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# Chemically Controlled Acidation
# of Oil Wells

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THE past three years have witnessed the acid treatment of approximately three thousand lime wells in the United States and Canada for the purpose of increasing oil production. The acid treating, or, as it is popularly known today, acidation or acidizing of wells, has resulted in successful treatments in a large percentage of cases, especially in the areas containing the purer limestones of Michigan, Texas, Oklahoma, Kansas, Louisiana, Ohio, Illinois, Kentucky, and Ontario. The increased oil production due to these acid treatments ranges from a few to over one thousand barrels per well per day, averaging 448 per cent increase for all of the wells treated to date.

Several papers have already been published on the acidation of oil wells, but they have dealt mainly with field experience and production. An article by the Pure Oil Company (6) notes the early acid treatments of oil wells in the Michigan field near Mt. Pleasant. Swindell (7) discusses field conditions relative to acid treating and results in the Seminole area. Cunningham (3) gives the history and results of the first acid treatments. He also discusses the chemical reactions, treatments, and value of acidizing vs. shooting of wells. Best (1) describes the technical knowledge necessary if the wells are to be acidized in a scientific manner to assure the maximum increase in production. The article also discloses the various methods of introducing acid into the well and problems on water control. Covell (2) has shown that the use of acid to stimulate oil production from Michigan lime wells requires a study of several factors: an analysis of the formation to be treated, the selection of a suitable type of acid and its amount, the time of treatments with respect to date of well completion, and finally an economic analysis of the results.

The object of this paper is to present the chemical background and laboratory developments required to give the

acidation of oil wells its present status. There was no progress of commercial importance in this field until a scientific study of the problem had been made in the laboratory, even though as early as 1894 lime wells were treated with uninhibited concentrated hydrochloric acid for the purpose of increasing oil production. Most people connected with the oil industry are familiar with the patent issued to Frasch (4) which specified the use of hydrochloric acid in limestone formations. Since that time practically every commercial field has had, at one time or another, some producer attempt the application of acid treatment in an effort to increase the porosity of the rock and eventually increase oil production.

## DEVELOPMENT OF ACIDATION

The control and technic, both by chemical and physical means, of directing the acid into the well and thus making it a constructive agent rather than a destructive one was not perfected on a commercial scale until about 1932. The work which lead to the practical development of chemically controlled acidation of oil wells began in 1929, owing to the demand for increased production of natural brine which forms the basis of raw materials for The Dow Chemical Company. The demand for more natural brine brought the problem to the attention of both the chemical and physical research laboratories in order to develop a method of opening up the crevices of producing rock other than by the use of explosives.

The brine is produced for the most part from a sandstone of very high silica content, which contains a small percentage of calcareous material. Being a chemical company, its first thoughts were to find an acid which would be effective. As is the usual procedure on any research problem, the literature was searched, with the conclusion that all previous attempts to acid-treat wells had met with failure. The experiments were begun with the full knowledge that some-

thing new had to be developed to overcome the reasons for the failure of the several previous attempts with various commercial acids.

The research work was narrowed down to the use of acid by two methods: In the first place, it was fed into the well along with a stream of brine which carried the brine and acid mixture back into the producing formation. It was hoped that the acid would react with calcareous material in the rock and thus increase its porosity.

For the second method a charge of acid was fed directly into the well, and a certain head of brine or oil pumped in on top. At first the difference in head of the two fluids was relied upon to bring about sufficient pressure to feed the acid back into the rock, and later, by the application of mechanical pressure, this was more completely accomplished.

The lack of a large percentage of calcareous rock in or adjacent to the brine formation prevented the treatment from showing very great promise for improved production. However, for a well which had previously been discarded as a nonprofitable producer, it was possible to increase its production some 25 per cent, thereby making the well a paying investment.

In addition to the research which developed into the two major methods described above, work was carried on to determine the best type of acid to use, as well as the strength of acid which could be used. Hydrochloric acid was looked upon with favor because it was commercially available and because soluble salts were formed as a result of its reaction with limestone. At the same time there were drawbacks which required much study before it was possible to put this acid into practical use.

