Scale—Its Occurrence and Methods of Control

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CAUSES OF SCALE

Scale is a term commonly used in the petroleum industry to define insoluble, inorganic salt deposition in water or water-containing systems. Normally this deposition is composed of the salts of calcium, magnesium, iron and barium.

Oil field brine water contains many and varied inorganic salts in solution, the most common being calcium and magnesium. If, for any reason, the concentration of these salts is increased or the solubility of the salts is decreased, the equilibrium is upset and precipitation takes place. This precipitation is commonly called scale. The physical factors which may cause precipitation are temperature, pressure, evaporation and condensation. Temperature variations and pressure changes are the two most common causes. The solubility of most salts increases with an increase in temperature. A sudden drop in pressure can cause an upset of equilibrium and may result in precipitation.

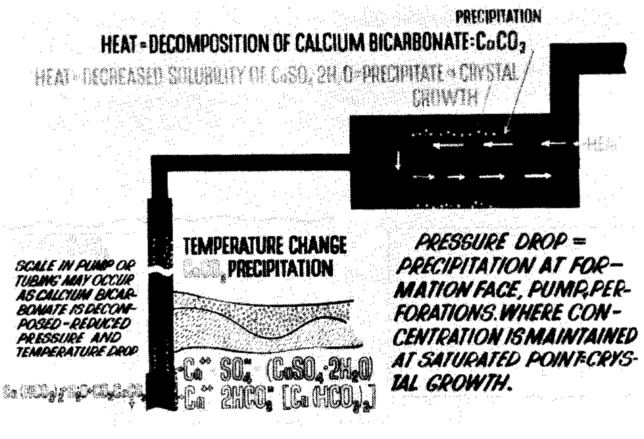

FIG. 1

TYPES OF SCALE

The two most common types of oil field scale are calcium carbonate ($CaCO_3$), and calcium sulfate ($CaSO_4$). Calcium carbonate precipitation is caused by a shift toward the carbonate in the carbonate-bicarbonate-carbon dioxide equilibrium. Thus, under a high partial pressure of carbon dioxide, large amounts of bicarbonate can be held in solution. Reduction of this pressure, or an increase in temperature, will permit release of carbon dioxide from solution leaving calcium carbonate which precipitates out as a scale (Fig. 1).

The formation of calcium sulfate scale is somewhat different. $CaSO_4$ scale occurs frequently when two waters are mixed, one containing calcium ions and the other sulfate ions. As one of these waters is added to the other, a point may be reached where the concentration of calcium sulfate is greater than its solubility, thus causing the formation of a precipitate. Salt content or pressure-temperature factors may cause gypsum to dissolve in internal formation waters to a point of saturation which may cause crystal growth or precipitation when this equilibrium is upset (Fig. 1). Methods have been developed in recent years for predicting precipitation of calcium sulfate (gypsum) scale from various waters and varied conditions (Fig. 1).

From an analysis of the water in question, along with temperature data, calculated predictions can be made toward scaling tendencies at a particular point. The other prevailing type of scale, especially in hydrogen sulfide environments, is iron sulfide. Iron sulfide is precipitated as the result of the reaction of iron with hydrogen sulfide that occurs naturally in many underground waters. It may also be produced by sulfate reducing bacteria. The source of iron would be downhole oil well equipment (Fig. 2).

Problem Scales

Problem sulfates are anhydrous calcium sulfate or anhydrite ($CaSO_4$), gypsum ($CaSO_4 \cdot 2H_2O$) and barium sulfate ($BaSO_4$). Anhydrous calcium sulfate, or anhydrite ($CaSO_4$), is generally found in certain formation waters as dispersed particles or in high temperature systems (boilers, etc.) because of dehydration of gypsum. Gypsum is found in a wide variety of systems and at various points within these systems, such as formation face, pumps, tubing (Fig. 3), flow lines, treaters and any other equipment.

Barium sulfate is a problem in some areas, but is not as prevalent as gypsum. This is the most insoluble of the sulfate salts and is most generally found when two or more waters are mixed together (Fig. 2), one containing a soluble barium salt, (e.g., barium chloride), and another containing a soluble sulfate. Barium sulfate is rarely produced, as such, in sufficient quantity to cause scale deposition unless colloidally dispersed in quantities sufficient to deposit scale when produced from a given formation.

