Gyp Removal - An Old Problem - A New Solution

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INTRODUCTION

The deposition of scaling materials from brines produced with oil has been a serious problem for many years. Compounds, such as calcium sulfate, calcium carbonate and barium sulfate, have been found in many wells, including injection wells, producing wells and waste disposal wells, and also plant water systems. The effect that these scales have on a well depends largely on the scale in the system. Scales may restrict and completely choke off production in the tubing, flow lines, tubing perforations, at the formation face or in the casing perforations. Scales have been known to deposit in fractures and the formation some distance from the wellbore.

Scale Identification and Composition

One of the most important factors in dealing with scaling problems is an accurate determination of the material being deposited. There are essentially two methods used in the laboratory for the identification of scales; one involves the use of an instrumental method and the other the use of chemical methods.

The instrumental method used is that of X-ray diffraction. It is the fastest method and requires the least amount of sample. With the second method, that of chemical analysis, the scale is decomposed and dissolved in chemical solutions. The various compounds contained in the scale sample are then analyzed by standard gravimetric or titrimetric methods.

Due to the time and expense involved in analyzing scale samples in the laboratory, it often becomes necessary to determine the composition of the scale in the field. Mineral scales can generally be divided into two classes based on the reaction of the scale with hydrochloric acid or the ability of hydrochloric acid to remove the scale. This division separates the scale into either (1) acid-soluble, or (2) acid-insoluble deposits. Table 1 shows the common acid-soluble and acid-insoluble scales encountered in the oilfield. This, of course, is a simplified division because seldom is pure calcium sulfate or calcium carbonate found deposited. Usually the deposit will be composed of one or more of the major inorganic components plus varying amounts of corrosion products, congealed oil, silicates, and paraffins. However, separation into an acid-soluble or acid-insoluble deposit is adequate to determine the type of scale removal treatment necessary.

Scale Formation

Prior to production, well fluids remain in a static undisturbed state in the formation. Scale deposits occur as a result of disturbing this chemical equilibrium. As production is initiated, environmental changes such as a pressure drop occurring near the wellbore allows dissolved gases to come out of solution. These changes destroy the state of equilibrium, and deposits form as the salts reestablish equilibrium under the new conditions. For example, calcium carbonate scale can occur as a result of a pressure drop at the wellbore. Calcium carbonate does not exist in the formation brine as calcium and carbonate ions, but as calcium and bicarbonate ions. A change in pressure allows CO_2 to escape from solution and thus calcium carbonate scale can be formed as expressed by the equation:

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

The concentration of uncommon ions, such as chlorides, can influence the deposition of calcium sulfate. The presence of uncommon ions at low concentrations increases the solubility of gypsum. For example, at 80°F, the maximum solubility of gypsum in sodium chloride occurs at a concentration of 14 per cent. However, should the concentration of chlorides in the brine exceed or be less than this limit, it would decrease the solubility of gypsum. The uncommon ion concentration can increase in a brine as a result of the expansion and evaporization of gases thus resulting in vaporization of the water and decreasing the total volume of solution. In addition, however, the maximum solubility of gypsum in a given brine system is dependent upon the total downhole conditions of pressure, temperature and total dissolved solids.

Scale deposits may also occur as the result of mixing incompatible waters. Waters from different zones may become mixed in the wellbore, or injection water may mix with formation water. In water injection wells, brines from several sources may be combined and result in incompatibility problems which eventually form scale. Incompatibility of mixed brines results when one water contains a high concentration of calcium or barium, while the other water contains a high concentration of sulfate or bicarbonate ions in solution. As these waters mix, the final solution becomes saturated with calcium sulfate, barium sulfate or calcium carbonate, and deposition occurs.

Corrosion and microbial reaction products can result in deposition of various iron scales such as iron oxides and iron sulfide. Sulfate-reducing bacteria yield a source of hydrogen sulfide which in turn can precipitate iron which is in solution or reacts with the steel.

