

OIL WELL CEMENT ADDITIVES: Critical Review of the Common Polymers

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ABSTRACT

Oil well cementing is a critical operation required for successful completion of oil or gas wells. The longevity and integrity of wells depend on good cementing operations. Several chemicals known as oilfield additives are needed to modify the API properties of cement slurries for optimum performance. These additives fall into the following broad categories: retarders, accelerators, extenders, densifiers, dispersants, fluid loss control agents, lost circulation agents, strength retrogression prevention agents, free water/free fluid control agents, expansion agents, and special additives. Various additives have been developed to perform specific functions for the above mentioned different categories during cement slurry design. This paper review significantly the multifunctional use of polymers for improving API properties such as rheology, fluid loss and free water of cement slurries used for oil well cementing operations.

Keywords: Additives, Oil well cementing, Rheology, Free water, Fluid loss

1.0 Introduction

Oil well cementing is considered as one of the important operations performed in the construction of a wellbore (Garnier, 2007) and (Looten, 2004), hence, high-quality cement slurry is required so that oil production is economically and safely achieved over the well's lifetime (Ridha et al., 2010). According to Nelson et al., 1990, poor quality cement slurry may lead to remedial cementing hence, increasing the time and cost of cementing operation; apart from remedial operations, poor quality cement slurry can also cause severe havoc in completion operations by loss of lives and facilities. Depending on the application of the well cement, there are varieties of additive that can be used to design cement slurry characteristics; hence, optimum cement slurries design for desired properties could be achieved with the aid of several

chemicals to adjust the slurry properties (Brandl et al., 2012). Over the years various type of additives including polymers have been used to improve API properties of the cement slurry. Polymers are widely used in oilfield applications for improving the properties of drilling fluid and cement slurry; it acts as fluid loss and gas migration control agent in the cement slurry. When cement slurry is placed across permeable formation under pressure, water tends to leave the slurry into the permeable formation, in particular when pumping has ceased and the slurry is static, but not yet set. If this fluid loss is not controlled in oil well cementing operations, the rheology, thickening time and density of the cement slurry will change, hence resulting in failure in cementing jobs. Design properties of slurries are significantly influenced by the water content; thus, slurries that lose water can also be subject to a loss or degradation of design properties. Polymeric materials help to retain the key characteristics of their cement slurries, including viscosity, thickening time, density and compressive strength development. According to Halliburton 2009, a polymer is effective in freshwater and saltwater slurries; it is also ideal for circulating jobs and for deep liner cementing, maintains fluidity, eliminates premature dehydration, and prevents bridging in a tight annulus in cementing operations. It helps to control fluid loss without breaking foamed cement structures. Also, it prevents retardation of compressive strength development; and acts as a dispersant and gel breaker as well. In addition to the listed qualities, polymeric materials are used as surfactants, emulsifiers, lubricants, corrosion inhibitors, flocculants, deflocculants. This paper describes the polymers that are commonly used for improving API properties of the cement slurry.

1.1 Materials and Method

The basis of the research was on the residue source of data from conference proceedings, textbooks, journal papers, unpublished materials, and recognized websites. The adopted method includes reviewing the broad categories of polymeric additives used for oil well-cementing operations.

1.2 Common Polymers and its uniqueness

A polymer is water soluble additive used in drilling and cementing operations to increase the viscosity of the aqueous phase and/or lowering the filter cake permeability of the drilling fluid and cement slurry, thus reducing the rate of filtration. This additive is commonly added to cement formulations to; disperse cement particles, modify the setting time under temperature and pressure conditions in the well, control filtration losses of the liquid from the

cement slurry during and after placement, compensate for shrinkage of the cement as it sets and hardens, improve interfacial bonding between cement and casing, and control influx and migration of formation fluids into the cement column during setting (Cowan et al, 1993). However, polymer efficiency decreases with increasing temperature.

