METHODS AND MEANS FOR INTRODUCING CORROSION INHIBITORS INTO OIL WELLS


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This invention relates to the treatment of metal surfaces against corrosion and more especially concerns a method for protecting oil well tubing and other equipment exposed to the production stream of a well against corrosive action of the brine frequently present in petroleum deposits. More particularly the invention is concerned with an improved method and apparatus for injecting certain inhibitor metal ions into an oil well by a suitable vehicle solution, such as the oil well brine itself, bringing such ions into contact with the walls of the production tubing and other equipment requiring treatment.

The invention is herein illustratively described by reference to its presently preferred form as applied to the treatment of specifically different types of oil wells, but it should be understood that certain of the novel aspects of the invention have broad application and that certain variations and changes in the disclosed method and apparatus may be made without departing from the essential features involved.

In many oil, gas and condensate fields the production of fluids from subsurface formations is accompanied by extremely severe corrosion of the ferrous metal tubing and attendant equipment contacted by the production discharge of a producing well. In these fields it was formerly necessary to make extensive and costly replacements of corroded equipment at more or less regular intervals, although more recently discoveries have been made which, although with somewhat cumbersome and expensive methods of application as hereinafter outlined, have enabled the effective treatment of oil well tubing against corrosion. Something of the basic problems involved, certain inhibitor substances formerly proposed and used and certain methods of introducing those substances generally are disclosed in the following United States patents: 2,635,698, Method for Inhibiting Corrosion, G. H. Rohrbach et al., Apr. 21, 1953; 2,635,996, Corrosion Inhibitor, G. H. Rohrbach et al., Apr. 21, 1953; 2,635,997 Corrosion Inhibitor, G. H. Rohrbach et al., Apr. 21, 1953; 2,635,998 Corrosion Inhibiting Composition, G. H. Rohrbach et al., Apr. 21, 1953; 2,636,000, Corrosion Inhibitor Containing Arsenious Oxide and Potassium Hydroxide, G. H. Rohrbach et al., Apr. 21, 1953; 2,635,999, Corrosion Inhibiting Composition Containing Arsenious Oxide and Potassium Hydroxide, G. H. Rohrbach et al., Apr. 21, 1953.

It is generally recognized that corrosion of tubing is mainly the result of attack by the brine which accompanies the produced petroleum products. This brine contains carbon dioxide in solution as well as organic acids rendering it acidic. Also, hydrogen sulphide will often be present, increasing the corrosive action. The produced fluids of an oil well are free of oxygen because this gas has long since been consumed by chemical reaction at the elevated temperatures and pressures in subsurface formations to produce oxyacidic compounds and the oxides of carbon, such as carbon dioxide.

It has been the practice to minimize corrosion in oil wells by adding corrosion inhibiting chemicals to the fluid mixtures produced from the subsurface formations so that these fluids are rendered less corrosive to the well equipment which they subsequently contact in discharging through the well. Many different types of chemicals have been used as corrosion inhibitors, but among the most satisfactory are salts of metals which are more passive than iron in the electromotive series and which function by being reduced at the iron surfaces to form a resistant film of the metallic state of the inhibitor.

Valent arsenic salts are presently being used extensively in the oil fields with excellent results as corrosion inhibitors, while others such as antimony salts show considerable promise.

A variety of methods are used for injection of the inhibitor ion-producing metal salts into the production fluids in oil wells. In those wells which have open annuli, the corrosion inhibitor in solution form is generally pumped or otherwise injected into the well bottom through the open annulus and is carried upwardly with the production stream into spreading contact with the tubing surfaces in order to become adsorbed on those wells having packed-off annuli, production of the well is stopped and the corrosion inhibitor introduced through the production tubing itself. This has been done either by pumping the inhibitor solution to the well bottom and permitting it to mix and flow upwardly with the production stream when the well is again produced, or by dropping the inhibitor in a solid form through the production tubing to the well bottom and then producing the well.

