US 20120217012A1

(19) United States

(12) Patent Application Publication

(10) Pub. No.: US 2012/0217012 A1

(43) Pub. Date: Aug. 30, 2012

DARBY

(54) METHOD OF INTRODUCING TREATMENT AGENTS INTO A WELL OR FLOW CONDUIT

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(21) Appl. No.: 13/034,546

(22) Filed: Feb. 24, 2011

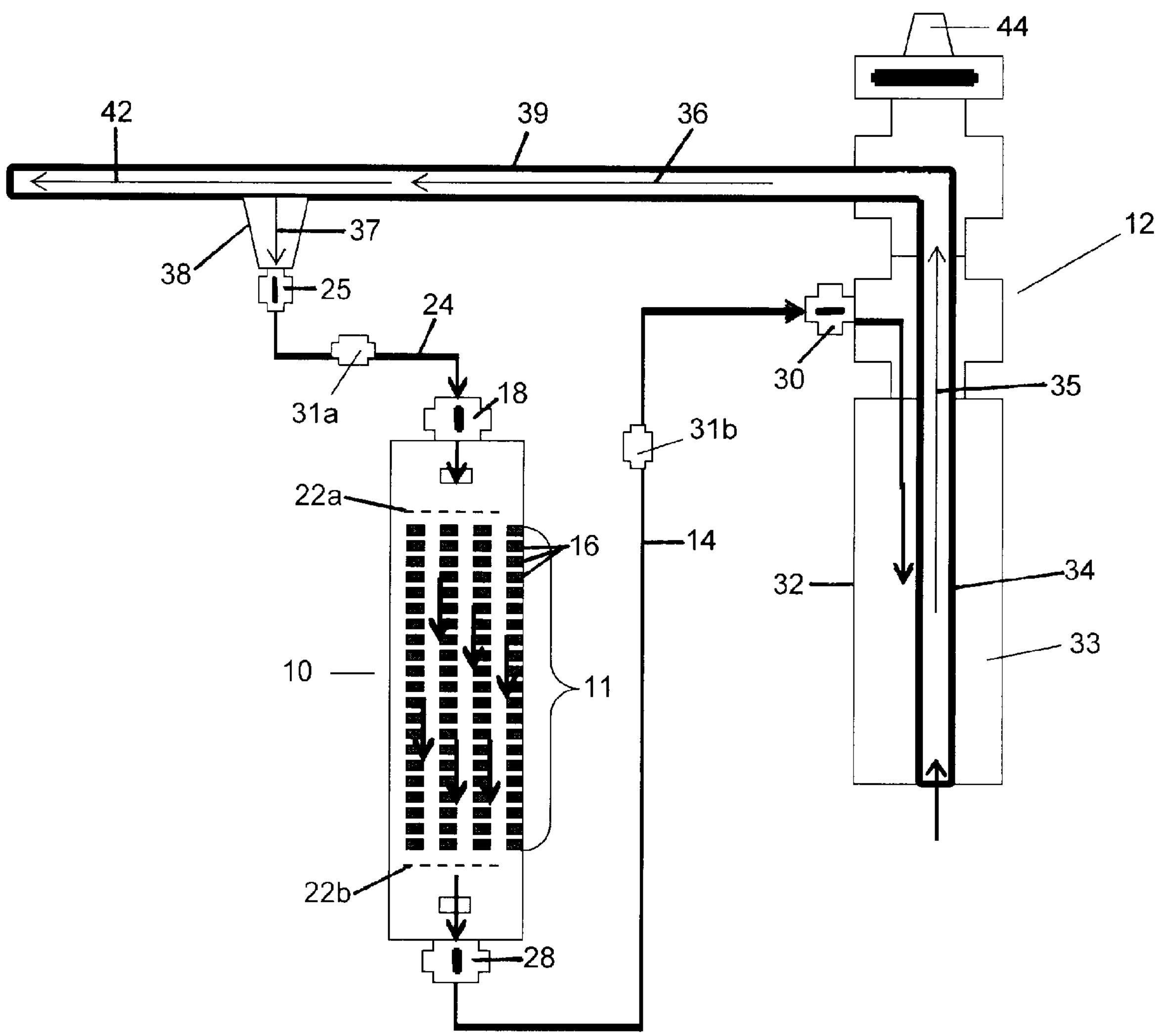
Publication Classification

(51) Int. Cl.
E21B 43/16 (2006.01)

(52) U.S. Cl. 166/305.1

(57) ABSTRACT

A treatment agent retained in a housing may be slowly and continuously released into a targeted area in a well or in a flow conduit. The housing contains a confinement area. Movement of the treatment agent is limited in the confinement area by a retainer.



