Chemical Control of Scale in Producing Wells and Lease Equipment

By BUZ CANON
United Chemical Corp. of New Mexico
Hobbs, New Mexico

Scale has been a major operating problem in producing wells practically as long as water has been produced along with oil and gas. At the present time, thousands of wells in the Permian Basin are being treated to combat this scale problem. The purpose of this paper is to acquaint the field operating personnel with some of the reasons why scale is formed, the chemicals which have been used in the past for scale treatment, and the chemicals which have been recently developed. Also, a good portion of the discussion is devoted to the results of the use of these newly developed chemicals. Because of the limitation of time, this paper does not include remedial type treatments such as acid treatment of carbonate scale, or acid and certain additives for treatment of sulfate scales. Possibly this subject can be covered at a later date.

Basic Theories of Scale Formation

For thousands of years, water was trapped in the oil bearing formations and became saturated under the extreme reservoir temperatures and pressures encountered. The pressures created by the earth's overburden ranged up to several thousand pounds and literally "squeezed" the available minerals from the rock into the water. Temperatures at the formation also increased the solubility of the water, but since by comparison, the temperatures were not as extreme as the pressures, this increased solubility was secondary to that caused by pressure. Wells were then drilled and production began to move this water along with the oil and gas to the well bore. Reservoir conditions were changed from their state of equilibrium and as the water moved into the well bore, casing, tubing, or pumping equipment, considerable pressure drops occured. This caused the super-saturated or overloaded water to drop out a hard scale. The scale deposit sometimes greatly retarded production and almost always interfered with normal producing operations. Too, on some leases, scale deposition did not occur until the fluid was moved into the surface lines and equipment. Scale deposits became apparent on other leases, only in the heaters or treaters where heat was applied. These variations in location on scale deposits are due to existing or changing conditions of temperature, pressure, and the composition of the water. Also, the fact that carbonates are more soluble in water at high temperatures, whereas sulfates are more soluble at low temperatures is important to where scale actually lays down.

The composition of scale in most Permian Basin production is usually found to be either of two general classifications: carbonate or sulfate. The carbonate type scale is acid soluble and is usually referred to as calcium carbonate because calcium (usually along with some magnesium) acts as the binding element. The sulfates (calcium sulfate, barium sulfate, etc.,) commonly called gyp, are more troublesome as they are not acid soluble. However, they can be fractured and removed by products later discussed in this paper. The governing factor, of course, over the type scale formed in various producing wells is the type producing formation and minerals found therein: carbonate scale from limestones, etc., and sulfate scale from pay zones containing anhydrite.

Past Chemical Treatment

Generally, the scale treating compounds which have been used during the past few years were either mild acid solutions or basic phosphate type chemicals. The mild acids; acetic, citric, etc., have been fairly effective on calcium carbonate scale but naturally do not have any effect on acid insoluble scales such as calcium sulfate. Some of these compounds have surfacing agents, wetting agents, etc., added to increase their effectiveness. A compound can be tested to determine if it is the mild acid type by adding some soda, sodium hydroxide, or calcium carbonate. If there is a bubbling or fizzing action, normal to acid deterioration, then it is an acid type compound. These materials are being used with satisfactory results in the Fullerton, TXL, and other fields where calcium carbonate scales are found. However, in the fields near Plains and Denver City, Texas, or others where sulfates are predominant, these compounds have not proved effective.

The most widely used treating compounds of the past (and still widely accepted today) are the phosphates. This material is usually in dry form, ready to mix with water for use. The principle of phosphate treatment is that it temporarily inhibits the precipitation of insoluble compounds and adsorbs on the surface of the growing crystal nuclei and prevents agglomeration. This is commonly referred to as the "threshold effect", as the prevention of precipitation only lasts from several minutes to several hours, depending on conditions. These materials, to be used with any degree of effectiveness, must be constantly added to the system and are not, at the concentration used, effective in dissolving or removing scale that has already been deposited. Too, it is possible for the phosphates to revert to common precipitating or tho-phosphate, laying down a coating of scale that is not soluble in acid and is extremely hard to remove. Several operators in the Eunice-Oil Center area used this type material for several years. The general result was that scale was found to still be present, but it was softer and easier to remove. Also, where without treatment, a treater or flowline had to be cleaned every 30 days, the phosphate treatment extended the maintenance period to 90 to 120 days. One operator in the Monument area is presently using phosphates with good results. The water being treated here has a very low hardness and excellent procedures for continuous treatment are being employed.

