A comprehensive review of polyacrylamide polymer gels for conformance control

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Abstract: Polymer gels have been designed and successfully applied to improve sweep efficiency and to reduce excessive water production by minimizing reservoir heterogeneity. Based on their compositions and application conditions, polyacrylamide polymer gels can be classified into three types: in-situ monomer-based gel, in-situ polymer-based gels, and preformed particle gels. Initially, in-situ monomer gels which are mainly composed of acrylamide were developed for water shutoff. Conventional in-situ polymer gels include metal-cross linked polyacrylamide gels and organic-cross linked polyacrylamide gels. Preformed gels include preformed particle gels, pH sensitive microgels, and micro- and nano-gels. A few directions are suggested for future research on novel gels, such as gels used for in-depth fluid diversion and gels for severe reservoir environments.

Key words: polyacrylamide (PAM); monomer-based gel; polymer gels; preformed particle gels; conformance control; in-depth fluid diversion; enhanced oil recovery

Introduction

As the rate of discovering new reservoirs decreases, improved and enhanced oil recovery (IOR/EOR) techniques are becoming increasingly important for mature oilfields. IOR/EOR processes often involve the injection of materials not present in the reservoirs such as polymers, foams, solvents, surfactants, etc. Conformance control is a key IOR/EOR method and is defined as any technique that encourages movement of normally unswept remaining oil or gas and brings the drive closer to the perfect conforming condition. In order to achieve the preferred conforming condition and produce more oil and gas, water production must be minimized since it becomes a major problem as hydrocarbon reservoirs mature. In the United States, on average, more than seven barrels of water are produced for each barrel of oil with a general oil recovery of 20–30%[1]. Treatment of the produced water significantly increases production costs. Controlling water production has been an urgent task for the oil industry.

Reservoir heterogeneity is one of the most important reasons for low oil recovery and early excess water production. Reservoirs with induced fractures or high permeability channels, commonly called thief zones or streaks due to extensive water flooding, are quite common in the mature reservoirs. Many methods have been applied to mitigate excessive water production problems and to EOR. They include polymer flooding, alkaline-surfactant flooding, foam flooding, gel treatments, and so on. Among these methods, polyacrylamide polymer gel treatment is a common and cost-effective method because the process can reduce water cut by sealing the thief zone and redistributing the water drive. Polymer gel treatments can be divided into two main categories: i) permeability blockers, and ii) relative permeability modifiers (RPM), which is also known as disproportionate-permeability-reduction (DPR). Permeability blockers are often used for near wellbore water control and flow paths diversion. The second type of gel system reduces the permeability of water flow to a greater extent than that to oil or gas.

Many polymer gel systems have been developed to address various reservoir conditions, including temperature, the ionic composition and pH of formation water, the presence of either carbon dioxide or hydrogen sulfide, and the adsorption of chemicals on reservoir rock. The primary purpose of the review is to review polymer gel development process and their applications, from which the investigators interested in gel treatments can develop better gels to meet the current needs of mature oilfields.

1. Current polymer gel technology

1.1. Conventional in-situ monomer gels

Some earlier applications used acrylamide monomer sys-
tems that polymerized in-situ for conformance control. When they were placed into formation with 4% to 10% total dissolved solids, the monomer and crosslinker solution had an initial viscosity similar to water (i.e., 1-1.3 cp). Because of its initial low viscosity, theoretically it could easily penetrate into all zones in the formation’s in-depth regions. However, because monomer gelation is a free-radical initiated rapid process, controlling the gelation was difficult under high temperature reservoir conditions. A retardant such as potassium ferricyanide was usually added to prevent premature gelation. Because acrylamide is neurotoxin and suspected carcinogen, Halliburton Co. has since developed a less toxic, acrylate-based, temperature-activated monomer system. The system, called PermSeal®, has a controllable gelation time when temperature is up to 93.3 °C, and it remains stable in temperatures up to 148.9 °C for one year. The system required a high monomer concentration (4%-10%) because the gels formed from low concentration systems were slightly water soluble and had lower gel strength. Therefore, the material cost was expensive and concern with operation risk results in a decreasing utilization. The oil industry demanded a more cost-effective treatment.

