D31 OIL & GAS PRODUCTS

TECHNICAL MANUAL

HISTORY OF BACTERIA IN THE OIL FIELD

The use of microorganisms in the oil field is not a new phenomenon. The addition of microorganisms and nutrients, such as molasses, to oil wells for stimulation purposes dates to the 1940's.1 Since then the principal areas of research in petroleum microbiology have been the biodegradation of oil by microorganisms and the control of undesirable microorganisms in oil wells. These undesirable microorganisms include sulfate reducing bacteria and slime forming bacteria which can add to lift costs through the corroding of tubulars and the souring of production. The latest research effort has focused on microbially enhanced oil recovery (MEOR).

Everyday corrosion mitigation, paraffin inhibition, scale inhibition, and demulsification can be achieved today through the use of microorganisms. Treatment with microorganisms often proves more economically feasible than with standard production chemicals. It is also much safer for workers and the environment. Sometimes, treatments with microorganisms correspond with an increase in production. This leads to the further development of MEOR possibilities.

The National Institute for Petroleum & Energy Research (NIPER) has completed studies that indicate approximately 27% of the reservoirs in major oil-producing states have potential for MEOR.2 The wells that stand to gain the most from MEOR are the stripper wells. These wells can greatly benefit from the cost-effective methods of MEOR.

The MEOR that can most immediately help the stripper wells are the downhole soak or squeeze treatments that can contribute to production stimulation. These treatments are designed to help the wells from sticking due to paraffin deposition. They are not designed to stimulate them well. The stimulations are a result of the wellbore region clean-up by the bacteria. The paraffin must have specific physical characteristics for stimulation to occur.

A large body of literature with concomitant increase in the number of workers in the field has documented that MEOR is a viable process. Research has mostly been directed toward the use of microorganisms in water floods to increase oil recovery through the improvement of oil and water movement in the reservoir. The reduction of interfacial and inter-surface tension is one aspect of MEOR. An increase in the permeability of reservoir rock is another aspect. 3, 4, 5, 6 Specialized areas have involved the use of microorganisms to selectively plug formations to reduce water infiltration. 7

At first, MEOR was highly dependent upon the type of reservoir and its physical and chemical characteristics. Although it still influences the performance, these restrictions are beginning to loosen as technology expands the treatment horizons for MEOR. The federal and some state governments are also helping the cause by providing tax breaks for new methods of enhanced oil recovery. These and continuing improvements should see the further use of MEOR.

MICROBIAL CULTURE PRODUCTS

The Para-GeoBac microbial culture products of Division 31 GEO-BAC contain naturally occurring, non-genetically engineered microorganisms. The cultures are nonpathogenic and exhibit minimal environmental toxicity. The products are mixtures of microorganisms and may contain several different principal strains that produce changes in the characteristics of crude oil or water relevant to oil field production. All of the products are rigidly controlled for the presence of undesirable bacteria.

Microbial products are not chemical products, and they require the development of a new technology and methodology for their successful use. A critical point is that the user must remember that these are living products. Microorganisms must be treated in a manner similar to the treatment of most living organisms. Extremes of heat and cold must be avoided during storage in order for the products to remain effective. The shelf life of the products is normally six months, depending on storage conditions. Another point to remember is that microorganisms are ubiquitous in the environment and care must be taken to keep Division 31 GEO-BAC products clean and free of outside contamination.

The bacteria that comprise the Para-GeoBac product line are generally of the dimensions of one to four micrometers in length and 0.1 to 0.3 micrometers in width. Most of the strains are motile (they can move via their own propulsion system--a rotating organelle called a flagellum and are thus capable of swimming toward a structure that may function as a point of attachment or as a food source. Some bacteria produce an extracellular polysaccharide, which is known as a capsule. Para-GeoBac bacteria produce minimal amounts of this material. Bacteria occur in three basic shapes: coccus or ball shaped, rods, and spirals. The bacteria present in the Para-GeoBac product are all rods or spirals.

Bacteria exhibit a remarkable diversity in their metabolism. They can use a variety of food sources under a variety of environmental conditions. Some bacteria require oxygen for growth. These are known as obligate aerobes. Other bacteria cannot live in the presence of oxygen; these are known as obligate anaerobes. Still other bacteria can live in the presence or absence of oxygen. These organisms are known as facultative anaerobes. The principal bacterial strains present in Para-GeoBac products are facultative anaerobes. They can survive and even multiply in anaerobic environments such as oil wells. The growth of Para-GeoBac microorganisms under aerobic and anaerobic conditions using crude oil as a sole carbon source. The growth rates (mean cell division time) of the various strains in the products vary from 30 minutes to 4 hours.

Bacteria require a carbon source of some type for growth. These may be complex organic compounds such as carbohydrates (sugars), proteins, and amino acids. They can also use various hydrocarbon compounds such as alkanes and alkenes. Degradation of microbial food sources can occur under both aerobic and anaerobic conditions. A variety of different biochemical pathways exist for the degradation of alkanes via oxygen dependent (aerobic) pathways. The exact pathways present in the Para-GeoBac product when using anaerobic metabolism are held as proprietary. It can be stated, however, that under anaerobic conditions, both organic acids and alcohols, both of which are recognized surfactants and paraffin solvents, are produced.