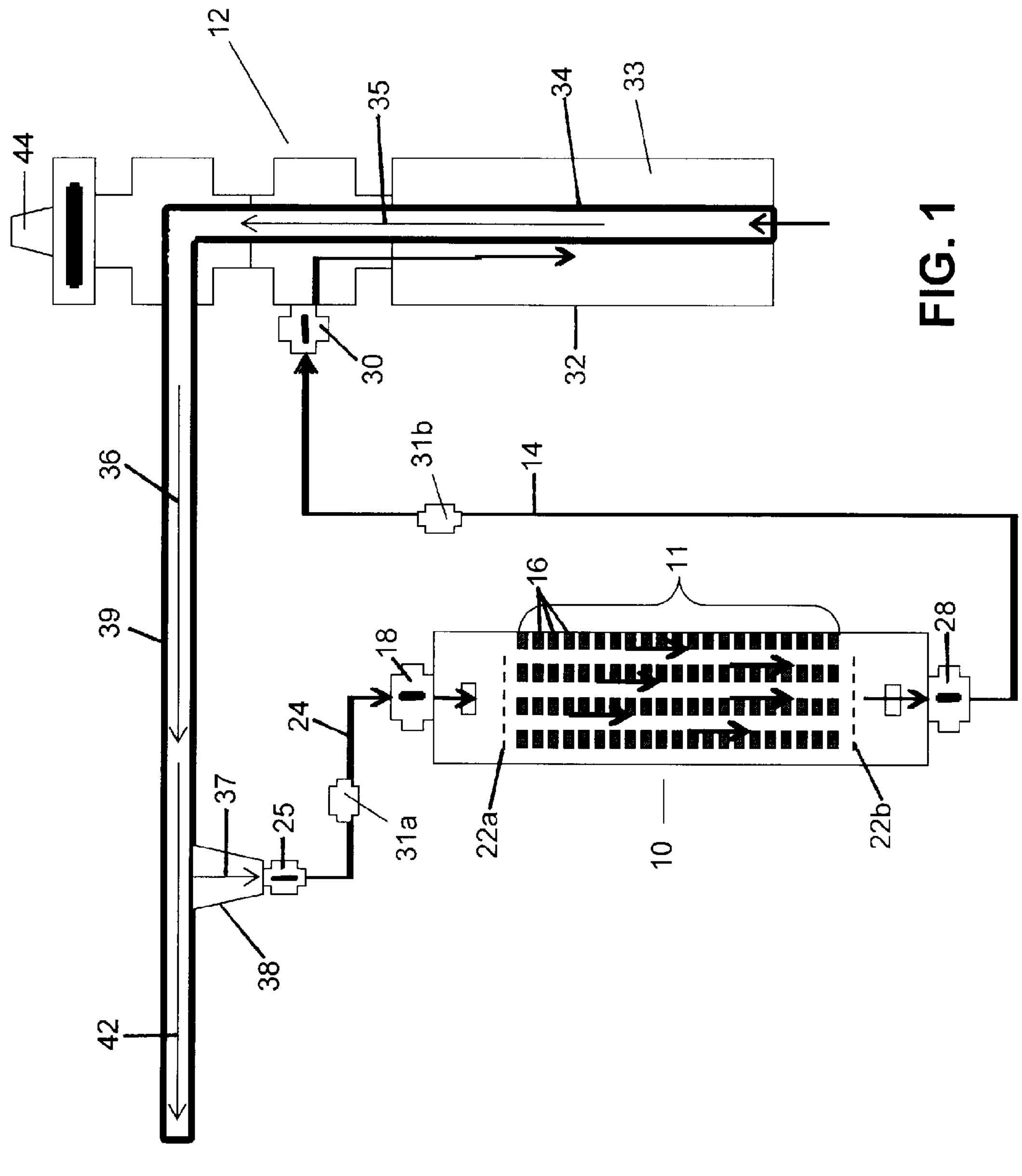

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FIG. 1

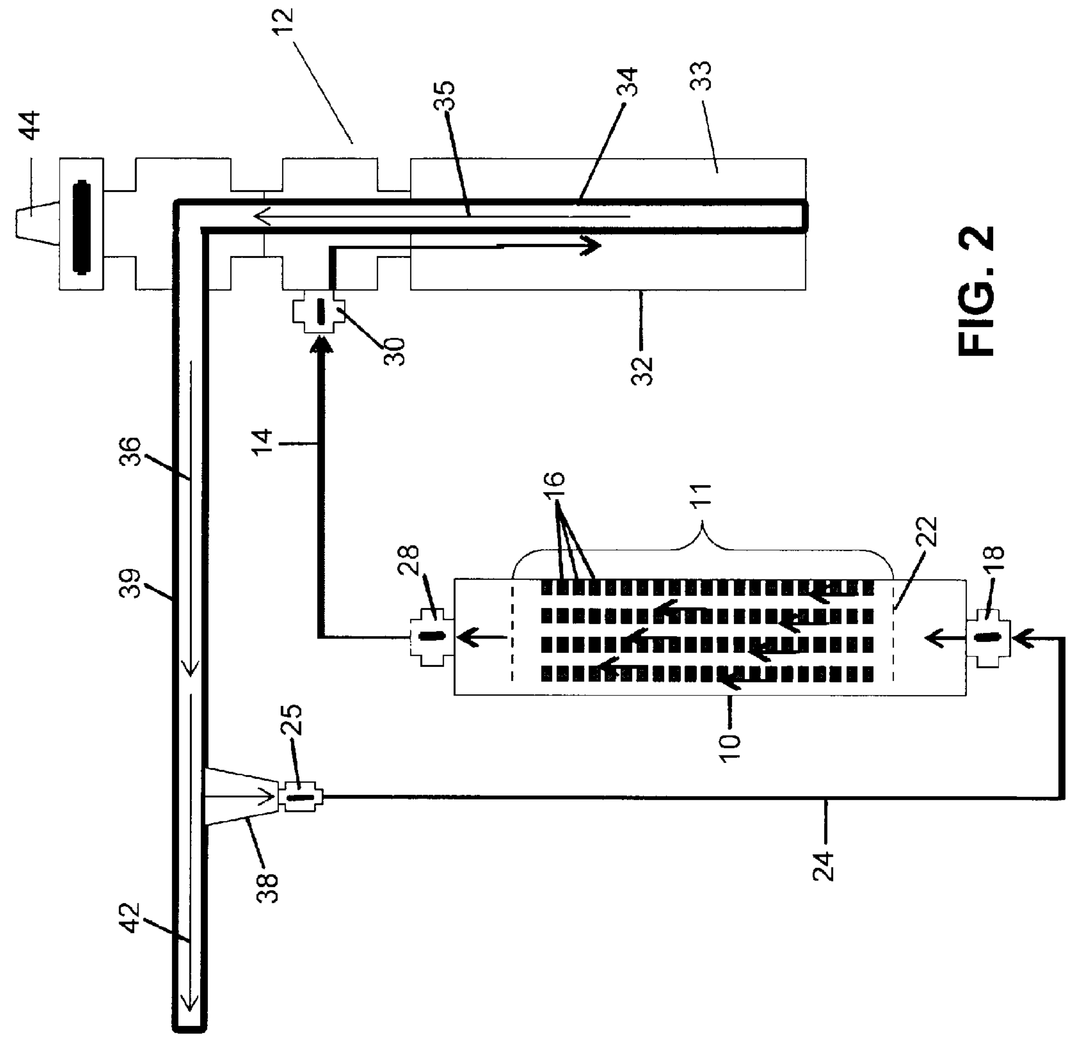

FIG. 2

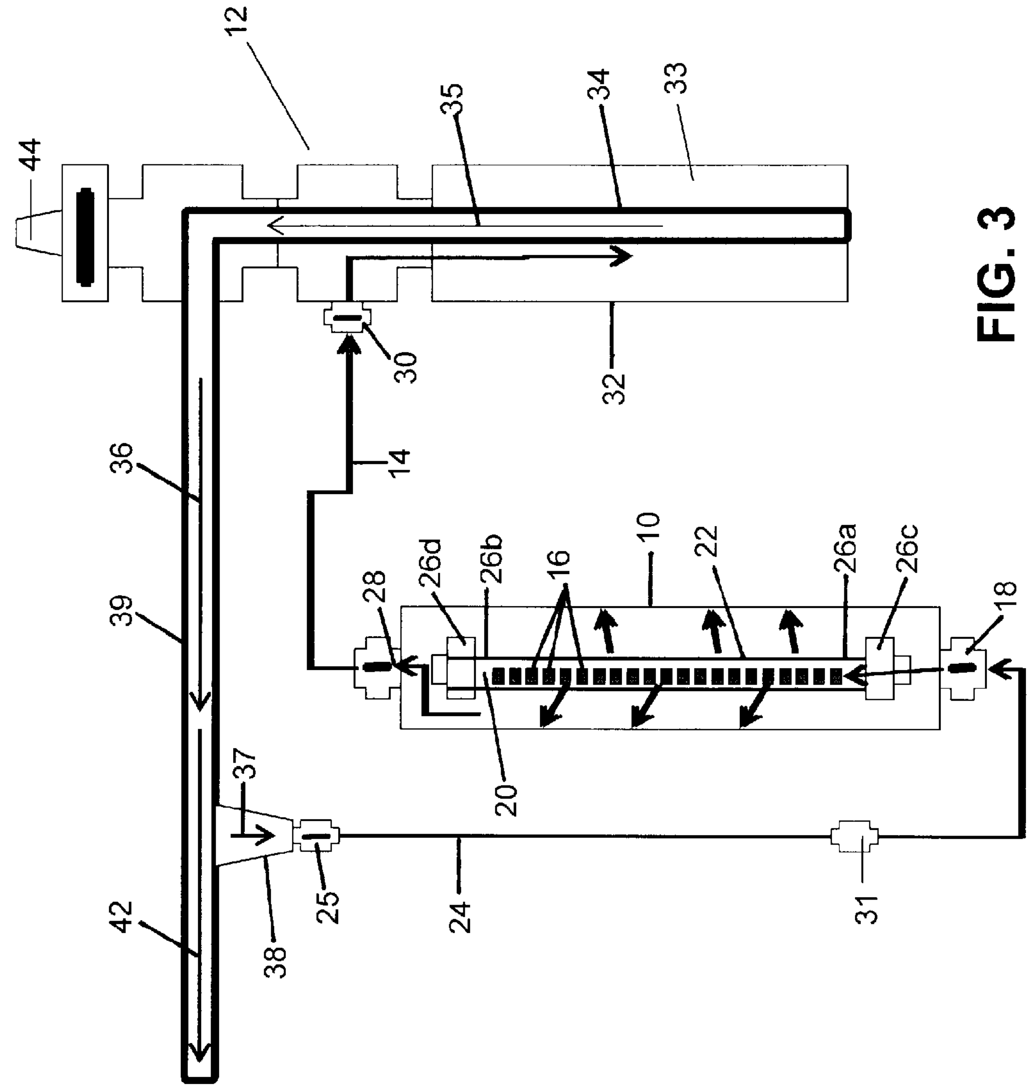

