Operational Problems Associated with Polymer Applications In Oilfield EOR Projects

by

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ABSTRACT

Water soluble polymers find three major applications in oilfield enhanced oil recovery projects. Two of these applications involve reservoir fluid mobility control while the third involves profile control via reservoir heterogeneity modification. All polymer applications in the oilfield require certain operational practices to ensure that the polymers can function as designed. Many of the design criteria involved in polymer applications include production and injection equipment modifications in conjunction with reservoir fluid chemistry considerations. Finally, the proper choice of specialty chemicals to support injection and production of oilfield polymers is essential to the ultimate success of the projects.

Two types of polymers are used in oilfield applications, the hydrolyzed polyacrylamides and the xanthan polysaccharides. Although each have their own specific advantages and disadvantages, the injection water quality requirements are essentially identical for both polymer types. A combination of specialty chemicals and specialized equipment is often required to meet the strict water quality requirements. In any system compatibility of all components is essential. This paper will discuss the water qualtiy requirements and the problems involved in designing a compatible system.

On the production side of polymer applications, compatibility is again of paramount importance. Saleable oil can only be attained if emulsions that are stabilized by the interactions of polymer, surfactants, solids, water, oil and bacteria can be resolved. Obtaining disposable or reusable water while minimizing produced fluid corrosivity is also a major consideration. Once again, systems must be designed that can effectively employ specialty chemicals (e.g. demulsifiers, water clarifiers, corrosion inhibitors, scale inhibitors, biocides), and mechanical techniques that minimize operational problems.

INTRODUCTION

When applying polymers or any flooding chemicals in oilfield enhanced oil recovery operations, the assurance of system compatibility is essential. Compatibility implies that all of a given system's components can function as designed without interference. Addition of any new components must maintain system compatibility and functionality. Any new component that adversely affects the system functionality can be considered incompatible and not suitable for addition to the system.

Thus, in designing and implementing an oilfield EOR system which incorporates specialty treating chemicals, flooding chemicals and specialized equipment, A "Total Systems Approach"① must be adopted to ensure that every component in that system can function as it has been designed. For example, any specialty chemical that adversely affects polymer functionality should be considered incompatible and should not be applied to the system. Likewise, any equipment that adversely affects polymer functionality should be removed. Alternate choices must be made to perform the desired function. This concept of total system compatibility is paramount to the successful operation of any oilfield polymer application.

Polymer Applications

The application of water soluble polymers in oilfield EOR applications can be divided into three distinct categories. The first involves the use of the polymers to impart mobility control during waterflood operations[1-8]. By imparting viscosity to the water drive, the polymers can help minimize the adverse effects of high mobility ratios (viscous fingering). In addition to viscosity modification, certain polymers have been shown to impart a reduction in water relative permeability and to impart resistance to water flow[1-8]. Residual resistance[8] to water flow can be important during reinstatement of waterflooding after polymer augmentation.

It is a combination of the viscosity and permeability alteration capabilities of the polymers that make them effective for mobility control agents in surfactant and caustic flood operations [9-12]. In these applications, the mobility control provided by the polymers is essential to ensure piston-like displacement of the banked residual oil. The polymers themselves can optimize sweep efficiency.

The final category for polymer application involves the use of modified polymers to form layered or bulk gels in-situ to alter reservoir heterogeneity [13-16]. Applications in both injection systems and on individual production wells have successfully improved areal sweep efficiency and decreased production water/oil ratios.

Polyacrylamides and Polysaccharides

At present there are two basic types of polymers being applied in oilfield EOR applications. The most commonly employed polymers are the polyacrylamides, most of which are employed as 30% hydrolyzed versions. In terms of cost, the viscosity functionality is optimized at the 30% acrylate level and 70% acrylamide level. This 30% level can be achieved during manufacture by hydrolysis of the polyacrylamide or by copolymerization of acrylate and acrylamide.

The polyarylamides can be obtained in three physical forms from the manufacturers. Molecular weights can range from hundred thousands to millions. Ease of hydration and ease of injection system operations are factors which should be considered seriously before a particular physical form is chosen. Careful laboratory core studies will predetermine the choice of molecular weight. The system that can minimize contamination by oxygen, bacteria, and suspended solids and minimize shear degradation and hydration problems will be the one that ultimately employs the functionality that has been purchased.

