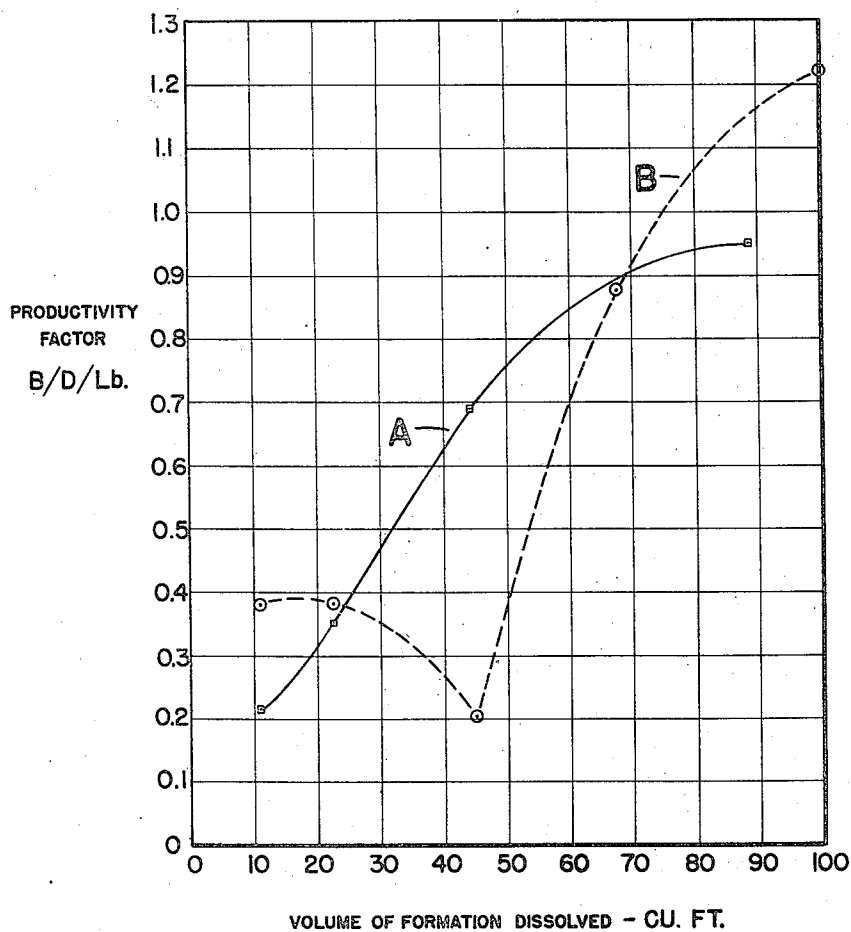
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ACID TREATING WELL

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ACID TREATING WELL

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The present invention is directed to a method of acid treating the desired formations penetrated by a borehole.

In completing oil wells, it is sometimes necessary and often desirable to treat the producing formations in order to increase or induce the flow of fluid therefrom. For a number of years, acid has been employed for this purpose, particularly when the producing formations are of a limestone or dolomitic nature, and also occasionally when sandstones are encountered.

It is an object of the present invention to devise a method of acid treating producing formations in order to induce or increase the production therefrom in a more satisfactory manner than has heretofore been accomplished.

A further object of the present invention is the stage treatment of formations with acid in order to obtain funnel-shaped drainage channels communicating through the producing formation into the borehole in order to obtain a substantially constant pressure differential between the reservoir and the bore of the well when producing fluid.

A further object of the present invention is to utilize a plurality of acids of differing rates of reaction in sequence to obtain drainage channels of more satisfactory shape in oil producing formations than has heretofore been possible and, hence, increasing the productivity of the treated formations.

Other objects and advantages of the present invention may be seen from a reading of the following description taken in conjunction with the drawing in which the sole figure comprises a pair of curves indicating the improved results to be obtained in the practice of the present invention as compared with conventional acid treating processes.

