

UNITED STATES PATENT OFFICE

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CHEMICAL TREATMENT OF OIL WELLS FOR
THE PREVENTION OF CORROSION AND
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of PennsylvaniaNo Drawing. Application January 2, 1946,
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4 Claims. (Cl. 252-8.55)

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This invention relates to the chemical treatment of oil wells for the prevention of corrosion and scale and more particularly to the use of aqueous solutions containing an alkali metal hydroxide and an alkali metal septaphosphate for treating oil well liquids to make them non-corrosive and non-scale-forming.

In order that this invention may be more fully understood I shall first give a brief description of an oil well and then point out how the problems of corrosion and scale formation arise in the operation of such a well.

Producing oil well subsurface equipment comprises an outer casing and an inner tubing through which the oil well liquids are produced. The casing is cemented or sealed for some distance above the oil zone so that water from adjacent rock formations may not contaminate the well fluids. Several casings are sometimes necessary to seal off water and to facilitate drilling of the well. In such a case, only the innermost or smallest casing extends to a depth near the oil zone where it is cemented. The tubing, or production pipe, is not cemented but is chiefly supported at the well head and thus has no obstruction at the bottom. From this it is readily seen that when liquid is introduced at the well head into the annulus between the tubing and the casing, it will travel to the bottom of the well to be produced with the well liquid through the tubing. Since this annulus is open to the oil-producing formation, a force pump must be used to inject a treating solution when the well is flowing by its own pressure. If, however, the well is being produced by a pump at the bottom of the tubing, the liquid level in the well may be near bottom and only moderate or no pressure will be present in the annulus. Under the latter conditions a treating solution may be fed by gravity into the annular space between the tubing and the casing.

Scale deposition takes place mainly on bottom hole pump parts and on the inside of the tubing. This scale appears to have two modes of origin.

1. Supersaturation occurs in the oil well brine as it leaves the oil formation and enters the pumping mechanism under reduced pressure.

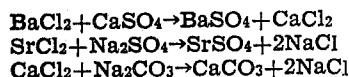
2. Two incompatible compounds are commingled by means of a casing leak which allows foreign water to come in contact with the oil well brine.

In the first case the scale is composed mainly of alkaline earth carbonates and sulfates, with admixtures of iron carbonate, iron sulfide, silica and fine sand, silt or other sediment. Physical

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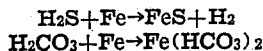
causes of the reactions are thought to be loss of heat, loss of pressure, evaporation and agitation. Loss of pressure releases carbon dioxide from calcium bicarbonate and ferrous bicarbonate causing scale containing calcium carbonate and ferrous carbonate to deposit. Calcium sulfate in solution is transformed into calcium sulfate scale by evaporation of water and loss of heat.

In the second case the scale is composed mainly of alkaline earth sulfates sometimes with carbonates and a smaller portion of inert material. If two waters carrying incompatible compounds are mingled in the well bore, precipitation of solid material will result as indicated by the following equations:

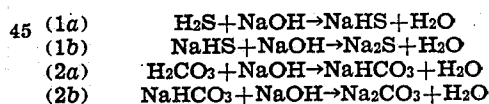


Calcium carbonate scale will also deposit when fresh water from near the surface saturated with calcium bicarbonate leaks into the well bore and mingles with a salt brine.

Serious oil well corrosion, when not due to hydrogen sulphide seems to occur when pH values of effluent brines are well below 7.0. Such corrosion usually may be greatly reduced by raising pH values of the brines by the addition of an alkali. Although the addition of an alkali to oil well brines may have the effect of minimizing corrosion, only a few of the direct causes of corrosion seem to be definitely proven. The following equations indicate the principal reactions that are believed to cause corrosion in oil well equipment:



Hydrogen sulfide and carbonic acid are common in oil well brines and contribute to cause the low pH values of these brines. The addition of an alkali will neutralize these compounds and raise the alkalinity, or pH value, as indicated in the following equations:



In treating oil well liquids with alkali, only sufficient alkali should be added to the oil well brine to produce Reactions 1a and 2a, because if sufficient alkali is added to produce Reactions 1b and 2b rapid scale formation will result. When oil wells are producing relatively large volumes of brine the rate of chemical treatment may be easily

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adjusted to proper proportions. However, some wells produce only a few barrels of brine per day, and chemical treatment is invariably in excess of that required. Furthermore, some oil wells after chemical treatment continue to give trouble from subsurface corrosion unless excess alkali is used. In either event, over-treatment with alkali causes excessive scale formation which may result in more operating expense than corrosion without chemical treatment. It is unfortunate that alkali anti-corrosion treatment for oil wells often results in the formation of scale in such large volume that scale trouble is more expensive than corrosion.