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FIG. 3

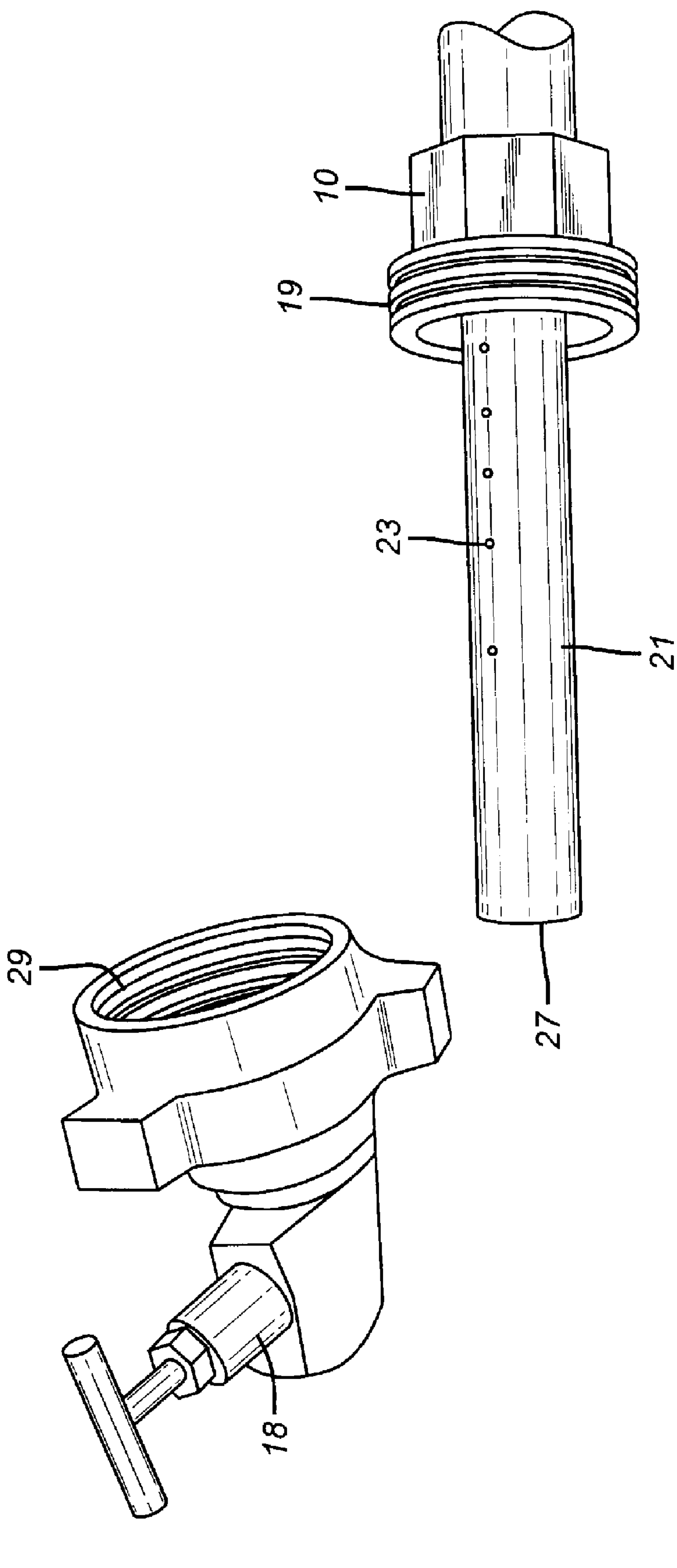

FIG. 4

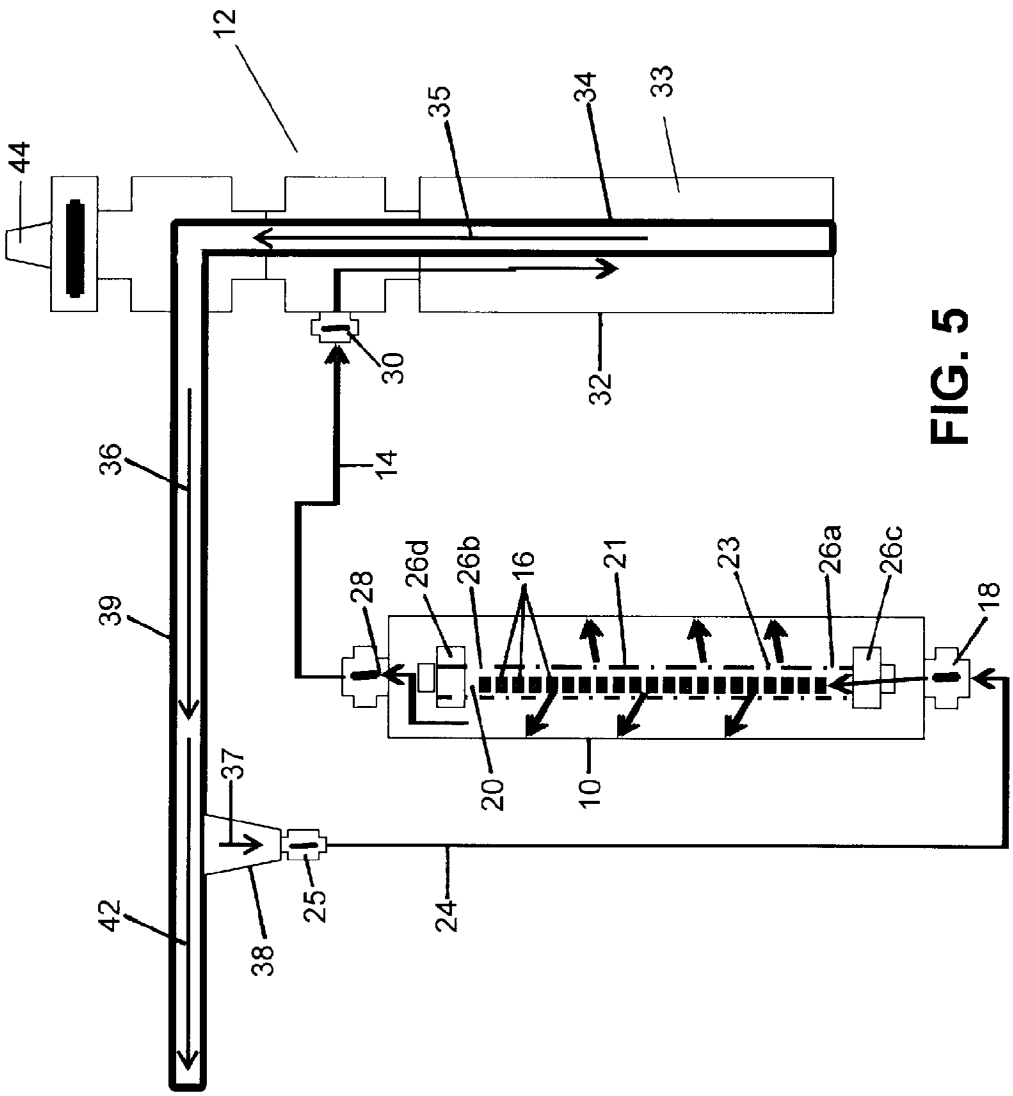
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FIG. 5

