Corrosion Inhibitors — Selection And Application

By J. D. CRAWFORD
Cardinal Chemical Company
Odessa, Texas

Theories and hypothesis of the corrosion process in relation to the oil field will not be discussed at length in this paper since other papers are to deal with this phase of corrosion control. Many excellent papers have been given in recent years concerning the theories and mechanisms of corrosion and should be studied diligently by the corrosion engineer who intends to try to understand his field of work. Many excellent papers have been published in technical and trade journals and specifically in Corrosion, the official publication of the National Association of Corrosion Engineers.

To simplify corrosion and corrosion inhibitors, one may say that corrosion is an electrochemical process in which a given metal seeks its lowest stable free energy state and a corrosion inhibitor is a substance which possesses ability to insulate or otherwise prevent action of the electrochemical cells. A corrosion inhibitor may be one of several types of substances; it may be a synthetic resin coating, a more noble metal alloy or coating, cathodic protection, inorganic inhibitors or organic corrosion inhibitors. The organic corrosion inhibitor relies upon a portion of its molecule to physically and/or chemically absorb onto a metal surface to the extent that the electrical circuit is broken and in turn prevents the loss of metal at the anodic area. The majority of commercially available inhibitors are based on polar and semi-polar molecules, but vary somewhat in the general structure of the molecule from manufacturers viewpoint.

The ability of a given molecule to absorb chemically or physically onto a metal surface depends upon the nature of the surface charge, the magnitude of charge of the polar portion and the proximity of the inhibitor molecule and metal surface. It is reasonable to assume that all inhibitor molecules present in a given system cannot become oriented properly on metal surfaces of the system, unless a static condition exists and then only a portion of the total number will be absorbed at any given instant. The various motions and vibrations characteristic of all molecules is likely to cause the inhibitor molecule to re-enter solution and unless a sufficient excess is present, the absorbed film may become incapable of restraining the corrosion process. This condition is most likely to exist in a dynamic system receiving periodic "slugs" of inhibitor and in more or less static systems containing insufficient inhibitor to prevent or overcome the tendency of the molecule to re-enter solution.

Organic corrosion inhibitors in the petroleum industry, while relatively new, have saved the industry untold millions of dollars in extended life of equipment and greatly minimized loss in production due to down time. Keen competition in the inhibitor industry has been a very real factor in the research and development of new and better inhibitors and will continue to be the prime factor in stimulating the search for the ultimate in corrosion inhibitors. In recent years hundreds of compounds have been introduced and in many cases, because of the laborious task of evaluating and testing, some have become obsolete by the time testing of the inhibitor was completed. In other instances, very good inhibitors may have been passed up without testing because of time required and reluctance to test a new compound. The urge to get on the band wagon has no doubt prompted the birth of many inhibitor manufacturers and the introduction of many worthless or mediocre inhibitor compounds, which in turn has necessarily cast a shadow of doubt by some operators when a new compound is introduced. This sort of thing however, has largely been eliminated by competition within the industry.

Corrosive oil wells cannot be determined as such by rule of thumb or by any means of pre-determination, generally speaking. In many areas however, with a knowledge of past experiences, it might reasonably well be expected that a given well is or will become corrosive. Certain factors in production may indicate that a well is potentially corrosive because of records of experiences in similar situations in the same general area or in many cases the same general conditions. At the same time, we may find in a very corrosive field a number of wells that are essentially non-corrosive and in other non-corrosive fields a few very corrosive wells. To cope with this situation, one should be careful to periodically survey pulling records and to note the success of offset operators who are producing under similar conditions.

In corrosion mitigation a careful study of water-oil ratios and type of corrosion present is most important and whether the corrosive agent is hydrogen sulfide, carbon dioxide, oxygen, or combinations of two or more of these gases. The presence of these dissolved gases may indicate potential corrosion and in most cases combinations of any two or more do present a corrosion problem. Particularly in the case of hydrogen sulfide-oxygen, hydrogen sulfide-carbon dioxide combinations, severe corrosion should be expected.

