

# United States Patent

[11] 3,548,943

[72] Inventors Theodore A. Simon;  
Edwin A. Richardson, Houston, Tex.  
[21] Appl. No. 850,253  
[22] Filed Aug. 14, 1969  
[45] Patented Dec. 22, 1970  
[73] Assignee Shell Oil Company  
New York, N.Y.  
a corporation of Delaware

[54] **ELECTROLESS METAL BONDING OF  
UNCONSOLIDATED FORMATIONS WITH  
BACKFLOW**  
5 Claims, No Drawings

[52] U.S. Cl. .... 166/292,  
166/300  
[51] Int. Cl. .... E21b 33/138

[50] Field of Search..... 166/292  
—295, 300, 285

[56] **References Cited**  
**UNITED STATES PATENTS**  
2,781,850 2/1957 Nowak et al. .... 166/295  
3,100,527 8/1963 Hilton et al. .... 166/295  
3,393,737 7/1968 Richardson ..... 166/292

*Primary Examiner*—Marvin A. Champion  
*Assistant Examiner*—Ian A. Calvert  
*Attorneys*—George G. Pritzker and J. H. McCarthy

**ABSTRACT:** A method of consolidating an incompetent or unconsolidated formation, over a wide temperature range, by subjecting the formation to an incremental electroless metal plating process wherein between such treatments the formation is subjected to a backflush treatment.

# ELECTROLESS METAL BONDING OF UNCONSOLIDATED FORMATIONS WITH BACKFLOW

## BACKGROUND OF THE INVENTION

In the U.S. Pat. Nos. 3,393,737, 3,438,440, 3,438,441 and pending applications Ser. No. 692,726 filed Dec. 27, 1967, now Pat. No. 3,500,926, and Ser. No. 705,907 filed Feb. 16, 1968, now U.S. Pat. No. 3,500,927, electroless metal plating techniques are described for consolidating unconsolidated formations. The metal plating process provides advantages relative to resin consolidation techniques for consolidating earth formations as described in such papers as Jr. Pet. Tech. May 1966, p. 545 entitled "Review of Sand Consolidation Experience in Southern Louisiana" by J. L. Rike, or Jr. Pet. Tech. Dec. 1961, paper entitled "Large-Scale Laboratory Investigation of Sand Consolidation Techniques" by W. F. Hoover, or Jr. Pet. Tech. Dec. 1966, page 1537 article entitled "Studies of a New Process to Consolidate Oil Sands with Plastics" by B. R. Treadway or as described in U.S. Pat. Nos. 3,412,796, 3,419,072, 3,378,071, 3,373,813, 3,310,111, 3,282,338 and the like. In essentially all of the resin consolidation processes for consolidating incompetent formations, rigs are required, curing time is difficult to control, the resin coating or binding material is not resistant to temperature changes encountered in the treated formation or to water stability or the influence of corrosive acids and the like. This results in costly operations of restrictive use and benefit and therefore makes the electroless metal consolidation techniques described in the above-mentioned references more attractive since metal consolidated formations require no rig, the formations thus treated are not affected by temperature changes and are water stable and impart high compressive strength to such metallized consolidation formations.

## SUMMARY OF THE INVENTION

It has now been discovered that further unexpected improvements in electroless metal plating techniques in order to consolidate formations can be achieved by an incremental electroless metal plating of unconsolidated formations so that in the initial electroless metal plating only the first-contacted portions of the treated formation are consolidated and in between such electroless metalization treatments the formation is subjected to at least one backflush treatment in which a liquid, such as the expended plating solution, capable of entraining and removing any impurities or debris present along the face of the formation or in the passageways from the borehole to the formation is backflowed from the formation to the well and thereafter the electroless metal plating cycle is repeated. By this process incompetent formations are metal consolidated to a high compressive strength and spatial uniformity of treatment which results in a consolidated formation resistant to the action of water, corrosive liquids, etc.

