CORROSION CHARACTERISTICS AND CONTROL IN DEEP, HOT GAS WELLS

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INTRODUCTION

For the purposes of this paper, deep, hot gas wells will be considered to be those that fall within the following ranges of conditions: Deeper than 10,000 feet; hotter than 200°F bottomhole temperature (BHT); and bottomhole pressure (BHP) higher than 5,000 psi. Corrosive wells also contain an aggressive acid gas (H_2S or CO_2) in amounts of 0.1% or greater. In addition, water production considerably aggravates corrosion especially if it is a heavy brine. When corrosion is observed, it is found to occur anywhere between the bottom and top of the hole, sometimes even continuously from bottom to top of the hole; rarely ever concentrated in just the top 2,000 or 3,000 feet which is normal for gas condensate wells.

In general, the rate of corrosion is aggravated by increasing partial pressure of CO_2 or of H_2S. In some pure CO_2 systems (H_2S free), a passivation effect is observed when especially pure water and high pressure/temperature conditions are realized. However, even very small amounts of H_2S (ppm's in the gas phase composition) can cause activation of the corrosion due to CO_2 which affects the passivation effect. Corrosion rate is also aggravated by increases in temperature, in water production rate, and especially by the production of heavy brines. Heavy brine production indicates that a considerable volume of aqueous electrolyte is contained in the hole in contact with the CO_2 or H_2S and thereby causes considerable aggravation in both the area of steel which is corroding as well as the rate of corrosion.

When the production temperature is relatively high and the liquid production (condensate or brine) is low, especially with high pressure in the hole, the flow conditions in the hole are essentially single-phase (i.e., there is not any considerable amount of separated liquid phase flowing in the hole). Of course, the formation is also dry. In addition to this, the gas phase is not effectively saturated with liquids so that many solvents commonly used for batch inhibitor treatments suffer evaporation when injected into the gas phase in the hole. This evaporation can have a considerable influence on the distribution of the inhibitor in the hole and from that on the effectiveness of corrosion control. In these wells where corrosion exists it must be caused by a mist of very fine droplets of a highly concentrated brine solution. When the droplets contact the steel surface, they are especially prone to stick to the surface and not to evaporate and thereby provide a continuous electrolyte phase in a very local area for high penetration rate pitting.

The most effective inhibitor treatments are made with continuous addition of the inhibitor carried in enough solvent so as not to evaporate completely and thereby to act as a distributor for the smaller volume of inhibitor compound. At the lower end of the temperature and liquid production rate scale, batch tubing displacements are useful for corrosion control if done frequently enough so that corrosion control is not seriously lost between treatments. For these treatments, the longest life will be obtained by depositing the most inhibitor in the hole since inhibitor removal processes are the dominating feature determining length of effective corrosion control per treatment. In holes where oil does not condense upstream from the flow choke but where corrosion occurs bottom to top, limited batch treatments (i.e., those where less than a tubing full of liquid is used) are not found to be useful.

Corrosion monitoring is necessary because corrosion rates are high and replacement is hazardous and expensive. Monitoring at the surface with instruments or coupons mounted in the flowlines or separators is not as useful as iron counts are because surface corrosion rates are much lower than the downhole corrosion rates due to the lower temperature and pressure conditions. The most serious drawback to corrosion control in wells making significant amounts of H_2S is in the difficulty of monitoring downhole corrosion rates. Some special techniques have been tried for monitoring downhole corrosion in sour systems but these have met with less than total success.

Conditions in the Hole

Conventional gas wells drop pressure and temperature as the gas flows uphole until condensation occurs somewhere near the top. At the water condensation point, corrosion occurs if the partial pressure of CO_2 is as much as 1 psi. Partial pressure of CO_2 is derived from the total pressure and the mole percent (per the chemical analysis) using the formula,

$$P_{CO_2} = P_{total} \text{ X Mole Percent } \quad 100$$

i.e., 1 psi partial pressure of CO_2 can come from:

100 psi total pressure at 1% CO_2 which implies 100 X 0.01 = 1 psi

or 1,000 psi total pressure at 0.1% CO_2 implies 1,000 X 0.001 = 1 psi

or 10,000 psi total pressure and 0.01% CO_2 implies 10,000 X 0.0001 = 1 psi

Sometimes the corrosion resulting from a partial pressure of CO_2 of 1 psi is not judged to be severe enough to worry about because the time, trouble, and expense of replacing equipment is judged to be less than the time, trouble, and expense of an inhibitor program. At temperatures in the lower range, 1 psi CO_2 partial pressure will give a general corrosion rate (i.e., non-pitting) of 2-8 mpy (mils penetration per year). The pit penetration rate at the same time may run in the neighborhood of 20-80 mpy which would give a tubing lifetime, for quarter inch pipewall thickness, of 3-13 years, provided pitting is heavy, or of 30-125 years, if it is absent. In low pressure, low temperature wells, even three-years-to-pit-penetration is a long time compared to the usual workover period so when the tubing is out of the hole anyway, it can be inspected and those few corroded joints layed down without too much expense.

On the other hand, at high temperatures and pressures and high CO_2 partial pressure, especially if a heavy brine is produced, the downhole corrosion rates can go as high as 50-500 mpy general attack, and 500-5,000 mpy pit penetration rate. These rates lead to failure even of heavy walled tubulars in a few weeks, both because of the high corrosion rate and because of high pressure and stresses due to the depth of the wells. Full penetration does not have to occur before failure does because the tubing metal is in a heavily stressed condition.

Corrosion conditions for H_2S are as bad as CO_2 or worse, except that H_2S has a terrible tendency to form iron sulfide scales under which corrosion is always in the pit penetration range (5X to 25X as fast as the general corrosion rate). Furthermore, these scales impede the inhibition process when allowed to form before inhibitor treatment. Proper downhole metallurgy is a must because of a tendency of H_2S to embrittle many alloys. Although inhibitors can slow down cracking (i.e., stretch out the time to failure), they cannot prevent it entirely. Furthermore, in a severe cracking situation where failure can occur in a week to a month or so, even if the inhibitor program provides 90% protection (10X the lifetime), the time to failure is extended only as far as 70-300 days. This is not enough protection to be feasible in the engineering sense so the solution to the sulfide cracking problem is to use the lower strength, less alloyed steels. This means that inhibition of general and pitting corrosion is required since all but a few very expensive alloys (Hastelloy) will crack in sour wells.

In deep, hot gas wells, the major obstacle to a good inhibition program is the tendency of the hole to be extremely dry upstream from the surface flow choke. Furthermore, if only small volumes of liquid are put into the hole, they will tend to evaporate completely at the point of injection into the hot gas. Corrosion is not inhibited by vaporized inhibitors. Many non-vaporized inhibitors are deposited as a gunk at the injection point when the solvent used with them evaporates. Thus, it is necessary to call upon knowledge of the phase behavior in the hole in order to design a workable inhibitor treatment.

