Well Depositions
Formation, Removal and Prevention

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INTRODUCTION

Scale

A preferred definition of scale is: a solid or encrusting deposit resulting from precipitation in water solution of materials native to the water.[1] These inorganic scale depositions have been a costly problem in the petroleum industry since its beginning. Scale depositions not only restrict production but often cause inefficiency or failure in production equipment. Once these scales are formed, removal must be accomplished by one of two methods, either chemically or mechanically. Both of these removal processes add to the overall cost, therefore reducing the margin of profit.

In recent years, progress has been made in scale prevention products and techniques. Scale prevention, in part, is a form of preventative maintenance.

Paraffins

The natural formation of any organic accumulation in oilwell tubing, surface flow lines or other production and storage equipment is called a paraffin deposit. Paraffin is derived from Latin "parum affinis", which means small affinity.[2]

Paraffinic hydrocarbons were so named because of their resistance to attack by acids, bases, and oxidizing agents. In oilfield operations, the paraffins which are troublesome are principally composed of mixtures of long chain hydrocarbons.

A production cost increase results from paraffin deposition because of:

(1) A decrease in flow capacity.

(2) Expense of periodic deposit removal.

(3) Non-productive down-time.

By preventing the formation of these deposits, the value of preventative maintenance is apparent.

The most successful approach to paraffin inhibition has been directed toward the use of wax crystal modifiers. The application of these crystal modifiers has not been entirely effective in inhibiting the formation of paraffin deposits. This is probably due to the varied physical characteristics and nature of the paraffin material.

FORMATION, REMOVAL AND PREVENTION METHODS

Scale Formation

The major components of oilfield scale deposits are calcium carbonate, calcium sulfate and/or barium sulfate. These scale deposits result primarily from environmental changes during the production of well fluids. Dissolved solids may drop out of solution and form scale because of any of several different reasons. Some of the reasons are temperature and/or pressure changes or mixing of different brines.

Calcium carbonate scale formation can occur as a pressure drop occurs in the vicinity of the wellbore. Calcium carbonate does not exist in a brine solution as calcium and carbonate ions but as calcium and bicarbonate ions. A change in pressure allows dissolved gases such as CO_2 to escape from solution resulting in the formation of calcium carbonate. This precipitation can be expressed by the equation:

$$(1)\ \underset{\text{Calcium Bicarbonate}}{Ca(HCO_3)_2} \rightleftarrows \underset{\text{Water}}{H_2O} + \underset{\text{Carbon Dioxide}}{CO_2} + \underset{\text{Calicum Carbonate}}{CaCO_3}$$

The loss of CO_2 content affects the equilibrium of the calcium bicarbonate resulting in the formation of calcium carbonate.

The deposition of calcium sulfate may be caused by any one or a combination of the following:

(1) Decrease in pressure.

(2) Decrease of $CaSO_4$ solubility in higher concentrated brine solution.

(3) Evaporation.

(4) Mixing of incompatible waters.

The precipitation of calcium sulfate can be expressed by the following equation:

(2) $\underset{\text{Calcium}}{Ca^{++}} + \underset{\text{Sulfate}}{SO_4^{--}} \rightarrow \underset{\text{Calcium Sulfate}}{CaSO_4}$

Barium sulfate is formed when a mixing of incompatible brines takes place. Brines become incompatible if one water contains a high concentration of barium ions, and the other water contains a high concentration of sulfate ions. When the two waters mix, the final solution becomes saturated with barium sulfate and deposition occurs.

The chemical composition of a scale deposit may be any of several different kinds of combinations. In addition to calcium carbonate, calcium sulfate and barium sulfate, other deposits that form either singularly or in mixtures are: strontium sulfate ($SrSO_4$), various iron compounds such as iron carbonate ($FeCO_3$), iron sulfate ($FeSO_4$), iron sulfide (FeS), iron oxide (Fe_2O_3) and numerous silicates with variable chemical formulas.

Iron scales such as iron oxide and iron sulfide do not occur so much from equilibrium changes in the system but are generally products of corrosion.

TABLE I

NEW SOLVENT WELL TREATMENT HISTORIES

					PRODUCTION			
				VOLUME	BEFORE		AFTER	
AREA	FIELD	FORMATION	SYSTEMS*	GALLONS	O	W	O	W
West Texas	North Cowden	San Andres	I	750	3	4	35	50
	Levelland	San Andres	II	2000 (Injected into formation)	11	1	38	10
	Slaughter	San Andres	II	1000	6	16	18	30
	North Cowden	San Andres	I	500	9	50	25	95
	Denver Unit	San Andres	II	1500	10	20	41	42
	Denver Unit	San Andres	II	500	8	55	28	99
	Denver Unit	San Andres	II	1000	38	5	67	7
	Cedar Lake	San Andres	II	1000	0	0	90	0
	Moss Unit	San Andres	I	500	13	55	61	129
New Mexico	Chas. Drab #3-P	Abo	II	300	0	0	8	0
	Langley	Abo	II	750	22	28	32	58

*System I — Low temperature

System II — High temperature

Scale Removal

The initial step in scale removal is to obtain samples of the deposit and determine its composition. Some scale deposits such as calcium carbonate and iron compounds can be removed by acid treatments. Iron deposits are generally not completely acid-soluble but are loosened from the pipe and broken down allowing removal by circulation or flushing.