The most troublesome insoluble magnesium salt is magnesium carbonate. Fortunately, $MgCO_3$ scaling is not often of great significance in oil producing equipment. The sulfate salt of magnesium is highly water-soluble and may be the source of the sulfate ion when waters containing calcium or barium in solution are mixed together (Fig. 2). In this manner, the magnesium sulfate salt may be a potential scale problem. Troublesome

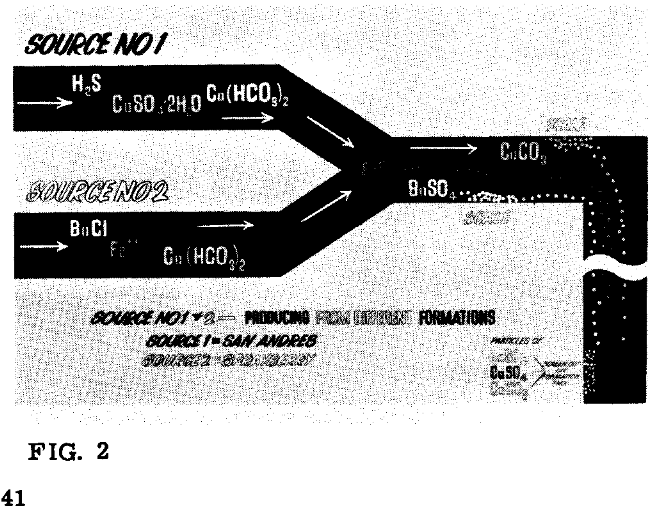

FIG. 2

insoluble iron salts most prevalent are ferrous sulfide (FeS), red iron oxide (simply represented Fe_2O_3), black or magnetic iron oxide (Fe_3O_4) and, in some cases, its carbonate salts.

In most instances, control of insoluble salt deposition depends on reduction of concentration of solute (dissolved solids). Reduction of dissolved solids concentration may be accomplished by employing one or more practical methods such as the addition of solvent, coagulation and precipitation, sequestering, dispersion, ion exchange and by pH control.

METHODS FOR CONTROL

In some systems, the most effective method for control of scale deposition is dilution with fresh water; however, fresh water is not always the most convenient or most economical medium of control. Except for excessive transportation costs, many producing oil wells with severe scale problems could be successfully treated with fresh water. Cooling tower and boiler chemical treatment is generally augmented with fresh water; a certain amount of water is bled off periodically or continuously, and replaced with fresh water.

Because of evaporation or high temperatures, so-called "fresh" water generally causes scaling in cooling tower and boiler water and must be chemically treated for protection of equipment and to maintain efficiency. Even though fresh water treatment is an effective scale prevention measure, most cases require auxiliary chemical treatment. In certain instances, exclusive chemical treatment is most practical and most economical.

Many producing oil wells which could be effectively treated with fresh water to prevent scale deposition cannot be economically treated, not only because of the lack of available fresh water, but because of corrosion problems which arise from the introduction of oxygen into the otherwise air-free system. Gypsum or calcium sulfate and sodium chloride deposits are the results of saturation and not decomposition, as is calcium carbonate. These deposits can usually be controlled by dilution with fresh water.

The use of coagulants and precipitation chemicals has been widely followed in industrial water conditioning and to some extent in the oil industry, as a means of preventing scale and formation plugging. Most waters available for injection into oil reservoirs contain insoluble inorganic salts and dispersed soluble inorganic salts in solution. These salts and other suspended matter will eventually cause scale or formation plugging.

If the supply water is allowed to remain stagnant for a sufficient period of time in an open pit, most of these solids will accummulate at the bottom of the storage reservoir; however, this is a slow process and it requires large storage capacity. For this reason, along with the inadequate settling of all suspended matter, coagulating chemicals are used. Because of inadequate settling or fallout of suspended matter, a variety of coagulants are often employed to accelerate precipitation.

