SCALE CONTROL TECHNOLOGY — A REVIEW

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WHAT IS SCALE?

For years, all oilfield scales were called gyp, and gyp meant trouble. Times and methods may have changed, but gyp, or scale, still means trouble. Scale can be anything that precipitates from water. We have seen scale deposits that were pure rock salt and others that were much more exotic, such as zinc phosphates, sodium carbonate, and occasionally minute traces of gold and silver, but these are unusual. Everyday oilfield scales are calcium carbonate, calcium sulfate or gypsum, and barium sulfate. Strontium sulfate is occasionally found, usually in conjunction with barium sulfate. Corrosion products, too, can be found in scale-like deposits.

Scale deposits are the result of water instabilities—supersaturated solutions are dropping out some of their burden of dissolved salts in order to approach equilibrium. Precipitation will continue until stability has been achieved. In a flowing system with continual replenishment of water, scale deposits can continue to grow, in some cases completely blocking the flow line (Fig. 1).

WHAT DOES IT DO?

What does scale do? It causes trouble in any number of ways. Scale reduces the diameter and sometimes plugs flow lines and tubing. Scale can plug perforations and gas anchors in producing and injection zones as well as restrict heat transfer in heater treaters, radiators, and heat exchangers. Deposits can result in channeling through water filters, reduced flow rates and ineffective filtration. Corrosion attack can be intensified by an overlying scale deposit.

Scale creates jobs for those in the business of preventing and removing scale. It occupies at least part-time attention from many people. Much time and effort have gone into studies of scale problems, and this is fortunate, for now we benefit. In addition to a better understanding of the reasons for scale deposits, we also have available numerous techniques and chemicals to prevent, control, and remove scale depositions. The possibilities are many and varied, but with judicious use, they can usually lead to a satisfactory solution of the scale problem.

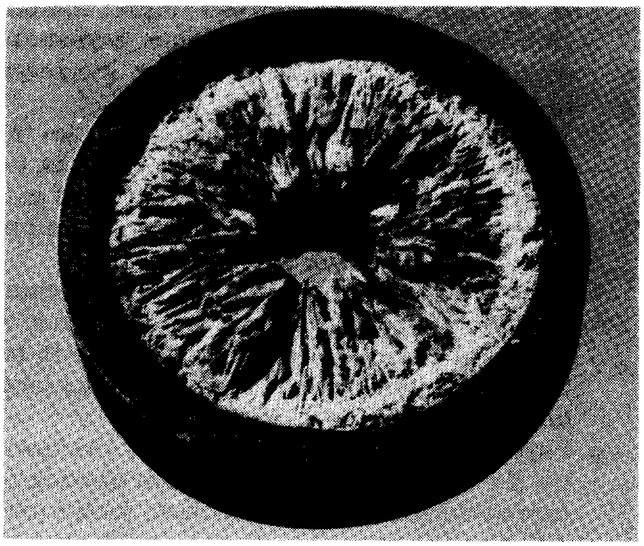


FIG. 1—CALCIUM SULFATE DEPOSIT IN FLOWLING

WHAT CAUSES SCALE DEPOSITION?

Calcium Carbonate

Calcium carbonate deposition is affected by:

1. Concentrations of calcium, carbonate, and bicarbonate ions. Calcium carbonate can precipitate from the combination of calcium ion with either carbonate or bicarbonate ions,

as shown by these two equations:

$$Ca^{++} + CO_3^{=} \longrightarrow CaCO_3\downarrow \qquad (1)$$

$$Ca^{++} + 2(HCO_3)^{-} \longrightarrow CaCO_3\downarrow + CO_2 + H_2O \qquad (2)$$

Only when concentrations of these ions exceed the solubility limit and the solution becomes supersaturated can precipitation take place. That limit of solubility is affected by each of the parameters listed here. The first is, of course, the concentrations of the ions which can form calcium carbonate.

