Biobased Additives in Oilwell Cement

A. Vázquez and T.M. Pique

1 Introduction

Oil and gas are usually extracted from the earth through very deep holes known as wellbores. Wellbores are drilled into a subterranean formation that is an oil or gas reservoir. Typically, a wellbore must be drilled 100/3000 m. The greater the depth of the formation is, the higher the temperature and pressure on the well. After the hole is drilled, a steel pipe, also known as casing, is placed inside the wellbore. The casing provides structural integrity to the borehole (the wall of the wellbore).

Between the borehole and steel casing, cement slurry is placed for sealing the annular space, annulus. After it sets, the cement slurry forms an annular sheath of hardened and impermeable cement. It provides zonal isolation, isolates porous formations, supports vertical and radial loads to the casing, protects the casing from corrosion, and bonds its exterior surface to the walls of the wellbore (Rincon-Torres and Hall 2013; Fink 2015). Figure 1 represents the casing, the borehole, the cement slurry, and the formation. It schemes the placing of the cement slurry between the casing and the different formations.

The cement slurry, also known as cement paste, is a mix of Portland cement, water, and additives. Portland cement was patented in 1824 as artificial cement produced by burning a blend of limestone and clay. It is often referred to as hydraulic cement because it hydrates when mixed with water. It is first a thick slurry. Subsequently, as a result of chemical reactions between water and chemical compounds present in the cement, it sets and hardens. This hydration reaction is responsible for the impermeable, resistant, solid, hardened cement paste. The final product is a synthetic rock insoluble in water under normal conditions, with low permeability

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S.N. Goyanes, N.B. D'Accorso (eds.), *Industrial Applications of Renewable Biomass Products*, DOI 10.1007/978-3-319-61288-1_7

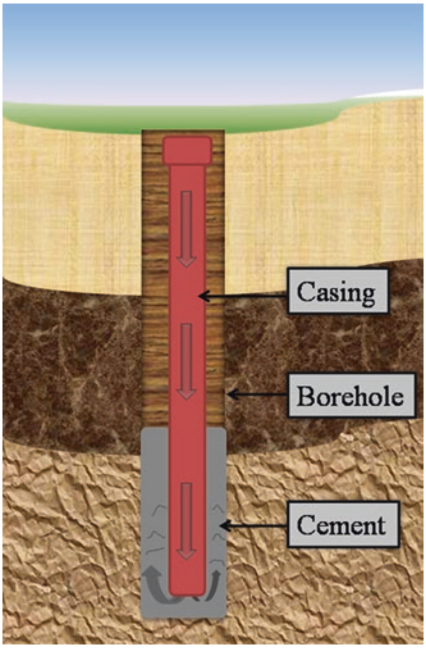


Fig. 1 Scheme of the placing of the cement slurry between the casing and the different formations

and extraordinary compressive strength (Robertson et al. 1989). In most of the world, oilwell cement is manufactured according to the chemical and physical standards given by the American Petroleum Institute (API): API Standards 10A "Specifications for Oilwell Cements and Cement Additives" (American Petroleum Institute 1979).

The water to cement ratio (w/c) is a very important parameter of the cement slurry, since it governs the mechanical properties of the hardened material. The lower the w/c is, the higher the final compressive strength. It also controls the flow behavior of cement before it sets, if no additives are added. It provides workability and the ability of the cement paste to be mixed, transported, placed, compacted, and finished before the initial setting time begins. In the oilwell cement industry, the usual w/c is between 0.38 and 0.46 (Fink 2015). Many desirable properties can be obtained by selecting the adequate w/c, although, to extend the offered properties of the cement paste, additives and admixtures are used (Vorderbruggen et al. 2016).

Finally, there are the additives. Oilwell cement must sometimes be pumped into 2000/3000 m deep wellbores where the temperature goes up to 200 °C and pressures to 140 MPa. Pumping might take more than 6 h and setting immediately after pumping is crucial to avoid gas migrations. Some boreholes are so weak that they cannot support the hydrostatic pressure of the fluid column exerted by the cement slurries with densities higher than 1.00 kg m^{-3}. There are also circumstances where high-density slurries are needed. Each formation and borehole condition needs tailored oilwell cement slurry. Its particular requirement is achieved by the use of additives.

Additives, in the oil and gas industry, are all additions to cement and cement slurries. Unlike in the construction industry, in the oil and gas industry, there is no differentiation between additives (larger additions) and admixtures (less than 5 % by weight of cement additions, usually chemical admixtures) (Bensted 1996).

Additives would be defined, then, as non-cementitious materials added to the cement slurry to optimize some specific property. The term is so broad that it includes slag, silica fumes, hollow glass, quartz, different chemicals, foams, and many different types of polymers. They can act on the cement hydration, accelerating or decelerating it, making the cement paste fluid with a low w/c, making it more viscous or more cohesive, and even shear thinning, depending on the material added and its interaction with the cement slurry. In the hardened state of the cement paste, these can be added to reduce the cement content, reduce the hardened material density, make it resistant to supercritical CO_2, and increase its mechanical properties (Ramachandran 1996).

Additives can control, for example, the thickening time for a projected temperature and pressure condition; hence, the slurry remains pumpable throughout the time required to place the cement. Thickening time is the open time, the time needed to manipulate the slurry after mixing the cement with water. As soon as cement contacts the water, viscosity starts increasing with time because of the hydration reaction. When viscosity is too great, the slurry is no longer pumpable. Thus, it is necessary to place the cement within a certain period of time after mixing. The viscosity can be regulated with the proper additive added in an amount fixed for that special cement slurry design for the particular conditions of the wellbore. The thickening time is influenced by temperature and pressure; consequently, it is important to know the conditions in the wellbore. If the cementing remains incomplete, expensive hard work must be done to fix it (Fink 2015).