It is accordingly an object of this invention to provide a solution for "down the hole" treatment of oil well liquids which will counteract both corrosion and the formation of scale. A further object is to provide a solution that will inhibit the corrosiveness of oil well liquids and at the same time not cause the formation of scale. A still further object is to provide a method of treating oil well liquids to retard corrosion and scale formation on metal equipment in the bore hole. Other objects will appear hereinafter.

These objects are accomplished in accordance with the present invention by utilizing an aqueous solution containing sodium hydroxide and sodium septaphosphate ($\text{Na}_7\text{P}_7\text{O}_{22}$) in "down the hole" treatments of oil wells to counteract corrosion and scale formation on metal equipment. I have found that it is usually sufficient to add from 3 to 7 pounds of sodium hydroxide to each 100 barrels of oil well brine to bring its pH value within the range of 7.0 to 8.0 and thus reduce corrosion. I have further found that with each pound of the caustic there may be used at least 1 ounce of alkali metal septaphosphate to place the proper concentration of scale inhibitor in the effluent brine. Since sodium septaphosphate will not readily dissolve in a strong caustic soda solution it is necessary to dissolve these chemicals separately and then to mingle the two solutions after the caustic solution has cooled. I have found that a very desirable treating solution can be made by separately dissolving 1 pound of sodium hydroxide in one gallon of water and 1 ounce of sodium septaphosphate in 50 to 100 cubic centimeters of water and then adding the septaphosphate solution to the caustic solution with stirring. When this treating solution is fed into a producing oil well at the rate of 6 gallons per 100 barrels of brine produced, the concentration of sodium septaphosphate will be 10.7 milligrams per liter in the effluent brine. This concentration is more than sufficient to suppress precipitation of scale-forming compounds.

It is feasible to employ treating solutions that contain much less than 1 pound of sodium hydroxide and 1 ounce of sodium septaphosphate per gallon. These concentrations of caustic soda and sodium septaphosphate are very close to maximum solubilities for these compounds when they are used in the same solution; hence, the above described solution is one of nearly maximum strength. In the treating process the use of more than 6 pounds of caustic soda per 100 barrels of oil well brine may be necessary in some instances. In such an event, the resulting increased concentrations of sodium septaphosphate in the effluent brine is not harmful. A more dilute treating solution may contain greatly reduced concentrations of caustic soda and sodium septaphosphate for oil wells of slow corrosion rate and low brine production. For example, 3 pounds of caus-

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tic soda per 100 barrels of effluent brine may be ample anti-corrosion treatment for some wells. Thus, 0.3 pound of caustic may be required per day if a given well is making 10 barrels of brine per day. This amount of caustic soda may conveniently be dissolved in several gallons of water if fed by gravity to the well, or in as little as 1 quart of water if a small chemical pump is used. In either event, sufficient sodium septaphosphate is used so that the brine will contain not less than 5 milligrams per liter of septaphosphate as it is produced. In the case of a well producing 10 barrels of brine per day a treating solution having a sodium septaphosphate content as low as 0.028 ounce (avoirdupois) per gallon may be used. This shows that a treating solution to be used in wells that produce small amounts of brine may feasibly contain as little as 0.3 pound of caustic soda and 0.028 ounce of sodium septaphosphate per gallon. It will therefore be appreciated that the concentrations of alkali metal hydroxides and of alkali metal septaphosphates in the treating solutions may be widely varied in the practice of the present invention.

Hydration or reversion of the septaphosphate to orthophosphate in this treating solution is so slow that the solution may safely be made up at 2-week intervals. The rate at which sodium septaphosphate reverts to sodium orthophosphate at 70° F. in an alkaline solution containing 1 pound per gallon sodium hydroxide is indicated in the following table.

Per cent reversion of sodium septaphosphate to sodium orthophosphate in a solution that contains 1 ounce of sodium septaphosphate and 1 pound of sodium hydroxide per gallon

As mixed	3 days	7 days
1.42	1.81	2.78

The above data prove that a very satisfactory and stable treating solution may be made by adding small amounts of sodium septaphosphate to a strong caustic soda solution. Usually, from 5 to 10 milligrams per liter of sodium septaphosphate are sufficient to suppress scale precipitation in oil well brine. If 6 gallons of this treating solution are used to every 100 barrels of brine produced, the septaphosphate content of the effluent brine will be 10.7 milligrams per liter.

