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ELECTROLESS METALIZATION OF UNCONSOLIDATED EARTH FORMATIONS

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ABSTRACT OF THE DISCLOSURE

A method of consolidating an incompetent formation by metalizing or metal plating the formation by an electroless metal plating process using a metal plating solution. The formation is activated by contacting it with a metal-forming sol solution, the metal of this solution being the same as in the metal plating solution.

This invention relates to treating incompetent or unconsolidated formations such as unconsolidated subsurface formations and more particularly to treatment of loose or incompetent earth formations surrounding well bores so as to consolidate said formation into a permeable, thermally and hydrolytically resistant consolidated formation for improved and efficient recovery of fluids therefrom.

BACKGROUND OF THE INVENTION

It is well known that many difficulties are encountered in producing or recovering fluids from incompetent earth formations due to collapsing or sloughing of the well bore walls. Numerous means have been employed to alleviate this and among the methods and devices used to prevent collapsing and sloughing of unconsolidated formations is the use of perforated pipe liners, gravel packing or tubular screens or by injecting resin-forming materials such as phenol-formaldehyde resins or epoxide resins which function **20** as bonding and consolidating agents for weak formations.

Another method employed involves subjecting the incompetent formations to elevated temperatures so as to cause fusion of constituents therein, e.g., silica sand particles, to provide bonding agents.

Still another means is to form carbonized or coked materials which act as binders to hold the formation as an integral consolidated mass.

Essentially these methods for consolidating incompetent earth formations have serious limitations as, for example, the mechanical devices mentioned tend to become plugged and generally are incapable of preventing fine particles from entering the production well. Also, these devices require cleaning and constant attention. The use of resin consolidating materials requires special equipment and a treatment process necessitating the presence of a drilling rig. This process is also time consuming and costly. In essence the same applies to thermal means of consolidating formations as mentioned above or other similar means known to the art. Thus, conventional thermal and chemical means of consolidating loose or incompetent formations are generally inefficient, ineffective, costly and generally cause a decrease in permeability of the formation. Also, these means of consolidation of formations lack desired resistance to changes in stress, strains, pressure and temperature conditions normally encountered in producing effluent from such formations.

A more effective and unusual method of consolidating formations and protecting surfaces such as tubing string and equipment used in oil recovery is by the electroless metal bonding process described in copending patent applications Ser. No. 579,223, filed Sept. 14, 1966 issued as U.S. Patent 3,393,737 on July 23, 1968; Ser. No. 579,-432, filed Sept. 14, 1966 U.S. 3,385,363 issued May 28, 1968; Ser. No. 692,686, filed Dec. 22, 1967 U.S. Patent 3,438,440 issued Mar. 15, 1969; Ser. No. 692,670, filed Dec. 22, 1967 U.S. Patent 3,438,441 issued Mar. 15, 1969 and Ser. No. 692,726, filed Dec. 22, 1967. The present invention also relates to an improved consolidation process using an electroless metal bonding process which is exceedingly effective and is also useful in metal coating surfaces so as to protect them from corrosion, wear and the like.

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SUMMARY OF THE INVENTION

An object of the present invention is to provide an improved method of consolidating loose or incompetent subsurface formations.

Another object of the present invention is to consolidate loose formations with a metallic binding agent which is resistant to hydrolysis and is capable of withstanding great pressures, strains and stresses.

Still another object of the present invention is to bind the grains of loose formations with a catalytic polyvalent metallic binding agent which is resistant to corrosion and is not effected by hot fluids such as water, steam and the like and is also resistant to high thermal temperatures caused by combustion drives and the like.

Still another object of the present invention is to form a catalytic polyvalent metallic consolidated subsurface earth formation having good permeability and good compressive strength, for the recovery of hydrocarbon fluids therefrom particularly when using thermal drives such as hot water or steam in the recovery process.

Still another object of this invention is to metalize formations at a controlled rate and to extended or great depths of penetration of said metal consolidation so as to protect natural materials against dissolution particularly at high temperatures.

Still another object of this invention is to metalize tubing strings and equipment used in oil recovery processes by the process of this invention so as to protect such equipment from corrosion and chemical damage.

Still other objects and advantages will be apparent from the description and examples illustrating the present invention.

