PREDICTING AND PREVENTING OILFIELD SCALES

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INTRODUCTION

Various types of scales have long been a harassing problem throughout the oil field. Their buildup in the formation as well as along the wellbore decreases production by blocking the flow of oil, either by skin damage in the formation or by plugging off the perforations and lowering pump efficiency. If a tendency for the formation of scale can be predicted, it may save time as well as money in the treatment of that well.

The basic types of scale encountered are calcium sulfate ($CaSO_4$), barium sulfate ($BaSO_4$), and calcium carbonate ($CaCO_3$). Their precipitation is mainly due either to the mixing of two different formation waters or the mixing of injected water with formation water, the latter being the more frequent case. Scale is not always found downhole; frequently, it may be found in flowlines, separators and other surface equipment.

Scale deposits are usually deposits of inorganic salts that result from the combination of a few parameters. Changes in pressure, temperature and mineral compositions of the waters are the parameters that affect the rate at which scale precipitates. Time is another factor often overlooked; the chemical reactions that produce scale are not spontaneous.

SULFATE SCALE

Sulfate scale is the result of water being supersaturated with calcium and sulfate ions rather than being unstable with its chemical components, as is the cause for carbonate scale. However, at a specific chloride concentration level in the water, only so many of the calcium and sulfate ions can be held in solution. As the flood front invades the formation, it has a diluting effect on the already present formation water. Since the injected water is usually fresher than the formation water, it is also diluting the chloride concentration. Dilution of the chloride concentration of one water by another water without diluting the calcium and sulfate ion concentrations will cause calcium sulfate scale to precipitate. It is then easy to see that the tendency for water to precipitate calcium sulfate or barium sulfate increases when the sulfate content of the water is increased.

Several parameters have been mentioned pertaining to the growth of scale crystals downhole. Some of these parameters have a direct bearing on the growth of the scale crystals while others do not.

Calcium sulfate has an inverse solubility with respect to heat. As the bottomhole temperature is increased, the amount of precipitation can also be increased. Therefore, as the solubility of calcium sulfate decreases, the amount of scale precipitation is naturally going to increase.

Pressure, on the other hand, can not satisfactorily be handled in the calculations for predicting a calcium sulfate scale. Pressure also affects the amount of carbon dioxide (CO_2) in solution; however, carbon dioxide has little to do with the formation of a sulfate scale. The carbon dioxide in solution adjusts the pH of the water, but pH also has little to do with the formation of sulfate scale.

Time can be a variable factor in scale growth. It can either be an advantage or a detriment, depending on the stage of the crystal development.

Predicting a tendency for gyp to precipitate can be done easily by the use of a few equations developed by Skillman, et al. These equations are highly dependable since they take into account the thermodynamic solubility of gyp over a range of conditions.

The first step in these calculations is to figure the ionic strength, U. The total ionic strength is the sum of the individual ionic strengths of the chemical components. Basically, $U = 1/2\Sigma C_i Z_i^2$.

Where : C_i = Concentration of each ion

Z_i = Ion's valence

More generally, it is possible to sum up the reported concentrations and convert them to ionic strengths by the following values:

	When Reported As	
Ion	mg/l	meq/l
Na	2.2×10^{-5}	5×10^{-4}
CA	5.0×10^{-5}	1×10^{-3}
Mg	8.2×10^{-5}	1×10^{-3}
Cl	1.4×10^{-5}	5×10^{-4}
HCO_3	$.8 \times 10^{-5}$	5×10^{-4}
SO_4	2.1×10^{-5}	1×10^{-3}

