USE OF INHIBITORS FOR DOWNHOLE CORROSION CONTROL IN GAS WELLS

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ABSTRACT

Factors to be considered in the selection of inhibitors and treating techniques used to control downhole corrosion in gas wells are discussed with special attention to deep, hot wells. Corrosion monitoring is recognized as a complex but necessary part of any corrosion control program.

INTRODUCTION

In concept, corrosion control in gas wells and surface systems transporting gas is straightforward and involves four main parts. An effective inhibitor must be used, enough inhibitor must be used, the inhibitor must be replenished often enough, and finally, the inhibitor must reach all metal surfaces subject to corrosion. The fact that there are many corrosion inhibitors in use, a number of techniques for applying inhibitors, and many opinions on required frequency and volume of inhibitor shows that there is still much to be determined and/or agreed on in this area. Related questions on monitoring and operating problems caused by inhibition treatments are also not resolved to everyone's satisfaction. Consideration of factors involved in gas-well treating should be useful in selecting treatments for specific wells and fields.

APPROACHING THE PROBLEM

The nature of gas wells has changed considerably since the 1953 NGAA book on gas-well corrosion came out.[1] At that time wells deemed probably corrosive were the deeper ones—below 7,200 feet, with wellhead temperatures greater than 130° F and wellhead pressures greater than 2,700 psi. Attack of these wells (mainly along the Gulf Coast area) was believed due both to CO_2 and organic acids. The 1958 API-NACE book "Corrosion of Oil- and Gas-Well Equipment" gave a cutoff point of 7 psi partial pressure of CO_2 below which no corrosion due to CO_2 would be expected.[2] In the past few years many gas wells have reached depths, pressures, temperatures, and acid-gas production rates well out of the ranges routinely found during the 1940's and 1950's. Production from below 20,000 feet with bottom-hole temperatures in excess of 350° F, pressures of 15,000 psi or more, and acid-gas concentrations accounting for 40% or more of gas production are no longer rare. Although old inhibitor chemistry and application techniques may not be adequate in some newer wells, the basic problems are the same: inhibitor adequacy, inhibitor transport, reduction of inhibitor-caused operating problems and meaningful corrosion monitoring. These are complicated by new needs for inhibitor thermal stability and for phase-behavior data in temperature-pressure regions not previously studied.

Some calculations and experimental measurements and observations are useful in putting downhole corrosion-control problems in focus. A 10,000 ft tubing string of nominal 2-1/2-in.-I.D. tubing (actual 2.44 in. I.D. 6.4 lb/ft) will contain 58 bbl (325 cu ft) and will have a surface area of 6,388 square feet. A 25,000 ft string of 4.00 in. I.D. (11.6 lb/ft) will contain 388 bbl (2,180 cu ft) and will have a surface area of 26,200 ft. If the gas contains no water vapor or hydrocarbons heavier than pentane, the gas volumes in the tubing string and volumes of water and typical diesel necessary for the existence of a liquid phase downhole for a 10,000 ft well with 2-1/2-in. tubing as shown in Table 1.

A typical condensate will usually supply a liquid phase with about half the volume required for diesel.

TABLE 1—EFFECT OF TEMPERATURE AND PRESSURE ON LIQUID VOLUME REQUIRED TO GIVE A LIQUID PHASE

Temperature, °F	Pressure, psi	MSCF in Tubing	Bbl for Liquid in Tubing: Water	Bbl for Liquid in Tubing: Diesel
175	5,000	91	6	33
	10,000	181	7	31
275	5,000	78	7	44
	7,500	118	9	40
	10,000	157	10	38
325	7,500	110	10	44
	10,000	146	11	41

Although produced gas is rarely absolutely dry in water and usually contains some heavier hydrocarbons, the volumes of liquid required are much greater than usually believed and cast doubts on the effectiveness of the batch treatments using only a drum or two per treatment. This situation is compounded in very deep, hot wells where the presence of a liquid phase cannot safely be guessed at or calculated. In these cases, expensive laboratory measurements using highly specialized high-pressure, high-temperature cells give the only really reliable data on phase behavoir needed to select inhibitor, diluent, and volume of diluent needed to give a constant liquid film. Failure to properly understand the factors involved has led to severe attack in parts of the tubing strings where condensation of liquid water (and thus corrosion) first occurs.

The rate of fall of inhibitor solution in batch treatments has been a subject of speculation. It is known that inhibiting treatments do not always fall in spite of shut-in periods of days or months. This appears to result from an emulsion block in the tubing and has been prevented in some cases by spearheading the inhibitor slug with demulsifier. When the inhibitor does fall (and it usually does), the fall rate is on the order of 1,000 ft/hr for a viscous inhibitor up to a maximum of 3,000 ft/hr for a very fluid inhibitor. Delays of two or three hours may be experienced if downhole constrictions such as flow-rate control valves are present. These measurements were used in a series of tests pumping radioactively tagged inhibitors down one tubing string and following the fall rate with a sensor on a wire line.[3,4] Other results during these tests showed that viscosity is much more important in determining fall rate than specific gravity so that very thick, dense (11 lb/gal) liquids fall much more slowly than do very fluid, lighter (8 lb/gal) liquids.