The age of some producing fields is a corrosion yardstick so to speak, while in others, corrosion becomes apparent at the very outset of production. How may a corrosion engineer pre-determine future problems that may be encountered if this be true? A number of factors can be of importance and should be determined as nearly as possible in the mitigation of a corrosion problem. Of these factors the most important to note is water-oil ratio, hydrogen sulfide (1) carbon dioxide and oxygen content of produced fluids. This information, when used in conjunction with pullings records, caliper surveys, iron counts and/or coupon surveys, may prevent or at least minimize the loss of valuable production due to down time because of corrosion damage of equipment.

When the need for inhibitors or other types of protection from corrosion is established, the long range economic justification of such treatment is naturally the first point to be considered by management. In many cases, this has no doubt been the cause for discontinuing production of many marginal wells over the entire country in the past few years. Marginal production in corrosive areas, however, may by proper selection of inhibitor and proper treatment, be placed in a paying bracket by reducing lifting cost due to corrosion. We owe it to ourselves and to future generations to prevent the premature death of an oil well, when by conscientious work this can be prevented.

Within the past few years it has become more and more apparent that one type of corrosion inhibitor is not suited for all types of corrosion. Initially all corrosive wells were treated with oil soluble inhibitors and because of a limited knowledge of the mechanism of corrosion, this type of inhibitor was accepted as being sufficient to control the problems at hand. As time and techniques progressed it became apparent that the oil soluble type inhibitor was not the answer to all producing well corrosion problems. In answer to this need, corrosion inhibitor manufacturers began the search for more versatile and better inhibitors and today many types of inhibitor compounds are available to the producing companies. Even though the problem is not solved by any means, steps in the right direction have been made. Only a matter of time and experience will prevent unnecessary loss of equipment in the future.

Many methods of determining corrosion rates have been proposed and used in the field the last few years. All of these methods have worked with some degree of success in many fields and in others have not shown any correlation with actual loss due to corrosion. The coupon method is satisfactory in some cases, especially (1) where bottom hole temperatures are not excessive (2) where paraffin deposition is not too heavy (3) in sour (H_2S) pumping wells (4) wells that do not carry a high water leg in the annular space. In the latter case pump corrosion may be excessive and may not be detected by coupons.

The iron count method has been and is at present widely used as a corrosion detection device in sweet oil and gas wells, but cannot be relied upon to tell the complete story. Where iron bearing waters are not present, the iron count may be relatively accurate; but in most cases cannot be used for other than relative or comparative values. (2)

At present a number of electronic corrosion measuring devices are being tested in the field and may prove to be the ultimate answer to corrosion detection and measurement. Whether or not down hole corrosion can be accurately measured or detected remains to be seen.

Most operators use pulling records to establish corrosion damage and need for protection. This method of detection, while most expensive and time consuming, is the only definite method of establishing extent of damage down hole and resulting maintenance cost because of such damage. Once the problem is ascertained, the next step should be to select the most economical long range method of protection. Generally there are three or four methods to be considered i. e. inhibitors, coatings, alloys and cathodic protection. Only inhibitors will be considered within the scope of this paper, since any one method could easily be and is the subject of many published papers and discussions.

Should the most practical solution to the problem be control by the inhibitor method, a number of points should be considered before initiation of a treating program. Some of the most important points to be considered are (1) water-oil ratios (2) volume of total fluids to be lifted (3) well temperatures (4) whether the well is "sour" or "sweet" (5) what zone is most heavily damaged by corrosion; i. e. pump, tubing, annular space tubing and/or casing, flow lines or combinations of two or more of these corrosive areas (6) type of completion.