In condensate gas wells the problem is different, since water is present as a liquid only in the top portion of the tubing, viz., above the zone of water condensation, and the corrosion inhibitor is needed on the tubing surfaces only above this zone. The problem is to spread the inhibitor on such surfaces and not wastefully below them. The vapors which exist at lower levels will not carry the desired inhibitor ions, so that merely dropping a solid metal salt, for instance, to the bottom of a gas condensate well will not result in any appreciable treatment of the tubing surfaces. This is true inasmuch as the water in which the salt is soluble at the well bottom travels upwardly only as a vapor until the zone of water condensation is reached. By arranging for the solid metal salt to sublimate on the tubing as it falls down the string, however, inhibitors have been effectively dispersed in gas condensate wells with some success.

It is recognized that there are many difficulties and shortcomings of presently used methods of introducing metal salt inhibitors into oil wells. In the condensate wells it is virtually impossible to treat all the corrosion-vulnerable surfaces without permitting quantities of the metal salt to fall as waste below the zone of condensation. A solid form of the inhibitor can perhaps be made which will soften quickly at well temperatures, but there is no certain way of determining how far down the tubing the inhibitor will fall before it is substantially completely dispersed on the tubing wall. Hence there is a certain way of determining that all of the vulnerable surface area is protectively covered nor that a large amount of waste is not occurring. Baskets or wire catchers may be placed in the tubing to prevent fall of the inhibitor beyond a given point, such as the beginning of the zone of condensation and thereby provide a desirable inhibitor substance at that point which gradually dissolves in the production stream over a limited period of time and provides continuing treatment of the tubing for a short period. However, these devices are not positive safeguards inasmuch as they must be of open or perforated construction in order to permit production of petroleum...
through the well tubing, and particles of inhibitor can still drop through the openings as waste. Also, such devices obstruct the tubing passage and tend to restrict production. A further difficulty resides in the manufacture of inhibitors in solid forms having a specific shape, softening characteristics, and specific density to fall and remain down the tubing at the desired location against the forces of the production stream.

While the metal salt inhibitors may be injected in liquid form into open annuli and packed-off annuli wells, further difficulties and objections are encountered there. Water solutions of the salts of arsenic and antimony are highly poisonous and must be handled by elaborate precautions and with great care. The relatively poor solubility characteristics of these salts present further problems. Arsenic salts, the preferred inhibitor salts, can be maintained in concentrated solution only by use of strongly caustic solutions, which introduce another extreme hazard in handling. Antimony salts cannot be maintained in concentrated solutions which are stable, and the treatment of a well to be effective even for a short period with these salts requires such very large quantities of solution as to make their use generally impractical.

Perhaps the greatest objection to existing or former methods for injecting certain inhibitor metal substances into oil wells, however, is that the treatment procedure must be repeated very often, usually daily, in order to insure constant protection against corrosion. The cost of such frequent services is relatively high and in extreme cases may even approach or exceed the savings realized through reduced maintenance costs by the use of any inhibitors.

It is a general object of the present invention to provide an improved method for injecting metal ion inhibitors into oil-wells which will eliminate the above-mentioned and other disadvantages of previous methods. It is a further object to provide an injection method and means readily adaptable to any of the types of oil wells encountered.

A very important object of the present invention is a method and means for providing continuing treatment of oil wells over long periods of time without interrupting well operations and without requiring the attention of an operator nor the transportation of expensive equipment to a well at regular short intervals. In this connection the invention provides a positive, convenient and easily controlled means for injecting the active inhibitor element at the desired well in a process capable of continuing without aid or attention over a long period of time.

With the foregoing and other objects in mind, the present invention is predicated on the observation that the desired inhibitor action realized from the use of certain metallic salts such as those described in the above-mentioned patents, results from the presence of metal ions which the salts produce when dissolved. These metallic ions, selected from the group comprising arsenic and antimony, are reduced to the metallic state on the ferrous metal tubing surfaces of the oil well and form a highly effective corrosion inhibiting film on those surfaces. In accordance with the present invention, the desired inhibitor metal ions are produced for introduction into the well at any desired location by subjecting a body of the inhibitor metal element in its metallic or solid state to electrolysis, and in that manner slowly releasing the ions at a desired or controlled rate rather than in the relatively sudden complete manner attending the dissolution of a metal salt. The body of inhibitor metal is formed and arranged as the anode of an electrolytic cell and, because of the relatively small quantities of ions required for effective inhibitor action in the well if supplied substantially continuously, constitutes a relatively enormous store of ions which will last a long time when released at a rate not greatly exceeding the corrosion prevention requirements of the particular well. Such a process may be carried out with minimum inconvenience and expense and once set into operation under conditions adjusted to the requirements of a particular installation will continue to provide effective corrosion protection efficiently over long periods of time without any attention.

