Scale and Paraffin -- Causes and Methods of Control

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Since this paper deals with a dual subject, it must necessarily be considered accordingly. Scale and paraffin—causes and control involves widely differing formation principles and control methods and must receive separate treatment. Principles of scale formation and control measures will be considered first.

SCALE—CAUSES AND METHODS OF CONTROL

What Is Scale?

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

Oil field brine water contains 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.

Normal 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. 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.

The formation of calcium sulfate is somewhat different. This 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.

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, in most cases, be downhole well equipment.

Most Severe Scales

Problem sulfate scales are anhydrous calcium sulfate or anhydrite ($CaSO_4$), gypsum ($CaSO_4 \bullet 2H_2O$) 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, flow lines and treaters.

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 more generally found when two or more waters are mixed together, 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 water containing calcium or barium in solution are mixed together. In this manner, the magnesium sulfate salt may be a potential scale problem. Troublesome 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 dissolved salts. 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.

Control Methods

In some systems, the most effective method of control of scale deposition is dilution with fresh water however, fresh water is not always the most convenient or most economical medium. Except for excessive transportation costs, many producing oil wells with severe scale problems could be successfully treated with fresh water.

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 result 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 dispersed insoluble inorganic salts and soluble inorganic scale forming ions in solution. These salts and other suspended matter will eventually cause scale or formation plugging if not sufficiently reduced below precipitation point.

If the supply water is allowed to remain stagnant for a sufficient period of time in an open pit, most of these solids will accumulate 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.

Clarification by Coagulation

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, where as the floc itself is a chemical reaction. Aeration in the open pit storage system helps remove such undesirable gases as hydrogen sulfied 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 radicals 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.

Chelation

Chelation may be defined as the reversible reaction between a polyvalent metal ion and an organic polyaminocarboxylic acid or salt, or other active organic molecules, 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 solution 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 come into importance, primarily due to treating economics. Many other compounds such as citric, gluconic, lactic acid and some anionics and nonionics have been used for sequestering various metal ions with a great deal of success.

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 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 sequestering agents.

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

There are several different ways in which organic chemicals prevent scale formation other than precipitation, 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. The dispersion technique is widely used for scale prevention in oil field producing equipment and waterflood operations, but is not so successfully used in high temperature and high degree systems such as boilers. When used in conjunction with sequestering agents, 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 by this method.

Ion-Exchange

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 are attracted to the anode. These ions exist throughout the solution and act almost independently. For example, magnesium sulfate ($MgSO_4$) 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.

PARAFFIN—CAUSES AND METHODS OF CONTROL

What Is Paraffin?

Paraffin or wax is commonly found in many varied types of crude oil production. Wax deposits are generally composed of two distinct classes of wax-forming materials which are paraffinic and asphaltic. Paraffin deposition in producing equipment is predominantly found in the Permian Basin and generally throughout the mid-continent area. Asphaltic wax deposition in producing equipment is found predominantly in the West Coast area and at scattered points in other areas.

Chemical composition of these wax deposits is so complex and varied that no attempt will be made to give this specific information. Extensive research has failed to give exact composition of these compounds but has given general classification.

Cause of Deposition

Deposition of paraffin and asphaltic wax in production equipment is essentially caused by loss of solution properties. This may be caused either by temperature or pressure reduction or both or by reduction in solvent properties of the fluid which is holding the wax in solution.

As pressure and or temperature are reduced, the normal solution equilibrium as it exists in a given formation reservoir is upset and crystallization and precipitation can occur. This precipitation can and does allow wax particles to adhere to piping and causes, in many cases, rapid plugging or restriction of the normal flow of oil or produced fluids. Crystallization and precipitation can occur at any point from the formation face to the point of storage, usually tubing and flow lines being the most troublesome areas of paraffin or wax deposition. Fallout in storage is also a problem because of high bottom build-up and also prevents adequate water dropout.

Solvent Removal

Prevention and removal of paraffin and wax have over the years become a not too well respected art. Solvents used several years ago of the chlorinated type such as carbon tetrachloride, were efficient solvents but were found to be the cause of severe corrosion on the processing and refining industry, and consequently have been outlawed for use in the production field.

Carbon bisulfide has been widely used for many years and has proven to be next best to the chlorinated solvent. However, unlike the chlorinated solvent, carbon bisulfide is very dangerous to handle from a fire and explosion standpoint. Extreme caution must be taken in handling this material.

Various other less efficient solvents have and are being used which are not hazardous to handle. These include aromatics of various types and even straight chain paraffin type hydrocarbons. The terpenes have probably proved to be the best of the aromatic solvents.

Solvent removal is a temporary solution to the problem and must be repeated as often as the problem presents itself. In many cases, solvent removal of deposits is the most economical method of control but in many cases, it can be more economical to prevent deposition than to remove it.

Prevention

Recent developments in paraffin and wax prevention technology make it possible to economically treat most systems to prevent undesirable deposition. Various surfactants have been successfully incorporated into paraffin treatment compounds which prevent premature crystallization and precipitation of waxes and also cause minute paraffin particles or crystals to remain dispersed in the solution.

These paraffin dispersants are effecitve and relatively inexpensive for the results obtained. In order to obtain the expected results it is necessary to inject these compounds into a system on a continuous basis and should be injected at a point in the system before or ahead of the deposition area. This method affords maximum dispersion of wax particles when and where they do begin to precipitate.

GENERAL CONCLUSIONS

Scale and paraffin (wax) can be chemically controlled in most cases if proper treating techniques are used along with the proper chemicals and application equipment. Both scale and paraffin deposition can be removed by batch or slug treatment with the proper chemicals but neither one can be prevented by this type of treatment. Many good chemicals are available for treatment of scale and paraffin for batch removal and for prevention of deposition. Economics of individual circumstances often determine the best method to use, but few installations are non-receptive to control by chemical treatment.