Calcium sulfate scale deposits are removed from oil field equipment including downhole pipe, tubing and casing as well as subterranean formations with a scale-removing composition comprising an aqueous alkaline solution having a pH of about 9 to about 14 and a chelating agent comprising DTPA in an amount from 20 to 40 % by weight, preferably 20 %. When the scale-removing solution is contacted with a surface containing a scale deposit, substantially more scale is dissolved at a faster rate than previously possible.
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METHOD FOR REMOVING CALCIUM SULFATE SCALE

Many waters contain alkaline earth metal cations, such as barium, strontium, calcium and magnesium, and anions, such as sulfate, bicarbonate, carbonate, phosphate, and fluoride. When combinations of these anions and cations are present in concentrations which exceed the solubility product of the various species which may be formed, precipitates form until the respective solubility products are no longer exceeded. For example, when the concentrations of the calcium and sulfate ions exceed the solubility product of calcium sulfate, a solid phase of calcium sulfate will form as a precipitate. Solubility products are exceeded for various reasons, such as evaporation of the water phase, change in pH, pressure or temperature and the introduction of additional ions which can form insoluble compounds with the ions already present in the solution.

As these reaction products precipitate on the surfaces of the water-carrying or water-containing system, they form adherent deposits or scale. Scale may prevent effective heat transfer, interfere with fluid flow, facilitate corrosive processes, or harbor bacteria. Scale is an expensive problem in many industrial water systems, in production systems for oil and gas, in pulp and paper mill systems, and in other systems, causing delays and shutdowns for cleaning and removal.

The incidence of calcium sulfate scale is worldwide, and it occurs principally in systems handling subsurface waters. Because of this, the calcium sulfate scale problem is of particular concern to the petroleum industry as water is generally produced with petroleum and as time goes on, more petroleum is produced by the waterflooding method of secondary recovery, implying even greater volumes of
produced water. The scale may occur in many different places, including production tubing, well bore perforations, the area near the well bore, gathering lines, meters, valves and in other production equipment. Calcium sulfate scale may also form within subterranean formations such as in disposal wells. Scales and deposits can be formed to such an extent that the permeability of the formation is impaired resulting in lower flow rates, higher pump pressures, and ultimately abandonment of the well. In some cases, production can be halted when valves and pumps are stuck—creating a potentially dangerous situation.

Calcium sulfate scale is particularly troublesome in some U.S. oil fields in West Texas.

Various proposals have been made in the past for dissolving calcium sulfate scale, commonly known as anhydrite and gypsum.

In common practice, calcium sulfate scale is converted to an acid soluble form by soaking in a carbonate or organic solution. The converted sulfate scale is then treated with dilute hydrochloric acid to remove the converted scale. Calcium sulfate scale is not directly soluble in hydrochloric acid. This conversion process, followed by acidification is not very efficient in removing thick layers of calcium sulfate scales.

U.S. Patent No. 3,660,287 describes a method for dissolving calcium sulfate containing scale with a mixture of an EDTA salt and a water soluble inorganic carbonate salt. The concentration is preferably that equivalent to form about 0.02 to 0.03 molar EDTA solution at a pH from about 6 to 14.

U.S. Patent No. 3,684,720 describes a method for dissolving calcium sulfate-containing scale with a scale converting agent and EDTA. Suitable converting
agents include the ammonium and alkali metal carbonates, bicarbonates, phosphates, oxalates and hydroxides.

Low concentrations of the chelating agents are used in the range of 0.05 to 5.0.

Although many of these known compositions will remove scale, the rate of dissolution is slow and the amount of scale dissolved is small.

The present invention is particularly effective in dissolving calcium sulfate scale from oilfield equipment using an aqueous solvent containing 20 to 40% by weight DTPA or salts thereof.

The present invention is directed to the method to remove calcium sulfate scale comprising contacting the scale with an aqueous solution having a pH of about 8 to about 14 and from about 20 to 40% by weight of a chelating agent comprising DTPA or salt thereof.

