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PREVENTION OF HARD SCALE FORMATION IN OIL WELLS

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The present invention relates to the prevention of hard scale deposits in oil wells and more particularly to a method of preventing corrosion of and the formation of scale deposits on metal parts in oil wells.

Many oil wells experience serious and expensive losses of material and time because of the formation of deposits of hard scale on the metal tubing and casing in the well and also because of corrosion of the metal parts by the liquids present in the well. An investigation of the waters associated with oils in the oil producing localities has disclosed that the compounds which are chiefly responsible for the corrosion of the metal parts installed in oil wells are hydrogen sulfide, organic sulfide and/or sulfur; or sulfuric acid, carbonic acid or other mineral acids associated with oxygen. All of these compounds are active in destroying iron and steel parts. It has been found that when these underground waters contain hydrogen sulfide a reaction takes place in the well resulting in the formation of iron sulfide. Ferrous sulfide thus formed tends to cling to the metal parts especially in spots where there is an impurity in the iron or steel. The iron sulfide thus present in contact with the metal parts of the well sets up an electric couple when immersed in the salt water or electrolyte which is present in the well. The current set up by this couple passes from the iron sulfide to the iron at the point of contact, thence from the iron to the electrolyte, (salt water and hydrogen sulfide) carrying iron into solution, and thence back to the iron sulfide, completing the circuit. Corrosion has been found by experiment to be many times more rapid in the presence of iron sulfide in contact with iron due to this electrolytic action.

Many oil wells in addition to experiencing corrosion of the tubing and deposition of the iron sulfide or "soft scale" are also troubled with the formation simultaneously of a "hard scale" which forms on the tubing as a very tough and very hard deposit greatly resembling boiler scale. Hard scale deposits sometimes form coatings of nearly an inch in thickness in a comparatively short time, and in wells in which such deposits are encountered the pulling and replacing of the tubing becomes a very expensive job. The extra weight of the tightly adherent scale adds materially to the strain on the joints of the metal tubing, which are also weakened by corrosion. This added strain due to the weight of the scale coupled by weakened joints causes frequent and very expensive parting jobs. Thus the deposition of a one-eighth inch thickness of scale will increase the weight of a string of tubing approximately 30% and the upper joints of the string must thus sustain this additional weight (about one and one-half tons in the case of a twenty-five hundred foot string). These deposits of hard scale materially shorten the life of the tubing because the scale deposited on the upper part of the working barrel offers strong opposition to the removal of the travelling valve and cups from the barrel and necessitates the use of extra pull, which in turn also causes frequent parting jobs on the strings. Moreover these hard scale deposits greatly interfere with the proper operation of the pumping apparatus and in many cases where the tubing has been removed for cleaning it is unfit to rerun for the reason that the scale is so hard and clings so tenaciously to the tubing that it is almost impossible to dislodge it by ordinary means (as boiler flue cleaners, hammers and the like).

One object of the invention is to provide a method for preventing the losses in oil well operation caused by the corrosive action of the liquids in the well on the metal of the casing, tubing and pumps installed in the well. To accomplish this object one feature of the present invention contemplates the prevention of corrosion of the metal parts in oil wells by lowering the hydrogen ion concentration of the brines or waters associated with the oil in the well to a point necessary to afford protection of the metal. To accomplish this, compounds which have an alkaline reaction in water are preferably introduced into the well in a way to bring them in contact with the brines or water in the well.

Another important object of the present in-

vention is to provide a method for preventing the formation of scale deposits on the metal parts of oil wells, thereby avoiding the losses mentioned above.

It has been found that wells which give the greatest trouble due to the deposition of hard scale are generally those which have casing leaks. An analysis of the hard scale deposits formed in such wells has shown that in most cases the deposits consist chiefly of strontium, calcium or barium sulfates. Apparently these deposits of insoluble alkaline earth sulfates are formed in the following manner:— The top waters encountered in the wells, that is, the waters in sands above the oil producing sands and which are presumably shut off from the producing sand by the casing, may for example carry varying amounts of strontium chlorid (which is a soluble salt) in solution. When a leak develops in the casing due to corrosion or some other cause these top waters find their way into the oil producing sand. The waters in the producing sand may carry soluble sulfates which are absent in the top waters. These soluble sulfates react with the soluble strontium chlorid carried in the top waters to form insoluble strontium sulfate. Ordinarily the precipitation of strontium sulfate on the metal parts in the well would be expected to take place rather rapidly with the formation of a granular or pulverulent precipitate. However, due to the high concentration of chlorid ions both in the top waters and in the waters associated with oil in the producing sands, and also due to the comparatively small excess of sulfate ions, the strontium sulfate which is formed crystallizes out slowly and deposits in the form of a very hard and compact crystalline scale.