While it is biochemically well established that hydrocarbons can be degraded under aerobic conditions, there is increasing evidence that degradation can also proceed by anaerobic pathways. This is extremely important, because the downhole region of oil wells is anaerobic. The work of Ward and Brock, and Tiedje has provided increasing evidence that anaerobic degradation of hydrocarbons is biochemically feasible. Lack of attention to its importance is probably due to the difficulty in working with anaerobic bacteria and the prolific publishing of workers studying oxygen-depending processes. Even in the hazardous waste bioremediation area, anaerobic degradation has become an accepted alternate method.

The changes produced in petroleum are not detrimental to the oil in terms of its acceptance by petroleum refiners or buyers. Produced oil treated with Para-GeoBac has been sold for years with no discernible effect on the oil, refineries, or transport facilities. The changes produced in the oil, while significant in terms of parameters such as viscosity or API gravity, are generally a small percentage of the various petroleum constituents.

DESCRIPTIONS OF SPECIFIC PRODUCTS

Para-GeoBac[a]

This is the original oil field microbial product. While initially developed for paraffin control, it has also been used for production increases, scale and corrosion control, and emulsion breaking. It was developed to control paraffins in the carbon ranges of sixteen to twenty-two (C16 to C22). As with all Para-GeoBac products, paraffin ranges are approximate and represent a distribution curve of activity. Activity can be found at higher paraffin lengths as well.

Para-GeoBac X

This product was developed to work on a wider spectrum of higher alkanes than Para-Bac. It is active in the C16 to C40 carbon number region. For most applications, it can replace Para-Bac. It has also been used for production increases, scale control, corrosion control, and emulsion breaking.

Para-GeoBac XX

This product was developed specifically to control higher molecular weight alkanes (C40 to C58). As with all Para-GeoBac activities, these ranges represent the expected maximum area of activity, and some activity may be found on paraffins outside these ranges.

Para-GeoBac XXX

Para-GeoBac XXX was developed to cover virtually any extremely high molecular weight paraffins. It covers ranges from C45 to C60+ paraffins. As these paraffins are generally found in small amounts in most crudes, the dosage with this product is adjusted accordingly. It is generally used as a minority fraction of a product dose. For example, a dosage regimen which has a maximum likelihood of working on any paraffin would be 75% Para-GeoBac X and 25% Para-GeoBac XXX. Para-GeoBac XXX is rarely used by itself as it may not control the more common types of paraffins.

Litho-GeoBac

This was developed originally for water flood injection treatments. It is designed to control calcium carbonate, calcium sulfate, and barium sulfate scales. It has the ability to control some forms of corrosion such as under deposit and mild oxygen. Since its inception it has found a broad field of application in oil wells and other petroleum production systems. It also has nominal paraffin control activity.

Para-GeoBac+, Para-GeoBac X +, and Para-GeoBac XX +

These products combine the scale controlling activities of Litho-GeoBac with the paraffin controlling activity and range of the respective Para-GeoBac products. These products allow for simpler and perhaps more cost-effective treatment than either Para-GeoBac or Litho-GeoBac alone. The " + " formulation is not available with Para-GeoBac XXX.

GEO-PB-M-1000

This is a composite product of Para-GeoBac and M-1000 microbial strains. This product has found utility in some emulsion applications as well as degradation of low levels of certain contaminating hydrocarbons such as toluene, benzene or xylene in certain situations.

Corroso-GeoBac

This is an extra-strength version of the " + " products It has a better filming activity, a broader range of paraffin control, and better chelating activity than the " + " products. The filming activity is roughly four times greater than Litho-Bac. Its paraffin control ranges approximate a mixture of 75% PBX and 25% PBXX and it has roughly twice the chelating (anti-scaling) activity of " + " products. It has been used to control calcium carbonate, calcium sulfate, and barium sulfate scale.

Sulfo-GeoBac

This MBI product line is designed specifically for the removal of hydrogen sulfide and its reaction products from gas, oil and water. Some products within this line are specifically targeted to control sulfate reducing bacteria by metabolic competition or inhibition without the use of biocides. The Sulfo-GeoBac products are targeted for field treatment of SRB contaminated reservoirs and above ground production systems.

Ben-GeoBac

This product has been developed to target the deposition of select asphaltenes and paraffins. It is effective in controlling specific types of asphaltic depositions and improving the flow properties of specific low gravity crudes. Ben-GeoBac is usually used in conjunction with other Para-GeoBac products in downhole treatments. Ben-GeoBac has also been successfully used to treat tank bottoms.

GEO-Force Blue

This biocide is formulated to control SRB populations, and their associated H2S concentrations, in oil wells and production equipment. GEO-Force Blue will also kill MBI products, therefore, it should be applied so as not to interfere with regular paraffin, scale, or corrosion treatments.

PARAFFIN CONTROL

NATURE OF THE PROBLEM

Crude oil consists of a complex mixture of various types of hydrocarbons. These consist primarily of alkanes (linear or branched saturated hydrocarbons), alkenes and alkenes (linear or branched unsaturated hydrocarbons), and cyclic aliphatic or aromatic hydrocarbons. Certain sulfur, nitrogen, and oxygen compounds are also present (McCain 1973). The amounts of these various compounds vary with the oil produced from different formations and different geographical locations.