Downhole Phase Conditions

Except in marginally warm wells, there are two surprise conditions in the hole which complicate the corrosion control to a considerable extent. The first surprise encountered is that corrosion can and usually does occur anywhere in the hole, including the bottom reaches of the tubing. It is not concentrated in the top 2 or 3,000 feet where condensation has been found to occur in past production experience. The second surprise condition is that condensation does not always occur in the hole, but rather often occurs after the surface choke. This condition raises the question, why is there any corrosion if the hole is essentially gas filled and dry of liquid phase? A study of the principles of phase behavior in natural gas wells provides a basis to answer the questions and to explain the surprises.

When multi-component vapors and liquids are in thermal equilibrium, the composition of the fluids is an important variable. The composition of gas well fluids is quite complex but it is possible to understand what occurs in principle by understanding the behavior of simpler binary or ternary mixtures of gas well components.

Figure 1 shows illustrative vapor pressure curves for a low boiling point compound, a high boiling point compound, and for a mixture of the two. If the normal vapor pressure of a single compound is measured over a range of temperatures, what is found is that there is a unique set of pressures and temperatures at which both liquid and vapor can co-exist in equilibrium. Single component curves for a low boiling point compound and for a high boiling point compound are shown in Figure 1. For any point along the curve when a system is at pressure and temperature equilibrium, vapor and liquid will co-exist. However, if the system is set to any higher temperature or lower pressure corresponding to a point below the curve, the liquid will evaporate and the system will be entirely gas phase. On the other hand, adjustment to higher pressure or lower temperature to a point above the curve will produce entirely liquid phase conditions when equilibrium is established.

As different points along the curve are tested, one temperature will be identified which is the highest point at which a pressure can be found to produce any liquid phase. This point is known as the critical point. Above the critical temperature, no amount of pressure will produce liquid phase conditions. At the critical temperature, the pressure required is known as the critical pressure. The critical temperature and pressure are unique properties for each compound. At the critical point, all properties of liquid and vapor phases are identical, e.g., density, molar volume, etc..

When a mixture of high and low boiling compounds is made and vapor pressure experiments are carried out, the vapor pressure line now becomes a region of mixed vapor and liquid (see Figure 1). If a test cell with a window is used to test any temperature which intersects the mixture region and the pressure is lowered progressively from a point above the region, there will be observed a point where the first small bubbles of vapor occur. This point is on the upper curve of the mixture region. Repeat experiments at different temperatures will establish a bubble point curve. If, at fixed temperature, the pressure is initially set below the two phase region, and then increased isothermally, a point will be found where the first droplets of liquid form. This is known as the dewpoint for that temperature.

Repeat experiments at different temperatures will establish a dewpoint curve. At any particular temperature, if the pressure is increased in stages beyond the dewpoint, variable but increasing amounts of liquid phase will be found until the bubble point curve is reached. Thus, in the mixed phase region, the composition is variable with regard to the amount of liquid and vapor contained in the system as the pressure is varied at constant temperature or vice versa.

The point where the dewpoint and bubble point curves meet is known as the pseudocritical point. Due to the bulging of the dewpoint and bubble point curves, sometimes there is a region of mixed phases which extends beyond the pseudocritical point. Thus, there is a temperature, called the cricondentherm, beyond which no condensation occurs but which does not correspond to the pseudocritical temperature. There is also a pressure, called the cricondenbar above which there is always liquid condition (provided the temperature is less than the pseudocritical temperature).

Several features of the mixture regions should be compared to the curves for the individual compounds. First of all, the bubble point curve lies lower on the pressure scale than the vapor pressure curve of the low boiling point compound. Correspondingly, the dewpoint curve of the mixture lies higher on the pressure scale than the vapor pressure curve of the high boiling point component. Thus, when the low boiling point component is present, the high boiling point component vaporizes more readily than it would by itself. Similarly, the low boiling point component condenses more readily than it would by itself. Furthermore, the liquid/vapor region out to the pseudocritical pressure extends to higher temperature and pressures than the critical point of the low boiling component and to higher pressures than the critical point of the high boiling component. When the percentage composition of low boiling and high boiling components is changed, the location of the pseudocritical point moves towards higher pressures for larger amounts of low boiling component. Consequently, the mixed phase region also swings upward for high percentages of low boiling component in the mixture and downward for high percentages of high boiling point component. (See Figure 4).

When the mixtures have more than two components, and particularly when they include water, CO_2, H_2S or inert gases (nitrogen, helium, etc.), additional complexities develop because of differing mutual solubilities. For example, CO_2 and H_2S can react chemically with water and some types of nitrogenous hydrocarbon species. In addition, separate aqueous liquid phases (brines) and solid phase (hydrates) can develop. When significant amounts of CO_2 or H_2S are present in the well fluids, high boiling point liquids are especially volatile.

However, produced water always carries some inorganic salt which cannot be considered at all volatile and must, therefore, be carried to the surface in the form of a light mist of small droplets of a highly concentrated brine. When vaporized water condenses, it dilutes the total dissolved solids (TDS) concentration. This brine mist supports the downhole corrosion due to the acid gases wherever droplets collect at imperfectations on the surface of the pipewall. Some wells produce brines which have very high TDS content. These must have a heavy population of droplets carried in the gas, and therefore, contact the tubing walls in more numerous locations causing a greater area of corroding steel. For this reason the iron content always goes up when the TDS level increases. Of course, the need for good corrosion control increases as produced brine TDS goes up, because when more area corrodes there is a greater probability that some areas will corrode at a locally severe rate.

Limited analyses of samples with unknown degrees hydration under surface conditions indicate that the downhole brine concentration is most probably in the range of TDS concentrations from 150,000 to more than 500,000 ppm. Note that when an attempt is made in the laboratory to experimentally produce a 500,000 ppm brine containing sodium, calcium and magnesium salts at ambient temperature and pressure, the samples are either inhomogenous (contain a solid phase) or are not liquid. Thus, the mist may very well be a metastable melt of some yet undefined kind or else the high pressure solubility of the well fluids tends to produce a previously unknown stable liquid, electrolyte phase.

A flowing gas well establishes an operating line of pressure and temperature changes which can be drawn on a P-T curve corresponding to the pressure drop in the tubing and to the corresponding temperature drop (due to expansion cooling). Usually the temperature and pressure changes are relatively small on this line. A second operating line is established in the surface equipment right up to the separator outlet to the condensate stock tank. For wells where the formation temperature is higher than the cricondentherm, the formation contains a single gaseous hydrocarbon phase. If the operating pressure and temperature line in the tubing crosses into the mixed phase region, tubing condensation occurs. (See Figure 2).