The present invention has been found particularly suitable for treating limestone, dolomite, and similar carbonate formations. In conventional acid treating processes employing hydrochloric acid, it has been found that the hydrochloric acid reacts at such a rate that it is substantially all consumed in the vicinity of the well bore. This phenomenon is encountered even though one of the known inhibited and retarded hydrochloric acids is used for the acid treating step. In accordance with the present invention, carbonate formations are given a plurality of acid treatments, acids of different reaction rates being employed in order to produce satisfactorily shaped drainage channels extending a substantial distance from the borehole.

One of the preferred ways of carrying out the present invention is to first treat the limestone or dolomite producing formation with a relatively small volume of a relatively active acid, such as hydrochloric, to remove obstructions within the borehole and to enlarge the capillaries in the producing formation immediately adjacent the borehole. Following this step, the spent acid is flushed from the well and a larger volume of acid solution of a very slow reaction rate is then injected into the formation. This slower reacting acid is forced into the formation a substantial distance from the borehole and is allowed to react with the carbonate. The spent solution obtained from the very slow reacting acid is then flushed from the formation. If the acid sludge cannot be satisfactorily removed by the flushing step, it will be desirable to follow the second acid treating step with a cleaning step in order to remove the acid sludge from the capillaries of the formation, so that fluid may flow readily there-through into the bore of the well. If desired, the sequential treatment described above may involve the use of strong acid in several stages, and also the employment of weak acid in several stages.

It is to be understood that in the procedure as described above it is not necessary to employ only two acids of different strengths. It will often be desirable to employ three or even more acids of different reaction rates in order to convert the capillaries of the formation into a funnel shape so that the pressure gradient through the formation, when the well is being produced, will be substantially constant.

The capillaries within the producing formations may also be enlarged to the desired funnel-like shape by reversing the sequence in which the charges of different acids are used and initially employing a charge or charges of a very slowly reacting acid and following it with charges of acids of increasing activity. When such a procedure is employed, the slow acting acid is forced out into the formation a substantial distance from the borehole, and is allowed to react until it is spent. The very slow reaction of the acid causes it to enlarge the capillaries in the producing formation a substantially uniform amount as far as the acid penetrates. The spent sludge is then removed from the formation and a charge of acid of greater activity forced into the borehole. This acid will not penetrate as far as the first acid, because its increased activity causes it to be spent before traveling this distance. The capillaries will accordingly be enlarged adjacent

the borehole a greater amount than they are enlarged a considerable distance away from the borehole. The spent fluids are now removed from the well and the procedure repeated with acids of increasing activity.

The number of different stages in which the treatment is carried out may be varied at the option of the operator to give optimum results. Under some circumstances a treatment with a slow reacting acid followed by a treatment of rapid reacting acid will be desirable, while under other conditions several separate treatments of the slow reacting acid followed by several treatments of the rapid reacting acid will be advantageous. Often it will be desirable to use three or more acids of differing strengths instead of only two acids, employing any of the procedures outlined above with respect to the two acids. In using stages of acid treatments it is advantageous, although not essential, to clean the acid sludge from the formation after each stage to leave the formation clear for the subsequent acid step and for production after the acid treating is complete. For best results the capillary passages in the formation should be generally funnel shaped and substantially free from sludge when the treatment is completed.

A comparison of an embodiment of the present invention with a conventional acid treating process will now be given in connection with a discussion of the drawing of the present application.

In the drawing, the curve designated A represents a well treated with a commercial inhibited hydrochloric acid, and curve B represents an adjacent well in the same field treated in accordance with applicant's process involving charges of acids of different activity.