The volume of inhibitor needed can be calculated, but the calculations must be interpreted with care. The tagged inhibitor experiments showed that good protection was obtained if the active ingredient of the inhibitor formed a film at least 3 mil (0.003 in.) thick.[3] This would amount to only about a gallon of inhibitor per 1,000 sq ft of surface. It is probable that at least 10 times that amount (i.e., a drum per 10,000 ft of tubing) is needed for adequate distribution of inhibitor with enough excess to give feedback over a long enough period to make it worthwhile. In general, the cost of inhibitor even at $150 to $400 per 55-gal drum is much less than the expenses related to shut-in time, pump costs, and sometimes solvent or nitrogen. If complete effectiveness or extended treatment life were assured, much higher treatment costs would be justified.

APPLICATION TECHNIQUES

Continuous

Several gas wells, particularly some expensive, deep wells are set up for continuous injection of inhibitor solution through a chemical string or occasionally through the tubing-casing annulus. In some cases this is the only alternative with a hope of success, since very high flow rates and high temperatures would make any periodic treatments very shortlived. This treating technique allows for treatment without shut-in and, within the range pumps being used, allows wide flexibility in the rate of chemical treatment. There are shortcomings in this system however. Provision must be made for injection of enough inhibitor-diluent solution to carry around. Unless there is a valve in the bottom of the kill string, there is no assurance that the kill string will be either full or empty, so inhibitor feedback will be most probably erratic. If there is a valve on the bottom, it will probably plug. Unless a large volume of inhibitor solution is pumped during so-called continuous treatment, the treatment may not be "continuous." Even the large volumes cited earlier may be inadequate in the very deep, hot, high-pressure wells. Inhibitors, selected for continuous treatment in deep, high-temperature wells must be not only effective at treatment temperatures, but they must stay soluble in the diluent for up to several weeks at downhole temperatures. Severe downhole deposit buildups caused by either lack of solvent or reaction by the inhibitor with itself or anything else are unacceptable in the long run. In practice, neat (undiluted) corrosion inhibitor is rarely used in continuous treatment, since solvent is needed to carry the inhibitor downhole. Inhibitor diluted in a suitable solvent is much more stable than is neat inhibitor. It is even more difficult to add small amounts of inhibitor at a reasonably "known" rate than it would be to add larger amounts. Morover, because of the large inhibitor inventory represented by a full kill string or annulus, concentrations of 1% to 5% inhibitor in a suitable solvent would permit much easier control and have a greater chance of success than neat inhibitor. Ideally, continuous treatment appears to be foolproof. In practice, careful monitoring is needed to make sure the inhibitor is getting around and is giving the anticipated protection.

Tubing Displacement

Tubing displacement calls for filling the tubing string from the top to move a solution of inhibitor under positive pressure over the entire length of the tubing string. This can be a uniform solution of inhibitor in a suitable diluent or dispersant—usually diesel, condensate, or water—or it can be a spearhead of concentrated inhibitor forced down by liquid or, in some cases, gas. The advantages of tubing displacement are that the entire tubing string is contracted by inhibitor and that shut-in time is only slightly more than the pumping time needed to fill the tubing string. Disadvantages include the possibility that the resulting hydrostatic head is greater than bottom-hole pressure (thus keeping the well from coming back on), the cost of nitrogen (if it is used as a displacing fluid), the possibility of formation damage when the inhibitor solution contacts it, and the cost of the pump trucks and larger volumes of fluid needed. The cost of nitrogen may run from $800 to $2,000, but this may be more than compensated for by the cutting of the shut-in time by several hours (e.g., from 12 hours to 2 hours) as compared to batch treatments. The fact that this method ensures contact of all of the internal tubing surface removes a major source of doubt and makes this system most attractive. We have now reduced our unknowns to only three—the inhibitor effectiveness and thermal stability as applied under well conditions, the required inhibitor volume, and the required frequency.

As one example of tubing displacement, corrosion inhibitor was dissolved in lease condensate to make a 2% solution. The entire tubing string was pumped full of this solution, and the wells were shut-in for a period of time determined for the convenience of the field and gas plant operator. In the case of weak wells, nitrogen gas is mixed with the inhibitor solution as it is pumped in to decrease the hydraulic head so that the well will come back on more easily.

In a second, less usual, case an oil-soluble corrosion inhibitor was followed by a slug of water and finally pushed downhole with nitrogen. The well was brought back on stream slowly at first to allow a second application as the inhibitor flowed back. Actual shut-in time was kept to a minimum that was limited to hookup time, pumping time, and time needed to disconnect the treating rig.

Batch Treatment

The batch treatment, in all of its variations, is probably the most widely used gas-well treating technique. Volumes used range from a few gallons to a significant fraction (one third or more) of the tubing volume. Problems associated with the use of small diluent volumes and inadequate shut-in times are apparent from considerations discussed earlier.