In most crude oils, alkanes are the predominant fraction. These range in size from methane, a single carbon alkane, molecular weight 18, which is a gas at room temperature up to compounds with molecular weights in excess of 1000 which melt at temperatures more than 90o C. A chart illustrating the properties of various alkanes is given in Table. Compounds which contain fewer than six carbon atoms display high vapor pressures and exist as either gases or very volatile liquids. Compounds from C7 to C12 generally comprise what is known as the transport fluid fraction of crude oil and are generally considered to be the most valuable fraction of the crude oil. These alkanes are used in the manufacture of gasoline, diesel fuel, kerosene, jet fuel and oils.

Above C12, the alkanes become progressively less volatile and generally become higher in viscosity. Above C16 or above C20 (depending upon the authority), alkanes are collectively referred to as paraffins or waxes.

Alkanes of molecular weights higher than that of C20 have melting points that fall within ambient ground temperatures. Due to this property, they tend to solidify in oil and form microcrystalline aggregates which may begin to precipitate out of the crude oil. The smaller alkanes act as paraffin solvents and hold these paraffinic components in solutions. If the paraffinic solubility of the crude oil drops below a certain point, these aggregates will grow and eventually precipitate out of solution and onto the surface of production structures. These can be formation face, casing, tubing, flow lines, separators, tanks or pipelines. Precipitates can reach levels where actual plugging can occur.

The oil well can be viewed as essentially a giant reverse distillation apparatus. A hot liquid holding many different compounds in solution is cooled as it rises to the surfaces. The rate and amount depend upon the depth and temperature of the well. Oil well downhole temperatures can vary from near ambient in the case of shallow wells to temperatures more than 100° C. Temperature drops in the fluid can be gradual, if rising through uniform rock or rapid, such as passing through water bearing zones. Low pressure zones, where gas breaks out of solution, will also cause the rapid cooling of oil. At some point, and this point may be at the formation face or in the pipeline above ground, the " cloud point " can be reached. The cloud point of an oil is the temperature at which the paraffin crystals first begin to crystalize. Below this temperature is the “pour point ". This is the temperature at which the paraffin crystals begin to grow, precipitate, and accumulate. Such accumulation can eventually block the flow of crude oil and / or increase the operational pressures on devices moving the oil past such accumulations.

Conventional treatments for paraffin control are based on three different methods. These are hot oiling, chemical paraffin solvents or dispersants, and mechanical cutting. Hot oiling involves the injection of oil heated to high temperatures (>100° C) into the well (or into the occluded line or tank). The hot oil melts the paraffin deposits accumulated in the well or on the tubulars and allows it to be brought back into solution. This material can then be produced out of the well. Hot oiling involves some loss in production time due to the shut-in of the well during the inflow of the hot oil. There is also a significant danger involved in the process since the hot oil is explosive.

A more serious and long term problem is the possibility that it may cause formation damage. The oil that is usually used for hot-oiling operations comes from tank bottoms. This oil is itself highly paraffinic. Heating the oil simply volatilizes the light ends which are responsible for the paraffin solvency of the oil. Therefore, the oil pumping downhole has little paraffin solvency left and will probably deposit more paraffin than it dissolves. Any paraffin removed was probably just melted and redeposited somewhere else. In addition, the Joules-Thompson Cooling Effect shows that the oil will only remain hotter than the surrounding formation to about 3000 feet, depending upon the bottom hole temperature. A better alternative is to use hot water with a surfactant added to it to keep the melted paraffin dispersed. This too, however, has its limitations, as hot water will only remain hotter than the surrounding formation to about 3000 to 3500 feet, depending on the bottom hole temperature. As the hot oil is pumped in and forced back into the formation, it may carry with it paraffin that will resolidify in the formation8 and reduce the porosity and permeability of the rock. This can lead to permanent production loss.

Chemical paraffin solvents directly dissolve the paraffin by the use of chemicals such as xylene which solubilize paraffins and which can carry a high level of paraffin without precipitation. These compounds have significant toxicity associated with them and must also be reapplied periodically in order to dissolve accumulations. Paraffin dispersants are similar compounds but are surfactants which dissolve paraffin accumulations somewhat similarly to detergents dissolving grease. These compounds may also have some degree of toxicity associated with them but are generally considered somewhat safer than solvent chemicals. Reapplication is necessary for continued control. Both attack the paraffin after they have been deposited.

Mechanical removal involves the use of paraffin cutting tool or "butter knife" which mechanically cuts paraffin accumulations from the well. Such tools are limited to areas that can be accessed and inserted in the well involved production downtime. This is the last resort to removing paraffin.

The Para-GeoBac bacterial culture products represent a different approach to paraffin control. These products utilize viable (living) microorganisms to control paraffin accumulation in oil wells. They rely on metabolic activity and metabolic products of bacteria for their effectiveness. The principal strains used in the products are facultative anaerobic bacteria. This means they are capable of growth in the presence or absence of oxygen. If oxygen is present, some of the strains will tend to use it as an electron acceptor and remove it from solution. If no oxygen is present, organic molecules or other electron acceptors present may be utilized. The organisms present in Para-GeoBac products have been specially selected and adapted to perform the product’s task of paraffin control. With Para-GeoBac products, the paraffin chains are attacked before they have a chance to crystallize, provided that the bottom hole temperature is high enough.