Figure 1 is a graph which shows the effect of chelant concentration on the rate of calcium sulfate dissolution.

Figure 2 is a graph which shows the effect of pH of the solvent on the rate of calcium sulfate dissolution at various concentrations of chelant.

According to the present invention, calcium sulfate scale is removed by direct dissolution using DTPA as the chelating agent. The method is particularly useful for the removal of such scale from oil field equipment used to bring oil and/or water from subterranean formations to the surface. The method may, however, also be used to remove scale from the formations themselves, especially in the regions surrounding production and injection wells, as mentioned above. The method may also be used to remove scale from above-ground equipment both in the oil field and elsewhere, for example, from boilers and heat
exchangers and other equipment exposed to scale-forming conditions.

The scale itself is usually in the form of an adherent deposit of the scale-forming mineral on metal surfaces which have been exposed to the water containing the scale-forming components. These components comprise alkaline earth metals including calcium, strontium and barium together with variable amounts of radium, depending upon the origin of the waters. As noted above, certain oil fields particularly contain calcium sulfate scale.

The present invention is directed to a method for the removal of calcium sulfate scale with an aqueous solvent which comprises a DTPA as the chelant or chelating agent which forms a stable complex with the cation of the alkaline earth scale-forming material. The chelant may be added to the solvent in the acid form or, alternatively, as a salt of the acid, preferably the potassium salt. In any event the alkaline conditions used in the scale removal process will convert the free acid to the salt.

We have found that if the concentration of the chelant in the solvent is in the range of from 20 to 40% by weight, and preferably between 20 and 30%, the solvent is very active in dissolving calcium sulfate scale in place.

The scale removal is effected under alkaline conditions preferably at pH values of from about 9.0 to about 14.0, with optimum values being from about 12 to 14, preferably about 12.

The preferred solvents comprise about 20% by weight of diethylenetriaminepentaacetic acid (DTPA), or salt of this acid, as the chelant. The pH of the solvent is then adjusted by the addition of a base to the desired value, preferably to about pH 12. We have
found that it is important to avoid the use of sodium cations when operating at high pH values, above pH 8, and instead, to use potassium or, alternatively, cesium as the cation of the scale-removing agent. Potassium is preferred for economy as well as availability. Thus, the normal course of making up the solvent will be to dissolve the chelant in the water to the desired concentration, after which a potassium base, usually potassium hydroxide is added to bring the pH to the desired value of about 12. This aqueous composition can be used to remove scale from the equipment, or alternatively, pumped into the subterranean formation when it is the formation which is to be subjected to descaling.

The aqueous solution containing the composition can be directed down a wellbore to remove calcium sulfate scale which has fouled the tubular equipment e.g. piping, casing etc., and passage ways. Prior to being directed into the wellbore, the composition may be heated to a temperature between about 25°C to about 100°C, although the temperatures prevailing downhole may make pre-heating unnecessary. Once within the tubular goods and the passageways requiring treatment, the composition is allowed to remain there for about ten minutes to about 7 hours. After remaining in contact with the equipment for the desired time, the composition containing the dissolved scale is produced to the surface and may be disposed of as required, possibly by re-injection into the subsurface formation. This procedure can be repeated as often as required to remove scale from the equipment.

In one procedure for circulating the solvent through the tubular goods in the well the solvent is pumped down through the production tube and returned to the surface through the annular space between the
production tubes and the casing (or vice versa). Also, the cleaning solution may be pumped down through the production tubing and into the formation, thereby cleaning the well, including the well casing, and the formation pore space by dissolving barium sulfate present as it flows over and along the surfaces that need cleaning. The spent composition containing the dissolved, complexed calcium together with any other alkaline earth metal cations which may have been present in the scale, especially radium, can be subsequently returned to the surface, for example, by displacement or entrainment with the fluids that are produced through the well after the cleaning operation. In an alternative manner, the cleaning solution may be applied batchwise fashion, for example, by flowing the solution into the well and optionally into the pore spaces of the adjacent earth formation and there keeping the solution in contact in non-flowing condition with the surfaces that are covered with barium sulfate scale, for a period of time sufficient to dissolve the scale.