In the processes of metal coating and metal consolidation of formations by the electroless processes described in the above copending applications, the surfaces to be treated are first activated or catalyzed with an activating solution which can be a palladium-activating solution and should also contain a reducing agent, e.g., hydrazine, sodium hypophosphite, lower aldehydes or the like. Such activator solutions can be palladium chloride and/or stannous chloride solutions or corresponding bromide, nitrate or sulfate solutions. Other such activator fluids can be aqueous solutions containing gold, ruthenium, rhodium, platinum or any of the so-called metallic dehydrogenation catalysts and a reducing agent such as hydrazine with or without the presence of protective colloids, e.g., soluble gums such as gum arabic tragacanth; proteins, e.g., gelatin, albumin, starch, glucosides or the like. The porous mass can be first treated with an acid solution such as sulfuric or hydrochloric acid solutions alone or in conjunction with the activator solutions. The pH of the activator solution can vary over a wide range and can be controlled by the presence of lower acids such as formic or acetic acids, acetic anhydride and salts thereof and mixtures thereof or by basic materials. The activator solutions are preferably acidic aqueous solutions such as palladium chloride-hydrazine solutions acidified with acetic or formic acid. Once the surfaces have been activated or catalyzed in this manner, the surface is contacted with a metal plating solution as described ι the copending applications so as to metalize and bond ıe treated surfaces into a consolidated formation.

It has now been discovered that instead of activating ıe surfaces to be protected and consolidated with pal- ıdium solutions or other expensive solutions, that the ıetalization reaction can be initiated by metal sol-form- ıg solutions, e.g., nickel, cadminum or iron sol-forming ›lution which can be metal hydrosols or organosols and ıe metal sol initiators should preferably correspond to ıe metal used in the subsequent metal plating solution.

The activating metal sol-forming solutions such as ickel sol-forming solution can be formed by any suitable ıeans such as, for example, by a modified Kelber reaction 'hich consists of reducing a nickel salt in a polyol solu- on, e.g., glycerine, ethylene glycol, triethylene glycol, olyalkylene oxides, e.g., polyethylene oxide or poly- ropylene oxide, in the presence of a reducing agent ıch as hydrazine and a protective colloid, said solution ontaining also a small amount of a chelating agent such s a nitrogen base compound or a hydroxy or carboxy rganic compound capable of chelating with the nickel ›n and prevent its precipitation. It has been discovered ıat if a small amount of such a metal sol solution is dded to a metal plating solution as described in the ›opending applications, electroless deposition of metal n the surfaces to be coated or consolidated takes place nd the surfaces are effectively coated and consolidated 'ith a metal bonding agent such as nickel, cobalt, iron nd the like.

In consolidating oil-bearing loose formations for the ›covery of hydrocarbon fluids therefrom by means of 'ells completed therein, it is preferable that prior to enetrating such formations with metal-deposition solu- ons as mentioned above, that such formations be pre- :eated with an acidizing fluid and/or preflushing fluid so s to displace oil and connate-water in areas desired to e consolidated by injecting therein suitable acidizing olutions and/or preflushing solvents. The metal plating olutions can be injected into the loose formations with r without spacer fluids between them. It is preferable ıat the formations be pretreated with a suitable acidizing olution or solvent, prior to penetrating the loose forma- ions with a metal sol-forming solution, followed by ıjecting a catalytic metal-deposition solution as will be ully described below.

Metals deposited by the process of this invention on ›ose sand grains in unconsolidated earth formations ›rm excellent binding agents which consolidate the ›ose and grains into stable permeable integral formations apable of sustaining great compressive forces and resist- ng damage to the formations caused by thermal drives. Also, the metal coatings on the grains form impermeable ayers that protect the grains from destruction by hot luids such as hot water and/or steam. The metal coating of siliceous components in earth formations also prevents lissolution of the silica that is contacted by hot aqueous luids when such fluids are flowed through the earth ormations, for example, in recovery by hydrocarbon luids therefrom.