Formations which can be metal consolidated by the electroless metal process of the present invention include any unconsolidated earth formation and preferably comprise underground incompetent formations penetrated by at least one well borehole from which fluids are to be recovered or into which fluids are to be injected. By consolidating such formations with a metal bonding material by the process of the present invention, improved and more efficient fluid recovery such as crude oil, natural gases, mining solutions and the like can be achieved.

Briefly outlined, the new and improved process of metal consolidating incompetent or unconsolidated earth formations by the electroless metal plating technique of the present invention comprises an improvement in treating a permeable incompetent or unconsolidated earth formation by pumping or injecting an activated electroless metal plating solution through a conduit within a well penetrating said formation and into an adjacent portion of the earth formation to be consolidated, wherein the improvement is provided by the following steps:

1. Pumping through the conduit and into the earth formation an amount of activated electroless metal plating solution that is sufficient to plate metal on any unconsolidated grains in the portion of the earth formation that is first contacted by fluid flowing from the conduit to the formation and consolidate those grains into an integral permeable mass but is insufficient to cause more than a selected degree of reduction in the permeability of the first contacted portion of the earth formation;
2. Backflowing fluid from the earth formation into a portion of the well in which solids entrained by the backflowed fluid are at least to some extent removed from the flow path of fluid flowing from the conduit to the earth formation;
3. Pumping at least one additional portion of activated electroless metal plating solution through the conduit and into the earth formation; and
4. Repeating steps (1) and (2), if required, to provide the desired extent of consolidation of the formation.

In the above definition, the term "activated metal plating solution" refers to a solution of electroless metal plating components in contact with activating components. Such a solution is preferably formed in situ by pretreating the sand grains or rock with a solution of the activating components and injecting a solution of the metal plating components into the pretreated zone. However, a solution of some or all of the activating components can be mixed with a solution of some or all of the plating components prior to the injection into the earth formation.

The activating components of such an activator solution are materials capable of catalyzing or activating the sand grains to be consolidated in the formation by the metal plating solution and can include any of the activator solutions described in U.S. Pat. Nos. 3,393,737, 3,438,440 or 3,438,441 of which preferred are aqueous solutions containing palladium chloride or stannous chloride to which can be added hydrazine, buffers, stabilizers and the like. The activator solution should be so formulated as to be resistant to catalytic deactivation even in the presence of 0.5 ppm or more of constituents such as hydrogen sulfide, or cyanide.

A preferred activator solution designed to effectively metal plate, preferably nickel plate, unconsolidated sand grains of an earth formation is one capable of depositing on the sand grains a colloidal palladium metal and such an activator solution is illustrated by:

TABLE 1.—COMPOSITION OF ACTIVATOR SOLUTION

| Component                                            | Quantity per barrel of solution <sup>a</sup> |
|------------------------------------------------------|----------------------------------------------|
| Water.....                                           | 40.7 gallons.                                |
| Gum Arabic <sup>b</sup> .....                        | 20.6 gms.                                    |
| Hydrazine hydrate (85%).....                         | 256 cc.                                      |
| Palladium chloride solution <sup>c</sup> .....       | 636 cc. <sup>1</sup>                         |
| Omit when buffers are used:                          |                                              |
| NiSO <sub>4</sub> ·6H <sub>2</sub> O.....            | 3.5 pounds.                                  |
| 90% formic acid or glacial acetic <sup>2</sup> ..... | ~160-320 cc.                                 |
| Buffers:                                             |                                              |
| Formic acid (90%).....                               | 640 cc.                                      |
| Sodium formate.....                                  | 7 pounds.                                    |
| or                                                   |                                              |
| Acetic acid (glacial).....                           | 6.4 liters.                                  |
| Sodium acetate.....                                  | 10.5 pounds.                                 |

NOTE: Chemicals are preferably added to the water in the order listed with complete mixing and dissolving before adding the next chemical.

<sup>a</sup> Contains 10.2 grams PdCl<sub>2</sub>/bbl. of activator solution.

<sup>b</sup> Requires about 15 minutes to dissolve.

<sup>c</sup> Contains 1.6 gms. PdCl<sub>2</sub>, 10 cc. conc. HCl, 90 cc. distilled or deionized water/100 cc. PdCl<sub>2</sub> solution.

