CHEMICAL SUPPORT FOR CARBON DIOXIDE ENHANCED OIL RECOVERY PRODUCTION OPERATIONS

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ABSTRACT

As with all EOR techniques, the injection of carbon dioxide into oil bearing reservoirs causes fundamental changes in the chemical and thermodynamic properties of the reservoir fluids, not only as they exist in the reservoir, but also as they are produced. Additionally, because of the dynamic nature of CO_2 flooding, the produced fluids (gas, oil and water) will change continually as various areas are swept and produced. Thus, producing wells, satellites and production batteries will experience constantly changing fluid conditions throughout the life of the project. Although various portions of the production system can approximate equilibrium, change is inevitable.

Given these conditions, chemical programs used in production operations must be designed with flexibility in mind. Chemical treatments must accommodate produced fluids whose tendencies to deposit scale, corrode steel, deposit paraffin and form emulsions are changing. This paper will address changes that must be made to transform traditional production chemical programs into systems that can maintain the efficient production in CO_2 enhanced recovery.

INTRODUCTION

The scope of this paper will be limited to considerations that should be made to anticipate changes in production operations that may result as producing wells begin to respond to CO_2 injection. Specifically, the changes that must be made in production chemical treatment programs will be discussed. The discussion will include considerations for chemical choice, methods of application and performance monitoring. Injection side operations will not be discussed.

As with the design of any chemical program, a complete and thorough understanding of the production system, including the physical mechanics and the reservoir fluid chemistry is essential. Without a clear understanding of the existing production operations, it is impossible to anticipate potential problems and develop possible solutions. A knowledge of operational experiences on similar projects can allow some extrapolation. However, extrapolations are nothing more than educated guesses. Their reliability is generally low due to reservoir variability. Often the best one can hope for is accurate prediction of the possible trends in changes that will develop as floods mature.

Given that enhanced oil recovery processes cause changes to occur, it is essential that these changes be monitored, especially changes that could mean the development of upset conditions or equipment failure. Properly designed monitoring programs should detect change and elicit response. A response might involve altering both physical and chemical programs within the production facility. For example, a rise in a producing well fluid level might require changing the corrosion inhibitor application technique from batch addition to batch addition with circulation. It might also involve changing from a rod pump lift method to a submersible pump lift method. Each change should evoke a planned response.

Pre-Flood Assessment

Prior to the implementation of a CO_2 flood, a complete review of the production facility equipment should be undertaken. Well completion configurations, system metallurgy, vessel sizes and pressure ratings should be analyzed in light of the proposed flood. Chemical programs should be reviewed and updated. Methods of chemical application should be especially noted; i.e., squeezes, batch with circulation, continuous slipstream flush, etc. Past gas and fluid analysis and previous operational problems related to the chemical programs should be reviewed.

As CO_2 injection progresses, a series of physical and chemical changes begin to occur at the producing wells and throughout the production facility. Below are some of the changes that can occur:

Physical Changes

1. Increase in reservoir pressure at producing wells
2. Increase in producing well fluid level (well can begin to flow)
3. Increase in Gas Oil Ratio
4. Increase in the amount of produced solids (sand or iron sulfide)
5. Decrease in Water Oil Ratio

Chemical Changes

1. Complete change in produced water ionic make-up (particularly HCO_3-, CO_3=, SO_4=, Ca++, Mg++, Ba++, Sr++)
2. Shift in produced water pH to a buffered minimum
3. Increased CO_2 content as a percentage of the produced gas
4. Increased corrosivity to mild steel
5. Change in the produced oil physical and chemical characteristics
6. Increased incidence of paraffin and asphaltene deposition
7. Increased tendency for emulsion formation

It is very difficult to predict which, if any, of these changes will occur and to what extent they will affect production operations. However, knowing that they may occur and being prepared to deal with their adverse affects can mean the difference between a project that is constantly upset and a project that responds to operational problems with strategic solutions. By monitoring certain parameters closely, most operational problems can be anticipated and dealt with before an upset occurs.