Many factors must be considered for designing cement slurries, for example, the desired compressive strength of the hardened cement paste. This must be higher than the axial forces or crush loadings that are expected to be exerted against it. As it was established before, the rheology of the slurry should be such that the viscosity is not too high so it can be pumped, but it is enough to maintain the slurry as a uniform suspension. The slurry should not be dehydrated, losing water to the permeable formations, so that the cement slurry retains the cement filtrate (water and the dissolved ions from dissolution of the aqueous phase of cement). This particular dehydration is known as fluid loss, and there are many additives, known as fluid loss agents, designed to prevent it. The most used are cellulose ethers. Furthermore, the consistency of the slurry should reduce the free fluid, minimizing the volume of fluid that separates from it and collects at the vertical surface on the top of a slurry column. This effect is also known as bleeding.

Wellbore cementing is an example of a material design that consists in 6–12 different, single-action components: cement, water, and additives. The diverse variety of additives include accelerators, dispersants, fluid loss agents, gas migration additives, latexes, retarders, and weighting agents, among others. It is wise to notice that additives might interact with each other when mixed together. This interaction must be studied before implementation.

Some of these additives, the chemical admixtures in particular, are biobased and come from renewable biomass products. Not only due to environmental regulations but also due to the recent increase in environmental consciousness, these products are more consumed nowadays, also because many of them have some unique properties that make them irreplaceable (Vorderbruggen et al. 2016). In this chapter, additives used in the oilwell industry for tailoring the cement slurries are described, and some of the most important biobased ones will be particularly addressed.

2 Additives

2.1 Retarders

Setting is the period during which the cement reaction with water generates sufficient hydration products so that these percolate. There is an initial setting time, also referred to as a thickening time, before which the slurry should be placed, and a final setting time, after which the slurry is already a hardened artificial rock.

Retarders are additives that delay the initial setting time; hence, there is more time to place the slurry. These are needed in the oilwell drilling when wellbores are to be cemented in 1000/3000 m or more in depth with high temperatures and pressures, when the cementing operation might require a long period of time. It is well known that the setting time shortens with high temperatures (Fig. 2). Successful placement of the slurry requires that it remains fluid and pumpable at high temperatures for the sufficient amount of hours to fill the annulus; thereafter, the initial setting time of the cement slurry must be adjusted to each cementing operation. Additionally, after the slurry has been pumped into place, it is required that is sets at a normal rate. Then the time of initial set and the thickening time should be retarded; thus, the slurry remains pumpable for the necessary time, and yet the period of time between initial and final setting time should not be modified. The passage of the slurry from a liquid to a solid state should occur rapidly to guarantee complete seal and prevent any unwanted fluid or gas flow. This can be achieved by adding the accurate dosage of specific retarders to the cement slurry.

2.2 Fluid Loss Control

Fluid loss refers to the unwanted leakage of the fluid phase of the cement slurry into formations across the surface of the borehole. When the slurry dehydrates, w/c is altered, changing the whole slurry design and affecting the quality of the hardened cement. It can cause failure due to premature setting, immobilizing the slurry before it reaches the desired position. It can also be detrimental to water sensitive shale sections of the wellbores that may weaken and break down due to

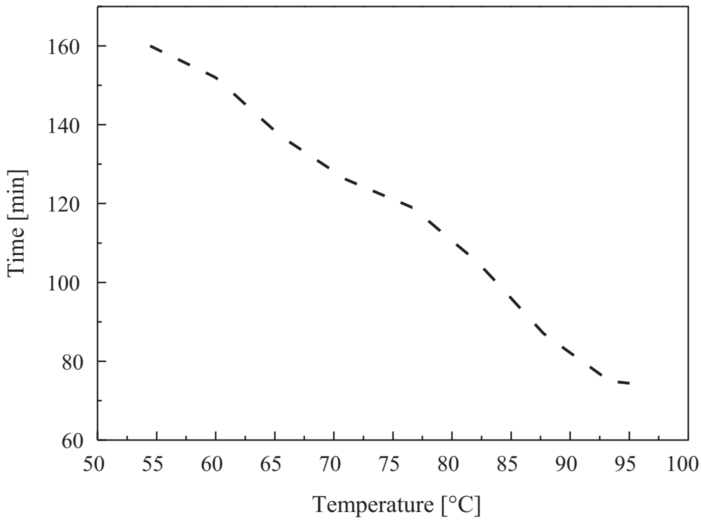


Fig. 2 Effect of temperature on time of initial setting of neat Portland cement with a w/c 0.6 (Adapted from Craft et al. 1934)

the filtration of liquids into clays that can swell causing partial or complete blocking of the wellbore.

Fluid loss control refers to treatments designed to reduce the undesirable leakage, and it has been achieved by two basic mechanisms (Rincon-Torres and Hall 2013). The first one is based on increasing the viscosity and the suspension stability of the cement slurry using high polymer concentrations. The second one is by developing a filter cake in the borehole surface using fluid loss additives to plug the pore throats of the formation. Fluid loss additives retain the key characteristics of the cement slurries, including viscosity, thickening time, density, and compressive strength development, all of which are affected by the amount of water on the cement slurry (Navarrete et al. 2000).

2.3 Free Water Control

Another mechanism, which is detrimental to the w/c ratio, is the sedimentation of cement particles down to the bottom of the pumped slurry and supernatant water on the surface of the cemented borehole due to the different densities. These can also affect the w/c and the stability of the cement suspension. One of the objectives of a slurry design is to keep the annular column with a homogeneous cement suspension until it sets; thus, a proper cement placement and, therefore, hydraulic annulus seal are obtained.