<sup>1</sup> Or 400 cc. of 35% hydrazine.

<sup>2</sup> As needed for pH=4.4.

The electroless metal plating solution composition can be varied over a wide range and can be formulated to suit bottom hole temperatures or formation temperatures which can range from about 50° F. to above about 400° F. and generally range between about 60° F. and about 250° F. Thus, depending on the temperature in the formation, at a low temperature range

(60–130°F.) an ammoniacal nickel plating system is preferred and at intermediate and higher temperatures acetate or formate containing nickel plating systems are preferred. Typical compositions of electroless nickel plating solutions are illustrated by the following examples:

TABLE 2.—COMPOSITION OF LOW TEMPERATURE PLATING SOLUTION

|                                                         | Quantity per barrel of solution |
|---------------------------------------------------------|---------------------------------|
| Component:                                              |                                 |
| H <sub>2</sub> O.....                                   | 35.9 gallons.                   |
| NiCl <sub>2</sub> ·6H <sub>2</sub> O.....               | 13.28 pounds.                   |
| NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O..... | 15.95 pounds.                   |
| NH <sub>4</sub> Cl.....                                 | 21.9 pounds.                    |
| 30% NiI <sub>2</sub> .....                              | 2.19 gallons.                   |
| Solution density.....                                   | 1.06 gm./cc.                    |
| Solution pH.....                                        | 8.7.                            |

TABLE 3.—COMPOSITION OF PLATING SOLUTIONS FOR INTERMEDIATE AND HIGH TEMPERATURES

|                                                         | Quantity per barrel of solution |                |
|---------------------------------------------------------|---------------------------------|----------------|
|                                                         | Formate system                  | Acetate system |
| Component:                                              |                                 |                |
| NiSO <sub>4</sub> ·6H <sub>2</sub> O.....               | 29.5 pounds.                    | 29.5 pounds.   |
| NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O..... | 42.2 pounds.                    | 42.2 pounds.   |
| Succinic acid.....                                      | 4.6 pounds.                     | 4.6 pounds.    |
| NaOH (30% solution).....                                | 0.937 gal.                      | 0.937 gal.     |
| Sodium formate.....                                     | 15.77 pounds.                   |                |
| Sodium acetate·3H <sub>2</sub> O.....                   |                                 | 31.6 pounds.   |
| Water.....                                              | 36.42 gal.                      | 34.74 gal.     |
| Solution density.....                                   | ~1.15 gm./cc.                   | ~1.15 gm./cc.  |
| pH range.....                                           | 3 to 4.                         | 4 to 5.        |

In carrying out the metallizing process of this invention the formation is preferably preflushed to condition it and/or remove foreign mater therefrom and this can be accomplished by injecting into the formation a hydrocarbon oil and alcohol mixture to displace hydrocarbons and water-wet the zone to be consolidated. Also a spacer fluid can be used between the activator solution and the metal plating solution. A suitable preflush includes injecting at least five pore volumes of diesel oil and at least five pore volumes of isopropyl alcohol to displace hydrocarbons and water-wet the zone to be consolidated.

After injecting enough plating solution to consolidate the first-contacted portion, the pressure is reduced within the conduit of the well and backflow from the treated zone is initiated by reducing the downhole pressure within the conduit to less than the fluid pressure within the formation, in order to effect removal of debris, etc. and, subsequently, an additional portion of plating solution is injected into the treated zone to effect further consolidation.

In respect to a resin sand consolidating operation, such a backflowing operation is normally undesirable and contrary to the prior teachings and conventional practices. It is advantageous in the process of the present invention only because the metal plating process is uniquely capable of providing a relatively strong consolidation in the first-contacted portions during the relatively short time in which the plating solution is being injected. This is essential in order to keep a relatively large proportion of sand from being washed into the well during the backflowing operation. During the initial injection of the metal plating solution, most of the solution enters the portions of the earth formation that are the most receptive to fluid. Even where an earth formation is uniformly permeable, at least some portion is apt to be somewhat unreceptive because particles of debris (which have sizes ranging from microscopic to macroscopic) are screened out to form an impermeable layer covering that portion or the passageways leading to it. The first few inches of the portions entered by the plating solution are converted to integral porous masses and, during the backflowing, they remain intact