If the tubing operating line does not cross into the two phase region but the operating line in the surface equipment does, condensate is produced in the separator but not in the tubing. (See Figure 2). If the reservoir is hot enough relative to the mixed phase region, no liquid hydrocarbon is produced even at separator pressure. These latter two types of wells fall into the deep, hot category.

One other type of well sometimes encountered is the retrograde well. This type is illustrated in Figure 3. When the dewpoint line has a large bulge towards higher temperatures and the reservoir temperature lies between the cricondentherm and the pseudocritical temperature, then it is possible to recross the dewpoint line on decreasing pressure from the mixed phase region into the gas phase region even though the temperature has fallen. This evaporation with decreasing pressure is known as a retrograde condition and can lead to relatively narrowly defined wet areas in the hole. Maybe a few thousand feet around the 10,000 foot mark will be wet and corrosive but above and below this zone, the hole is very dry. Or maybe the corrosive, wet region will fall at 15,000 feet. Examples of all of these downhole conditions have been found in the author's experience.

How Phase Conditions Affect Inhibitor Applications

Most inhibitor applications involve some means for adding a small volume of the inhibitor to the wellbore contained in a much larger volume of a solvent/diluent/carrier. Both intermittent batch and continuous addition schemes are used. Inhibitors are formulated to be pumpable over a wide range of ambient temperatures (frequently over the range from -30°F to +140°F). In addition, many times, flash point or other restrictions require even more specialized formulations. Consequently, what is received in the drum is not often 100% active inhibitor ingredient. The formula also contains solvents designed to provide the required ancillary properties. For this reason, the actual volume of inhibitor ingredient injected into the hole is usually very much on the low side and therefore a solvent/carrier is used. A film thickness of inhibitor which provides very good corrosion protection is of the order of 5 to 30 mils (a mil is a thousandth of an inch) so even though it is dilute in the drum, there is plenty enough inhibitor for corrosion control provided it can be distributed properly for surface contact. The solvent/carrier should be selected with some care because if it evaporates significantly there may not be enough liquid volume in the hole to get an evenly coated distribution of inhibitor.

If gas well conditions were similar to distillation conditions, it would seem that it should be possible without too much trouble to provide enough volume of even low boiling point materials by simply allowing for enough solvent/carrier to evaporate and saturate the gas well fluids and then providing some extra to remain liquid and to carry the inhibitor to all the places it needs to reach. Relatively straightforward correlations exist to predict the vapor pressure at elevated temperatures using Trouton's Rule. The predictions are based on a single-component assumption that the liquid and vapor are in equilibrium along the vapor pressure line (i.e., not within a mixed phase region). They predict low because they fail to account for the effects of the normally gaseous components on the dewpoint of the normally liquid components. For example, using a condensate from the author's experience with an API gravity of 54.5° produced at a BHT of 280°F, and a BHP of 7,500 psi, at a rate of

METHOD OF ESTIMATION OF VOLUME TO SATURATE VIA DISTILLATION ASSUMPTION

$$L_N \frac{P_2^0}{P_1^0} = \frac{\Delta H_M}{T_1 R} X T_1 X \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

P_2^0 IS VAPOR PRESSURE AT TEMPERATURE T_2

P_1^0 IS VAPOR PRESSURE AT TEMPERATURE T_1

$\frac{\Delta H_M}{T_1}$ IS TROUTON'S CONSTANT = APPROXIMATELY 21

R IS THE GAS CONSTANT EXPRESSED IN APPROPRIATE UNITS = 1.987

$$P_2^0 = 14.7 \text{ EXP}\left[\frac{\Delta H_M}{T_1 R} X T_1 \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

$$\text{BBLS/MMCF} = \frac{\text{MOLES/MMCF X MOLE FRACTION X MW}}{\text{\#/MOLE}}$$

MW IS MOLECULAR WEIGHT, #/MOLE

MOLE FRACTION IS ESTIMATED AS P_2^0/WELL PRESSURE

349 barrels per million cubic feet, whose mean average boiling point (MABP) is 243°F and whose molecular weight (MW) is 114, the calculation estimates a vapor pressure at temperature of 58.6 psi or a production rate of 8.8 barrels per million cubic feet (using the calculation scheme shown in the example where the ratio of the vapor pressure to the total pressure of the well is used to estimate the mole fraction of the condensate in the well fluids).

Tests were done in a windowed pressure cell using produced fluids from the subject well recombined to formation conditions, followed by staged reduction of pressure at constant temperature. The results showed a retrograde dewpoint at 280°F and 4,038 psi. The condensate had a bubble point pressure at 280°F of 75 psig but as little as 20% reservoir fluids mixed with it raised the bubble point to 1,013 psig. Thus, a 3 to 4 times increase in the ratio of barrels of condensate per million cubic feet would be required to produce liquid in the hole from bottom to top. That is to say, around a thousand barrels of condensate per million cubic feet would have to be injected into the well on a continuous basis in order to use condensate as the carrier for a continuous inhibitor treatment.

Many times kerosene or diesel fractions are used as solvent carrier for inhibitor treatments. These hydrocarbons have boiling points in the neighborhood of 476°F mean average boiling point and API molecular weights in the neighborhood of 175. Calculation of barrels per million cubic feet required under distillation pressure conditions, show a vapor pressure of 0.6 psi at 280°F and a saturation requirement of 0.15 barrels per million cubic feet. However, if the kerosene calculation were to be off by the same ratio as the condensate (i.e., 1,000/8.8 = 113.6; it could be more than that), then somewhere around 17 barrels of kerosene would be required to saturate the vapor of each million cubic feet of gas. In addition to that, an extra 10 to 20 barrels per day would be needed to carry the inhibitor. For wells producing in the 2 to 20 MMCFD range, these requirements are very costly.

Some continuous inhibitor treatments have used a very heavy solvent derived from heavy gas oil or even higher boiling components provided from a refinery. Even these require from 30 to several hundred barrels per day to provide saturation plus. Comparative calculations for a gas oil boiling at 968°F MABP (range, 850-1,100°F) with an API molecular weight of 352.8 gives 0.0001 psi vapor pressure at 280°F and 0.05 barrels per million cubic feet for saturation. However, under these conditions, both the light condensate and the non-condensable gases (e.g., methane/ethane) contribute to raising the dewpoint of the gas oil and thus the estimation by calculation is even farther off than for the original condensate was. The calculated estimates are quite consistent with distillation practice where the vapor phase is derived from the material contained in the liquid phase but not when methane, ethane, and condensate are present.