1.2. Conventional In-situ Polymer/Gels

In the 1970s, Philips Co. (now ConocoPhilips) pioneered the first in-situ polymer gels using partially hydrolyzed polyacrylamides (HPAM) and aluminum citrate, which were the precursors for conformance control\[2\]. Since then, in-situ polymer gel systems used in conformance control have attracted more attention. These systems essentially had two components: high molecular weight polymers and crosslinkers. Corresponding to some internal or external stimulation, the crosslinking agent connected itself to two adjacent polymer molecules chemically or physically linking them together. An in-situ three-dimensional network was thus established under reservoir conditions. The network displayed a unique liquid-like behavior on molecular length scales while maintaining solid-like macroscopic properties.

Since then, numerous in-situ gel systems have been developed for oilfields. The most prevalent gel system was related to polyacrylamide (PAM), a synthetic polymer. Polysaccharides (biopolymers) such as starch, xanthan, guar, lignin and cellulose, and silicate gels with organic modification were also used in the oil industry. The raw materials, performance properties, and processing costs placed these polymers at a considerable disadvantage relative to PAM-related gels. Crosslinker types in the in-situ PAM system can be divided into two categories: metallic and organic crosslinked systems.

1.2.1. Metallic cross-linked PAM system

In pure state, polyacrylamide is electrically neutral and comprises a carbon-carbon backbone hung with amide groups. When exposed to a small amount of alkaline solution or vulnerable to elevated temperature, some of the amide groups in PAM tend to convert to carboxylate groups. PAMs used in in-situ gel systems are all partially hydrolyzed to carry a negative charge. Therefore, it can form an ionic bonding with multivalent cations. The proportion of amide groups that transformed into carboxylate is defined as the degree of hydrolysis and typically varies from 0% to 60%. Efficient cross-linkers are multivalent metal ions such as Al(III), Cr(III), Fe(III), and Zr(IV). These multivalent ions can be found in the form of simple inorganic ions or within soluble chemical complexes in solution. When added to an HPAM solution, metal ions will react with carboxyl group. The rate and extent of the reaction depend on the ligand within the cross-linker structure. Intramolecular cross-links are initiated if the metal ion-carboxyl complex further associates with another carboxyl group on the same polymer chain. The metal ion-polymer complex thus obtained is called a pre-gel aggregate. Intermolecular cross-links build up and continue to grow into a three-dimensional network if the concentration of pre-gel aggregates is more than the critical overlap concentration.

In the early 1970s, aluminum sulfate was used to cross-link HPAM. However, this material is highly pH dependent. When aluminum sulfate and HPAM are mixed at surface facilities in acidic condition, no gel forms and the mixed solution can be successfully injected into the reservoir. When the fluids penetrate into the formation, however, pH increases rapidly and gelation takes place simultaneously with no control. Therefore, the gel system can only be applied to the area very near the wellbore as a permeability blocker. To obtain better gelation control, Cr(VI) and HPAM gel systems have been widely employed. Cr(VI) ion is inert with respect to the cross-linking reaction, but it can be converted to a Cr(III) ion through the injection of a redox agent. In the ideal case, it can be injected deep into the formation before gelling. In field applications, however, it has several drawbacks. First, a sufficiently long gelation time cannot be achieved for this system in high-temperature reservoirs. Second, the gel system is sensitive to oilfield interferences, especially H2S. Worst, Cr(VI) has been reported to be carcinogenic\[3\].

In 1984, Sydansk\[40\] in the Marathon Oil Co. established and patented a new polymer-gel system using HPAM/Cr(III) acetate. His system achieved great success in the oilfields. The acetate group has a structure very similar to that of the carboxylate groups on the HPAM polymer. Therefore, Cr(III) ions are under the attraction of both the acetate ligand within the complex and the carboxylate groups on the HPAM. These two forces slow the cross-linking reaction and make the gelation time controllable. The HPAM/Cr(III) acetate gel system is a total upgrade package over inorganic Cr(III) compounds and Cr(VI) chemical complexes. It is insensitive to pH from about 2 to 12.5 and also has some degree of resistance to chemical interferences, such as ions in the formation fluids, H2S, and CO2. More importantly, the gel strength and gelation time are controllable and the system can be applied to high-temperature reservoirs (124 °C or even higher). For