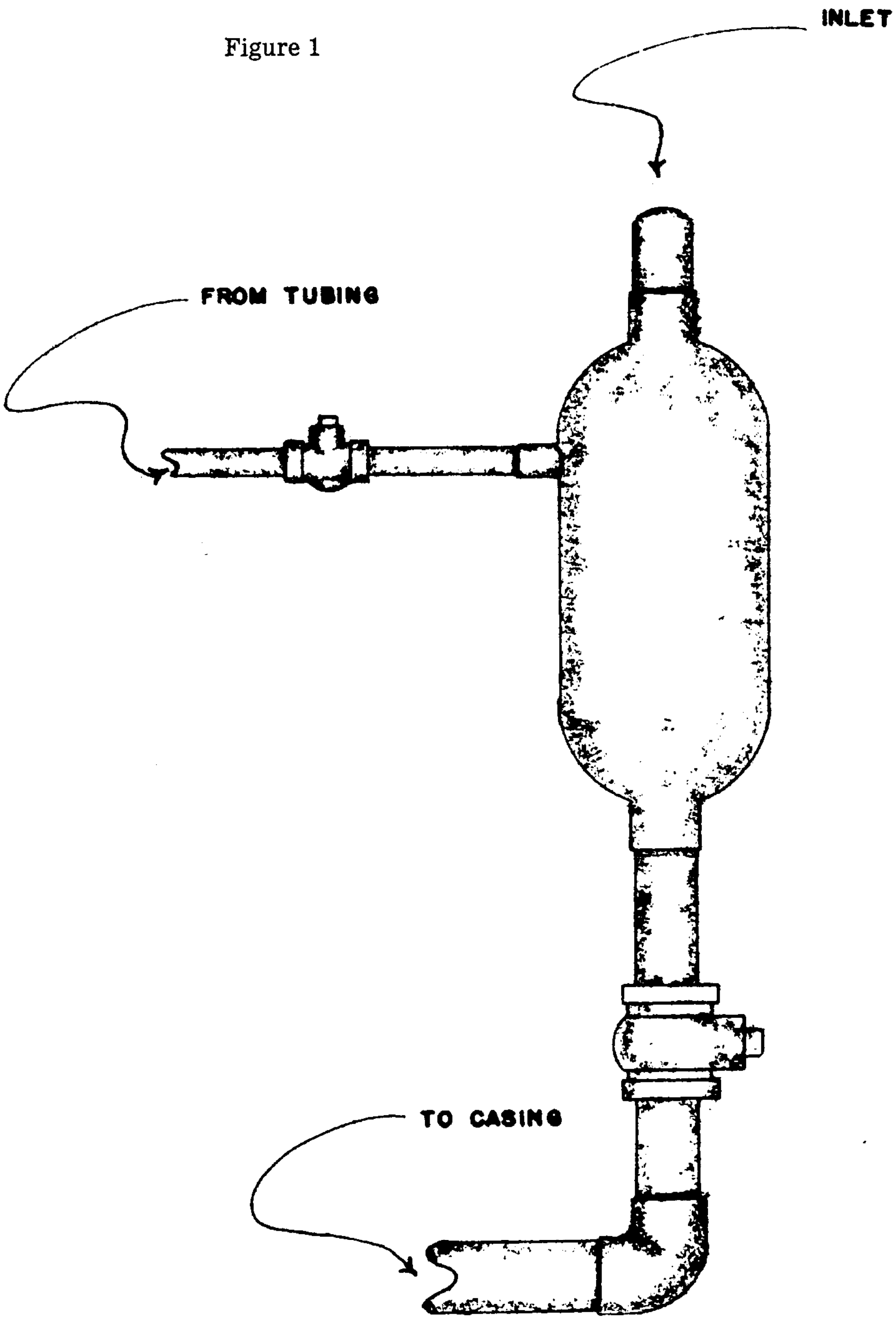
The manner in which a well is completed is largely a determining factor in type of inhibitor most practical to use and is not always the most beneficial type from a protection economics in equipment loss standpoint. Upon compiling all available information, as to need for inhibitor protection of equipment, type and severity of corrosion to be dealt with, volumes of fluids to be treated, the next step to methodically follow should be selection of the proper type inhibitor. Type inhibitor is not to be construed as a particular brand name, but rather chemical and physical types and is meant to include oil soluble-water insoluble, oil soluble-water dispersible, water soluble-oil dispersible and water soluble-oil insoluble.