Preferably electrolytic displacement of the inhibitor ions forms the metallic electrode into solution in accordance with the improved method is effected by application of externally generated electromotive force between the cell electrodes; however, by certain well known principles it is possible by a proper selection of cathode material to realize an electrolytic displacement of metallic ions from an anode of one of the desired inhibitor metals without any externally applied E. M. F. Displacing the desired inhibitor ions into solution by means of applied voltage constitutes a method which lends itself to certainty in the control of the rate of injection of inhibitor ions at any desired value within wide limits and also a convenient basis automatically regulating the selected rate of ionic displacement if desired, namely by automatic electric current regulating apparatus incorporated in the external source of voltage.

The electrochemical reaction taking place when voltage is applied to the inhibitor metal anode and the opposing cathode is represented as follows:

\[ M = M^{n+} + n e \]

wherein M is the metallic state of the metal, M\(^{n+}\) is the water soluble metal ion having a positive charge of \( n \) units and \( n e \) is the number of electrons given up by one metal atom in passing from the metallic state into the ionic state, that is from M to M\(^{n+}\). In the case of arsenic and antimony electrodes the respective electrode reactions at the anode would be As\(\rightarrow\)As\(^{5+}\) + 5e and Sb\(\rightarrow\)Sb\(^{3+}\) + 3e.

In the preferred embodiment of the invention the electrolyte into which the inhibitor metal ions are displaced electrolytically is the water contained in the well or separated from the production stream of the well. This water is generally highly conductive to electricity because of its appreciable salt content and its weak acidity; moreover, it is oxygen-free. When a direct current of electricity is passed through this brine between an anode of metallic or antimony and a cathode, for example, the desired metal inhibitor ions are formed at the anode surface while hydrogen gas is liberated at the cathode surface. Of course, metals other than iron may be used for the cathode, and in this connection those metals which are not themselves attacked by corrosive action of the well brine and which have low corrosion potentials are particularly suitable, since the potential required to operate the inhibitor ion-hydrogen cell is then kept low. In many instances, however, it is convenient to use iron for the cathode due to its mechanical properties and in some cases because it enables making the well tubing itself a cathode. Carbon or graphite cathodes are also suitable, though for obvious reasons are usually less practical than iron even if the cell is located entirely outside the well, since the structural and other mechanical characteristics of carbon or graphite do not compare with iron.

If necessary or desirable, electrolytes other than the well water or brine may be used. Regardless of the source of the electrolyte and of the specific location of the electrolytic cell (i. e. whether externally of the well i. e. above ground, at the bottom of the well, or inside the well tubing at a suitable position therein, the important consideration is the continuous or intermittent generation of inhibitor ions at a desired or controlled rate over long periods by electrolytic action and the introduction of such ions, likewise continuously or intermittently, into the tubing for creating the corrosion inhibitor film therein. For reasons of convenience and cost the desired ions preferably will be generated substantially at the condensation level in a gas condensate well, at the
bottom of the tubing string in the case of a packed-off annulus well and above ground (or at the well bottom) in the case of an open annulus well.

In a basic sense the invention provides a novel method and apparatus for treatment of metal surfaces and especially to the prevention of corrosion and similar effects over prolonged periods of time.

These and other features, objects and advantages of the invention, including certain details of the illustrated methods and apparatus for practicing the same, will become more fully evident from the following description by reference to the accompanying drawings, particularly to a gas condensate type well, wherein the inhibitor anode is located part way down the well.

Figure 4 is a vertical sectional view of a modified inhibitor ion-hydrogen cell.