The liquid polyacrylamides are usually oil external emulsions which are inverted into the water phase during hydration. A typical arrangement is shown in Figure 1. Note that the systems are closed to minimize oxygen contamination and that static mixers are employed to attain essentially instantaneous hydration. Polymer incorporation into the water stream is done downstream of the triplex water injection pump to minimize shear degradation.

Polyacrylamides can also be obtained as semi-solid gels or as concentrates. The commercially available gel logs (28-30% solids) are copolymers that are ground and extruded during hydration. A typical arrangement is shown in Figure 2. The system employs a grinding phase to initially hydrate the polymer. The polymer is then mixed and diluted to a lower concentration (usually 0.6%) and finally injected into the water stream at use concentration (usually less than 1000 ppm). Polyacrylamide concentrates, generally prepared on-site from the acrylamide monomer, employ a similar hydration scheme.

The final form is the solid polyacrylamides which can be purchased as powders or microbeads. Hydration of the solids is significantly more difficult than the other forms. Generally hydration involves hopper feed of the solid, mixing and finally hydration tanks that allow enough residence time to fully solubilize the polymer as a concentrate (usually as 5-6% solids). Finally the concentrates are added to the water stream at use concentration. A typical dry solids polymer system is shown in Figure 3. These solids systems suffer in that hydration of the polymers is more difficult than the other forms and oxygen incorporation via the hopper is unavoidable.

The polysaccharides are also available as solids or as concentrates. Most of the commercially available polysaccharides are fermentation products of the bacterium Xanthomonas campestris. However, functionality characteristics can vary greatly depending upon the molecular component make-up. Various manufacturers have created many different types of polysaccharides to suit a broad array of application requirements. Generally, plugging problems associated with bacterial debris in the early biopolymer floods have been overcome with recent upgrades in biopolymer quality and functionality.

Basically, the solid forms of polysaccharides are hydrated the same as the solid polyacrylamides and involve all of the same inherent problems. The polysaccharide concentrates can be hydrated without hydration tanks by diluting the broth (generally 3% solids) to around 6000 ppm and then diluting again to use concentration (usually less than 1000 ppm). This hydration process can be employed in a continuous stream.

The following sections will address injection and production operational problems as separate discussions.

Front End (Injection-Side) Operational Problems

Water Quality - Oil and Suspended Solids

As in any oilfield waterflood operation, the removal of oil and suspended solids is necessary to minimize injectivity problems. Injectivity problems can be significantly complicated when polymer applications are employed. The natural tendency for the polymers is to adhere to the solids and agglomerate. This is basically due to charge phenomena.

In systems that employ waters containing oil and/or suspended solids, efficient removal to 1.0 ppm oil and 1.0 ppm suspended solids is considered optimal although expensive. Generally, during waterfloods the permeability characteristics of the waterflood injection zone predetermines the parameters for water qualtiy. However, during polymer applications the need to attain very high quality water is more pronounced.

The technology currently exists to attain very high qualtiy water via air flotation and filtration. Steamflood EOR operations routinely attain water which contains less than 1.0 ppm oil and less than 1.0 ppm suspended solids for steam generator feed. This water clarification technology is directly applicable to polymer flood operations and is recommended. In the water clarification processes, specialty chemical flotation aids and filter backwash surfactants significantly improve the efficiency of the flotation units and filters. A water treatment scheme is shown in Figure 4.

Scale Inhibition

Generally, in systems that mix two or more waters for polymer flooding, scaling tendencies of the blend should be claculated and any positive tendency should be treated with an inhibitor. Most of the commercially available inhibitors, the phosphates and phosphonates are compatible with the different polymers. However, in specific cases compatibility should be verified.