There are two forms of derivatized polymeric cellulose which have been found useful in well-cementing applications, namely; single-derivatized hydroxyethyl cellulose (HEC), carboxymethylcellulose (CMC) and twice-derivatized Carboxymethyl hydroxyethyl cellulose (CMHEC). Single-derivatized cellulose provides fluid loss control and shortens transition time to help address shallow water flow concerns. Twice-cellulose derivatives have been used for many years as cement retarders, but they are generally effective to 120⁰C (250⁰F), although the usefulness of the two materials depends on their retardational character and thermal stability limits. Cellulose derivative and dispersant are developed for primary or squeeze operations between 60⁰F (15.6⁰C) and 300⁰F (148.9⁰C). Apart from the single and twice-derivatized cellulose, Hydroxypropyl guar (HPG) has been found useful in well cementing applications (Brandlet et al., 2011; Reddy et al, 2012). In fracturing fluids, the polymer acts as a carrier for proppants. However, most of the polymers suffer thermal thinning problem and lose their viscosity at high temperature. Hence, such type of multifunctional additives does not show any effect on fluid loss and thickening time at 94⁰C.

A nonionic synthetic polymer such as polyvinyl alcohol (PVA) is an effective water control enhancer. At high well temperatures, cationic polymers such as polyethyleneimine (PEI) are frequently adopted. These polymers can control fluid loss at temperatures up to 225⁰C (437⁰F) but they also encourage slurry sedimentation (Parcevaux et al, 1985).

1.3 Hydroxyethyl Cellulose (HEC)

Hydroxyethyl Cellulose is named after its two components: cellulose and hydroxyethyl side chains. Cellulose itself is a non-ionic water-soluble, long-chain molecule polymer consisting of repeating anhydroglucose units, as shown in Figure 1.1. It is pseudoplastic in aqueous solutions. Its molecule can easily be hydrolyzed by an acid catalyst and it is widely used in the petroleum industry for the design of cement slurry. It reduces hydraulic friction of the slurry and minimizes water loss to the formation and act as free water as well as gas migration control agent in cementing operations. It can also thicken, suspend, bind, emulsify, form films, stabilize, disperse without lump and provide protective colloid action. It can be used to prepare solutions with a wide range of viscosities. It has outstanding tolerance for

dissolved electrolytes. Hydroxyethyl Cellulose is cellulose in which both ethyl and hydroxyethyl groups are attached to the anhydroglucose units by ether linkages. It is prepared from cellulose by treating with alkali, ethylene oxide, and ethyl chloride. It is either hygroscopic white, slightly yellowish or grayish in colour, odourless granules or fine powder with a molecular weight of 250,000. It is insoluble in boiling water and ethanol. This is commonly used at temperatures up to approximately 82°C (180°F) for fluid-loss control and may be used at temperatures up to approximately 110°C (230°F) Bottom Hole Circulation Temperature (BHCT), depending on the co-additives used and slurry viscosity limitations. Above 110°C (230°F), HEC is not thermally stable. HEC is typically used at a concentration of 0.4 to 3.0% by weight of cement (BWOC), densities ranging from 16.0 to 11.0 lbm/gal, and temperatures ranging from 27 to 66°C (80 to 150°F) BHCT to achieve a fluid loss of less than 100 cm³ /30 minute.