Figure 5 is a vertical sectional view of a further modified cell.

In Figure 1 a producing oil well of the open annulus type is illustrated in which brine-petroleum mixtures flow from the producing formation 10 into the well bottom 12 and upwardly through the production tubing 14. An oil-water separator trap 16 is set in the surface flow line 18 for removing the producing tubing 14 and constituting an effective extension of such tubing. Some of the produced brine will settle in the bottom of the trap, and this water is drawn off at a slow rate approximating the rate at which it accumulates therein through a pipe 20 by a pumping unit 22 by which it is injected into the iron cell vessel 24. The metal anode 26 which will dissolve electrolytically to give the desired metal inhibitor ions, selected from the group comprising arsenic and antimony, is positioned inside the iron cell vessel at a desired spacing from the surrounding interior of the chamber or vessel. Suitably insulated from the chamber walls, the metal anode 26 is connected to an insulated wire 28 which runs through a packing gland 30 out the top of the vessel 24 and to the positive terminal of a variable direct-current source 32, which may comprise any suitable type of direct current generator or converter. The negative terminal of the direct-current source 32 is connected to the vessel 24 by means of another insulated wire 34, enabling the ferrous metal walls of the vessel to function as a cathode. The negatively charged vessel 24 is insulated from the pipes 20 and 36 leading to it by means of insulated connecting flanges. The water stream pumped at least intermittently and preferably continuously from the trap 16 into the vessel 24 during well production is charged with ions therein by at least intermittent and preferably continuous application of voltage to the cell electrodes. Such brine carrying the desired inhibitor metal ions discharges or is dispersed or spread into contact with all of the metal surfaces of the oil well and related equipment subjected to corrosive attack and provide continuing protection against corrosion while the well produces.

Moreover, by this arrangement the extremely potent metal corrosion inhibitor ions such as arsenious (trivalent) arsenic ions are continuously fed into the well bottom at a rate which may be readily controlled. Such control is effected simply by adjusting or controlling the electric current flowing between the inhibitor metal anode 26 and the ferrous metal cathode comprising the interior of the iron cell vessel 24. This electric current flow and consequently the rate of inhibitor action may be readily varied by any suitable means, of which there are many well known types, for adjusting the voltage of the direct-current voltage supply 32. Further, the rate of the electric current flowing in the cell may be provided in order to regulate the ionic generation rate from the metallic anode at a desired constant value which yields the optimum (sufficient but not wastefully excessive) rate of generation of inhibitor metal ions for effective inhibitor action in the well equipment. The techniques by which such current regulation may be accomplished are well known and require no description herein.

The iron cell vessel 24 is constructed with an easily removable top (not illustrated in detail) permitting replacement of an inhibitor metal anode 26 which has become spent over a period of time. Such replacements will be very infrequent, because of the vast store of inhibitor ions comprised in a relatively small solid inhibitor metal anode at the low rate of generation of these ions necessary in the system for effective corrosion inhibiting action. Moreover, at the low rate of dispersement of ions required for effective inhibitor action in a well the amount of electrical energy consumed by the system is relatively small as an item of operating expense.

It will be noted that the process of extracting electrolyte in the form of brine separated from the petroleum in the production stream of the well and of passing this electrolyte through the electrolyte cell containing the inhibitor metal anode before injection back into the well is also a factor in the over-all process minimizing the operating expense involved. The conditions under which this preferably continuous or substantially continuous process is carried out, including the magnitude of electric current passed through the electrolytic cell, can be so adjusted, especially after a little experience in a particular field, that corrosion in the tubing and related equipment is effectively prevented without wasting electrical energy, inhibitor metal, and other elements which enter into the determination of cost. However, even under poorly adjusted operating conditions wherein there is some unnecessary waste, the efficiency of the present method greatly exceeds that of former methods. This is particularly true because the continuous reduction of inhibitor ions to the metallic state on the well tubing surfaces may be established and maintained at the required value to offset the continuing tendency for the inhibitor film on the protected tubing to dissipate during production of the well.