An unconsolidated mass of sand grains is preferably :onsolidated by the process of this invention by im- ›regnating the mass with metal sol-forming liquid and hen with a catalytic metal-deposition solution contain- ng chemicals inclusive of metal ions and a reducing ıgent so as to chemically deposit within the mass a metal :oating which consolidates the mass or the two liquids :an be injected simultaneously. The amount and dis- ›osition of the deposited metal should be sufficient to ›ind the sand grains into a consolidated mass capable of ıustaining compressive forces of many hundreds of pounds ›er square inch. Also by this means the sand grains are :oated with an impermeable layer of metal that protects hem from being dissolved by hot aqueous fluids. The metal plating solution can contain a small amount of a non-catalytic metal salt to control the reaction rate of the plating or the non-catalytic metal containing solution or deactivator solution can be added after the metal plating solution has been injected into the formation and the metal plating process has been in progress for a desired interval of time.

For the most effective results it is desirable to flow a plurality of pore volumes of both the metal sol solution and a catalytic metal plating solution and if desired a deactivating soution through the interval of the formation into which the well is opened and preferably flow pore volumes of each of said solutions through generally shaped zones, e.g., cylindrical or spherical zones having a diameter of from about 1 to about 5 feet around to open portions of a well borehole.

The results of effecting a chemical-reduction deposition of metal within a porous earth formation that surrounds the borehole of a well are such that is a particularly advantageous process for treating such an earth formation. Where the earth formation is unconsolidated, the metal deposition provides a method of consolidation in which the chemical coats are not more than those of sand consolidation procedures which have proven to be economically advantageous. Where the well is to be employed in the injection or production of hot fluids, the metal deposition provides a treatment that (a) consolidates any unconsolidated portions of the earth formation; (b) metal plates any siliceous components and prevents the dissolution of silica that tends to occur whenever a hot aqueous fluid is flowed through a siliceous earth formation that was naturally consolidated or was consolidated by a conventional sand consolidation procedure; (c) metal plates and improves the stability of any intergranular bonding material that has been formed within the earth formation; and (d) reduces the heat loss that occurs within the tubing string of the production wells that extends into communication with the earth formation by depositing on the tubing strings a reflective metal plating that reduces the thermal emissivity of the tubing string.

In general, a chemical-reduction deposition of metal within a porous mass of earth-formation material is an advantageous procedure for improving the strength and stability of the moss. The electroless metal-deposition treatment provides a convenient and relatively economical procedure for binding a sand into a mold in which to solidify a molten material, such as a molten metal, for increasing the thermal or electrical conductivity of a mass of earth-formation material or for dispersing and fixing metals that are to be utilized as catalysts, activators, property indicators, or the like, within such a porous mass, etc.

PREFERRED EMBODIMENT OF THE INVENTION

The process of metal plating unconsolidated earth formations into consolidated form can be effected by the following sequential steps for consolidating a zone around a borehole:

(1) Inject if necessary an acidizing fluid such as a mud and thereafter wash the formation with several pore volumes of solvent such as isopropyl alcohol to achieve desired injection rate;

(2) Preflush the formation also if necessary or desirable with conventional liquids such as several pore volumes of hydrocarbon oil, e.g., diesel oil, and/or solvent such as isopropyl alcohol;

(3) Injecting a metal sol-forming solution, which metal sol-forming solution can be a metal hydrosol or organosol solution for consolidation of sand grains which metal sol solution is capable of subsequently initiating an electroless metal plating process comprising the injection into the unconsolidated sand grains of an electroless metal plating solution;

(4) Inject an electroless metal plating solution;

(5) Inject if necessary spacer fluid which is preferably an ammonical buffer solution;

(6) Inject water; and,

(7) Consolidation of formations by metalization is thereafter effected.

In permeating a porous mass by the process of the present invention with a metal sol-forming liquid, each element of the mass is preferably contacted with at least several pore volumes of the liquid. Metal hydrosol or organosol solutions should contain reducing agents such as hydrazine or sodium hypophosphite or lower aldehyde, e.g., formaldehyde, and an organic base chelating agent such as alkanolamines. Such a solution can be illustrated by a nickel sol solution formed by reducing a nickel salt in glycerine with hydrazine in the presence of a protective colloid such as gelatin and a chelating agent such as ethanolamine. Other such metal sol-forming solutions can contain cobalt, iron, copper sols or the like and a reducing agent such as hydrazine and the protective colloids can be soluble gums such as gum arabic or gum tragacanth; proteins, e.g., gelatin, albumin, starch, glucosides or the like and chelating agents can be alkanolamines, e.g., ethanolamine, propanolamine, etc., or polycarboxylic acids.