2. Salinity. As the salinity of the water increases, solubility of calcium carbonate increases — up to a point; about 150,000 mg/l sodium chloride. Beyond this, calcium carbonate solubility decreases with further increases in salinity.
3. Temperature. Calcium carbonate has an inverse solubility with temperature; that is, as temperature increases, the solubility of calcium carbonate decreases. It is just the opposite for most other substances.
4. The acidity of the solution or pH. Calcium carbonate is readily soluble in acid. Thus, it is logical to expect calcium carbonate to be increasingly soluble as the acidity of the solution increases.
5. Partial pressure of carbon dioxide. As shown by Eq. (2), the release of carbon dioxide is part of the precipitation reaction. As the partial pressure of carbon dioxide in the system increases, the equilibrium of this reaction will be driven to the left. The effect will be to increase the solubility of calcium bicarbonate and limit precipitation of the insoluble calcium carbonate.

CALCIUM SULFATE

Calcium sulfate exists in several crystalline forms. These include gypsum, which is $CaSO_4 \cdot 2H_2O$; hemihydrate, $CaSO_4 \cdot 1/2H_2O$; and anhydrite, $CaSO_4$. Although the solubility curves (Fig. 2) of these crystalline forms versus temperature show that above about 40°C (104°F), anhydrite is the thermodynamically stable form, we know from experience that gypsum is the form most likely to precipitate up to a temperature of about 100°C (212°F). Above this temperature, hemihydrate becomes less soluble than gypsum and will normally be the form precipitated. This can, in turn, dehydrate to leave a scale of anhydrite. So, for solubility limits, we can look to gypsum at temperatures below 100°C and hemihydrate above this temperature. Anhydrites can, of course, be directly precipitated and do so from quiescent systems above about 121 to 135°C (250 to 275°F). In the presence of a boiling heat transfer or an agitated system, anhydrite can appear at lower temperatures. Some of the factors which influence calcium carbonate solubility also affect calcium sulfate. Calcium sulfate solubility is affected by:

1. Concentration of calcium and sulfate ions. Only when these concentrations exceed the solubility limit for one of the forms of calcium sulfate will scale deposition be found.
2. Salinity. The effect of dissolved salts on calcium sulfate solubility is much the same as with calcium carbonate. A maximum is reached in the neighborhood of 125,000 mg/l sodium chloride. Beyond this, solubility decreases with increasing salt concentration.
3. Temperature (Fig. 2). Gypsum shows a different response to temperature than did calcium carbonate. Solubility of gypsum increases with temperature up to about 40°C. Beyond this, the solubility relationship becomes inverse and decreases with further increases in temperature.
4. Magnesium ion concentration. The presence of magnesium ions in the salt solution has a direct effect on the solubility of calcium sulfate. This is in addition to the effect of salinity. Explanations for this have been offered;[1] however, these are beyond the scope of this paper.
5. Total pressure. Increases in calcium sulfate solubility are caused by increases in total pressure on the system. The effect is physical as the size of the calcium sulfate molecule is reduced by increasing pressure.[2] Thus, substantial pressure is required. For instance, at 100°C, the solubility of anhydrite in distilled water is approximately 0.0758 percent at 1 atmosphere pressure. Increasing the pressure to 100 atmospheres increases the solubility to about 0.09 weight percent. Even so, pressure drops can sometimes be responsible for deposition of calcium sulfate in producing systems.

Barium Sulfate

Solubility of this nearly insoluble compound is affected by:

