Secondary Recovery Stimulation Techniques and Chemicals

J. R. RUCKER and H. R. BRISCOE
Dowell Division of the Dow Chemical Company

INTRODUCTION

Waterflooding is the most commonly used secondary recovery technique. Its use has grown rapidly and there are currently waterflood projects underway in nearly all oil-producing areas. Since waterflooding involves the injection of large quantities of water into underground formations, many problems are encountered which are not normally associated with producing wells. Until the past few years some of these problems were not correctly diagnosed and methods of maintaining or increasing injectivity were limited to conventional acidizing and hydraulic fracturing techniques. Within the past three or four years, however, stimulation techniques have been developed primarily for problems related directly to water injection wells. Two of these new injection well stimulation methods have been widely used and have proved highly successful. The first of these removes permeability damage caused by bacterial activity. The second increases relative permeability of the formation to water by removing much of the residual oil saturation from the formation near the wellbore of the injection well.

BACTERIAL DAMAGE

Bacterial activity can result in the creation of large amounts of organic material and tremendous loss in wellbore permeability. The primary contributing factor involved with bacterial problems is the rate at which microorganisms can reproduce. With the right conditions of temperature, nutrient availability and environment, bacteria can create as many as 96 generations in 24 hours. Such activity can completely plug-off a wellbore with organic residue. In addition to causing permeability problems, bacteria indirectly can induce severe corrosion problems. To relate in specific terms the relationship between bacteria and permeability damage, consider the size of the majority of pores in a typical sandstone. A conservative estimate is that 85 per cent of the pores in a sandstone have a diameter of less than five microns. The size of the most common bacteria is of the same order. Sulfate-reducing bacteria have a diameter of about one micron and a length of about three to five microns. Many other types of the aerobic variety are as long as 15 to 25 microns. In fact, due to their size and tremendous number, bacteria are literally filtered onto the face of a wellbore. Bacterial plugging occurs not only on the face of the formation but also within the matrix of the rock.[1,2] Although there is some disagreement as to the maximum depth of penetration, studies[2] have shown that live bacteria may migrate within cores at a rate of up to 1½ in. per day. There is evidence of extensive formation penetration by bacteria in both producing and gas storage wells. The large amount of hydrogen sulfide produced by some gas wells, which earlier had produced none, indicates infection of the formation by sulfate-reducing bacteria. Although bacterial plugging is a well-recognized phenomenon, it has seldom been taken into consideration when designing stimulation treatments for water-injection wells. Acidizing will usually increase injectivity of wells damaged by bacteria; but only partial restoration of the original permeability is obtained. In core test studies carried out by Kalish, et al,[1] various procedures were used in an attempt to restore permeability to cores damaged by bacteria. Of the techniques studied, acidizing followed by reverse flow provided the best results. This treatment, however, resulted in recovery of only 20 to 65 per cent of the original permeability. His examination of bacteria exposed to hydrochloric acid showed that the individual cells tended to disperse and shrink; however, they did not actually dissolve. Cerini[3] also studied methods of dissolving bacterial residue. He found that this type material was not soluble in hot hydrochloric acid, but was dissolved by boiling sodium hydroxide or oxidizing solutions such as aqua regia and boiling mixtures of sulfuric and chromic acids.

When the nature of the material responsible for injection-well plugging is taken into consideration, it becomes evident that a need exists for a stimulation treatment capable of dissolving both organic and inorganic plugging residue. In answer to this problem, a two-stage treatment employing an oxidizing stage to remove bacterial depqsits and an acid stage to dissolve the remaining inorganic material has been developed.[4]

In developing the oxidizer stage of this treatment, various oxidizing agents were examined for possible use. Sodium hypochlorite was found to be far more effective in dissolving bacterial residues than any of the agents tested. Unfortunately, solutions of this mixture were extremely corrosive to steel and caused deep pitting of the metal surface. However, an inhibitor was found which reduced corrosion to acceptable rates and eliminated pitting.

