Modern Inhibitor Programs For Modern Petroleum Production Systems

DR. R. R. ANNAND
TRETOLITE DIVISION, Petrolite Corporation

INTRODUCTION

Treatises are available which describe in detail the chemical structures which have been found to be corrosion inhibitive. The number and diversity of these compounds is quite large. However, when practical applications are considered, the number of truly different chemical types decreases considerably. In fact commercially available inhibitors for petroleum production systems are largely derived from a limited number of raw materials from the production of amines and natural-product carboxylic acids. Oxyalkylation is a frequently used modification.

In the author's experience covering ten years of research, field testing, and development, those factors which make one inhibitor work better than another in field use are more likely to be physical rather than chemical. Thus if two compounds are in the right chemical structure class for the kind of corrodent, how well the compound matches the needed dispersibility, thermal stability, and other compatibility features is going to be more important than small differences in the chemical structure. It is still necessary to match the chemical structure of the inhibitor to the chemistry of the corrodent, but once this is done, the problem is not solved until the physical properties match the application. Thus, for example, corrosion due to dissolved oxygen must be combatted with different types of compounds than for corrosion due to dissolved H_2S or CO_2. However, once this choice is effectively made, then the match between the method of application and the properties controls the success of the program.

The required choice of the proper chemical structure for the corrodent to be inhibited is only made through extended laboratory testing. This is one of the important functions of the inhibitor supplier, and cannot be readily carried out in the field. On the other hand, the proper choice of a match between the physical properties of the inhibitor and the mechanical features of the production equipment requires cooperative effort between the inhibitor supplier and the producer. The parameters which should be considered in making this match are the subject of this paper because field matching is required.

BATCHWISE INHIBITOR TREATMENTS OF OIL AND GAS WELLS

Batchwise inhibitor treatments are most often used because the total number of possible variations is quite large. This number of variations provides great latitude for matching available manpower with the economics of treatment and with the proper inhibitor for effective corrosion control. Batchwise treatments are used in both oil and gas wells by introducing a volume of chemical into the well so that it contacts all of the surfaces which should be protected. When good contact is made under the right kind of conditions, the inhibitor forms a long-lived protective film and corrosion rates remain very low between treatments.

When selecting the proper inhibitor for batchwise application to a corrosion problem, it is necessary to match both the chemical and physical properties of the available inhibitors to the chemical and physical features of the corroding system. For example, even when CO_2, H_2S and O_2 are present in gas gathering systems, corrosion is significant only where liquid water collects. Gas phase corrosion (attack of steel or other alloys) is not important at temperatures below 350-400° F. On the other hand, very pure water without any dissolved salt, or acid gases, or oxygen is relatively uncorrosive. However, when water, oxygen, and H_2S all occur together corrosion rates are very rapid indeed. Thus to properly choose an inhibitor, it is necessary to know what is causing the corrosion and where it occurs. When these facts are known, a compound, with the proper chemical and physical properties to achieve control, can be selected.

The nature of the inhibitor must be adapted to the corrosion conditions. Compounds which are effective as inhibitors against oxygen corrosion are different from those which are effective against H_2S and CO_2 and these in turn are different from those required for mixtures of H_2S and O_2. In many cases, water-soluble inhibitors work more effectively when a hydrocarbon phase is also present because a more protective film is formed. The rate of formation of the protective film and the life of the film are both important variables for batchwise and other treatments. Experience has shown that dispersed compounds (either in oil or in water) form a film more rapidly and are retained in the film longer than those which are completely soluble. In all cases, protective films which are formed in the presence of the corrosive elements are more persistent than those formed by coating the metal externally and then immersing in the corrodent. Probably it is because of this feature that even the best filmers provide better corrosion control when low concentrations of inhibitors are continually present in the fluids during the time between batch treatments. By appropriate adjustment of volume of inhibitor and of flush, this condition can be achieved without continuous injection pumps even in wells which are pumped off so that no fluid stands continuously in the annulus.

Batch Treatment of Pumping Wells

In treating oil wells, the chemical may be used in undiluted form or diluted with solvent or emulsified in water. If used undiluted, it may be either oil or water soluble, but a flush of produced fluids or recirculation of well fluids is ordinarily necessary to ensure that the chemical reaches the bottom of the well. The recirculation time will vary from one-half to eight hours for treatment volumes varying from one quart to ten gallons. The usual path which the inhibitor follows is to fall through the annular space between tubing and casing and then to return through the bottomhole pump with the produced fluids.

If the chemical is diluted, the choice of diluent will depend upon whether the chemical is oil or water soluble. Inhibitors are routinely diluted with water, brine, produced fluids, crude oil, or local solvents. In this application the treatment volume is usually between 1 and 30 gallons with a flush of produced fluids used to insure that the chemical gets all the way to the bottom of the well. The flush volume may range from 0 to 10 barrels. Usually with the larger volumes of diluted chemical, it is not necessary to flush.

Some inhibitors are easily emulsified, and therefore can be applied in emulsified form in much the same way as the diluted inhibitors. These compounds are usually classified as oil-soluble/water-dispersible. They may be emulsified with water, brine, or produced fluids having a high water content. One of the prime objectives of using emulsified inhibitors is to enable the inhibitor to fall through a standing column of hydrocarbon found in the annular space where wells are not pumped off. For this purpose a treatment volume of 5 to 30 gallons may be used with 0 to 10 barrels of flush from the produced fluids.

