Sulfate-Reducing Bacteria...Their Role In Corrosion & Well Plugging

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INTRODUCTION

Microorganisms are causative agents of many problems associated with the primary and secondary recovery of oil. Bacteria of the genus Desulfovibrio, commonly referred to as sulfate-reducing bacteria, are responsible for many of these troubles.

The Desulfovibrio are a rather hardy and rugged bacteria. Being strict anaerobes they grow and increase in numbers in the absence of oxygen; however, they can exist and survive in an aerobic environment. Petroleum crudes as well as other organic materials can be utilized as a necessary carbon source. Inorganic sulfates are used as the hydrogen acceptor in energy producing reactions.

Sulfate-reducing bacteria have been found in soil, fresh and ocean waters and sediments, sewage, oil producing formations, drilling muds, cooling towers, and a host of other places. Migration through oil bearing cores is proof of their mobility. Some species are tolerant to high temperatures. Growth of sulfate-reducing bacteria has been observed in a pH range of 5.5 to 9.5, and some investigators have reported growth outside these limits.

TWO BASIC PROBLEMS

Sulfate-reducing bacteria pose two basic problems in the production of oil — (1) injection well plugging and (2) corrosion of iron and steel. Large numbers of sulfate-reducers can be deposited on an injection well sand face. Further, a chemical reaction between the soluble mineral constituents in a flood water and the end products of the metabolism of this bacteria often results in the formation of insoluble materials that are capable of plugging oil sands. The corrosion of oil production and water injection equipment is frequently due to the presence of this type of bacteria, as will be shown.

Plugging

Injection of water into an oil producing horizon for the secondary recovery of oil, or the injection of produced water into a non-oil bearing formation for disposal can be a failure if the sand face becomes plugged with suspended material* (*Injection sand face, injection well, injection water, etc. will refer to secondary recovery injection systems, salt water disposal systems, and their corresponding components.) Sulfate-reducing bacteria frequently represent a significant plugging agent in producing brines and injection waters since these fluids often offer a suitable medium for their growth. The plugging potential is much greater for "tight" or low permeability horizons.

In formations that have high permeability and porosity factors, plugging by sulfate-reducing bacteria (and other species as well) can occur even when the bacteria are much smaller than the pore spaces. Surface phenomena, such as difference in an electric charge or potential, can cause the bacteria to be adsorbed on the sand particles. Thus, the cadavers of sulfate-reducers are often responsible for a loss of injectivity in injection wells.

Another, and far more common, cause of plugging of injection wells is the deposition of large amounts of insoluble iron sulfide on the sand face. While this type of deposition is not always the result of bacterial activity, the responsibility frequently is traced to the action of sulfate-reducing bacteria. During the growth of this organism inorganic sulfates are reduced ultimately to hydrogen sulfide gas. This gas reacts with soluble iron found in most oil field brines to form insoluble, black iron sulfide — a potential plugging agent.

Bacteria deposited downhole and causing reduced injectivity can be removed by the application of acids, detergents, or oxidizing materials. Water-wet iron sulfide deposited on an injection sand face is readily dissolved by muriatic acid. However, when the iron sulfide has been made oil-wet, its removal is not so simply achieved.

The occurrence of oil-wet iron sulfide is quite common since produced waters often contain small amounts of oil because of incomplete oil-water separation. If oil-wet iron sulfide is to be removed, organic solvents or powerful detergents must be used to remove the oil so that subsequent acid treatment will be effective.

Oil producers know that cleanup and well restimulation procedures are costly. Certainly no operator wants an injection well to become plugged. Some steps that can be taken to reduce input well plugging by controlling the growth of sulfate-reducing bacteria will be reviewed later.

Corrosion

Exposed metal surfaces in oil producing, oil gathering, oil-water separation, and water injection systems are subject to corrosion. As mentioned earlier, much of the corrosion observed in these systems has been traced to the action of sulfate-reducing bacteria. In many instances they are the sole cause of corrosion; but more often they are an accelerating or contributing factor in a situation where a corrosive potential is already present.

Sulfate-reducing bacteria play a dual role in corrosion; (1) they act as cathodic depolarizers and (2) they produce the corrosive constituent hydrogen sulfide.

1. Cathodic depolarization — The aqueous corrosion of iron is an electrochemical process. It requires electrically connected anodic and cathodic areas immersed in an electrolyte plus an effective depolarization of the cathode. Some local anodes and cathodes invariably are present on iron and steel surfaces while many others are formed during service (e.g., as the result of deposits).