Corrosion Inhibition

The problem which causes most concern in production operations that will produce CO_2 flood oil is corrosion. Carbonic acid corrosion of mild steel is well documented.[1,2] The increase in CO_2 partial pressure that occurs during CO_2 flooding will probably increase corrosivity or at the very least change the corrosion mechanisms. Most of the available data regarding shifts in corrosivity associated with increases in CO_2 partial pressure are similar to those shown in Figure 1. It must be noted that most of the data regarding CO_2 corrosivity has been developed in the laboratory and not on producing oil wells. The magnitude of the change in corrosivity seen in the field will depend upon the brine chemistry, the reservoir temperature, the presence or absence of H_2S, the CO_2 flooding pressure, fluid velocities and produced fluid volumes. Many producers who have operated CO_2 floods do report increased corrosivity.[6-9,11,12,14] However, most increases have been controllable. Designing production systems that can protect against increased corrosivity can be accomplished in many different ways.[4] Monitoring the performance of the corrosion control program is always essential.[3-5,12]

Corrosion control programs designed for CO_2 floods have included combinations of metallurgy, plastics, coatings and chemical inhibitors.[6,10] Because of the expense involved, exotic metallurgies are not often employed in producing wells. Thin film epoxy coatings and spray metal coatings are extensively employed. Fiberglass rods are also receiving more wide-spread acceptance as are fiberglass and polyethylene piping for surface facilities. Regardless of the program that is employed, most facilities rely on chemical corrosion inhibitor programs to supplement the other corrosion control measures for the protection of exposed mild steel.[7-9]

Many producers have found that traditional corrosion inhibitor formulations employed during primary and secondary recovery operations can be effective when chosen and applied properly during CO_2 floods.[10-13] Generally, a combination of laboratory screening tests and field trials are required to choose the proper inhibitor and the method of application. The application of the inhibitor becomes very important because of the highly corrosive nature of the CO_2 saturated produced fluids.

Several factors make the application of chemical corrosion inhibitors difficult in CO_2 floods. First, the fact that the producing well water oil ratios will drop as tertiary oil is recovered means that inhibitors might have to be changed from chemicals that perform well in high water cut regimes to chemicals that perform well in lower water cut regimes.[12] Thus, water soluble inhibitors may have to be replaced with oil soluble or water dispersible inhibitors as the oil cut goes up and is replaced again as it goes back down. Second, because of increasing reservoir pressures and increasing annular fluid levels, getting inhibitors down the annulus and back around can become impossible.[4,5,17] Unless the inhibitor gets to all of the exposed mild steel surfaces, including the casing at the perforations, the pump, the rods and the production tubing, the components can be placed at risk of corrosive failure. These components are generally the most expensive components in the entire facility. Techniques that involve the circulation of inhibitor-in-oil solutions,[11,12] downhole capillary injection (Figure 2)[8], slipstream continuous addition or squeezed applications[7] have all been employed with varying degrees of success. Pressured-up wells that are flowing through the annulus present special problems. Squeeze treatments[15] or capillary injection treatments are the only workable techniques that can verify effective application. Finally, wells that begin to deposit scales and paraffins or to produce large amounts of solids[9,14] may require special programs to address the complications that solids cause; e.g., underdeposit corrosion and erosion-corrosion.

In order to choose the proper inhibitor, a reliable performance monitoring technique must be employed, both during the field trials and throughout the flood.[5,12] There are many methods available for monitoring corrosivity. However, many are not suited for detecting the rapid changes in corrosivity that can occur during the different stages of a CO_2 flood. Generally, a combination of techniques is most reliable. The various weight loss techniques do not alert to short-term changes and cannot differentiate between general corrosion and the pitting type corrosion that can occur in wet CO_2 systems. Iron counts can indicate changes in corrosivity, but they have limited value in systems that contain hydrogen sulfide. Copper ion displacement (CID) tests can verify the presence of an inhibitor film but are not useful in day-to-day monitoring. The electrochemical techniques that employ linear polarization are very useful in determining instantaneous corrosion but they require constant water contact and can give erratic corrosion rates due to iron sulfide films. Potentiodynamic linear polarization techniques can differentiate pitting from general corrosion, however, they are time consuming and they require a certain degree of expertise to operate the instruments and interpret the results. Electrical resistance techniques are versatile but they cannot differentiate pitting from general corrosion; they don't give instantaneous corrosion rates and they can give false readings as a result of conductive scale deposits.