From past records it has been fairly well established that corrosive wells producing small volumes of water and below 40-50 percent, an oil soluble inhibitor should be used to best advantage as a general rule. Wells producing 40-70 percent water and mildly corrosive can generally be treated successfully with an oil soluble inhibitor; but in cases of severely corrosive wells of this type, oil soluble-water dispersible inhibitors have shown to be much more effective. Above 70 percent water cut, the severity and type of corrosion plays an important role in selection of proper inhibitors. Mildly corrosive wells may be treated with oil soluble inhibitors with very good results in some cases, but in this critical situation it cannot be expected to be the rule by any means. In this water to oil area a deciding factor is the volumes of fluid concerned and is the best method of determining the type inhibitor most likely to give the desired protection.

With water-oil ratios in the range of 50-90 percent and where large volumes of total fluid is being lifted, it is most likely that an oil soluble-water dispersible inhibitor will give the best protection. By employing this type compound one is assured treatment of both the water and oil phase, which in turn insures an inhibitor-oil film on metal parts in contact with treated fluids. Percentage of water to oil in the range of 80-100 percent and where large volumes of fluid is being lifted, a water soluble-oil dispersible corrosion inhibitor should be considered. In this type of system the phase almost continually in contact with metal equipment is the corroding or water phase. With the insurance of inhibitor in the corroding phase, it is most likely that the minor or oil phase will have the chance to film metal parts because of the nature of the inhibitor molecule. A portion being oil soluble, when once attracted to a metal surface, the oil phase naturally tends to spread over the surface, hence oil wetting and protecting metal equipment from the corrosive elements contained in the brine or water phase. Regardless of what type corrosion inhibitor is selected for use in a given well a rigid treating program should be set up and diligently executed. Provision should be made for flushing and/or circulating the inhibitor wherever economically and technically possible in pumping wells. Flush fluids should in the majority of cases be production from the treated wells. A simple lubricator is shown in Figure 1.

Many producing oil wells, subject to corrosion attack both in "sweet" and "sour" areas, are difficult to treat effectively with any type of liquid cor-

Figure 1



MANUAL LUBRICATOR

rosion inhibitor because of extremely high annular fluid columns. In such instances bottom hole treatment may, for all intents and purposes, be completely lacking in concentrations sufficient for protection of pumps, tubing anchors, etc. Whether or not the well is pumping off or lowering the annular fluid column appreciably during a given production cycle is also a gauge as to the possibility of pump contact with inhibited fluids. A number of specialized inhibitors have recently been introduced to meet this particular situation and a number of treating devices have also been introduced with varying degrees of success, but will not be discussed here. Figure 2 demonstates oil soluble, water dispersible, water soluble and oil dispersible - water dispersible characteristics of inhibitor compounds.

Inhibitors especially designed for bottom hole treatment include both liquid and solid forms. Liquid inhibitors of this type are generally water soluble or dispersible and have a specific gravity of 1.1 or greater, which permits the liquid to fall in droplets through the oil phase and into or through the water phase, thus insuring bottom hole treatment. Heavy liquids may be used to advantage in wells having too little clearance in annular space for solid type inhibitors to fall freely, but the tendency of a liquid to adhere to casing and tubing will prevent adequate treatment unless thorough flushing of the inhibitor is performed. Some companies are experimenting with various mechanical devices to carry concentrated inhibitor to the bottom of high pressure and condensate wells periodically and releasing in the concentrated state. This method has given apparently good results thus far. At least treatment at the bottom of the well is assured, but length or period of effective treatment may vary. In testing most operators treat by this method monthly or semi-monthly. The inconvenience and possibly fouling in stick inhibitor type treatment is eliminated almost entirely by this means of application.

Pellet type inhibitors have in recent months gained widespread interest for the treatment of pumping wells where high fluid levels and high water production are encountered, and as outlined earlier, which are difficult to treat effectively as far as bottom hole equipment is concerned. The pellet has definite advantages over the liquid in treating this type of well and may be briefly outlined as (1) ease of application (2) assurance of bottom hole treatment (3) residual action between treatments because of low rate of solubility (4) water soluble or dispersible. Low annular clearance and high casing pressure has made pellet application impractical in some instances, but over all the pellet has definitely help solve a specific problem. Operators report that pumps, rods and other equipment not previonsly receiving adequate protection from liquid inhibitors, are giving much longer service after pellet treatment and in numerous instances, effects of corrosion have for all intents and purposes been eliminated. An actual case history of pellet treatment of a high fluid level well in West Texas over a two year period is shown in Figure 3.