Well A was treated as follows: The limestone producing formation was packed off in the manner conventional to the art and 1,000 gallons of inhibited hydrochloric acid forced into the producing formation. The acid was allowed to remain in position until its reaction with the carbonate formation was complete, the acid sludge removed, and a second charge injected. The second charge consisted of 1,000 gallons of the same acid, and after the reaction had been allowed to go to completion and the acid sludge removed, a third treatment of 2,000 gallons of the same acid was given, followed by a cleaning step and a 4,000 gallon treatment with the acid. As will be seen from the curve, each charge increased the productivity of the well, the total of 8,000 gallons of acid resulting in a productivity factor of 0.95.

Well B was given a preliminary treatment of 1,000 gallons of the same inhibited hydrochloric acid used in treating well A. After the sludge resulting from this treatment was cleaned out of the well, two charges of a mixture of mono- and di-chlor-acetic acid mixture were used, a first charge of 2,000 gallons, and a second charge of 4,000 gallons. After each injection of acid into well B, an attempt was made to remove acid sludge from the well, but the difficulty in removing the sludge was such that a substantial amount remained within the well and caused the productivity of the well to be actually decreased.

In order to clean the acid sludge from well B, after using the mono- and di-chlor-acetic acid mixture, a charge of 3,000 gallons of inhibited hydrochloric acid was forced into the formation to aid in the removal of sludge from the capil-

larities of the formation. As shown by the curve, the cleaning step was successful and increased the productivity of the well so that its final productivity factor was approximately 25% higher than that of well A.

The drawing clearly shows that the utilization of an acid having a slow rate of reaction in treating a well gives an increased productivity factor over the use of conventional inhibited hydrochloric acid. In the drawing the productivity factor is plotted against volume of formation dissolved in order to properly compare the treatments of wells A and B. The points on the curve indicate the addition of the charges of acid to the wells. A given volume of the mono- and di-chlor-acetic acid mixture used in treating well B will, of course, not dissolve as much carbonate formation as the same volume of commercial inhibited hydrochloric acid. The drawing indicates that when sufficient acid is employed in each well to dissolve 90 cu. ft. of formation that approximately 20% greater increase in productivity factor is obtained by utilizing the slow reacting acid, as above described.

The drawing also clearly shows that substantially no improvement could be expected in the treatment of well A by employing increased amounts of hydrochloric acid, because the productivity curve has leveled off so that it is substantially parallel with the axis. It will be apparent that, if desired, additional treatments of slowly acting acids may be given well B and will result in an increased productivity factor because the end of curve b is sloping sharply upward, having a shape similar to the curve of well A after its treatment with only enough hydrochloric acid to dissolve 45 cu. ft. of limestone formation.

As has been previously suggested, it will sometimes be desirable to reverse the sequence of treatments and inject slow acting acid into the well first and follow it by another stage or treatment in which a more active acid is employed. For example, instead of employing the mono- and di-chlor-acetic acid mixture in the second stage, it may be used for a first stage treatment, and hydrochloric acid as the second stage.

It will be apparent that I do not intend to limit the present invention to the specific acids listed above. Other acids which react relatively rapidly with the formation, as well as other acids which react relatively slowly with the formation, may be employed in carrying out the process.

It will also be evident that the present invention is by no means limited to the two stages above described. Under some conditions a larger number of stages will be desirable. A specific example of a sequence of acids which have been found useful for such stage operation is as follows, the acids being listed in order of increasing activity and ionization constant:

Acid	Ionization constant at 25° C.
Lactic acid.....	$K_a = 1.38 \times 10^{-4}$ at 25° C.
Mono-chlor-acetic acid.....	$K_a = 1.55 \times 10^{-3}$
Di-chlor-acetic acid.....	$K_a = 5.0 \times 10^{-2}$
Tri-chlor-acetic acid.....	$K_a = 2.0 \times 10^{-1}$
Hydrochloric acid.....	K_a large

While I have disclosed examples of specific materials which have been found suitable for practicing the present invention, these examples are given by way of illustration only and are not to be construed as limiting the scope of the invention.