The exact biochemical mechanisms involved in the control of paraffin by the Para-GeoBac products have not been completely elucidated. It can first of all be due to the variety of strains utilized in the products. It is likely that the various processes which have been identified play selectively significant roles in different types of crude oils. Several products of bacterial metabolism can act as paraffin solvents. These include alcohol, aldehydes, ketones and fatty acids.

Second, bacteria which metabolize hydrocarbons produce various types of surfactants (emulsions and related compounds) which appear to be involved in the transport of these compounds across the cell membrane. These compounds are glycolipids, lipids or carbohydrates which actively bind to crude oil and alter its oil-water behavior.

Third, the cell surfaces of many bacteria are hydrophobic and actively adhere to hydrophobic surfaces such as those of oil droplets, metal surfaces or minerals. This adherence is often an essential requirement for growth and will also alter the behavior of oil-water mixtures. Both the production of biosurfactants and cell-surface hydrophobicity are involved in the demulsification properties of bacterial suspensions. This is covered in more detail under the section on demulsification, tank bottoms, and BS&W.

CORROSION

BACKGROUND

Corrosion of oil field production equipment is a complex phenomenon with a variety of causes. The increase in water production seen in older producing fields and the widespread use of water flooding has greatly exacerbated the problem. Corrosion is a function of the concentration of carbon dioxide, oxygen, hydrogen sulfide, sulfate reducing bacteria, or a combination thereof in water. Many other parameters of oilfield chemistry affect corrosion including chloride level, pH, temperature, and overall condition of the metallic surfaces of the well.

GENERAL CORROSION BASICS

In a simplistic sense, the driving force that causes metals to corrode is that the formation of a metallic structure requires energy which is stored in the structure. When a metal corrodes, this energy is returned to its surrounding environment. Only the rate of energy exchange is different. The diversity of types of corrosion is related to the nature of the metal as well as its environment. While the types of corrosion vary greatly, most corrosion in an aqueous environment can be viewed as an electrochemical phenomenon. The corrosion cell has four constituents, an anode, a cathode, an electrolyte, and a metallic pathway. All four items must be present for corrosion to take place. The term anode refers to that portion of the metal surface that is oxidized and corroded (metal loss). The cathode is the portion of the metal that is reduced. An electrolyte is an aqueous solution that can conduct electricity by the movement of ions. The metallic pathway can be any piece of metal that connects the anode and cathode.

Corrosion starts when potential is created between the anode and the cathode due to a dissimilarity in the metal or its immediate environment. This potential creates a current (electron flow) through the metallic pathway from the anode to the cathode. When electrons begin leaving the anode, metal ions are released into the electrolyte. Electrons travel on the metallic pathway to the cathode where positively charged ions, such as hydrogen, have gathered. The electrons that have traveled to the cathode begin combining with the positively charged oxidizers in solution around the cathode. If the electrons are removed from the cathode, the corrosion process will continue to proceed. In the corrosion of iron, the anode (metallic iron) will produce positively charged Fe++ ions which will go into solution, leaving behind two electrons (e-) for each iron atom. These electrons will flow through the metallic pathway. At the cathodic surface these electrons will react with neutralizing positive ions, such as hydrogen ions in the water. This neutralization can result in the formation of hydrogen gas and sometimes a net alkaline solution due to the accumulation of hydroxyl ions.

TYPES OF CORROSION

Oxygen Corrosion

Oxygen corrosion represents one of the most straightforward elements of the corrosion equation. Molecular oxygen is a relatively strong electronegative element that is an oxidizing agent. (Many other compounds are oxidizing agents, such as sulfide, which are completely dissimilar to oxygen). In its free form in water oxygen reacts readily with metallic iron to form insoluble ferric hydroxides.

$4Fe + 6H_20 + 3O_2 \Rightarrow 4Fe(OH)_3$

$2Fe(OH)_3 \Rightarrow Fe_2O_3 + 3H_2O$

Oxygen is an excellent cathodic depolarizer, meaning that it readily removes electrons from the surface of the cathode. The removal of electrons from the surface of the cathode in turn facilitates the corrosion process. Oxygen can enter into the production system through the use of fresh water in downhole operations, leaks in casings, leaks in flow-lines and stuffing boxes, and through tanks without gas blankets.

Carbon Dioxide Corrosion

The presence of carbon dioxide in production systems is common. The concentration of carbon dioxide can directly affect the pH of the produced water. Carbon dioxide is present in the form of carbonate and bicarbonate when the pH of the system is between 8.3 and 9.6, or just bicarbonate when the pH of the system is between 4.5 and 8.3. Carbon dioxide will act as a depolarizer in its acid form, carbonic acid. Carbon dioxide corrosion often occurs in combination with hydrogen sulfide. The areas of corrosion are widespread and look like long straight trenches in the surface of the metal. Carbon dioxide corrosion is most prolific in CO_2 floods after breakthrough.