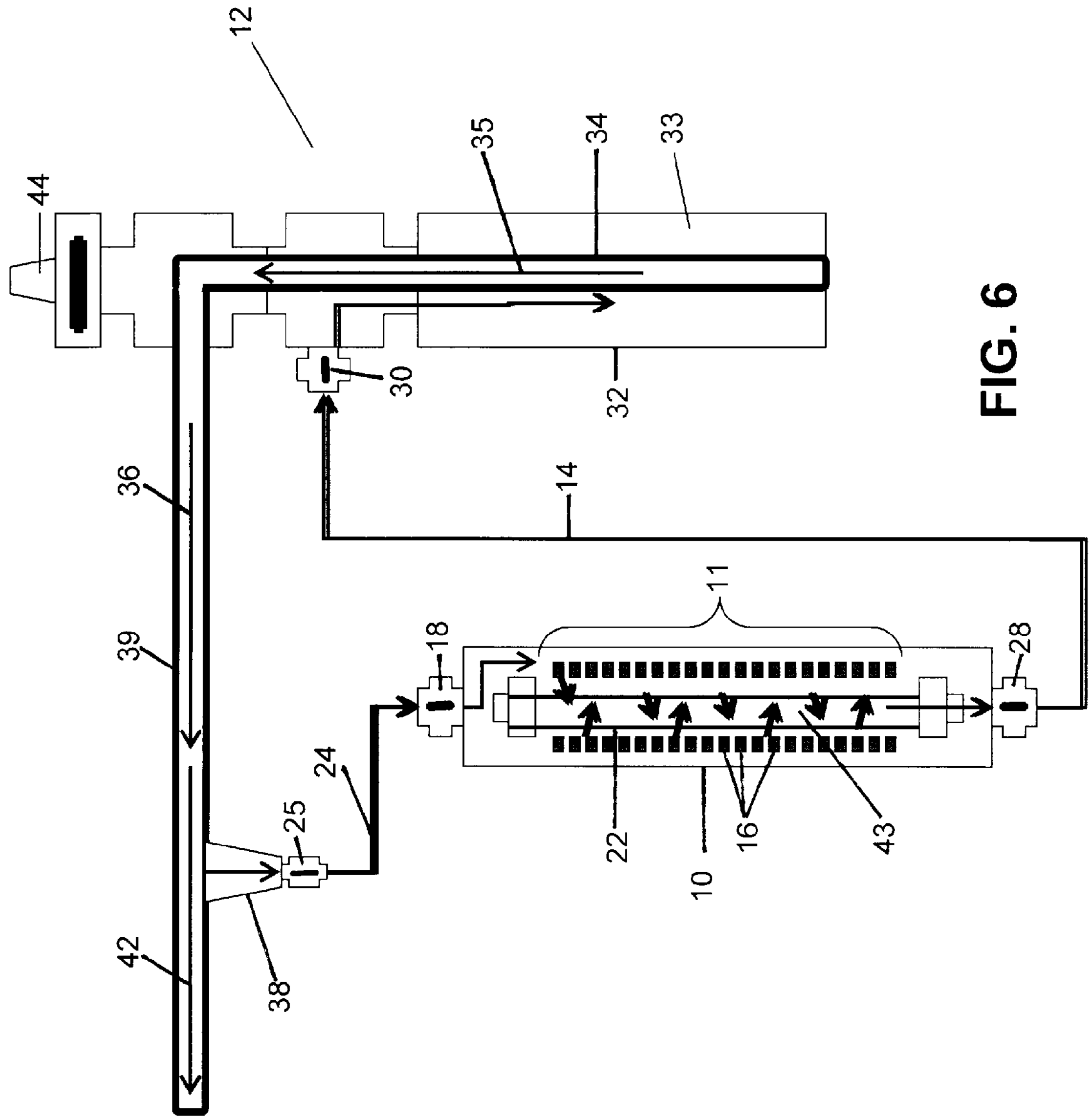


FIG. 6

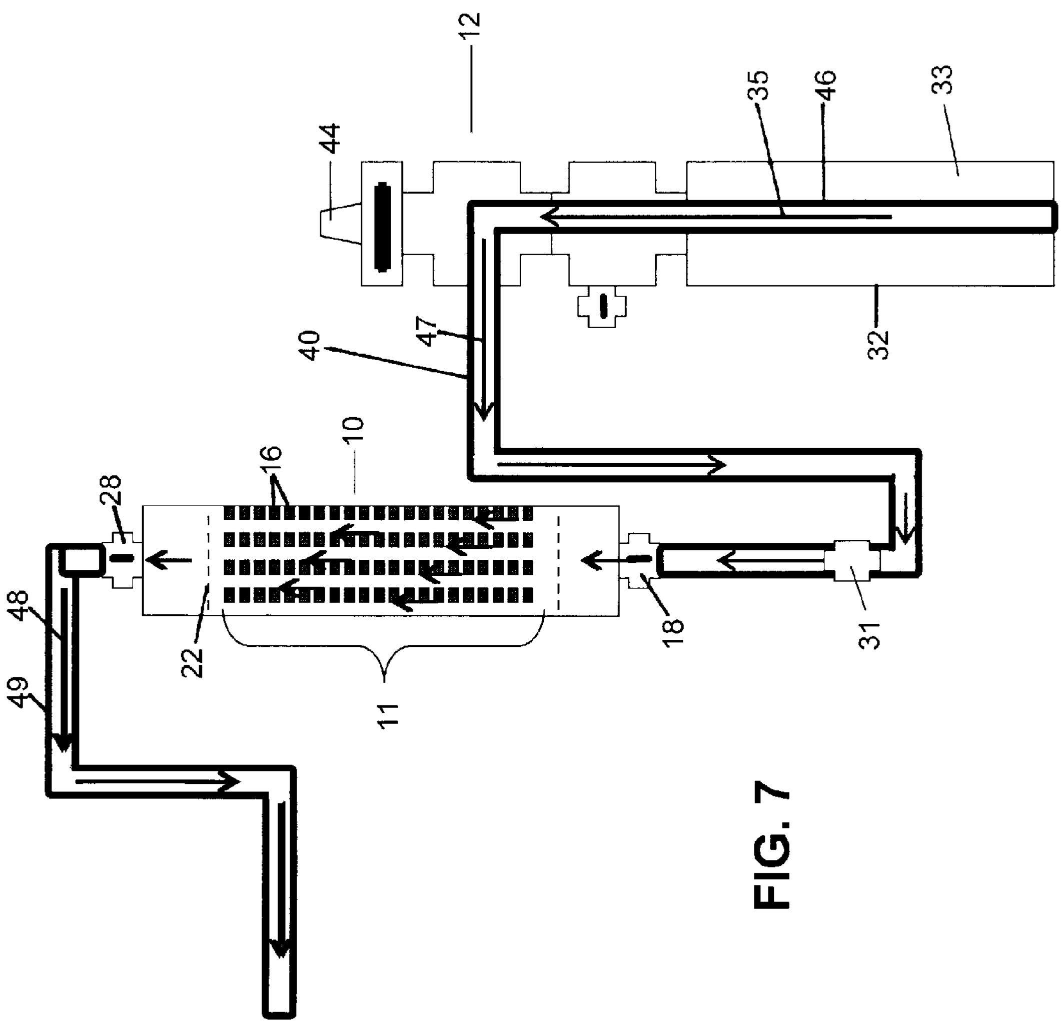


FIG. 7

METHOD OF INTRODUCING TREATMENT AGENTS INTO A WELL OR FLOW CONDUIT

FIELD OF THE INVENTION

[0001] The invention relates to a method of introducing a chemical treatment agent into a well or into a flow conduit which extends from a well.

BACKGROUND OF THE INVENTION

[0002] Oilfield fluids (e.g., oil, gas, and water) are generally complex mixtures of aliphatic hydrocarbons, aromatics, hetero-atomic molecules, anionic and cationic salts, acids, sands, silts, clays and a vast array of other components. The nature of these fluids, combined with the severe conditions of heat, pressure, and turbulence to which they are often subjected, are contributory factors to the formation and deposition of contaminants, such as scales, salts, paraffins, corrosion, bacteria and asphaltenes in oil and/or gas production wells. Such contaminants also form in equipment and flow conduits used in gas production and oil production. For instance, mineral scale deposits (such as calcium carbonate, calcium sulfate and barium sulfate) often precipitate from produced oilfield water in oil and gas wells and create blockages in flow paths, especially in production flow conduits such as well tubing, well casing and flow lines. Such blockages lead to a restriction in such flow conduits. The formation and deposition of such unwanted contaminants decrease permeability of the formation, reduce well productivity and can completely block the well tubular in severe cases. In addition to mineral scale deposition, other problems caused by oil field water include corrosion, bacterial growth, paraffin deposition and asphaltene deposition.

[0003] A common site for the formation and deposition of such contaminants in oil or gas wells is the annular space between the production tubing and casing. The annulus may be a static area or may produce gas or liquid. In low pressure gas wells, such as coal bed methane wells, the gas is produced up the annulus and the liquid (water) is allowed to fall to the liquid level and is removed via a submersible pump up the tubing. Such undesirable substances as salt, scales, paraffins and asphaltenes form due to pressure and temperature changes at the perforations. Alternatively, such substances form due to comingling of incompatible waters from one set of perforations to another. The formation and deposition of such contaminants decrease permeability of the subterranean formation and reduce well productivity. For instance, in some completions, the presence of scale in the annulus may make it difficult or impossible to remove the tubing for servicing.

[0004] In addition to being formed in oil and gas wells, such contaminants further form in flow conduits used in the production of oil, gas and other fluids. For instance, an acute problem develops when such contaminants develop in flow conduits used in gas and oil production, refineries and other fluid processing facilities.

