Field Evaluation of Microbial Problems and Effective Chemicals for Their Control

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ABSTRACT

In many instances today, a waterflood operator faces two basic problems: first, whether corrosion and plugging of filters, flow lines, and water injection wells are biological in origin; and, second, how to evaluate the effectiveness of a bactericide treatment.

The first of these two problems is usually solved by sending, for examination, samples of water to a microbiological laboratory. Frequently, it takes several days for the sample to reach the laboratory and thus makes it impossible to determine an accurate original bacterial count. Another method for solving this problem has been to set up a laboratory in the field. While this method is effective it is often very expensive and can be done only at infrequent intervals. A third solution has been the development of a "suitcase laboratory" which is portable and can be used by personnel in the field.

It is only after finding that a microbial problem does exist and determining the type of organism that is causing the difficulty that the operator is in a position to select and evaluate various chemicals for microbial control.

In most instances, nitrogen containing compounds such as quaternaries, amines, diamines, and imidazolines are effective in fresh water systems. These materials have the added qualities of being corrosion inhibitors and surface active agents. However, in general, the nitrogen containing chemicals are not effective in hard water systems. Chlorinated phenol type chemicals have proved to be effective in hard water brines.

INTRODUCTION

The microbiological examination of waterflood injection waters is a valuable aid to the field engineer. Micro-organisms is these waters are capable of creating problems which, if not controlled, can decrease operating efficiency and reduce water injection rates.

Transporting water samples brings about a change in the microbial population, and this change may lead to erroneous data upon which the engineer will base his evaluation. To alleviate this problem, there has been developed a "suitcase laboratory" which permits microbiological examinations to be made in the field.

Bacterial Corrosion Problems

Bacterial corrosion is known to occur by at least two general conditions: Figure 1 (1) shows a galvanic corrosion cell under anaerobic conditions. With no oxidizing agent present, hydrogen accumulates at the cathode stifling further corrosion. Sulfate reducing bacteria are capable of removing this hydrogen and using it to reduce sulfate to sulfide. In this manner, these bacteria obtain energy for further growth and activity. Removal of the hydrogen from the metal surface allows iron to go into solution at the anode. A pit may result at this point; and the pit may eventually penetrate the pipe.

The second corrosion condition can occur when hydrogen sulfide produced by the bacteria reacts with ferrous ions in the water to form insoluble ferrous sulfide. This product may be deposited on the pipe wall and create metal dissimilarities which result in formation of other galvanic cells (2).

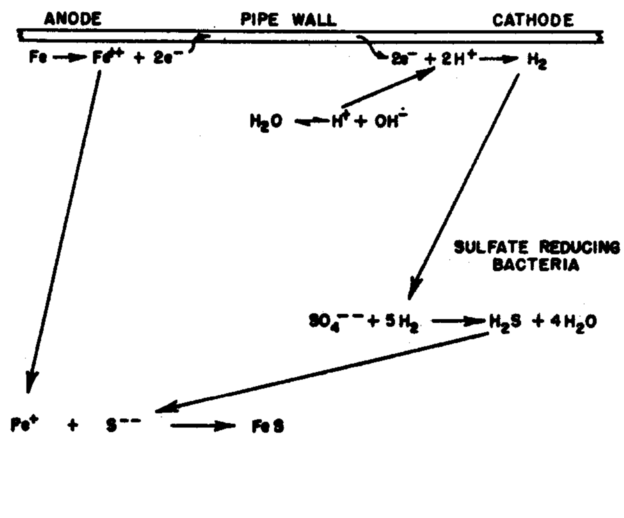
Microbial Plugging Problems

Plugging of filters, flow meters, and injection wells can result from just the physical mass of microorganisms, from insoluble by-products of their activity, or from a combination of both. Core studies of water before and after sterilization were made on one company's water-flood injection waters (3); and definite plugging was encountered using the non-sterile water. Other evidence has indicated that 100,000 bacteria per ml of water can plug some injection well sand faces (4).