Iron in solution can be precipitated if oxygen is introduced into a system, or iron oxides can form on the metal surfaces when exposed to oxygen.

The physical form of a scale deposit is dependent upon the manner in which it was deposited. Scale does not form spontaneously, rather it occurs in stages. Initially, a calcium ion combines with a sulfate or carbonate ion to form a molecule. The molecules combine to form micro-crystalline nuclei that act as growth sites. The scale nuclei combine at these sites to form clusters. As the clusters grow and become too heavy to remain in solution, they precipitate or become deposits.

The final crystal habit or form of the scale may be categorized as: (1) soft, thin deposits (2) dense, laminated deposits and (3) crystalline deposits.

The thin, soft scales are often deposited rapidly and contain imperfections in their crystal lattice. These imperfections result from the scale being deposited with paraffin, silicates, or oil trapped and included within the crystal lattice. The dense, laminated deposits are the result of slow growth which results in a crystal form which has few imperfections and the lattice structure is extremely compact. The final form that a scale deposit takes can significantly affect effort to remove the scale.

TABLE 1

Oil Well Scale Deposits

Acid Soluble Deposits	Chemical Formula	Mineral Name
Calcium Carbonate	$CaCO_3$	Calcite
Iron Carbonate	$FeCO_3$	Siderite
Iron Sulfide	FeS	Trolite
Iron Oxide	Fe_3O_4 $(FeO \cdot Fe_2O_3)$	Magnetite
Iron Oxide	Fe_2O_3	Hematite
Magnesium Hydroxide	$Mg(OH)_2$	Beucite

Acid Insoluble Deposits	Chemical Formula	Mineral Name
Calcium Sulfate	$CaSO_4 \cdot 2H_2O$	Gypsum
Calcium Sulfate	$CaSO_4$	Anhydrite
Barium Sulfate	$BaSO_4$	Barite
Strontium Sulfate	$SrSO_4$	Celestite
Barium Strontium Sulfate	$BaSr(SO_4)_2$	. . . .

SCALE REMOVAL

Acid Soluble Scales

The initial step in scale removal is to obtain a sample of the deposit to determine its composition. Scales which fall into the acid-soluble category, such as calcium carbonate and iron oxides, can be removed with hydrochloric acid. If a major portion of the deposit is composed of iron oxide, a sequestrant and pH control agent should be added to the hydrochloric acid to prevent reprecipitation of the iron as the acid spends.

Acid Insoluble Scales

Unfortunately, the acid-insoluble scales, such as calcium sulfate, barium sulfate and strontium sulfate, are not as easily removed. Gypsum (calcium sulfate) can be removed effectively by chemical treatment; however, barium sulfate and strontium sulfate cannot be removed unless the scale is highly contaminated with gypsum or calcium carbonate scales. These scales can be removed with a mechanical approach such as hydraulic jetting, underreaming, drilling, or by fracturing through the deposit.

There are three types of chemical treatments used to remove gypsum:

1. Inorganic converters which react with gypsum to form an acid soluble reaction product
2. Organic converters which react with gypsum to produce a water-dispersible reaction product or pumpable mud
3. Solvents which form a soluble complex with the calcium ion.