[0005] A number of approaches have been used to inhibit and/or remove contaminants. For example, in oil and gas production, the technique of "downhole squeezing" is commonly used to address oil field scale formation, wherein a slug of the treatment composition is injected into the annulus, using a pre-flush, squeeze, and overflush treatment before the well can be returned to normal function. However, the overflush process often flushes a significant portion of the treatment agent such the remaining treatment agent is gradually removed from the surface as oil production continues. Thus, further descaling treatments are typically required.

[0006] Another method of treating deposits, such as mineral scales, is to apply chemicals directly to the well tubular. Such applications are commonly applied to the tubing or casing of pumping wells, either continuously or in batch form. However, this often requires specialized and expensive pumping equipment as well as associated piping and containment.

[0007] Alternative treatment methods have therefore been sought for introducing treatment agents into oil and/or gas wells as well as flow conduits used in the production of oil and gas.

SUMMARY OF THE INVENTION

[0008] In an embodiment, treatment agent retained in a housing may be slowly and continuously released into a targeted area in a well or in a flow conduit. Within the housing there is a confinement area wherein movement of the treatment agent is restricted. Mobility of the treatment agent may be limited by a retainer. The retainer may be a screen, a porous media or any other device which is capable of minimizing migration of the treatment agent outside of the confinement area.

[0009] The treatment agent is at least sparingly soluble in the fluid entering the housing. A portion of the treatment agent is dissolved in the entering fluid and thus becomes free to exit from the confinement area. Fluid exiting the housing contains dissolved treatment agent. The exiting fluid enters flow conduits and targeted areas of a well where the treatment agent is needed. Thus, unwanted deposits are removed or the formation of such deposits is inhibited or reduced with the treatment agent.

[0010] In one embodiment, the housing is situated between the flowline and the casing of the well. Fluid from the flowline may be permitted to flow through the retainer and over the solid treatment agent to dissolve an amount of the treatment agent. The chemically laden water may then be drained into the annulus of the well to treat the well and conduits exiting the well.

[0011] Suitable treatment agents include those capable of addressing the undesired effects caused by scale formations, salt formations, paraffin deposition, emulsification (both water-in-oil and oil-in-water), gas hydrate formation, corrosion, asphaltene precipitation and paraffin formation for slow release into the well or flow conduits. Other suitable treatment agents include foaming agents, oxygen scavengers, biocides and surfactants.

[0012] In an embodiment, the treatment agent may be retained in the housing in a receptacle. The retainer relatively restricts the movement of the treatment agent in the housing to the receptacle while permitting fluid flow into and out of the receptacle. At least a portion of the fluid entering the housing may flow directly into the receptacle.

[0013] In another embodiment, the treatment agent may be directed to flow over the treatment agent in the receptacle within the housing. Upon being moved over and/or across the receptacle, dissolved treatment agent may combine with the fluid. The fluid exiting the housing contains the dissolved treatment agent.

[0014] In another embodiment, the combination of receptacle and retainer may be defined by a structure resembling a perforated sleeve which rests within the housing. For instance, the receptacle may be a tubing which resides in the housing. The retainer may consist of small openings in the tubing. The small openings communicate with the interior of the receptacle. The treatment agent resides within the interior of the receptacle. Treatment agent, upon being dissolved, may then combine with the fluid. The fluid exiting the housing may contain the dissolved treatment agent.

[0015] In another embodiment, the confinement area(s) may be defined by the space between each of the inner walls and retainer. A flow pathway may exist between the confinement area(s). Fluid entering the housing flows over the treatment agent in one or both of the confinement areas and exits the housing with dissolved treatment agent.

[0016] In another embodiment, a treatment agent may be delivered to a flow conduit downstream of a well. Fluid pumped out of the well may enter a housing containing a confinement area. The treatment agent may be retained within a confinement area of the housing. As fluid moves through the housing and through the confinement area, a portion of treatment agent is dissolved in the fluid.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] In order to more fully understand the drawings referred to in the detailed description of the present invention, a brief description of each drawing is presented, in which:

[0018] FIGS. **1** and **2** are schematic representations of methods of delivering a treatment agent into a well and flow conduit using a housing having treatment agent retained in the housing.

[0019] FIG. **3** is a schematic representation of a method of delivering a treatment agent into a well and flow conduit using a housing having treatment agent retained in a receptacle within the housing.

[0020] FIG. **4** illustrates a representative housing containing a receptacle for a treatment agent and a retainer.

[0021] FIG. **5** is a schematic representation of a method of delivering a treatment agent into a well and flow conduit using a housing having a perforated sleeve.

[0022] FIG. **6** is a schematic representation of a method of delivering a treatment agent into a well and flow conduit using a housing having a fluid flow pathway, the treatment agent being retained between the fluid flow pathway and the wall of the housing.

[0023] FIG. **7** is a schematic representation of a method of delivering a treatment agent into a flow conduit using a housing having treatment agent retained in the housing.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0024] Treatment agents may be introduced into a targeted area of a well or in a flow conduit extending either from a well or into a well in embodiments of the invention. The treatment agent is contained within a housing. Fluids flow into the housing and exit the housing with a portion of dissolved treatment agent. (The term "dissolved" used herein shall include solids which are dissolved, solubilized or entrained in the exiting fluid.) The housing is located outside of the well so no intervention into the well is necessary. The method may be run continuously or be conducted intermittently. The treatment agent may be monitored and replenished as needed. Since the housing containing the treatment agent is external to the well, filling the housing is easy, requiring no special tools.

[0025] The treatment agent is typically in a solid or semi-solid state and is at least sparingly soluble in the fluid traveling through the housing The treatment agent may be of any form including beads, pellets, flakes, slurries, balls, rods, sticks or blocks. The size and shape of the solid is not critical to the success of the method provided the treatment agent can be at least partially dissolved in the fluid which passes over the confinement area or through the confinement area. In one embodiment, the treatment agent is a pellet approximately one inch in diameter and 3/8 inches tall.

[0026] A representative embodiment is depicted in FIG. **1** which shows housing **10** separated from well **12** by flow conduit **14**. Treatment agent **16** is retained in housing **10**. Treatment agent **16** is confined in housing **10** in confinement area **11**. Retainer **22** relatively restricts the movement of the (solid) treatment agent in housing **10** outside of confinement area **11** while permitting flow of fluid into and out of confinement area **11**. In a preferred embodiment, retainer **22** is located on both ends of the confinement area, shown as **22*a*** and **22*b***.

[0027] Retainer **22** may be a screen, a porous media or any other device which is capable of minimizing migration of the treatment agent outside of the confinement area **11**. Exemplary porous medium include porous filters or a porous solid, such as sand, diatomaceous earth, ground or crushed shells of nuts like walnut, coconut, pecan, almond, ivory nut, brazil nut, etc.; ground or crushed seed shells (including fruit pits) of seeds of fruits such as plum, olive, peach, cherry, apricot, etc.; ground or crushed seed shells of other plants such as maize (e.g., corn cobs or corn kernels), etc.; processed wood materials such as those derived from woods such as oak, hickory, walnut, poplar, mahogany, etc. The mesh of the screen, porosity of porous medium or diameter of other devices for retainer **22** is selected such that the treatment agent is relatively unable to freely move outside of confinement area **11**.

[0028] Fluid from passageway conduit **24** enters housing **10** through housing entrance flow regulator **18**. The fluid consists typically of oil, water or a mixture of oil and water. In an embodiment, the fluid may be water originating from a production flow line **35**. Treatment agent **16** in housing **10** is at least sparingly soluble in the entering fluid.

[0029] In an embodiment, fluid stream **35** may be pumped out of well **12** by a submersible pump (not shown) or pump jack **44**. A portion of fluid stream **36** in flowline **39** may be diverted. Diverted fluid stream **37** may then pass into housing **10**, into flow conduit **14** and back to casing **32** via the pressure differential in flowline **39** and well casing **32**. The technique of diverting fluid from a fluid stream back to the casing of a well is commonly described as slip stream.