The formation can be pretreated with a mud acid (410 cc. concentration HCl+590 cc. H_2O+32 grams

NH_4F+2 cc.

amine corrosion inhibitor or any suitable acidizing fluids such as described in U.S. Patents 3,215,199; 3,236,305; 3,249,536 and 3,251,415.

The metal sol-forming solution may be injected prior to or simultaneously with the metal plating solution. In treating a subsurface earth formation it is preferable to precede the above steps by a conventional oil- and connate-water-displacing procedure such as described in U.S. Patent 3,294,166 for sand consolidation with epoxy resin. Since this procedure generally displaces oil and connate-water films from the tubing string, such a pretreatment ensures that some metal deposition will occur in the injection tubing string when the metal-deposition solution is injected into the treated porous mass through said tubing string in the well bore in communication with the porous mass, and therefore some thermal-emissivity reduction can be provided in respect to the thermal properties of the tubing string.

The metal plating solution can be in the basic pH range of 8–14, preferably 8–10, or acidic pH range of 2.5–5. The basic pH regulators can be aqueous ammonical solutions containing ammonium hydroxide, ammonium chloride and mixtures thereof and the acidic pH regulator can be formic or acetic acid, acetic anhydride or salts thereof. Control of pH aids in forming more uniform metal deposition through the formation and to greater depths. The reaction rate of metal deposition on the surfaces to be consolidated is most effective when the pH of the solution is about 8 or 9 and the temperature is in the range of from about 35° F. to about 125° F., and at a pH of 2.5–5 when the temperature of the formation is above 125°, preferably between about 150 and about 200° F.

The metal plating compound can be a polyvalent metal compound of which preferred compounds include nickel, cobalt and copper compounds and mixtures thereof, e.g., nickel and/or cobalt chloride and/or sulfate. These metal compounds are reduced by such reagents as hydrazine, hypophosphorous acid, hypophosphites, e.g., sodium hypophosphite or alkaline solution of molybdenate, formate and/or hydroxy carboxylates, e.g., hydroxyacetate. The concentration of the metal-containing compounds and the reducing agents in aqueous solutions can be varied over a wide range such as from 1 to 50%, respectively, and preferably from 5 to 40% each.

To keep the hydrogen evolution to a minimum during the reaction, the reducing agents in the metal-plating solutions should be kept at a minimum generally not in excess of 10% of the total electroless metal plating solution. Also, hydrogen evolution can be effectively suppressed and the life of the metal-plating reaction increased by addition to such aqueous solutions buffering and chelating agents such as hydroxy carboxylic acids and polycarboxylic acids and their salts, e.g., citric, tartaric, maleic, gluconic and succinic acids or ammonium or alkali metal salts of said acids such as sodium citrate, sodium succinate and the like. However, the gas can be effectively eliminated from the area being metalized by applying pressure of 200 pounds or more on the system.

To promote wetting of the surfaces to be metalized by the electroless process of the present invention, wetting agents can be used such as reaction products of alkylphenol and alkylene oxide, e.g., nonyl phenolethylene oxide reaction product wherein the number of ethylene oxide units in the molecule ranges from 4 to 20; sulfated alcohols; sulfonates of fatty acids having from 12 to 18 carbon atoms, e.g., sulfonated oleic acid; sulfonated mineral oil fractions and the like.

Also, using hypophosphites as the reducing agent its concentration should be controlled since depending in part on the phosphorus content of the solution the metal being plated can be in the form of an alloy of metal-phosphorus nickel phosphide. High concentrations such as above 10% of hypophosphite in the metal plating solution tends to form these alloys.

The metal-plating consolidation process of the present invention can be also used to improve earth formations which have been previously consolidated by various resins or plastics such as epoxy resins or various other types by forming on the resin coated surface a metal coating that renders the consolidated formation resistant to hydrolysis at elevated temperatures, such as those encountered when hot water and/or steam is injected into such systems for secondary recovery of hydrocarbon fluids such as petroleum oil. The metalization of resin or plastic consolidated formations is effectively accomplished by the process of the present invention. This is particularly desirable in cases where resins used to consolidate formations are thermally stable but are hydrolytically unstable and tend to disintegrate on prolonged exposure to steam or hot water. The same applies to formations consolidated with quartz or other types of consolidators.

The following example illustrates the invention.