   When corrosion occurs, iron atoms lose an electron and enter the electrolyte as ferrous ions at the anode. The electrons flow through the metal to the cathodic areas where hydrogen ions accumulate and gain an electron to become neutral hydrogen atoms. If the corrosion cell is to continue to function, some means of removal of the hydrogen atoms must be present — the cathode must be depolarized.

   In acidic solutions depolarization takes place by the

Fig. 1

evolution of hydrogen gas. In neutral or alkaline solutions (i.e., above a pH of about 5) this evolution ceases to be an appreciable factor. However, dissolved oxygen is a very effective cathodic depolarizer and in many systems it is almost a prerequisite for a sustained attack.

In the absence of oxygen, sulfate-reducing bacteria can serve as the cathodic depolarizer. These microorganisms consume the hydrogen in their metabolic reduction of sulfate. Thus, sulfate-reducing bacteria permit a sustained attack on iron and steel under anaerobic conditions.

2. Sulfide production — Sulfate-reducing bacteria also contribute to the attack of iron and steel in oxygen-bearing waters. In such cases, they produce hydrogen sulfide in local anaerobic areas (e.g., under loose deposits). The dissolved hydrogen sulfide thus introduced markedly increases the corrosiveness of the oxygen-bearing water to iron and steel. Further, hydrogen sulfide tends to react with dissolved iron to produce ferrous sulfide which is decidedly cathodic to iron. Local corrosion cell activity on the metal surface is intensified by the deposition of iron sulfide.

Employing the mechanisms outlined above, sulfate-reducing bacteria play a major role in the severe and extremely common pitting type of corrosion. Fig. 1 shows a section of pipe that has been pickled to expose typical severe pits caused by sulfate-reducing bacteria. Frequently the pit is covered with scale and corrosion products in the form of a tubercle.

Fig. 2 is another excellent example of typical corrosion caused by sulfate-reducing bacteria. The lower half of the pipe section shown has been cleaned and pickled to reveal the pitted surface. The upper half of the pipe is covered with a thin, compact scale of corrosion products. The layer of this scale nearest the viewer is mainly iron oxide since the pipe carried a water that contained oxygen. The layers nearest to the metal surface consist of ferrous sulfide. Many tubercles are evident. In the center of the pipe a tubercle has been broken revealing a pit that has completely penetrated the pipe. The metal surface immediately under this tubercle was anodic — the portion of the pipe where metal entered into solution. This area was also anaerobic and contained actively growing sulfate-reducing bacteria.

As iron entered into solution at the anode it reacted with hydrogen sulfide produced by the bacteria and was deposited as iron sulfide. This material accentuated the cathodic area at the extremities of the tubercle. Growing sulfate-reducers were aggressively depolarizing these cathodic areas thus permitting an accelerated electron flow from the anode to the cathode. This was accompanied by concentrated corrosion at the anode. The "drilled-hole" leak resulted.

In Fig. 3, the scale and corrosion layers have been removed from the specimen. Anaerobic areas where sulfate-reducers were growing are now obvious by the dark regions containing iron sulfide. Also, numerous pits are seen that can be matched with the tubercles of the corrosion layer. Perhaps the most striking part of this figure is the large pit near the center right hand edge of the pipe that is now exposed but was hidden under a tubercle in Fig. 2. This pit is partially covered by a layer of iron sulfide and it has almost penetrated the thickness of the pipe.

A variation of this situation is exemplified by systems that inject a fresh or brackish water until it is necessary to commingle the supply water with a connate water when large volumes of the latter are produced. In the majority of cases the produced water contains a significant number of sulfate-reducing bacteria. Corrosion products, calcareous scale, or even corrosion inhibitors may be laid down as a deposit.

It is possible for sulfate-reducers to penetrate the film, become established, and flourish. The type of corrosion illustrated in Fig. 2 and Fig. 3 can then occur. Many variations of these examples may be found but the end result is always corrosion ... caused by or accelerated by sulfate-reducing bacteria.

OCCURRENCE

How do these bacteria get into water injection and producing wells and systems? Where do they come from? It remains an unresolved question as to whether sulfate-reducing bacteria are indigenous to oil producing horizons. Today many subsurface formations do contain these bacteria, probably as a result of previous oil field operations.