If used in sufficiently high concentrations, organic sequestering agents, such as ethylene-diamine-tetra-acetic-acid, could be used to dissolve most scale. However, the use of this material as a scale solvent is, except in very special cases, completely out of the question because of cost.

Development of Surface Active Chemicals

As recently as three years ago, there did not appear to be a single scale treating compound which was the answer to all types of scale. The mild acid compounds were effective on carbonates but not on sulfates. Phosphate materials required continuous injection and offered the distinct disadvantage of reverting to ortho-phosphate which could be detrimental.

About this time, experimentation was initiated on a new combination of materials. It has long been a fact that water is one of the best solvents known, and it was felt that there should be some compound which, when added to water, would overcome localized conditions and enable water to carry more hardness in solution and thereby "make the water work" in removing and preventing scale. The result of this development work is a new theory of treatment and a series of surface active compounds to combat scale. Also, patents have recently been issued covering this new composition and method of scale control. (Patent No. 2,777,818.)

The unique feature of these newly developed compounds

is that they are effective on both carbonate and sulfate scales. They are in liquid form and contain no acids or caustics and thereby are easy to handle and do not agitate corrosive conditions. Yet, they remove scale (sulfates included which are even acid insoluble) as well as prevent further deposition. The theory of the action of these compounds was prepared by Dr. John J. Singer after study of field results and considerable laboratory work. It can be explained as the "surface adsorbtion effect." That is, the compound, when added to water, adsorbs on the surface of the scale and begins to fracture it into minute particles. These particles stay in suspension and move out of the well bore with the fluid produced. If these particles are calcium sulfate, they will be dissolved and an increase in the hardness of the water will be observed. This is due to the fact that calcium sulfate becomes more soluble in water as temperatures decrease and, of course, temperature will be dropping as the fluid moves to the surface and through the flow lines. This increase in hardness has actually been recorded on many sulfate type treating problems at Oil Center, Fullerton Field, Wasson Field, etc. One well in the East Hobbs Field has been treated with several standard scale treating compounds without success. Production was down and operating costs were such that the well was about to be abandoned. As a last resort, treatment with the surface active compound was started. The hardness of the water began a steady increase from 100 grains/gal. and levelled off at about 250 grains/gal., definitely indicating that scale was being removed. After four months treatment, the well was producing 65 BOPD and, now, after over two years, is still producing about 40 BOPD. In the case of calcium carbonate scale, the same breaking up of the structure occurs but, since carbonates are considerably less soluble in water than sulfates, most of the particles remain in suspension rather than being dissolved by the water. No increase in water hardness is normally apparent. At the same time, this surface adsorption effect is removing deposited scale, the water is being treated to tie up the contained hardness to prevent further scale deposition. The several materials in the compound prevent growth of crystal nuclei and act as suspending agents to prevent precipitation as well as cause the initial fracturing of the scale.

The many advantages of these surface active compounds for combating scale are readily apparent and include:

1. No longer essential to treat continuously as scale can be removed as well as prevented.
2. One single product to work on all types of scale. Only the amount of treatment need be changed from well to well. This reduces stocking requirements and complications of handling.
3. Not harmful to employees handling material, as no acids or caustics are present.
4. No corrosion acceleration since some corrosion inhibition possible.
5. Production increases possible where treatment removes scale from formation face and bottom hole equipment.
6. Economical to use. Chemical costs are usually comparable with other treating compounds. Overall maintenance costs greatly reduced due to treatment.

At the present time, a large percentage of the scale in the Permian Basin producing wells and lease equipment are being treated with these surface active compounds. They are being applied in batch-large volume water treatments, with simple lubricators, and chemical injection pumps. A general description of the results of these treatments for various applications is as follows.