With previous methods requiring frequent (usually daily) treatment of the wells it was usually necessary to greatly exceed the required concentration of ions in the well initially in order to be certain that a sufficient residue of the inhibitor would still remain in the well by the end of the period between successive treatments. Thus the production stream of the well immediately following an injection of inhibitor metal salts under the former method would carry with it many times the concentration of ions necessary for effective inhibitor action, in order that the discharge at a later time would possess the necessary concentration.

Should the rate of extraction of brine by the trap 16 and delivery by pump 22 to the electrolytic cell vary, the concentration of ions being produced in the cell will likewise vary if the magnitude of direct current between the electrodes remains substantially unchanged. However, the total number of inhibitor ions generated by the cell under these conditions over any period of time, hence the rate of injection of ions into the well would
remain substantially constant due to the substantially fixed relationship between quantity of ions displaced and quantity of electricity utilized. It is therefore unnecessary to regulate carefully the rate of flow of brine in the electrolyzing fluid circuit comprising the trap 16, the pipe 20; the cell, the pipe 36 and the well casing.

Due to the present disclosure and appended claims it should be appreciated that the best results from the invention are achieved if the process of generating ions and of conveying those ions to the well are carried out substantially continuously. At the same time, however, interrupted or intermittent operation is possible and is not precluded.

In Figure 2 the method is applied to a well which may be either of the open annulus or the packed-off annulus type. In this case the metal anode 26a comprising the inhibitor element is suspended in an electrically insulating container 44 of porous or open construction, attached to the bottom of the string of production tubing 14 by suitable means not illustrated in detail. The insulated conductor 46 extends from a point of connection to the anode 26a upwardly through the annular space between the well casing 38 and production tube 14 for connection to the positive terminal of the variable direct-current source 32. The negative terminal of this source is connected to the metal tubing 18 at the top of the well by the insulated conductor 48. The production tubing string 14 serves as an electrical conductor, and its lower regions generally adjacent the anode 26a are thereby placed at a potential negative with respect to such anode. This is also true of the lower end regions of the casing string 38, since this casing is also of metal and is necessarily in electrical contact with the tubing 14 at one or more points. Together the lower ends of the casing 38 and tubing 14 provide cathode surfaces essentially of iron which cooperate with the inhibitor metal anode 26a, both being immersed in the well liquid immediately below the ends of these tubes. Thus, electric current passes through the well liquid and metal inhibitor ions are liberated at the anode 26a, whereas hydrogen is liberated on the surfaces of the casing 38 and 36.

The fluid in the bottom of the well which immerses the opposing electrode surfaces is not essentially brine as it was in the case of the arrangement illustrated in Figure 1, but rather consists of a mixture of brine and petroleum in a ratio which varies at different wells. It is found, however, that the electrolytic action achieved and the generation of inhibitor metal ions from the anode 26a takes place in the desired manner here just as it does in the arrangement of Figure 1. The electrical resistance through the combined petroleum and brine bottom of the well is greater than it is in the case of electrolyte comprising essentially brine, and a slightly higher potential is ordinarily required, therefore, in order to produce ions at the necessary rate, but this is easily accommodated in any practical case simply by increasing the voltage of the electric current source 32 above that used in the previous example. Some additional increase in this voltage may be necessary if the electrical resistance of the combined tubing strings 14 and 36 is relatively high (i.e., in a very deep well), but this may be avoided if desired by extending the conductor 48 from the negative terminal of the source 32 directly to the lower surface area of the tubing 14. The inhibitor metal ions liberated at the anode 26a flow directly up the production tubing 14 with the production stream of the well and, as in the previous example, provide a desired deposit of metallic inhibitor on the tubing 14, as may be the case in the corrosion-vulnerable surfaces. The rate of liquid flow through the discharge tubing 14, hence the rate of change of the body of liquid functioning as electrolyte in the electrolyzing zone of the cell comprising the anode 26a and the lower surface areas of the strings of tubing 14 and 36 does not greatly affect the rate of liberation of inhibitor ions, since that is a direction function of the rate of exchange of electrical charge, that is the magnitude of electric current-flowing.