The removal of calcium sulfate scale can be accomplished by using converting solutions. Two general types are carbonate and hydroxide solutions. These solutions convert the calcium sulfate to an acid-soluble material, thus requiring a subsequent acid treatment.

Recent development has introduced a new solvent for removing calcium sulfate scale. The solvent consists of two systems formulated to meet a wide temperature range (20°F to 200°F). System I is used at low temperatures (90°F and below). System II is used at high temperatures (90°F and above). This solvent is a water-base solution designed to chemically remove calcium sulfate deposits, eliminating the use of follow-up acid treatments. The solution dissociates and flocculates the calcium sulfate deposits allowing removal by circulation or swabbing. A treatment of this type is advantageous in reservoirs with close oil-water contact where the use of acid might cause excessive water production. Although acid treatments are not necessary when this solvent is employed, we would like to point out that the dissociated scale is converted to an acid-soluble material. Field evaluation of this product was conducted in the Permian Basin and results are shown in Table I.

TABLE II

OILWELL SCALE DEPOSITS

DEPOSIT	CHEMICAL FORMULA	REMOVAL CHEMICAL	CAUSE OF SCALE DEPOSIT
Calcium Carbonate	$CaCO_3$	Hydrochloric Acid	Mixing of brines, changes in temperature and pressure.
Calcium Sulfate	$CaSO_4$	Converting Solutions - carbonate, caustic New Solvent.	Same as above.
Barium Sulfate	$BaSO_4$	No removal chemical known.	Mixing of brines.
Strontium Sulfate	$SrSO_4$	No removal chemical known.	Mixing of brines; changes in temperature and pressure.
Iron Carbonate	$FeCO_3$	Hydrochloric Acid plus sufficient amount of iron sequestering agent.	Same as above.
Iron Sulfide	FeS	Hydrochloric Acid plus sufficient amount of iron sequestering agent.	Corrosion of well equipment by sour crude or hydrogen sulfide gas.
Iron Oxide	Fe_2O_3	Same as above.	Reaction of oxygen with dissolved ferrous iron.
Sodium Chloride	$NaCl$	Water or 1-3% HCl.	Evaporation of water.
Magnesium Hydroxide	$Mg(OH)_2$	Hydrochloric Acid	Excessive amounts of oxygen enters the well or alkaline fluids in the well. High temperature.
Silicates	Variable	Mud-Acid	Changes in solubility due to cooling of brines by pressure drops.

Barium sulfate deposits can not be removed chemically. Their removal is best achieved by mechanical methods such as under-reaming, drilling, or by fracturing. Table II lists the most common scale deposits, chemical formulas, removal chemicals and general cause of their deposition.

Scale Prevention

The most effective and economical method used to prevent the deposition of scale involves using chemicals which exhibit the "threshold effect"[3]. This involves the coating of the small microcrystalline nuclei with the inhibitor, which in turn controls their growth. This keeps large particles from forming and maintains them in solution at concentrations above the normal precipitation level. Chemicals which exhibit the "threshold effect" and which are used as scale inhibitors are the polyphosphates, organic phosphates and synthetic organic polyelectrolytes.

Solid polyphosphates are placed into the formation during fracturing treatments. After being placed into the formation, the polyphosphates, being slowly soluble, are produced back with the water as it flows through the formation, thus preventing the deposition of scales. Generally, 5-20 ppm of the dissolved phosphates in water is necessary to prevent scale deposition. However, some types of scale may be prevented with less than 5 ppm. Field experience gives the most reliable information on the results that can be expected when using this type polyphosphate chemical.

One of the arguments against using the solid polyphosphates is the placement method which is relatively expensive and not always possible. Too, the use of acids before and after polyphosphate placement is not recommended because acids promote the reversion to the orthophosphate which combines with calcium in water to form insoluble calcium phosphate.

In recent years, the use of liquid inhibitors has proven to be effective for scale control. Included in this group are the organic phosphates and synthetic organic polyelectrolytes. The success of scale control depends on the adsorption of the inhibitor on the rock matrix and slow desorption into the produced fluids. The adsorption properties of all inhibitors are not equally effective. Many scale inhibitors are effective in preventing scale but have poor adsorption properties. Figure 1 shows the relative adsorption/desorption rates of two liquid inhibitors on Berea sandstone. Placement of liquid inhibitors may be performed by either the matrix squeeze technique, fracturing, or by metering the liquid into water injection systems.