The characteristics of the individual lease (perhaps even of the individual well) determines the kind of chemical inhibitor which should be used. Thus, if H_2S is present in the produced fluids, it is important to choose an inhibitor which is good for this kind of corrosion. If CO_2 or oxygen are causing the corrosion, inhibitors appropriate for these corrodents should be chosen. If the produced fluids have a very low water cut, then an oil-soluble inhibitor would probably be more effective than a water-soluble one. On the other hand, in those situations where a high volume of produced fluids stands in the annulus, and where the water predominates in the produced fluids, frequently a water-soluble inhibitor is more effective than an oil-soluble one. Inhibitors function by forming a protective film at the metal surface; thus how long the film lasts after no more inhibitor is present in the fluids, is an important property of the compound.

One of the most economically important questions which must be satisfied by the chemical inhibitor treatment is how frequently must the well be treated. Our experience in looking at the individual application in detail, shows that the most important feature of the behavior of the inhibitor which has an influence on the frequency of treatment is the amount of feedback coming from the annulus. Once a good inhibitor film is laid down on a metal surface, only a few ppms of inhibitor are required to keep it in repair in most cases. Thus, the length of time (number of days) the inhibitor feeds back from the annulus has an important bearing on the time between treatments. Also, the concentration of the chemical produced by feedback is important. Even if a chemical is used which does not have a long film life, if a high concentration is returning from the annulus, the effective treatment life in the well can be quite long.

Two other characteristics are also important; they are the initial concentration which produces the protective film and the detergency of the chemical. It can be demonstrated in the laboratory that high concentrations of inhibitors generally produce more rapid filming (more rapid reduction of corrosion rate) than low concentrations do. Therefore, when the chemical is batched in and circulated, if a high concentration is present, a good film is more likely to be produced than if a low concentration is present. Furthermore, deposits of paraffin, scale, etc., tend to prevent formation of a good inhibitor film. Thus, if the chemical has a high detergency, i.e. removes the deposits and prevents their further formation, it will have added effectiveness.

In some produced fluids and in some types of equipment, emulsion stabilization or emulsification caused by the corrosion inhibitor slug is a problem unless specially formulated compounds are used. Usually a highly oil-soluble or highly water-soluble compound will not cause emulsion problems. However, those which are oil-soluble and water-dispersible (or perhaps vice versa) will sometimes cause problems. If it is necessary to use this kind of product (say for detergency) then a formulation containing a demulsifier is necessary to combat the emulsification characteristic. Needless to say, the demulsifier additive must not interfere with the corrosion protection or cause an adverse change in the frequency of treatment.

To sum up the batchwise inhibitor treatments of oil wells, it is possible to generalize the factors which must be taken into account in the design of inhibitor protection for any oil well. In all but the special variations of the batch treatment discussed below, a volume of inhibitor is introduced into the annulus of the well. The total volume of fluid contained in the annulus, and the distance through which the inhibitor must fall through this fluid to reach the produced fluids, are both important factors which will determine which compounds are effective. Furthermore, the production rate (total fluids) will determine how much inhibitor is necessary per treatment and to some extent will determine the frequency of treatment. In those cases where the producing days are prorated this will have a bearing on the frequency of treatment also.

The composition of the annular fluids will be important. For example, if the annulus is full of oil and an oil-soluble inhibitor is used, either of two situations will have to develop before any inhibitor comes around through the production stream: (1) Several successive batches or one large batch of chemical will have to be put into the well to produce a high concentration of chemical in the annulus so that inhibitor is pulled through the pump into the production stream; or (2) a big enough flush volume should be used to move the upper layers of inhibitor-containing fluids down to a place where the pump can pick them up. Of course, if the annulus is filled with both water and oil, then an inhibitor emulsion (in water) can be used to get the inhibitor through the oil phase into the water phase, and therefore, closer to the pump. A relatively large volume of emulsified fluid or of flush in this case will help considerably.

The amount of time available for the recirculation will have an influence. In not enough time is available to completely replace the annular fluid, then the amount of inhibitor used will have to be chosen to provide a high concentration in the annular fluid. By this means, that amount of this fluid which does come around into the production string has enough inhibitor in it to produce a good protective film. When the appropriate information is available covering all of these factors, it should be possible to select an inhibitor which will provide good economic protection. It is still necessary, however, to have laboratory or field test data showing that the inhibitor will inhibit the corrosion when it is made properly available to the corroding surfaces.

Batch Treatment of Gas Wells

The controlling variables in the types of applications of inhibitors to gas wells are the kind of well completion and the thermal stability of the inhibitor relative to the bottomhole temperature. When concentric strings are available so that a continuous treatment is possible, this is preferable. If concentric strings are not available, continuous treatment is eliminated and the well must be treated, therefore, by some form of a batch application.

There are at least five types of batchwise treatments used in gas wells. They include simple batching of standard gas well inhibitors (plus solvent sometimes); tubing displacement; inhibitor squeeze treatments; atomized inhibitor squeeze treatments; and heavy inhibitor treatment. Each of these is related to the other in the sense that a limited volume of compound is put into the well in one batch and then the well is allowed to flow for a period of time until the next batch of inhibitor is put down. The chemical nature and equipment required vary considerably, depending upon the kind of application.

In the treatment where a standard gas well inhibitor compound is pumped into the tubing and allowed to fall to the bottom while the well is shut in, it is usually diluted with either lease condensate, diesel, or perhaps some other cheap solvent. The dilution ratio can range from 1 + 1 to 1+9 (inhibitor plus solvent). The final volume of the diluted inhibitor may range from 50 to 500 gallons. This volume is pumped into the well as rapidly as possible and the well is left shut-in for time periods ranging up to 48 hours. Except for heavy inhibitors, gas well inhibitors are generally oil soluble.