One other point that should be mentioned is that corrosion monitoring devises that evaluate corrosivity on the surface may not be very sensitive to the corrosion that is occurring downhole. Corrosivity can be significantly worse downhole where CO_2 partial pressures and temperatures are higher. Establishing a correlation between surface measurements and actual downhole measurements may be very important. Specially designed downhole retrievable coupons can be used for this purpose (Figure 3).

The optimum corrosion monitoring system may be approached by combining several techniques which together can monitor instantaneous corrosion, differentiate pitting corrosion from general corrosion, and give simple, reliable corrosion rates without complicated or time consuming procedures.

Scale Inhibition

Predicting whether chemical scales will deposit during production operations is difficult enough in systems that are under simple reservoir pressure depletion. During CO_2 flooding, these predictions are complicated significantly by factors such as:

1. Solubilization of CO_2 in the reservoir water resulting in the increase of dissolved carbonate species and decrease in pH
2. Reservoir anhydrite solubilization releasing Ca^{++} and $SO_4^{=}$ into the water
3. Reservoir calcite solubilization releasing Ca^{++}, HCO_3^{-} and $CO_3^{=}$ into the water

4. Reservoir pH decrease destabilizing soluble Ba++ and SO_4= in the brine
5. Produced water pH increase during CO_2 flash-off in the production well
6. Cooling in the production wellbore associated with CO_2 flash-off

All of these elements make it difficult to predict whether or not CO_2 injection will cause scales to deposit. The only really effective means of predicting deposition is through constant monitoring of changes in the water chemistry of the fluids being produced. By monitoring certain sensitive components, it is possible to identify an increase in the scale forming components in the water and recognize potential scale problems. Having no feeling for the water chemistry can mean sudden and unexpected scale deposition that can result in many unnecessary workovers or scale clean-ups.

As with the application of other chemicals, the choice of scale inhibitor will be dictated by the nature of the scale and the produced water chemistry. Both static and dynamic screening tests are available that can approximate the production system in choosing the most likely candidate for the job. Field trials on strategic wells are always recommended.

Applying scale inhibitors to the production system can be as complicated as applying corrosion inhibitors, for basically the same reasons. Squeeze applications of inhibitors can be very effective and can last for many months and sometimes years.[16] Performance monitoring is accomplished by verification of inhibitor levels in the produced fluids. Scale inhibitor residuals can be monitored in the produced fluids and graphed versus time after the squeeze. It should be remembered that the continuous presence of scale inhibitor is necessary to ensure that deposition does not occur. At predetermined minimums, the wells must be resqueezed.

Paraffins/Asphaltenes

Paraffin and asphaltene components in the reservoir crude can also undergo significant changes during CO_2 flooding.[18,19] Medium and higher molecular weight hydrocarbon components can be displaced during high pressure miscible displacement. Consequently, crude components that weren't displaced prior to CO_2 flooding can be mobilized and produced. Heavy ends can be left behind as the front passes and later produced with the WAG cycle.[9] The low pH effects of dissolved CO_2 in the reservoir water can also cause asphaltene components in the crude to crosslink and precipitate.

Paraffins and asphaltenes that are solubilized during multiple contact miscible extraction can become less soluble when pressure drops occur at the production wells. The loss of the hydrocarbon light ends and CO_2 can cause deposition in wellbores and production equipment. The cooling associated with CO_2 flash-off in the wellbore can also cause deposition because of the relatively high melting points of these type hydrocarbons. The deposits can cause plugging problems and make electrochemical corrosion monitoring difficult.

Compounds that control paraffin and asphaltene deposition are generally segregated into categories which describe their functionality. They can act as detergents, dispersants and crystal modifiers. Once the chemical composition of the deposit is determined, a chemical can be recommended. Once again, tests that simulate the production facility are used to screen possible chemical candidates.

Although batch treatments are used most often for clean-ups, squeeze and continuous techniques are more effective preventative measures. Monitoring performance is generally done by physical inspection during workover. Paraffin deposits can exist as one component in a scale deposit.

Oil Dehydration And Water Clarification

Complications with oil dehydration and water clarification during CO_2 flooding most often result from the increased production of solids with breakthrough. These solids may be mineral scales, iron sulfide fines, paraffin, asphaltenes, reservoir fines, drilling mud solids or formation sand and clays. Some CO_2 floods in sandstone reservoirs have reported significant increases in sand production.[9,14]

Solids complicate oil and water separation by forming pads at the oil water interface in the free-water-knock-outs and heater treaters. In general, chemical programs that have been employed prior to the implementation of the CO_2 flood should be reevaluated. The gross changes in the oil and water chemistry of the produced fluids may mean that the demulsification and water clarification chemicals will no longer be effective. The chemicals may also have to be modified slightly to deal with the produced solids.