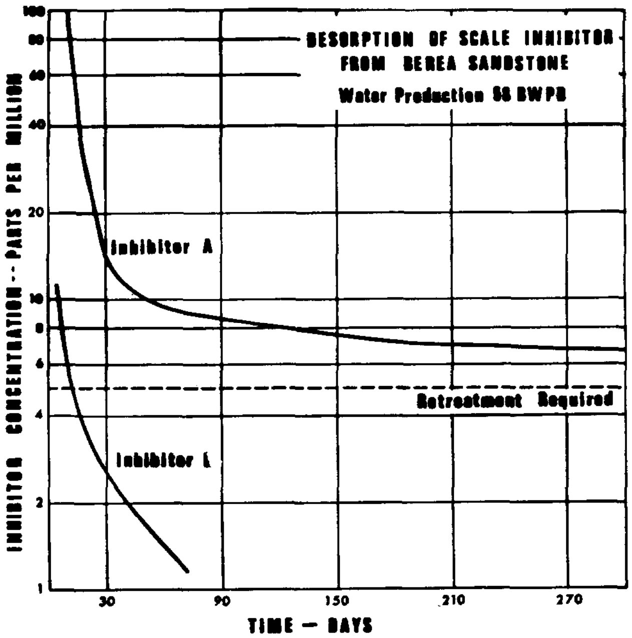

FIGURE 1

Paraffin Formation

Paraffin is a deposit which is not soluble or dispersible by the crude oil under the conditions in which deposition occurred.[4] The paraffin normally consists of high molecular weight hydrocarbons, both straight chain and branched, resins and asphaltic materials of undetermined nature.

In consistency, the deposit may vary from a soft, sticky material to one which is hard and brittle. Deposits are usually black, although lighter colors are sometimes observed. Under the conditions of temperature, pressure and oil composition occurring in the reservoir, the paraffin is in solution. As the oil flows to the surface, there is generally a reduction of temperature, pressure and the amount of dissolved gases contained in the oil. Reduction of temperature and gas break-out have been shown to be factors causing reduced solubility of the paraffin in the crude.[5]

Thus, as the crude containing paraffin rises to to the surface, the solubility of the paraffin may be exceeded. Deposition will begin at the point where the temperature falls below its cloud point and will continue as long as there is a further drop in the solution power of the crude for the paraffin. The amount of deposition, as well as its location of the bulk, in subsurface or surface equipment, will depend on the amount of paraffin originally in the crude, the manner in which pressure and temperature of the crude are reduced and other properties of the crude and of the paraffin.

Paraffin Removal

The three most commonly used methods for paraffin removal are: (1) thermal, (2) mechanical, and (3) solvent applications. However, each of these methods is limited to both immediate effectiveness and long lasting solution to the paraffin problem. The thermal treatment merely removes the accumulation by relocating it, which may or may not provide the desired results. The mechanical approach, which utilizes various tools such as paraffin hooks, knives and augers, merely eliminates the problem for a short time span. Solvent applications (wetting agents and dispersants) are often helpful with minor paraffin problems, but even here, usually only provide temporary relief. Each removal treatment has some advantages and some disadvantages and should be thoroughly evaluated before employed.

Paraffin Prevention

Inhibition of paraffin has by no means been solved. Many chemicals have been brought forward which have shown promise; however, all have had limitations.

In the past, chemical dispersants have had some success inhibiting the formation of paraffin. The dispersant concept is an approach that utilizes chemicals to cause paraffin crystals to repel one another preventing them from forming clusters.[6] Reasons for some failures have been due to misapplications and failure of the chemical to contact the proper place in the most effective concentration.

The most promising new paraffin control chemical is from the group known as wax crystal modifiers. This basic chemical and variations of the same are polymeric materials such as polyethylene. These wax crystal modifiers actually combine with the paraffin molecules and modify the growth of the wax crystals. This modification causes a lowering of the cohesive forces between the wax crystals themselves and in many cases, even causes a lowering of the adhesive force between the wax crystals and the available surface.[7]

Research is continuing in an effort to find more efficient methods and/or chemicals for paraffin prevention.[8,9]

SUMMARY AND CONCLUSIONS

1. Scale and paraffin deposits can reduce production or injection of fluids.
2. Scale and paraffin deposition can result from several causes. These deposits are usually mixtures of one or more components.
3. Most well deposits can be effectively removed by chemical or mechanical means.
4. Scale and paraffin deposits can be effectively controlled under most conditions.
5. The new solvent has proven effective for removing calcium sulfate scale.
6. In many instances, prevention of scale and paraffin is more economical than their removal.

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