A number of gas wells on the Gulf Coast are treated with a drum or less of inhibitor, sometimes mixed with a barrel or two of diesel or condensate. The chance of successful treatment is probably greater where the volume of diluent is 15 to 30 bbl. A number of gas wells in West Texas are being successfully treated using two drums (55 gal) of an oil soluble-water dispersible inhibitor dispersed in 10 to 30 bbl of water. Other deep, hot wells are being treated with two or three drums of water-soluble inhibitor dissolved in 10 to 25 bbl of water. The choice of water or hydrocarbon diluent depends on hydrocarbon cost and the relative volumes needed to maintain a liquid phase, as well as the solubility or dispersibility of the desired inhibitor in the different diluents.

Squeeze

It is possible to displace inhibitor solution into a formation using hydrocarbon, water, or even atomized in nitrogen. The inhibitor used should be very stable, thermally, and very soluble in both the diluent used in the squeeze and in the produced fluids leaving the formation. It would seem to be necessary to have a liquid phase leaving the formation for a squeeze to be successful in order to obtain returns. Squeeze treatments are often not much longer lasting than effective tubing displacements. There is concern that squeeze treatments will cause formation damage in some cases, although this is the exception. The Gulf Coast area has reported successful use of nitrogen squeezes in several areas, although here, too, there is at least one area where apparent formation damage has occurred.

MONITORING

Monitoring corrosion in gas wells particularly deep, hot wells is a challenge. Measurements made on the surface using coupons, hydrogen probes, flush mounted PAIR probes, and Corrosometer probes at the best usually give the corrosivity of the produced fluids at completely different conditions in terms of flow velocity, temperature, pressure, and turbulence than is seen downhole. Measurements at the surface can be used to detect return of inhibitor and the relative effectiveness of downhole treatments as reflected on the surface. They do not indicate if the inhibitor reached all of the steel or if it is effective at bottom-hole conditions.

Iron counts caught at the surface are held in varying degrees of esteem. If there is a large volume of water produced, if there is coated tubing, if there is a high sulfide content with little CO_2 present, or if care is not exercised in catching fresh samples, iron counts usually have little value. In areas where the main corrodent is CO_2 and water production is in the range of 10 to 100 BWPD, iron counts often give valuable data on the relative effectiveness of treatment downhole. Unfortunately again, they do not determine if treatment reached bottom or if corrosion is in the form of pitting.

In those areas where iron counts are relevant, an effort should be made to determine the iron-count value representing complete protection and to set up a treating program to keep iron counts from greatly exceeding that value. After the well has discharged any foreign water left by drilling or completion operations, the well should be inhibited in the best possible way. This is usually by tubing displacement and possibly multiple treatments within a short period of time. The lowest values obtained shortly thereafter should represent complete protection. Any treating technique that can control iron counts to within 5 or 10 of that value can be used. The wells should be treated often enough to maintain an almost complete film (i.e., iron counts should not greatly exceed the minimum value), since it is easier to repair and maintain such a film than it is to rebuild one after corrosion has been out of control for a while.

Tubing calipers can offer valuable data, particularly if run every year or on a definite schedule. These call for well shut-in time and cost money, and there is always the possibility of losing a fish in the hole anytime wireline work is done. The wells should definitely be inhibited immediately following caliper surveys (and any other wireline work) to repair any lost protective film.

INHIBITOR SELECTION

There are a number of adequate inhibitors for treatment of routine gas wells. There are fewer adequate inhibitors for very deep, hot wells. Inhibitors should be chosen primarily on the basis of their effectiveness, and the inhibitor-diluent combination must be such that it will stay essentially intact until it comes in contact with the metal to be protected. A very real problem in the field arises if an inhibitor causes operating problems on the surface. Inhibitors, like most surface active materials, may stabilize foam, emulsions and reverse emulsions. Although many surface "gunking" problems result from paraffin and sand production, interaction of returning inhibitor and condensate can lead to formation of tarry-like materials in some cases. Gas-treating facilities are particularly vulnerable to bed fouling or glycol or amine foaming if inlet-separation facilities are not adequate.

Most laboratory tests (such as wheel tests) represent only the first stage in screening inhibitors and will show gross inadequacies. Any new inhibitor should be closely followed. The chance of making a good selection is greatly enhanced by conferring with individuals in other areas having similar gas wells, who have a successful program already established. The final judgment of the success of the inhibitor and treatment selection must take place in the field, not the laboratory.

CONCLUSION

So how should a gas well be treated? Since gas wells are usually packed off and do not have a kill string, continuous treatment is usually not an option. Tubing displacement with an adequate concentration of a suitable inhibitor (such as 2% in a suitable diluent) should give protection for one to three months as a rule. A recent breakthrough using a spearhead of a specially formulated inhibitor, followed by water, and pushed down by nitrogen is proving very effective in the corrosion control of a number of deep wells. Squeezes—particularly nitrogen squeezes—may give up to four or five months' protection, although this is optimistic.

Batch treatments should use at least enough total fluid to give a liquid film all of the way to the bottom of the hole and at least a drum of inhibitor for each 10,000 ft. Periodic tubing-caliper runs should be used to verify the effectiveness of any tubing treatment—particularly batch treatments.

REFERENCES

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