CONCLUSIONS

In general, chemical programs at producing fields that will undertake CO_2 flooding should be reviewed and updated. Potential changes in mechanical configuration, pressure, temperatures and produced fluid characteristics should be taken into consideration as the new program is established. Production systems must be analyzed individually, taking into consideration the unique chemical and physical characteristics. Some guidelines are as follows:

1. The system corrosivity will change. New inhibitors and applications techniques may be required. Monitoring corrosivity is essential. Continuous inhibitor addition to protect exposed mild steel well components may be necessary.
2. Because of changes in the produced water chemistry, scaling tendencies will also change. Reservoir heterogeneity and rock composition will play a large part in determining whether or not scales will deposit. In scaling systems, continuous inhibition will be required.
3. Miscible displacement of reservoir oil by CO_2 can result in the solubilization of paraffinic components not produced during primary and secondary production. Paraffin deposition may become severe in producing wells as a result of cooling and loss of solubility during the pressure drop.
4. In crudes that contain asphaltenes, precipitation and deposition may occur as a result of crosslinking at low pH and loss of solubility during multiple contact extraction.
5. Changes in produced oil and water characteristics may require a complete change in the oil dehydration and water clarification programs. Dealing with produced solids may become necessary.

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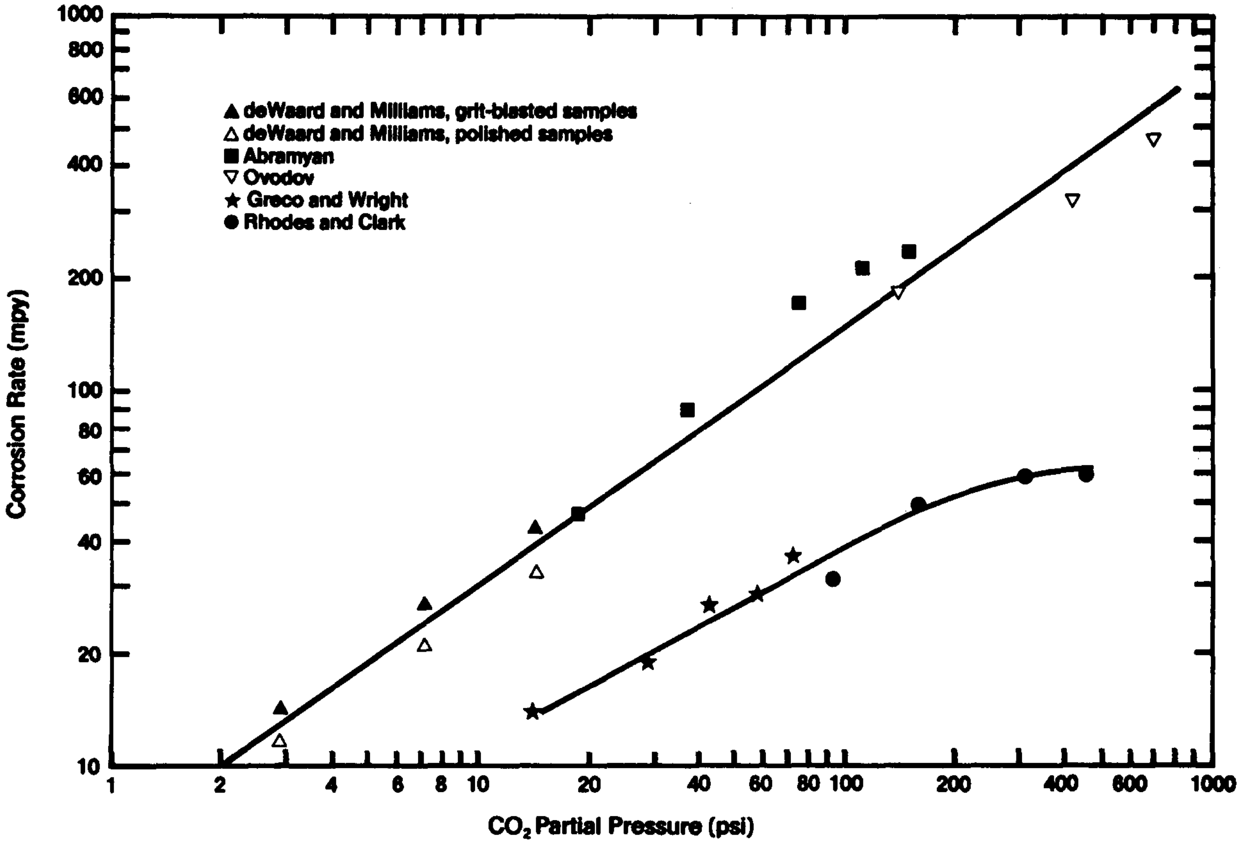