Insoluble by-products of microbial activity include iron sulfide and iron hydroxide. Ferrous sulfide is formed when hydrogen sulfide, produced by sulfate reducing bacteria, reacts with soluble ferrous ions in the injection water; this iron sulfide creates especially difficult plugging problems when a little oil is also present in the water. Iron hydroxide results from iron bacterial growth in the injection water system. These bacteria oxidize soluble iron from the water and produce large amounts of ferric hydroxide -- up to 500 times their own weight (5). This ferric hydroxide is precipitated in sheaths surrounding the organisms or in ribbons extruded from the cells, and the resultant mass is a very good plugging agent. Iron bacterial growth is prevalent in river sand water used for injection purposes

FIGURE

ANAEROBIC BACTERIAL CORROSION (FROM BOGTSTRA (1))



Detection of Microbial Problems

When an operator encounters a possible microbial problem, his first step should be to determine what organisms, if any, are actually involved. This determination is accomplished by a complete microbiological examination of the waterflood system, and the results of such an analysis will also indicate what type organisms are involved. The operator is now in a position to evaluate available chemical control measures.

METHODS OF MICROBIOLOGICAL ANALYSIS OF WATER

Microscopic Examination (6)

This technique makes it possible to detect significant numbers of microbes which may not respond to usual laboratory cultivation media. It also permits an estimation of the number of organisms present as an aid in preparing plate count dilutions.

Plate Count Technique (6)

This method is designed to cultivate or grow the general aerobic bacterial population. By this means, bacterial colonies develop and can be visually counted. The number of bacteria present in the original water sample then can be calculated.

Extinction Dilution Technique

The principle of this method is to dilute a measured quantity of water until it is improbable that any of the original bacterial population is still present. When this diluting is done in a systematic or serial manner and into a nutrient medium, it is possible to establish a growth-no growth range for the bacteria, i.e., the greatest dilution which theoretically contains but a single organism. This organism multiplies in the nutrient diluting solution and imparts a cloudiness or turbidity; but the next greater dilution will remain clear since there was not an organism present to grow and produce turbidity.

MICROBIOLOGICAL LABORATORIES

There are, in essence, three types of microbiological laboratories: the stereotyped typical laboratory that is housed in a permanent structure and has a staff of technical personnel, the mobile laboratory, and the so-called "suitcase laboratory"

The Typical Laboratory

Because of its permanent nature, this type laboratory has several advantages such as adequate work space and specialized but bulky equipment, i.e., electron microscope, steam sterilizer, etc. It has the disadvantage that samples for analysis must be transported to it.

The Mobile Laboratory

The mobile laboratory is just what the name implies: a truck, trailer house, or station wagon outfitted as a laboratory. Some of these are quite elaborate but they are still limited in the scope of work that they can perform. That they can travel to the area where lab services are needed is a distinct advantage. This eliminates the time lag between obtaining and processing samples.

The Suitcase Laboratory

The "suitcase laboratories" (Figure 2) vary in size, versatility, and analytical methods but all of them fill a need. They are easy to transport and are on the spot for making analyses in the field. Because of their size, they are relatively inexpensive to equip and maintain.

Adequate technical service is an important part of a chemical sales program today. For this reason, there has been developed a "suitcase laboratory" which provides the essential test for waterflood injection waters.

C-1 analyses are possible with the "Suitcase Laboratory." This kit is equipped to permit a sales group to make general aerobic and sulfate-reducer counts in waterflood injection water. In addition, chemical analyses for pH, soluble iron content, total hardness, chlorides, hydrogen sulfide, and amine or quaternary concentrations, can be made. Provision is made for utilizing the membrane filter technique of preparing water samples for microscopic examination. However, these filters must be sent to the central laboratory for evaluation.

The C-2 "suitcase" testing method allows microbiological analyses to be made by using the "extinction dilution" technique. The test is performed in the following manner (Figure 3):

a) One ml of the water sample is drawn into a sterile disposable syringe and injected into a serum bottle containing 9 ml of sterile growth medium.
b) After mixing, 1 ml of solution is withdrawn from this bottle (number 1) with a new sterile syringe and injected into a second serum bottle of medium (bottle number 2). This bottle is designated as the 1:10 dilution, i.e., it now contains one-tenth of the organisms present in the original 1 ml water sample.
c) This procedure of using a sterile syringe to remove a milliliter of solution from the previous bottle and adding it to the next bottle is continued until any organisms present in the original water sample have been diluted 1:10,000,000.

Eight inoculated serum bottles will result from these manipulations. They represent dilutions of the organisms present in the original water sample corresponding to the numbers given in Figure 3.

By this technique, a water sample containing 100 organisms per milliliter would cause turbidity in bottles Nos. 1, 2, and 3 but not in bottle No. 4. That is, the 1:100 dilution of the organisms would allow one organism to be present to grow. However, the next higher dilution (1:1000) would have very little chance of being inoculated. In this manner, the range of microbial contamination is easily determined.