Scaling problems have been noted in several systems that have employed base hydrolyzed polyacrylamide. These problems have been especially acute in systems where waters exhibit mild calcium carbonate scaling tendency. The shift in pH that results during polymer dilution or the addition of HCO_3^- from the polymer can be sufficient to precipitate scale. Plugging and polymer agglomeration on the precipitated scale particulates can result. Commercially available scale inhibitors have been successfully employed in these polymer applications.

Hydration

Incomplete hydration of polyacrylamides or polysaccharides can cause serious injection well plugging problems. Poor choice of polymer molecular weight can also cause plugging complications. Poorly hydrated or partially hydrated polymers do not utilize the viscous functionality of the polymer molecules. Thus, the designed mobility control cannot be attained.

If unhydrated or poorly hydrated polymer "fish eyes" are injected they can foul the near well bore reservoir pores by entering them and swelling as they become fully hydrated in time. Workovers to repair a polymer plugged injection well typically employ specialty chemicals that can oxidize the polymer and cleave the polymer backbone. Treatments can also include surfactants to remove oil fouling and to liberate freed particulates so that they can be removed from the plugged well.

Generally, the liquid emulsion polymers present no hydration problems if surfactant inverters (activators) and static mixers are employed properly. The gel logs and concentrates must efficiently employ a shear mixing step to get to use concentration. The solid polymers must employ hoppers, mix tanks, hydration tanks and dilution tanks in order to minimize the possibility of poor hydration. The solids are clearly much more difficult to hydrate [17]not to mention the tendency for the hoppers to cause oxygen ingression.

Oxygen

Numerous investigators have shown that oxygen exclusion from the polymer injection stream is essential[18-28]. This fact holds true for polyacrylamides and polysaccharides, especially in higher temperature reservoirs (greater than 130°F).

Basically, oxygen causes three types of problems in polymer injection systems. First, oxygen can cause significant oxidative degradition of the polymer molecule in higher temperature reservoirs. In extreme cases all of the polymer funtionality can be lost to oxidative degradation especially in systems whose waters contain transition metals which can become involved in free radical reactions. Free radicals have been implicated as a necessary component for oxidative degradation.

Second, oxygen can cause corrosion of any mild steel components involved in the polymer injection system. Cathodic depolarization of the mild steel components by oxygen is well documented and can be catastrophic.

Finally, oxygen can support the proliferation of aerobic and faculative anaerobic organisms which can lead to plugging problems in injection systems and degradation of polymer functionality. Although polysaccharides are known to be particularly susceptible to biodegration, [21,29-32] recent evidence in our labs[41] and others[34] indicate that aerobic, facultative anaerobic and even sulfate reducing bacteria (SRB) can be involved in polyacrylamide degration. The stimulatory effect of polyacrylamide upon SRB growth has also been documented.[35]

Ideally, closed systems which contain no inherent dissolved oxygen should have no problem with oxygen. However, leakage is inevitable. Every attempt should be made to minimize oxygen ingress. In systems that employ waters with existing dissolved oxygen (surface waters and shallow fresh waters), removal of oxygen by mechanical or chemical means is necessary. Sulfite oxygen scavengers have proven effective when applied properly.

Biocides

As has been mentioned, exclusion of oxygen is important to inhibit the proliferation of aerobic and faculative anaerobic organism (those that can utilize oxygen for growth). As a rule, aerobic organisms particularly fungi can readily cleave the bonds in both polyacrylamide and polysaccharide molecules. This usually results in significant loss of viscous functionality.

The fact that polysaccharide can support bacterial growth has been documented by many investigators.[21,29-32,36] However, significant increases in bacterial contamination within systems that employ polyacrylamide has been documented at numerous polyacrylamide polymer floods. It is becoming widely accpeted that incorporation of a compatible biocide to any system which employs polymers is essential to minimize microbial complications.[18,21-23] These complications can manifest themselves in several different ways including injection well plugging (biofilms), viscosity loss, and increases in hydrogen sulfide concentration (attributable to SRB).