1. The concentrations of barium and sulfate ions

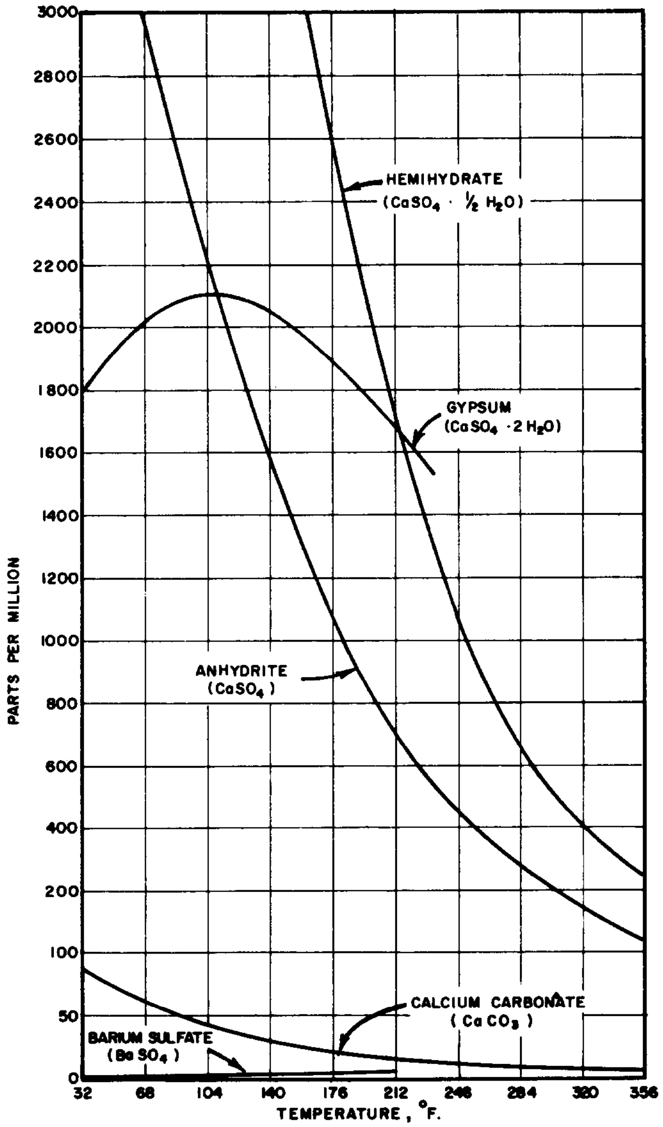


FIG. 2—SOLUBILITY OF CALCIUM CARBONATE, CALCIUM SULFATE AND BARIUM SULFATE

2. Salinity. Severalfold increases in solubility can result from increasing the salinity of the system. Even so, barium sulfate has extremely limited solubility.
3. Temperature. Unlike calcium sulfate and calcium carbonate, barium sulfate tends to increase in solubility with temperature. Although this increase can be severalfold, solubility remains at a low level.
4. Total pressure. There is only limited documentation on the effect of pressure on the solubility of barium sulfate. There have been instances in producing systems where pressure drops have resulted in barium sulfate deposition from what had previously been stable sytem. We can offer no data on the pressures required.

HOW CAN WE TELL IF SCALE WILL FORM?

Take any given water system, whether it be water injection system, cooling tower, or producing system. How can we know if scale will form? There are several possible ways:

1. Wait and see. If nothing happens, you are home free. If scale does form, be ready to do something about it immediately. Timely action can prevent real headaches later on. Actually, this is always good practice. Keep your eyes open. Inspect the system at every opportunity. Thin deposits of scale can be a portent of things to come. Absense of any scale can be an indication of a scale-free system or of successful treatment.
2. Ask somebody — somebody who can give you a straight answer; someone in the area who is handling the same water. If he is having problems, you can expect problems. If he has no problems, perhaps you, too, will be as fortunate.
3. Use the factors affecting solubility from the paragraphs above to calculate the limiting solubility of scale formers in the water. Calculation procedures have been developed by researchers for each of these common scale-forming compounds. Each of these procedures uses a constant known as the solubility product. Chemists have found that the product of the concentrations of scale-forming ions is always more or less equal to a constant at a given temperature. For instance, the solubility product for calcium carbonate at 25°C (77°F) is:

$$[Ca^{++}]\,[CO_3^{=}] = 0.87 \times 10^{-8} \qquad (3)$$

where the square brackets represent ionic concentrations in gram-ions per liter. From this equation we can see that if the calcium concentration is high in a given solution the carbonate solution at the solubility limit must be low. Solubility calculations, then, for each of the three scale-forming salts begin with this solubility product constant in some form, then introduce corrections for each of the affecting parameters described in the preceding sections. Langelier[3] has given us a method for calculating calcium carbonate solubility in fresh water. Stiff and Davis[4] extended this work to permit similar calculations of solubility in brine solutions. Stiff,[5] Metler and Ostroff,[6] Carlbert and Matthews,[7] and others have derived procedures for use with calcium sulfate. Ostroff[8] has given a method for barium sulfate solubility calculations.