Large Volume Water Treatment

Experience has shown that, on wells that produce a small percentage of water (trace to 5%), sufficient water must be added along with the chemical to effect removal of the scale. In the Welch, Prentice, Spraberry and Wasson Fields, regular treatments at 7, 15, or 30 day intervals, using 1 gallon of the surface active compound to each 10 barrels of water injected, have resulted in considerable savings in well service work due to scale. Also, in most cases, there are also an increase in production since a sufficient volume of treatment was added to reach into the formation. One operator in the Prentice field reported that treatment of several wells at regular 15 day intervals resulted in 200 BPD increase. Several operators in the Spraberry area have brought wells making 15 BPD or less up to 30 BPD (one particular well came up to 140 BPD - and is still holding up) with single 100 barrel water treatments containing 1 gallon of chemical per 10 barrels of water.

It should be pointed out here that for many years, wells have been treated with fresh water to remove salt deposits and this water may have also removed a slight amount of scale. However, the main body of the scale (which was water insoluble and in some cases even acid insoluble) continued to build up and the operator eventually was in trouble as neither water nor acid would remove this deposit. The addition of only a small amount of these surface active compounds (1 gallon to each 10 barrels of water) will prevent this from happening and will result in obtaining several times the amount of work possible using only fresh water and will enable a more complete removal of salt and scale.

Lubricators

Lubricators are being employed on most pumping wells being treated for scale. A lubricator, of course, refers to any type of vessel used for injecting a volume of chemical solution into the casing-tubing annulus under pressure. A few common names are boll-weevil lubricators, logs, pressure pots, etc. Most lubricators afford a batch type treatment where the chemical solution runs into the annulus in a few minutes. Others are fixed with pressure equalizing lines and a needle valve so that continuous feed may be maintained. The batch type treatment is satisfactory on most pumping wells except those where the fluid level is at the pump. These type wells require more continuous feed to obtain good results.

The surface active chemicals being lubricated into pumping wells are usually either mixed with water or flushed down with produced fluid. Adequate treatment with this method has eliminated scale on tubing and in bottom hole pumps and in several cases removed scale from the face of the formation and resulted in a production increase. At the same time, scale in flow lines, manifolds, and treating equipment was also removed and prevented.

Several pumping wells on a lease in Apco-Warner field were being treated once per day through a lubricator. Shortly after treatment started, the wells began to flow. Also, before treatment, valves in the manifold had to be turned at least once per day with a twenty-four inch wrench or they could not be turned at all. Treatment cleaned up these wells and surface equipment and eliminated periodic maintenance expense. A well near Oil Center, N.M. had to be pulled at regular 2 month intervals due to barium sulfate scale on the pump. Lubrication of treatment into this well daily has reduced pulling jobs only to when the pump is worn through normal operation. Also, analysis of the produced water showed an increase in the barium content of over 40% after treatment, indicating that barium sulfate scale was definitely being picked up. These are but two of several hundred similar cases.

Chemical Injector Pumps

Chemical pumps are employed where continuous injection is required such as in gas lift wells and lease treating equipment or in cases where high casing pressures make lubricators unsafe.

Many gas lift wells are being successfully treated with the

surface active compounds by feeding them continuously into the input gas stream. The tubing has been kept clean and the valves prevented from becoming inoperative due to scale deposits. Naturally, with less restriction to flow through tubing and good valve operation production was maintained and pulling jobs to replace scaled up valves were eliminated. Treatment of one particular gas lift well increased production from 70 BOPD to 100 BOPD while producing over 1,000 BWPD.

A lease near Hobbs, N.M. had a heater-treater which was being pulled every 30 days to remove 2-in. or more of scale from the fire tube. A chemical pump was set to continuously put treatment into the manifold up-stream of the treater. Three 30-day inspections were made after treatment and each time only a few gallons of sloughed off scale were found. The 30-day inspections were discontinued and scale free operation has been maintained. Many other successes are on record where proper treatment with the surface active compounds has eliminated well pulling, fire tube failures, and clean outs due to scale, dump valve sticking, and plugged water lines.

In summary, it is widely recognized that scale is a major problem in producing operations and can result in considerable well servicing expense, lease maintenance work, and lost production. However, there are available chemicals which can eliminate scale deposits - even the very troublesome calcium sulfate or gyp - at a very economical cost. There is no longer any reason why scale should be troublesome to an operator!