FIELD EVALUATION OF MICROBIAL PROBLEMS

Visual Inspection

Visual inspection of the physical setup and condition of a water handling system will often point out areas that present microbial problems. Many times these sources of possible contamination can be eliminated simply by better "housekeeping". For example, heavy accumulations of sediment or sludge in tanks provides an ideal source of microbial contaminants. If one removes this source, the possibility of microbial problems is reduced.

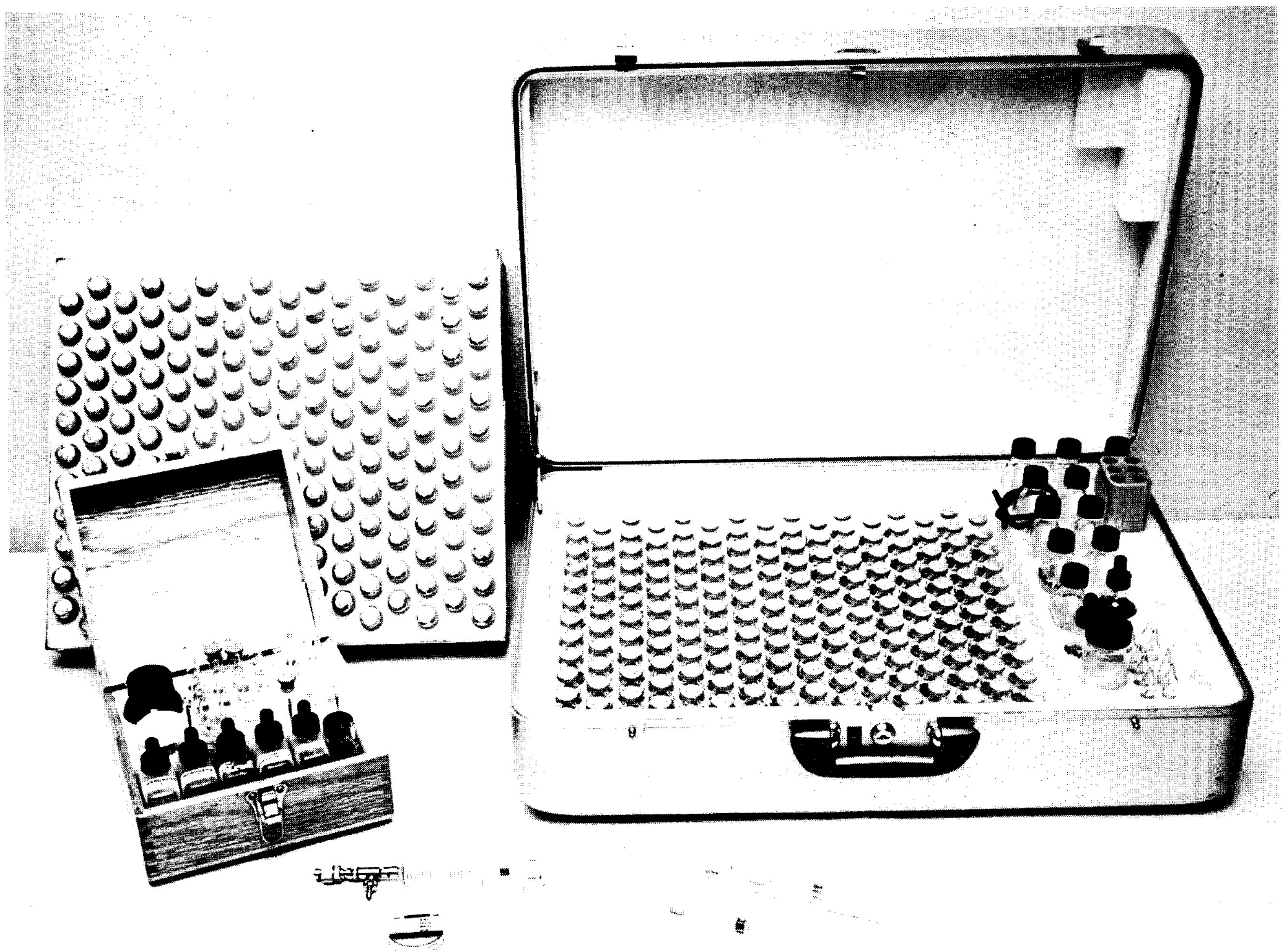


Fig. 2 Suitcase Laboratory

Laboratory Information

The second step is the obtaining laboratory information that will determine the extent of microbial contamination. In this step the "suitcase laboratory" is of great help. Water samples are obtained at selected points throughout a water system and cultured by the extinction dilution technique. Both the general aerobic bacteria count and the sulfate-reducer count are determined for each water sample. In this manner, it is possible to compare the degree of microbial contamination present from the supply water source all the way through the system to the injection well head.