These calculations and the answers which they provide should be considered as guidelines only. Each of the calculations is based upon an analysis of the water or waters involved. Conditions at the time of analysis are rarely, if ever, the same as those in the water system. Even if the calculations were perfect in describing solubilities (and they are not), the result would only be indicative of solubility at the time of analysis. Consequently, these calculations should be used as guidelines rather than as absolute fact.

HOW CAN WE CONTROL SCALE?

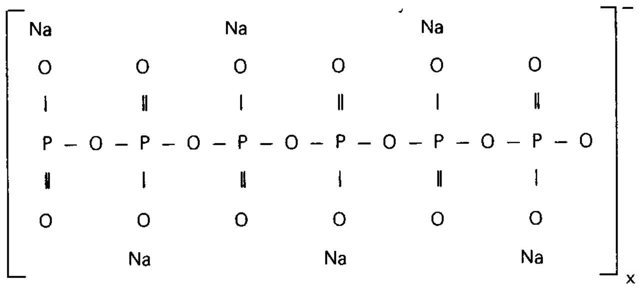
In concept at least, scale control is quite simple. This paper has described the factors which affect solubility of the different scale formers. All that is needed is to vary one or more of these parameters to insure that no scale is deposited. Sometimes this is practical. More often, though, it is impractical or even impossible. By removing all of the calcium from the water, there would be no calcium carbonate or sulfate deposits. Ion exchange water softeners are proof of the effectiveness of this treatment, but how can this be done in a producing well? As a second choice, something can be done which will interfere with precipitation of the crystalline scale materials; stabilize the condition of supersaturation. Such an approach is usually more practical than is attempting to alter the conditions directly affecting solubility. Scale control chemicals are commercially available for use to stabilize the condition of supersaturation. For the most part, they operate under threshold conditions; that is, very small quantities of chemical are able to control precipitation from considerable excesses of scale-forming ions. Basically, their action is one of adsorption on the microcrystalline nuclei to inhibit growth to full-fledged scale crystals. The effect is to stabilize the supersaturation. The reasons why they work this way are beyond the scope of this paper. Usually however, the effects can be seen under the microscope as a distortion of the minute crystals formed.

WHAT ARE THE CHEMICALS TO CONTROL SCALE BY THIS THRESHOLD ACTION?

Most of the scale-control chemicals are phosphorus compounds and are similar to the phosphates which have become a dirty word in the ecophile view of detergents. Several forms of these compounds are used.

Inorganic Polyphosphates

Poly means many, so polyphosphate means many phosphate bonds linked together. In sodium polyphosphate, the most common form, these bonds are joined in the following manner.



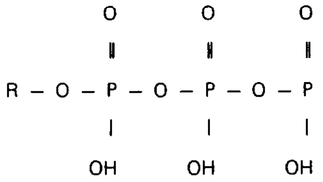
Note that the phosphorus bond is joined directly to the oxygen. In this way, long chains of oxygen-phosphorus linkages can be formed.

The solution rate of the polyphosphate molecule can be reduced by replacing all or part of the sodium ions with calcium, magnesium, or other ions which reduce the solubility of the basic phosphate compound. In this form, these chemicals are known as controlled solubility polyphosphates.

In a sense, the polyphosphates can be considered a first generation development. When polyphosphates are dissolved in water, there is a tendency for them to hydrolyze to the ortho-phosphate form, sometimes known as reversion. In the ortho-phosphate form, precipitation can take place with calcium ions. The rate of this reversion is increased by elevated temperatures and/or acidic conditions.

Organic Phosphate Esters

Organic chemicals are based upon a linkage of carbon atoms. Such a linkage can be of considerable complexity or contain only one or two carbon atoms. A typical organic phosphate ester compound sketched below shows this carbon linkage as an R. There is a distinct similarity in this molecule and the inorganic polyphosphate:

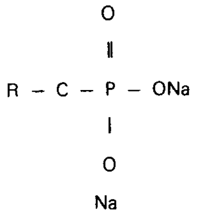


$$R-O-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}$$

Phosphate esters are generally more stable than are the polyphosphates; hence, they can be expected to withstand elevated temperatures and not revert to the ortho-phosphate state. However, phosphate esters may be incompatible with some brines and, in some formation squeezes, can produce emulsion blocks.