In the third type of situation, as illustrated in Figure 5, the inhibitor metal anode 26b is suspended inside the production tubing string 14 at a desired point between the well bottom and the well head. In the case of a gas condensate well, this electrode would be positioned near the lower end of the condensation zone where water begins to form as liquid, simulating the condition conducive to corrosion which is identical to that permitting the ionizing process to be carried out in order to combat corrosion. The electrode is carried inside an electrically insulating container such as an insulating perforated or open mesh plastic basket 50 which prevents direct electrical contact between the metal anode and the wall of the tubing 14. An insulated electrical conductor 52 extending from the positive terminal of the direct-current source 32 extends down through the production tubing 14 for making an electrical connection with the anode 26b. This insulated conductor may also serve as a means for the physical suspension of the anode basket 50 in the well. A second insulated electrical conductor 54 is connected at ground level between the negative terminal of the direct-current source 32 and the metallic tubing 14. Thus the production tubing serves as an electrical conductor and as casing there in the case of Figure 2. As in the preceding example, positive inhibitor metal ions are liberated from the anode surface by electric current flow through the production fluid of the well. These positive ions are carried upwardly through the production tubing 14 and constantly wash over the corrodeable surfaces of such tubing and any other corrodeable surfaces contacted by the well production in order to form the desired inhibiting film thereon.

It has been found that antimony can be cast into a suitable electrode form by pouring the molten metal around a center contact rod made of a metal lower in the electromotive series, such as copper or silver, or around a rod of carbon. Such cast metal electrodes will function satisfactorily in the arrangements illustrated in Figures 1, 2 and 3. However, in the case of arsenic, the preferred inhibitor metal, the casting of a suitable anode is not an easy task. Metallic arsenic is brittle, and it is extremely difficult to cast because of its boiling point being lower than its melting point except at high pressures. Alloys of arsenic with other metals in the instance in 50%–20% range respectively, exhibit better casting characteristics but are not as suitable as antimony in that respect. Moreover, the pure metal is preferable for the process of the present invention.

This difficulty with manufacturing an anode from pure metallic arsenic may be easily overcome for present purposes, however, by forming the anode in the manner illustrated in Figure 4. In that example the iron core vessel 54 is of similar construction to that shown in Figure 1, but the positive conductor 28a leading from the positive terminal of the direct-current source 32, extends through a packing gland 56 in the side of the vessel and is connected to the side wall of a cylindrical container 58 of carbon or graphite. This carbon container is in the form of an open cup having an aperture in its bottom which snugly receives the tube 60 for admission of brine from the pipe 20 into the cup's interior. This tube 60 is of suitable electrical insulating material such as a corrosion resistant plastic or hard rubber. The carbon cup 58 is supported out of direct contact with the ferrous metal casing 54 by means of a solid rubber or plastic insulating ring preventing annular space to prevent the electrolyte from entering between these two elements differing in electrical potential. The walls of the ferrous metal vessel 54 function as cathode and for that purpose the vessel is connected by the insulated wire 34a leading to the negative terminal to the direct current source 32.
Lumps or particles of arsenic metal 64 are placed in the carbon cup 58 through the removable vessel lid 42 and make electrical contact with the cup. Pure arsenic metal in lump or powder form is commercially available and by the illustrated arrangement for holding a quantity of it, inside the positively charged carbon cup, is enabled to function as the anode of the electrolytic cell. Such an electrode is virtually as efficient electrolytically as a cast solid arsenic electrode and is manufactured at much lower cost. Due to the conductivity of the carbon cup 58 and its inability to dissolve in an anodic reaction, the carbon vessel acts merely as an electrical conductor and container for the divided anodic material. The latter is thereby enabled to produce the desired arsenic inhibiting ions carried off by the stream of brine flowing constantly through the cell.