Hydrogen Sulfide Corrosion

Hydrogen sulfide-based corrosion is another example of corrosion produced through the presence of an acidic substance. Hydrogen sulfide in oil and gas wells can be of geochemical or microbial origin. Dissolved hydrogen sulfide gas disassociates in water to form an acid.

$H_2S \Rightarrow H^+ + HS^-$

The sulfide ion is highly reactive with any free cations and will readily react with iron to form iron sulfide. Highly insoluble in water, iron sulfide will form black precipitates which are shed in the water phase of production. Such precipitates can be quite hard and can form thick deposits which can stick rods and plug tubing. The precipitates usually become oil-wet. When oil-wet, the iron sulfide can hang in the oil-water interface, causing oil-carryover and injection system plugging.

Microbially Mediated Corrosion

Certain specific groups of bacteria are associated with corrosion. These include principally the sulfate reducing bacteria or SRBs. Certain other types of bacteria are associated with the formation of slime layers and biomass which may be involved in plugging of screens, filters or pumps. Sulfate reducing bacteria (represented by the various genera in Table 2) generate, as part of their growth, sulfide by the reduction of sulfate. These organisms are obligately anaerobic and do not grow in the presence of oxygen. They generally utilize organic compounds as growth substrates. These bacteria have a long history of corrosion in the oil industry. Many genera such as Desulfotomacum are thermophilic (capable of growth at elevated temperatures) and thus are capable of surviving and multiplying downhole. They tend to attach to surfaces and multiply in colonies on surfaces. Their corrosion damage stems not only from the indirect production of hydrogen sulfide but also from the creation of a localized anodic environment under the colony. The increased iron in the water, from the localized corrosion cell, is then available for reaction with hydrogen sulfide to form iron sulfide.

CORROSION CONTROL

Neutralizing the corrosion cell can be used to reduce corrosion processes. This is known as cathodic polarization. It can occur naturally or through the use of inhibitors or linings. The protective cover (inhibitor or lining) acts as a barrier to the oxidizing agents (depolarizers), thus slowing the removal of electrons from the cathode. By slowing the removal of the electrons (increasing polarization), the corrosion process can be greatly retarded. Likewise, if this polarization is reduced, corrosion rates will increase.

Cathodic Protection

The goal of corrosion control is to increase metal passivity. This refers to the loss of chemical reactivity exhibited by certain metals and alloys under specific environmental conditions. One of the means of accomplishing this is by reversing the current flow from the anode by applying an external electrical current. This is known as cathodic protection. This system has been successfully applied to protect casing strings, storage tanks, and pipelines. Typical downhole corrosion mitigation is achieved using inhibitors.

Chemical Inhibitors

Chemical treatments for corrosion involve the use of either a water or oil soluble filming agent. These are generally molecules with surfactant type properties that readily coat surfaces and thus minimize the contact of the metallic surface with the electrolyte fluids. Desirable properties of such chemicals are good filming activity, good dispersibility in water, good cleaning ability and the formation of tenacious films which will last for extended periods of time. There are two ways in which to apply chemical inhibitors, batch and continuous treatments (inhibitors can also be squeezed, but it is rarely economical).

Batch treatments are generally how chemical inhibitors are applied. A batch treatment will introduce a large concentration of chemicals into the well at one time. This initially high concentration is responsible for the primary coating of the metal. There is very little chemical left in the annulus after the primary coat is applied. The chemical that is remaining in the annulus is responsible for repairing the primary coating. The drawback of batch treatments is that the lower amount of inhibitors is sometimes not enough to effectively inhibit corrosion throughout the entire production string. This "spotty" protection can often cause localized corrosion (pitting) which can cause premature failure of equipment; however, it should be noted that localized corrosion can occur in the absence of inhibitors due to solids or material deformities. The continuous treatment of inhibitors is usually applied with a "side stream flush". The inhibitor is applied down the wall of the annulus with the aid of a chemical pump. To help the inhibitor reach the fluid column at the bottom of the well a side-stream flush is supplied by circulating a small amount of production, usually totaling about two to five barrels per day. This method of treatment allows for the continuous application of the optimal amount of inhibitor on the production string at all times. The disadvantage of this method is that chemical pumps are prone to malfunctions, a chemical inventory must be kept, chemicals are always on site, and a third-party is usually responsible for keeping the chemical pot full of inhibitors.

Corrosion Control using Corroso-GeoBac Bacteria

Corroso-GeoBac is a bacterial culture intended for use in the prevention of carbon dioxide and sulfide-based corrosion, control of calcium carbonate, calcium sulfate, and barium sulfate scales, as well as control paraffin deposition. It acts to protect tubing and rod strings by sequestration and removal of corrosive components from metal surfaces. It is compatible with all other Para-GeoBac products at the dilutions recommended below. Corroso-GeoBac can also treat injection systems in the same manner as above while improving injectivity with its high surfactancy.

It is recommended that Corroso-GeoBac be used in sufficient quantities to obtain an initial concentration (based on total fluid produced or present) of 1000 to 5000 ppm. For best results, the product should be used with a minimum dosage frequency of every two weeks. Maintenance dosages should be determined by regular monitoring with weight-loss coupons or iron counts and by visual inspection of the treated material as the level of product is decreased to the optimal level. In general, it can be expected that the lower limit of product efficacy is 100 ppm based upon total fluid produced.