Chemical Analysis

The third step is to obtain a chemical analysis of the water samples used for microbial testing. Changes in pH, iron content, and hydrogen sulfide content of the water often can be correlated with microbial activity. The degree of hardness of a water is one of the criteria that determines whether a quaternary or amine type bactericide can be used effectively; for this reason, it is included in the analyses. The test for chlorides has been found to be helpful in fresh water systems and is especially useful in helping to establish salt water encroachment.

Analysis for quaternary or amine concentration is made when these materials are being used in a treating program and indicates whether the desired concentration of chemical is present throughout the system. Periodic microbiological and chemical checks of a system that is receiving bactericide treatment are necessary to determine if the treating program is giving adequate control. The "suitcase laboratory" is especially adaptive to this field monitor type of testing.

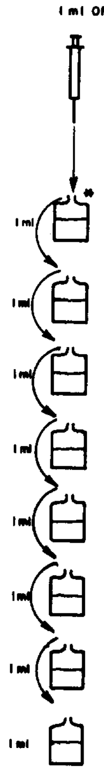
It is essential to make the microbiological examination of a water sample as soon as possible after it is taken, for changes in microbial count occur rather rapidly in a water sample (7, 8, 9). The examination is made easily and rapidly in the field using the extinction dilution technique of the "suitcase laboratory".

Characteristics of Waterflood Microbiocides

For a chemical to be used effectively as a microbiocide in waterflood operations, several criteria should be met:

1) The chemical must be economically effective in the specific water in question. This effectiveness is usually shown by a laboratory time kill test using the injection water.
2) The chemical must be compatible with the water in question. The presence of calcium and/or magnesium ions at over 1000 ppm will inactivate some bactericides. Other chemical treatments -- i.e., scale control with phosphates -- will also inactivate certain bactericides.

FIGURE 3
EXTINCTION DILUTION TECHNIQUE



BOTTLE NO.	DILUTION FACTOR	GROWTH INTERPRETATION
1	0	1
2	1:10	10 per ml
3	1:100	100 per ml
4	1:1000	1000 per ml
5	1:10,000	10,000 per ml
6	1:100,000	100,000 per ml
7	1:1,000,000	1,000,000 per ml
8	1:10,000,000	10,000,000 PER ml

* Each bottle contains 9 ml of dilution fluid

3) The chemical must not significantly plug the injection formation. For this possibility actual core tests are usually used.
4) The toxicity of the chemical should not impose severe handling problems.
5) The chemical, if a liquid, should have a low freezing point. In many cases, this is accomplished by packaging the chemical in alcohol instead of water. However, this requirement is not as significant as in past years when heating facilities were unavailable.

If a chemical meets these criteria, the operator may want to use it in a field test. Usually, a 60 day trial in an injection water is used. For proper evaluation of the test, periodic microbial checks of the water should be made during the test.

Effective Waterflood Microbiocides

For this presentation, the microbiocides have been grouped according to their principal functional groups.

(Chlorine) - Chlorine is a very effective bactericide and algicide and will generally control growth at 0.2 ppm or less. The chemical can be used in gaseous form as chlorine gas or in a solid form as the hypochlorite. The calcium salt of hypochlorite is the most common solid form of chlorine used; but, as with all solid microbiocides, treating is more difficult than with a gas or liquid. For this reason, hypochlorites are normally used only for batch type treatments. Chlorine gas is being used for microbial control in several waterfloods. Initial equipment purchase for gaseous chlorination is relatively high but, in the long run, treatment costs are quite low

Use of chlorine in waterflood systems does have some definite disadvantages which have restricted its usage. The chemical is a very strong oxidizing agent and can produce corrosion problems unless the flow lines are lined or made of plastic. In addition, if the injection water contains soluble ferrous iron, it may be oxidized to the insoluble ferric state with resultant plugging problems.