The inorganic converting agents used for gypsum removal are the carbonates and hydroxides. The inorganic converters have been used for many years and represent a classical approach in removing gypsum. With the carbonate solutions, the gypsum is converted to calcium carbonate which is removed with a subsequent acid treatment. The carbonate solutions are relatively inexpensive and have been used in many wells with satisfactory results. However, the carbonates may not be as effective as other type solvents on dense, laminated gypsum scales. Because of a lack of penetration of the treating solution, repeated applications may be necessary. The hydroxides (sodium and potassium) have also been used with fair success. The hydroxides convert the gypsum to calcium hydroxide which is soluble in acid. In some cases, the calsium hydroxide reaction product will slough away from the surface of the gypsum, while in others a tightly adhering coat is formed on the surface of the deposit which interferes with the reaction and must be removed with acid. Some wells treated with hydroxides have shown a decrease in effectiveness with repeated treatments because of a buildup of calcium hydroxide sludge within the interstices of the gypsum and on the surface of the deposit. This effect is more pronounced when an acid stage is not used to remove the reaction product. This buildup of reaction product or sludge limits the penetration of the hydroxide solution. In addition, this residual amount of gypsum and reaction product provides a site for further deposition to occur, which results in a deposit that is considerably more difficult to remove. With the carbonates and hydroxides, an acid stage is usually required to insure removal of the calcium carbonate or calcium hydroxide reaction product.

Organic converters, such as sodium citrates, potassium glycolates and a newly developed converter, represent a new approach in removing gypsum. They differ from the inorganic converters in that an acidizing stage is not usually required for removal of a reaction precipitate. The reaction products formed tend to slough away from the surface of the gypsum to form a dispersion or pumpable mud. The reaction products can then be circulated or swabbed from the well. The sloughing away of the reaction product from the gypsum surface also allows for better penetration of the solvent. Reaction products of this type are readily dispersible in water. Consequently, residual amounts of the reaction product not removed when the spent solvent is circulated or swabbed from the well can be removed as a dispersion in the produced water once production is resumed. However, if a well treated with an organic converter should become plugged, the reaction precipitate can be dissolved with hydrochloric acid.

The solvent type treatment for removal of gypsum differs from the inorganic and organic converters in that an insoluble reaction product is not formed. Solvents or chelating agents, such as EDTA Na_4 (ethylenediaminetetraacetic acid tetrasodium salt) and NTA Na_3 (nitrilotriacetic acid trisodium salt) and a new solvent type chelating agent, remove gypsum by extracting and complexing the calcium ion. The calcium removed is then held in solution as a stable complex. The solvents are more expensive than the previously mentioned converter type treatments. However, they are applicable in removing gypsum in certain instances, e.g., removing gypsum from a fracture or formation where solid reaction precipitates could possibly cause plugging.

Laboratory Investigation

A comparison of the three types of gypsum removal chemicals has been conducted in the laboratory with two West Texas field scales and a quarried gypsum from Southard, Oklahoma. Results of the tests are shown in Table 2. The inorganic converters did not remove a significant amount of gypsum without acidizing before and after the 24 and 48 hour solvation periods, respectively. The 30% KOH solution formed a tightly adhering coat of calcium hydroxide which did not slough and required acidizing to be removed. The 30% NaOH solution appeared to penetrate the gypsum test samples more readily and a small amount of calcium hydroxide

TABLE 2

Comparison of Various Types of Chemicals Used for Gypsum Removal

Vol. = 100 ml
Solvation Period: 24 and 48 hrs.
Concentration = Wt. %
Temperature = 72°F

Gypsum Removed (lbs/gal)

	24 Hrs.			48 Hrs.		
Solvent Types	Scale #1	Scale #2	Scale #3	Scale #1	Scale #2	Scale #3
Inorganic Converters*						
12% NH_4HCO_3-$NaCO_3$	0.06	0.0	0.03	0.06	0.1	0.03
30% KOH	0.00	0.0	0.0	0.00	0.0	0.0
30% NaOH	0.23	0.17	0.17	0.50	0.4	0.17
Inorganic Converters**						
12% $NH_4HCO_3NaCO_3$	0.35	0.37	0.40	0.6	0.74	0.80
30% KOH	0.33	0.0	0.50	0.5	0.30	0.65
30% NaOH	0.50	0.6	0.52	0.9	0.80	0.75

Gypsum Removed (lbs/gal)