A well being drilled with a mud contaminated with sulfate-reducing bacteria will, in effect, permit the inocculation of every formation that is penetrated. When casing is set and the well is completed, the areas or zones outside the casing that are able to support the growth of this microorganism

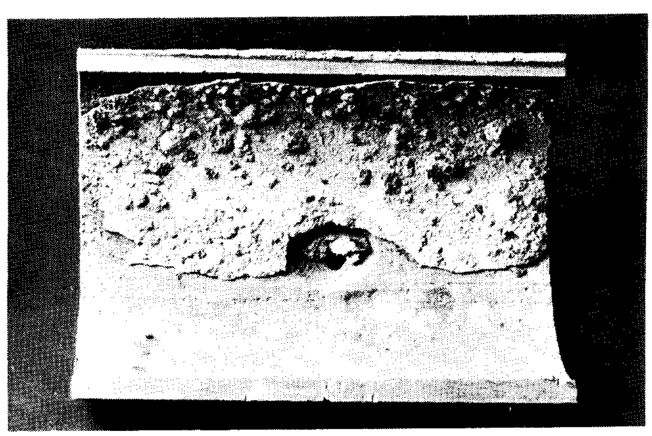

Fig. 2

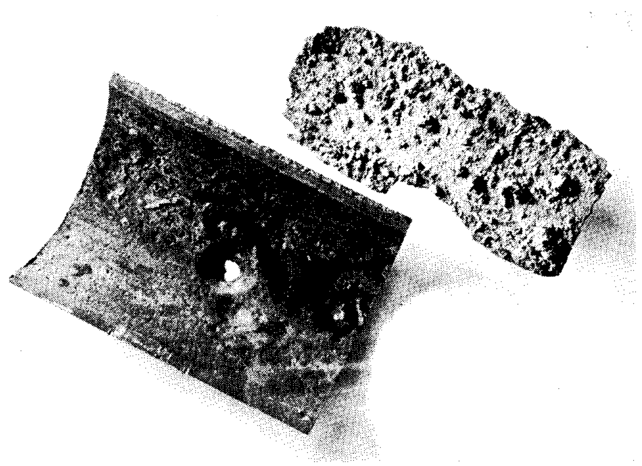

Fig. 3

will do so. If the environment in the producing formation is favorable, the bacteria may become established there. It is then possible for them to migrate through the zone, eventually appearing at an offset well.

Each area outside the casing that is conducive to the growth of sulfate-reducers is susceptible to leaks as a result of external casing corrosion caused by their activity. Further, the bacteria may migrate from the well bore and completely infiltrate a potential water source formation. They would then represent a potential hazard to any future operation that might make use of water from the infiltrated zone.

Another route whereby these organisms enter a water-flood injection system is through the conversion of a contaminated producing well to a water injection well. While the water being injected might be free of these bacteria, it is possible for them to become established in the injection system, since they are motile and could migrate up the tubing of the converted well. Subsequently they can become established in the storage tanks and eventually throughout the entire injection system.

Commingling of uncontaminated supply water with a produced water that carries sulfate-reducers is yet another avenue whereby this organism enters an injection system.

DETECTION

What are the first symptoms indicating that sulfate-reducing bacteria are present? Can their presence be detected by field personnel?

Positive detection of sulfate-reducing bacteria can only be made by reliable laboratory tests.

The American Petroleum Institue in May, 1959 outlined in RP 38 a "Recommended Practice for Biological Analysis of Water-Flood Injection Waters." Methods were suggested to detect the presence of sulfate-reducing bacteria in disposal or injection waters and in produced fluids. Fig. 4 illustrates a typical positive sulfate-reducing bacteria culture made from a sample of injection water using the A. P. I. procedure.

A black spot occurs in the immediate area around the growing sulfate-reducing bacteria. Hydrogen sulfide produced by the bacteria reacts with iron in the culture media to form the insoluble, black iron sulfide — in effect making the "colony" readily discernible by the unaided eye.

A number of "symptoms" can be observed in the field by operating personnel that will give evidence of the possible presence of these harmful microorganisms. The presence of sulfate-reducing bacteria might be suspected if the following conditions are observed:

1. Any produced or supply water that is black or contains black suspended particles (iron sulfide).
2. The presence of sour gas (hydrogen sulfide) in the water of any injection system.
3. A sour crude, sour gas, or sour water well.
4. Pitting type corrosion if black deposits are present and especially if the black film rubs off rather easily, revealing a bright silvery metal underneath.