Most experience with gas wells leads to the conclusion that if any of the tubing is covered by a standing column of liquid when the well is shut in, it is only a very small proportion, perhaps less than 10 per cent. Otherwise the well drowns and must be bailed or otherwise stimulated to get it to produce after treatment. Recent radiotracer experiments in dual completions using a gamma logging tool to log the inhibitor show that high density is not necessary for the inhibitor to fall to the bottom of gas wells of any depth down to at least 25,000 feet. The inhibitor solution runs down the tubing walls but does not fall through the gas.

The results from many radiotracer experiments show that the time required for flow to the bottom varies with the total volume of inhibitor plus solvent. Flow rate is also dependent on viscosity. A low viscosity gives a high flow rate. The maximum observed flow rate has been 3000 feet per hour for a mix of one drum of a standard gas well inhibitor plus seven barrels of lease condensate.

The total amount of inhibitor used must match that required to plate onto the pipe walls. For this reason one drum of inhibitor is recommended for each 10,000 feet of tubing to be covered. This amount of inhibitor should be diluted with from 5 to 10 volumes of solvent (lease condensate, diesel fuel, or other). There is enough leeway in these dilutions so that any tubing size up to and including four-inch diameter can be accommodated. However, for depths less than or more than 10,000 feet, the volume of inhibitor should be adjusted proportionately. For example, one-half drum (plus 5-10 volumes of solvent) is used for 5000 feet; two drums (plus solvent), for 20,000 feet, etc.

The proper shut-in time will depend on the fall rate of the inhibitor plus the hold-up time for any chokes or other small bore constrictions in the tubing string. Our experience shows that for a standard gas well inhibitor used at the rate of one volume plus five to ten volumes of solvent, allow 10-15 minutes shut-in time for each 1000 feet of tubing. Add 1-2 hours for each small bore constriction and allow 40-50 minutes of shut-in time for each 1000 feet below the first constriction. The allowance for constrictions is an arbitrary average from our experience, but in the absence of undue blockage of the choke bore it should prove adequate. Low viscosity and low surface tension both contribute to fast flow through small bore constrictions.

The compound chosen for this use should be a good inhibitor for the corrodent present in the well (CO_2 or H_2S). It should be appropriately stable at the well temperature (no undue tendency to form gunks). A dispersed compound (not completely soluble in the solvent but not thick and syrupy either) will plate out more effectively than a soluble compound but the dispersion should have good stability.

When the well is turned back to production much of the inhibitor comes back as a slug of high concentration in the first produced fluids. This can sometimes lead to troubles in downstream equipment in the form of deposits, emulsions or foams. Thus, one of the properties that the inhibitor should have is that it should be compatible with the downstream equipment such as dehydrators, gas plants, etc. As a minimum, the compound should probably contain a demulsifying component to combat emulsion and/or foam problems caused by the large concentration of inhibitor returned in the first slug.

Since one of the objectives of the batch treatment is to get a maximum time period between treatments, it is desirable to have an inhibitor with a long film life. Most inhibitors with long film lives are also ones which have a decreased solubility in highly aliphatic solvents. They require, instead, aromatic solvents. The aromatic/aliphatic character of condensates, diesels, and other cheap solvents varies considerably from location to location in the country and perhaps from time to time, depending upon the refinery runs. The compound should be compatible with highly aliphatic solvents and with the condensate from the well. It is not strictly necessary that it be completely soluble. However, if a hazy-type dispersion is formed, it should be stable and not separate into two phases during the required time period. This time period is determined by the total number of hours from make-up of the solution all the way through the time when the well is turned back on. Thus, if the inhibitor is to be made up the day before the well is to be treated, and the well is to be shut in for 48 hours, it is necessary that any dispersion formed should be stable for at least 72 hours. This requirement usually means that the compound must be soluble in the diluent. Thus, where it is necessary to have maximum solubility/stability for maximum time (several days), it is best practice to check the compatibility of the inhibitor and the solvent to be used. This can be done by making up a small sample of inhibitor plus diluent in the desired ratio and checking for haziness. If there is a haze, there should be no separation during the desired time period. Compatibility with the lease condensate can be checked similarly.

Variations of the Batch Treatment

There are four variations which fall under the definition of batchwise treating given above but which are done sufficiently differently to warrant further discussion. They are tubing displacement, inhibitor squeeze, encapsulated inhibitors and heavy inhibitors. Each of these types of treatment involves a particular combination of chemical properties and treatment method. The choice of type of treatment to be used is always governed by economic consideration as well as the type and availability of surface equipment, and of the kind of well completion, or production method.

Tubing Displacement—In this treatment the inhibitor (usually diluted) is pumped into the tubing and then pushed all the way down to the formation face by pumping solvent behind the inhibitor. The well is then turned to production whereupon the inhibitor recontacts the tubing surface on the way back up. The diluent and follow-up solvent may be condensate, diesel, or some other readily available solvent. Thus the solubility requirements are similar to those for the batch treatment although usually the length of time during which the inhibitor/solvent combination must hold together is minimum (from a few hours up to one day). Sometimes the inhibitor is deliberately emulsified in water and this emulsion is used instead of the usual solution. For this type of application it is preferable to use water which has a low total dissolved solids content because a stable emulsion is most easily formed with this kind of water.