While the hard scale deposits encountered in the wells of certain oil fields are made up largely of strontium sulfate, barium or calcium sulfates and likewise the insoluble carbonates of these alkaline earth metals are also found to cause serious trouble due to hard scale deposition in wells in other localities. Likewise it has been found that in some localities the soluble alkali sulfates may be present in the top waters and the soluble chlorides in the bottom waters of the well.

Since in general the hard scale deposits appear to occur in oil wells only when there is mixing of water produced with the oil or from below the oil horizon with water from the upper sands which are presumably shut off by the casing (water string), the most obvious method of preventing the formation of this scale would appear to be to completely exclude the "top water" or the "bottom water" from the well. However, this obvious method of treatment is not always possible or practicable. It is only in exceptional cases that it is possible to completely shut off water produced from below the oil sand as by plugging. It is never possible to completely shut off by plugging water produced with the oil in the oil sand. It is frequently possible to obtain a complete shut off of "top water" when the casing is not seriously corroded and when there is a good casing seat. In such cases complete shut off of "top water" can be accomplished by pulling and replacing leaky joints, and reseating the casing. A complete shut off of either "top" or "bottom" water will in almost every case definitely prevent such scale formation. Evidently however corrosion in many fields is so severe that it is dangerous to attempt to pull casing and it is therefore extremely expensive and hazardous to attempt to shut off water by either of the methods outlined above, particularly as the results are not sure and the well may be lost.

Another object of the present invention is to provide a comparatively cheap and economical method of preventing scale formation and of allowing economical production in oil wells when a water shut off such as that above referred to is not practicable.

To accomplish this object another feature of the invention contemplates treating the well liquids to avoid precipitation of insoluble alkaline earth salts whenever possible, and in cases where such treatment is not possible effecting the rapid precipitation of the insoluble salts and further treating the precipitates formed to prevent the building up of scale on the metal parts of oil wells and to allow for removal of the precipitated matter from the well by suspension in the water and oil pumped from the well.

With these and other objects and features in view the invention consists in the method of preventing corrosion and hard scale formation in oil wells hereinafter described and particularly defined in the claims.

Essentially the method for treating oil wells to prevent formation of scale deposits and corrosion constituting the present invention in its preferred form comprises adding to the liquids in the well a reagent comprising a mixture of a neutralizing agent for lowering hydrogen ion concentration and a material capable of reacting with the soluble alkaline earth salts present in the liquids of the well to form a light, flocculent and non-adhering or non-scaling precipitate. The preferred reagent consists of a mixture of caustic soda and a tan bark extract such as hemlock, oak or the like. Other reagents suitable for use in accordance with the method of the present invention are the alkaline solutions of tannic acid and similar organic acids or compounds such as tan bark extracts of chestnut, oak and similar materials and the alkaline reacting solutions of sodium aluminate, sodium silicate and similar inorganic compounds capable of reacting with magnesium, calcium, strontium and barium

salts to produce light, flocculent and even gelatinous precipitates.

The amount of reagent which it is necessary to employ and also the composition of the reagent and the proportions of alkaline compound and of flocculating compound employed in making up the reagent are determined by the volume and analysis of the water associated with the oil in the particular well to be treated, by the volume production of the well, and by the character and amount of corrosive and scale-forming compounds respectively present in the well.

Under certain conditions it has been found that the formation of the precipitates of insoluble alkaline earth salts tending to form hard scale deposits in oil wells can be prevented by a modification in the method outline above. Thus if the "bottom" or "top" waters of the well under theatment contain a low sulfate and a comparatively low chlorid concentration, for instance and if the top (or bottom) waters contain strontium chlorid and sodium chlorid, for instance, in relatively large proportions, the mixture of the two waters may just barely result in the slow precipitation of insoluble strontium sulfate. Under such conditions it has been found that the addition of a concentrated brine (such as sodium chlorid) in relatively small proportions will serve by building up the chlorin ion concentration to force back the dissociation of the strontium chlorid to the point where the comparatively low concentration of SO_4 ions is insufficient to cause principitation of undissociated strontium sulfate. Thus this modified treatment results practically in increasing the solubility of strontium sulfate by the addition of brine to the mixture of top and bottom waters in amounts such that no precipitation of strontium sulfate will occur. This method of scale prevention is only economically possible when the total amount of strontium sulfate which can possibly be formed by admixture of the top and bottom well waters is quite small and exceeds to only a slight extent its solubility point under the conditions of the particular chlorid concentration of the mixture. It is believed that this method would be readily applicable if the precipitate material under treatment were calcium sulfate and would be less applicable, though still possible under special conditions in the case of barium sulfate, because of the relative solubilities of the three salts.