Figure 1 - Uniform corrosion rate of carbon steel as a function of CO_2 partial pressure (graph taken from Reference 1)

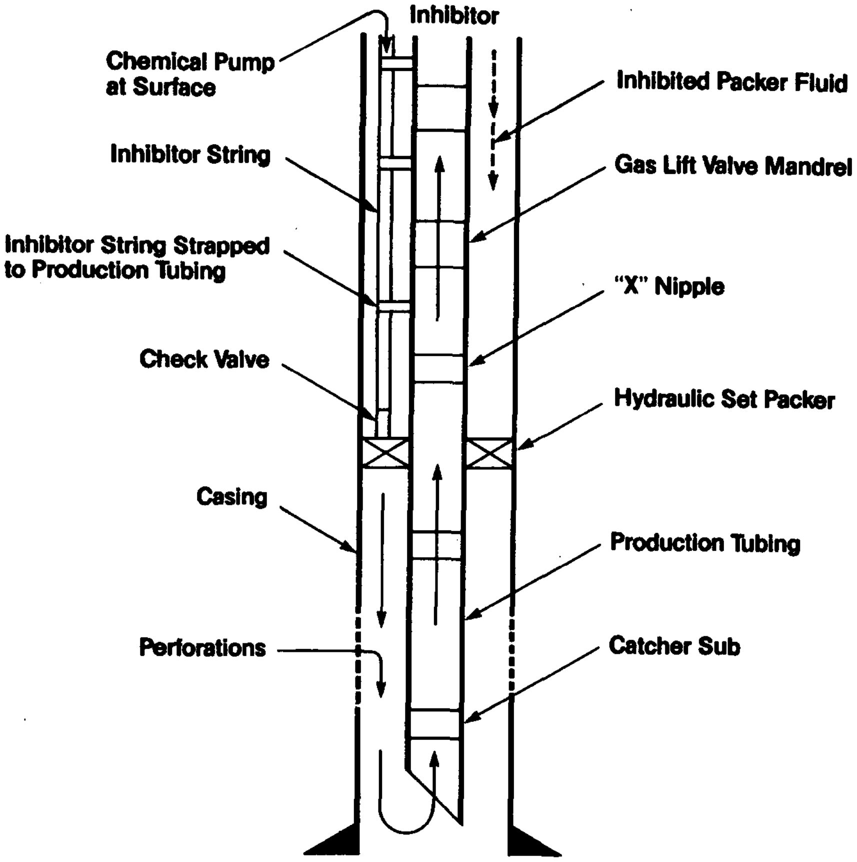

Figure 2 - Down-hole capillary corrosion inhibitor addition. Note: inhibitor must go past perforations

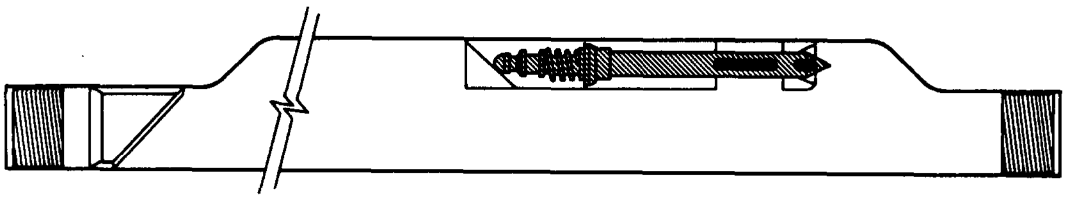

Figure 3 - McMurry-Hughes side pocket mandrel with modified pocket and corrosion monitoring carrier