The separation of the different specific gravity particles can be prevented if the viscosity of the slurry increases. An additive that increases the viscosity can enhance the ability of the fluid to suspend and carry particles without sedimentation. There are several kinds of viscosity increasing additives. These can be referred to as viscosifying agent, viscosifier, thickener, gelling agent, or suspending agent.

2.4 Dispersants

Cement slurry is a non-Newtonian fluid. It actually behaves as a Bingham's fluid. It presents an initial high shear stress that has to be overcome with pumping energy during the placing in the annulus. Sometimes, due to different additions or wellbore conditions, this initial shear stress is too high. To lower it down, dispersants are added to the slurry. Dispersants, also known as water reducers, are additives that increase the slurry's fluidity without adding additional water or reduce the water content and, hence, the water to cement ratio for a given fluidity in order to increase the hardened slurry's strength.

Dispersants interact with cement particles leading to its adsorption on the cement particle surfaces. The electrical charge repulsion of adsorbed dispersant molecules can prevent flocculation of cement particles, promoting their homogeneous dispersion in fresh cement slurries. Figure 3 is a schematic representation of the electrostatic repulsion.

Dispersants have a thinning effect that can ease the mixing and placing of the slurry. These can lower the friction and the pressure during pumping. They can also be used to reduce the pressure exerted on the borehole protecting depleted or weak formations and preventing circulation lost.

2.5 Lost Circulation Materials

Lost circulation is another serious problem cement slurries have to overcome. It is the reduction or total loss of the slurry during cementing operation. It occurs in high permeability formation, with vugs or naturally fractured formation and unconsolidated zones. It can also happen when the hydrostatic pressure of the cement slurry exerted over the borehole exceeds the fracture gradient of the formation. In each of these cases, slurry can flow and circulate outside the annulus failing to seal the space between the formation and the casing. Figure 4 represents a wellbore where the slurry can be lost during the cementing operation.

There are different ways to avoid the loss of circulation of the slurry. Lightening the slurry's density is one way. With low-density slurries the pressure drops by friction during the slurry placement, allowing to mitigate the circulation loss since, by reducing this pressure, the pressure exerted by the cement slurry on the formation is also reduced. Another alternative is the use of thixotropic cement slurries, sensitive to shear stress, which gelates when the shear ceases. These slurries develop high gel strength as soon as they flow into a formation by plugging the area. Another option is to use fast-setting cement. Moreover, some materials and fibers have been successfully used to avoid circulation loss because they

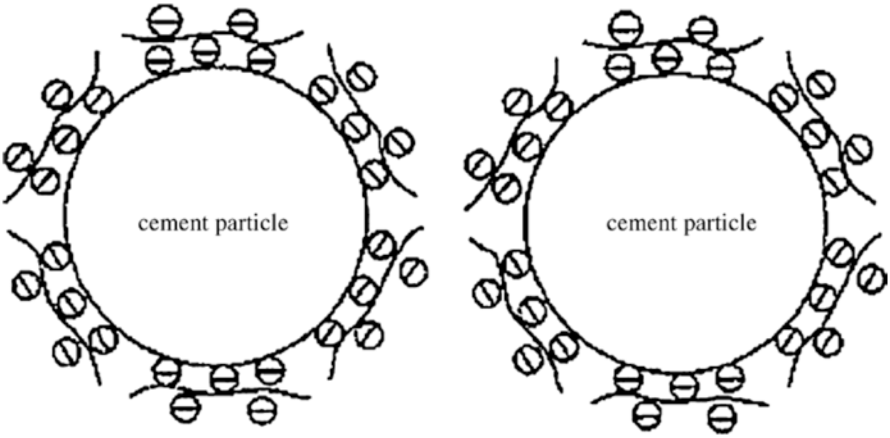


Fig. 3 Electrostatic repulsion: a schematic representative of two cement particles adsorbed with dispersants or water reducer molecules (Ouyang et al. 2006)

act as bridging agents tamponing some borehole voids, avoiding that the slurry circulates outside the annulus (Abbas et al. 2004).

2.6 Lightweight Additives

As mentioned before, some weak formation require low-density cement slurries; thus, the hydrostatic pressure of the fluid column is low enough for the formation to resist. These slurries avoid or minimize circulation loss. The lightweight slurries require also less energy to transport and pump. To lower the slurries' densities, these can be foamed by injecting gas, usually nitrogen, into the slurry. The density drastically falls but also the slurry's mechanical strength. Adding additional water to the cement slurry is a common mean of reducing its density. The cement slurry will thus require water-extending additives. These help maintaining the slurry stability and compensate the low compressive strength due to the high w/c. Some of these extenders are lightweight aggregates such as hollow glass microspheres and fibers, which also can contribute to reduction of the cement slurry density.

3 Biobased Additives

3.1 Cellulose

In the construction chemical industry, cellulose products are very important. Cellulose is mostly used in the form of ether derivatives, specially carboxymethyl cellulose and methyl cellulose. Other than ethers, very small quantities of cellulose products are used, such as micro and nanocellulose fibers (Plank 2005).

Fig. 4 Scheme of a wellbore with permeable formations with vugs and natural fractures, where the slurry can lose during the cementing operation (Abbas et al. 2004)

3.1.1 Cellulose Derivatives

Cellulose ethers have been used in the oilwell cement industry for decades. A patent from 1953 claims the use of alkyl hydroxylalkyl cellulose mixed ethers, where the alkyl group contained 1–4 carbon atoms and the hydroxyalkyl group contained 2–4 carbon atoms, as set retarding agent using it within 0.5–5 % by weight of cement (bwoc) (Kaveler 1953). Another patent in 1957 claimed the use of sulfoalkyl cellulose ethers and their salts as cement set retarders but also as thickening time extending and fluid loss control agents (Kaveler 1957). Not only sulfoalkyl cellulose ethers were reported as fluid loss control and thickening time extending agents and set retarders, carboxymethyl hydroxyethyl cellulose (CMHEC) was reported as well, and nowadays it is still used for this purpose (Rust and Wood 1959; Vázquez and Pique 2016).