A reason for this is illustrated in Figure 4. When a low boiling point composition and a high boiling point composition are mixed in various ratios and vapor pressure curves are determined, what is found is that the pseudocritical points of the mixtures change location toward higher pressures and lower temperatures as less and less of the high boiling point component is present in the mix. Thus, when a light condensate mixes in the wellbore with a heavy gas oil added as inhibitor carrier, the low boiling point components raise the dewpoint line of the mixture above the bubble point curve of the heavy gas oil (HGO). In order to get a significant change in the percent of liquid phase at high temperatures, large mole fractions of HGO have to be added. When the condensate molecular weight is between 100 and 150, and the HGO molecular weight is around 350 to 400, an even greater volume penalty is taken because a barrel of HGO, molecular weight 350 and density about 350 pounds per barrel, provides only one mole per barrel. On the other hand, a condensate, molecular weight 150 and density about 280 pounds per barrel, provides 1.9 moles per barrel. Thus, it takes almost twice as many barrels of HGO per barrel of condensate to mix with the condensate in the wellbore and provide a 50 mole percent mix. Thus, if 350 barrels per million cubic feet of condensate are produced, it would take almost 700 barrels per million cubic feet to provide a 50 mole percent mix in the hole. To acquire a liquid condition at 280°F would perhaps require a 20% mix or 0.4 barrels HGO per barrel of condensate. This amounts to 40 barrels of HGO for each 100 barrels condensate produced per day. From the results of these estimates, it is not surprising to learn that even heavy specially selected solvents require large volumes to saturate the gases and provide an extra amount for a continuous liquid phase. Furthermore, after the liquids are separated at the surface, it is necessary to provide some form of distillation separation of the light condensate from the heavy gas oil in order to be able to reuse it. If significant volumes of condensate are produced, a small refinery is required for this step. Not all gas well locations can support these logistics.

Phase Behavior Applied to Design of Inhibitor Treatments

The first requirement for a corrosion inhibitor for application to deep, hot gas wells is that it must be thermally stable indefinitely and also flowable under downhole conditions even when neat active ingredient is left behind. For batch applications, it is also desirable to have a very, very low vapor pressure at well temperatures so that inhibitor evaporation does not remove protective film in too short a time. If the vapor pressure under distillation conditions is sufficiently low (in the range of 10^{-4} to 10^{-5} psi), then if enhanced downhole volatility is experienced (due to the effects of gaseous and condensate components), perhaps evaporation will be sufficiently slow to leave inhibitor in the hole for 25 to 30 days. This amounts to about two gallons per day evaporation rate or 0.2 gallons per million cubic feet in a 10 MMCFD well for a one drum treatment. In order to realize this long and effective treatment life, a 50-60 gallon quantity of inhibitor must be left in the hole after the well is returned to production and it must cover the corrosive area completely if metal loss is to be well controlled. That is to say, the amount of inhibitor left behind in the hole after the treatment is an important variable relative to how long a treatment lasts. In addition, how effectively that inhibitor is distributed on the corrodable surface is a variable related to how closely the corrosion is controlled. Both of these features are related to downhole phase behavior of the inhibitor active ingredient and of the mixture of inhibitor and solvent/carrier relative to the method of application.

The types of applications which have been used for gas wells covers a wide range including batch and continuous methods such as: 1) Low volume, pump and fall; 2) Tubing displacement; 3) Inhibitor carried or pushed with nitrogen; 4) Continuous injection; and 5) Formation squeeze. In the type of wells encountered in the past, there was a continuously available liquid phase in the tubing bore which carried the inhibitor and distributed to all of the surfaces which needed protection. In the deep, hot wells discussed here, the tubing bore and especially the formation experiences an essentially dry condition with very little liquid to carry and distribute the inhibitor. Thus, special phase behavior requirements are placed on the inhibitor and on the solvent/carrier used in the application. These requirements are overlayed with modern logistic and economic considerations. Because of these latter considerations, two of the more popular modern treatment media are water and nitrogen used either as pusher or as carrier for the inhibitor mixture.

The Short Batch Method of Application

Traditionally, this method has used 5 to 50 barrels of inhibitor solution containing 1/2 to 5 drums of inhibitor carried in water (as a dispersion of oil soluble inhibitor or perhaps as a solution of a water soluble compound) or diesel or sometimes condensate. The inhibitor mix is pumped into the shut-in well and allowed to travel to bottom. Radiotracer investigations reported in the literature have shown that the liquid mix bridges over at the top of the hole and fills the tubing bore. Then a film of liquid falls down the tubing walls proceeding from the bottom of the filled column as a bubble of gas rises through the center of the liquid column. These processes are illustrated in Figure 5. To get proper distribution of inhibitor from top to bottom of the string requires about one drum of inhibitor mixed in 7 to 10 barrels of diluent for each 10,000 foot of depth. If significant evaporation of diluent occurs in the hole, then even larger treatment volumes are required to get even distribution of inhibitor top to bottom. Of course, if corrosion only occurs high in the hole, then proper distribution all the way to bottom and consequent large volumes are not requirements. Even so, in especially hot wells, there is a tendency for flash evaporation of diluent to form tiny bubbles and a stabilized foam at the bottom edge of the liquid column of inhibitor mix. Many times these foams prevent proper fall of the mix because they are too stiff to run down the tubing walls. Sometimes the addition of a properly chosen surfactant helps.

The combination of possible evaporation and of not falling to bottom makes it difficult to achieve good corrosion control by this method applied to deep, hot wells where corrosion occurs deep in the hole. Possibly with appropriate use of water or of a special solvent with a very high boiling point, the method would be more attractive. Due to the fact that gases always contain water vapor, when water is used as solvent/carrier, fewer moles are required to achieve complete saturation than if diesel or other solvent is used which is not contained in the gas. Furthermore, one barrel of water (8.4 pounds per gallon and 18 pounds per mole) contains 19.6 moles of water; whereas one barrel of diesel (6.3 pounds per gallon and 175 molecular weight) contains 1.5 moles of hydrocarbon. Thus, it is 10 times easier to increase the mole fraction of carrier in the hole by injection of a few barrels of water than by injection of diesel. Water is also cheaper than diesel or other solvents and less hazardous to pump. However, truly water soluble corrosion inhibitors are sometimes less effective than oil soluble compounds. Thus, frequently oil soluble/water dispersible compounds are chosen for use with water as a carrier.

For wells in the mid to upper range of the deep, hot category, it is desirable to put in enough diluent to displace from 1/4 to 1/2 of the tubing volume (for a 20,000 foot well, the range is from 20 barrels for 1/4-full 2-3/8-inch tubing to 120 barrels for 1/2-full 4-inch tubing). After the mix is pumped, the well is shut-in for 4 to 8 hours for each 10,000 feet of tubing. This recommended volume provides for guaranteed treatment of the top 1/4 to 1/2 of the tubing surface as well as allowing for approximately half the diluent to evaporate as the solution falls leaving enough liquid to distribute evenly. Of course, the gas that is displaced from the tubing back into the formation does not have to be saturated and this lowers the evaporation volume requirement. When full coverage is achieved, the indicated corrosion rate (as measured by iron count) will be reduced to at least as low as 25% of the uninhibited value.

