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3,213,017

METHOD OF INHIBITING DEPOSITION OF
SODIUM CHLORIDEPaul H. Ralston, Bethel Park, Pa., assignor to Calgon
Corporation, a corporation of PennsylvaniaNo Drawing. Filed Sept. 26, 1962, Ser. No. 226,451
8 Claims. (Cl. 252-8.55)

This invention relates to inhibiting deposition of sodium chloride from saturated solutions thereof onto metals in contact with such solutions. It is particularly applicable to the inhibition of salt deposition from oil-field brines onto oil well equipment.

Highly concentrated brines low in carbonates and sulfates are found in many oilfields of the United States and other areas. Such brines have long caused a difficult and costly deposition of relatively pure sodium chloride on the insides of well tubing, rods, pumps, and other equipment in contact with it. The underground brines found in association with crude oil are commonly at temperatures considerably above surface temperatures. They are frequently highly concentrated with sodium chloride and may contain appreciable amounts of other chlorides. As the brine-oil mixture flows upward in the wellbore, the temperature is reduced and the saturated solutions tend to deposit solid sodium chloride on the inside of the tubing. Under such conditions, it is not uncommon for the deposit of sodium chloride to build up inside the tubing within two or three weeks to the point where fluid production is impossible. At this point or before, the tubing and other equipment must be removed from the well and cleaned. Such an operation is costly and troublesome.

I have discovered that the addition of a small amount of an alkaline earth metal molecularly dehydrated phosphate (or such a phosphate fused with an alkali metal molecularly dehydrated phosphate) to saturated brines will inhibit the tendency of such brines to plug oil wells by deposition of sodium chloride. The use of my invention is not limited to the oilfields. It is applicable wherever it is desired to interfere with sodium chloride deposition from saturated sodium chloride brine.

My invention was demonstrated in experiments in oil wells in North Dakota, where highly concentrated brines exhibiting very low sulfate and carbonate contents are quite common. In one such experiment, several hundred pounds of a glassy molecularly dehydrated phosphate having a molar ratio of $A_2O:MO:P_2O_5$ of 0.25:0.85:1 (where A is an alkali metal and M is an alkaline earth metal) was placed in an anchor consisting of two-inch perforated tubing and hung at the bottom of the tubing string immediately below the downhole pump. The well was kept in production for 63 days, which may be compared to prior periods of production at the same rate lasting an average of about three weeks without treatment. Salt deposition which finally occurred in the tubing was limited to the level of 700-1075 feet.

In another experiment, about 240 pounds of a molecularly dehydrated phosphate having a molar ratio of $A_2O:MO:P_2O_5$ of about 0.38:0.92:1 and a particle size of $\frac{1}{4}$ "- $\frac{1}{2}$ " mesh were placed in a 78' slotted anchor at the level of about 6530-6610 feet. Temperature at this level was approximately 200° F. At the end of 97 days, the tubing string and anchor were pulled because of corrosion in the tubing rather than salt deposition, which was not serious. About one hundred pounds of the phosphate was undissolved. Temperature of the brine at the surface throughout the test was about 80° F. Oil production per day during the above test averaged about 30 barrels, while the brine flow was in the range of 50 to 100 barrels, usually about 90 barrels. Concentrations of

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phosphate (expressed as PO_4) varied from about 2-20 mg./liter. The equilibrium composition of the filtered brine averaged about 173,000 mg./liter of calcium and magnesium chlorides and 169,000 mg./liter sodium chloride. Brine at the bottom of the well comprised about the same calcium and magnesium content, while the sodium chloride content was about 10-15% higher.