Cellulose ethers (CE) are available in the construction industry as methyl cellulose (MC), methyl hydroxyethyl cellulose (MHEC), methyl hydroxypropyl cellulose (MHPC), hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC), Na-carboxymethyl cellulose (CMC), Na-carboxymethyl hydroxyethyl cellulose (CMHEC), ethyl cellulose (EC), and ethyl hydroxyethyl cellulose (EHEC). Cellulose ethers are obtained by the substitution of the hydroxyl groups of cellulose that can be replaced with, for example, methyl, hydroxypropyl, hydroxyethyl, and carboxymethyl groups. The etherificated cellulose becomes a water-soluble polymer. Figure 5 represents the structure of some water-soluble cellulose ethers used in the construction industry.

The most used in the oilwell cement industry are HEC and CMHEC. HEC is a very good fluid loss control agent and can perform under diverse salinity conditions up to

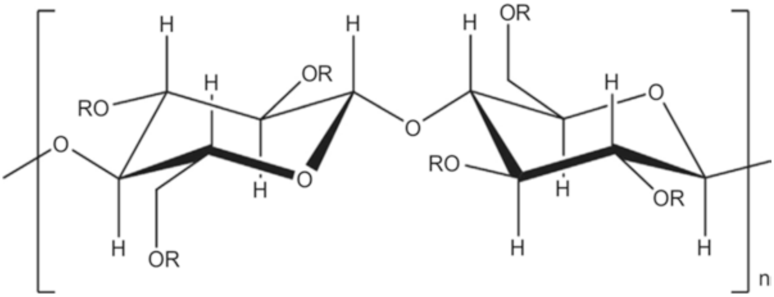


Fig. 5 Structure of water-soluble cellulose derivatives (R = H for cellulose and R = H, ($-CH_3$), ($-CH_2$-CH_2OH), ($-CH_2$-$CHOHCH_3$), or ($-CH_2$-COOH) for methyl cellulose, hydroxyethylmethyl cellulose, hydroxypropylmethyl cellulose, or carboxymethyl hydroxyethyl cellulose, respectively) (Vázquez and Pique 2016)

150 °C. Nevertheless, when using HEC, dispersants have to be added to the cement slurry to control its thickening effect. HEC can enhance the viscosity of the cement slurry, which is not always desirable for pumpable slurries. Typical HEC products used in well cementing have a degree of substitution (DS) of 1.5–2.5. When using CMHEC, the carboxylic group introduces a set retarding effect on the cement slurry among its fluid loss control capacity. Typical commercial products used in well cementing exhibit a degree of substitution (DS carboxymethyl) of 0.3–0.4 and a molar degree of substitution (MS hydroxyethyl) of 0.3–2.0 (Plank 2005).

Figure 6 represents some of the results of a research conducted by Bülichen and Plank. It shows the measurement of the fluid loss of CMHEC according to the American Petroleum Institute (API) specifications. Fluid loss decreases from 1163 ml at 0.1 % bwoc CMHEC, to 42 mL at 0.5 % bwoc CMHEC. The concentration of CMHEC needed to achieve an API fluid loss of below 100 ml/30 min at 27 °C was found to be 0.4 % bwoc. The columns in Fig. 6 represent the amount of polymer retained from the filtrated volumes of cement slurries containing CMHEC at 27 °C (Bülichen and Plank 2012). The same research was done for HEC. For this biopolymer fluid loss decreases from 318 ml at 0.4 % bwoc HEC to 36 mL at 1.0 % bwoc HEC. The concentration of HEC needed to achieve an API fluid loss of below 100 ml/30 min at 27 °C was found to be 0.7 % bwoc (Bülichen and Plank 2011).

Recently a new derivatized-cellulosic polymer has been tested in field cases. Cellulose was modified, so the additive fulfills many of the cementing slurries' desired properties such as fluid loss control, dispersability, free water control, and lightweight, for use in wells up to 120 °C. This was achieved by modifying cellulosic material after an in-depth structure activity study of the polymer. The molecular substitution and degree of substitution of the ether side chains structures were tuned along with its molecular weight. The size of the particles was also optimized to control the hydrolysis rate of the polymer (Vorderbruggen et al. 2016). This means that the cellulose-based additives are still an actual research topic; it is still being tuned and optimized to reach the perfect additive.