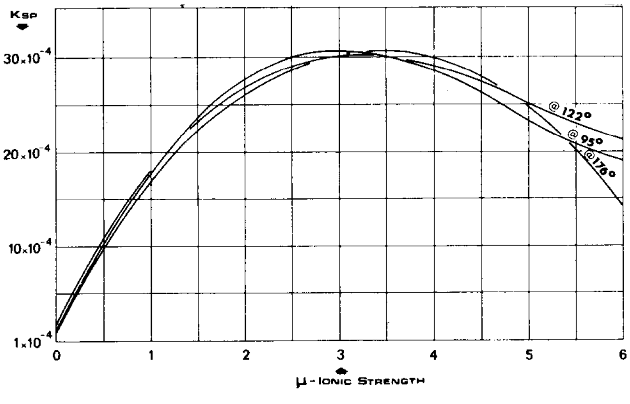
Once ionic strength has been figured, the K value can be taken from Fig. 1, (from Skillman, et al). Now the excess common ion factor, X, can be calculated by the following equation:

$$X = | 2.5\,Ca - 1.04SO_4 | \times 10^{-5}$$

With the solubility product constant, K, and the excess common ion factor, X, having been determined, the solubility of gyp under the reservoir conditions may now be determined. This solubility of gyp, S, can then be calculated by:

$$S = 1000 \; [\sqrt{X^2 + 4K} - X]$$

This solubility is given in milli-equivalents per liter (meq/l).



FIG– 1—Ksp VS. IONIC STRENGTH

These results must then be interpreted to give the scaling tendencies. The solubility, S, calculated is the minimum concentration of sulfate needed for precipitation. Therefore, if a water analysis indicates the sulfate content is greater than the calculated solubility, there is a positive tendency for gyp to precipitate. Conversely, if the reported amount of sulfate is lower than the calculated solubility, there is a tendency for gyp not to form.

CARBONATE SCALE

Calcium carbonate develops by a completely different process. This scale is the result of the two mixed waters being unstable. A water is said to be stable if it neither dissolves nor precipitates calcium carbonate. The water may be stable at one point in the reservoir but then become unstable just a few feet away. Magnesium carbonate may also precipitate to form scale; but the magnesium is more soluble than calcium, and therefore, will stay in solution longer while the calcium will precipitate out.

Calcium carbonate is likely to precipitate under three conditions: (1) with an increase in temperature, (2) with a decrease in the partial pressure of carbon dioxide (CO_2), and (3) with a decrease in the total dissolved solids. As the temperature increases, calcium carbonate becomes less soluble and will drop out of solution. Calcium carbonate is even less soluble than calcium sulfate under a normal operating range of temperatures.

Pressure is a major cause of carbonate scale. As the pressure is increased, more and more carbon dioxide is held in solution. If the water becomes supersaturated with carbon dioxide, the CO_2 exists as a weak carbonic acid (H_2CO_3) which can be corrosive. If the carbon dioxide becomes too low, it will upset the carbonate-bicarbonate (CO_3-HCO_3) equilibrium as well as the pH. Carbon dioxide dissolves in water to form these products in the following manner:

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$
$$H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$
$$HCO_3^- \rightleftarrows H^+ + CO_3^{-2}$$

The total dissolved solids content is another thing to keep in mind. The higher the total dissolved solids content, the greater the solubility of calcium carbonate in water and the lower the scaling tendency. This will hold true until the dissolved solids reach a maximum concentration of approximately 200,000 ppm.

Predicting a carbonate scaling tendency can be done easily with the use of the Langelier equation for stability index. This equation takes into account the concentrations of the various ions as they are reported on the water analysis. The Langelier equation is given in terms of a stability index:

$$SI = pH - K - pCa - pAlk$$

Where: SI = stability index
K = constant that is a function of temperature and ionic strength
$pCa = -\log[Ca]$, or $\log 1/[Ca]$
$pAlk = -\log[Alk]$, or $\log 1/[Alk]$
pH = measured pH

The alkalinity concentration is a combination of the hydroxyl, carbonate and bicarbonate ion concentrations. The figures for pCa and pAlk may be obtained from the graph in Fig. 2 and the constant, K, may be obtained from the graph in Fig. 3 (both from Stiff and Davis).

Once all these values have been found and put into the equation, a number, either positive or negative, can be calculated for the stability index. If this calculated value is zero, then the water is in chemical balance. If the number is negative, this will indicate a corrosive tendency of the water. If the number is positive, then a scaling tendency is indicated.