In a well where the strontium (calcium, barium) and sulfate ions are present in their respective waters in relatively large amounts, but at the same time in quantities nearly proportional to their reacting weights and in the presence of relatively high chlorine ion concentration, the same slow crystallization of the alkaline earth sulfates will take place when the waters are mixed, and this slow crystallization will result in cementing and hard scale formation. To meet this situation another modified method of treatment has been devised which comprises adding sodium sulfate to the well water mixture. The addition of sodium sulfate increases the concentration of SO_4 ions and results in driving back the dissociation of the insoluble strontium or other alkaline earth sulfate, with the resultant decrease in the solubility of this compound and its rapid precipitation. The tendency under these conditions will be toward the formation of a finely divided pulverulent precipitate of strontium sulfate which will not have as great tendency to "grow" on the tubing or on other crystals to form a scale. This lessened tendency to form scale is further aided by addition of the preferred caustic soda-tannin (sodium tannate) reagent. The two reagents may be applied in any suitable way, as by mixing the sodium tannate or similar reagent with the sodium sulfate in a solution of suitable concentration for treatment.

In treating one well it has been found that a reagent comprising thirteen parts by weight of sodium hydroxid to one part of tannic acid, when added to the well in proportions of one hundredth of one per cent by weight of the daily water production of the well, is entirely satisfactory both in inhibiting the corrosive action of the well waters and in preventing the deposition of calcium and strontium carbonates and sulfates on the metal parts. Experiments at another well have shown that tan bark extract by itself is not effective in preventing the deposition of strontium sulfate, but that when the tan bark extract is admixed with caustic soda in the proportions of 10 lbs. of the powdered extract (60% or better soluble tannins) to 2½ lbs. of the sodium hydroxid, and this mixture made up to a volume of about twenty barrels by solution in fresh or salt water, the treatment of the well over a twenty-four hour period with that amount of reagent prevents completely the deposition of hard strontium sulfate scale and is also effective in preventing extensive corrosion in the well.

At another well a reagent comprising two parts by weight of caustic soda and one part by weight of tannin extract (60% soluble tannins) dissolved in water to 25–35° Bé. has given satisfactory results. At this well the treatment consisted in adding four to five gallons of the above reagent per day continuously to the well waters by means of a specially designed treating device stationed at the casinghead. The strong solution is dripped continuously into the casinghead and washed down by a fine stream of salt water from the well (about three barrels per day). Another reagent successfully used under conditions of greater corrosive action and a somewhat

less marked scaling tendency consisted in ten parts by weight of caustic soda and three parts by weight of tannin extract.

The question as to whether the reagent 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 agent 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 concentrated reagent 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.

The caustic alkalis in general, and particularly caustic soda, are very strong neutralizing agents for the acidic compounds present in oil well brines. The caustic alkali component of the preferred types of reagent used in accordance with the present invention is therefore effective in preventing corrosion. The tannic acid and tan bark extracts are not in general effective by themsleves as corrosion preventing agents, in fact under certain conditions they themselves cause corrosion, but when they are neutralized with caustic soda in excess the resulting mixture has been found to be very effective not only in preventing corrosion but also in preventing the deposition of the hard scales of calcium, strontium or barium sulfates and carbonates on the metal parts in the well. Moreover the reagents used in this process are in general very effective in removing soft iron sulfid and also non-sulfid deposits from the iron tubing and dispersing this material in the form of a suspension in the fluid in the well, so that the iron sulfide or non-sulfide material is thereafter removed with the fluids pumped from the well. Likewise the present reagents are very effective in causing the formation of light, flocculant non-adherent precipitates of the insoluble calcium, strontium and barium salts present in the brines, causing them to remain suspended in the water or oil and be pumped out with the fluid. The non-scaling precipitates formed from the alkaline earth salts of the brine by reaction with the present reagents also have a tendency to envelop or be absorbed on any alkaline earth sulfate or carbonate crystals or on iron sulfide particles which may form in the well and thus to prevent such crystals from cementing to the tubing or casing or to each other.

The removal of the iron sulfide and of non-sulfide deposits from the metal parts of the well has the effect of greatly reducing the speed of corrosion. Thus when a well giving trouble due to corrosion and the metal parts of which are coated for example with iron sulfide scale is treated by the present process for the first time, the water pumped from the well after treatment is usually black with suspended iron sulfide which is so finely divided as to be practically in colloidal suspension. This pumping of black water from the well may proceed for several days, but if the treatment is continued it will be observed that the water gradually loses color as the scale of iron sulfid is removed.