Figures 1 and 2 show the results of two series of tests made with sodium hypochlorite to improve the permeability of cores damaged by bacterial residues. The residue used in these tests was recovered from the treating plant of a waterflood near Bartlesville, Oklahoma, and was predominantly organic in nature. Cores were damaged by injecting into them a brine solution containing a dispersion of the bacterial deposit. In the test series shown in Fig. 1, the core was first damaged and then treated with sodium hypochlorite. This treatment produced a significant increase in permeability; however, only about 34 per cent of the original permeability was recovered. The core was next treated with 15 per cent hydrochloric acid which resulted in a further increase in the permeability. Following the two-stage treatment, about 85 per cent of the original permeability was restored. Since these were sandstone cores, permeability increase from hydrochloric acid injection was not expected; Berea sandstone has a solubility of less than 15 per cent in 15 per cent hydrochloric acid.

In the core test series shown in Fig. 2, a core damaged by the same bacterial residue was treated with acid. The acid treatment

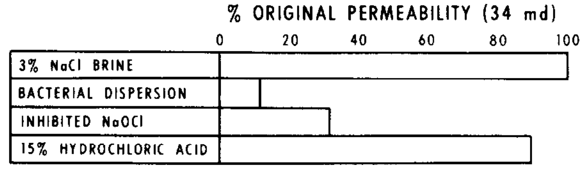

FIGURE 1
Treatment of Berea Sandstone Core to Remove Permeability Damage Resulting from Injection of Bacterial Residue

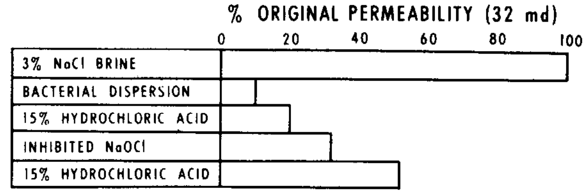

FIGURE 2
Treatment of Berea Sandstone Core to Remove Permeability Damage Resulting from Injection of Bacterial Residue

failed to increase permeability. Following this treatment, sodium hypochlorite was injected into the core. Although this caused a three-fold increase in permeability, only about 11 per cent of the original permeability was recovered. This illustrates the necessity of preceding the acid stage with an oxidizing treatment.

The importance of the acid stage, however, cannot be overemphasized. Although the oxidizer disintegrates and dissolves the organic portion of the plugging material, it has essentially no effect on the inorganic residue. Only limited improvement in injectivity can be obtained with the oxidizer alone. The acid then dissolves the inorganic portion of the plugging material. The acid also has one other important function; it neutralizes the basic sodium hypochlorite solution and prevents precipitation of calcium salts often found in formation water.

Treating Technique

Analyses of injection pressure data from oxidizer-acid treatments indicate that a minimum contact time of 45 minutes should normally be provided between the oxidizing solution and the treated zone. Since a typical treatment employs 25-50 gallons of oxidizer per foot of treated interval, the solution is normally injected in five equal stages with a 15-minute pause between stages. The oxidizing solution is followed by a water spacer and then by a quantity of 15 per cent hydrochloric acid equal in volume to that of the oxidizing solution. All materials are injected at a low pump

TABLE 1

Case Histories

Date	Treatment	Injection Rate Before Treatment	Injection Rate After Treatment	Remarks
		Aux Vases Sand, Wayne County, Illinois		
1964	Put on injection	---	670 BWPD @ 700 psi	Declined in 3 months to 348 BWPD @ 700 psi
July, 1966	Fractured with 5000 gal water, 8000 lbs sand	12 BWPD @ 1100 psi	450 BWPD @ 1100 psi	4 months later well down to 150 BWPD @ 1100 psi
July, 1967	750 gal NaOCl, 750 gal 15% hydrochloric acid	7 BWPD @ 1100 psi	789 BWPD @ 450 psi	
Three months following treatment well taking 376 BWPD				
		McClosky Lime, Wayne County, Illinois		
Jan., 1967	1000 gal 15% hydrochloric acid	135 BWPD @ 1400 psi	395 BWPD @ 1500 psi	
July, 1967	1000 gal NaOCl, 1000 gal hydrochloric acid	325 BWPD @ 1510 psi	600 BWPD @ 1450 psi	
Three months following treatment well taking 492 BWPD at 1450 psi				
		Kirkwood Sand, Lawrence County, Illinois		
April, 1965	600 gal 15% hydrochloric acid	39 BWPD @ 780 psi	122 BWPD @ 600 psi	Rate declined rapidly following treatment
July, 1966	500 gal 15% hydrochloric acid	55 BWPD @ 920 psi	119 BWPD @ 900 psi	Rapid decline
April, 1967	100 gal NaOCl, 700 gal 15% hydrochloric acid	55 BWPD @ 950 psi	261 BWPD @ 500 psi	No decline
Six months following treatment well taking 283 BWPD @ 500 psi				
		McClosky Lime, Wayne County, Illinois		
Sept., 1966	1000 gal 15% hydrochloric acid	12 BWPD @ 1000 psi	395 BWPD @ 900 psi	Declined to 44 BWPD in three months
July, 1967	750 gal NaOCl, 750 gal 15% hydrochloric acid	15 BWPD @ 1000 psi	720 BWPD @ 50 psi	
Three months following treatment well taking 513 BWPD				