When choosing a biocide for incorporation into a polymer flood, three essential criteria have been identified.[41] First, the biocide must be compatible with the polymer that is being employed. The implications are that the biocide not cause loss of viscosity or screen factor (screen viscosity) upon aging at reservoir conditions. Second, the biocide must effectively kill the inherent microbial flora. An optimum kill would be greater than 99%. The kill efficacy should be determined for aerobic, anaerobic and sulfate reducing bacteria, preferrably on-site using field fluids. Finally, the biocide should provide persistent protection of the polymer as it may encounter new reservoir microorganisms. Generally, the oxidizing biocides cannot fulfill these criteria. Compatibility with inherent hydrogen sulfide and/or carbon dioxide is also necessary.

Polymer flood injection systems should ideally employ two compatible biocides to minimize the chances for adaptation by the microorganisms that are unaffected by a single biocide treatment, namely that unkilled 1%. Generally 100% kill is not economically attainable nor maintainable. This point basically stems from the fact that new microorganisms can be picked-up by the system from a myriad of sources.

The most common compatibility problem that occurs in polymer flood injection systems involves oxygen scavengers and biocides. The sulfite type oxygen scavengers as reducing agents can readily react with the aldehydes, the halogen type oxidizing biocides and the sulphur containing biocides. Quaternary amine biocides are incompatible with the polymers and should be avoided.

In systems that contain oxygen, the oxygen should be first scavenged and then a polymer compatible biocide can be applied just prior to polymer dilution. Biocides should be applied to the deoxygenated water prior to any polymer dilution or hydration step to minimize biocontamination in diluted polymer.

Metal Ions

Chelation of transition metal ions to prevent redox degradation or crosslinking of the polymers is often necessary. The most troublesome ions are Fe++, Fe+++, Al+++, Cr+++, and $B_4O_7^{=}$. Other divalent cations can adversely affect polyacrylamide functionality by adsorption and precipitation. Various investigators have employed chelators and sequestering agents to deal with the interference caused by these ions.[26,37]

In contrast, it is the crosslinking tendency of these ions that is employed during profile modification applications of the polymers. Here sequestering agents are employed to alter the kinetics of the crosslinking mechanism.

Shearing

Shear degradation can adversely affect the viscous functionality of polyacrylamide. Polysaccharides are relatively insusceptible to shear degration. Most commercial applications of polyacrylamide currently employ coiled tubing to throttle polyacrylamide injection. This practice controls flow by employing the tubing friction as a pressure drop. Valves have proven to be unacceptable because of their shearing effects. Various other technologies including specialized injection well completions, mixing facilities and limits on injection rates have been employed to minimize polyacrylamide shear.[21,36,38-40]

Back End (Production-Side) Operational Problems

General

The injection of EOR flooding chemicals can considerably alter the physical and chemical characteristics of the produced fluids. The various types of polymer applications have caused or altered scaling tendencies, microbial activity, emulsion problems and corrosion problems. One point that cannot be overstressed is that during implementation of the polymer applications, the produced fluids will change. The relatively constant produced fluid chemistry conditions that existed during primary and waterflood stages become fully dynamic during polymer applications. Fluids can change on a daily basis. The nature of the flooding chemicals and reservoir oil and water chemistry will determine how significant the change in produced fluid characteristics.

The common misconception, or hope, that once the polymers, caustics and surfactants are injected they're gone is not true. The chemicals will be produced in some form or fashion. Generally, caustic/polymer and surfactant/polymer floods create profound differences in the produced fluid characteristics. Polymers do not in and of themselves change the oil and water chemistry. However, they do cause other significant changes in the produced fluid physical characteristics.

Emulsions

Destabilizing produced emulsions to obtain saleable crude oil and injectable water is the primary objective in handling polymer enhanced produced fluids. One fact that must be acknowledged is that several flood processes, specifically surfactant/polymer and caustic/polymer floods, are designed to create tight, stable emulsions in-situ. Resolving these emulsions requires a combination of specialty chemical demulsifiers, heat and quiescent residence time.[42] The emulsions themselves can exist as oil or water external moities as they are produced. The type in large part predetermines the equipment and chemistry that will be required to break the emulsion.