The life of a treatment will depend first of all on how much total inhibitor is left in the hole. Many times, analyses of inhibitor returns immediately after the treatment show that 80% or more of what went into the hole is produced right back out almost immediately. This leaves only 20% to provide protection in the hole. This condition is especially true when not much of the inhibitor mix falls below the injection depth. As the inhibitor mix falls to bottom, a thin liquid film is formed — approximately 0.030 inches thick. When the well returns to production, some of this liquid is swept off by the gas flow but much of it is evaporated into the undersaturated formation gas leaving solvent-free inhibitor behind so that with a successful application, only 20% or so of the inhibitor is brought back out of the hole immediately.

The in-well inhibitor film removal processes are: Washing by produced fluids; evaporation into the gas phase; and corrosion processes. Thus, a well which produces a high volume of liquid in the hole (this could be significantly less than the volume measured at the separator) especially if a brine; or which is quite corrosive; or quite hot will show a much shorter treatment life than one on the other end of the range. To offset these effects with inhibitor selection, a compound is needed which has a very low effective vapor pressure under tubing conditions, which is as insouble as possible in the wellbore fluids, and which significantly lowers the corrosion rate of that part of the metal surface which is filmed.

The Tubing Displacement Method

By this method of treatment a tubing full of fluids is pumped into the well with the objective to displace inhibitor completely top to bottom so as to insure contact with the tubing surface. The most common mode of treatment is to use inhibitor-free solvent to push to bottom 2 to 20 barrels of a concentrated inhibitor solution (5 to 20%; sometimes 100% inhibitor is used). Diesel or condensate are the most frequently chosen solvents for the inhibitor mix, although sometimes special aromatic or higher boiling point solvents are chosen. Water, nitrogen, or natural gas (from another well operating at higher pressure) are frequently used to push the mix to bottom. Diesel and condensate are also used for this.

Although it is fairly certain that each square foot of the surface is contacted with inhibitor when this method is used, it is not certain how much film is left behind. If the volume of inhibitor mix is too small and it is pushed with a non-miscible solvent, then there may be a lack of adequate distribution of inhibitor to all the necessary areas of the tubing surface because of spiralling flow down the hole or other factors. These factors are especially likely to occur when neat, oil soluble inhibitor is pushed with water or gas. On the other hand, if a good solvent for the inhibitor is used to push with, the film left behind when the few gallons of inhibitor mix passes will be washed off when the many gallons of solvents passes behind it. Of course, some of the inhibitor will be redistributed from bottom by the flow of gas when the well is returned to production.

The inhibitor mix chosen for these treatments should be relatively non-volatile in the hole so that as little as possible evaporates and as much of the liquid volume as possible is available to film onto the tubing surface. When a liquid displacement is made, the gas volume in the hole decreases to a small volume so that there is no problem achieving saturation on the down trip. However, as gas flows out, displacing the push fluid, redistribution of inhibitor is aided by non-volatile mix. In order for the treatment to be effective for a long time, the same volatility principles apply to the active ingredient (that is, non-solvent components) of tubing displacement compounds as for limited batch compounds. The immiscible push mode produces the best retention of inhibitor in the hole but runs the risk of misdistribution so that not all the corrodable areas are covered. Thus, it is particularly important to see at least 75% reduction in iron counts immediately after the treatment in order to be confident that significant control is achieved.

A variant tubing displacement mode is to dissolve 0.5-4.0% inhibitor (1 to 4drums) in a tubing volume of solvent (50 to 250 barrels) which is then pumped into the well. For this mode, water has been used to carry water soluble or oil soluble-water dispersible inhibitors and diesel, condensate or gas oils have been used to carry oil soluble inhibitors. If a completely soluble compound is used, it is difficult to leave behind a major fraction of the inhibitor which is pumped into the wellbore. One way to maximize the amount of inhibitor left behind is to bubble gas through the column of liquid by flowing the well slowly when it is turned to production in order to allow as much downhole evaporation as possible instead of rapid displacement. Probably the best way to maximize inhibitor left in the hole is to use an inhibitor dispersion which breaks at high temperature and keep the well shut-in until the mix comes to temperature and the dispersion breaks to deposit water insoluble inhibitor on the tubing walls. For this application, it is desirable to have a minimum volatility active inhibitor ingredient.

Typical inhibitor patterns are shown in Figure 6. If the downhole corrosion as determined by iron ppm's is not reduced at least to 25% of the unprotected value, it is probable that the full tubing surface has not been covered with inhibitor and thus corrosion proceeds unabated on some areas. Usually in this case the treatment life will also be much too short as judged by the time until the iron ppm's reach 100% of the unprotected value. Even if the iron levels shortly after treatment reach a low of 25% or less of the unprotected level, the length of time until they climb again to high values may be too short due to using the wrong inhibitor (vapor pressure too high at well temperature and pressure) or the wrong technique (too little inhibitor left in the hole).

What is more desirable is for the iron counts to bottom out well below the 25% level and to retreat before they pass the 50% level so that uncontrolled corrosion is not allowed over a significant part of the corrodable surface. If the iron count for the fully unprotected surface is not known because the well has always been treated with inhibitor except under upset conditions, a retreat level should be chosen which is no more than four times the minimum iron level (e.g., 12.5% goes to 50% or when 5 ppm minimum increases to 20 ppm). When the iron ppm's are not allowed to rise much before retreatment, on successive treatments the curves will usually trend downward until a comfortably low level is routinely maintained.

If the iron loss per 10,000 feet of tubing is kept below 1 pound per day, experience has shown that downhole corrosion is usually very well controlled. The pounds of iron loss per day is calculated according to the scheme shown. One pound per day corresponds to about 2 mpy (mils penetration per year) if corrosion is generally distributed top to bottom in 10,000 feet of 2 inch i.d. tubing. Frequently corrosion is either of the pitting variety or localized to a fraction of the total tubing area. In this case, typically about 10% of the area will be involved and one pound of iron per day will correspond to about 20 mpy pit penetration rate. In wells which make less than 10 barrels of water per day, it should be easily possible to keep the metal loss to well below one pound of iron per day. In wells making as much as 1,000 barrels of water per day, one pound per day of metal loss is difficult to achieve. Ten ppm carried in 100 barrels of water per day corresponds to 0.35 pounds per day.