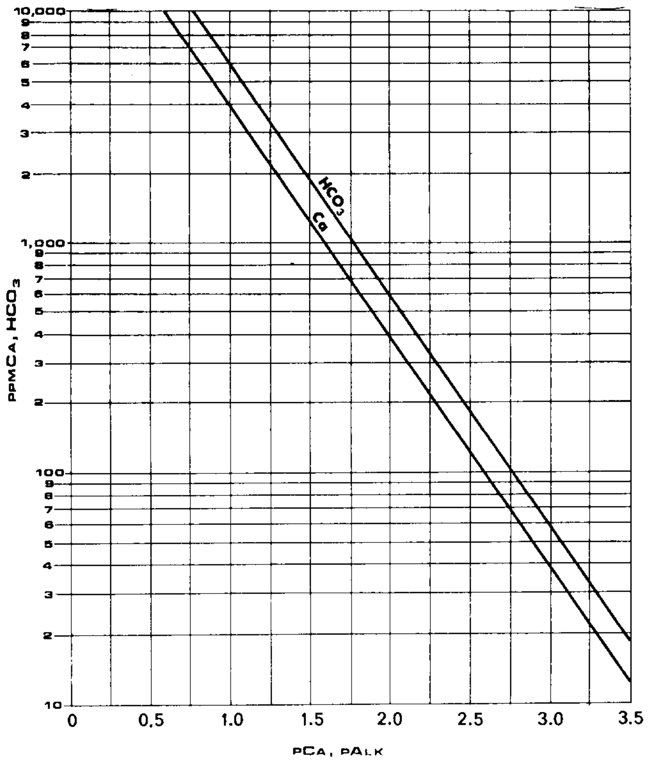


FIG. 2—pCa, pAlk VS. PPM Ca, HCO_3

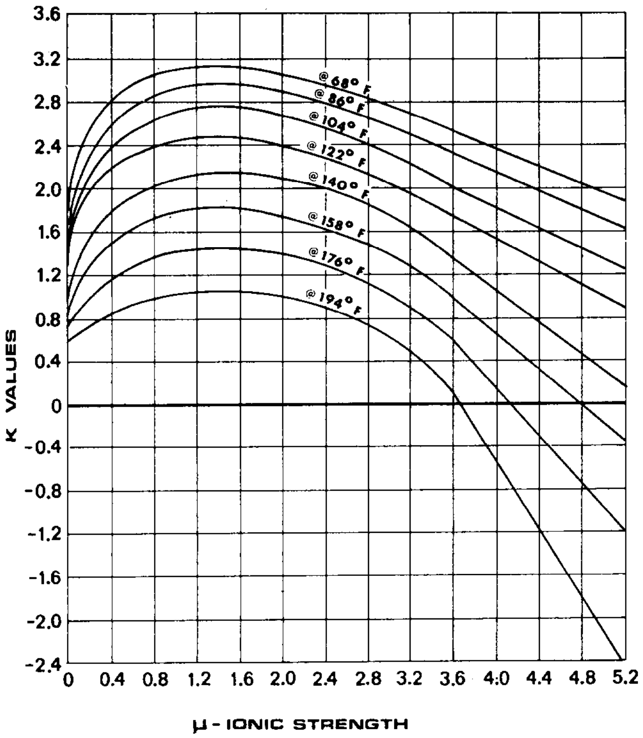


FIG. 3 — K VS. IONIC STRENGTH

With the scaling tendency having been predicted, it is now up to the engineer to remove it from the wellbore. There are various chemicals and acids on the market that can easily treat the well for the scale buildup. Removing the scale may not be as big a problem as inhibiting the well against future scale buildup. There are also various inhibitors on the market, each having different makeups and properties.

TYPES OF COMMERCIAL INHIBITORS

There are four main types of inhibitors available commercially. These are inorganic phosphates, organic phosphates, phosphate esters and polyelectrolytes.

Inorganic Phosphates

Inorganic phosphates, commonly known as polyphosphates, work on the principle of the threshold-effect treatment. As the scale crystals begin to grow, the phosphate ions cling to the nuclei of these developing crystals and inhibit against further growth. Thus, it is possible for a small amount of phosphate to tie up a large amount of scale-forming material.

