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TREATMENT OF DEEP WELLS

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The present invention relates to the treatment of deep wells, such as oil, gas, brine or water wells, to increase the output therefrom. It is more especially concerned with the treatment of wells in which the mineral-bearing stratum consists of a limestone or other calcareous formation, or is contiguous to such a formation.

An object of the invention is to counteract some preventable natural causes for the decline of yield of a well. A familiar example is the decline of production of an oil well. When it is first drilled into an oil-bearing stratum, the release of pressure upon the oil deposit may cause the well to flow naturally for a certain length of time. The flow will gradually recede from the initial high point to the point where natural flow does not produce a sufficient yield, and thereafter pumping will be resorted to, until the continued decline in output renders further operation unprofitable. In many cases, however, the stoppage of oil output is caused, not by exhaustion of the oil supply, but by the building up of solid deposits of wax or the like in the channels and pores of the oil-bearing rock which obstruct and finally may cut off altogether the flow of oil to the well.

Various methods have been used for opening up or cleaning a clogged well hole, such as drilling, "shooting" with explosive or by chemical treatment. The first two methods mentioned have the disadvantage that the pump rod and tube must be removed prior to applying the treatment, in addition to which, in the case of using an explosive, there is danger of damaging the casing. The chemical methods heretofore proposed have either not been found effective to clear the hole or they have involved the use of corrosive substances which are injurious to the metal parts of the well structure.

As an illustration, a chemical method is described in United States Patent 556,669, according to which the flow of an oil well in a limestone formation is increased by treating with a quantity of an acid, such as hydrochloric acid. The acid has the effect of attacking and dissolving the rock, thereby enlarging the cavity at the bottom of the well, or the channels and pores in the rock through which oil flows to the well. In actual practice, however, this method has never been generally adopted, due to the fact that the acid attacks the metallic casing, pump tube, etc. about as actively as the rock, and causes serious damage thereto.

We have now found that the last-mentioned method may be adapted for use in increasing or restoring the flow of oil wells by suitable modification without material injury to the casing or other metallic parts of the well. The treatment can be carried out at less cost and with better results than any of the methods heretofore employed. The invention, then, consists of the improved method hereinafter fully described and particularly pointed out in the claims.

In carrying out our improved method we employ a mineral acid, preferably hydrochloric acid, inasmuch as the latter upon reacting with the calcareous rock forms water-soluble salts which remain in solution and are removed from the well with the spent acid. To the acid we add a small amount of a substance capable of inhibiting attack of the acid upon metal surfaces, e. g. of iron or steel, copper, etc., with which it comes in contact. As the inhibiting agent we prefer to use an arsenic compound soluble in the acid solution, examples of which are arsenic acid, H_3AsO_4, arsenic trioxide, As_2O_3, or a soluble arsenate or arsenite, such as the corresponding alkali metal salts. The amount of arsenic compound added may be varied, but we have found that from 1 to 5 per cent thereof, based upon the weight of the solution, will be satisfactory for the purpose. Other inhibitors which may be used are cyanides, organic nitrogen bases such as aniline, phenyl-hydra-

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zine, pyridine, quinoline, acridine and derivatives thereof, organic sulphur compounds, such as mercaptans, as well as various by-products of industrial processes, such as sludge acid from oil refining and residues from acid sulphite paper manufacture, etc.

The strength of the aqueous hydrochloric acid solution, in general best adapted to the purpose in hand, may be between about 5 per cent and about 20 per cent, and preferably should be between 10 and 15 per cent although other concentrations may be used, if desired. With such strength of acid the corrosive action thereof upon metals, particularly iron or steel, can be largely or substantially inhibited by adding thereto a relatively small amount of an arsenic compound or other inhibiting agent. Consequently, the acid can be introduced into the well through the pump tube, so that the latter need not be withdrawn prior to the treatment. It is sufficient merely to pull the pump rod and valves, and to pour the acid solution into the well through the tube. Due to the presence of the inhibitor there will be no substantial attack upon the pump tube, or upon the well casing if the charge of acid rises high enough in the well to contact with the casing.

The acid solution is preferably added in amount calculated to fill the bore of the well to a depth not exceeding the thickness of the mineral-bearing stratum. In order to force the charge of acid out of the pump tube into the bore of the well against the head of oil standing in the hole, it may be followed by a charge of oil, water or other liquid sufficient to overcome the head, or pressure may be applied by other suitable means, e. g. by air pressure or by means of a pump. When introduced into the bottom of the well, the acid attacks the rock structure and dissolves or disintegrates it, thereby enlarging the pores and channels in the rock, or opening up new channels. The action of the acid upon a limestone formation causes the evolution of a considerable volume of carbon dioxide gas. This gas may be allowed to escape up the casing, or the latter may be capped off, thereby creating a gas pressure within the well which assists in forcing the acid into the pores and crevices of the rock. After the action of the acid has practically ceased, the spent solution containing the dissolved salts may be pumped or bailed out. In many cases it may be desirable to repeat the treatment one or more times. By making successive additions of smaller amounts of acid solution, and pumping out the spent acid between charges, a greater cumulative effect may be produced than by the use of a single larger charge. It is not necessary, however, to add the acid solution through the pump tube, as any other convenient way may be employed. For instance, the pump tube may be withdrawn and a dump bailer used to lower a charge of acid into the base of the bore.