[0030] Fluid flow may optionally be metered into housing **10** such as by use of a metering valve **31** located upstream of housing **10** along passageway conduit **24**. Alternatively, a metering valve may be located downstream of housing **10** along flow conduit **14**. In an embodiment, multiple metering valves may be present upstream **31**a and downstream **31**b. The location of the optional metering device(s) serves to assist in the control of fluid into and/or out of housing **10**.

[0031] The fluid containing dissolved treatment agent flows downwardly and exits housing **10** through exit flow regulator **28**. The exiting fluid enters flow conduit **14** and then enters the well through well flow regulator **30** where it continues to pass into annulus **33**. Fluid stream **35** in piping **34** containing dissolved deposits may exit the well and then enter flowline **39** extending from well **12** with the assistance of the submersible pump or pump jack **44**. Diverted fluid stream **37** enters well access point/valve **38** off of flowline **39**. Diverted fluid stream **37** then enters passageway conduit **24** through passageway conduit flow regulator **25**. The remaining portion of the fluid continues through flowline **39** as exit fluid stream **42**.

[0032] The treatment agent in the fluid exiting housing **10** through exit flow regulator **28** removes unwanted deposits or inhibits or reduces the formation of such deposits in the well and flow conduits leading into and out of the well.

[0033] The direction of fluid flow through the housing and over or into the confinement area is not critical. The inlet to the housing may be either at the top of the housing or the bottom or side with an outlet opposite the inlet. The inlet and outlet may be on the same side of the housing.

[0034] As an example, FIG. **2** illustrates an embodiment wherein fluid from passageway conduit **24** enters housing **10** through housing entrance flow regulator **18** which is located at the bottom of the housing. The fluid flow proceeds in an upwardly direction through the housing and exits housing **10** at exit flow regulator **28** located at the top of the housing. In another embodiment (not shown), fluid from passageway conduit **24** enters the housing through a side connector located at the side of the housing. The fluid containing dissolved deposits may then exit through a second side connector located at the other side of the housing.

[0035] A pump may be located towards the bottom, top or side of the housing to circulate or assist in the movement of the production fluid through the confinement area containing the treatment agent. While a pump may be used to aid in moving fluid through the well production system, in a preferred embodiment, a pump is not used for moving the diverted fluid through the housing into the confinement area. A highly advantageous feature of the embodiments of the invention is that movement of diverted fluid into the housing, through the housing and up to the well flow regulator does not require a pump.

[0036] Referring to another embodiment shown in FIG. **3**, treatment agent **16** is confined in housing **10**. Treatment agent **16** is retained in housing **10** in receptacle **20**. Retainer **22** relatively restricts the movement of the treatment agent in housing **10** to receptacle **20** while permitting fluid flow into and out of receptacle **20**. Retainer **22** may be a screen, a porous media, small apertures or other fluid permeable devices as previously described. Inlet and outlet fittings and valves for the confinement area, retainer and housing may be used. As illustrated, receptacle **20** may be secured to housing **10** at its anterior end **26***a* and posterior end **26***b* by nuts and bolts **26***c* and **26***d* or manifold and other conventional attachment methods.

[0037] Fluid from passageway **24** enters housing **10** through housing entrance flow regulator **18**. At least a portion of the fluid passes directly into receptacle **20**. Treatment agent **16** in receptacle **20** is at least sparingly soluble in the fluid. The fluid containing dissolved treatment agent may then exit the housing via exit flow regulator **28**. One or more metering valves may assist in the control of the fluid to the housing or to the casing of the well.

[0038] In contrast to the diverted fluid from passageway conduit **24** directly entering receptacle **22** as shown in FIG. **3**, the fluid, upon entering the housing, may be directed to flow over the treatment agent **16** in receptacle **20**. After freely moving over receptacle **20**, the fluid stream containing dissolved treatment agent exist housing **10** at exit flow regulator **28**. The exiting fluid enters conduit **14** and then passes into the well through well flow regulator **30**. The fluid flows into annulus **33**.

[0039] In another variation of the embodiment of FIG. **3**, the fluid from passageway conduit **24** enters housing **10** through housing entrance flow regulator **18** located at the top of housing **10** and the exit flow regulator **28** is located at the bottom of housing **10**.

[0040] The size and shape of the housing as well as the size and shape of the retainer or receptacle are not critical. Exemplary housings include steel cylinder of a diameter between 1½ and 36 inches. The length of an exemplary housing is between from about 6 inches to 500 feet. The receptacle and/or retainer may be of any size or composition suitable for holding the solid form of the treatment agent and which is compatible with the production system. The interior diameter of the receptacle must be suitable to hold the solid treatment agent and be of a shape and size to fit inside the housing.

[0041] The combination of receptacle **20** and retainer **22** may be defined by a perforated sleeve structure within a housing. Referring to FIG. **4**, the receptacle may be a tubing **21** which resides in housing **10**. The retainer consists of small openings **23** which communicate with the interior **27** of tubing **21**. The treatment agent **16** resides within the interior of the tubing. The diameter of openings **23** is such that dissolved treatment agent may be combined with the diverted fluid stream. Housing **10** may consist of two separate mating sections **19** and **29** to assist in the refilling of treatment agent **16** in the housing.

[0042] FIG. **5** illustrates an embodiment of using the housing of FIG. **4**. Referring to FIG. **5**, treatment agent **16** is confined in housing **10** in a receptacle defined by tubing **21** which may be composed of a metal or alloy. Treatment agent **16** is retained in housing **10** within the receptacle. The diverted fluid stream enters into tubing **21** through openings **23**. Tubing **21** may be secured to housing **10** at its anterior end **26***a* and posterior end **26***b by* nuts and bolts **26***c* and **26***d* or manifold and other conventional attachment methods. Fluid from passageway conduit **24** enters housing **10** through housing entrance flow regulator **18**. At least a portion of the fluid passes directly into the interior of tubing **21** which contains treatment agent **16**. Treatment agent **16** is at least sparingly soluble in the diverted fluid stream. The fluid containing dissolved treatment agent may then exit the housing via exit flow regulator **28**. Flow of fluid into and out of the housing may be regulated by a metering device.

[0043] FIG. **6** illustrates another embodiment wherein the confinement area **11** containing treatment agent **16** is located between the inner wall of housing **10** and retainer **22**. A flow pathway **43** extends from generally the top of the housing to the bottom of the housing. The fluid pathway is preferably an unobstructed channel for the continuous flow of the fluid. Diverted fluid from passageway conduit **24** may enter the housing through housing entrance flow regulator **18**. While FIG. **6** shows the entrance connector as being on the top of the housing and the exit flow regulator **28** being on the bottom of the housing, the entrance connector could also be on the bottom of the housing and the exit connector on the top of the housing as well as the entrance connector may be on the side of the housing with the exit connector being on the other side of the housing.

[0044] The fluid from housing entrance flow regulator **18** flows over treatment agent **16** in confinement area **11** and ultimately leaves the housing through exit flow regulator **28** as it moves down flow pathway **43**. The solid treatment agent is separated from flow pathway **43** by retainer **22** as previously described. Fluids exiting the housing through exit connector **43** contain dissolved treatment agent. Retainer **22** may further be defined by the perforated sleeve structure of FIG. **4**.

[0045] FIG. **7** illustrates another embodiment wherein a treatment agent may be delivered to a flow conduit downstream of a well, such as a production well. As illustrated, fluid stream **35** in well tubing **46** may be pumped (such as by a submersible pump, not shown, or pump jack **44**) out of well **12** and into flowline **40**. Flowstream **47** in flowline **40** passes into housing **10** via housing entrance flow regulator **18**. Treatment agent **16** is confined in housing **10** in confinement area **11**. Movement of treatment agent **16** within housing **10** is restricted by retainer **22**. As the fluid moves upward through the housing and through the confinement area **11**, a portion of treatment agent **16** is dissolved in the fluid. The fluid exits housing **10** through exit flow regulator **28** as fluid stream **48** in exit conduit **49**. Fluid stream **48** contains dissolved treatment agent. Metering valve **31** may be positioned upstream and/or downstream of housing **10** to assist in the control of fluid into and/or out of housing **10**.