	24 Hrs.			48 Hrs.		
Solvent Types	Scale #1	Scale #2	Scale #3	Scale #1	Scale #2	Scale #3
Organic Converters*						
30% New Converter	1.2	0.90	0.7	3.0	1.7	1.50
30% Na Citrate	0.35	0.56	0.5	0.88	1.0	0.78
30% K Glycolate	0.36	0.50	0.5	0.45	0.66	0.94
Solvents*						
30% New Solvent	0.62	0.62	0.4	0.85	0.80	0.75
30% Na_4EDTA	0.23	0.31	0.25	0.43	0.45	0.36
30% Na_3NTA	0.01	0.04	0.01	0.01	0.04	0.01

Scale #1 = quarry deposit, Southard, Oklahoma
Scale #2 = large crystal from Jordan Field, Andrews Co.
Scale #3 = small needle like crystals from Magutex Field, Andrews Co.

*No acidizing after each solvation period.
**Acidized for 2 hours in 15% HCl after each solvation period.

sloughed away from the gypsum surface. However, acidizing the test samples resulted in a larger amount of calcium hydroxide being removed. The ammonium bicarbonate-sodium carbonate mixture formed a layer or coating of calcium carbonate on the gypsum surface that did not slough and required acid to be removed.

The organic converters were more effective in physically removing or disintegrating the gypsum as a result of the respective reaction products sloughing from the surface of the gypsum. Sodium citrate and potassium glycolate, while more effective in this respect, did not remove appreciably more gypsum than did the inorganic converters when followed by acid. The new converter is more effective than either the sodium citrate or potassium glycolate and is also more effective than the inorganic converters, even when they are followed by acid.

The solvents are not as effective as the new organic converter. However, a new solvent has been developed which is more effective than the EDTA and NTA acid salts. This new solvent will remove approximately the same quantity of gypsum as the inorganic converters followed by acid.

Table 3 shows a relative cost comparison of the three types of gyp-removal treatments. The chemical cost of removing 1 lb of gyp was calculated for each chemical. The value obtained for the most economical treatment was divided into each cost figure, thereby defining the cost ratio. Obviously, the most economical treatment will have a cost ratio of 1.0.

Field Results

To determine the effectiveness of the new organic converter and solvent, a field evaluation of the products was conducted in the Permian Basin and some typical production data are shown in Table 4.

Often, the success or failure of a gypsum-removal treatment is dependent upon having sufficient volume and concentration of treating solution. Shryock and Knox[4] have presented

TABLE 3

Relative Cost Comparison for Removing Gypsum

Solvent Types Inorganic Converters	Cost Ratio*
12% NH_4HCO_3-$NaCO_3$	2.1
30% KOH	4.2
30% NaOH	2.0
Organic Converters	
30% New Converter	1.0
30% Na Citrate	5.1
30% K Glycolate	11.1
Solvents	
30% New Solvent	4.9
30% Na_4EDTA	20.9
30% Na_3NTA	345.3

*Cost Ratio - These values were calculated on the basis of prevailing chemical prices as of February, 1970.

charts to enable determining the quantity of scale downhole. For example, a 2-in. ID pipe having scale 0.5-in. thick would contain 0.016 cu ft of gypsum per ft. Gypsum weighs 144 lb per cu ft, so each linear foot of pipe would contain (144 lb cu ft x 0.016 cu ft = 2.3 lb per linear ft) 2.3 lb of gypsum. The 2-in. ID pipe containing 0.5-in. gypsum scale would have a capacity of 0.044 gal. per linear ft. Consequently, several treatments would be required to remove this quantity of gypsum scale. In cases as drastic as this example, circulating the solvent over the scaled interval would be the most practical approach. The volume and concentration of treating solution necessary to circulate would depend on the length of the scaled interval, tubing volume and fluid level in the annulus.

The treatment time required to remove a particular deposit will vary, depending on the treatment technique, concentration of treating solution, and final crystal habit of the gypsum. Generally, circulating the treating solution increases the rate of removal with either the converting agents or solvent treatments. Treatment time can best be determined by conducting a simple laboratory solubility test in which a preweighed sample of the deposit is placed in contact with varying concentrations of treating solution and this amount of gypsum removed as a function of time determined gravimetrically.