The dilution ratio for the inhibitor mixture ranges from 1 + 1 to 1 + 6 (inhibitor plus solvent). The final volume of mixture will range from 50 to 350 gallons. Several more drums of solvent are required to fill up the tubing as the compound is pushed down. A large-volume high-pressure pump is required for this operation in order to carry it out in a reasonable period of time. For very deep wells or for wells where the formation is hydrocarbon sensitive, a nitrogen in water disposition has been used as the push vehicle for the inhibitor mixture. Sometimes the well is shut in after the inhibitor reaches the bottom; usually a 24 hour shut-in period is the maximum time allowed.

In this case also most of the inhibitor mixture comes back as a slug of high concentration when the well is turned back to production and, therefore, the composition probably should contain demulsifying components to combat emulsion and/or foam problems in the downstream equipment. As with the other methods, the compound should be the kind of compound that readily produces a protective film at the dilution used. It should also be one that has a long life. Thermal stability requirements of this application are not great but the compound should inhibit effectively at the bottomhole temperature. It should also be a good inhibitor for the kind of corrodent present in the well and for the kind and amount of water produced.

Inhibitor Squeeze—Inhibitor squeeze treatments are used for gas wells perhaps more frequently than for oil wells. In this application the inhibitor must be completely compatible with the solvent used and with the produced hydrocarbon so that gunks are not formed which might impair productivity of the well. Also, the thermal stability requirements in a gas formation are usually maximum in that the temperatures will be higher and the residence time may be from two months to two years. Successive squeezes usually produce longer lived treatments than the first one.

In this kind of treatment an inhibitor solution is forced into the formation with a pump working against the natural pressure. Following this, an overflush of fluids is put behind the inhibitor to provide displacement of the chemical into the formation. The inhibitor is retained in the formation and then is slowly released into the produced fluids over a long period of time. The mechanism of retention is usually due to adsorption and absorption involving the inhibitor and the clay binding for the formation sands. Some of the inhibitor is known to be retained permanently in the formation. If properly done, one-third or more of the inhibitor will be readily released. In general, the inhibitor is made up as a solution in some readily available hydrocarbon diluent. The solution ratio for the inhibitor solution ranges from 1 + 1 to 1 + 10 (inhibitor volume + solvent volume). The final volume of the inhibitor solution mixture is one to two barrels. The amount of overflush is determined on the basis of the volume contained by the tubing; from 0 to 5 tubing volumes may be used.

The factors which determine the effectiveness of the squeeze treatments are those which concern the interaction between the inhibitor and the clay-binding materials primarily, and the inhibitor compatibility with the diluent and the produced fluids secondarily. Thus, the treatment life will be longer if there is a large volume of inhibitor reversibly retained in the formation. This is true because there will be inhibitor available to the produced fluids for a longer period of time and because the concentration of inhibitor returning in the fluids will be higher and, therefore, more likely to be protective.

A high clay content in the formation solids will lead to a high irreversibility of absorption of the inhibitor, and therefore to a low return concentration and a shorter treatment life. Usually upon multiple treatment, clays tend to become saturated with inhibitor and treatment life becomes longer. Furthermore, if large overflush volumes are used, the inhibitor is displaced more widely in the formation and, therefore, is more likely to adsorb irreversibly to the clay. Of course, a long film life characteristic of the inhibitor compound itself will add to the total treatment life. Inhibitor compounds with low solubility in the produced fluids will tend to reside in the formation for a longer period of time and thereby prolong treatment life if the concentration of returning inhibitor is adequate.

The inhibitor compatibility factor needs to be considered from two other standpoints also. If the inhibitor/solvent combination does not make a reasonably good solution then the ease of squeezing may be affected because a large pressure surge occurs when the inhibitor reaches the formation. If the formation is easily fractured, this surge may lead to some incipient fracturing and subsequent alteration of reservoir characteristics. On the other hand, there are some compounds which cause clay to swell or are otherwise incompatible with formation components. If these were to be used as squeeze inhibitors, they could cause plugging.

A variation of the inhibitor squeeze is to use an inhibitor which is atomized into a stream of nitrogen so that the gas contains a stable aerosol of inhibitor when it is squeezed into the formation. One of the advantages of this process is that the pressure surge seen in normal squeezes when the inhibitor reaches the formation interface is much, much lower in this type of squeeze so that the danger of fracturing the formation is much, much less. The nitrogen gas is used to push all of the inhibitor into the formation but no overflush solvent is used.

The inhibitor is made up as a solution in a relatively high-boiling solvent so that good atomization of the chemical is obtained in the gas stream. Total volume of inhibitor will be one to seven barrels. Much of this comes back to a high concentration in the first few days of production just as it does from a standard squeeze. All of the other remarks with regard to stability of the inhibitor and compatibility with formation fluids apply equally well to this kind of treatment as to the standard squeeze.

Encapsulated Inhibitors—In this variation of the batch treatment, a liquid inhibitor surrounded by an encapsulating shell is used. The individual particles are weighted to a density which will allow them to fall through brine. A batch is introduced into the well to fall through the annular or tubing fluids so the capsules rest on the bottom and slowly release their inhibitor from that point. The inhibitor goes into the produced fluids and contacts the production equipment to form a protective film. The weight and size of the capsules must be such that they will not be readily washed out by the velocity of the fluid if they are to be used in a location above the perforations.