Methods of Inhibitor Application Using Nitrogen Gas

Nitrogen gas is frequently used to push a slug of inhibitor mix to bottom. The principles of this mode are the same as for the other tubing displacement methods. The other mode of nitrogen application is to displace the gas in the hole with nitrogen gas containing a mist of inhibitor solution. One to four drums of inhibitor are used contained in a 2% to 50% solution. Nitrogen is taken to the well site in liquid form and expanded into gaseous form at a pressure slightly greater than that in the well. Displacement is calculated from the gas law modified to account for deviations of nitrogen from an ideal gas. The inhibitor mix is aspirated into the flowing gas as droplets and carried with it to bottom. Rapid displacement helps ensure that the mist droplets penetrate all the way to bottom. After the well is shut-in for a few hours, the inhibitor mist settles onto the tubing walls. It is desirable to resume flow in the well at a relatively slow rate and then build up to full flow rate. In this way, solvent evaporation fixes the active inhibitor ingredient on the tubing walls with only a minumum amount swept back out of the well. Thus, this method offers the best possible utilization of inhibitor. Evaporation and other removal processes operating after a nitrogen treatment are identical to those operating after a short batch or tubing displacement treatment.

Method of Continuous Treatment With Inhibitors

The most effective and reliable method of corrosion control is to continuously add inhibitor to the bottom of the producing string of tubing in an adequate amount to cover the surface and with an amount of liquid carrier adequate to produce a liquid phase condition in the hole. When these conditions are met, the periodic corrosion rate highs and lows found in the batch methods are avoided. Thereby overall metal loss is significantly less over the life of the downhole equipment and thus the chance for premature failure is much reduced. In one case in the author's experience, corrosion has been reduced to essentially zero over more than five years of continuous inhibitor treatment in several sour wells. The uncontrolled corrosion rate in this case had lead to failure in less than six months. Both the inhibitor and a special low volatility solvent were extensively tested at bottomhole temperature and pressure before application to the wells.

CALCULATION OF POUNDS OF IRON LOSS PER DAY

$$\#Fe/DAY = PPM\ Fe \times 10^{-6} \times BWPD \times \#/GALLON\ WATER \times GALLON/BARREL$$

$$\#Fe/DAY = PPM\ Fe \times BWPD \times 3.5 \times 10^{-4}$$

PPM Fe IS OBTAINED FROM THE IRON COUNT

BWPD IS NUMBER OF BARRELS OF WATER PRODUCED PER DAY

IF 10 PPM OF IRON ARE FOUND IN 100 BWPD

$\#Fe/DAY = 10 \times 100 \times 3.5 \times 10^{-4} = 0.35$

IN 10,000 FEET OF 2" I.D. TUBING, 1 #Fe/DAY

CORRESPONDS TO 2 MPY IF CORROSION IS GENERALLY DISTRIBUTED BOTTOM TO TOP OR TO 20 MPY PIT PENETRATION RATE IF ABOUT 10% OF SURFACE IS CORRODING AT A LOCALIZED RATE

As noted in the discussions of phase behavior, even carriers which are especially good at saturating the downhole fluids require from 1 to 100 barrels per million cubic feet of produced gas with the larger ratios required for higher temperatures or pressures. This translates to injection rates in the range of tens to hundreds of barrels per day. Thus, the supply system: tankage, high pressure pumps, heat tracing, is an important part of the overall reliability of treatment. Most applications have an open annulus or kill string kept full by the surface pumps. However, some applications have used bottomhole valves. Keeping these valves open and functional requires some considerable attention.

In sour wells, it is attractive to use a specially designed solvent/carrier for the inhibitor with selected low downhole volatility and good solvency for elemental sulfur. Some sour wells tend to form plugs of sulfur in the hole and the sulfur solvent action is required to prevent this plugging. This solvent is then recovered, reconditioned to remove sulfur and to adjust inhibitor concentration, and then reused. Since high molecular weight goes along with low volatility and also with a high melting point, it is necessary to use a heated solvent delivery system in order to keep it flowable. It is also desirable to have a non-formulated inhibitor with a high percentage of active ingredient since any normal solvents in the formula will be lost in the hole.

If the elemental sulfur content in the solvent is allowed to build up too high as it recycles through the well, vulcanization-type reactions can take place where sulfur atoms are inserted into C-H and C=C bonds in the solvent and/or the inhibitor. These reactions proceed at high temperatures. When both solvent and inhibitor molecules are linked together by sulfur, insoluble gunks can form. The hottest location is downhole, so build up of tars in that area can occur with high sulfur content in the solvent. Of course, when the solvent is saturated with sulfur, it will no longer remove it from the gas. These problems are avoided by treating the inhibited solvent with an aqueous base solution in order to remove the sulfur.

In general, deposits downhole have been a minor but recurring problem even with water and condensate carrier. Mineral scales can form due to reaction of downhole brines with constituents carried in the solvent such as: 1) Basic sulfur wash solution carried in emulsion form in the special hydrocarbon solvent and reacting with calcium from the downhole brine to form calcium carbonate scale; 2) Sulfate carried in the carrier and reacting with downhole barium; 3) Calcium plus carbonate carried in soluble form in the injection water collected on the surface but precipitating downhole due to the inverse solubility versus temperature effect in calcium scales. In addition, when water is the carrier, dissolved oxygen must be removed down to below 0.1 ppm in order to prevent downhole corrosion in the injection circuit due to that source.

It is necessary to maintain good control of the variables by analyzing both the injected fluids and the produced fluids for inhibitor content, dissolved oxygen, dissolved sulfur, and for dissolved iron. In sweet systems where no FeS precipitates, frequent reliable iron analyses will predict downhole success or failure. In sour systems, special techniques are necessary for corrosion rate monitoring. Special sampling and analysis techniques have been used for FeS counts as well as various radiotracer techniques. There is definitely a need for improvement here since measurements of corrosion rate at the surface have proved useless in predicting downhole corrosion rates.

Thus, in hot, sour wells a proven continuous injection technique is the most responsible choice when carefully monitored for inhibitor and sulfur content and where the interruptions are absolutely minimized. In order to have good analytical monitoring, a qualified Analyst is required who has been furnished methods proved to be applicable to the inhibitor, the solvent, and the produced fluid stream (especially in the case of iron sulfide counts). For these reasons, it is almost mandatory to have careful prior planning of the inhibitor injection prior to the operating phase of a well so that corrosion control is instituted from Day One.

For continuous injection applications, inhibitor usage rates range from 5 to 50 gallons per day. For this level of usage to be economical, the inhibitor must be both thermally stable and corrosion effective. Stability demands are especially severe where a long residence time in a hot annulus or where recycle is employed. Oil soluble compounds carried in oil should remain stable even after wellbore gas has dissolved into the oil at full bottomhole temperature and pressure. Water soluble compounds should remain soluble at full wellbore pressure and temperature especially in the presence of heavy downhole brine. Dispersions of oil soluble-water dispersible compounds should remain viable under annular or kill string conditions. To determine these properties requires testing in high pressure, high temperature equipment containing both liquid and gas phases. It is especially important that the inhibitor ingredient not gunk up because even at a low injection rate of five gallons per day inhibitor with a 25% active content, if most of the active ingredient remains at bottomhole deposited on the tubing due to gunking, then as much as one cubic foot would accumulate in a week. If that amount spread out over the tubing surface in an immovable layer which is 0.1 inch thick, about 280 feet of tubing would be coated. Probably this would cause some restriction of gas flow.