Organic Phosphonates

The phosphonate compounds, of which there are many, incorporate a carbon linkage attached directly to the phosphorus rather than through an oxygen atom:



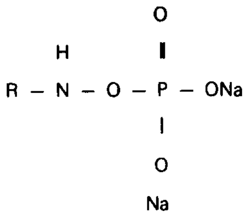
$$R-C-\underset{\underset{\underset{Na}{O}}{|}}{\overset{\overset{O}{\|}}{P}}-ONa$$

Because of their slightly different linkage, phosphonates have a high heat stability, excellent water solubility in high calcium waters, and do not seem to cause emulsion blocks on squeezing.

To summarize to this point, the inorganic polyphosphate is characterized by a P-O-P linkage, the phosphate ester by an R-O-P linkage, and the phosphonate linkage is R-C-P.

Organic Amino Phosphates

These materials are intended not only to provide scale control but also corrosion control. As with all organics, the hydrocarbon skeleton of the molecules can assume a variety of forms and links. The phosphate ester portion of this molecule will be the same as in the organic phosphate ester. In addition, there is a nitrogen-hydrogen linkage included in the molecule to enable it to serve a dual function of corrosion and scale prevention.



$$R-\overset{H}{N}-O-\underset{\underset{\underset{Na}{O}}{|}}{\overset{\overset{O}{|}}{P}}-ONa$$

Organic Polymers

Polymers are long-chain compounds composed of repeating groups. Polyacrylics are one form of polymer which can by used as a scale-control agent. These, too, are believed to work by an adsorption mechanism to prevent crystal growth. Since various polymers can function in this way, no characteristic grouping can be drawn.

EDTA Compounds

This class of scale-control agents is based upon the ethylene diamine tetraacetic acid molecule. These materials do not act by a threshold mechanism but rather by a chelating mechanism wherein one molecule of sequestrant reacts with one atom of calcium to form a soluble complex. In this way, the calcium is unable to combine with a carbonate or sulfate ion and precipitate. Treatment with EDTA compounds is quite limited in oilfield service because of the excessive quantities required. They are, however, used to dissolve calcium sulfate deposits.

WHY ARE THERE DIFFERENT SCALE-CONTROL CHEMICALS?

Each of these different types of compounds and even the individual compounds within a given type provide different characteristics which can be utilized in scale prevention treatment.

Inorganic polyphosphates for many years provided the chief means of scale control. These have now largely been superseded by the organic phosphate compounds. Inorganic controlled solubility phosphates, however, still fill a specific need where continuous treatment is required, but continuous injection cannot be provided. Caution is advised in the use of the inorganic polyphosphate because of the reversion characteristic.

The organic phosphate esters provide scale prevention approximately equal to the inorganic materials. In addition, these are in liquid form, thus simplifying handling and injection. They have no tendency to revert and are more stable at elevated temperatures. When used in a squeeze technique to place the chemical within the formation, there is some tendency to produce emulsion blocks, apparently due to incompatibilities between high concentrations of the organic phosphate and formation waters.

Phosphonates also have high heat stability and do not seem to cause emulsion blocks when squeezed.

HOW CAN WE USE CHEMICAL TREATMENT?

Basically, chemical treatment can be by one of three techniques: (1) continuous feed, (2) batch feed, and (3) squeeze.

Continuous Feed

Chemical is added constantly to the water. A liquid can be fed through an injection pump, or metered by means of a slowly soluble controlled solubility polyphosphate.

Batch Treatment

This is exactly what the name implies: chemical treatment introduced in a batch at regular intervals. This approach relies upon the adsorption of chemicals to the system at the time of treatment to the followed by a slow desorption to provide the necessary treating concentration.

Squeeze

When squeezing, liquid chemical is displaced into the formation to be adsorbed onto the formation surface. Subsequently, when the well is returned to production, flow of fluid past the adsorbed chemical causes it to slowly desorb into the stream to give the necessary treating concentration. Similar treatments can be carried out by displacing controlled solubility polyphosphate particles into a fractured formation where they will contact produced fluids, slowly dissolve and give the necessary treating concentrations.