As outlined above, alkali metal hydroxides are used for corrosion prevention in oil wells, while alkali metal septaphosphates are used for preventing scale deposits. The necessity for a combination treatment arises because of the fact that corrosion and scale deposition may occur within the same oil well. In addition, it has been found that alkaline anti-corrosion treatment in itself causes rapid scale accumulation. This acceleration of scale formation is due to excess alkali or caustic, which is in turn due to lack of treatment control or to excessive alkali necessary for corrosion protection.

In preparing and using a treating solution containing an alkali metal hydroxide to prevent corrosion and an alkali metal septaphosphate to prevent the accumulation of scale deposits, it is desirable to observe the following precautions:

(a) Sufficient alkali should be present to provide corrosion protection in the oil well brine produced over a 24-hour period or longer.

(b) The solution should be of sufficient volume to be adjusted to proportionate mingling with the oil well fluid, but the volume should not exceed that easily transported or handled by small chemical pumps at the well.

(c) The solution should not freeze at prevailing temperatures in the winter time.

(d) Sufficient alkali metal septaphosphate should be dissolved in the caustic solution so that the precipitation of scale-forming compounds will be inhibited in the well liquids when excess alkali is used.

The proper rate of treating solution injection may be attained either with a chemical pump or by allowing the treating solution to drip by gravity from a small drum into the well head. A chemical pump is used when an oil well is flowing under natural pressure and the gravity system is used when the oil well is being pumped or not produced under pressure.

The question as to whether the treating solution shall be added continuously or periodically to the well liquids can only be determined by conducting separate tests to determine the most economical method of carrying out the treatment at each well. Despite the fact that a periodical treatment of the well liquids with the treating solution necessarily results in extensive periods in which there is a low percentage neutralization of the corrosive compounds of the well liquids, in general, it has been found that in the long run the periodic rather than the continuous method of carrying out the treatment is most economical. In general it has been found that it is not necessary to maintain complete neutralization of the acidic compounds of the well liquids for the full twenty-four hours of the day, particularly in wells which are only pumped during the normal working day of eight or ten hours. It has been found that the scale cleansing effect occurring during the short periods of high neutralization immediately after the periodic addition of the concentrated treating solution to the well liquids leads to the formation of protective ferrous hydroxide films which afford protection, with the result that the ill effects of low neutralization for the hours elapsing between additions of treating agent are minimized.

Resort may be had to such modifications and variations as fall within the spirit of the invention and the scope of the appended claims.

What I claim is:

1. A method of treating oil wells to retard corrosion and scale formation on metal equipment in the bore hole which comprises introducing an aqueous solution containing an alkali metal hydroxide and an alkali metal septaphosphate into the well fluids near the bottom of the production pipe, the alkali metal hydroxide being present in an amount sufficient to inhibit the corrosion of

said metal equipment and the alkali metal septaphosphate being present in an amount sufficient to inhibit the formation of scale on said metal equipment.

2. A method of treating oil well liquids to render them non-corrosive and non-scale-forming which comprises adding an aqueous solution containing sodium hydroxide and sodium septaphosphate to said oil well liquids, the sodium hydroxide being present in an amount sufficient to inhibit the corrosion of said metal equipment and the sodium septaphosphate being present in an amount sufficient to inhibit the formation of scale on said metal equipment.

3. An aqueous solution for treating oil well liquids in an oil well to make them non-corrosive and non-scale-forming which contains an alkali metal hydroxide and an alkali metal septaphosphate, the amounts of alkali metal hydroxide and alkali metal septaphosphate in said solution being sufficient to inhibit corrosion and scale formation when said solution is introduced into said oil well liquids.

4. A method of treating oil wells to retard corrosion and scale formation on metal equipment in the bore hole which comprises introducing an aqueous solution containing an alkali metal hydroxide and an alkali metal septaphosphate into the well fluids near the pump, the alkali metal hydroxide being present in an amount sufficient to inhibit the corrosion of said metal equipment and the alkali metal septaphosphate being present in an amount sufficient to inhibit the formation of scale on said metal equipment.

LESLIE CLINE CASE.

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