rate and at a pressure below that required to fracture the formation.

Original field tests with oxidizer-acid treatments were carried out in the Illinois Basin. Since that time, the technique has been used widely in many waterflood areas. Field results indicate that this treatment often increases injectivity to a higher level than is obtained with other methods. Furthermore, slower rates of decline in injectivity have been observed. Typical results are shown in Table 1.

RESIDUAL OIL SATURATION

Another problem inherent with waterflooding or applying optimum injection rates is residual oil. Since waterflooding is obviously performed in oil-bearing formations, two-phase flow becomes a problem. The relative permeability to water in an oil-bearing core is limited to about 40 per cent of the absolute permeability to water, the absolute permeability to water being that permeability obtained if the porous media were saturated with water. If water is flowed through a core containing oil, the water saturation will increase until it reaches about 70 per cent. Because of the poor mobility ratio of water to oil, there will remain a 30 per cent saturation of residual oil. This amount of residual oil restricts the effective permeability to water. By removing 100 per cent of the residual oil within a 10-foot radius of the wellbore, the effective water permeability can be increased by a factor of two or three. This can be accomplished by utilizing a micellar dispersion especially designed for use in injection wells.[5]

In order to see how 100 per cent of the residual oil can be removed, a discussion of micellar dispersions is needed. The type of micellar dispersion used in injection wellbores is the water or brine innerphase variety. The innerphase is in the form of a micellar which has a diameter of four microns. A refined hydrocarbon is used for the outerphase. The type of micellar dispersion used in injection wells is miscible in either oil or water. As the micellar dispersion is pumped into the wellbore, a favorable mobility ratio allows it to contact all of the porosity available. The residual oil and the refined hydrocarbon mix on contact. The water that is contacted is taken into the micelles of water or brine until the small four micron droplets (micelles) expand to the point that they burst. At this point, the micellar dispersion inverts and becomes a water or brine outside phase with the hydrocarbons being carried on the inside. In this manner, an almost complete removal of residual oil and considerable increase in water permeability is obtained.

Figure 3 is a graph with relative permeability to water and oil curves plotted for the Bartlesville Sand in Oklahoma. The solid black lines are where actual values were plotted. The dotted lines were extrapolated to show what the relative permeabilities would be if varying percentages of residual oil (irreducible oil saturation) could be removed. When all the oil (100%) is removed, the relative permeability to water becomes 1.0 or equivalent to absolute permeability (single-phase flow). Various solvents are capable of removing oil in the range indicated by the solid lines. Only the micellar dispersions, however, are capable of removing residual oil in the range indicated by the dotted lines.

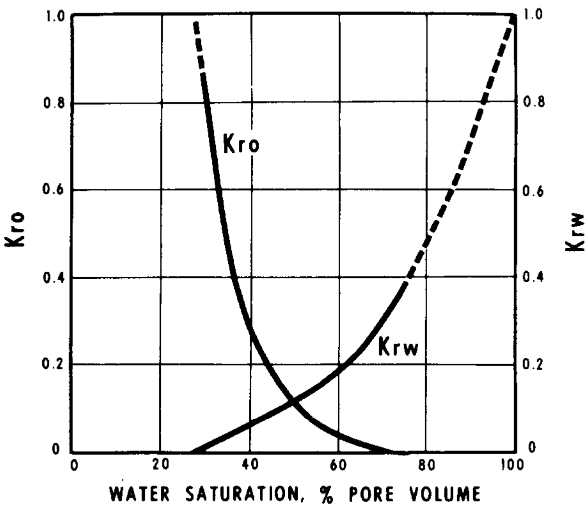

FIGURE 3

Relative Permeability to Oil and Water at Various Water Saturation Levels of Bartlesville Sandstone Core