Any of these symptoms justifies further examination and laboratory tests to determine the extent, if any, to which sulfate-reducing bacteria are contributing to the problems being experienced.

"Why wait for trouble?" A far wiser and safer approach is to determine at the beginning, and regularly during the life of any water injection or oil producing system, the presence and significance of sulfate-reducing bacteria. One sulfate-reducing bacterium ... one positive test, can be the "warning light" that a potentially serious problem can arise. Only a complete water survey by competent specialists can determine the significance of the presence of sulfate-reducing bacteria. Maintaining a close watch for future developments will enable corrective steps to be taken before costly damage results.

CONTROL

When field and laboratory tests show that sulfate-reducing bacteria are present in a water injection or oil producing system, it is necessary to ascertain the significance of their presence and the extent of their activity. In systems that are protected against corrosion through the use of cement or plastic line pipe and tubing and corrosion resistant alloys, the corrosive action of sulfate-reducers is not as critical a consideration as their potential to cause well plugging. It should be noted that some cements and plastics are subject to deterioration by bacterial activity. Each injection system, each producing well or gathering system will have its own limit or "critical number" of sulfate-reducers that can be tolerated before serious trouble develops.

How can sulfate-reducing bacteria be controlled in an injection system? Treating chemicals are available that will kill or inhibit the growth of these harmful bacteria. Products of the former type are called bactericides and those of the latter, bacteriostats.

Generally, it is much more desirable to treat a sulfate-reducer problem with an effective bactericide rather than with a bacteriostat since the chances of a "resistant strain" becoming established is much greater when bacteriostats are used. Employing modifications of the methods outlined

Fig. 4

in API RP 38, it is possible to test in the laboratory, under conditions approaching those that will be encountered in the field, a number of commercially available bactericides to determine which one should be given a field trial. This approach permits oil producers to arrive at a successful treatment in the shortest possible time via the most direct route.

Any use of a bactericide should be carefully followed by regular bacterial analyses to be certain the desired control is being obtained and to permit an early detection of any "resistant strain" of the bacteria that may evolve. Should periodic bacterial checks reveal an increase in the number of sulfate-reducers, the chemical treatment can be changed to a second product that will be effective.

If the bacteria become tolerant to the second chemical (as determined by regular bacterial analyses) the reapplication of the first bactericide will usually be effective in achieving control. It is important from the standpoint of economics and the achievement of successful control to change bactericides on the basis of results from regular periodic bacterial analyses and not on the basis of time alone.

Initial treatment with a bactericide will provide little or no real benefit unless the following important points are considered:

1. A bactericide cannot kill bacteria unless it comes into intimate contact with them. Therefore, it is desirable to clean the system to remove old corrosion films, scale deposits, and debris before instituting a bactericide treatment.
2. Sludge in tank bottoms generally provides an ideal "breeding ground" for sulfate-reducing bacteria. This sludge should be removed and, if possible, the tanks thoroughly cleaned before application of a bactericide.
3. Graded bed filters are frequently found to be the "source" of many sulfate-reducing bacteria. Filter operation in conjunction with a bactericide treatment should be properly carried out so that no "refuge" is provided for the bacteria in the filters.
4. Before a bactericide is used in any water injection system, its compatibility with the water to be treated should be determined. Many good bactericides that are available produce insoluble products when added to various oil field brines. These insoluble materials coat graded bed filter media, thus reducing the effectiveness of the filter. They are also potential plugging agents when "filtered out" on the injection sandface.

SUMMARY

Sulfate-reducers are a hardy and widely distributed type of bacteria found in oil producing and water injection systems. They frequently are the cause of a very severe type of pitting corrosion and are responsible for the plugging of injection wells. Entrance into water injection systems can be via contaminated drilling muds, supply water, or produced fluids.

Situations that should be suspect of the presence of sulfate-reducing bacteria are (1) "black water" or water that contains particles of suspended iron sulfide, (2) sour gas (hydrogen sulfide) injection systems, (3) soul oil, gas or water wells and (4) pitting type corrosion, especially where tubercles and iron sulfide are evident. Positive identification of the presence of sulfate-reducing bacteria can be obtained by employing the methods outlined in API RP 38.

Each water system has its own "critical number" of sulfate-reducing bacteria that can be tolerated. Control can be achieved through a wise choice of the equipment to be used and through the use of an effective bactericide. Regular periodic bacterial analyses coupled with experienced and judicious interpretation of the results can provide the best guide toward maintaining an adequate control of these harmful microorganisms.

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