The paraffin controlling activity of the product is equivalent on a volume basis to approximately 75% of Para-GeoBac X and 25% Para-GeoBac XXX. Its spectrum of activity can thus be expected to treat most paraffins commonly deposited. The addition of Corroso-Geo Bac to Para-GeoBac treated wells may further improve paraffin control, in addition to providing corrosion inhibition.

As all living products are sensitive to environmental extremes, this product may show reduced efficacy when used in temperatures in excess of 140° F. The customer is referred to the Division 31 GEO-BAC bulletin "Product Storage and Handling Information" for further direction in the care and handling of the bacterial products of Division 31 GEO.

It is the policy of the Research and Development department of Division 31 GEO-BAC to continually improve our products. Thus, the specifications and microbial content of this product may be changed without notice.

DEMULSIFICATION, TANK BOTTOMS, AND BS&W

A frequent problem in oil production is the formation of stable emulsions between crude oil and produced water. Restrictions on the presence of water in oil by transport and processing systems have led to perpetual and costly efforts to reduce emulsions. Conventional treatments include the use of heat (such as in heater treaters and chemelectrics), demulsifiers, or a combination of the two. Some demulsifiers are made of cationic agents like alums or acids, and some are organic chemicals such as polyamines (cations). Alkyl benzene sulfonates (anions) and substituted polyalcohols (nonionic) are other demulsifiers. Other physical methods for breaking emulsions include the use of centrifuges or ultrafiltration, but these two methods are very rarely found in the oil field. Demulsification is a complex problem centering on the enormous variability in the petroleum and water components of the emulsions.

Emulsions broadly fall into two types: water-in-oil (W/O) and oil-in-water (O/W). (Figure 9). It has been shown that bacteria can demulsify both oil-in-water and water in-oil emulsions. The activity is related directly to the bacterial cell itself rather than any extracellular product of the cell. Cairns et. al. has developed a model for the demulsification of emulsions via bacteria in which bacterial cells act as wetting bridges between droplets in the continuous phase. Contact of an emulsion droplet with a bacterial surface causes a spreading of the droplet across that surface causing eventual contact and coalescence with other droplets contacting that surface. The activity of bacteria would thus be affected by the relative hydrophobicity of their surfaces.

It is likely that this model can be expanded by the contribution of the various products of bacterial metabolism such as biosurfactants, organic acids, and alcohols. The degradation of solid particles by bacteria can also contribute to emulsion destabilization. Surfactant and solvent molecules can contribute to demulsification by increasing the wetting efficiency of either bacterial surfaces or droplet surfaces. Contact angles of bacterial cells are observed to fall below the critical micelle concentration (CMC) of a given surfactant for a given hydrophobic substance. Since in almost all practical situations a very low concentration of bacteria relative to the total volume of crude oil is used, the concentrations of any biosurfactants will stay low, well below the CMC. It is unlikely that the bacterial treatment will enhance emulsions and in practice this has seldom, if ever, been seen.

Emulsion breaking with Para-GeoBac^{a} products has been very successfully in the case of tank bottoms and BS&W. This material, which is composed of a mixture of crude oil, water, mineral particles, and foreign matter, frequently collects in the bottom of tanks. These tank bottoms are most often caused by water-in-oil emulsions. The tenacious emulsions that form are due to mineral particles, which are known to stabilize emulsions (Figure 12), and are sometimes due to congealing oil. The conventional method for cleaning tanks can be costly, damaging to equipment, and dangerous to personnel. Para-GeoBac and other Division 31 GEO-BAC products have been used successfully to reduce BS&W and tank bottom levels in a safe and economic manner. Use of Para-GeoBac in downhole treatments has been shown to reduce BS&W accumulations in production storage tanks as well.

H2S CONTROL BY GEO-BAC PRODUCTS

Hydrogen sulfide (H2S) is a common component of oil field production. It can be naturally occurring, or it can be an indirect result of sulfate-reducing bacteria metabolism. It is a corrosive, and dangerous gas that must be controlled for optimal production to proceed. It can be detected at concentrations as low as 1 ppm. It deadens the human sense of smell at 30 ppm, thus making it extremely dangerous. In urban areas, its rotten egg odor induces complaints from the surrounding population. It is toxic at levels as low as 280 mg/m3 and is implicated in cases of poisoning in tanks, pits and other areas of low ventilation. It is also highly reactive to metals. It is important to appreciate the chemical parameters of the reactions to understand the complex relationships between hydrogen sulfide, oxygen, and various bacterial catalyzed processes.

In alkaline solutions in the absence of any bacterial species and organic matter, the following reaction can occur.

$H_2S + 2O_2 \Rightarrow H_2O + 2S$ (elemental sulfur)

Under acid conditions the following reaction can occur.

$H_2S + O_2 \Rightarrow H_2SO_4$ (sulfuric acid)

Note that both of these reactions require oxygen to occur. Reaction (2) tends to yield a more acidic solution and is a more predominate reaction in nature. It is also catalyzed in nature by various members of the genus Thiobacillus, which can grow under extremely acid conditions. They can also function under anaerobic conditions.