Polymers tend to stabilize emulsions by existing as precipitated or agglomerated solids that are neither oil nor water soluble. As such they tend to hang at the oil-water interface as oil-wet or water-wet particles, much as iron sulfide can. Polymers also act to flocculate and coat suspended particles that may be present in the produced water. These particles can be reservoir fines, clays, scale particles and iron sulfide particles. The flocculated particles can tend to drag oil into the water which can mean the loss of saleable crude and plugging during reinjection. They can also act to drag water into the oil and cause LACT rejection of the crude or refinery reinjection for excess basis sediment (BS).

Most treatment schemes involve specialty chemical applications to break down the polymers and ultimately force them into the water phase for disposal or reinjection. A typical production treating arrangement is shown in Figure 5. The schemes generally involve draw-off capabilities to treat the interfaces separately. Filtration of polymers from production streams is generally not feasible because of media plugging.

Bacteria

Bacterial proliferation in production systems that contain polymers is very common. Not only can the polymers serve as nutrients, they also act as very effective deposits under which bacteria can thrive. Production rods and tubing that get coated with polymer laden solids can experience catastrophic failure, especially in the presence of SRB. Pitting failure is very common.

Successful treatments employ specialty chemical to kill the bacteria and keep the solids from adhering. The biocide programs have been coupled with corrosion inhibition programs. Once again compatibility is essential for systems employing multiple chemicals in the presence of polymer. Slugged and continuous treatments have both been effective depending on the system.

Scale Inhibition

Generally, scales that occur in conjunction with polymer applications result from changes in the water chemistry that occur when caustics are applied or as flooding waters alter reservoir water chemistry. Although the number of caustic/polymer applications is limited, experiences with caustic floods without mobility control (i.e. no polymer) have shown that carbonates and hydroxide scales can be common. Silicate scales of magnesium have also been identified in orthosilicate alkaline flooding. Fresh waters have caused produced fluids to scale by incorporation of bicarbonate, sulfate and other scaling components during polymer applications.

Successful treatments have involved application of specialty chemical scale inhibitors by both squeeze and continuous addition.

Corrosion Inhibition

Corrosion control in production systems that are experiencing polymer invasion can be extremely complex. Polymer agglomerated solids, sulfate reducing bacteria (SRB), hydrogen sulfide, oxygen, and carbon dioxide can all be contributing complications. What makes the corrosion significantly more troublesome in the polymer applications is the fact that the polymer agglomerated solids create ideal circumstances for underdeposit mechanisms to predomiante. The pitting type corrosivity can be catastrophic.

Successful type treatment schemes inevitably employ complex specialty chemicals that can address and control the various types of corrosion mechanisms that might be involved. Identification of the mechanisms is the first necessary step. Because of the increased surface area that the agglomerated polymer solids provide, maintaining presistent protective films can be difficult. Monitoring of troublesome systems is essential.

Another complication that must be addressed is the fact that many commonly employed corrosion inhibitor types are cationic in nature and as such present compatibility problems when applied to systems that contain anionic polymers. A complete review of prepolymer corrosion protection programs is recommended. The successful schemes have for the most part had to resort to continuous inhibitor application when inherent corrosivity cannot be diminished. Prevention of oxygen ingression and control of bacterial contamination and solids can greatly reduce corrosivity.

CONCLUSIONS

The application of polymers in oilfield enhanced oil recovery operations can be very successful. However, careful consideration ofthe entire system, a "Total Systems Approach"Ⓣ, is essential to minimize complications.

The process of applying polymers in the oilfield has become significantly more efficient in recent years. Preserving the integrity of the polymer functionality so that it can provide optimal performance in the reservoir is the primary task. The development of polymers that are more resistant to degradation in ongoing. Polymers with enhanced functionality are also being developed at economical costs.

Dealing with polymers in produced fluid streams is necessary in most polymer applicatons. Designing efficient production systems coupled with specialty chemical applications that anticipate polymer breakthrough can make the endeavor more manageable.