I claim:

1. A method of treating a petroleum producing water-insoluble carbonate formation comprising the steps of preliminarily treating said formations with commercial inhibited hydrochloric acid, removing the products of reaction from the formation, injecting an acid capable of dissolving the water-insoluble carbonates and having an ionization constant of a lower order of magnitude than said hydrochloric acid in said formation, removing the products of the reaction from said formation, and producing said well.
2. A method in accordance with claim 1 in which the slowly reacting acid is a mixture of mono- and di-chlor-acetic acids.
3. A process in accordance with claim 8 in which the first acid used is a mixture of mono- and di-chlor-acetic, and the second acid used is hydrochloric acid.
4. A method of treating underground water-insoluble carbonate formations adjacent a bore hole comprising the steps of dissolving substantial amounts of the water-insoluble carbonates adjacent said bore hole in each of a plurality of stages and employing acids capable of dissolving water-insoluble carbonates and having ionization constants of differing orders of magnitude in successive stages and removing the products of the reaction from the formation after each stage.
5. A method of acidizing oil producing water-insoluble carbonate formations comprising the steps of preliminarily treating a petroleum producing water-insoluble carbonate formation with an acid capable of dissolving water-insoluble carbonates and having a relatively large ionization constant, removing the products of the reaction from the formation, subsequently treating said formation with a second acid capable of dissolving carbonates and having an ionization constant of a lower order of magnitude than first acid and removing the products of the reaction from the formation.
6. A method of treating a petroleum producing water-insoluble carbonate formation comprising the steps of treating the formation in stages and employing in said stages acids capable of dissolving water-insoluble carbonates, the acids used in successive stages having ionization constants of progressively increasing orders of magnitude and removing the products of the reaction from the formation after each stage.
7. A method of treating a petroleum producing water-insoluble carbonate formation penetrated by a bore hole comprising the steps of separately injecting a first acid capable of dissolving water-insoluble carbonates and having a relatively large ionization constant into said formation and a second acid capable of dissolving water-insoluble carbonates and having an ionization constant of

a lower order of magnitude than said first acid into said formation, whereby passages extending a substantial distance from the bore hole and increasing in size adjacent said bore hole are produced in said formation, removing substantially all of the products of the reaction from the formation after each acid treating step, and subsequently producing said well.

8. A method of treating a petroleum producing water-insoluble carbonate formation comprising the steps of injecting a charge of a first acid capable of dissolving water-insoluble carbonates and having an ionization constant of a low order of magnitude into said formation and forcing it a substantial distance from the bore hole, allowing the acid to react with the formation until it becomes spent, removing products of said reaction from the formation, subsequently injecting into said formation a charge of a second acid capable of dissolving water insoluble carbonates and having an ionization constant of a higher order of magnitude than said first acid, allowing it to react therewith, removing the products of reaction from the formation, and producing said well.

9. A method of treating a petroleum producing water-insoluble carbonate formation adjacent a bore hole comprising the steps of separately injecting charges of several acids into said formation, said acids being capable of dissolving water-insoluble carbonates and having ionization constants of progressively increasing orders of magnitude, allowing each charge to become spent, removing the products of the reaction after each acid charge is injected and before the subsequent charge is added to the well, removing the products of the reaction after the last charge has been spent, and producing petroleum from said formation.

10. A method of treating a petroleum producing water-insoluble carbonate formation adjacent a bore hole comprising the steps of separately injecting charges of several acids into said formation, said acids being capable of dissolving water-insoluble carbonates and having ionization constants of progressively decreasing orders of magnitude, allowing each charge to become spent in the formation, removing the products of reaction after each acid charge is injected and before the subsequent charge is added to the well, removing the products of the reaction after the last charge has become spent, and producing petroleum from said formation.

11. A method in accordance with claim 1 in which the slowly reacting acid is a mixture of mono- and dichloracetic acids and in which the products of the reaction of this acid with the formation are removed by treating the formation with commercial inhibited hydrochloric acid.

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