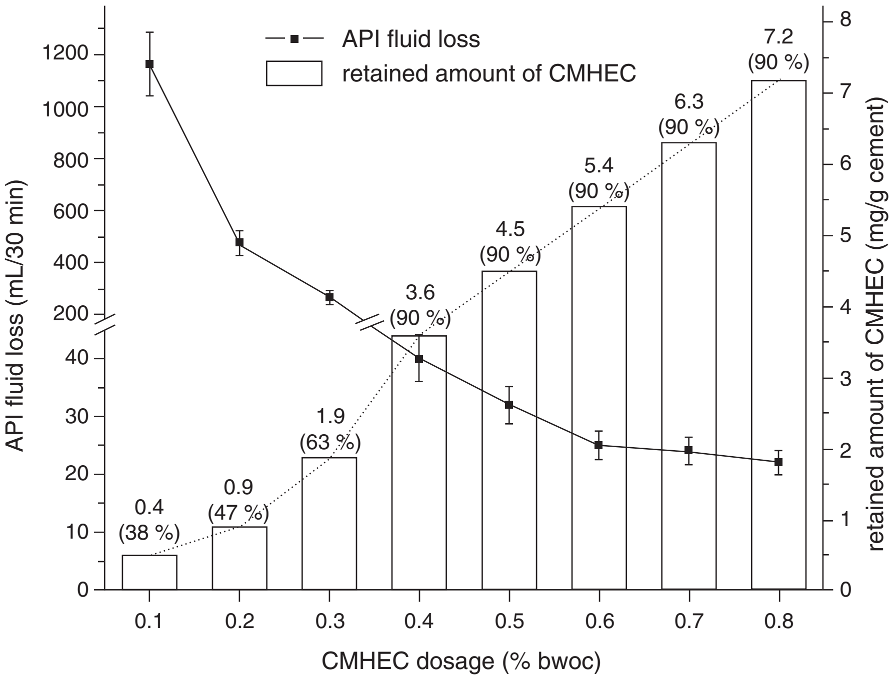


Fig. 6 Fluid loss measured according to API specification and the retained amount of CMHEC as a function of polymer dosage (Bülichen and Plank 2012)

3.1.2 Micro- and Nanocellulose Fibers

Cellulose fibers and their derivatives constitute one of the most abundant renewable polymer resources available on earth. The use of cellulosic fibers to reinforce cement-based materials has been widely applied. Many types of natural fibers are commonly used to reinforce construction materials (Gómez Hoyos and Vázquez 2014). Bensted stated that the most common lost circulation controllers employed in the North Sea in 1996 were, among mica and calcium carbonate, walnut shells, while in Asia, coconut shells and sugar cane were also frequently utilized (Bensted 1996). Sugar cane fiber, for example, can reduce the density of the cement slurry, the free water, and the fluid loss content and prevent the lost circulation problem acting as a bridging agent (Samsuri and Phuong 2002).

Microcrystalline cellulose was found to increase the amount of hydration products when added to a cement-based material, thus increasing its impermeability, since hydration products grow to fulfill the cement porous structure. It was also found that the initial shear stress of the cement paste grew 260 % when 3.0 % of microcrystalline cellulose was added (Gómez Hoyos et al. 2013).

With the advances of nanotechnology, the use of fibers in oilwell cementing has reached to the use of nanofibers, especially of nanocellulose (NC). Nanocellulose materials have repetitive molecular structure composed of a linear backbone of β(1→4)-linked d-glucose units. Its chemical structure is plotted in Fig. 7.

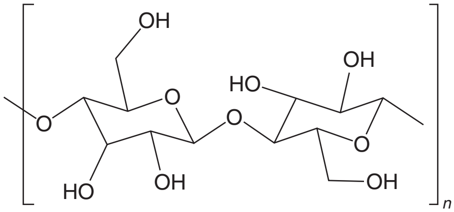


Fig. 7 Chemical structure of nanocellulose materials (Lafitte et al. 2013)

Nanocellulose is a rather interesting material since it has a large surface-to-volume ratio, high strength and stiffness, very low thermal expansion coefficient, low weight, low density, high aspect ratio and is biodegradable. It can be obtained from every cellulose source, specially from lignocellulosic fibers, including a family of sea animals called tunicates, some algae and bacteria, such as bacteria from the *Acetobacter* species (Charreau et al. 2013).

Extraction of nanocellulose from lignocellulosic fibers is one of the most studied topics in the literature today since this particular nanocellulose is renewable and abundant, and the cost of the raw material is low. Nanocellulose from wood and natural fibers has traditionally been extracted mainly by acid hydrolysis and via mechanical treatment. When extracted by acid hydrolysis, the so-called nanocrystalline cellulose (NCC) or cellulose nanowhiskers (CNW) are obtained. These are rodlike particles with diameters in the range of 2–20 nm and 100–600 nm in length. Cellulose nanowhiskers are characterized by high crystallinity, and their aqueous suspensions display a colloidal behavior (Vázquez et al. 2015).

Cellulose nanowhiskers are of high strength, low density, and thermally stable above 180 °C, which is highly important for oilwell materials. Then, it can be used as a cement reinforcement and to prevent circulation loss of the cement slurry. Furthermore, because the product is insoluble in aqueous solution and its ability to enhance viscosity is via hydrogen-bonding interactions, the cellulose nanowhiskers can be used in cement slurries for thixotropy and to improve its static suspension ability (Rincon-Torres and Hall 2013). Figure 8 shows the effect of different percentages of cellulose nanofibrils on the cement slurry's viscosity. Being τ_0 the initial shear stress of the cement paste, it is established how the shear stress of the slurry increases almost exponentially with the addition of small amounts of cellulose nanofibrils (Gomez Hoyos 2013).

Additionally, Gómez Hoyos studied the cement paste modified with 0–0.4 % bwoc of cellulose nanofibrils by means of dynamic mechanical analysis between a temperature range of 25 °C and 200 °C (Gómez Hoyos et al. 2017). It was demonstrated that the storage modulus of the modified cement paste was relatively constant until 100 °C, the same as the unmodified cement paste. After the analysis, FE-SEM images were taken from the tested samples and smaller cracks were found for modified cement paste. Furthermore, cement paste modified with 0.4 % bwoc of cellulose nanofibrils showed the smallest amount of microcracks. This sample had the highest storage modulus and lost only a 10 % of it at 200 °C.