Many producing wells deposit not only gypsum, but also paraffin or heavy hydrocarbons and various forms of iron oxides or sulfides. Removal of these materials immediately preceding the gypsum removal will enhance the total results of the treatment.

Paraffin removal has been economically accomplished by the use of a special blend of aromatic solvents, either alone, or dispersed with an iron-sequestering hydrochloric acid solution. Volume usually used is 1000-2000 gallons. If the tubing can be lowered to a point near the bottom of the openhole section or below the perforated interval, these preflushes may be dumped in the annulus and circulated with the downhole pump. If this is not possible, or if the well is on gas lift, the preflush may be spotted partially in the casing and partially in the formation, and allowed to soak for 24 hours. After recovery of the preflush with the downhole pump or gas lift, the gypsum converter or solvent is applied, using the same technique and volume. A 48-hour soak or circulation time may be necessary if the deposit is thought to be very thick or dense.

TABLE 4

Well Treatment Histories

Area	Treating Solution	Field	Formation	Volume (gal.)	Production Before O	Production Before W	Production After O	Production After W
West Texas	New Converter	Cedar Lake	San Andres	1000	80	6	238	7
		Cedar Lake	San Andres	1500	44	177	67	183
		Cedar Lake	San Andres	1500	93	8	122	14
		Cedar Lake	San Andres	1500	60	17	102	30
		Geo. Smith	Clearfork	2000	36	36	67	38
		Slaughter	San Andres	1500	11	3	55	6
	New Solvent	Dollarhide	Clearfork	1000	50	28	62	24

Injection wells are treated with the spot-and-soak technique. The solvents are particularly adapted to this type well since there is no solid residue. If disintegrators are used in injection wells, back-flowing is advisable to remove the insoluble residue.

Selection of wells to be treated should be based upon data other than a drop in production or a decrease in injectivity. Pressure buildups or drawdowns may be used to establish the existence of damage near the wellbore.

CONCLUSIONS

1. Scale deposition can result from several causes. Three of the more common causes are mixing of incompatible waters, pressure drops, and the uncommon ion effect.
2. Scale removal treating solutions can be divided into three categories: (1) inorganic converters, (2) organic converters, and (3) solvents.
3. Based on relative cost comparison data, the new organic converter is the most economical treatment for removing gypsum. The new solvent, while more expensive than the new organic converter, may find application in special cases.
4. Laboratory and field test data have shown that the newly developed organic converter and solvent are effective in removing gypsum deposits.

REFERENCES

1. Yuster, S. T.: The Gypsum Problem in Water Flooding, Producers Monthly, April, 1939, p. 27.
2. Ostroff, A. S.: Compatibility of Waters for Secondary Recovery, Producers Monthly, March, 1963.
3. Lasater, R. M., Gardner, T. R., and Glasscock, F. M.: Scale Deposits are Controlled, Oil and Gas Journal, January 15, 1968.
4. Shryock, Stan and Knox, J. A.: Stimulating Water Injection Wells, Oil and Gas Journal, January 4, 1965.
5. Slaton, Leo, Lasater, R. M., and Knox, J. A.: Scale Deposition and Removal, Producers Monthly, September, 1965.
6. Smith, C. F., Nolan, T. J. and Crenshaw, P. S.: Removal and Inhibition of Calcium Sulfate Scale in Waterflood Projects, J. Pet. Tech., November, 1968.
7. Fulford, R. S.: Effects of Pressure Drop on Gypsum Scaling in Oil Wells, J. Pet. Tech., June, 1965.

ACKNOWLEDGMENT

The authors express appreciation to Halliburton Services for permission to prepare this paper and to those of the organization who helped secure data and offered suggestions for the preparation of this paper.