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EFFECTIVE CHEMICALS FOR MICROBIAL CONTROL IN SECONDARY RECOVERY

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by

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Abstract

In recent years the problem of biological control in secondary recovery has received a considerable amount of attention. In many cases, the success of a waterflood has depended upon the ability of the operator to control microbial growth.

The waterflood operator is faced with two basic microbiological problems: (1) bacterial corrosion and (2) microbial plugging of filters, flow lines, and water injection wells.

The waterflood operator must first establish that his problem is biological by a complete microbiological examination of the waterflood system. After finding that such a problem exists and determining the type of organism that is causing the problem, the operator is in a position to 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. The materials have the added qualities of being corrosion inhibitors and surface active agents. In general, the nitrogen containing chemicals are not effective in hard water systems. Chlorinated phenol type chemicals have proven to be effective in hard water brines.

Introduction

Microorganisms in secondary recovery waters are capable of creating problems which, if not controlled, could decrease operating efficiency and reduce water injection rates. Waterflood operators must know how to detect these problems and how to combat them.

Bacterial Corrosion Problems

Bacterial corrosion is known to occur by at least two general mechanisms: (1) Figure 1 shows a galvanic corrosion cell under anaerobic

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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 which may eventually penetrate the pipe.

The second corrosion mechanism 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, creating 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 byproducts of their activity or from a combination of both. Core studies with water before and after sterilization were made on one of Continental Oil Company's California waterflood injection waters (3). 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 byproducts 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). The ferric hydroxide is precipitated in sheaths surrounding the organisms and the resultant mass is a very good plugging agent. Iron bacterial growth is prevalent in river sand water used for injection purposes.

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 is accomplished by a complete microbiological examination of the waterflood system. 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.

Characteristics of Waterflood Microbiocides

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

1. The chemical must be economically effective in the specific water in question. This 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.

3. The chemical must not significantly plug the injection formation. We usually test this possibility with actual core tests.

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. This 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. It 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. They are particularly effective against sulfate reducing bacteria (6) and fungi. In one instance, control of sulfate reducing bacteria by tetrachlorophenate in producing wells reduced pulling job frequency by 59% (7). Corrosion studies showed that the sulfate reducing bacteria were responsible for more than 77% of the corrosion that had been taking place in these wells. 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 briney 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. In order to prevent the possibility of chlorophenates from getting into produced fluid, some companies will not allow their use in waterflood operations.

Formaldehyde

Formaldehyde was one of the first chemicals used in waterflood operations for microbial control. Initially the chemical usually controls growth in the injection water, but it is very common for resistance to quickly develop. 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 2. Note the sharp decrease in the bacterial count following cessation of treatment.

Formaldehyde is also difficult to handle in the field. It will severely irritate the skin upon contact and the vapor is irritative to the eyes and nose.

Organic Sulfur Compounds

This group of chemicals have been used for several years in the paper mill industry to control microbial activity in pulp processing and are now being sold for use in waterflood operations. They have not as yet been widely accepted for this application. This is principally due to 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 than are the monoamines but are less water soluble. Laboratory core data has indicated that the diamines do tend to plug (7). At least one manufacturer is now marketing a diamine that is claimed not to have this plugging tendency. We are presently treating one injection water for microbial and corrosion control with one of these new diamines. No plugging problems have been detected.

Quarternary Ammonium Compounds

Quarternaries, 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. They are used as microbiocides in mouthwashes, contact eye lens washes and in hospital disinfection.

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 and magnesium does not always develop, for Continental Oil Company has very effectively used a quaternary microbiocide in a 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 amines and quaternaries, but, in general, the imidazolines are better corrosion inhibitors and not quite as effective against microorganisms.

Alcohols

The low molecular weight alcohols, i.e., methyl, ethyl and isopropyl alcohols, are effective microbiocides in 70% solutions. They are not effective in concentrations that could be used in waterflood operations. 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 the shorter chain structures but, at present, are too expensive for use in waterflood operations.

Combinations

The combination of two or more bactericides, commonly used in waterflood operations, do 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

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 to a significant extent have been discussed. We are constantly striving to discover new and better microbiocides and increase the effectiveness of the ones currently available. The groups of effective microbiocides for waterflood usage will grow with these new developments.