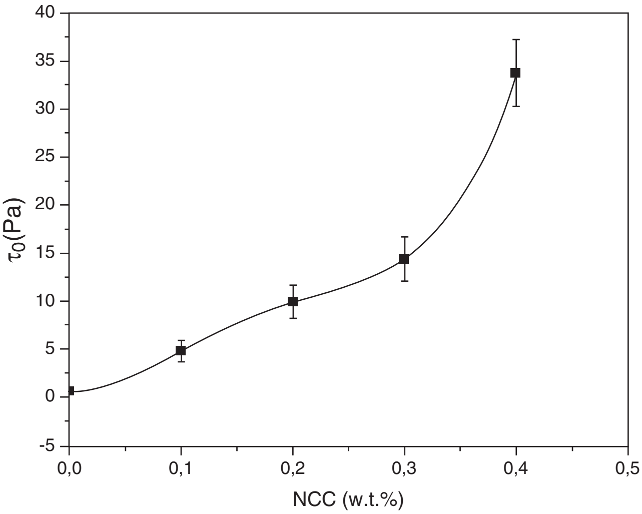


Fig. 8 Effect of different percentages of cellulose nanofibrils on cement slurry in its initial shear stress (Gomez Hoyos 2013)

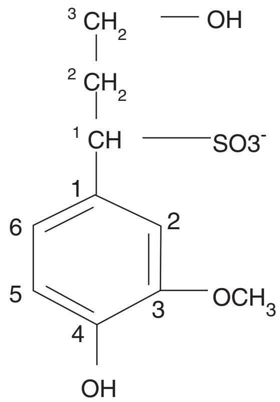
Surface modification of nanocellulose may be employed to increase or attenuate one or more enhancing properties of the abovementioned uses. Some cement slurries can even be additivated with more than one NCC with different surface modifications. Nanocellulose is usually used at concentrations between 0.01 % bwoc (Lafitte et al. 2013).

3.2 Lignin

Lignosulfonates are produced from lignin, a biopolymer contained at 20–30 wt% in wood. Pure lignin is a water-insoluble anionic surfactant obtained during wood pulping. Its surface activity may promote surface adsorption, foaming, and further particle dispersion. Lignosulfonate is the main component in the liquid waste from chemical pulp mills. It contains both hydrophilic groups (sulfonic, phenylic hydroxyl, and alcoholic hydroxyl) and hydrophobic groups (carbon chain) as it is represented in Fig. 9.

Lignosulfonate-based admixtures are the largest admixtures used, by volume, in the construction industry, typically used in dosages between 0.1% and 0.3% bwoc in concrete. They have been used as dispersants for more than 70 years (Aitcin 2000). They are low cost and can reduce up to 15% of the water content of a cement mixture, which means, decrease the w/c, increasing the mechanical properties of the hardened material, without affecting the workability during the cementing operation. These admixtures influence both the dispersion of the cement in the presence of water and the hydration rate of the cement, becoming the most used water-reducing/water-retarding admixture in the concrete industry (Vázquez and Pique 2016).

Fig. 9 Typical structural unit of lignosulfonate (Ouyang et al. 2006)



Due to their natural product source, they have to be processed because they can vary in performance from batch to batch (Vorderbruggen et al. 2016). Sulfomethylation with sodium sulfite and formaldehyde is the most common process to obtain an optimized water-soluble lignosulfonate. It yields Na-lignosulfonates (NL) or Ca-lignosulfonates (CL) with a degree of sulfonation between 0.5 and 0.6. Lignosulfonates in solution have a wide range of molecular weights. The highest the molecular weight is, the highest the water-reducing capacity in the cement paste (Ouyang et al. 2006).

It is well known that surface activity and foaming capability of the water reducers have a positive effect on the solid particles dispersing into liquid. In order to improve the water-reducing ratio of lignosulfonate, Ouyang et al. proposed to modify the lignosulfonate molecules by increasing the amount of sulfonic group, thereby altering its surface and foaming activities (Ouyang et al. 2006).

The retarding mechanism of NL is explained since lignosulfonates form complexes with calcium ions available in the cement matrix, which precipitate onto the surface of cement. Thus, the access of water to these sites is blocked and further growth of the cement hydration products is inhibited. The higher the amount of polymer precipitated on the surface, the greater the retardation (Recalde Lummer and Plank 2012).

3.3 Microbial Polysaccharides

Microbial polysaccharides are additives economically competitive with natural gums, produced from marine algae and other plants, in the oilwell industry. Plant- and seaweed-derived gums used traditionally are affected by environmental factors; there are exceptions, of course, such as carrageenan, a high molecular weight polysaccharide derived from seaweed (Fink 2015). Microorganisms, on the contrary, can be grown under controlled conditions and offer a wide range of polymers with unique structural properties. Xanthan from *Xanthomonas campestris*, sphingans (gellan, welan, diutan, rhamsan) from *Sphingomonas* sp., and cellulose from *Acetobacter xylinium* are some of the microbial polysaccharides extensively studied due to their commercial importance (Kaur et al. 2014).

Biopolymers made by fermentation usually have a shear-thinning type of viscosity; this is what makes them so important in the oilwell industry. This means that most of the microbial biopolymers increase the yield point and show a low plastic viscosity. This is particularly useful in oilwell slurries because low viscosity when being pumped is desirable, since it decreases the pumping energy and prevents the circulation loss, and high viscosity is desirable when the pumping is over, because it favors the gel strength and the stability of the slurry (Plank 2004).