In the squeeze procedure, chemical characteristics must be tailored for each application; that is, the solution rate of controlled solubility polyphosphates must be such that it will match the downhole temperatures. Also, liquid chemicals must be capable of adsorption and desorption from the formation surfaces.

Regardless of the treatment method used, treating chemical must be present in the solution at all times to effectively prevent scale deposition.

WHAT DO I ASK FOR; HOW DO I USE WHAT I GET?

Table 1 shows a number of available commerical chemicals arranged according to the type of formulation. The manufacturer's recommended method for use, whether it be continuous, batch, or squeeze, is shown as are the scale forms against which it can perform. As this table reveals, not all chemicals are suitable for use against all scale forms. Polymers, for instance, are best used against barium and calcium sulfate deposition.

Use concentrations to a great extent depend upon the active ingredient concentration in the chemical. Generally speaking, concentrations of 5 to 15 ppm should be used based upon water volumes. For calculating actual concentrations based upon ppm figures this rule of thumb can be quite handy: 1 ppm is equal to 0.35 lb/1000 bbl.

HOW CAN I BE SURE OF TREATING SUCCESS?

The answer to this is: No way. You can minimize your chances of failure by following these guidelines:

1. Select the chemical which has the desired characteristics, one which is recommended for use against your type of scale. Use it as recommended.
2. Select the chemical with proven success, either in your operations or other operations known to you. This is not always possible. Sometimes you will find it necessary to do your own field testing in order to find an appropriate chemical.
3. Be sure the chemical is compatible with other chemicals used in this system. Be sure the chemical is compatible with the water.
4. Be sure the chemical gets into the system. Are chemical pumps working? Are injection lines plugged? Are the chemical pots filled?
5. Be sure the chemical is distributed throughout the system. The majority of these chemicals can be determined in the water by analysis. In most cases, this information is provided by the chemical supplier. If the chemical is not distributed through the system, there is no way it can prevent scale. By analysis, you can learn if you are achieving effective concentrations where they are needed.

WHAT HAPPENS IF I DO GET SCALE?

Hopefully, this will not happen, but if it does, you will have two choices: live with it or get rid of it. Let's consider the latter. Simplest scales to remove are those composed of calcium carbonate. Calcium carbonate is readily soluble in acid. Hydrochloric acid is available from numerous sources and can be injected into the well by pump truck. Dry acids are also available which can be mixed with water and run into the well with much less equipment cost. We recommend that spent acid be removed from the well in order to prevent reprecipitation later.

Solution of gypsum is more involved. Gypsum is only slightly soluble in hydrochloric acid. Various scale converters or solvents for calcium sulfate (gypsum) are now commercially available, including the inorganic converting agents which are commonly carbonates and hydroxides.[9] These react with the gypsum to convert it to either calcium carbonate or calcium hydroxide which can, in turn, be removed by acidizing. Organic converters are also used, such as sodium citrate, potassium glycollate, and potassium acetate. These, too, are converters rather than solvents, but the reaction product frequently tends to slough from the surface to form a dispersion or pumpable sludge which can be circulated or swabbed from the system.

Solvent-type treatment using EDTA can also be used to dissolve the scale. Some of the commercial materials for such use are listed in Table 2.

Barium sulfate poses a unique problem in that it is only very slightly soluble and largely unaffected by the above-noted converters. Hence, barium sulfate deposits must usually be removed mechanically.