The problem of acid strength became of far more importance than occasional observation in the beginning had indicated. For instance, highly concentrated hydrochloric acid put into a well, with little or no water, did two things: It worked so rapidly in some formations that it did not penetrate into the pores any distance but merely increased the size of the bottom of the hole; and the water formed by the reaction back into the pores of the rock was not sufficient to dilute the calcium chloride salt to the point where it could be easily brought out and open up the formation for increased production. In other words, it had a greater tendency to seal the well than to open it.

Connected directly with the problem of strength of acid was the necessity of developing an inhibitor which would retard or eliminate the action of the acid on the metals employed in the well but at the same time would not retard the action on the formation to be attacked.

During these experiments on the brine-producing sand formation, neighboring oil well owners became interested, and, as a result of the combined efforts of The Dow Chemical Company and The Pure Oil Company, oil production was increased. The patents relating to this procedure taken out by both companies were licensed to Dowell Incorporated (5). The oil, however, was produced from a limestone formation at a much greater depth than the brine. The results obtained were interesting, if not phenomenal, from the start. However, the apparent possibility of making an error of a few feet one way or another in depth when working at a distance of over a half-mile, immediately suggested the possibilities of chemical action taking place where it might do harm rather than good.

In many wells the casing used to close off the upper water formation from the oil-producing sand is embedded in a limestone formation and apparently is sealed at this point. However, since there is as great a possibility of the acid's attacking the seat of the casing in the limestone formation as there is of its attacking the limestone which produces the oil, the need of a careful diagnosis and expert control in the treatment of a valuable oil well is apparent. Difficulties due to water, unspent acid, plugs, and paraffin were also encountered.

With the solution of these problems, it then became both practical and economical to increase oil production by chemically controlled acidation. In the discussion of the treatment given to oil wells, no attempt will be made to give an exact treatment for any particular well, since every well is different, even though it is an offset in the same pay formation. However, an attempt will be made to discuss the various materials and reasons for using them in various types of wells that are encountered.

## SELECTION OF INHIBITOR

The first and unquestionably the most important factor from the standpoint of economical oil well treatment is the inhibitor used. Inhibitors for acids have been used for metal pickling to retard the action of acids for a great many years. The word "retard" is used advisedly, as that is the exact function which these partial inhibitors perform. No attempt was made to eliminate the action of acid on metal entirely but merely to slow it down, as the pieces of metal were taken through the bath and brought out at the other end of the line.

In the early work the well-known arsenic compounds were used, but it was found that they were not sufficiently inhibiting to prevent excessive losses due to acid attack on the metallic surfaces. It finally developed, in order to assure safety, that two or three materials had to be used in the same solution to accomplish the desired inhibition. At the present time both organic and inorganic inhibitors are used, of both the soluble and insoluble types. The value of the inhibitor lies in its long-time protection of the equipment against possible acid pocketing at various points in the casing and tubing, such as joints, casing seats, etc.

The entire situation would be comparatively easy for the oil companies to cope with if the tubing and casing were destroyed or badly attacked within the first 30-day period. Even though actual operation on a commercial scale has been going on since 1932, when many oil well owners bought carboys of acid and dumped it into wells, those wells are being lost 2 years later as a result of using uninhibited acid. Unquestionably the percentage of lost wells due to the use of uninhibited acid is greater after 1 or 2 years than of those which are ruined within the 30- to 60-day period after initial treatment.