[0046] FIG. **7** may be modified by having the entrance connector and exit connector being at the top and bottom, respectively, of the housing such that the flow of flowstream **47** extends from top to the bottom of the housing. Alternatively, the entrance connector may be located on one side of the housing with the exit connector being on the other side of the housing.

[0047] In another modification of the embodiment of FIG. **7**, treatment agent **16** may be contained within a receptacle, such as that illustrated in FIG. **3**, having a fluid permeable retainer. Flowstream **47** may then pass into housing **10** and flow into or over the receptacle. The fluid containing dissolved solids may then exit the housing via exit flow regulator **28**.

[0048] In another modification of FIG. **7**, the treatment agent may be retained in housing **10** in a tubing having openings for passage of dissolved fluids. The dissolved solids exit the housing via exit flow regulator **28** in the exiting fluid. Exemplary of such a housing is that shown in FIG. **4**.

[0049] In one embodiment, the oil or gas well treated is a low pressure coal bed methane well where the flow line containing the water for treatment is at a higher pressure than the casing. Drainage of the treatment agent into the targeted area of the well may be effectuated using available system pressures. The pressure differential between the flow conduit and casing makes unnecessary any specialized pumps or equipment.

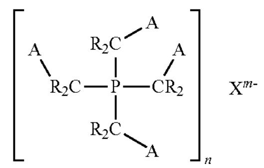
[0050] The treatment agent may be any chemical that is used to treat an oil or gas well. Preferably, the treatment agent is one which is capable of inhibiting the formation and/or deposition of such contaminants as scales, corrosion, salts, paraffins and asphaltenes. In addition, the treatment agent may be a biocide and thus the method may be used to eliminate the presence of bacteria. Further, the treatment agent may be one which is capable of removing such contaminants.

[0051] The method may further be used to remove deposited contaminants which forms on flow conduits. For instance, during the production of oil and gas from wells, it is not uncommon for scales, rust, salts, paraffins and asphaltenes to be deposited onto internal surfaces of flow conduits or vessels. The method may be used to inhibit the deposition of such materials and/or remove such deposits upon their formation.

[0052] Exemplary of treatment agents used in the foamed treatment composition are one or more inhibitors or removal agents for such unwanted deposits as scales, rust, salts, paraffins and asphaltenes as well as biocides.

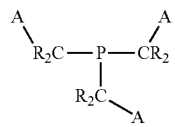
[0053] The treatment agents may be any of those commonly known in the art. In a preferred embodiment, the treatment composition is used to remove scales (such as iron sulfides or mineral scales like calcium carbonate) or inhibit the formation of scales. Suitable scale inhibitors or removal agents include phosphates, phosphate esters, phosphoric acid, phosphonates, phosphonic acid, phosphonate/phosphonic acids, polyacrylamides, salts of acrylamido-methyl propane sulfonate/acrylic acid copolymers (AMPS/AA), phosphinated maleic copolymers (PHOS/MA), salts of a polymaleic acid/acrylic acid/acrylamido-methyl propane sulfonate terpolymer (PMA/AMPS) as well as mixtures thereof. Phosphonate/phosphonic acid type scale inhibitors are often preferred in light of their effectiveness to control scales at relatively low concentration. Polymeric scale inhibitors, such as polyacrylamides, salts of acrylamido-methyl propane sulfonate/acrylic acid copolymer (AMPS/AA), phosphinated maleic copolymer (PHOS/MA) and sodium salt of polymaleic acid/acrylic acid/acrylamido-methyl propane sulfonate terpolymers (PMA/AMPS) are also effective scale inhibitors. Sodium salts are preferred.

[0054] Further, preferred as scale inhibitors and/or scale removal agents are alkyl-substituted phosphonium compounds and alkyl-substituted phosphines such as alkyl-substituted phosphonium compound of formula (I):



(I)

[0055] or alkyl-substituted phosphines of formula (II):



(II)

[0056] wherein X is an anion; n is the valency of X represented by m; each A are the same or different and are selected from the group consisting of —OH, —OR^{-1}, —OS_3R^1, —$PO_3(R^1)_2$, —COON, —$COOR^1$, SO_3H, —PO_3H_2, —CH_2COOH, substituted alkyl, aryl or substituted amino groups; each R and each R^1 is independently selected form the group consisting of hydrogen, a C_1 to C_{20} alkyl, aryl, substituted alkyl or aryl, carboxy or carboxy ester. Such compounds include those disclosed in U.S. Patent Publication No. 2008/0135476, herein incorporated by reference.

[0057] In a preferred embodiment, the alkyl-substituted phosphonium compounds for use as treatment agent are tetrakis(hydroxymethyl)phosphonium sulfate (THPS), tetrakis (hydroxymethyl)phosphonium chloride, tetrakis(hydroxymethyl)phosphonium bromide, tetrakis(hydroxymethyl) phosphonium acetate and tetrakis(hydroxymethyl) phosphonium phosphate.

[0058] Further, treatment agents acidic in nature, such as mineral acids, may be used for the removal of scales. Suitable mineral acids include sulfamic acid. Caustic scale removal agents may also be used. Such caustic removal agents, of particular applicability in the removal of sulfate scales, include sodium hydroxide, chelants such as EDTA, glucoheptanate and urea.

[0059] Suitable salt inhibitors include nitroliotriacetamide and its salts, such as those set forth in U.S. Pat. No. 7,028,776. Other salt inhibitors include fructans and derivatives thereof, including inulin or an inulin derivatives such as carboxyl-containing fructans like carboxyl-containing inulin as well as carboxyalkyl inulins Such inhibitors include those set forth in U.S. Patent Publication No. 2009/0325825, herein incorporated by reference.

[0060] Treatment agents for the inhibition and/or removal of paraffins include, but are not limited to, ethylene/vinyl acetate copolymers, acrylates (such as polyacrylate esters and methacrylate esters of fatty alcohols) and olefin/maleic esters.

[0061] Suitable corrosion inhibitors or rust removal agents useful for the practice of the invention include but are not limited to fatty imidazolines, alkyl pyridines, alkyl pyridine quaternaries, fatty amine quaternaries and phosphate salts of fatty imidazolines.

[0062] Exemplary hydrogen sulfide scavengers include triazines, maleimides, formaldehydes, morpholinos, amines, amino derivatives, carboxamides and alkylcarboxyl-azo compounds, such as those disclosed in U.S. Pat. No. 6,063,346; U.S. Pat. Nos. 5,128,049; and 7,264,786, all of which are herein incorporated by reference.

[0063] Exemplary asphaltene treating chemicals include but are not limited to fatty ester homopolymers and copolymers (such as fatty esters of acrylic and methacrylic acid polymers and copolymers) and sorbitan monooleate.

[0064] Suitable foaming agents include, but are not limited to, those which are amphoteric, anionic and cationic. Preferred anionic foaming agents include betaines, alkyl ether sulfates, oxyalkylated sulfates, alkoxylated alcohol sulfates, phosphate esters, alkyl ether phosphates, alkoxylated alcohol phosphate esters, alkyl sulfates as well as alpha olefin sulfonates. Included as amphoteric surfactants are glycinates, amphoacetates, propionates, betaines and mixtures thereof. Cationic foaming agents are especially useful where the treatment agent employed is also cationic. For instance, cationic foaming agents have particular applicability with cationic biocides. Suitable cationic foaming agents include alkyl quaternary ammonium salts, alkyl benzyl quaternary ammonium salts and alkyl amido amine quaternary ammonium salts.

[0065] In one embodiment, the treatment agent may be a composite having a water soluble or oil soluble chemical agent adsorbed onto a water-insoluble or oil insoluble adsorbent. The composite may be those disclosed in U.S. Pat. Nos. 7,491,682 and 7,493,955, herein incorporated by reference. The water insoluble adsorbent may be any of various kinds of commercially available high surface area materials having the affinity to adsorb the desired treatment agent. Typically, the surface area of the adsorbent of the well treating composite is between from about 1 m^2/g to about 100 m^2/g.