In a few cases, the injected volume of carrier has been very small relative to what must be required to saturate the wellbore. In these cases it is evident that the carrier simply serves to carry the inhibitor through the injection circuit (kill string or annulus) but not through the production tubing. Since it can be demonstrated that inhibitor is returning in the right amount, there is no downhole build-up. In most cases corrosion is not well controlled because the inhibitor has totally volatilized in the hole and, therefore, is not available to inhibit the corrosive downhole phase. In a few well documented cases, however, corrosion is controlled. This must mean that these active inhibitor ingredients are not totally volatile downhole but are able to move with the fluids to film adequately on the tubing surface. Laboratory distillation of these compounds has shown vapor pressures at well temperature in the neighborhood of 10^{-4} to 10^{-5} atmospheres. Calculated estimates of evaporation rate for one such well based on this vapor pressure and assuming a 114X downhole enhancement, show about six gallons per day evaporate out of 30 gallons per day injected. (See the earlier example for the method used to calculate).

Application of Inhibitors Through Capillary Tubing

High alloy, high strength capillary tubing is available for use in gas wells by coupling it to the tubing at bottomhole and running it into the hole with the tubing string. A high pressure liquid pump is used at the surface to inject neat chemical at bottomhole by pumping through the capillary tubing. Because of friction losses, as much as 20,000 psi injection pressure is required to overcome downhole pressure and to put up to 20 gallons per day of chemical into the wellbore. To maintain adequate flow rate, the viscosity of the chemical must remain low (a few centipoise) while contained in the capillary tubing and it must be free of solids. For this latter reason, very fine pore size filters are incorporated into the system to prevent plug-ups.

Up to now these applications have been used for cooler, low pressure wells. However, because of the evidence reported above, where some compounds appear to have a low enough vapor pressure, it now appears possible to use the method for some deep, hot wells in the lower end of the range. It must be recognized that low volatility, good thermal stability, and low solids requirements are extremely stringent for this application.

Inhibitor Squeeze

This method has found use in conventional gas wells and may be considered for the deep, hot variety. However, since the formation is most likely to be gaseous and undersaturated, there are many possibilities for causing blockage due to the fluids injected or deposition of non-volatile inhibitor which cannot move with the gas. Perhaps it would work to use a nitrogen squeeze containing inhibitor mist with a highly non-volatile, but fluid compound in the mist. Overall, the process is not very attractive.

The Importance of Corrosion Monitoring

Uncontrolled corrosion in deep, hot gas wells has been the cause of failure in periods of time as short as a few weeks. Frequent experience has seen a few months to failure. Furthermore, the failures are hazardous and the strings are expensive to replace to say nothing of the lost production profits. These reasons are justification for the inhibitor application, but they are even more of a justification for seeing to it that the inhibitor applied is working the way it is supposed to so that a failure will not be the first sign that it is not working. Careful monitoring will provide data to allow verification of control.

Among the methods of monitoring which are available for corrosion are:

1) Careful iron analysis of produced fluids;
2) Downhole caliper surveys;
3) Inspection of tubing pulled from the hole.

Much experience has cast heavy doubt on the following methods of monitoring:

1) Coupons mounted downstream from the choke;
2) Corrosometer probes in the flowlines;
3) Electrochemical probes in the flowlines;
4) Hydrogen probes downstream from the choke.

It's possible that coupons can be useful when mounted in the tree upstream from the choke.

In sweet wells (no black iron sulfide), the best method to date has been frequent iron analyses using a well developed technique. A good method is to catch samples in clean quart size polyethylene containers to which a teaspoonful of citric acid has been added. Analyses can then be carried out at a convenient time without danger of loss of iron due to adsorption on the container or to precipitation as air-oxidized iron (III) hydrous oxides (rust). For the initial application, samples should be taken at least as frequently as every other day until the control pattern is established. After optimization of the inhibitor procedure is complete, sampling frequency for long term monitoring can be adjusted to weekly.

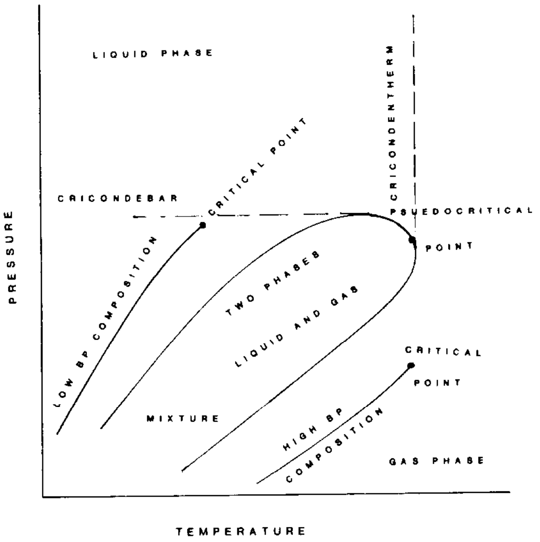
In our hands, good results have been routinely obtained using citric acid with the Hach method of iron determination in the field. The field analyses have been reproduced in the laboratory by another operator using the Hach method and by a third operator using the Atomic Absorption method. However, a matrix interference occurs in the Atomic Absorption method due to the citric acid which must be standardized and corrected. No interference due to the inhibitor has been found to date. A discussion of the significance of the ppm's of iron in the produced fluids is contained in another section of this paper.

It is possible to modify the sampling method and the analyses for iron to account for wells which produce iron sulfide. Downhole radioactive tubing subs of various kinds have been used coupled with analysis for radioactivity on the surface. But basically, caliper surveys and inspection of pulled tubing are the least equivocal methods to judge corrosion control by. It is also desirable to monitor by chemical analysis to insure that good quality inhibitor mix is going downhole and that the proper amount of inhibitor is returning in the produced fluids. These data can frequently catch problems before they show up in any other type of data.