When treating the liquids in the well according to the present invention it has been found that it is necessary for best results that the treating agent diffuse rapidly through the liquids in the well. This result is accomplished according to the present invention by adding the treating agent to a brine or salt water which has a specific gravity substantially the same as the specific gravity of the water in the well to be treated. In making up a reagent the desired specific gravity for the purposes herein described is obtained either by adding a salt such as sodium chlorid, which is stable under the conditions in the well, or by using water from the well to be treated. In the latter case a calculated excess of caustic soda is added to compensate for the calcium salts precipitated by the caustic or other neutralizing compound used.

The treating agent may be added to the well in various ways. The determination of the manner of adding the treating agent depends largely on the number of hours that the well is pumped each day. Thus the procedure generally adopted in treating wells which are pumped from two to twelve hours per day consists in adding the calculated amount of treating agent as a strong solution to the well just after the shut down of the pump, and washing down the chemical with about one barrel of either fresh or salt water. Wells which are operated twenty-four hours a day are provided with a special form of treating device consisting essentially in a chain bucket pump driven from the crank shaft or other moving part of the well and designed to feed strong chemical in regularly distributed amounts throughout the pumping period. The chemical is washed to

the bottom of the well with a fine stream of salt water from the lead line. For treating wells having a pumping period of ten to twelve hours a day a combination method of treatment is generally used, comprising the continuous addition of a regulated small amount of chemical during the course of the pumping period followed upon shut down by an additional charge which is washed down with salt or fresh water in amount sufficient to provide treatment for the incoming water at the bottom of the well during the period in which the pump is idle.

It has been found that cups, whether of leather or composition, have a much longer life in wells treated by the method of the present invention, since only soft fine grained precipitates are formed which are pumped out of the well readily without injuring or scoring the cups or the barrel. The cups in wells which are not treated often last but a short time, due to abrasive action of the gritty and granular products of corrosion and the hard scale flakes or chips formed on the metal parts adjacent the cups and jarred loose during the operation of the pump. The barrel of the pump and the cups are not lubricated by the present chemical treatment but the cups and working barrel are subjected to service under conditions substantially normal to a well not troubled with corrosion or hard scale formation. The life of the cups, balls, valve seats and barrels in wells treated in accordance with any of the methods outlined above is noticeably increased thereby and the savings due to such increased life are large.

It is often the case that the oil wells which give the greatest trouble due to corrosion and to the formation of hard scale deposits on the tubing and casings, are also the source of much trouble and expense due to the formation of stable emulsions of the oil-in-water type, commonly known as BS emulsions. Accordingly one feature of the present invention which is sometimes employed in the treatment of wells subject not only to corrosion and to the formation of hard scale deposits but also to the formation of BS emulsions in pumping, consists in admixing with the treating agent hereinbefore described a small amount of cresylic acid or similar compound having a lowering effect on the surface tension of the water forming the dispersed phase of such BS emulsions and having consequently a breaking action on the emulsion. The proportions of neutralizing agent or alkali, tan bark extract and cresylic acid or other emulsion breaking agents which are used in preparing the reagent for treating a given well are determined in each case by analysis of the well liquids and by tests carried out to determine the nature of the emulsions formed on pumping.

In some of the claims the expression "chemical hard scale inhibitor" has been used as a generic term to define chemical reagents of the type above described (such as a caustic solution of tannin or certain alkali metal salts) which when added to oil well liquids are capable of reacting with or changing the character of insoluble alkaline earth salts or other potential hard scale-forming components of the said liquids, as above described, so as to produce light and flocculent non-scale-forming precipitates, or so as to inhibit the formation of hard scale-forming precipitates.

The invention having been thus described, what is claimed as new is:

1. The method of treating oil well liquids to render them non-corrosive and non-scale-forming which comprises adding to the well liquids a reagent comprising a mixture of an alkali metal salt and a caustic alkali solution of tannin in amounts sufficient to cause precipitation of the insoluble alkaline earth salts from the well liquids in a pulverulent and non-scale-building form.

2. A method of treating oil well liquids to render them non-scale forming consisting of adding to the liquids a reagent comprising a salt water solution of an alkali and a tan bark extract in quantities and proportions sufficient to effect 80% to complete neutralization of the acidity of the oil well liquids and to prevent hard scale deposition of calcium, magnesium, strontium and barium sulfates and carbonates.

3. A method of treating oil well liquids to render them non-scale-forming comprising mixing with the well liquids an alkaline brine solution of a tan bark extract in which the brine has substantially the same specific gravity as the well water.

4. A method of treating oil well liquids to prevent the formation of hard scale deposits on metal parts in contact with the liquids which comprises mixing with said liquids an alkaline solution of a tan bark extract.

5. The method of treating oil well liquids to render them non-scale-forming comprising adding a strong caustic alkali solution of tan bark extract to the well and washing the agent down the well with water.

In testimony whereof I affix my signature.

JOHN C. WALKER.