Sodium Salts of Chlorinated Phenols

Chlorophenates are solids but are quite water soluble and are particularly effective against sulfate reducing bacteria (10) and fungi. In one instance, control of sulfate reducing bacteria by tetrachlorophenate in producing wells reduced by 59 per cent pulling job frequency (11). Corrosion studies showed that the sulfate reducing bacteria were responsible for more than 77 per cent of the corrosion that had been taking place in these wells. However, chlorophenates give no direct corrosion protection.

Chlorophenates are relatively inexpensive microbiocides. In addition, they are not affected by water hardness and can be used in briny injection waters.

Even with these attributes, this group of chemicals has not been widely used in waterflood operations. Operators are reluctant to handle the material as purchased (flake form) because of severe nose and throat irritation problems that occur. Some of the chlorophenates are now being marketed in ball form which may eliminate this toxicological objection.

Chlorinated hydrocarbons poison the catalytic process in petroleum cracking. To prevent the possibility of chlorophenates getting into produced fluid, some companies will not allow their use in waterflood operations.

Formaldehyde

Formaldehyde was one of the first chemicals used for microbial control in waterflood operations. Initially, the chemical usually controls growth in the injection water, but it is very common for resistance to quickly develop. And not only do bacteria become resistant to the formaldehyde, they use it as a food source. An example of such an incident is shown in Figure 4. The sharp decrease in the bacterial count following cessation of treatment should be noted.

Formaldehyde is also difficult to handle in the field. Contact with the skin will cause severe irritation, and the vapor is irritative to the eyes and nose.

Organic Sulfur Compounds

In the paper mill industry, this group of chemicals has for several years been used to control microbial activity in pulp processing and are now being sold for use in waterflood operations. However, they have not as yet been widely accepted for this application, principally because the lack of laboratory techniques to demonstrate their effectiveness. Without supporting laboratory data it is difficult to justify a field trial.

Heavy Metals

Chromium, zinc, mercury, silver, copper, and tin are all effective microbiocides. Colloidal silver has been suggested for use in water treatment but high cost has prevented its use. Copper sulfate has been used in surface waters for algae control but copper is not very effective against bacterial growth. Some metal organics will effectively control growth in secondary recovery waters, but water insolubility and high cost have prohibited their usage.

Amines and Diamines

This is the first group of microbiocides that serves a multiple function in injection waters. The amines and diamines are effective bactericides, corrosion inhibitors, and surface active agents.

Amines are convenient chemicals to handle in the field and are currently being used in several waterflood areas. Some of the amines and diamines are more oil soluble than water soluble; therefore, in closed injection systems utilizing these chemicals, it is necessary to use gas instead of oil blankets in the water storage tanks.

The diamines are more effective microbiocides but are less water soluble than are the monoamines. Laboratory core data has indicated that the diamines tend to plug (11); however, at least one manufacturer is now marketing a diamine that is claimed not to have this plugging tendency. One injection water is presently being treating for microbial and corrosion control with one of these new diamines, and no plugging problems have been detected.

Quaternary Ammonium Compounds

Quaternaries, like the amines, provide benefits beyond that of microbial control. These chemicals are cationic (have a positive charge) and plate out in a very thin film on the walls of the injection flow system. By this filming action these structures provide good corrosion protection.

Quaternaries are very surface active and act as detergents. This characteristic results in flow line cleanup and helps to prevent meter and filter plug-ups.

The quaternaries are relatively non-toxic and are used as microbiocides in mouthwashes, contact eye lens washes and in hospital disinfectants.

However, there is no universal microbiocide and quaternaries will not function effectively in all waterflood injection waters. As a rule, quaternaries are used only in fresh water systems because water hardness, over about 1000 ppm, inactivates them. This inactivation mechanism by calcium are magnesium does not always develop, for a quaternary microbiocide has been very effectively used in a sea waterflood (3).
sea waterflood (3).

Quaternaries are thus effective microbiocides that provide three services for the price of one. This is probably the principal reason that this group of chemicals is the most widely used for microbial control in waterflood operations.