Under anaerobic conditions, the following reaction can occur.

Fe (or other metals) + $H_2S \Rightarrow FeS + 2H$

In nature, the primary source of sulfur exists as sulfate ions or as organic sulfur which is comprised of the sulfur containing amino acids, cysteine and methionine.

Free sulfate ions can be assimilated directly by a variety of aerobics or anaerobic processes. In the aerobic process, the sulfate ions go directly to organic sulfur, bypassing sulfide generation. Most sulfide production occurs by bacteria under conditions of anaerobic respiration where sulfate is used as an electron receptor and not as a co-metabolite of organic sulfur metabolism. The limiting factor for most microorganisms which cause H_2S production in nature becomes the number of free sulfate ions which are present in the water. Bacteria which are capable of assimilating sulfate directly will effectively sequester and compete with microorganisms. This is one principal mechanism by which organisms, which are heterotrophic and can directly assimilate sulfate, are able to limit sulfide production by sulfate-reducing bacteria. This assimilation is facultatively anaerobic and can occur in the presence and absence of light. Thus, competition for the sulfate can occur under both aerobic and anaerobic conditions. Because the production of sulfide is an anaerobic or microaerophilic process, competition for the sulfate ions can occur in environments different from those involved in sulfide production. (Figure 13)

A second, less important mechanism for the sequestration of H_2S is the light dependent process of bacterial photosynthesis. This process allows H_2S to be oxidized to elemental sulfur, organic sulfur, or sulfate by purple sulfur and green bacteria. In conditions where light is present, this may be an important mechanism of regulating the H_2S content of water.

SCALE CONTROL

The increase in water production and water flooding that is seen as producing oil and gas fields age has contributed greatly to the relative importance of scaling in production systems. "Scale" is the collective term used for various insoluble salts that form precipitates in oil field equipment in contact with water. These vary in chemical composition. Scale types and frequency are dependent upon the type of production, geographic region, as well as the geology of water origin. Scales can form in many areas; within the formation, at the formation face, the length of the tubing string, on sucker rods and in downhole pumps; it can form in surface vessels and on the heating surfaces in the heater treater. In the water handling system, scale can form in pumps, surface lines and formation faces in the injection reservoir.

Traditional treatments for scale involve mechanical removal (a very limited approach) and chemical treatment. Chemical treatment involves two basic types of treatment, acidization and chelation treatment. Acidizing is commonly performed as a scale removal method. It involves the application of mineral acids such as hydrochloric acid. It is expensive and involves handling dangerous chemicals. Chelation treatments involve the use of chemicals that bind divalent cations such as calcium, barium, and magnesium and prevent their deposition as scale. These treatments generally are not used for scale removal as is acidization, but they are used for the inhibition of scale formation. The chemicals used in oil fields today generally are of three types: (1) phosphonates, (2) polyphosphoric acid esters, or (3) polymers of acrylic or methacrylic acids.

Many factors influence the formation of scale. These include temperature, pressure, pH and presence of other ionic compounds notably sodium chloride (ionic strength). Chlorides can have differential effects on the formations of various types of scale. For example, increasing the concentration of chloride to 100,000 ppm generally increases the solubility of calcium carbonate, calcium sulfate and barium sulfate. The commingling of fresh water can thus promote scale formation. Fresh waters also often contain high levels of anions such as sulfate and carbonate, further aggravating the scaling problem. Above 150,000 ppm, chlorides can promote calcium sulfate scaling. Temperature also tends to increase the solubility of most scales. Temperatures above 100°F tend to promote calcium sulfate scale. Falling fluid temperatures, caused by gas escaping from solution as fluids rise through the well, tend to promote scale formation also.

The complexity of scale formation has led to the development of various types of indices to predict whether scaling will occur in a certain type of water. These include the Stiff-Davis index for calcium carbonate and the Skillman, McDonald, and Stiff index. These indices, commonly used in water analysis laboratories for oil fields, are of utility in predicting scale formation. These indices show only the tendency of waters to scale; they do not predict the formation of scale.

The chemical events involved in the formation of scale can be divided into three parts: (1)formation of micronuclei of salts (e.g. aggregates of calcium carbonate) suspended in aqueous phase or attached to surfaces, (2)growth of these micronuclei to a critical size that promotes aggregation with other micronuclei, and (3) formation of crystalline solids composed of these aggregated micronuclei on surfaces to form visible scale deposits. Conventional chemical scale inhibitors are threshold inhibitors, i.e., they inhibit the development of these micronuclei to critical size. They accomplish this by sequestering or celebrating available divalent cations so that growth cannot continue and by preventing precipitation of the micronuclei to heat transfer surfaces where temperature drops make scale formation likely. Scale inhibition can thus be summarized as each or all of the following activities.

(1) Anti-nucleation stops or modifies crystal growth

(2) Sequestration holds metal ions tightly, chelate calcium, magnesium, and other multivalent metal ions.

(3) Anti-precipitation ⍰ maintain solids suspended in water and prevents deposition on surfaces.