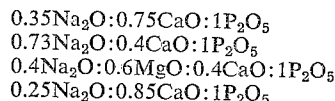
The ratio of metal oxide to P_2O_5 and the ratio of alkali metal oxide to alkaline earth metal oxide, are important as affecting the solution rate of the glass. Those familiar with the art will recognize that a slowly soluble treating composition is essential to permit continuous treatment over several months. The composition and amount should be chosen to fit the temperatures and flow rates to be encountered so as to impart to the brine a concentration of phosphate compound in the range of about 1 p.p.m. to about 25 p.p.m. Concentrations higher than 25 p.p.m., i.e. 50 or 100 p.p.m., may be used in brines having low calcium and magnesium contents, although such use may be uneconomical; in typical saturated oilfield brines containing substantial amounts of calcium, phosphate concentrations over about 25 p.p.m. are also uneconomical because of the tendency to form calcium phosphate, thus lowering the efficiency of the treatment.

Glassy alkali metal metaphosphates, such as sodium hexametaphosphate (having a ratio A_2O to P_2O_5 of from about 0.9:1 to 1.05:1) are slowly soluble without the addition of alkaline earth metals, and may be used in a particular size and amount sufficient to yield about 1 p.p.m. to about 25 p.p.m. alkali metal phosphate.

Generally speaking, in the $A_2O:MO:P_2O_5$ complex, the addition of more alkaline earth metal oxide renders the composition less soluble. An alkaline earth metal phosphate having no alkali metal content may be used. Such a composition may be described as a glassy phosphate having a molar ratio of $MO:P_2O_5$ of about 1:1, where M is an alkaline earth metal. Examples of such useful compositions have ratios of MgO or $CaO:P_2O_5$ of about 1:1.

Readily soluble forms of molecularly dehydrated phosphate, such as Calgon, may be used if means for continuous feeding are available. The composition may be dissolved on the surface and fed to the bottom of well through a "macaroni" tube with the aid of a small pump. However, since prepared solutions will revert to the orthophosphate form on long standing, considerable trouble could be incurred with frequent dissolving operations and continuous feeding; therefore, I prefer to use solid materials. Such readily soluble forms as Calgon have a $Na_2O:P_2O_5$ ratio of about 1.1:1. Any readily soluble alkali metal polyphosphate glass may be used where practical considerations permit.

The preferred compositions are glassy fusion products having molar ratios $A_2O:MO:P_2O_5$ of about 0.2-0.8 $A_2O:1.0-0.3MO:1P_2O_5$, where the sum of A_2O and MO is from about 1 to about 1.4. Examples of such compositions are:



The phosphate should be of a particle size which is practical to place in the well and which will not be drastically reduced in surface area throughout the desired period of treatment. Particles of $\frac{1}{8}$ " to 1" minimum thickness have been found quite satisfactory for the compositions, temperatures and flow rates encountered.

The composition may be placed anywhere below the level at which the salt is known to deposit. It will inhibit deposition of salt from the brine at all points lower in temperature than the temperature where the phosphate

is introduced. Although the dissolved sodium chloride content of the untreated brine at the well bottom may be considerably higher (i.e. 15%) than that of the brine at the surface, this does not mean all of the 15% of the salt is continuously deposited on the tube. Some of it is in the untreated brine in the form of small undeposited crystals. It is assumed that my invention enables some of this salt to remain in solution, or to resist depositing on the metal equipment.

Throughout the specification and claims, when I speak of "brine" and "saturated brine," I mean to include sodium chloride brines and saturated brines which may include other salts. A typical oil field brine may include substantial amounts of calcium chloride, magnesium chloride, etc. Such a brine is a saturated brine within the meaning of my disclosure whenever it cannot accept additional sodium chloride in solution at the prevailing temperature.

Having thus described my invention by way of the foregoing specific examples, it is to be distinctly understood that my invention is not limited thereto but may be otherwise variously practised and embodied within the scope of the following claims, which are to be considered part of my disclosure.

I claim:

1. Method of inhibiting the deposition of sodium chloride on oilfield tubing and equipment in contact with a saturated sodium chloride oilfield brine, which is low in sulfates and carbonates, comprising adding to said saturated sodium chloride oilfield brine prior to cooling at least about 1 part alkali metal phosphate per million parts of brine, said phosphate having a ratio of $A_2O:P_2O_5$ of from about 0.9:1 to about 1.05:1, where A is an alkali metal.

