A NEW TREATING TECHNIQUE TO RECOVER INJECTIVITY IN INJECTION WELLS DAMAGED BY POLYMER DEPOSITION

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ABSTRACT

A new treating method has been designed for use in wells in which injectivity has been decreased by deposition of polymer residue incurred in polyacrylamide polymer and copolymer treatments. This treatment consists of one or two stages: an oxidizer stage followed by an acid stage, or a combined acid-oxidizer stage. This treatment is effective against polyacrylamide polymer and copolymer deposits near the wellbore that will not respond to conventional treatments.

It is known that polymer injection can gradually lead to a decrease in injectivity. This injectivity decrease can be due to incompletely dissolved solid polymer, improperly inverted emulsion polymer, and/or deposition and adsorption on the rock face. These blockages can contain inorganic as well as organic components. An acidizing treatment is necessary for the inorganics while an oxidizer treatment is necessary to treat the organic constituent. The new treatment method consists of a strong oxidizer that is acid compatible. The pH of the oxidizer stage can be adjusted to suit the need of a given well. The pH adjustment can also control the release rate of the oxidizer.

These solutions are mildly corrosive to steel. The oxidizer and acid can be split into two stages if the mixture proves to be too corrosive, or if a stronger acid is desired. These treatments have been effective without the acid stage in polymer injection wells.

Laboratory data and preliminary well treatment results are presented to show the effectiveness of the oxidizer alone and with acid.

INTRODUCTION

The success of any injection project depends on the maintenance of good effective permeability whether it is waste disposal, reservoir pressure maintenance, chemical flood, polymer flood, or other applications. The loss of injectivity can be due to insoluble solids in injected fluids, precipitation generated by temperature or chemical changes, flocculated submicron particles, bacterial byproducts such as hydrogen sulfide and slime, poor quality polymer, and/or incorrect handling procedures.

The best solution for injectivity loss is prevention. Solids in the injected fluids can be controlled by good filtration techniques. Precipitation of solids such as iron sulfide or calcium sulfate can usually be prevented by careful engineering and operation control. Excessive oil carryover and paraffin deposition can cause injection problems. Remedial treatments for removing this type injectivity damage with hot oil, heat, or solvents can sometimes be avoided or reduced by judicial use of inhibitors or better control of separation facilities. Acid treatments are used to repair injectivity damage due to materials which are soluble or degradable in acid.

Water and polymer flooding operations are often plagued with injectivity problems. Bacteria are often present in these operations and their byproducts such as slime and hydrogen sulfide cause persistant problems. Regular monitoring and a good biocide program can prevent this problem. Once a project has been infested with bacteria, well cleanup is frequently required.

Polyacrylamides are the most common polymers used in EOR projects. Polyacrylamides are generally supplied as either emulsions or solids. An emulsion is a stable suspension of small droplets of concentrated polymer solution in an oil phase. To use this type polymer, the continuous oil phase must be broken (inverted) to release the polymer into the injection water. Partially or poorly inverted emulsion polymer is a major contribution to injectivity damage. The mechanics of completely dissolving a solid polymer are very important. Any undissolved or partially dissolved polymer can cause severe loss of injectivity. In either of these cases, a filtrate skin builds on the formation face which severely limits injectivity. Physical examination of this type filtrate reveals a tough, leathery composition which is resistant to chemical attack except by strong oxidizers.

Submicron solids can be floculated by polyacrylamides. This is not surprising since this is one of the predominate uses of polyacrylamides. The efficiency and effectiveness of the filtration system is very important as is the total undissolved solids which can not be removed by filtration.

Removal of injectivity damage caused by polymers and/or bacterial byproducts is normally attempted with acid or oxidizer treatments. The oxidizer most widely used is bleach (sodium hypochlorite). Bleach has been very effective in removing damage due to polymers.[1,2] Bleach treatments are normally performed at a very high pH to reduce corrosion, however some formations and/or injection waters are not compatible with this high pH fluid. Under normal circumstances, bleach treatments are safe to run with proper handling and procedures. It is important however to know that the reaction of bleach and a strong acid can release chlorine gas.

The mixed composition of flocculated solids consisting of both polymer and inorganic components is more difficult to treat than either of these individually. The oxidizer can attack the polymer it contacts but has little effect upon most inorganics. Acid can dissolve many inorganics but may have little effect on the polymer. Treatment with both acid and oxidizer enhances the probability that injectivity damage can be removed.

This paper describes a new process by which a strong oxidative compound (sodium perborate) is either applied alone or with acid to successfully repair injection damage.[3] Advantages of the system include (1) a slow release mechanism of the oxidizer, (2) broad useful pH range, (3) greater temperature range, and (4) improved safety.

CHEMISTRY

There are two types of oxidizers commonly used in injection well cleanup treatments. These are the hypohalites and the peroxygens. Sodium hypochlorite (ordinary laundry bleach) is the most common example of a hypohalite. It has been widely used to reduce injectivity losses due to bacterial slimes and/or other polymer blockages. It is readily available, and under normal conditions is fairly easy and safe to use if proper procedures are followed. However, it is highly corrosive to steel and is normally used at pH 13-14 in order to minimize the corrosion rate. Many formations cannot tolerate such high pH fluids and therefore limit its use. In addition to increased corrosion rates, gaseous chlorine can be liberated when used at a low pH, which can be dangerous owing to the toxicity of chlorine.