In order to demonstrate the calcium sulfate scale-dissolving capacities of the composition, several aqueous solutions have been tested in laboratory tests the results of which are described in the discussions which follow. The experiments described below were, except as noted below, carried out in a cylindrical glass vessel having a height of 10 cm and an internal diameter of 7.5 cm. Calcium sulfate or, when applicable, other sulfates or solid scale components, were agitated with the selected solvents and the rates of dissolution and final dissolved concentrations determined.

FIG.1 shows the effect of the amount of DTPA used on the rate of calcium sulfate dissolution at 70
degrees centigrade and pH 13. The results show that the solvent is very effective in dissolving calcium sulfate scale at a concentration range of 20 to 40% by weight, preferably between 20 and 30%.

FIG. 2 shows the effect of solvent pH on the rate of calcium sulfate dissolution (at 70 degrees centigrade) for solvents containing 20% and 40% DTPA. These results show that an increase in pH from 10 to 13 slightly increases calcium sulfate dissolution.

As noted above, the effect of cations is also very important to the success of the scale solvent, especially when added with the sizable portion of caustic required to adjust the pH to 12. Dissolution is enhanced as the size of the cation is increased, i.e. lithium, sodium, potassium and cesium. Lithium and sodium hydroxides in the presence of EDTA, or DTPA, and catalysts are not soluble at a pH of 12, the optimum value. Cesium is too difficult to obtain, both in quantity and price. Therefore, potassium hydroxide, in the form of caustic potash, is the pH adjusting reagent of choice.

One example of a preferred aqueous solvent which can be used comprises 20% by weight DTPA adjusted to a pH of 12 with potassium hydroxide.

The solvent containing the dissolved scale may be regenerated by acidifying the solvent in the presence of an anion which forms a precipitate of an insoluble salt of the alkaline earth metal of the dissolved scale. This method of regenerating the solvent is described in applicant's co-pending application Serial No. 07/593,136, filed October 5, 1990.
Claims:

1. A method for removing calcium sulfate scale comprising contacting the scale with an aqueous solution having a pH of about [8] 12 to about 14 and consisting essentially of diethylenetriaminepentaacetic acid (DTPA) or salt thereof present in a concentration of from about 20 to 40% by weight and potassium hydroxide of a chelating agent comprising DTPA or salt thereof sufficient to dissolve the scale.

2. The method as recited in Claim 1 where the pH is obtained by the addition of hydroxides of potassium.

3. The method as recited in Claim 1 where the chelating agent diethylenetriaminepentaacetic acid (DTPA) is present in a concentration of 20% by weight.

4. The method as recited in Claim 1 where the pH of the solution is adjusted to about 12 with potassium hydroxide.

5. The method as recited in Claim 1 where the pH of the solution is from 12 to 14.

6. The method as recited in Claim 1 where the pH of the solution is about 12.

7. The method as recited in Claim 1 where the solution is directed down a cased wellbore, from which scale is dissolved and subsequently dissolved scale is removed from the wellbore.
8. The method as recited in Claim 1 where the solution is contacted with a subsurface formation to remove scale from the formation.
GYPSOLV Dissolution vs pH

Solvent: Pentasodium DTPA

70°C, 7 hours

Scale Dissolved, g/l

pH Range

- 0.86 M CaSO₄, 20% Active DTPA
- 1.42 M CaSO₄, 40% Active DTPA
A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C02F 5/14
US CL :252/8.552

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/8.552

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C. See patent family annex.

Date of the actual completion of the international search: 13 NOVEMBER 1992

Date of mailing of the international search report: [Signature]

Name and mailing address of the ISA/ Commissioner of Patents and Trademarks
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