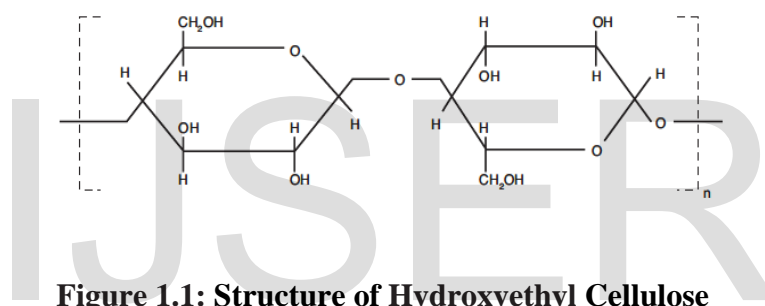


Figure 1.1: Structure of Hydroxyethyl Cellulose

1.4 Carboxymethyl cellulose (CMC)

Carboxymethylation of cellulose yields the well-known carboxymethylcellulose (CMC) also known as cellulose gum or tylose powder. It is an important industrial polymer that possess many desirable qualities such as emulsification, suspension, water maintaining, binding, and inspissations. CMC is used with a wide range of applications in flocculation, drag reduction, detergents, textiles, drugs, medicine, electrical elements, making printing, dyeing and oil well drilling operation. According to Batdorf J. B et al (1973) and Ott E. et al. (1964), CMC has many other uses besides food additives and products such as toothpaste, laxatives, diet pills, ice cream, water-based paints, detergents, soap powder. In fact, The 2009 EU Food Standard Agency approved CMC as an additive, labeled as E466 in the emulsifiers, stabilizers, thickeners and gelling agents category. CMC is a derivative of cellulose formed by its reaction with sodium hydroxide and chloroacetic acid which falls under carboxymethyl groups (-CH₂-COOH) bound to some of the hydroxyl groups of the glucopyranose monomers that make up

the cellulose backbone as shown in Figure 1.2; hence often used as its sodium salt. It has a number of sodium carboxymethyl cellulose (CH_2COONa) which is introduced into the cellulose molecule to promote water solubility. It is anionic and hydrophilic cellulose, usually in the form of powder or granule (easy to disperse and avoid blocking) and can achieve thickening and special rheological property without further treatment. It can be uniformly dispersed and thickened under stirring and provides excellent firm-forming properties and adhesion. Baar A. et al (1994); Kamide K. et al. (1985) and Reuben J. and Conner H. T. (1983) stated that various properties of CMC depend upon three factors: molecular weight of the polymer, average number of carboxyl content per anhydroglucose unit, and the distribution of carboxyl substituent along the polymer chains.

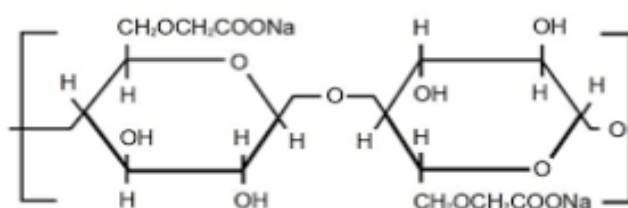


Figure 1.2: Structure of Carboxymethyl Cellulose

Kaistner U. et al. (1997) noted that CMC is mostly used in aqueous solutions, where useful characteristics such as high viscosity at low concentrations, defoaming, surfactant, and bulking abilities are applicable. However, in the solid-state CMC also has considerable application; mainly as film, paints and paper products. In this condition, CMC may be associated with other ions that will influence its physical–chemistry properties.

By carrying out experiments at 30°C before and after processing, Rao et al. (1981) were able to show that thermal processing has detrimental effects on the structure of CMC.

1.5 Hydroxypropyl guar (HPG)

"Guar gum" or simply "Guar" is galactomannan obtained by the thermo-mechanical treatment of the seeds of "Cyamopsis Tetragonolobus", a member of leguminosae family as noted by (Whistler and Hymowitz 1979; Kay 1979; Prem et al. 2005) and its species are cultivated in the semi-dry region of tropical countries, particularly in India and in Pakistan where the plant has been grown for centuries as food for both human and animals consumption, (Whistler and Hymowitz 1979). But guar gum increased its demand during the last few decades due to the development of different derivatives of guar gum like anionic and cationic derivatives. Guar is a polysaccharide with one of the highest molecular weights of all naturally occurring water-soluble polymers. The viscosifying effect of commercial guar gum preparations can vary enormously depending on the molecular weight of the galactomannan. Early