The phosphate ion has good adsorption properties in the formation. When the phosphate is pumped into the reservoir, it will encounter the calcium ions in the formation water where they will precipitate and form a gel. This is the gel that holds so well to the formation. The gel has a water-wetting property, thereby allowing more water to pass through. This is a small cleaning effect in the reservoir.

The disadvantage in using a polyphosphate is that it may undergo a reversion process. That is, it will hydrolyze and go from a polyphosphate to an orthophosphate. The orthophosphate has no inhibiting properties because it reacts with calcium to form an insoluble calcium phosphate ($CaPO_4$) which can plug up the formation. The rate of reversion increases with a lowering of pH or an elevation in temperature. If the amine molecule is added to the phosphate ion, it makes the new amine phosphate molecule more stable and less likely to hydrolyze.

Applications

Scale	Protection	Minimum-Conditions
$CaCO_3$	Excellent	2 - 5 ppm
$CaSO_4$	Fair	10 - 20 ppm
$BaSO_4$	Poor	50 or more ppm

Organic Phosphates

Organic phosphates, commonly known as phosphonates, do not have a reversion problem like inorganic phosphates. Phosphonates are a man-made product that have heat stability to at least 350°F.

While its advantages are heat stability, nonreversion property, and being able to be mixed with hydrochloric acid, there are a few disadvantages to consider. Phosphonates do not adsorb well to the formation. After they are flushed back into the formation, they come back readily with the produced water. So, in order for phosphonates to effectively inhibit against scale, the concentrations in the reservoir must be kept fairly high. However, under certain conditions, the well may be overtreated and a new compound, calcium triphosphate [$Ca(PO_4)_3$] will be formed. This compound has no inhibition properties. Also, no one is sure just how much phosphonate will tie up how much calcium.

Applications

Scale	Protection	Minimum-Conditions
$CaCO_3$	Good	5 - 10 ppm
$CaSO_4$	Good	15 - 20 ppm
$BaSO_4$	Excellent	20 or more ppm

Phosphate Esters

Phosphate esters are oil-soluble compounds that resemble phosphonates in a few ways, the major one being that when used excessively, they become inactive compounds. Esters provide excellent coverage in surface equipment or when batch-treated downhole. Since they are oil-soluble, they can be mixed with corrosion inhibiters while treating the well.

There are several disadvantages. The esters tend to form emulsions when mixed with oil and, therefore, need a de-emulsifier added when treating downhole. They also revert to inactive compounds at high temperatures above 250°F.

It is also believed that esters do not have a long shelf life.

Applications

Scale	Protection	Minimum Conditions
$CaCO_3$	Fair	Below 250°F
$CaSO_4$	Good	Below 250°F
$BaSO_4$	Good	10 - 20 ppm

Polyelectrolytes

Polyelectrolytes, or polymers, are the newest forms of inhibitors to be used. Since they are relatively new on the market, there is not as much information known about them.

As the name implies, the polymer is a long chain molecule that is able to tie up the calcium ion as well as cling to the formation. Polymers also provide excellent protection at low concentrations, usually

3-5 ppm. The polymer returns may also be monitored, but this can only be done through the use of a dialysis bath, a machine similar to the kidney dialysis machine. This, however, is a long and costly process. Polymers are an appealing food for bacteria and their use in the formation may enhance the problem of bacterial growth. At times, polymers show good heat stability, but this mainly depends on downhole conditions.

Applications

Scale	Protection	Minimum Conditions
$CaCO_3$	Fair	Up to 250° F
$CaSO_4$	Good	3-5 ppm, up to 250° F
$BaSO_4$	Good	Up to 350° F

General

Several studies have been done on the different types of inhibitors with some interesting results. The rating of inhibitors by their effectiveness is only relative and depends on test conditions. There is no ideal inhibitor. The selection of an inhibitor is always a compromise between its positive and negative characteristics. Scale inhibition is closer to being an art than a science.

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