while any loose grains (such as a layer of debris) are entrained in the backflowed fluid and are carried into the well. In the well, the debris in the backflowed fluid is allowed to settle and/or diffuse throughout a relatively large volume of fluid, so that the solids are at least to some extent removed from the flow path followed by fluid flowing from a conduit within the well to the earth formation. During the next injection of metal plating solution, even where some solids are dispersed within the fluid being injected, since the fluid tends to enter all- portions that are now receptive and since these portions include both the consolidated portions and the portions that were previously unreceptive to fluid, the plating is now extended into the previously unreceptive portions and the spatial uniformity of the treatment is improved.

The backflush step of the invention, which essentially is its essence, removes from the earth formation being treated any localized build-ups of debris and the like that prevent fluid from entering portions of the formation during the metal plating cycle thereby improving fluid injectivity, distribution of metal plating solution, and subsequently fluid (oil, etc.) production. The backflushing is accomplished by filling a conduit such as the tubing string in a well borehole with one or more relatively low density fluids such as hydrocarbons, gases or the like that provides a hydrostatic pressure of less than the formation fluid pressure and allowing fluid to flow from the formation to the conduit in order to remove impurities and debris from the formation being metal consolidated.

The backflush improves the injection profile and results a more uniform depth of penetration around the perforated zone. The sand in and adjacent to a perforation which has passed plating solution for a fraction (say one-third) of the design plating time will exhibit a consolidation strength somewhat in proportion to the time fraction (say 4,000 - 10,000 p.s.i.) and will not be affected by backflushing. Perforations that contain unconsolidated sand that prevented an entry of the plating solution tend to be removed by the backflowing fluid, which enters from the formation side, and the formations adjacent to them tend to be consolidated on the following plating cycle.

The solids entrained by the backflowed fluid may be only partially displaced away from the flow path of fluid flowing from the conduit to the earth formation. In such a partial removal from the flow path, the entrained solids may be allowed to settle below the flow path, by falling through the relatively static liquid in the borehole below the perforations, or simply redistributed and dispersed throughout the first portions of the fluid that will subsequently be injected into the earth formation. Such a redistribution is, in itself, effective in accomplishing the purposes of the invention.

#### PREFERRED ILLUSTRATIVE EMBODIMENTS FOR CARRYING OUT THE PROCESS OF THIS INVENTION

After injecting a predetermined portion (e.g., two-thirds, one-half or one-third) of a plating solution (but not less than about one-third) the formation is backflushed by a procedure such as the following:

##### USING SMALL WORK STRING THROUGH TUBING, SMALL ANNULUS OPEN TO PERFORATIONS

1. If the annulus is open and a small work string (say, 1-inch) is being used through tubing (say, 2 3/8-inch), displace work string with filtered diesel oil. Assure that a low weight fluid such as diesel oil is standing in the annulus.

2. Open tubing/work string annulus and produce approximately 10 barrels (some 2000 vertical feet of annular volume) into the mud tanks. Rate of backflush must be dictated by formation integrity.

3. Circulate annulus clean by pumping diesel down the work string (some five barrels per 1000 feet of depth).

4. Circulate two- to three-pore volumes of isopropyl alcohol (IPA) down the work string to bottom. The surface valve on the annulus should be closed when IPA is calculated to be at

the perforations (which may be after this or during the following steps, depending upon tubular size, well depth, etc.). Displace IPA into the formation with the following solutions.

5. Pump in two-pore volumes of activator solution shown on Table 1.

6. Pump in several barrels inert spacer solution.

7. Pump in balance of plating solution or repeat backflush sequence after the next predetermined quantity of plating solution has been pumped. The annulus now contains diesel oil and is now prepared to handle the next backflush.

#### WORK STRING HUNG IN CASING, ANNULUS OPEN TO PERFORATIONS

1. Displace tubing to perforations by pumping in diesel oil. Assure that annulus strands nearly full with light weight fluid such as diesel oil. Quantity required depends upon total (all stages) number of backflushes desired.