With the arrangement illustrated in Figure 1, when the electric current passing through the ion generating cell is increased, or the flow of brine is decreased, the concentration of metal ions in the stream of brine injected into the oil well will correspondingly increase. It is found that in some situations the volumetric flow of brine through the cell may decrease to the point that a given electric current magnitude in the cell the concentration of inhibiting metal ions in the brine can become so great that some of these will be reduced and deposited on the cathode surface. This effect is negligible for antimony and is small for arsenic except under extremely high current densities and low brine volumetric injection rates. It can also be made negligible for arsenic, however, by an arrangement such as that illustrated in Figure 5. While Figure 5 is diagrammatic and the details of the two electrodes, especially the anode, are not illustrated, the important feature to be noted lies in the positional relationship of the two active electrodes relative to each other and to the directional flow of brine through the cell. In this case the ferrous metal vessel comprises an upper section 54a and a lower section 54b, insulated at a connecting flange 54c from the upper section. The negative terminal of the electrical current source 32 is connected by an insulated conductor 34c to the lower section 54b. The lower section thereby is enabled to function as the cathode from which the upper section is electrolytically insulated. The inhibiting metal anode 2ac, connected by the insulated conductor 28b to the positive terminal of the current source 32 is suspended inside the vessel so that its entirety lies appreciably above the top of the cathode section 54b of the vessel. Since the flow of brine through the cell is upward the anode lies “downstream” from the cathode surface. Arsenic inhibiting ions liberated at the anode 2ac tend to be drawn directly out of the cell by the pipe 36 and have relatively little opportunity to come into contact with the active cathode surface for reduction thereon. Accordingly, this type of arrangement minimizes the opportunity for reduction of generated inhibiting metal ions, which in some situations wherein arsenic anodes are used tend to reduce the efficiency of the cell.

Passage of direct current is the simplest and the presently preferred method of generating inhibiting metal ions according to the invention. However, it is also possible to generate such ions by application of alternating voltage directly between an electrode of the inhibiting metal and a suitable cooperating electrode. In this case it is important that the conditions of electrolysis permit the inhibiting metal electrode to function as anode at least during part of the alternating voltage cycle, and that the cooperating electrode be chosen of a material which does not produce ions detrimental to the oil well equipment. With some inhibiting metals, two electrodes both of the inhibiting metal itself may be used and alternating current passed directly between them through the brine electrolyte. Under those conditions inhibiting metal ions are generated at one electrode and hydrogen gas at the other electrode during one half cycle of current flow, whereas the reverse reactions occur on the other half cycle. The two inhibiting metal electrodes are thereby dissolved at equal rates in generating the desired inhibiting metal ions.

With two arsenic metal electrodes, however, the reactions are more complicated when alternating current is employed. The electrode instantaneously serving as anode dissolves to give the desired trivalent inhibitor ions, but the cathode reaction generates not only hydrogen gas but arsenic hydride, AsH₃. This hydride provides some corrosion inhibiting action due to its reduction on the oil well ferrous metal surfaces to form an arsenic metal film thereon; however, it is less efficient for the protection than arsenic ions generated directly by electrolysis. The more suitable method with alternating current in the specific case of arsenic is to employ an electrode of arsenic metal cooperating with two separate electrodes of a conductor which cannot dissolve as an anode (carbon meeting this requirement) or of a conductor which causes rectification of the alternating current (aluminum meeting this requirement). With this latter arrangement alternating voltage is applied between the arsenic electrode and each of the two separate electrodes with opposite phase relationship, so that one of the latter is positive relative to the arsenic electrode while the other is negative relative to the arsenic electrode, and likewise, in a manner all of the arsenic metal is used to generate the desired inhibiting arsenic ions, since on each half cycle the arsenic electrode functions as anode relative to one of the two separate electrodes while hydrogen gas alone is liberated at the latter as alternately acting cathodes.