In the practical use of our method in the central Michigan oil field, where the oil is derived from a calcareous rock formation, we have successfully used hydrochloric acid solutions of 10 to 15 per cent strength to which was added a small amount, e. g. 1 to 5 per cent, of an arsenic compound. For example, to 4500 pounds of a 15 per cent hydrochloric acid solution was added 2 gallons of arsenic acid solution containing 21 pounds of arsenic calculated as As_2O_5. The mixed solution was charged into an oil well through the iron pump tube, being followed by a quantity of crude oil to force the acid solution out of the tube into the well. After the acid was exhausted, it was pumped out, and thereupon regular pumping of the oil was resumed. The production of the well was approximately doubled with one treatment.

The method has been used repeatedly for the treatment of low yield or exhausted oil wells in producing territory with a resultant increase of output amounting to as much as 75 to 200 per cent, and in some cases wells which have ceased to flow have been brought back with a resumption of natural flow. The treatment has been applied in the manner described without appreciable damage to the pump tube or well casing. The invention may also be employed similarly to increase the flow of gas wells and brine or water wells in cases where the mineral or water-bearing stratum, or the immediately adjacent strata, are of a limestone or calcareous formation, or of a nature such as to be acted upon and dissolved by hydrochloric acid solution.

Other modes of applying the principle of our invention may be employed instead of the one explained, change being made as regards the method herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. In a method of increasing the output of a well for producing a fluid mineral product such as oil, gas, water or brine, the step which consists in introducing into the well an aqueous hydrochloric acid solution to which has been added a relatively small amount of an agent capable of inhibiting action of the acid upon metals.

2. In a method of increasing the output of a well for producing a fluid mineral product such as oil, gas, water or brine, the step which consists in introducing into the well an aqueous hydrochloric acid solution to which has been added a relatively small amount of an arsenic compound capable of inhibiting action of the acid upon metals.

3. In a method of increasing the output of

a well for producing a fluid mineral product such as oil, gas, water or brine, the step which consists in introducing into the well a 5 to 20 per cent hydrochloric acid solution to which has been added from 1 to 5 per cent of an arsenic compound capable of inhibiting action of the acid upon metals.

4. In a method of increasing the output of a well for producing a fluid mineral product such as oil, gas, water or brine, the step which consists in introducing into the well a 5 to 20 per cent hydrochloric acid solution to which has been added from 1 to 5 per cent of arsenic acid.

5. The method for increasing the output of an oil well which comprises introducing into the base of such well a 5 to 20 per cent hydrochloric acid solution containing a relatively small amount of a corrosion inhibitor, permitting the acid to act upon the rock formation surrounding the well cavity and withdrawing the spent acid.

6. The method for increasing the output of an oil well which comprises introducing into the base of such well a 5 to 20 per cent hydrochloric acid solution containing a relatively small amount of an arsenic compound capable of inhibiting action of the acid upon metals, permitting the acid to act upon the rock formation surrounding the well cavity and withdrawing the spent acid.

7. The method for increasing the output of an oil well which comprises introducing into the base of such well a 5 to 20 per cent hydrochloric acid solution containing a relatively small amount of a corrosion inhibitor, permitting the acid to act upon the rock formation surrounding the well cavity while applying pressure upon the solution and withdrawing the spent acid.

8. The method for increasing the output of an oil well which comprises charging into the pump tube a quantity of a 5 to 20 per cent hydrochloric acid solution containing a relatively small amount of a corrosion inhibitor, expelling the acid from the tube into the bore of the well by applying pressure thereon, permitting the acid to act upon the rock formation surrounding the well cavity and withdrawing the spent acid.

9. The method for increasing the output of an oil well which comprises charging into the pump tube a quantity of a 5 to 20 per cent hydrochloric acid solution containing a relatively small amount of a corrosion inhibitor, expelling the acid from the tube into the bore of the well by applying pressure thereon, permitting the acid to act upon the rock formation surrounding the well cavity under pressure due to the gas generated thereby and withdrawing the spent acid.

10. In a method of treating a well for producing a fluid mineral product such as oil, gas, water or brine, the step which consists in introducing into the well an aqueous hydrochloric acid solution to which has been added a relatively small amount of an organic nitrogen base capable of inhibiting action of the acid upon metals.

11. In a method of treating a well for producing a fluid mineral product such as oil, gas, water or brine, the step which consists in introducing into the well an aqueous hydrochloric acid solution to which has been added a relatively small amount of an organic sulphur compound capable of inhibiting action of the acid upon metals.

Signed by us this 24 day of June, 1932.

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DISCLAIMER

1,877,504.—*John J. Grebe* and *Ross T. Sanford*, Midland, Mich. TREATMENT OF DEEP WELLS. Patent dated Sept. 13, 1932. Disclaimer filed Apr. 2, 1945, by the assignee, *The Dow Chemical Company*.

Hereby enters this disclaimer to claims 1 to 9 inclusive, of said patent.

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