One of the most corrosive agents known is iron chloride, formed by the action of hydrochloric acid on iron. It embeds itself under the oil film and continually permits corrosion to take place. No oil well owner should permit the use of any treatment on a well without first testing the inhibiting qualities of the acid employed. It should be insisted upon that, prior to forcing the acid into the well, a few cubic centimeters should be drawn off into a test tube in which a piece of clean iron is placed and allowed to stand for 15 to 30 minutes to determine whether the gas bubbles continue to be evolved and therefore whether corrosion will take place. Many experiments were made in connection with the use of old tubing and casing that were partially corroded with paraffin and oil sludge to determine the possibility of the use of uninhibited acid. Experiments have been conducted by flushing with oil first, then putting in acid, and following with the second oil treatment in order to clear the tubing. Both of these procedures would, undoubtedly, work satisfactorily if the tubing could be guaranteed to have a uniform coating that would not be washed off as a result of mechanical action so that the acid would not remain in joints or on the sides and thus reach the steel and attack it.

One company used an inhibited acid which caused corrosion at the rate of 0.108 pound loss per square foot per day. The hydrochloric acid alone causes a loss of 0.210 pound per

square foot per day, whereas the inhibitor used in all Dowell acids limits it to only 0.001 pound per square foot per day.

### SELECTION OF ACID

The next item of particular importance is the selection of a suitable acid and the determination of the most satisfactory concentration to be used. To acidize a well successfully, the products of the reaction of the acid and the pay formation must be soluble in water, and the acid must be sufficiently dilute to hold the products of the reaction in solution. Hydrochloric acid was selected as the most suitable acid because of its rapid action on lime formations and the fact that it forms sufficiently soluble salts. Fifteen per cent was found to be the most satisfactory concentration for general well treatment. This concentration of acid gives a 22 per cent calcium chloride solution when completely reacted with the limestone and is thus well within the limits of the saturation concentrations for all likely temperatures. The inhibited hydrochloric acid, called Dowell X, reacts with the pay formation, forming calcium chloride, carbon dioxide, and water, but prevents the reaction,

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$
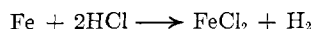
to the extent of 99 per cent.

The XX acid is the same as the X acid but contains a catalyst particularly effective in connection with dolomitic formations which are mixtures of magnesium and calcium carbonates. The action of hydrochloric acid on magnesium carbonate is slow and consequently does not accomplish the desired results except when an accelerating agent is present.

The XF acid is an inhibited, free-flowing hydrochloric acid and is used particularly in limestone formations where the rock pressure is low. In certain types of formation where this is the case, the regular acid can be forced back into the pores of the rock, but the products of reaction do not come out. The difficulty is that the acid acting on the limestone forms carbon dioxide and calcium chloride solution which exist side by side in the pores. The pressure required to force such an interspacing of gas and liquid from the pores is considerable and is dependent on four factors: (1) size of pores, (2) surface tension of the neutralized acid, (3) force of attraction between the neutralized acid and the walls of the pores, and (4) number of gas-liquid groups.

The XF acid was developed to reduce the pressure necessary to make the gas-liquid products of reaction flow more easily. This was accomplished by adding to the regular X acid, materials which would reduce the surface tension of the resulting brine or spent acid. Most technical men in the oil industry are familiar with the Jamin test which can be demonstrated easily with a capillary tube, filling it with alternating liquid and gas bubbles. A pressure is then applied and measured with a manometer in the system. Using neutralized XF acid, the manometer shows that only one-tenth the pressure is necessary to force it from the capillary tube as compared with the regular material.

The XG acid is an inhibited blend which is particularly

adapted for the cleaning out of casings and tubings where "gyp" formation is prevalent.[1] Gyp is generally formed in wells that contain brine and have high rock pressure. The calcium is present in the brine as the acid carbonate, and, as it approaches the surface, the pressure is reduced and carbon dioxide liberated. The bicarbonate is thus converted into the carbonate and deposited in the upper length of tubing, as indicated by the following formula:

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$
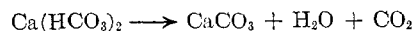
As soon as the X acid comes in contact with the gyp it reacts, liberates carbon dioxide, and immediately channels so that most of the acid drops to the bottom of the well unreacted. The XG acid is the regular X acid treated with an agent which causes foaming simultaneously with the formation of calcium chloride and the evolution of carbon dioxide. The foaming tends to buoy up the column of acid in the tubing and allow more time for reaction.