publications reported that the average molecular weight of guar gum vary enormously, depending on what method is used, but these are typically in the range of 0.25–5.0 million. The biological properties of guar galactomannan and other such polysaccharides are dependent on their behavior in an aqueous medium. Guar gum swells and or dissolves in a polar solvent on dispersion and form strong hydrogen bonds. In non-polar solvents, it forms only weak hydrogen bonds. The rate of guar gum dissolution and viscosity development generally increases with decreasing particle size, decreasing pH and increasing temperature. Hydration rates are reduced in the presence of dissolved salts and other water-binding agents such as sucrose (Bemiller and Whistler 1993). Guar gum in aqueous solutions shows pseudo-plastic or shear-thinning behavior which means a reduction in viscosity with increasing shear rate as shown by many high molecular weight polymers. This shear-thinning behavior of guar gum aqueous solution increases with polymer concentration and molecular weight. Also, guar gum in aqueous solutions does not show yield stress properties (Whistler and Hymowitz 1979). Aqueous solutions of guar gum at 1% concentration show a typical behavior of macromolecular biopolymer with dominating loss modulus (G'') over storage modulus (G') in a lower frequency range. The most significant characteristic of guar gum is its ability to hydrate rapidly in cold water systems to give highly viscous solutions. Guar gum forms a viscous colloidal dispersion when completely hydrated which is a thixotropic rheological system. Dilute solution of less than 1% concentration of guar gum are less thixotropic than solutions of concentration of 1% or higher (Glicksman 1969). As like the other gums, a viscosity of guar gum is dependent on time, temperature, concentration, pH, ionic strength and also on the type of agitation. High viscosity by a little addition, High pH stability, Gelling and water-tolerant by cross-link, Good compatibility to salt varieties, surfactants and solvents; High water retention, High lubricity and High sustainability of foam. Temperature is the most significant factor that affects the rate of hydration and maximum viscosity. Guar solutions reach maximum viscosity much faster when prepared at higher temperatures than those at lower temperatures. But the prolonged heat is also considered to have a degradative effect. In most of the cases, guar gum solutions prepared by heating have a lower final viscosity than the same solutions prepared with cold water and allowed to hydrate slowly. Temperature range of 25–40 °C is desirable for maximum viscosities of guar gum dispersion. The viscosity of 0.5% (w/w) guar solution at 25 °C is significantly higher than that of 37 °C (Srichamroen 2007).

Schlakman and Bartilucci (1957) examined thirteen different commercial samples and found great variation in the viscosity property, particle size and rate of hydration. A 1% aqueous dispersion of good quality guar gum may show a high viscosity value of 10000 cP (Parija et al. 2001). Hydration of about 2 hours is required in practical applications in order to reach maximum viscosity. Hydration rate largely depends on the particle size of guar gum

powder. Hence, for quick initial viscosity, very fine mesh guar gums are available (Glicksman 1969).

Guar gum mainly consists of the high molecular weight polysaccharides of galactomannans which are a linear chain of (1 → 4)-linked β -D-mannopyranosyl units with (1 → 6)-linked α -D-galactopyranosyl residues as side chains as shown in Figure 1.3. These galactose and mannose groups constitute the galactomannan portion of seed endosperm units in the ratio of 2:1 respectively. Each ring of the monosaccharide bears three free hydroxyl groups that are available for chemical reaction, two of them being in the "cis" position.

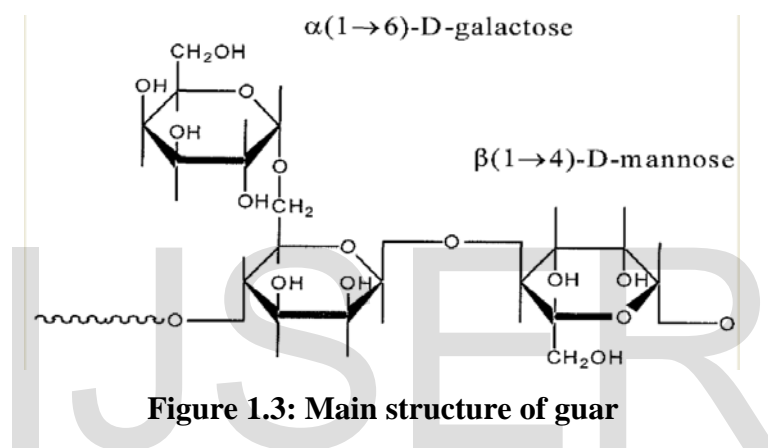


Figure 1.3: Main structure of guar

Hydroxyalkyl derivatives of guar are obtained by chemical reaction of the hydroxyl groups of the galactomannan chain with alkylene oxides (ethylene, propylene, butylene or higher oxides), in the presence of an alkaline catalyst (such as sodium hydroxide). The derivatization reaction may be conducted in the substantial absence of water or solvent (no water added) although the efficiency of the reaction is very low without the addition of water. Accordingly, the reaction is generally conducted in the presence of water to provide higher reactivity.