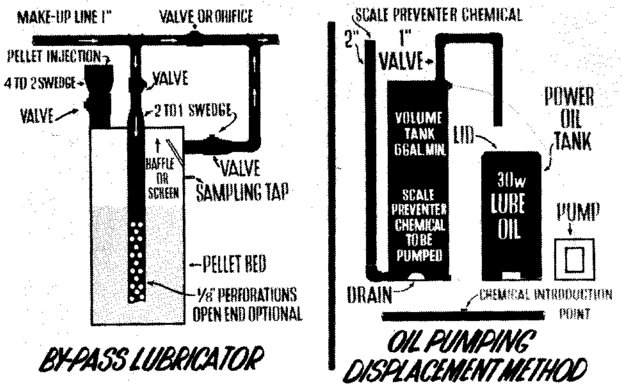

FIG. 3

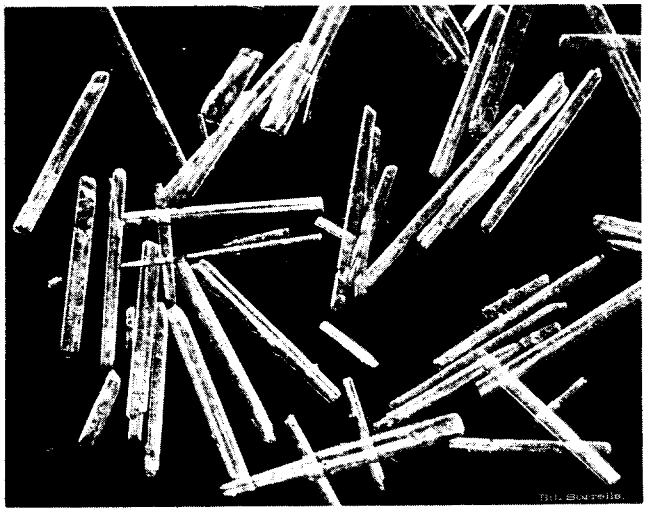

FIG. 4

Successful Coagulants

Successful coagulants include alum, hydrated lime, sodium aluminate, ferric sulfate or chloride. All these precipitate scale-forming salts, reduce hardness, alkalinity and remove turbidity by producing a jelly-like spongy mass called floc which traps suspended matter by mechanical action, whereas the floc itself is a chemical reaction. Aeration in the open pit storage system helps remove such undesirable gases as hydrogen sulfide and carbon dioxide. Iron and manganese are also oxidized and removed by coagulation or by long retention in storage.

Lime-soda ash is most commonly used for this type of treatment. The lime removes carbon dioxide and free carbonate radicals by precipitation of calcium carbonate when calcium hydroxide (lime) and carbon dioxide or the carbonate radical are combined. Soda ash (sodium carbonate) reacts with calcium in solution and precipitates as insoluble calcium carbonate. Sodium remains in solution as a soluble chloride, sulfate or hydroxide salt.

Iron salts, such as ferric sulfate, precipitate ferric-hydroxide floc over a wide range of pH values. But for each specific use, pH must be closely controlled. In practice this is done by feeding an acid or alkali such as lime, soda ash or caustic soda. Clay, activated silica, organic polyelectrolytes and other aids are used to foster coagulation. In general, coagulant aids help produce larger and heavier floc particles over wider pH ranges with greater ability to remove turbidity.

Since there are no simple rules to determine the choice of a coagulant, it is best to conduct tests under actual operating conditions to arrive at the lowest treating costs for best results. Even though scale prevention in disposal systems does not depend on complete removal of dissolved solids, suspended clays and other solids should be removed to prevent formation plugging.

Solids Removal Method

Four of water's most troublesome impurities are removed effectively by chemical reaction and combinations of lime, soda ash and caustic.

1. Calcium hardness precipitates as calcium carbonate and magnesium hardness as magnesium hydroxide.
2. Bicarbonate alkalinity is first converted to carbonate form and then removed as calcium carbonate.
3. Silica comes out as an insoluble silica-magnesium complex when it reacts with magnesium hydroxide.
4. Turbidity from suspended solids and magnesium hydroxide and calcium carbonate sludge is removed by settling and filtration.