ⓉTrademark - Petrolite Corporation

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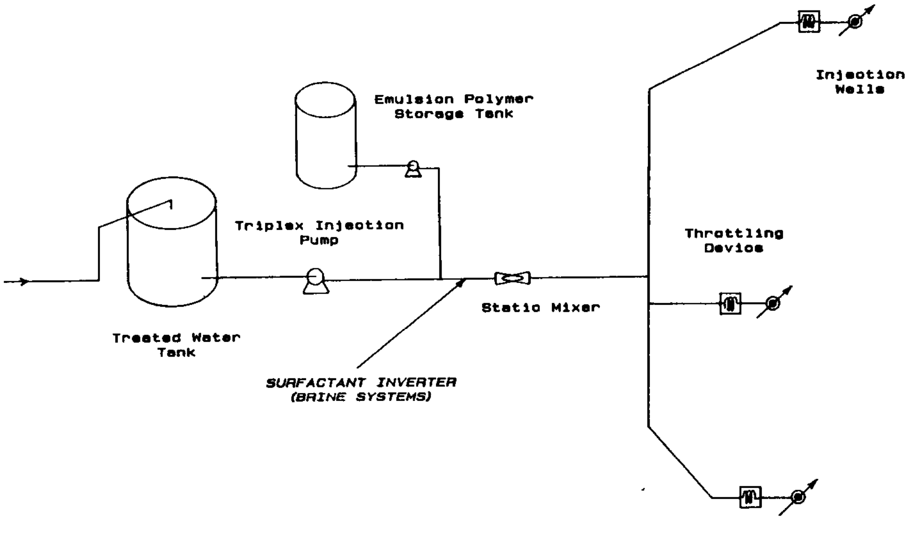