An alternate location is in the rathole below the perforations. In this case, the inhibitor must come through the capsule shell and then float through the rathole fluids to the level of the perforations at which point it is picked up and moved through the production equipment. The inhibitor release rate is always a function of temperature with higher temperatures leading to faster release. Thus, the kind of inhibitor contained in the capsules and the kind of capsules have to be matched to the bottom-hole temperature of the well. A long film life characteristic of the inhibitor is not particularly necessary but the inhibitor must have the right compatibility with the produced fluids.

A prefilming liquid treatment is frequently used. Also it is usually necessary for the capsules to reside in a rathole if a very long (weeks to months) treatment life is to be obtained. A rathole probably *decreases* the effectiveness of water-soluble inhibitors contained in capsules because the total rathole fluid must be brought up to a high concentration of inhibitor before enough is transferred to the produced fluids to maintain a good inhibitor film on the production equipment. However, once this has come about then long-lived treatments are possible.

Heavy Inhibitors—A recent addition to the arsenal of inhibitor treatments for gas wells is the use of heavy inhibitors. A heavy inhibitor is one that is formulated to have a high density relative to the formation fluids. The densities may run from 9 to 14 pounds per gallon. In the application, the inhibitor is pumped into the tubing without dilution and allowed to flow to the bottom of the well with production shut in. Shut-in times range from 2 to 48 hours, depending upon the depth of the well, the demand for production from that well, and the characteristics of the inhibitor. In recent experiments carried out by the Tretolite Company in cooperation with producers, it was found that the inhibitor *flows* down dry tubing in the upper parts of the well. If there is a standing column of fluid in the lower parts of the well, it then may fall through this column. However, the major time to get to the bottom is taken up by the process of flowing down the dry tubing walls and through the storm choke.

The thickness of the film flowing down the walls, the viscosity of the inhibitor, and the temperature of the formation all determine the rate of flow of the inhibitor. Due to the fact that a diameter reduction occurs at that point, storm chokes cause a serious impediment to the flow and may well be the single largest determining factor in the rate of flow all the way to the bottom of the well. From one-half to two drums of the inhibitor is used in the treatment. In our experiments we have found that a useful shut-in time for use in gas wells from 5000 to 15,000 feet treated with one drum of chemical is to allow 50-60 minutes shut-in time per thousand feet of tubing above the first small bore constriction (choke). Allow 2-5 hours shut-in for each constriction and 1.5-2 hours for each 1000 feet below the first constriction. These estimates should allow for differences between storm chokes, well temperatures, tubing diameters and other operating conditions but still ensure a reasonable time period for contacting all the walls of the tubing to produce a protective film.

We have found, however, that even when the well is flowing, the inhibitor will be deposited on the lightly coated sections of the tubing, both in the upper reaches and the lower reaches. When the well is returned to production, the major portion of the inhibitor returns as a highly concentrated slug but there is a considerable amount left in the hole which, if properly formulated, will repair patches of bare metal which may develop during the life of the treatment. Treatment lives vary from one to six months, or even longer.

Heavy liquid inhibitors are also sold for batch treating oil wells. In using these compounds for this purpose relatively large volumes (one-half to two drums) are put into the open annulus or pumped into the tubing (with the well shut in) so the liquid can fall to the bottom of the well. When located below the perforations, the inhibitor slowly releases active ingredients to the produced fluids, thereby providing a long treatment life. In order to be effective, the compound must have a density which is large relative to the density of the produced brine.

The inhibitor release rate will depend upon the amount of agitation at the point where the inhibitor resides, as well as on the bottomhole temperature and, perhaps, on the compatibility of the weighting agent with the chemicals in the well fluids. Thus, even though the compounds are difficultly soluble in water, agitation will disperse them and increase the release rate. High bottomhole temperatures function similarly. Those compounds which contain zinc or other heavy metals with insoluble sulfides may come apart in H_2S - containing fluids, and thereby release the inhibitor too rapidly. Zinc sulfide may be objectionable also if it tends to form deposits. If a large enough volume of inhibitor is used to reasonably fill a rathole below the perforations, then a very long treatment life can be obtained.

From the above description of the types of factors involved in the application of heavy inhibitors, it is apparent there are a number of features which a compound designed for this kind of treatment should have. First of all, the compound should have a minimum viscosity for maximum flowability in the upper parts of the hole. Higher density materials will flow faster, but viscosity is more important. Furthermore, the compound must hold together (not separate into its components) during its fall through the well fluid. If it does not hold together, it will be diluted or unduly dispersed and will not be available in high concentration for filming the tubing walls. Thus, it must be basically insoluble in both oil and brine but at least dispersible in brine (if not both) upon mechanical action. The greater the density of the compound, the more rapidly it will fall through the well fluids. Of course, the composition must be heavier than brine in order to fall through it at all. The composition should be such that it will readily form a long-lived inhibitor film as it flows down the upper parts of the tubing and falls through the lower parts.

Beyond these factors the composition should also have those properties which are necessary for any inhibitor used in oil and gas wells. That is, it should not have any plugging tendency when it comes in contact with formation materials. The compositions should probably contain a demulsifying component in order to combat emulsion and/or foam problems caused by the large concentration of inhibitor which returns when the well is put back on production. The weighting agents should not be heavy elements, such as lead or arsenic, because these cause difficulties in the refinery or petrochemical plant. For similar reason, halogenated hydrocarbon solvent cannot be used for obtaining high densities. The weighting agent and the chemical itself must be matched well for the chemical composition of the corrodent. That is, the chemical must be able to inhibit H_2S if H_2S is present, but H_2S should not cause a decomposition of the inhibitor. Of course, the composition should have adequate thermal stability and perform well as an inhibitor at the bottomhole temperature.