Microorganisms can produce substances that mimic many of these properties of scale inhibitors. For example, one of the products of microbial metabolism is organic acid, which can act as a chelating agent for divalent cations. The removal of metallic ions and the solubilization of calcium carbonate by microorganisms is a well-documented phenomenon. Microorganisms can also produce extracellular substances such as polysaccharides, polyphosphates, lipopolysaccharides, phospholipids, glycolipids, and proteins that have chelating, anti-precipitation, filming, and biosurfactant activities. By selecting appropriate organisms and/or altering their nutrients and growth conditions, the production and activity of these compounds can be enhanced. Litho-Bac, a scale inhibition product of Division 31 GEO, is an example of such a microbial culture product.

The total weight of scale deposited on corrosion coupons, as well as the precipitation of the simulated carbonate brine, is decreased by the addition of Litho-GeoBac prior to addition of calcium solutions. The activity against calcium sulfate and the effect observed against barium sulfate is also illustrated. There is little change in the pH of the solution throughout the process.

Litho-GeoBac has been used for scale inhibition in a variety of situations involving scale and corrosion. These include oil and gas wells as well as water injection wells and above ground production equipment. Two other groups of scale inhibiting products are produced by Division 31 GEO. These are Corroso-GeoBac, and the "+" products of Para-

Bac. Corroso-GeoBac is a combination corrosion and scale inhibitory product, and the “+ " products combine the anti-scaling activity of Litho-GeoBac with the paraffin controlling activities of Para-Bac.

SAFETY CONSIDERATIONS

There is sometimes concern for the use of bacteria for commercial applications. This concern usually arises due to the perception by many people that micro-organisms are dangerous and produce diseases. While it is true that many diseases are produced by bacteria, fungi or viruses, it is equally true that the total number of microorganisms that produce disease are a very small fraction of the total number of different species of bacteria. There are high numbers of bacteria of many different species in various environments such as soil, fresh and salt water that do not cause any apparent disease in any animal or plant and whose presence is not associated with any detrimental effect. In fact, microorganisms play the key role in recycling various compounds such as nitrogen, carbon, and oxygen in the environment. Without microorganisms, life could not exist as we now know it.

Microorganisms have been used in food production since recorded history began. Egyptian hieroglyphics describe beer and bread manufacture. In addition to the production of alcoholic beverages, various types of microbes are used to produce yogurts, cheeses, various oriental foods, vinegar, and breads. There are now commercial ventures in which microorganism biomass (cell bodies) are being used as food stuff. This is known as single cell protein (SCP). In industrial applications, microorganisms are used for antibiotics, insulin, and various types of food supplements such as amino acids and vitamins. The use of microorganisms in industrial applications is mushrooming (no pun intended) and the future holds the likelihood that they will be used in the manufacture of plastics, fabrics, and fuels as well as a range of other products.

Another group of microorganisms which have created concern are genetically engineered microorganisms (GEMs). These organisms are produced by technology which allows the recombination of deoxyribonucleic acid (DNA), the genetic material of living organisms, between different types of microorganisms and even between different phyla of organisms. For example, the human gene which codes for insulin can be introduced into the common intestinal bacterium, Escherichia coli, and be used to produce insulin of a higher purity than that formerly available from sheep. Such a product is now commercially available. GEMs are of growing commercial importance in a variety of commercial areas.

Concern over GEMs has come from the possibility that the introduction of foreign DNA may result in a "super bug" which may run amok or produce incurable infections or have some other environmentally damaging occurrence. Although no instance of this has occurred and is considered unlikely, such organisms are tightly regulated by the Environmental Protection Agency (EPA) and cannot be released into the environment without a lengthy review and approval process.

> In contrast to extensive public concern over GEMs, the use of naturally occurring microorganisms has caused little official concern. Indeed, so little concern is shown that the EPA has indicated that they have chosen not to regulate them at all. A copy of a letter to this effect is enclosed in this section. More recently, the EPA has reaffirmed this position in meetings with the Applied Biotreatment Association, an industry trade group.

None of the organisms found in the Division 31 GEO-BAC products are genetically engineered or pathogenic for animals, plants, or humans. In the history of the company, there has never been an incident of any adverse health effect being reported regarding our products. The principal strains found in the Para-GeoBac products were derived from a marine environment. Rigorous quality control procedures ensure that no foreign organisms are introduced into the product. An additional concern to oil field personnel has been the possibility that sulfate-reducing bacteria may be introduced or stimulated by our product. Each product lot is controlled for sulfate reducing bacteria (SRBs). There are no documented instances of the products either stimulating hydrogen sulfide levels or SRB counts in oil production system.

Para-GeoBac products have been tested in the standard American Public Health Association fish toxicity test. The product shows no toxicity at typical use concentrations. This is in contrast to the relatively high concentration of two commonly used oilfield chemicals (a paraffin solvent and a corrosion inhibitor).

Other relevant toxicity testing is available. These products are negative in the Ames carcinogen test as well.

The material safety data sheets (MSDS) for each of the products are found following this section. Our products are prepared with standard microbiological nutrients and minerals for growth. All of products are cultured in US facilities. The products are not directly obtained from any natural sources. While our exact formulations and types of bacteria used are held as proprietary information, we use no secret catalysts or other mysterious ingredients in our products. They are scientifically developed and scientifically prepared and quality controlled.

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