Research investigation shows that high viscosity guar gum derivatives can be obtained by treatment of guar gum with complex agents like organic titanates, chromium salts, and aluminum salts. These agents react with guar gum to form complexes with high viscosity gel. Increase in concentration of guar gum enhances the inter-molecular chain interaction or entanglement which leads to an increase in viscosity (Zhang et al. 2005). On doubling the concentration, guar gum shows a tenfold increase in viscosity (Carlson et al. 1962). Up to 0.5% concentration, guar gum solutions behave as Newtonian system whereas above this concentration level guar solutions behave as non-Newtonian and thixotropic systems. It is also

reported that viscosities of different concentration of guar gum at constant temperature reduces with an increase in shear rate (Srichamroen 2007). Guar gum solutions are stable over a wide pH range of about 1.0–10.5. This is due to its non-ionic and uncharged behavior. Final viscosity of guar gum is not affected by the pH, but the hydration rate shows variation with any change in pH. Fastest hydration is achieved at pH of 8–9, however slowest hydration rate occurs at pH above 10 and below 4 (Carlson et al. 1962). Guar gum solutions in brine behave the same as in water. Hydration rate is not influenced by salt; however, the presence of sodium chloride slightly increases the final viscosity of fully hydrated guar gum. Physiological buffer i.e. Krebs bicarbonate decreases the viscosity of 0.25% guar gum solution as compared to guar gum in water alone (Srichamroen 2007).

1.6 Polyvinyl alcohol

Poly (vinyl alcohol) (PVOH, PVA, or PVAI) is a water-soluble synthetic polymer. It has the idealized formula $[\text{CH}_2\text{CH}(\text{OH})]_n$ as shown in Figure 1.4 It is used in papermaking, textiles, and a variety of coatings. It is white (colourless) and odourless. According to Manfred L (2000), PVA is an atactic material that exhibits crystallinity. In terms of microstructure, it is composed mainly of 1,3-diol linkages $[-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{CH}(\text{OH})-]$ but a few percents of 1,2-diols $[-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{CH}_2-]$ occur, depending on the conditions for the polymerization of the vinyl ester precursor Manfred L (2000). Polyvinyl alcohol has excellent film forming, emulsifying and adhesive properties. It is also resistant to oil, grease, and solvents. It has high tensile strength and flexibility, as well as high oxygen and aroma barrier properties. However, these properties are dependent on humidity, in other words, with higher humidity more water is absorbed. The water, which acts as a plasticizer, will then reduce its tensile strength, but increase its elongation and tear strength. PVA has a melting point of 230 °C and 180–190 °C (356-374 degrees Fahrenheit) for the fully hydrolyzed and partially hydrolyzed grades, respectively. Polyvinyl alcohol is used as an emulsion polymerization aid, as protective colloid to make polyvinyl acetate dispersions. Injection molding of soluble containers for active release of detergents and agrichemicals, paper adhesive with boric acid in spiral tube winding and solid board production and thickener, modifier, in polyvinyl acetate glues