3.3.1 Xanthan Gum

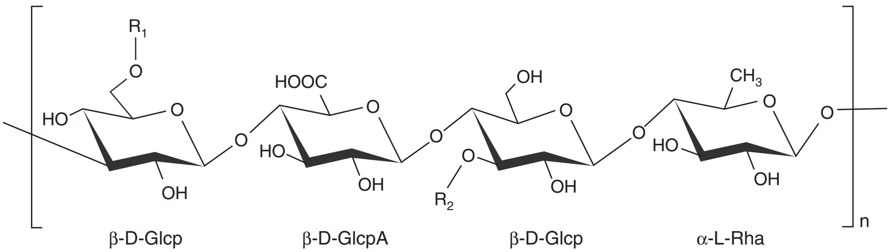
Xanthan gum was the first microbial biopolymer to be used in the construction industry and the most used nowadays. It is an exocellular biopolymer secreted by *Xanthomonas campestris*. The molecular weight of the gum is reported to be of approximately 2×10^6 Da, and it has a double helix molecular arrangement (Caenn et al. 2017). It was also stated that solutions of xanthan gum exhibits thickening properties with a pseudoplastic behavior. Xanthan gum has been used extensively in the oil industry as a viscosifier for different applications due to this unique rheological property. It is also very popular because of its suspension capabilities to water-based drilling fluids. The rheological behavior of xanthan-based fluids can be used, in addition, to control fluid loss.

Xanthan gum performs well in high viscosity systems but cross-links in the presence of calcium ions and high pH, both found in the cement slurry. It also presents some limitations; it is sensitive to high temperatures and has low tolerance to field contaminants (Gallino et al. 1996; Navarrete et al. 2000).

3.3.2 Welan Gum

Welan gum is one of the different variations of sphingans. Sphingans are structurally similar exopolysaccharides that have a comparable backbone structure except for the location of side chains as it is shown in Fig. 10. This gives the biopolymers different physical properties (Kaur et al. 2014).

It is an industrial grade of a bacterial polysaccharide gum produced by the growth of the *Sphingomonas sp*. It contains principally the neutral sugars l-mannose (L-Manp), l-rhamnose (L-Rha), d-glucose (D-Glcp), and d-glucuronic acid (D-GlcpA) in the molar ratios 1.0:4.5:3.1:2.3 (Dial et al. 2001). The welan molecule is rather stiff, whereby it becomes relatively insensitive to temperature and pH variation. This, together with its tolerance of high calcium ion concentrations, makes it ideal for applications in cement systems. It acts as a thickening, suspending, binding, and emulsifying agent, stabilizer, and viscosifier. It is used in oilwell cementing because it retains its stability and viscosity at elevated temperatures.



Name of sphingan	R_1	R_2
Gellan	H	H
Welan	H	←1)-α-L-Rha or ←1)-α-L-Manp
Rhamsan	←1)-α-D-Glcp-(6←1)-β-D-Glcp	H
Diutan	H	←1)-α-L-Rha-(4←1)-α-L-Rha

Fig. 10 Scheme of the structure of sphingan biopolymer showing different side chain and their linkage positions for gellan, welan, rhamsan, and diutan. *Glcp* is glucose, *GlcpA* is glucuronic acid, *Rha* is rhamnose, and *Manp* is mannose (Kaur et al. 2014)

Of all microbial biopolymers, welan gum was found to be the best to stabilize cement slurries and to prevent surface fluid loss at concentrations in the range of 0.01–0.9% bwoc (Kaur et al. 2014). Allen et al. claim that welan gum controls the water loss from cement slurries and remains stable until temperatures in the range of 93–127 °C (Allen et al. 1990). Üzer and Plank found that the stabilizing effect of welan gum only derives from its strong viscosifying effect on the aqueous phase of the cement slurry (Üzer and Plank 2016).

Welan gum can also stabilize a dispersant's suspension. Rapidly hydrating welan gum acts as a liquefied viscosity agent with the dispersant. Welan gum particles swell in the dispersant, resulting in a stable suspension without much viscosity increase; it is then used usually in cement slurry already containing dispersants. Nevertheless, due to its adsorption effect, it induces a retarding behavior in the cement setting (Allen et al. 1990; Kaur et al. 2014; Üzer and Plank 2016).

The use of low viscosity welan gum in cement slurries can also reduce the fluid loss. It can be obtained in a wide range of viscosities and still exhibit good fluid loss control. In some applications, the cement slurry is viscous enough; thus, additional viscosity induced by the additive would be undesirable. For these applications, a lower viscosity welan gum can be prepared which retains fluid loss control (Allen et al. 1990).

3.3.3 Diutan Gum

Diutan gum was isolated from the *Sphingomonas* genus in the 2000 decade (Navarrete et al. 2001). The chemical structure of the monomer is shown in Fig. 10. Diutan gum has an average molecular weight of 5×10^6 Da, which is much higher

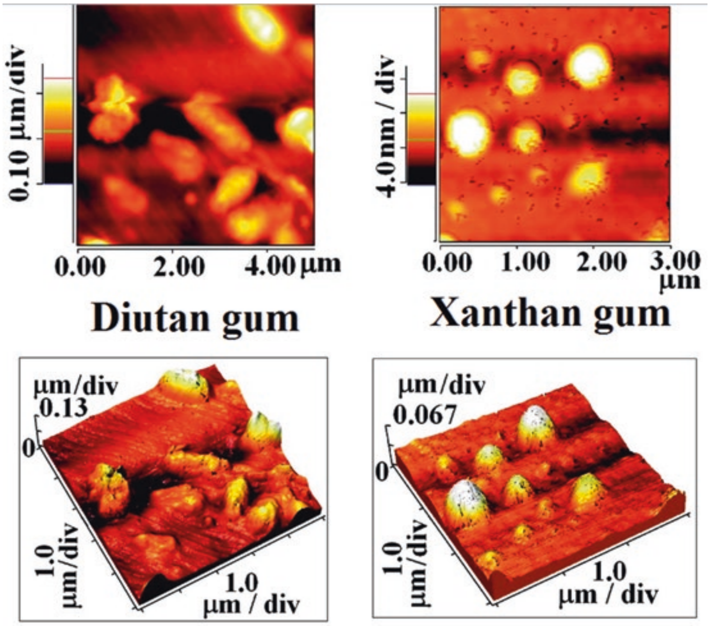


Fig. 11 Topological 2D (*top*) and 3D (*bottom*) images of diutan and xanthan gum (Adapted with permission from Mukherjee et al. (2010). Copyright 2010 American Chemical Society)

than those of welan and xanthan gum. Topological images of diutan gum, 2D and 3D, are shown in Fig. 11 and are compared with xanthan gum.