When planning for the solids removal method of preventing scale, water should be analyzed by a reputable laboratory, experienced in correlating scale deposition with water analysis. Water analysis and treatment recommendations should be completed prior to construction of reservoir or storage facilities.

Water treatment chemicals for cooling towers, boilers, and some disposal waters are generally used to lower the solubility product of scale-forming solids by precipitation as sludge. But in most oil field systems, such as producing oil wells, water floods, etc., this method is impractical both from an economic standpoint and because of difficulty in proper application. This problem is overcome by the use of organic chemicals with the power to remove certain ions from solution such as calcium, magnesium and iron as chelates.

Chelation

Chelation may be defined as the reversible reaction between a polyvalent metal ion and an organic polyaminocarboxylic acid to form within the molecule one or more ring structures incorporating the metal ion with at least one coordination bond. To sequester means to withdraw from circulation and has, for all intents and purposes, the same meaning as complex.

Chelation refers not to any one type of compound but rather a general type of reaction between metal ions and a variety of compounds known as chelating agents in which the metal ions are rendered chemically inactive. Possibly the best known class of sequestering or chelating agents is the ethylenediaminetetraacetic acid (EDTA) compounds which have only recently come into importance, primarily due to price reductions which have aided in treating economics. Many other compounds such as citric, gluconic, lactic acid and some anionics and non-ionics have been used for sequestering various metal ions with a great deal of success.

As shown in Fig. 2, precipitation of most insoluble salts may be prevented if the metal ion such as barium, calcium, or iron can be sequestered or chelated prior to its contact with precipitate-causing negative ions such as sulfate or sulfide. This may be accomplished in a system such as a producing oil well (Fig. 1), if the metal is complexed prior to precipitation of its salts. Point of treatment application should be determined first by locating point of scale formation in equipment, i.e., if scale is in the pump or tubing, treatment should be applied in the well bore.

When scale appears in the treater, chemical should be applied at the header or in gathering lines. If scale builds up at the formation face, treatment should originate inside the formation for best results. Chemical application inside the formation may be applied by squeeze or frac treatment in which sequestering chemicals are introduced into the formation. Fresh water may be used in some cases with good results by simply reducing the concentration of salts to a point below saturation.

Efficient scale control in oil field brines does not depend on complete removal or chelation of troublesome ions such as calcium and magnesium, but only in sufficient amounts to decrease saturation below precipitation point. This type of treatment is generally called threshold treatment when a concentration of only a few parts per million of a phosphate is used. In principle, it applies to many other chelants.

In contrast to calcium removal, barium and soluble iron should be removed from solution as completely as possible. Because of the extremely stable nature of barium sulfates when the two ions (barium and sulfate) come in contact even at low parts per million, precipitation will occur at normal brine pH. Iron oxide or sulfide deposits may be removed by acid treatment while barium sulfate will not react to this type of treatment.

Dispersion Technique

There are several different ways in which organic chemicals prevent scale formation other than precipitating, sequestering or chelating undesirable scale-forming solids. Some organics, such as lignins and starches and some nonionics, coat minute calcium, barium sulfate or other crystal particles with a protective layer which, in turn, prevents accumulation or adhesion of precipitated particles. The basic function of a dispersing agent is the reduction of cohesive forces between individual particles. In this manner it prevents agglomeration, permitting each particle to act as a separate entity. This mechanism is not fully understood but in many cases, dispersing agents apparently function by imparting a similar charge on the surface of solids, causing them to become mutually repellent.

Some organics form flocs with salts of magnesium, calcium, etc., which entrap these precipitates. Others distort crystal structures in such a manner that scale deposition is prevented. It has been shown that inorganics also distort calcium sulfate (gypsum) crystal formation so as to prevent scale at the point of formation. Fig. 4 shows typical gypsum crystals from an untreated water while Fig. 5 shows deformed poly-crystalline rosettes driven out of solution by a drastic five-fold supersaturation. This deformation occurred in the presence of controlled solubility phosphate.

The dispersion technique is widely used for scale prevention in oil field producing equipment and water flood operations, but is not so successfully used in high temperature, high pressure systems such as boilers and various heat exchangers. When used in conjunction with sequestrants, the dispersion principle has proved to be an effective water treatment in the oil field, since lower concentrations of chemical are possible through the combined principle application.