A variety of systems for flushing have been devised, but an elaborate array of flush equipment is not necessary for effective results. Many "home made" systems have been put to good use without an outlay of expensive equipment. The idea is solely to return production into the annular space from tubing or flow line and the

SOLUBILITY AND DISPERSIBILITY CHARACTERISTICS OF INHIBITOR COMPOUNDS.

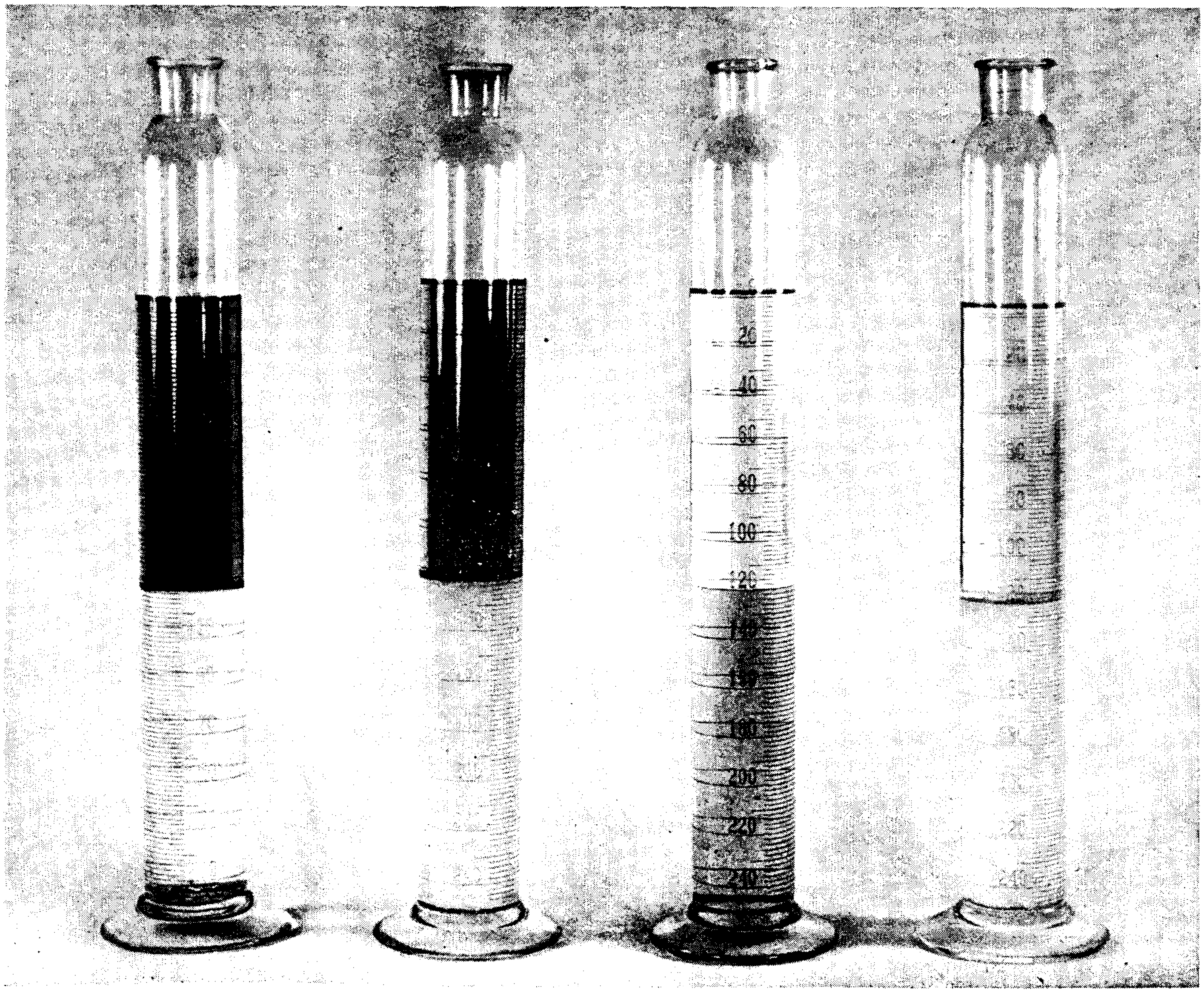
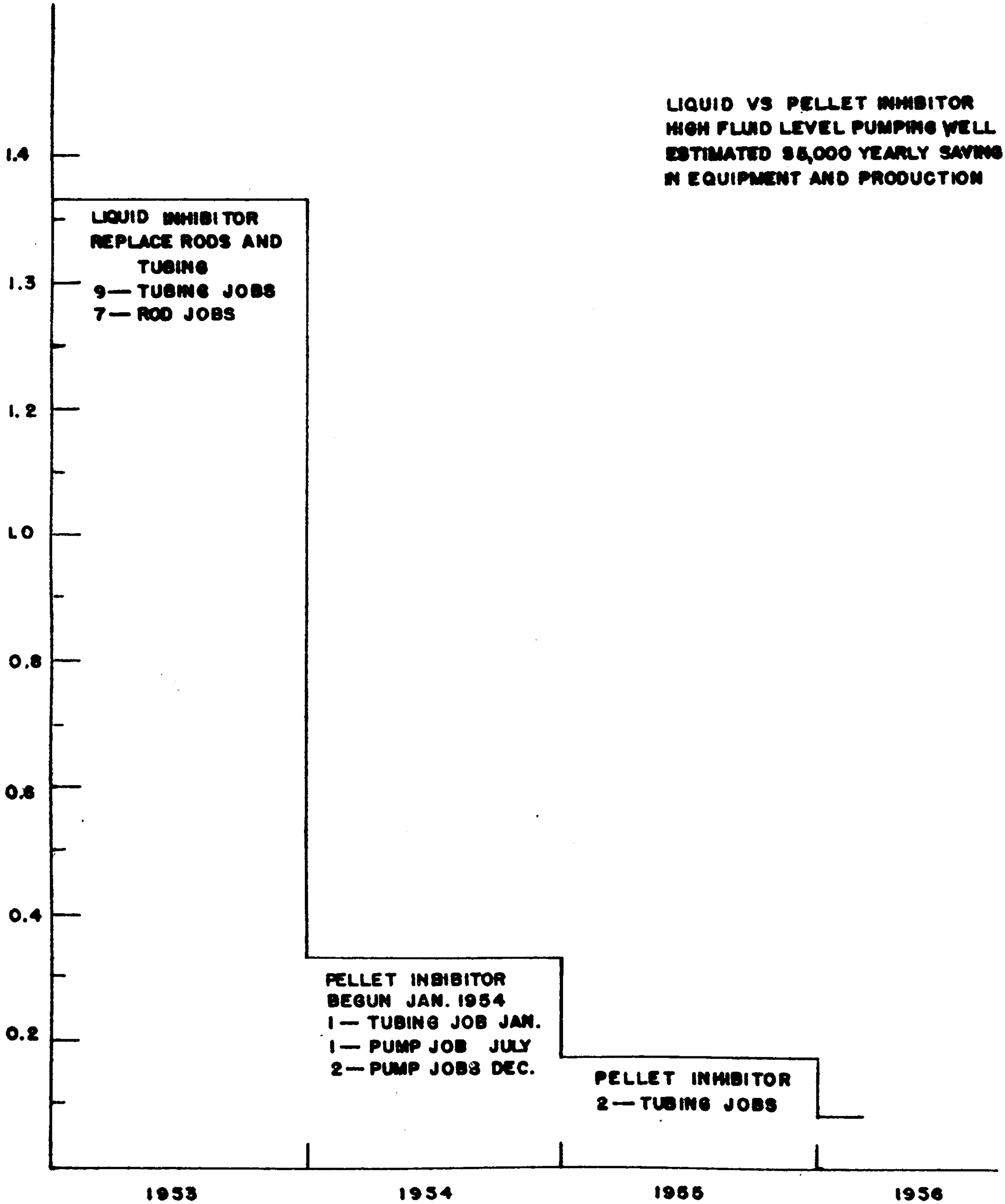