2. Open annulus valve and produce approximately ten barrels to mud tanks at a controlled rate.

3. Circulate three-pore volumes of IPA to bottom while bleeding at the same rate from the annulus valve. Close annulus valve when IPA is calculated to be at the perforations. Note that debris backflushed from perforations will be displaced higher into the annulus during circulation. The field engineer may find it desirable to circulate debris to surface if adequate diesel oil is available.

4. Pump in two-pore volumes of activator solution (table 1).

5. Pump in several barrels of inert spacer solution.

6. Pump in the balance of plating solution or repeat backflush sequence after the next predetermined amount of plating solution has been pumped. Assure that the annulus still contains adequate diesel oil for the remaining backflushes planned.

#### NO WORKOVER RIG, PUMPING THROUGH TUBING, ANNULUS PACKED OFF

1. Pump in a quantity of diesel oil calculated to permit backflowing approximately five barrels of spent plating solution from the formation at a minimum of between 200 and 500 p.s.i. underbalance.

#### ILLUSTRATIVE EXAMPLES

1. Backflush five barrels (or other amount desired) through the tubing to the mud tank. Shut in well for 15 to 30 minutes.

2. Assure that at least one barrel of diesel oil spacer remains in the tubing to separate the IPA from the plating solution. Normally, more than the required amount will be present. Pump in three-pore volumes of IPA.

3. Pump in two-pore volumes of activator solution.

4. Pump in several barrels inert spacer solution.

5. Pump in balance of plating solution or repeat backflush sequence after another predetermined amount of plating solution has been pumped.

In addition to well treatments designed to consolidate an unconsolidated sand, the present process can be used to (1) coat a partially or fully consolidated earth formation in order

to protect the formation grains and/or consolidating material from dissolution by hot aqueous fluid, (2) ensure the uniform spatial distribution within an earth formation of a metal to be utilized as a catalyst, a conductor of electricity or heat, or the like, (3) ensure the uniform spatial distribution of a metal that is being plated to a thickness sufficient to provide a selected degree of reduction in the permeability of a relatively permeable zone that amounts to a thief zone within an interval of lesser permeability, i.e., the process described in copending application Ser. No. 817,722, filed Apr. 21, 1969, and (4) consolidate grains of sand that were previously displaced (or are being displaced) through the perforations in a casing liner or the like to fill voids within the surrounding earth formation, etc.

We claim:

1. A method of electroless metal plating a permeable earth formation penetrated by a well borehole comprising:

a. injecting through the wellbore and into the earth formation an activating solution capable of activating the formation to effect electroless metal plating thereof;

b. injecting through the well and into said activated earth formation a portion of an electroless metal-plating solution;

c. reducing the pressure in the wellbore to effect backflow of fluid from the earth formation, whereby the backflowing fluid entrains and removes impurities and debris from the earth formation;

d. injecting activating solution capable of activating any newly exposed portion of the earth formation; and

e. injecting into the earth formation an additional portion of the metal-plating solution of b until metal consolidation of the formation is achieved.

2. The method of claim 1 wherein prior to step a the earth formation is preflushed with a liquid capable of cleaning the formation and water-wetting the formation surface to be consolidated.

3. The method of claim 2 wherein a spacer liquid is injected between steps a and b.

4. The method of claim 3 wherein the solution in step b is a nickel-plating solution and the activator of solution a is colloidal palladium.

5. A method of consolidating an incompetent earth formation penetrated by at least one well borehole in order to improve injectivity and oil recovery from the formation comprising:

a. injecting a preflushing liquid comprising of diesel oil and an alcohol to water-wet the sand grains of the formation;

b. injecting a palladium chloride solution to activate the sand granules;

c. injecting a spacer liquid;

d. injecting a nickel-plating solution containing a reducing agent in an amount less than that required to complete the consolidation;

e. reducing the pressure within the well borehole and backflushing liquid from the earth formation to remove debris from the treated formation; and

f. injecting at least one additional portion of plating solution d until formation consolidation is completed.