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TABLE 1—COMMERCIAL SCALE CONTROL CHEMICALS — PARTIAL LISTING

		SUGGESTED USE			SUITABLE TREATING METHOD		
Chemical Type	Chemical Name	Calcium Carbonate	Calcium Sulfate	Barium Sulfate	Batch	Squeeze	Continuous
Polyphosphate and Controlled Solubility Polyphosphate	Visco 27	X	X	X	X		X
	31	X	X	X	X		X
	40	X	X	X	X		X
	3701	X	X	X	X		X
	3705	X	X	X	X		X
	3708	X	X	X	X		X
	Calgon 15 RJ (Low Temp)	X	X	X	X		
	21 RJ (Low Temp)	X	X	X	X		
	37 P (High Temp)	X	X	X	X		
	Tretolite SP 1	X	X				X
	SP 142	X	X		X		
	SP 171	X	X		X		
	Baroid Surflo H-34	X	X	X			X
Organic Phosphonates	Visco 4DS-175	X	X		X	X	X
	Tretolite SP 181	X	X			X	X
	SP 188	X	X			X	
	SP 191	X	X		X	X	
	SP 203			X		X	X
	SP 223	X	X			X	X
	J&L Jetco Jetcote 92		X	X		X	X
	Jetcote 93 (Oil Soluble)		X	X		X	X
	Champion Gyptron T-27	X	X	X		X	X
	Calgon S-31	X	X	X		X	X
	S-71	X	X	X		X	X
	Baroid Surflo H-35	X	X	X	X	X	X
	Surflo H-351	X	X	X	X	X	X
	Surflo H-352	X	X	X	X	X	X
	Surflo H-353	X	X	X	X	X	X
	Surflo H-344	X	X	X	X	X	X

TABLE 1—COMMERCIAL SCALE CONTROL CHEMICALS — PARTIAL LISTING* Continued

		SUGGESTED USE			SUITABLE TREATING METHOD		
Chemical Type	Chemical Name	Calcium Car-bonate	Calcium Sulfate	Barium Sulfate	Batch	Squeeze	Contin-uous
Organic Phosphate Esters	Visco 935	X	X	X	X	X	X
	950	X	X	X	X	X	X
	951	X	X	X	X		X
	952	X	X	X	X		X
	953	X	X	X	X	X	X
	957	X	X	X	X	X	
	959	X	X	X	X	X	
	960	X	X	X	X	X	
	3749	X	X	X	X		X
	Tretolite SP-148	X	X			X	X
	SP 175	X	X			X	X
	SP 177	X	X			X	X
	SP 183 (Oil Soluble)	X	X			X	X
	SP 185	X	X			X	X
	SP 193	X	X				X
	SP 224	X	X			X	X
	J&L Jetco Jetcote 10)	X			X	X	X
	Jetcote 20) Oil Soluble	X			X	X	X
	Jetcote 40)	X			X	X	X
	Jetcote 60	X			X	X	X
	Jetcote 61	X			X	X	X
	Jetcote 90	X	X	X		X	X
	Champion Gyptron T-65	X	X	X			X
	Baroid Surflo H-395	X	X	X			X
Polymers	Visco 962	X	X		X	X	X
	Tretolite SP 178		X	X			X
	SP 180		X	X			X
	J&L Jetco Jetcote 80		X	X		X	X
	Arco Arcohib S-234	X	X	X	X	X	X
	Arcohib S-235	X	X	X	X	X	X
	Champion Gyptron T-50	X	X	X		X	X
	Cardinal Gyptrol 7	X	X	X		X	
	Gyptrol 8	X	X	X		X	
	Baroid Surflo H-381	X	X	X		X	X
Mixed Types	Tretolite SP 186 (Polymer-Phosphate Ester)			X		X	
	SP 205 (Polymer-Phosphate)	X	X	X			
	SP 219 (Phosphonate-Polymer-Ester)	X	X	X		X	X
	Champion Gyptron T-55 (Phosphonate-Polymer)	X	X	X		X	X
	Calgon S-61 (Phosphate-Phosphonate)	X	X	X		X	X
	S-91 (Organic Phosphate-Polymer)	X	X	X		X	X

TABLE 2—SCALE REMOVING CHEMICALS (PARTIAL LISTING)*

Name	Type	For
Visco 901	Organic Acid Salt	$CaSO_4$
Visco N-48-5	Organic Acid Salt	$CaSO_4$
Visco 900	Sulfamic Acid	$CaCO_3$
Tretolite SP 194	EDTA	$CaSO_4$
SP 221	Organic Acid Salt	$CaSO_4$
SP 170	Organic Acid Salt	$CaSO_4$
SP 29	Organic-Inorganic Acids	$CaSO_3$
SP 36	Organic Acids	$CaCO_3$
Calgon C-2	Organic Acid	$CaCO_3$
Cardinal Gypsol III	Organic Acid Salt	$CaSO_4$
Baroid Surflo H-392	Organic Acid Salt	$CaSO_4$

*This constitutes only a partial listing of available chemicals. The above information was supplied by the companies listed.