A great deal of work has been done and results have been obtained with hydrofluoric acid, especially for the sand type of well. However, it is well known that hydrofluoric acid reacts with sand to form silica gel in the bottom of the well, which stops up the well rather than increases the flow. Methods of eliminating this trouble have been developed, but, owing to their present status in the Patent Office, details cannot be given now. However, in the treating of sand wells, it must be taken into consideration that the results cannot be expected to be as phenomenal as in the limestone treatments where the rock formation provides channels and crevices, making it possible oftentimes to open an untapped pool or pocket of oil which would not be touched under the ordinary methods; with sand formation there is a certain amount of uniformity existing that, at best, will allow only an increase in the rate of production rather than the total amount to be recovered.

One of the most important accessories to well treatment is what is known as a blanket. In the normal treatment of a well, the tendency is for the acid to work straight down or, at least, on a downward curve rather than out into the formation. With a water layer underneath the oil-bearing strata, a considerable amount of care must be exercised to prevent the bringing in of water to the exclusion of the oil. One of the greatest hazards, aside from the effect on equipment in oil well treating, is the bringing in of water in excess of that being produced at the well at the time of treatment. In the original research work on the problem it was found that, by using a 40° Bé. calcium chloride solution to fill the lower section of the pay or the bottom of the hole, the X acid could be directed to the upper layers of the formation. The acid following the blanket does not penetrate it but floats on top. There is no chemical action involved but an adjustment of gravity which increases the protection to the well.

In addition to the problems encountered in the treating



SMALL TRUCK EQUIPPED WITH 500-GALLON TANK AND HIGH-PRESSURE PUMP

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[1] "Gyp" is a term used in the oil industry which has been erroneously derived from the word "gypsum." Gyp as found in the oil field is a definite calcium carbonate, whereas gypsum is calcium sulfate.

of brine wells, paraffin presents an additional difficulty in oil wells. There are two types of paraffin solvents which were developed to be used in connection with well treating— one at the time of well treating, the other for well maintenance. It is definitely known that there is selectivity among solvents. Therefore, it was necessary to obtain paraffin samples from various fields all over the country and to put them through the laboratory tests to determine the various solvents which, because of their selectivity, could be used in blending satisfactory materials for paraffin work.

Owing to the amount of insoluble material mixed with paraffin, it was necessary to develop the solvent with selectivity from the standpoint of solvent power and with the proper gravity for maintaining the insoluble materials in suspension so that they could be brought to the top of the well rather than be deposited at the bottom. The use of any of the petroleum products alone, while being good solvents and the natural solvents for paraffin deposits at the bottom of the hole, may cause trouble because of the insoluble materials present. Solvent Red, which is blended, is technically correct from the standpoint of gravity and selectivity, and excellent results have been obtained in various fields with it. The second type of paraffin solvent is one with organic acid so that it will attack the paraffin and the limestone. It is used where the hole has been covered with paraffin and the pores of rock stopped up around and near the surface. This is used during the treatment with beneficial results.

Other factors to be considered in well treatment are the use of special plugs, protections for the lead plugs that are already set in the hole, the proper method of protection for the casing seat, which may or may not be cemented, and particularly the known dimensions of the pay formation.

The above factors have been determined from actual well work, and in addition the technic for the handling of these various reagents has been developed by carefully trained men who are put in the field to do the actual diagnosing of the well.

The successful results without damage to wells or equipment through the use of materials and methods described above indicate the aid of chemistry in the oil industry.

### Literature Cited

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# Removal of Copper Sulfate from Water by Ferric Floc

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COPPER sulfate has been used for years to control algae growth in municipal raw-water supplies. A previous paper (1) reported the adsorption of copper sulfate by aluminum floc; considerable quantities of copper were completely removed by treating the water with alum, provided the filtered water possessed a pH of 6.3 or above.