An unconsolidated sand formation was first treated with mud acid and thereafter preflushed with diesel oil and isopropyl alcohol to remove crude and oil. Thereafter a nickel sol was prepared by reducing a 1% solution of nickel acetate in glycerine with hydrazine in the presence of about 0.5% ethanolamine. Consolidation was achieved by injecting this sol solution with a nickel plating solution comprising:

(a) 81.6 cc. H_2O
(b) 3.62 grams $NiCl_2 \cdot 6H_2O$
(c) 4.33 grams $NaH_2PO_2 \cdot H_2O$
(d) 5.95 grams NH_4Cl
(e) 4.75 grams (5.0 cc.) 29.4% weight NH_3 solution (conc. ammonium hydroxide)
(g) To this solution was added 0.36 grams of $FeSO_4$ solution to control metal plating rate.

Following the above procedure an unconsolidated sand formation was cobalt consolidated using a cobalt sol as the initiator and the cobalt metal plating solution comprised injecting:

(a) 856 cc./l. H_2O
(b) 38 grams/l. $CoCl_2 \cdot 6H_2O$
(c) 33 grams/l. $NaH_2PO_2 \cdot H_2O$
(d) 62.5 grams/1. NH_4Cl
(e) 52.2 cc./l. 29.4% weight NH_3 (conc. ammonium hydroxide solution).

Final flush was injected using about 5 pore volumes of e following solution:

ι) 905 cc./l. H_2O
ɔ) 66 grams/l. NH_4Cl
:) 55 cc./l. 29.4% weight NH_3 (conc. ammonium hydroxide solution).

In each of the above cases the compressive strength of :e formation was greatly increased and remained so for long period of time. Also, the permeability of the for-.ation was not effected so that fluid flow was excellent.

Notable features of the present invention are the control : the reaction rate of the electroless metal process so that :eat depths of consolidation can be achieved and also ιe metal plating process aids in reducing corrosion and эat loss of tubing strings used in the bore wells for when ιjecting the binding and activating fluids into the under-:ound production areas the tubing strings are metalized y the process of the present invention. As these fluids are ιjected into the loose formations the tubing strings are .so metalized with such materials as nickel or cobalt or ickel phosphide or cobalt phosphide or nickel-iron pro-ιctive metal coatings, as well as other parts of the equip-ιent and apparatus with which said metalizing fluids come ι contact.

The foregoing description of the invention is merely in-ınded to be explanatory thereof. Various changes in the etails of the described method may be made, within the :ope of the appended claims, without departing from the ɔirit of the invention.

I claim as my invention:

1. A method of consolidating unconsolidated earth for-ıations with metals by an electroless metal plating proc-ɜs comprising contacting and activating said formations ʼith (1) a metal-forming sol solution to initiate metal eposition on the surface of said formations and contact-ıg said formations with (2) an electroless metal deposi-on solution containing a reducing agent capable of metal onsolidating said formations by metal bonding the sand rains of the unconsolidated earth formations, said metal ı (1) and (2) being the same.

2. The method of claim 1 wherein the formation being onsolidated is an unconsolidated earth formation, the ıetal sol of the metal sol-forming solution is selected rom the group consisting of nickel sol and cobalt sol the olution being selected from aqueous and organic liquids containing a reducing agent and the electroless metal deposition solution being an aqueous solution containing nickel or cobalt salts and the reducing agent being selected from the group consisting of hydrazine, hydrophosphorus acid, alkali metal hydrophosphite, and lower aldehydes.

3. A method of consolidating an incompetent formation penetrated by a well borehole comprising:

(a) injecting into said formation from said well borehole, a metal sol-forming initiating solution comprising of a nickel sol formed by reducing nickel acetate in polyalcohol, said solution containing hydrazine as a reducing agent and an amine chelating agent; and

(b) injecting an aqueous electroless metal plating solution containing a nickel salt and sodium hypophosphite in an amount sufficient to nickel plate and consolidate the formation.

4. The method of claim 3 wherein the nickel salt in (b) is nickel chloride, or nickel sulfate.

5. The method of claim 4 wherein the polyalcohol is glycerine and the nickel sol solution contains therein a protective colloid and said chelating agent is an alkanolamine chelating agent.

6. The method of claim 5 wherein prior to injecting solutions (a) and (b) into the incompetent formation, an acidizing fluid and solvent are injected into the formation.

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