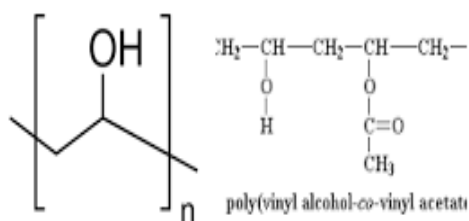


Figure 1.4: Structures of Polyvinyl alcohol polymer

1.7 Polyethyleneimine (PEI)

Polyethyleneimine (PEI) or polyaziridine, poly[imino(1,2-ethanediyl)] is a polymer with a repeating unit composed of the amine group and two carbon aliphatic CH₂CH₂ spacer. Linear polyethyleneimines contain all secondary amines, in contrast to branched PEI which contain primary, secondary and tertiary amino groups. Totally branched, dendrimeric forms were also reported by Yemuland O. et al. (2008). According to Davidson R. L et al (1968), PEI is produced on an industrial scale and finds many applications usually derived from its polycationic character. Boussif et al, (1995) reported that polyethyleneimine (PEI) a branched cationic polymer and has been shown to condense plasmids into colloidal particles that effectively transfect genes into a variety of cells in vitro as shown in Figures 1.7a, b, c respectively.

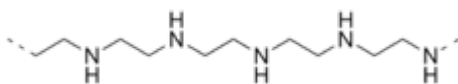


Figure 1.7(a): Structure of Linear PEI fragment

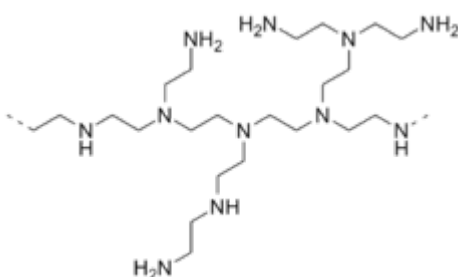


Figure 1.7(b): Structure of Typical branched PEI fragment

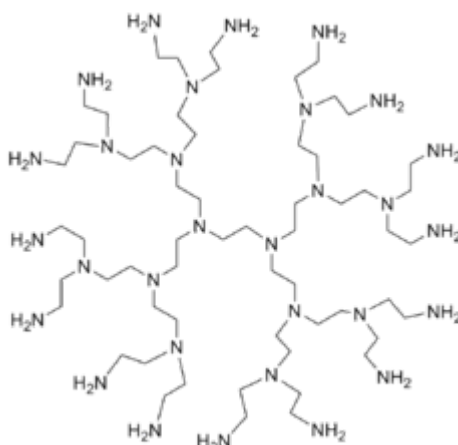


Figure 1.7(c): Structure of PEI dendrimer generation

The linear PEIs are solids at room temperature while branched PEIs are liquids at all molecular weights. Linear polyethylenimines are soluble in hot water, at low pH, in methanol, ethanol, or chloroform. They are insoluble in cold water, benzene, ethyl ether, and acetone. They have a melting point of 73–75 °C. They can be stored at room temperature. Zhuk, D. S (1965) reported that branched PEI can be synthesized by the ring opening polymerization of aziridine. However, depending on the reaction conditions the different degree of branching can be achieved. Linear PEI is available by post-modification of other polymers like poly (2-oxazolines) (Tanaka R. et al. 1983) or *N*-substituted polyaziridines (Weyts K. F 1988). According to Brissault, B.; et al. (2003), linear PEI was synthesized by the hydrolysis of poly (2-ethyl-2-oxazoline). Polyethylenimine finds many applications in products like detergents, adhesives, water treatment agents and cosmetics (Sigma-Aldrich. 2012). Also, its ability to modify the surface of cellulose fibers is added advantage. PEI is employed as a wet-strength agent in the paper-making process (Wågberg, Lars 2000). Madkour T. M. (1999) disclosed that it is also used as a flocculating agent with silica sols and as a chelating agent with the ability to complex metal ions such as zinc and zirconium.

1.8 Conclusions

The various polymers discussed in this work are among those used to retain the key characteristics that enhance the performance of Portland cement during oil and gas well cementing. This paper reviewed the broad classification of oil well polymers giving prominence to those commonly used in oil well-cementing jobs. The paper highlighted the commonly used oil well cement polymer additives as Hydroxyethyl Cellulose (HEC),

Carboxymethyl cellulose (CMC), Hydroxypropyl guar (HPG), Polyvinyl alcohol, Polyethyleneimine (PEI) and many others.

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