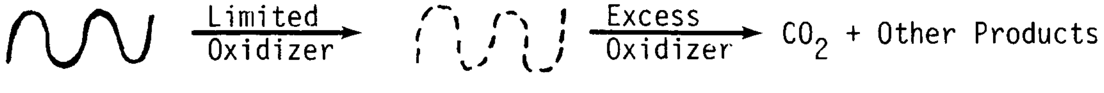
Although there are many peroxygens used in the laboratory, until recently the only peroxygen compound available in the field was hydrogen peroxide. This material is reasonably safe to handle at low concentrations (less than 10%); at high concentrations, much consideration must be given to its storage, handling, and use. Hydrogen peroxide also can give off a gaseous product, oxygen, upon acidification. Although it is molecular oxygen and non-toxic, it is sometimes hazardous. Hydrogen peroxide generally has lower corrosion rates on steel than does sodium hypochlorite and is normally used at a lower pH. However, dissolved iron catalyzes the decomposition of the peroxide and its conversion to molecular oxygen. For this reason, it is important to determine the amount of iron and/or metal ions present in the treating system. Under certain conditions, much of the activity of hydrogen peroxide can be lost due to this metal-ion catalysis. Therefore the hydrogen peroxide can be consumed in the tubing before contacting the blockage.

All peroxygen compounds are fairly unstable materials. They undergo a homolytic reaction generalized below to form oxide free radicals. These radicals are generally short-lived, highly energetic species which will react with even weak reducing agents. This homolytic cleavage type reaction shown below, is dependent only on the temperature when in simple solution. It is common to express the activity of these materials in half-lives at a temperature which permits selection of the best peroxygen for an application. There are many materials which can serve as catalyst for the homolytic cleavage of peroxide such as amines, transition metal salts, etc. Since most peroxygens are strong oxidizers, they are consumed by even mild reducing agents such as steel, sulfides, organics and the like. To design a well cleanup treatment with these materials, one needs to allow for some loss of oxidizer due to non-plugging contaminantes.

$$\mathrm{RO\text{-}OR} \xrightarrow[\text{heat}]{} 2\ \mathrm{RO.}$$

HOMOLYTIC CLEAVAGE OF A PEROXYGEN COMPOUND

The formation of the free radical is the first step in the oxidative degradation of polymers. This radical is thought to attach the polymer randomly causing breaking of the backbone via a very complex mechanism. It is important to note that the rate of polymer degradation is dependent on the concentration of radical ions and the polymer concentration. Under proper conditions, polymer can be completely oxidized to carbon dioxide. This is not necessary however, to achieve well cleanup. The breaking of the polymer backbone at a few random sites generally reduces the viscosity of the polymer sufficiently to allow well cleanup as depicted below.



POLYMER DEGRADATION VIA OXIDIZER

Sodium perborate is a relatively stable peroxygen when kept below 120°F. It requires a higher temperature to achieve homolytic cleavage to form radicals than hydrogen peroxide. This makes sodium perborate more suitable for use at higher temperatures where a slow release of radicals is desirable. It also tolerates acid quite well, therefore combinations of oxidizer and acid for well cleanup fluids can be formulated. Catalysis of the homolytic cleavage reaction can be achieved, resulting in effectiveness even at low temperatures.

While the hypohalites do not undergo the homolytic cleavage reaction to generate free halogen radicals, they do form free radicals by a similar mechanism. These radicals, like the oxide radicals, are short-lived, energetic species.

Effectiveness of sodium perborate and hydrogen peroxide in the degradation of polymers was investigated. A test was designed to give comparative data in a reasonably short time. It was performed by placing a five gram sample of a polymer gel in a six ounce jar and covering it with 100 grams of treatment fluid. This jar was sealed and placed in a temperature bath in order to maintain a constant temperature. It was observed visually on a regular basis to determine a qualitative degradation rate. When only a trace of material was remaining, it was reported as degraded.

The polymer chosen for use in this test was polyacrylamide since most of the reported injection problems involved this material. It is generally more difficult to oxidize than polysaccaharides and could be easily reproduced. A high molecular weight polymer was obtained by the polymerization of 4% acrylamide solution which resulted in a shape sustaining gel. Care was taken in obtaining the five gram samples which were used in the test to ensure that similar surface areas were achieved since degradation rate may also be dependent on surface contacted with the treating solution.

Results shown in Table 1 demonstrate that polymer degradation at 24 hours with sodium perborate is affected little by variations in pH. This observation promoted the evaluation of selected carboxylic acids in conjunction with the perborate. These results are shown in Table 2 and indicate that simple carboxylic acids can be used with sodium perborate without significant affect on the treatment oxidative properties. It was thought that some improvement in the solubilities of certain inorganic salts might be achieved by using selected organic acids.