In continuing this work it was of interest to know what effect the ferric floc would have on the removal of copper in the filtering process. It is well known that ferric floc is more insoluble at lower pH values than alum floc. We are not concerned here with coagulation in pH ranges over 7.0 because considerable copper alone without iron or alum coagulants will be removed by the floc, probably as a basic salt.

A 0.01 molar solution was prepared by dissolving 1.116 mg. of good-grade ferric ammonium sulfate in 1 liter of distilled water. A solution having a concentration of 0.1 mg. of copper ion per cc. was made by dissolving 0.3928 gram of $CuSO_4\cdot 5H_2O$ in 1000 cc. of distilled water. The buffer solutions were prepared according to Clark's method (2) from disodium and monosodium phosphate. These solutions were used in 50-cc. volumes at a definite pH, to which were added, in order, the copper sulfate solution with stirring, and then the solution of ferric ammonium alum with stirring. These solutions then stood 1 to 4 hours until the floc had settled. The supernatant liquid was filtered by decantation so that only about 40 cc. ran through, and very little of the floc appeared on the filter paper. Of these 40 cc., 10 cc. were used for the determination of copper by the ferrocyanide method and 10 cc. for the colorimetric determination of pH (3).

In some cases at the lower pH range there was considerable residual iron in the solution which interfered with the determination of copper by the ferrocyanide method. In these cases the iron and copper were separated by means of strong ammonium hydroxide; this is the usual procedure. The following data show the percentage of copper removed by various concentrations of ferric floc at various pH values:

| Test No. | | Buffered Water | | Filtered Water | |
|---|---|---|---|---|---|
| | pH | Ferric soln. | Copper soln. | pH | Cu removed |
| | | P. p. m. | P. p. m. | | % |
| 1 | 6.8 | 159.3 | 14.3 | 6.4 | 100 |
| 2 | 6.8 | 279 | 12.5 | 6.1 | 100 |
| 3 | 6.8 | 368 | 11.1 | 5.0 | 100 |
| 4 | 6.8 | 20.7 | 8.9 | 6.5 | 100 |
| 5 | 6.8 | 0.0 | 8.9 | 6.8 | 93 |
| 6 | 6.6 | 159.3 | 14.3 | 6.3 | 100 |
| 7 | 6.6 | 171.8 | 7.2 | 6.2 | 100 |
| 8 | 6.6 | 182 | 1.6 | 6.3 | 100 |
| 9 | 6.6 | 20.7 | 8.9 | 6.4 | 97 |
| 10 | 6.6 | 0.0 | 8.9 | 6.4 | 93 |
| 11 | 6.0 | 159.3 | 14.3 | 5.2 | 92 |
| 12 | 6.0 | 171.8 | 7.2 | 5.2 | 100 |
| 13 | 6.0 | 182 | 1.6 | 5.2 | 100 |
| 14 | 6.0 | 20.7 | 8.9 | 5.9 | 100 |
| 15 | 6.0 | 0.0 | 8.9 | 6.0 | 63 |
| 16 | 5.6 | 159.3 | 14.3 | <3.8 | 92 |
| 17 | 5.6 | 171.8 | 7.2 | <3.8 | 100 |
| 18 | 5.6 | 182 | 1.6 | <3.8 | 100 |
| 19 | 5.6 | 20.7 | 8.9 | 5.5 | 88 |
| 20 | 5.6 | 0.0 | 8.9 | 5.5 | 56 |
| 21 | 6.4 | 159.3 | 14.3 | 5.8 | 100 |
| 22 | 6.4 | 159.3 | 14.3 | 5.4 | 100 |
| 23 | 6.4 | 182 | 1.6 | <3.8 | 100 |
| 24 | 6.4 | 20.7 | 8.9 | 6.3 | 94 |

Comparison of the above results with those obtained in the previous paper (1) indicates that the iron floc is more efficient in removing copper ions from solution than is the aluminum floc. The pH range for this removal is wider, and smaller concentrations of iron will effect complete removal of copper ions. Copper ions have been completely removed from water at a pH value of 3.8; this was impossible with the aluminum floc.

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