2. Method of inhibiting the deposition of sodium chloride on oilfield tubing and equipment in contact with a saturated sodium chloride oilfield brine, which is low in sulfates and carbonates, comprising adding to said saturated sodium chloride oilfield brine prior to cooling at least about 1 part alkaline earth metal phosphate per million parts of brine, said phosphate having a ratio of $MO:P_2O_5$ of about 1:1, where M is an alkaline earth metal.

3. Method of inhibiting the deposition of sodium chloride on oilfield tubing and equipment in contact with a saturated sodium chloride oilfield brine, which is low in sulfates and carbonates, comprising adding to said saturated sodium chloride oilfield brine prior to cooling at least about 1 part of an alkali metal-alkaline earth metal polyphosphate per million parts of brine, said polyphosphate having a molar ratio of $A_2O:MO:P_2O_5$ of about 0.2-0.8 $A_2O:1.0:0-3 MO:1 P_2O_5$ where the sum of A_2O and MO is about 1 to about 1.4, A is an alkali metal, and M is an alkaline earth metal.

4. Method of inhibiting the deposition of sodium chloride on oilfield tubing and equipment in contact with a saturated sodium chloride oilfield brine which is low in sulfates and carbonates, by cooling of said saturated sodium chloride oilfield brine, comprising adding thereto prior to cooling at least about 1 part per million parts of brine of a readily soluble alkali metal polyphosphate glass.

5. Method of claim 4 in which the readily soluble alkali metal polyphosphate glass is a sodium polyphosphate glass having a ratio of M_2O to P_2O_5 of about 1.1:1.

6. Method of inhibiting the deposition on oil well tubing and equipment of sodium chloride from highly concentrated oil field brines low in sulfates and carbonates during flow upwards through a wellbore, in which there is a significant temperature drop normally causing such deposition, comprising placing a charge of an alkaline earth metal molecularly dehydrated phosphate in the well at a depth below that at which such salt deposition normally occurs, the amount of such charge and the particle size thereof being such that about 1 to about 100 parts phosphate per million parts brine are dissolved in the brine.

7. Method of inhibiting the deposition on oil well tubing and equipment of sodium chloride from highly concentrated oil field brines low in sulfates and carbonates during flow upwards through a wellbore, in which there is a significant temperature drop normally causing such depositions, comprising placing a charge of an alkali metal-alkaline earth metal glassy phosphate having a molar ratio of $A_2O:MO:P_2O_5$ of about 0.2-0.8 $A_2O:1.0-0.3 MO:1 P_2O_5$, where the sum of A_2O and MO is from about 1 to about 1.4, A is an alkali metal, and M is an alkaline earth metal, in the well at a depth below that at which such salt deposition normally occurs, the amount of such charge and the particle size thereof being such that about 1 to about 100 parts phosphate per million parts brine are dissolved in the brine.

8. Method of inhibiting the deposition on oil well tubing and equipment of sodium chloride from highly concentrated oil field brines low in sulfates and carbonates during flow upwards through a wellbore, in which there is a significant temperature drop normally causing such deposition, comprising placing a charge of an alkali metal phosphate having a ratio of A_2O to P_2O_5 of about 0.9 to 1 to about 1.05 to 1, in the well at a depth below that at which such salt deposition normally occurs, the amount of such charge and the particle size thereof being such that about 1 to about 100 parts phosphate per million parts brine are dissolved in the brine.

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60 JULIUS GREENWALD, *Primary Examiner.*

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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October 19, 1965

Paul H. Ralston

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 51, for "1.0:0-3 MO:" read -- 1.0-0.3 MO:
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Signed and sealed this 28th day of June 1966.

(SEAL)

Attest:

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