Diutan is a more efficient viscosifier than xanthan and welan gums at ambient temperature in low concentration, even in salt systems, usually present in wellbores, and at temperatures between 90 and 150 °C. The thermal stability of diutan can be improved to at least 160 °C by the presence of NaCl. Diutan is more elastic than xanthan gum and is more shear thinning than xanthan and welan, resulting in lower friction pressure losses at comparable concentrations (Navarrete et al. 2001).

Figure 12 shows the viscosity of different concentrations of xanthan, welan, and diutan gums in synthetic seawater at 24 °C. Viscosity increases with the concentration. The more viscous one is diutan, followed by xanthan and welan gums.

3.3.4 Bacterial Nanocellulose

As it was mentioned before, cellulose nanofibers can be obtained through lignocellulosic fibers or through microorganisms. Specific bacteria synthesize cellulose microfibrils as a primary metabolite. These overlap and intertwist to form a nonwoven mat with very high water content (Vázquez et al. 2013). Figure 13 shows a FE-SEM image of the freeze-dried bacterial nanocellulose mat.

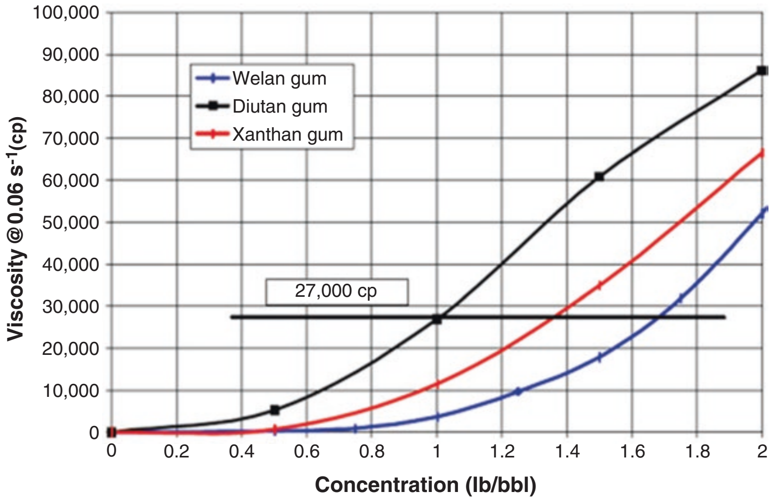


Fig. 12 Viscosity of different concentrations of xanthan, welan and diutan gums in synthetic seawater at 24 °C (Caenn et al. 2017)

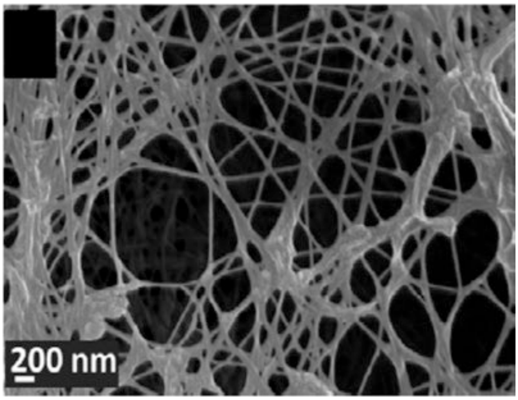


Fig. 13 FE-SEM images of freeze-dried bacterial nanocellulose (Menchaca-Nal et al. 2016)

No recent patent or papers were found that use bacterial nanocellulose in oilwell cement, but research is being done. In a recent conference, Martin et al. evaluate the modification of an oilwell cement slurry with 0.1% and 0.2% bwoc of bacterial nanocellulose. To introduce it to the slurry, the mat was mechanically mixed with the slurry's water. As a result, the shear stress increases dramatically, the free water diminishes, and the compressive strength was enhanced (Martin et al. 2016). Many more studies should be done, but the first results show promising.

4 Conclusions (Outlook and Future Trends)

The oilwell cement industry is very demanding on chemical admixtures. Biopolymers have fulfilled these demands and are wildly used in this industry, competing hand to hand with the synthetic ones. The most used are cellulose and lignin based, as well as in the general construction industry. Furthermore, the oilwell cementing industry has included the microbial biopolymers. The oilwell industry has always been ahead in technology due to its technical complexities. Therefore, there is to expect that microbial biopolymers will soon be accepted in the construction industry as well.

Biopolymers have an extra advantage over synthetic polymers. Lately, environmentally friendly products are more appreciated in many companies. An effort is being made to produce or use nontoxic, low emission, and leaching products that would be recyclable if needed and show no effects on the environment where they are fabricated and used. This applies to the construction chemicals used as additives in the oilwell cement industry.

Acknowledgments The authors acknowledge the Universidad de Buenos Aires/Facultad de Ingeniería (UBACyT 20020160100055BA), the Agencia Nacional de Promoción Científica y Tecnológica del Ministerio de Ciencia y Tecnología de la República Argentina (PICT-2016-4543) and the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET).

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