From the foregoing it will be clear that the present invention provides a method and apparatus for the effective, safe, convenient and versatile injection of inhibitor metal ions into oil wells for preventing corrosion of the ferrous metal surfaces subject to attack by the production stream brine. In this regard the former danger and inconveniences of handling the preferred inhibitor metal salts are avoided, since the metallic forms of arsenic and antimony employed in the present invention are safe to handle. Moreover, it is no longer necessary to carry and inject large volumes of poisonous solutions nor to undertake difficult manufacturing procedures for producing special solid forms of metal salts to be dropped into the well tubing as a means of tonic dispersal therein. Furthermore, the present invention more readily enables the selection of the precise point at which the inhibitor ions may be generated and introduced into the well, so that the different types of wells mentioned may be conveniently and efficiently treated with minimum waste. It will also be apparent that the method lends itself to positive and convenient control of the rate of injection of inhibitor metal ions into the well, since it is merely necessary to adjust, and automatically regulate if desired, the electric current passed through the electrolytic cell in order to secure the desired rate of ion generation. The method is not critical with respect to the variations in the rate of circulation of brine constituting the electrolyte since the primary determining factor in the rate of ion generation is the electric current magnitude. Nor is the method dangerous because of possible fires since the required voltages are not high; moreover, the absence of oxygen in the well fluids practically eliminates the possibility of combustion in regions in which the electrolysis is carried out.

Of perhaps greatest significance, however, is the advantage of continuity and the adaptability to automatic continuous protection of an oil well installation without the frequent attendance of service operators who in the past have been forced to make daily salt hikes in oil fields in order to treat each well usually once a day for effective and constant protection against corrosion. For example, in the present invention the treatment of a well producing one hundred barrels of water daily with
sufficient metal ions to maintain a concentration of ten parts per million by weight of inhibitor ions in the produced water would require an expendable inhibitor metal anode weight of only twenty-four pounds to treat the well for a period of sixty days. In other words, the invention offers an extremely compact treating system of low cost, since a tremendous store of desired inhibitor metal ions are present even in a relatively small solid metal electrode.

Having described the invention in its preferred form and aspects and by way of example, it will be readily appreciated by those skilled in the art that various changes and modifications in the method and in the details of carrying out the principles thereof in practice are possible, as well as variations in the applications of those principles to provide anticorrosion protection.

I claim as my invention:

1. The method of inhibiting corrosion of ferrous metal tubing surfaces in an oil well by the production fluids of the well, comprising the steps of producing a solution containing inhibitor metal ions capable of chemical reduction at said surfaces to deposit an inhibitor film thereon, wherein said solution is produced by passing electric current through an electrolyte between an anode comprising said inhibitor metal and a cathode, and com mingled said solution with the well production fluids during well production to be carried thereby into contact with said surfaces for chemical reduction thereon.

2. The method defined in claim 1, wherein the solution is produced and commingled with the well production fluids at least at intervals over an extended time period to maintain a corrosion inhibitor film on the tubing surfaces continuously during well production.

3. The method defined in claim 1, wherein the solution is produced and commingled with the well production fluids substantially continuously during production of the well.

4. The method defined in claim 1, wherein the inhibitor metal comprises arsenic.

5. The method defined in claim 1, wherein the inhibitor metal comprises antimony.

6. The method defined in claim 1, wherein the solution is produced and commingled at least at intervals over an extended time period during production of the well, and wherein the electrolyte is provided by separating briny water from the well production stream and passing such briny water electrolyte between the electrodes.

7. The method defined in claim 1 applied to a gas condensate well, wherein the production of the ion-containing solution is effected in the vicinity of the lower end of the gas condensation zone where water begins to form as liquid, the production liquids of the well serving as the electrolyte.

8. The method defined in claim 1, wherein the production of the ion-containing solution is effected at the bottom of the well.

9. The method defined in claim 1, wherein the production of the ion-containing solution is effected outside the well.

10. Apparatus for inhibiting corrosion of ferrous metal surfaces in an oil well by the production fluids of the well, comprising means forming an electrolyte cell for producing a solution containing inhibitor metal ions capable of chemical reduction at said surfaces to deposit an inhibitor film thereon, said means including an anode of said metal, a cathode, means forming a space containing electrolyte between said anode and cathode, means for passing electric current through said space between said anode and cathode, and means introducing an electrolyte into said space to produce said solution and thereupon commingling said solution with oil well production fluids at least at intervals during well production, at a location in said well from which to be carried by said production fluids into contact with said surfaces, thereby to prevent corrosion of said surfaces by said production fluids.

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