CONTINUOUS TREATMENT FOR OIL WELLS

There are several approaches to continuous inhibitor treatment. Perhaps the most common is where an inhibitor pump is pumping inhibitor directly into the annulus of an oil well, with provision for a continuous flush of produced fluids provided through a valve on the lead line. This type of treatment is particularly useful when the water volume is large compared to the oil volume and/or when the corrosion is particularly difficult to control. A successful application will be one in which the inhibitor has the proper solubility/dispersibility/detergency characteristics for the fluids pumped.

Thus, for high water volume wells, a water-soluble or water-dispersible inhibitor is probably necessary for this kind of treatment. If paraffin or sulfide deposits are also a problem then an inhibitor with a built-in detergency is useful. The volume which must be pumped to give the correct concentration of inhibitor in the fluid is usually adjusted by the settings of the pump and not by dilution of the compound. The total production is used as a guide for setting this volume; it may range from 1 or 2 ppm up to 50 ppm.

The volume rate of flow of the flush fluids has to be adjusted in order to adequately wash inhibitor down the annulus and around into the produced fluid stream. This volume should be higher for deeper wells and for those which contain a standing column of hydrocarbon than it is for shallow wells pumped dry. The adjustment is usually made by means of a needle valve on the lead line. The nature of the produced fluids is such that it is difficult to keep these valves functioning properly for long periods of time because they tend to plug up. Therefore, frequent attention to the setting of the valve is needed in order to maintain an adequate flush volume.

A second type of treatment is where the inhibitor pump works into a small diameter string of tubing called a "macaroni" string. This tubing will usually be approximately ¼-inch diameter and will extend from the surface down to the vicinity of the bottomhole pump. When it is used, a flush is not necessary so that greater reliability in distribution of the inhibitor is obtained. It is, however, more difficult to run tubing when a macaroni string is used. The same principles of inhibitor selection apply to this application as to the one where the pump works directly into the annulus. That is, the inhibitor should be properly selected for solubility/detergency characteristics and should be pumped at a rate which is proper for the concentration desired in the produced fluids.

Another application of inhibitors for continuous treatment is found in gas lift wells where the inhibitor is continuously pumped into the lift gas prior to going downhole. In this application enough inhibitor is pumped into the gas not only to inhibit the gas but also to inhibit the produced fluids. It is necessary to have an injection nozzle which will adequately atomize the compound into a rapidly flowing section of the gas stream so it will carry the full distance required from the point of injection to the lift valves. A 10-20 per cent dilution of an oil-soluble inhibitor is used or perhaps an oil-soluble/water-dispersible inhibitor. The diluting solvent should have a high-boiling point to prevent evaporation between the point of injection and the lift valves. On the corrosion protection leg (in the production tubing), the inhibitor should have the proper solubility/dispersency / detergency characteristics required by the corrosion conditions. Sometimes (but not always) the annular space below the lift valves can also be inhibited in this way. Other times, special precautions are necessary.

CONTINUOUS TREATMENTS FOR GAS WELLS

In this type of application for gas wells, the corrosion inhibitor compound or a dilution of the compound, is pumped continuously through a string of tubing all the way to the bottom of the well where it mixes with the produced fluids and returns through the production string. Since the in-well residence time may be as long as 60 days, good thermal stability is necessary. That is to say, the compound should not polymerize or otherwise form gunk at the bottomhole temperature. Thermal stability is always a function of time and dilution with longer times and higher concentrations leading to more likelihood of thermal breakdown. Thus, continuous injection of a concentrated compound represents the maximum requirement for good thermal stability.

It is also important that the inhibitor be able to inhibit corrosion at the high temperatures at the bottom of gas wells. This property is not necessarily related to the polymerization or gunking properties. It is equally possible that the compound could break up into little pieces rather than form long polymer chains and thereby become ineffective as an inhibitor. Often the polymer chains (gunks) are still good inhibitors.

Similarly, the compound should be compatible with the diluent for at least as long a time as the residence time in the tubing. It should be compatible with the condensate when it mixes at the bottom of the hole and it should not cause deposits, emulsions, or foams to form in any of the downstream equipment. Usually the concentration used for continuous injection is low enough that this is not a problem. However, inhibitors formulated with demulsifiers and antifoamers are available for use if this situation should develop.

The treatment level to be used should be determined by that amount required to maintain a *minimum* iron concentration in the water returned from the well. Usually the treatment levels range from 1-2 quarts per million cubic feet down to ½ to 1 pint per million cubic feet. Since workovers on gas wells are usually a good bit more expensive than workovers on pumping oil wells, the monitoring for corrosion should be more carefully done. The easiest way to do this is by determining the concentration of iron dissolved in the water coming from the well. When this is done it is never found that the iron goes absolutely to zero but rather it decreases to some low value under proper inhibitor treatment. The number of ppm's of iron at this low value will be determined by the relative corrosivity of the fluids, and the volume of fluids relative to the total area of pipe exposed. Dissolved iron contained in the fluids resident in the formation also will influence the reading. Thus, in some situations, 50 to 100 ppm of iron in the water represents a good protection because the iron levels will rise as high as 500 to 1000 under complete absence of protection, whereas in other wells one to two ppm's represent good protection and 20 to 30 ppm represent a badly underprotected condition.

INHIBITOR TREATMENTS FOR WATERFLOODS

A number of different compounds are used in treating flood waters for the prime purpose, or at least the secondary purpose, of preventing corrosion attack. Perhaps the most commonly encountered are inhibitors, scavengers, biocides, scale preventives, and detergents. Many times, one composition with multiple properties is used.