[0066] Suitable adsorbents include finely divided minerals, fibers, ground almond shells, ground walnut shells, and ground coconut shells. Further suitable water-insoluble adsorbents include activated carbon and/or coals, silica particulates, precipitated silicas, silica (quartz sand), alumina, silica-alumina such as silica gel, mica, silicate, e.g., orthosilicates or metasilicates, calcium silicate, sand (e.g., 20-40 mesh), bauxite, kaolin, talc, zirconia, boron and glass, including glass microspheres or beads, fly ash, zeolites, diatomaceous earth, ground walnut shells, fuller's earth and organic synthetic high molecular weight water-insoluble adsorbents. Particularly preferred are diatomaceous earth and ground walnut shells.

[0067] Further useful as adsorbents are clays such as natural clays, preferably those having a relatively large negatively charged surface, and a much smaller surface that is positively charged. Other examples of such high surface area materials include such clays as bentonite, illite, montmorillonite and synthetic clays.

[0068] The treatment agent is generally dried onto or into the adsorbent and the resulting solid chemical treatment or adsorbent is compressed or formed into spherical forms including balls or pellets or tablets.

[0069] The weight ratio of treatment agent to water-insoluble adsorbent in the composite is generally between from about 90:10 to about 10:90. The amount of treatment agent in the composite is that amount sufficient to effectuate the desired release into the flowing produced fluid over a sustained period of time. Generally, the amount of treatment agent released is from about 0.05 to about 5 (preferably from about 0.1 to about 2) weight percent based upon the total weight of flowing produced fluid. In some instances, the amount of treatment agent in the well produced fluid may be as low as 0.1 ppm. Such small amounts of treatment agents in the produced fluid released from the composite may be sufficient for up to 1,000 pore volumes and typically provides up to six months to twelve months of continuous inhibition of the unwanted deposit. Continuous release of the treatment agent further protects flow conduits and equipment from unwanted deposits which may otherwise be formed.

[0070] The amount of treatment agent within the housing is that amount sufficient to effectuate the desired result over a sustained period of time. Generally, the amount of treatment agent in the housing is from about 0.05 to about 50% by volume. The amount of treatment in the chemical laden effluent leaving the housing may be as low as 1 ppm to as high as several hundred ppms or several percent.

[0071] The method may be effective in the removal of contaminants on metallic as well as non-metallic surfaces. In one, the method is used to remove contaminants on metallic surfaces, such as high alloy steels, including chrome steels, duplex steels, stainless steels, martensitic alloy steels, ferritic alloy steels, austenitic stainless steels, precipitation-hardened stainless steels and high nickel content steels.

[0072] The continuous release of the treatment agent using the method described herein protects the tubular and equipment from unwanted deposits which may be formed.

[0073] Generally, the lifetime of a single treatment using the method described is between one and twelve months or several years.

[0074] The foregoing disclosure and description of the embodiments is illustrative and explanatory thereof, and various changes in the size, shape, and materials, as well as in the details of illustrative construction and assembly, may be made without departing from the spirit of the invention. Other embodiments within the scope of the claims herein will be apparent to one skilled in the art from consideration of the description set forth herein. It is intended that the specification be considered exemplary only, with the scope and spirit of the invention being indicated by the claims which follow.

What is claimed is:

1. A method of introducing a treatment agent in a well or in a flow conduit extending from a well comprising:

(a) retaining a soluble treatment agent within a housing located externally from a well;

(b) introducing fluid into the housing and moving at least a portion of the fluid over the retained soluble treatment agent, wherein at least a portion of the retained soluble treatment agent is dissolved in the fluid;

(c) flowing the fluid containing the dissolved treatment agent out of the housing; and

(d) flowing the fluid of step (c) into the annulus of the well or into a flow conduit extending from the well.

2. The method of claim **1**, wherein the fluid introduced into the housing in step (b) is water, oil or a mixture of oil and water.

3. The method of claim **1**, wherein the soluble treatment agent is retained in the housing by a screen or porous media.

4. The method of claim **1**, wherein the soluble treatment agent is retained in the housing within a perforated sleeve.

5. The method of claim 1, wherein the fluid is introduced into the housing at the top of the housing and wherein the fluid exits the housing at the bottom.

6. The method of claim 1, wherein the fluid is introduced into the housing at the bottom of the housing and wherein the fluid exits the housing at the top.

7. The method of claim 1, wherein the fluid is introduced into the housing at a side of the housing and wherein the fluid exits the housing at the opposite side.

8. The method of claim 1, wherein an unobstructed continuous channel extends from the top of the housing to the bottom of the housing.

9. The method of claim 1, wherein the soluble treatment agent is a composite of a water soluble or oil soluble treatment agent adsorbed onto a water insoluble or oil insoluble adsorbent.

10. The method of claim 1, wherein the soluble treatment agent is selected from the group consisting of corrosion inhibitors, scale inhibitors, paraffin inhibitors, gas hydrate inhibitors, salt formation inhibitors, asphaltene dispersants, foaming agents, hydrogen sulfide scavengers, oxygen scavengers, biocides and surfactants.

11. The method of claim 10, wherein the soluble treatment agent is a scale inhibitor.

12. The method of claim 9, wherein the water insoluble adsorbent is diatomaceous earth.

13. A method of delivering a treatment agent into the annulus of a well comprising:

(a) retaining a soluble treatment agent in a confinement area in a housing located externally from the well;

(b) introducing fluid into the housing and traversing the fluid over or through the confinement area and dissolving at least a portion of the treatment agent into the traversed fluid;

(c) flowing the traversed water containing the treatment agent into the annulus of the well; and

(d) releasing the treatment agent into the annulus of the well.

14. The method of claim 13, wherein the well is a production well.

15. The method of claim 13, wherein the soluble treatment agent is retained in the housing by a screen, a porous media or within a perforated sleeve.

16. The method of claim 13, wherein either:

(a) the fluid is introduced to the housing at the top of the housing and the traversed fluid containing the dissolved treatment agent exits the housing at the bottom of the housing;

(b) the fluid is introduced to the housing at the bottom of the housing and the traversed fluid containing the dissolved treatment agent exits the housing at the top of the housing; or

(c) the fluid is introduced to the housing at the side of the housing and the traversed fluid containing the dissolved treatment agent exits the housing at the opposite side of the housing.

16. The method of claim 13, wherein the soluble treatment agent is a composite of a water soluble or oil soluble treatment agent adsorbed onto a water insoluble or oil insoluble adsorbent.

17. The method of claim 13, wherein the soluble treatment agent is selected from the group consisting of corrosion inhibitors, scale inhibitors, paraffin inhibitors, gas hydrate inhibitors, salt formation inhibitors, asphaltene dispersants, foaming agents, hydrogen sulfide scavengers, oxygen scavengers, biocides and surfactants.

18. The method of claim 16, wherein the water insoluble adsorbent is diatomaceous earth.

19. A method of delivering a chemical treatment agent into a flow conduit downstream of a producing well comprising:

(a) moving produced fluid from the well through a flow conduit;

(b) transporting the produced fluid from the flow conduit through a housing containing a solid chemical treatment agent and dissolving a portion of the solid chemical treatment agent in the produced fluid, wherein the solid chemical treatment agent is retained in the housing during movement of the produced fluid through the housing; and

(c) delivering the produced fluid containing the dissolved chemical treatment agent into the flow conduit.

20. The method of claim 19, wherein the chemical treatment agent is retained in the housing by a screen, porous media or within a perforated sleeve.

21. The method of claim 19, wherein either:

(a) the fluid is introduced to the housing at the top of the housing and the traversed fluid containing the dissolved treatment agent exits the housing at the bottom of the housing;

(b) the fluid is introduced to the housing at the bottom of the housing and the traversed fluid containing the dissolved treatment agent exits the housing at the top of the housing; or

(c) the fluid is introduced to the housing at the side of the housing and the traversed fluid containing the dissolved treatment agent exits the housing at the opposite side of the housing.

22. The method of claim 19, wherein the chemical treatment agent is a composite of a water soluble or oil soluble chemical treatment agent adsorbed onto a water insoluble or oil insoluble adsorbent.

23. The method of claim 19, wherein the chemical treatment agent is selected from the group consisting of corrosion inhibitors, scale inhibitors, paraffin inhibitors, gas hydrate inhibitors, salt formation inhibitors, asphaltene dispersants, foaming agents, oxygen scavengers, biocides and surfactants.

24. The method of claim 22, wherein the water insoluble adsorbent is diatomaceous earth.

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