Figure 1 - Emulsion polymer injection system

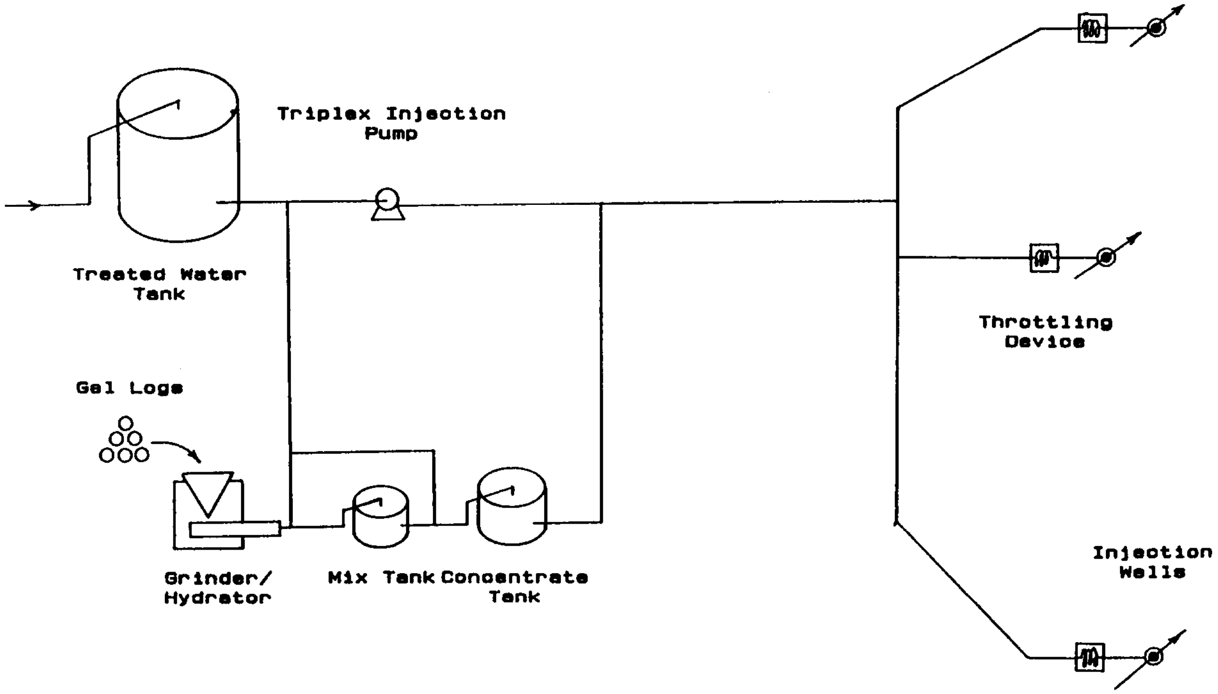

Figure 2 - Gel log polymer injection system

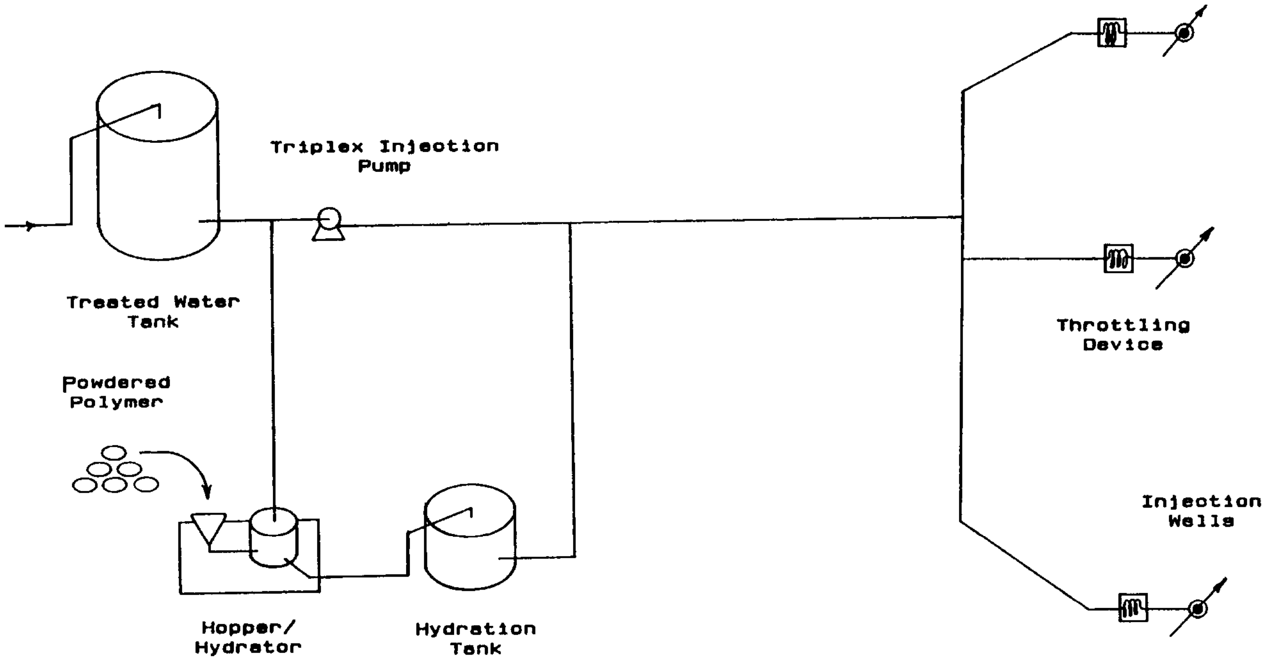