The composition should be soluble or at least easily dispersible in order to avoid deposition of gums and tars which would aggravate the corrosion problem. However, when the formation into which the water is injected will stand it, the use of dispersible compounds will sometimes provide better protection in extremely aggressive systems. Some of the multiple components injected into flood waters are basically incompatible until they have been diluted in the stream somewhat. For example, most inhibitors interfere with the action of bisulfite and its derivatives used as scavengers if they are mixed together at the time the scavenger is removing the oxygen. For another example, when chlorine or hypochlorite is used as biocide, both scavengers and inhibitors interfere by taking up some of the oxidative power of the biocide. Therefore, some care has to be applied in the application of multiple compounds to avoid one component cancelling out the effects of another.

Recently, scavenger compatible inhibitors have been developed. However, the usual solution to the inhibitor/scavenger interference is to inject the scavenger first and then the inhibitor is put in far enough downstream from the scavenger injection point to allow for adequate reaction time. The usual solution to the chlorine or hypochlorite interference with the inhibitor or scavenger is to use the hypochlorite or chlorine treatment as a periodic slug and to remove the inhibitor or scavenger during the period of time the biocide is in use. In any event, adequate attention needs to be paid to these features in order to promote proper control.

In some systems intermittent injection is perfectly acceptable particularly in the case of inhibitor, biocides and detergents. The general features of this process are essentially the same as with continuous injection. It is necessary to use an inhibitor which has a significant film life. Usually, water-dispersible inhibitors are more likely to have a long film life than completely soluble inhibitors. A biocide which works most effectively in slug treatment is a necessary choice for this type of approach also. When detergents are treated intermittently, care must be taken not to overload downstream filters or not to plug the formation with the accumulated material which is released by the detergent.

Chemical Requirements of Waterflood Compounds

Each of the types of components listed above which are used to treat flood waters are subject to some specific chemical requirements in order for them to be able to perform their function. The corrosion inhibitor should provide maximum corrosion protection for minimum concentration. For present purposes a corrosion inhibitor is defined as a compound which decreases the corrodibility of the metal by formation on it of a protective film. The inhibitor should be compatible with the water, i.e. it should not form gunks, or tarry deposits on the exposed equipment or most particularly, on the formation face of the injection well. The compound in the injection water should be compatible with the formation receiving water, particularly in the presence of iron sulfide or small amounts of entrained oil. It is often found that this oil/FeS mixture in combination with some types of inhibitors can be damaging to formation permeability. The compound may be completely soluble or it may be dispersible within the limits of compatibility described above. However, for intermittent injection it should exhibit an adequate film life and this usually means a dispersible compound.

The inhibitor should be compatible with all the other compounds used in the system and effective in their presence and it should keep the metal surfaces reasonably free of gross deposits of corrosion products such as iron sulfide, iron oxide, etc.

A scavenger is defined as a compound which reacts with and thereby decreases the corrosivity of the corrodent. Usually the chemical which is to be scavenged is dissolved oxygen from the air. However, other types of oxidizing species such as iron (III) and chlorine could be scavenged with an appropriate reducing agent (e.g., hydrazine). The scavenger should provide a maximum decrease in corrosivity for a minimum concentration of the compound in order to be economically feasible. It should be compatible with both the water and the formation into which the water is injected. Since the total residence time in a waterflood system will be short, the reaction time should be very short. Five minutes should be the maximum time at the temperature of the flood water. Of course, the scavengers should be suitably compatible with all the other compounds added to the water and effective in their presence. As mentioned above, this sometimes requires some manipulation for bisulfite and its derivatives used as oxygen scavengers in the presence of inhibitors.

The presence of H_2S in the water is a complication because H_2S and bisulfite (or its derivatives) react to form sulfur. This reaction uses up scavenger that would otherwise go to remove oxygen. Furthermore, usually H_2S will be present in large amounts and therefore it is not feasible to use an excess of scavenger to make up for that amount lost to the H_2S reaction. In addition, elemental sulfur which is produced in this reaction is prone to form deposits and to plug the formation. This is a serious concern because it is not easily removed by solvents or acidizing.

The solution to the problem is to put in the scavenger before mixing with the H_2S containing water. At least two minutes of reaction time should be allowed before mixing; it is preferable to have five minutes reaction time.

In some systems, it is not possible to eliminate the oxygen before mixing with the H_2S containing solution. In these systems it is necessary to have a special inhibitor. Chromates won't work; they don't inhibit the oxygen corrosion. Recently, a new type of compound has been developed for just this situation. These compounds are sulfo-phosphated organic inhibitors. They have been found to be very effective against mixtures of H_2S and O_2.

Biocides contribute corrosion protection by decreasing biological deposits (and thereby the pits which tend to grow under them) and by decreasing the H_2S concentration levels caused by sulfate-reducing organisms. The biocide itself may be corrosive (as are chlorine and hypochlorite) or inhibitive (as are most quaternary ammonium compounds) or indifferent (as are chlorinated phenols). These factors should be taken into account in planning the overall program. For example, as mentioned above, chlorine could remove inhibitor by reaction with it and therefore should not be added at the same time as inhibitor is added. However, a quaternary compound used as a biocide could very well reduce the amount of inhibitor necessary to maintain adequate corrosion control. As with the other additives, biocides should be compatible with the formation solids and with the water and as well as with all the other compounds, and it should be effective in their presence.