Imidazolines

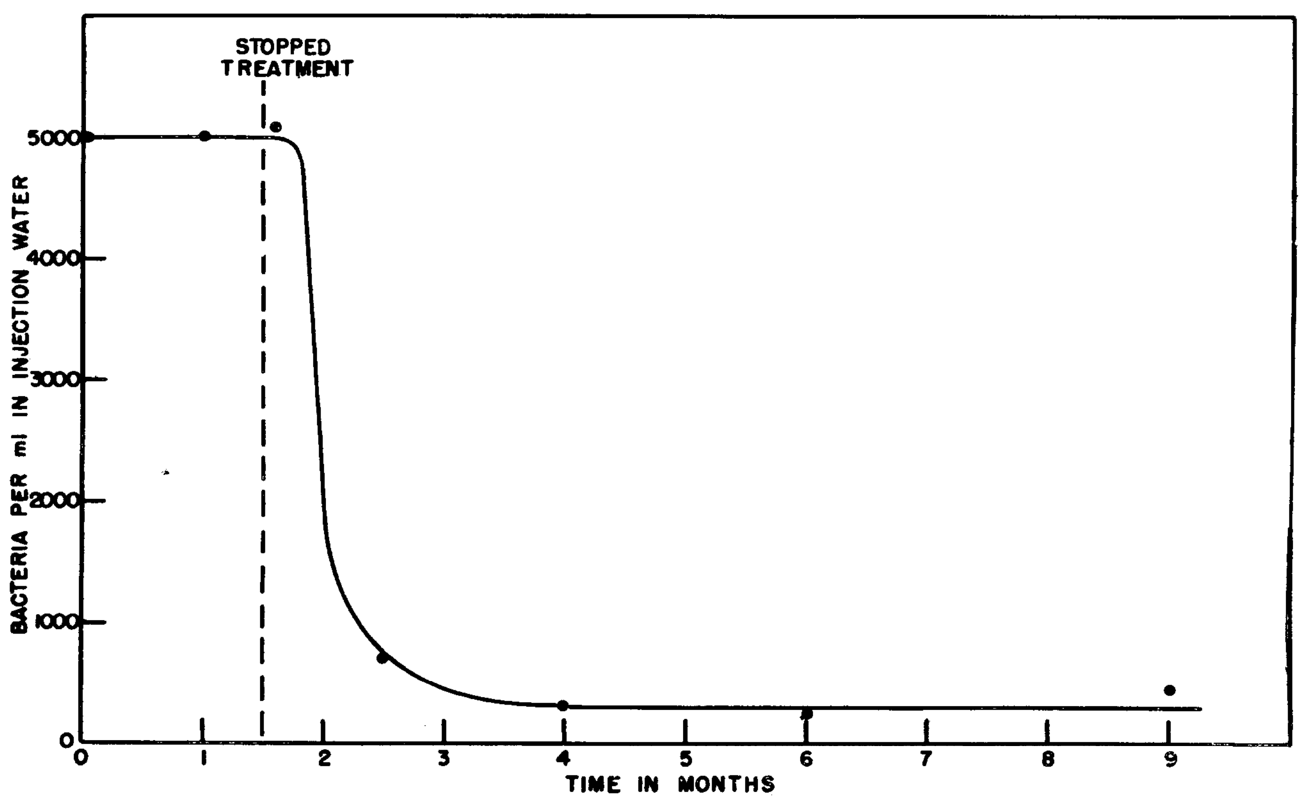
These are nitrogen containing microbiocides that are good corrosion inhibitors. The characteristics of these chemicals are very similar to those of amines and quaternaries; however, in general, the imidazolines are better corrosion inhibitors but are not quite as effective against microorganisms.

Alcohols

The low molecular weight alcohols--i.e., methyl, ethyl and isopropyl alcohols--are effective microbiocides in 70 per cent solutions; but they are not effective in concentrations that could be used in waterflood op-

FIGURE 4

FORMALDEHYDE TREATMENT OF A WATER FLOOD INJECTION WATER



erations. These alcohols are very good solvents for many bactericides and are used as such in many products. The higher molecular weight alcohols are more microbiocidal than are the shorter chain structures; but, at present, they are too expensive for use in waterflood operations.

Combinations

The combination of two or more bactericides, commonly used in waterflood operations, does not result in a product with exotic properties. The benefit that can be obtained with such a product is versatility. For example, if a quaternary and an organic tin were compounded, one would expect a quaternary product that could be effectively used in hard water.

Summary

Evaluation of microbial problems in a waterflood is one of several problems faced by the field engineer. Accurate and periodic microbiological examinations of the water are needed to make such an evaluation. The "suitcase laboratory" of the technical sales representative provides the necessary services to assist the engineer in this evaluation.

Not all of the types of microbiocides that are offered to the waterflood operator for use in his waterflood operations have been covered. However, the chemicals that have been effectively used in the field have been discussed. Laboratories are constantly striving to discover new and better microbiocides and increase the effectiveness of those currently available; and the groups of effective microbiocides for waterflood usage will grow with these new developments.

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