The effect of several possible additives on polymer degradation rate with sodium perborate treatment was determined. Some of these are presented in Table 3. Perusal of this data reveals that the polymer degradation rate can be either accelerated or inhibited.

The corrosivity of sodium perborate and sodium perborate/acetic acid treating solutions without corrosion inhibitors on steel was determined at 70 and 170°F. These are shown in Table 4.

ENGINEERING

Three considerations in designing a well cleanup treatment are temperature, formation type, and blockage type. The temperature of an injection well can limit the choice of an oxidizer. The normal cutoff temperature for hydrogen peroxide is about 120°F. Sodium perborate and bleach can both be used above 120°F. However some formations are not stable to high pH treating fluids therefore excluding the use of bleach. Blockages composed of mainly organics can be treated with just an oxidizer solution, however if significant quantities of inorganics are present a treatment sequence including an acid stage should be considered. These considerations usually limit the choice to one or two systems. The final element to determine is the desired depth of treatment penetration. Treatments are normally designed to treat a maximum of 3 to 5 ft radially into the formation because it is believed that the damage is a near wellbore phenomena.

Sodium perborate and sodium perborate/acid jobs are very simple to perform. Low corrosivity of the solutions allow the materials to be handled using conventional methods. The jobs are performed with conventional mixing and pumping equipment.

CASE HISTORY

A Louisiana emulsion polyacrylamide injection well with 170°F bottomhole temperature developed severe injectivity problems. A treatment with hydrogen peroxide followed by 15% hydrochloric acid did not remedy the damage. The damage was determined to be polyacrylamide mixed with iron and clay particles. The treatment was designed to dissolve the iron and clay particles and then degrade the polyacrylamide. It was suspected that much of the hydrogen peroxide was spent before it reached the zone to be treated. Sodium perborate was selected as the oxidizer due to its higher thermal stability. The treatment consisted of 3000 gal 15% hydrochloric acid, 1500 gal hydrofluoric acid, 2000 gal spacer, 10,000 gal 5% sodium perborate, and 2000 gal overflush. The well was shut-in for 12 hours. The well responded by increasing to 90% of the original injectivity.

CONCLUSIONS

Sodium perborate has been found to be an effective oxidizer for performing wellbore cleanup treatments. It is suitable for use over a broad pH range, and it has been found to be superior to other oxidants, particularly at temperatures greater than 140°F.

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Table 1
Effect of pH on Rate of Polymer[d] Removal by Sodium Perborate

Treatment pH[a]	Treatment	Polymer Degradation in 24 Hours (%)
10.2	4% Sodium Perborate[c]	100[b]
6.0	4% Sodium Perborate	100
4.0	4% Sodium Perborate	98

a. pH adjusted by addition of 10% NaOH or 10% HCl.
b. Polymer was gone in 2 hours.
c. Tetrahydrate form was used.
d. A 4% active polyacrylamide gel was used.

Table 2
Effect of Selected Organic Acids on Polymer[a] Degradation in 4% Sodium Perborate Solution

Treatment pH	Organic Acid[b]	Polymer Degradation (%)	
		6 hour	24 hour
3.0	Formic	90	100
4.3	Acetic	80	100
4.7	Propionic	80	100
3.4	Lactic	80	98
3.2	Glycolic	80	100
3.9	Citric	98	100

a. A 4% active polyacrylamide gel was used.
b. These were used at 5% concentration.

Table 3
Effect of Selected Additives on the Rate of Polymer[e] Degradation by 5% Acetic Acid/4% Sodium Perborate Solution

pH	Additive	Polymer Degradation	Time
10.2	none[d]	100%	2 hours
4.3	none	100%	24 hours
4.4	FeCl$_2$[b]	100%	6 hours
4.4	FeCl$_2$[b] + Corrosion Inhibitor[a]	100%	2 hours
4.0	FeCl$_2$+HCl[b]	100%	2 hours precip
4.0	Alkylpyridine[c]	10%	24 hours
4.0	Triphenylsulfonium Chloride[c]	50%	5 hours
2.5	MSA Inhibitor[c]	100%	3 hours
4.0	Methanol[a]	50%	5 hours
4.0	Diacetone Alcohol[c]	100%	18 hours
4.0	Propargyl Alcohol[c]	75%	18 hours
4.0	Ethylene glycol[c]	100%	18 hours
5.0	Monethylamine[c]	100%	18 hours

a. 1.0 percent by weight of aqueous composition.
b. 0.2 percent by weight of aqueous composition.
c. 0.1 percent by weight of aqueous composition.
d. No acetic acid present.
e. A 4% active polyacrylamide gel was used.

Table 4
Corrosion Data of Oxidizer Solutions on J-55 Steel

Corrodent		Temperature (°F)	Corrosion Loss (lb/ft²)	Exposure Time (hrs)
5% Acetic Acid	4% Sodium Perborate Fresh Water	70	.033	24
5% Acetic Acid	4% Sodium Perborate Fresh Water	70	.050	48
	2% Sodium Perborate 4% KCl Water	170	.0046	24
2% Acetic Acid	2% Sodium Perborate 4% KCl Water	170	.056	24