Figure 2

Figure 3


LIQUID VS PELLET INHIBITOR
HIGH FLUID LEVEL PUMPING WELL
ESTIMATED $5,000 YEARLY SAVING
IN EQUIPMENT AND PRODUCTION
1.4
1.3
1.2
1.0
0.8
0.6
0.4
0.2
LIQUID INHIBITOR
REPLACE RODS AND
TUBING
9—TUBING JOBS
7—ROD JOBS
PELLET INHIBITOR
BEGUN JAN. 1954
1—TUBING JOB JAN.
1—PUMP JOB JULY
2—PUMP JOBS DEC.
PELLET INHIBITOR
2—TUBING JOBS
1953
1954
1955
1956

most simple arrangement to accomplish this end is naturally best as long as the safety factor is not overlooked.

Flushing of inhibitor with production accomplishes several very important purposes. Two which are possibly the most important are (1) with proper selection of inhibitor the flush promotes a uniform treatment of well fluids; i. e. the well production is largely water and a water dispersible inhibitor is being used. Then by flushing with production, treatment of both phases is accomplished as intended by the manufacturer. The same analogy would be true with other types of inhibitor and other types of production. (2) Flushing inhibitor into the well affords treatment of annular space equipment; tubing and casing are exposed to treated fluids permitting a greater area of exposure than would be possible with injection of inhibitor alone. Annular space corrosion should be dealt with more specifically however. In many instances, circulation of well fluids for a period of several hours should be undertaken to insure an inhibitor-oil film on exposed metal surfaces. Effect of annular space corrosion on a tubing collar is shown in Figure 4.

In static systems such as an oil filled annular space treated with inhibitor, there should be no further addition of inhibitor required unless the system should require additional oil for some reason. Most inhibitors are stable under ordinary conditions and unless the temperature stability point is exceeded or is reacted with some foreign substance which would destroy its original properties, should remain effective indefinitely. As a direct contrast in respect to corrosion inhibitors, the dynamic system is generally a once through process and the protection or film forming qualities of the inhibitor depend upon its ability to absorb in the presence of high velocity fluids, which tend to carry the molecule away. An absorbed film may actually be eroded away, and if additional inhibitor is not present in the passing fluids by the time the film becomes too sparse to afford protection, corrosion may actually be accelerated at the exposed areas. Because of the relatively large anodic areas in relation to cathodic areas, a severe pitting condition may exist.

The treatment of annular space corrosion has been seriously undertaken by some of the major oil companies and good results have been obtained by widely differing methods of treatment, 3-4. As the science of corrosion control progresses, many innovations in present treating methods, techniques and corrosion treating chemicals will come into being. Even though a concentrated effort to control corrosion in the petroleum industry has been carried for only a few years, great progress has been made in fundamental theories of causes and control. Many technical groups have been organized within recent years, with the express purpose of studying control practices, actual field conditions and methods of determining extent of damage due to corrosion. Of these technical groups the National Association of Corrosion Engineers has set up a number of technical groups throughout the country to study the problem and to report findings periodically. A great deal of valuable information has been contributed by these groups and within the near future much more valuable data will be contributed to further the progress of corrosion control.

EFFECT OF ANNULAR SPACE CORROSION ON TUBING COLLAR.

Figure 4

1. Scot P. Ewing, "Electrochemical Studies of the Hydrogen Sulfide Corrosion Mechanism," Corrosion 11, No. 11, 51-55, 1955.

2. Corrosion 12, 149 T.

3. J. A. Caldwell, M. L. Lytle, "Internal Casing Corrosion in Sour Oil Wells," Corrosion 12, No. 2, 23-26, 1956.

4. H. E. Greenwell, Rado Loncaric, H. G. Byars, "Use of Ammonia To Prevent Casing Corrosion," Corrosion 11, No. 11, 491-496, 1955.