Treating Techniques

Micellar dispersions are normally used for the following purposes:

1. To convert producing wells to injection wells
2. To condition newly drilled wells for water injection

3. To remove damage caused by oil carry-over in produced injection water

In treating injection wells with micellar dispersions, quantities used vary from three to ten barrels of material for each foot of interval treated. The value, three bbl/ft, represents one pore volume of 15 per cent porosity for a six-foot radial distance from the wellbore. These are average figures for most sandstone wells. Formations having higher porosities will require greater volumes. In no case, however, are less than three bbl/ft recommended.

Micellar dispersions are injected at low pump rates and pressures less than those required to fracture the formation. Injection water is used as flush. Wells should not be back-flowed following treatment since this will allow formation oil to encroach back into the treated critical area surrounding the wellbore.

TABLE 2

Field Results of Micellar Dispersion Treatments in West Texas Area

Job Date	Formation	BWPD Injection Before	BWPD Injection After	Later Date/BWPD
3/3	Queen Sand	30	100	4/14/70-158
3/5	Queen Sand	44	143	4/14/70-177
4/17	Queen Sand	60	280	9/1/70-240
5/18	Greyburg	63	265	6/19/70-125
6/3	Greyburg	200	60	9/1/70-300 (pinched in)
6/16	San Andres	Producing	550 (pinched)	9/1/70-550 780 psi Holding 330
6/17	San Andres	Producing	---	9/1/70 - channeled
9/3	Eumont	125	---	9/25/70-300
9/3	Eumont	85	---	9/25/70-200
9/4	Eumont	55	---	9/25/70-250
9/28	Queen	0	97	
8/13	San Andres	Producing vacuum		9/28/70-600 400 psi No more water now

Field Results

Micellar dispersions have been used successfully to stimulate injection wells in nearly all waterflood areas. Typical results in the West Texas area are shown in Table 2.

An analysis of results from several areas leads to pertinent conclusions regarding micellar dispersions[6]:

1. They are not normally successful in limestone formations.
2. Injectivity increases often are greater than theoretically possible. This indicates that a secondary benefit of these materials is the removal of skin damage.
3. Low permeability sandstones sometimes will not accept the fluid at allowable pressures. This is believed to be due to the viscosity of the fluid. New, lower-viscosity dispersions now available may solve this problem.

CONCLUSION

New stimulation techniques developed primarily for water injection wells have solved many of the problems inherent in waterflooding operations. These techniques have proved successful in nearly all waterflood areas. Their use should be limited, however, to wells where an analysis of well conditions shows the problem to be one that can be solved by the application of these techniques.

REFERENCES

1. Kalish, P. J., Steward, J. A., Rogers, W. F. and Bennett, E. O.: The Effect of Bacteria on Sandstone Permeability, *Jour. Petr. Tech.* (July, 1964) 805-814
2. Myers, G. E. and Samiroden, W. D.: Bacterial Penetration in Petroliferous Rocks, *Producers Monthly* (April, 1967) 22-25
3. Cerini, W. F., Battles, W. R. and Jones, P. H.: Some Factors Influencing the Plugging Characteristics of an Oil Well Injection Water, *Petr. Tech.* 9, No. 3, T. P. 2028 of AIME, (1946)

4. Crowe, C. W.: New Treating Technique Removes Bacterial Residues from Water-Injection Wells, presented at the Spring Meeting of Mid-Continent District, API Division of Production, Amarillo, Texas, April 3-5, 1968
5. Gogarty, W. B., Kinney, W. L., and Kirk, W. B.: Injection Well Stimulation with Micellar Solutions, presented at SPE of AIME, Rocky Mountain Regional Meeting, Denver, Colorado (1969)
6. Moran, J. P. and Maxwell, W. J.: Field Results of Injection Well Stimulation Treatments Using Micellar Dispersions, presented at SPE of AIME Spring Symposium, Fort Worth, Texas (1970)