Most oil field brines contain tremendous concentrations of dissolved, potential scale-forming solids. For this reason, economics will not permit use of ion exchange as a preventive measure. However, in most cases, fresher waters for use in cooling towers, boilers, etc., may be treated economically and effectively by this method.

Ion-exchange Material

Soluble impurities which dissociate to form positively and negatively charged particles known as ions are called electrolytes. Positive ions are named cations because they migrate to the negative electrode (cathode) in an electrolytic cell. Negative particles are, therefore, anions since they're attracted to the anode. These ions exist throughout the solution and act almost independently. For example, magnesium sulfate ($MgSO4$) dissociates in solution to form positive magnesium ions and negative sulfate ions. Generally, all natural waters contain electrolytes in varying concentrations.

Ion-exchange material has the ability to exchange one ion for another, hold it temporarily in chemical combinations, and give it up to a strong regeneration solution. The first basic treatment in the ion exchange process is a softening, in which the water trades calcium and magnesium cations for sodium cations. This exchange process continues until the ion exchange material runs out of sodium. At this point, the water is no longer softened because calcium is no longer being removed from the solution; therefore, regeneration of exchange material becomes necessary. Ion exchange may be used to demineralize water completely if both cation and anion exchanges are properly employed.

The control of pH has been used for several years for the prediction and control of calcium carbonate scale in boilers and cooling towers. Oil field brine waters contain such high parts per million dissolved solids that earlier stability index of fresh waters did not apply. However, Stiff and Davis showed that the Langelier equation could be experimentally derived, which extended the method to include brine waters. This work has greatly aided analysts in predicting and controlling calcium carbonate scales in the oil fields.


FIG. 5

METHODS OF APPLICATION

We have discussed the general chemistry of how and why scale is formed, and the chemicals used for its control. The next step is to explain the methods of application. For the downhole application of scale preventive chemicals, an operator may select a material in either liquid or pellet form. Lubricators, similar to those used to inject corrosion inhibitors, are popular with oil field personnel. Usually, they are larger in size.

Most operators dilute the scale preventive with water. A large quantity of water and chemical will rapidly fall through the oil to the bottom of the annular space. Circulation of fluids is at times beneficial. Lubricators can be used for intermittent treatment but are impractical for continuous treatment. Sizes will vary according to the need. Pumping well lubricator capacities are usually between 5 and 15 gallons, whereas gas lift wells require from 15 to 50 gallons capacity.

Oil field chemical injection pumps are ideal for the downhole application of scale preventive chemicals. A continuous treatment, which is necessary in most cases, provides a constant concentration of chemical. When an operator treats intermittently and is successful in eliminating scale, the problem is usually minor in scope. To apply the chemical full-strength does not afford uniform distribution in the water being treated; also, excessive evaporation of chemical solvent often leaves a viscous active ingredient that can cause plugging of the pump.

A good method of application is to dilute the chemical with available brine or fresh water. This practice will eliminate the loss of chemical inside the casing and outside the tubing and help carry the chemical through the oil in the annular space. This procedure will also eliminate dehydration of chemical injected with the gas stream in a gas lift well.

Of the several disadvantages in using chemical injection pumps, the most prevalent is mechanical failure. Several scale chemicals on the market are either acidic or alkaline which creates packing and corrosion problems. Recent advancements in pump design have provided some resistance to these difficulties; however, dilution with water helps neutralize the chemical. Certain solvents used full strength or mixed with water will afford a very small amount of lubricating properties which cause abnormal wear. Field personnel also find it difficult to keep trash from entering the chemical pump reservoir.

A water solution of sodium hexametaphosphates, when being pumped over a 24-hour period, will revert to orthophosphate and precipitate out, which will cause plugging of the chemical pump. This problem can be prevented by oil displacement (Fig. 6A), instead of pumping scale preventives and water. Operationally, it involves a storage reservoir other than the one available with most chemical pumps. Lube or non-volatile oil is pumped from the oil reservoir to the second reservoir, which will contain scale chemicals or scale chemical-and-water. When the oil container is emptied, scale inhibitor is poured into the second container to force oil back into the original container. This can be used in treating either a low or high-pressure system. Pressure can be used instead of gravity to force oil back into the storage tank. Size can be adjusted to fit individual needs.