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FIGURE I

ANAEROBIC BACTERIAL CORROSION (FROM BOGTSTRA (8))

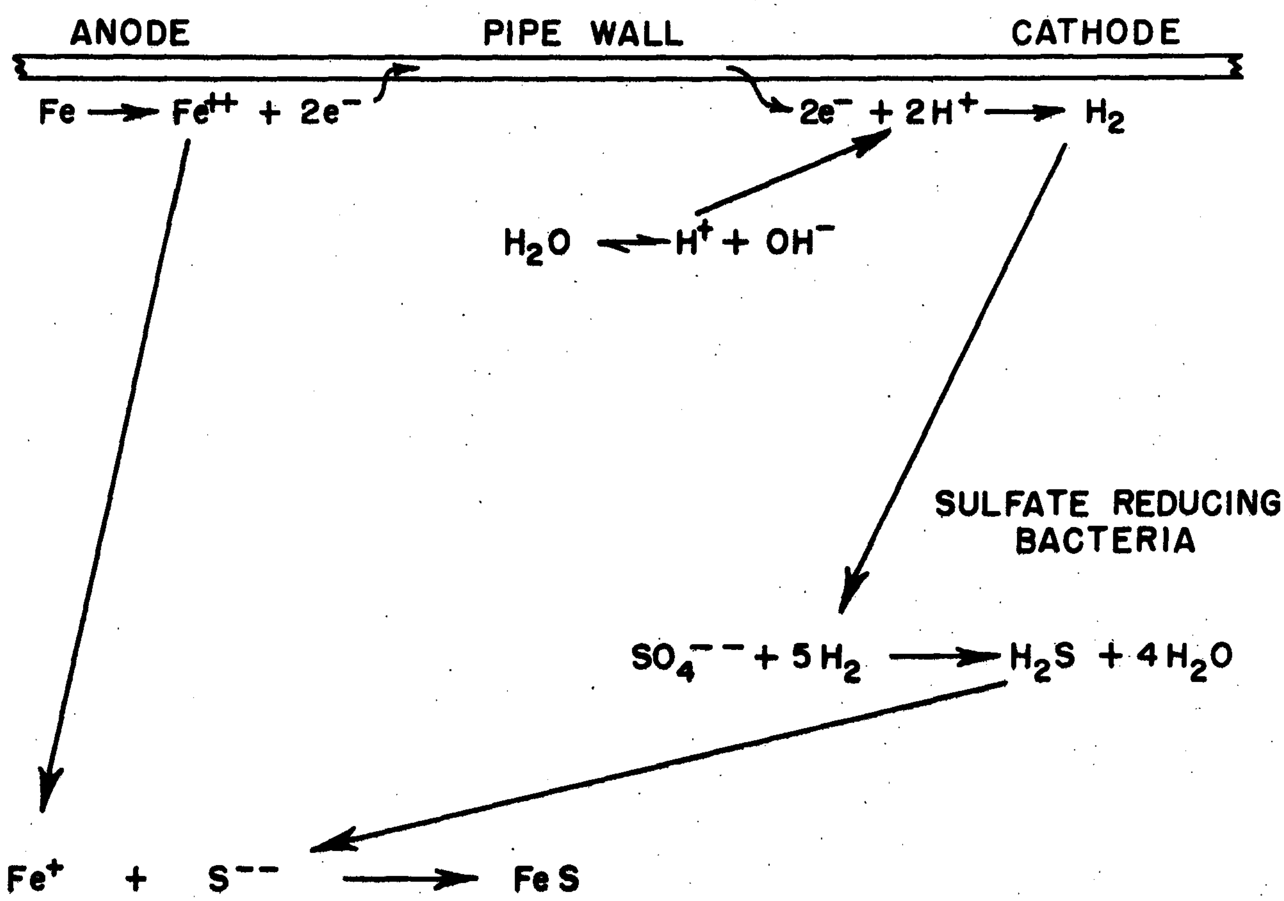

FIGURE 2

FORMALDEHYDE TREATMENT OF A WATER FLOOD INJECTION WATER