Scale preventives contribute corrosion protection by decreasing the deposits under which pits often grow. Sometimes carbon dioxide or acids are used to prevent carbonate scales. When these are used they may contribute extra corrosivity to the water and add to the protection load carried by the inhibitor. Whatever the compound is, it should be compatible with the formation, the water, and the other additives in the water, and it should be effective in their presence. Scale inhibitors are sometimes squeezed to get the advantages of batch treatments.

Detergent compounds are added (usually to other components) to keep the system clean and free of deposits. Thereby they contribute corrosion protection because they tend to eliminate those places where pits can grow. These compounds should also be compatible with formation and water and with the other compounds and effective in their presence. It is particularly important that the detergent does not interfere with the activity of the inhibitor by preventing it from laying down a protective film. Usually it is not a problem to find a detergent compound which will aid the inhibitor by removal of deposits. In fact, inhibitor detergent combinations are readily available.

Many times, combination additives are used. The most common combinations are as follows: Inhibitor/scale preventive; inhibitor/biocide; inhibitor/detergent; scavenger/detergent; and biocide/scavenger/detergent. These combinations must meet the same chemical requirements as the individual components.

Methods of Addition of the Compounds

The most often encountered method of treatment of flood waters is to continuously inject the composition into the water stream so as to produce a fixed concentration in the flood water. The usual injection point is just ahead of the suction to the high pressure pump. In these applications the stream concentration may range from 5 to 100 ppm. Sometimes the inhibitor is diluted with alcohol or water to from 5 to 50 per cent of its normal concentration. In large streams, it is important that the injection point be well chosen so that maximum mixing over a minimum distance is accomplished.

Another common injection point for corrosion control components is down the annulus of the source well followed with a continuous flush as would be used in the treatment of an oil well. In this case the corrosion control of the annulus may be an important feature of the application and may require special attention. If this is so, highly soluble inhibitors generally will provide less difficulty from deposits (and corrosion under same) than the dispersible compounds.

INHIBITION OF NATURAL GAS PIPELINES

There are really only two types of approach to the inhibition of natural gas pipelines. One of these is to treat with a liquid slug pushed down the line so as to lay down a film of inhibitor, and the other is to treat continuously with an atomized solution of inhibitor. The atomization approach is to be preferred because it guarantees a continuous access of inhibitor to the surface and therefore, uncertainties in the film life, etc., are not a problem.

Continuous Treatment

A diesel engine fuel injection nozzle is frequently used to provide the atomization of the compound into the gas stream. It is desirable to make a very stable aerosol so it will carry a long length down the line. Monitoring at various positions along the line with coupons is mandatory. The coupons should be checked for both weight loss and for pitting in order to get the maximum reliability for determination of corrosion protection.

Approximately a 10 per cent solution of inhibitor in a very good solvent should be used. The compatibility of the inhibitor and the solvent should be checked to be sure that the inhibitor is completely soluble (no haze apparent). Many of the better inhibitors for these applications are more soluble in the aromatic solvents than in highly aliphatic ones. Therefore, if the choice can be made between one with appreciable aromatic content and a solvent such as diesel fuel, the aromatic content solvent is preferable. If it is known there will be problems with water collecting in low spots, then an inhibitor which has some dispersibility in water is preferred in order to enhance the ability of the inhibitor to penetrate the water and inhibit corrosion in the low spots. For this situation, the amount of inhibitor to be used should probably be kept high. If possible to locate coupons or other corrosion monitoring devices in the low spots this should be done.

How far the inhibitor will carry down the line is determined by the kind of hydrodynamic flow and/or by the amount of liquids in the line. If the liquids are present, the inhibitor will go where the liquids go. If the line is almost dry then the amount of inhibitor plus solvent injected per day relative to the hydrodynamic flow conditions determines how long it takes to cover the pipe walls from one end of the line to the other. Under conditions of slow flow rate (feet per second) and little or no gas line liquids, it could take as long as 3 or 4 days to traverse a mile of 24-inch pipe. If the line is very long, multiple injection points are necessary to obtain adequate coverage.

The concentrations of inhibitor used range from 1 to 2 quarts per million cubic feet down to ½ to 1 pint per million cubic feet. When appreciable liquid phase is present, the proper volume of inhibitor to use is determined by the concentration produced in the liquid phase. This is only qualitatively related to the gas flow rate (MMCFD). Large amounts of liquids require larger volumes of inhibitor to produce an inhibitive concentration. The proper con centration should always be confirmed with coupon and/or inspection data. The lower injection rates will only be safe when confirmation is obtained.

Some of the pitfalls which must be avoided arise because the inhibitor application must be compatible with downstream equipment. If there is a gas plant at the end of the line, the inhibitor may cause emulsion problems. If there are solid bead absorbers, it can cause loss of activity. Extra hot, extra dry gas can evaporate the solvent too rapidly, and therefore, the inhibitor will deposit as a gunk before it gets to the end of the line. Proper selection of compounds and/or remedial measures such as the use of demulsifiers or anti-foamers at the gas plant will eliminate the problems.

CONCLUSION

In choosing an inhibitor composition for production systems, the "inhibitor" characteristics of the compound is only one of the many necessary properties. Solubility, dispersibility, thermal stability, and solvent compatibility are also dominant factors in choosing compounds for control of corrosion in oil wells, gas wells, gathering systems, and waterfloods. The composition must be a good inhibitor to do the job but if the application and the type of inhibitor are not properly matched, the inhibitor will never get to the job site.