The use of scale preventive pellets for downhole treatment is a satisfactory method of application. Sodium-calcium hexametaphosphates or other "controlled solubility phosphates" are manufactured in varied pellet sizes. These are dropped or lubricated down the annular space: the slow solution rate will create continuous treatment. Controlled solubility phosphates usually afford prevention of scale at a low parts per million with less frequency of application; however, they are higher in price than other types. Before using pellets the operator should check to see if there is ample space between the casing and tubing as bridging of pellets could be detrimental.

Bottom-hole temperatures should not exceed 150° F

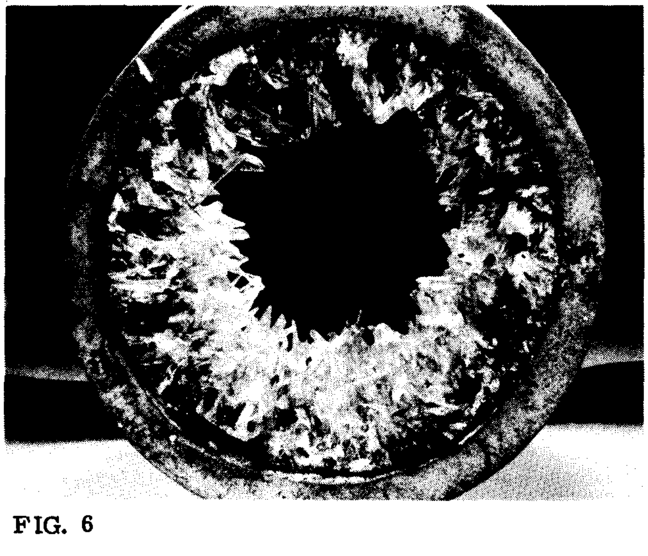
FIG. 6

especially when sodium hexametaphosphate is used. Rapid brine water reversion of metaphosphate, which has sequestering properties, to insoluble orthophosphate, which has no sequestering properties, occurs at normal operating temperatures. The stagnant void space below the perforations should not exceed 5 feet in depth because the chemical in solution has a tendency to remain within this void area. Occasionally this space below the perforations will be filled with sand or solids even though drilling records show several feet of void space.

Another field-proved method of preventing downhole scale is squeezing of the "controlled solubility phosphates" into the formation. The duration of effect will vary according to the quantity of pellets used, bottom-hole temperatures, and the volume of fluid passing over the pellets. Bottom-hole temperature should not exceed 180°F. If it is not feasible to introduce the pellets downhole, a bypass lubricator on the surface is a logical substitute. It is necessary that a portion of the production fluid continuously pass over the pellets.

Heater treaters and other separation equipment may be conveniently and effectively treated with slowly soluble scale preventive chemicals. Pellets or granular types may be conveniently introduced into flow line or directly into treater. Specific gravity of most chemicals of this type is great enough to insure their remaining on bottom of separator until solution takes place. In this manner, continuous treatment is attained with infrequent batch application of chemicals. Bypass feeders, such as shown in Fig. 6B, may be used successfully to insure continuous chemical injection into systems where batch treatment is not practical.

Often heater treater or separator scale is prevented when any of the bonafide water conditioning chemicals are introduced downhole. This method is preferred if scale deposition occurs in pumps, tubing, flow lines and equipment other than in the separator. Regardless of type of chemical used for scale prevention, application should, if possible, be made at a point in the system ahead of the scaling area. When adequate treatment is affected at a point prior to precipitation, more thorough water stabilization is afforded.

CONCLUSION

In conclusion, it should be emphasized that scale in oil field equipment can be economically and efficiently controlled, if not eliminated. The most important point to remember is diligent application of chemicals. Second, provide correct and necessary application equipment and rely, as much as possible, on water analyses for predicted water stability. Efficient forecasting will often prevent a plugged line or other failures due to scale.

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