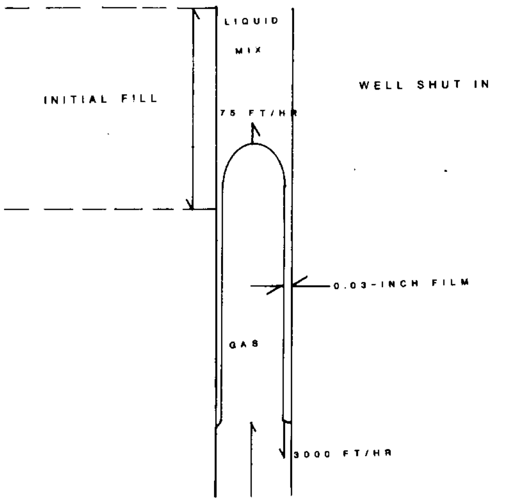
CONCLUSION

Deep, hot gas wells pose special problems in that corrosion is usually severe and proper care is needed in the choice and maintenance of a good inhibitor program. However, a sufficiently wide range of compounds and application techniques is available so that a producer can achieve any degree of control which he judges to be economically justified. Most reservoir specialists worry about squeezes of liquids into the type formations considered here. The continuous methods are the most trouble and also the most reliable. The short batch, pump and fall method is the least trouble and the least reliable. In between these extremes are good methods to control corrosion and allow for any of the completion or production peculiarities usually found in modern practice.

VAPOR PRESSURE CURVES

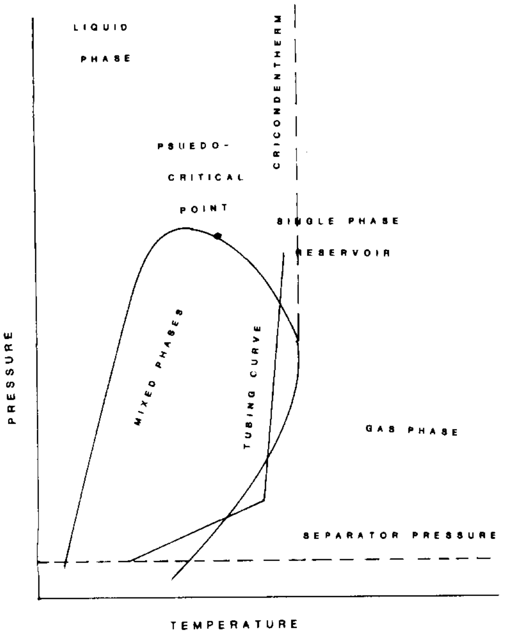


FALL CONDITIONS
FOR SHORT BATCH TREATMENT

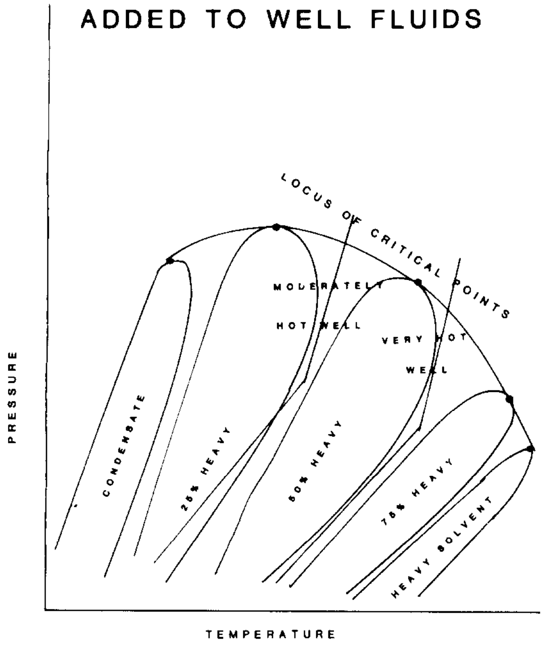


UPFLOW AT TURN ON
REDISTRIBUTES INHIBITOR

RETROGRADE OPERATING LINE



HEAVY SOLVENT
ADDED TO WELL FLUIDS



GAS WELL OPERATING LINES

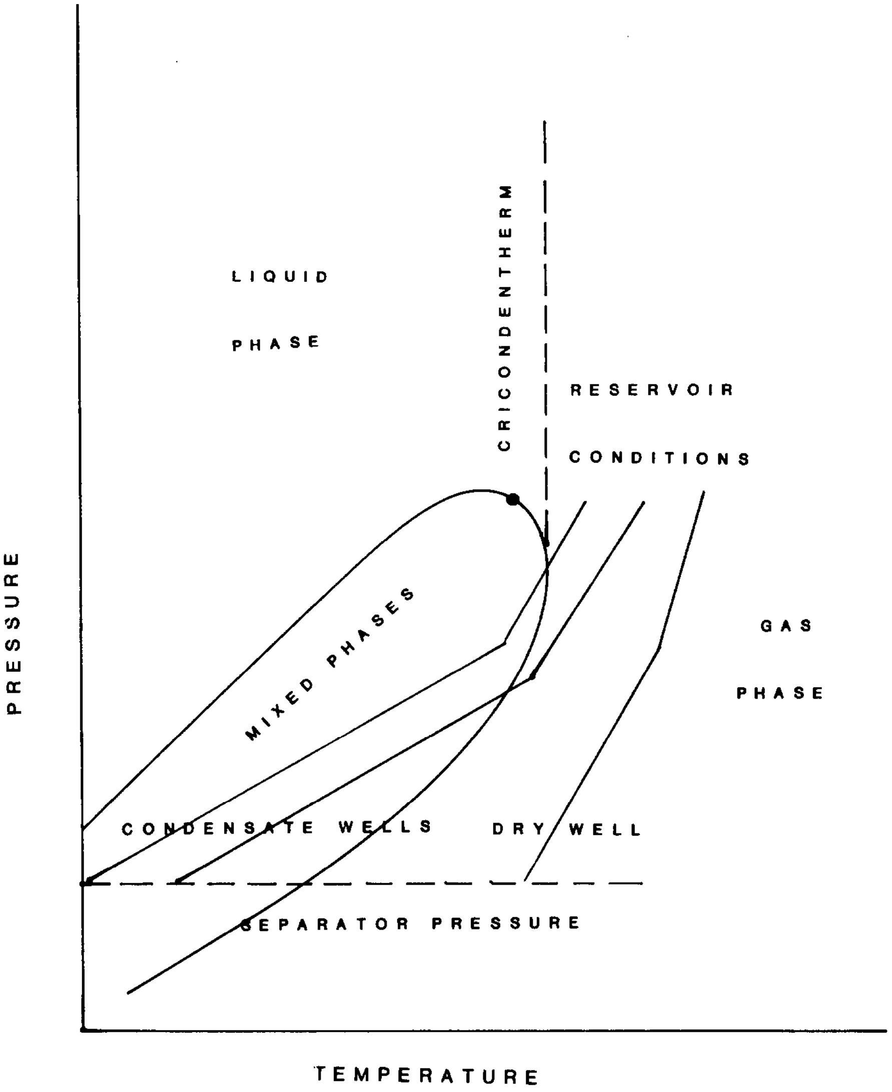


FIGURE 6

IDEALIZED IRON COUNT CURVES FOR BATCH TREATMENTS