Figure 3 - Dry powder polymer injection system

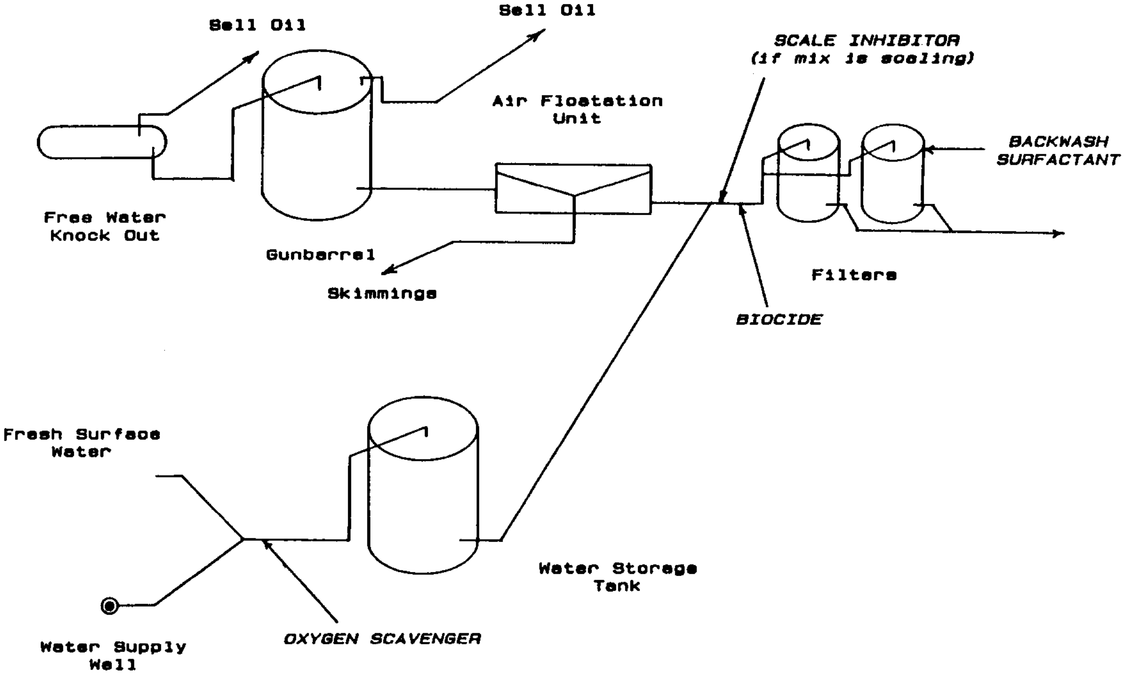

Figure 4 - Water pretreatment system

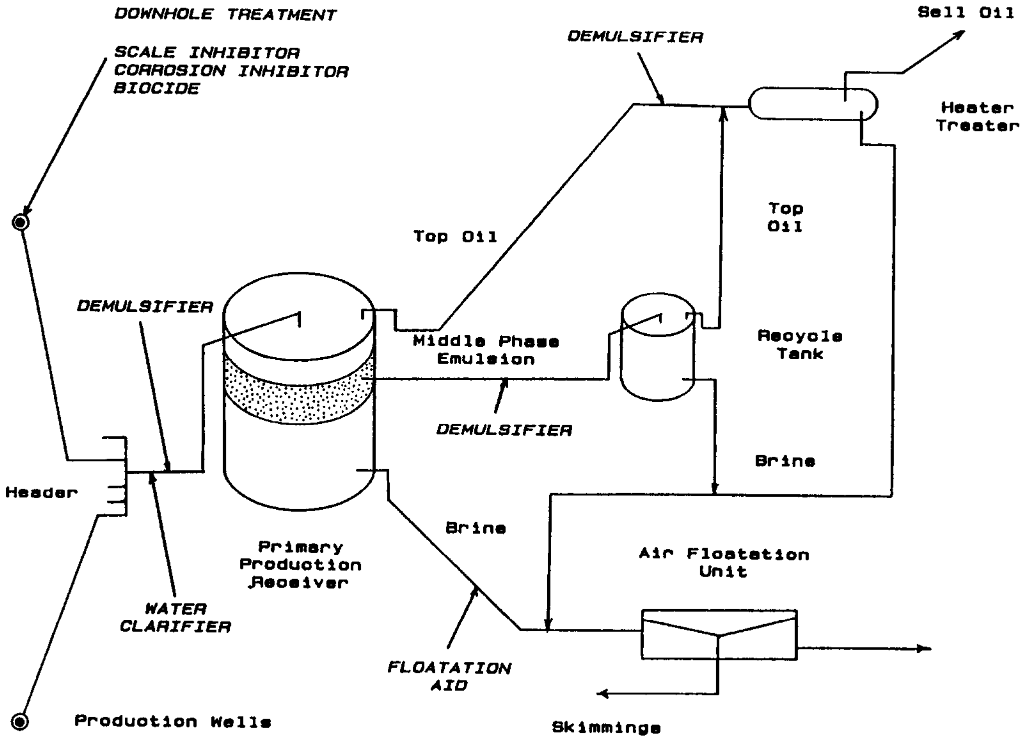

Figure 5 - Produced fluid treatment system