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Oil Well Cement Additives: A Review of the Common Types

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Abstract

Additives play significant role in oil and gas well cementing operations. There are varieties of cement additives that have been developed to allow the use of Portland cement in many different oil and gas well operations. In an attempt to formulate the appropriate cement slurry for any cementing job, the right additive must selected and the right quantity must be added. Additives have different functions and are broadly classified as accelerator, retarders, extenders, fluid loss agents, dispersants and many more. Each of the broad classification has different categories of additives that have been developed to perform almost the same function during cement slurry design. However, there some additives under each major type that are commonly used in cement slurry design for oil and gas well cementing operations. This paper reviews the broad classification of oil well additives giving emphasis to the commonly used additives during oil and gas well cementing operations.

Keywords: Accelerator; Additives; Dispersant; Extender; Retarder.

Introduction

In well cementing, Portland cement systems are designed for temperatures ranging from below freezing in permafrost zones to 662 °F (350 °C) in thermal recovery and geothermal wells [1]. They also encounter pressures ranging from ambient to 30 000 psi (200 MPa) in deep wells. Accommodation of such variations in conditions was only possible through the development of cement additives [2]. According to American Petroleum Institute Recommended Practice 10B, additives are materials added to cement slurry to modify or enhance desired property [3]. Cement additives selected for cementing operations are an integral part of sound well design, construction and well integrity [4]. Additives are available to enhance the properties of oil well slurries and achieve successful placement between the casing and the geological formation, rapid compressive strength development and adequate zonal isolation during the lifetime of the well [2]. According to Cowan and Eoff [5], additives are 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. There are different types of cement additives that have been developed to allow the use of Portland cement in many different oil and gas well applications [6]. Each major type has different types of additives that have been developed to perform almost the same function during cement slurry design. However, there are some additives under each major type that are commonly used in cement slurry design for oil and gas well cementing operations. This paper reviews the broad classification of oil well additives giving emphasis to the commonly used ones in oil and gas well cementing operations.

Materials and Method

The research was conducted using secondary source of data from journal papers, conference proceedings, text books, unpublished materials and recognised websites. The method adopted includes reviewing the broad categories of oil well cement additives giving prominence to the common additives.

Cement Additives and Common Types

The rate at which hydration occurs when water is mixed with cement can be altered using chemical additives [7]. Additives are chemicals and materials blended into base cement slurries to change the performance of the cement. Due to the inherent nature of base cements and because of the demands placed on the cement sheath throughout the life of the well, the performance properties of the cementing slurry are modified to address the specific and unique conditions of each well [8]. Many of the additives currently used are organic, polymeric materials which have been specifically formulated for use in well cementing operations [5]. Typical chemical additives for oil and as well cementing operations include; accelerators, retarders, extenders, fluid loss and loss circulation additives, dispersants, and many more [9].

Accelerators

Accelerator is a chemical additive used to speed up the normal rate of reaction between cement and water which shortens the thickening time of the cement, increase the early strength of cement, and saves expensive rig time. Cement slurries used in shallow wells where temperatures are low requires accelerators to shorten the time for "Waiting-on-Cement (WOC)" before drilling operation can be resumed [10-12]. In deeper wells the higher temperatures promote the setting process, and accelerators may not be necessary. Accelerators do not increase the ultimate compressive strength of cement but promote rapid strength development [6,13]. According to Bett [4], higher concentration of accelerators acts as retarders. However, Lake and Mitchell [14] were of the view that not all accelerators at high concentrations acts as a retarder. To Lake and Mitchell, regardless

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of the concentration of Calcium Chloride, it always acts as an accelerator. Accelerators are also required to counter the setting delay of other additives added to the slurry such as dispersants and fluid loss control agents [1,2]. Calcium Chloride and Sodium Chloride are the most commonly used [4]. However, Calcium Chloride ($CaCl_2$) is undoubtedly the most efficient and economical accelerator [1,13,15]. Other types of accelerators include; Sodium Metasilicate, Potassium Chloride and gypsum [2].

Calcium Chloride: Calcium Chloride ($CaCl_2$) is undoubtedly the most efficient and economical accelerator [1,13,15]. It is available in regular grade (77% Calcium Chloride) and anhydrous grade (96% Calcium Chloride). The anhydrous Calcium Chloride is in more general use because it absorbs moisture less readily and is easier to maintain in storage [16]. Calcium Chloride is generally added in concentrations of 2% – 4% by weight of cement (bwoc) (Table 1) but over 6% bwoc its performance becomes unpredictable and premature setting may occur [2]. To Anon [17], Calcium Chloride is effective at temperatures between 40 °F and 120 °F (4°C and 49°C) in concentrations of 2% to 4% by weight of cement (bwoc), or equivalent liquid concentrations of 40 gal/100 sk (2%). According Anon [6], Calcium Chloride is commonly used at 3% or less by weight of cement. To Bett [4], Calcium Chloride is used in concentration range of 1.5% bwoc - 2% bwoc. Higher concentration decreases thickening time and develops compressive strength faster [1]. According to Rike [10] $CaC1_2$ should be added to the mix water first to insure that no portion of the cement can accidentally include an excess fraction of $CaC1_2$, causing a premature set of part of the cement.

Sodium Chloride: Salt (NaCl) is a slight accelerator at low concentrations and becomes a retarder at high concentrations and also acts as a mild dispersant at all concentrations [10,14]. According to Lake and Mitchell [14], generally, NaCl acts as an accelerator at concentrations from 1% to 10 % by weight of water (bwow) with the commonly used concentration of NaCl as 3% bwow. To Bourgoyne et al. [16], maximum acceleration of NaCl occurs at a concentration of about 5% bwow for cements containing no bentonite. At concentrations above 5%, the effectiveness of sodium chloride as an accelerator is reduced. Saturated sodium chloride solutions tend to act as a retarder rather than an accelerator [16]. Seawater is extensively used offshore as it has 25 g/l NaCl but the concentration of magnesium of about 1.5 g/l must be taken into account [2]. The thickening time obtained with seawater usually is adequate for cement placement where bottomhole temperatures do not exceed 160 °F (71 °C). Cement retarders can be used to counteract the effect of the seawater at higher temperatures, but laboratory tests should always be made before this type of application [16]. According to Ludwig [18], a study conducted by API Mid-Continent District Committee on the effect of NaCl on oil well cement showed that small quantities of NaCl**,** up to about 4 percent by weight of cement (4% bwoc), greatly accelerate the rate of setting, whereas larger quantities, from about 8% to 10%, do not have a very great effect upon setting times. However, the most commonly used concentration of NaCl for cementing operation is 2% bwoc – 2.5% bwoc [4].

$CaCl_2$ %bwoc	91 °F	103 °F	113 °F
0	Thickening Time		
	4:00	3:30	2:32
2	1:17	1:11	1:01
4	1:15	1:10	0:59

Table 1: Calcium Chloride Thickening Time on Portland cement

Retarders

Retarders are chemical additives used to decrease the speed of cement hydration [19]. The cements commonly used in well applications do not have a sufficient long fluid life (thickening time) for use at Bottom Hole Circulating Temperatures (BHCTs) above 100 °F (38°C) [4,7]. For extending the thickening time, additives known as retarders are required [7]. Retarders inhibit hydration and delay setting, allowing sufficient time for slurry placement in deep and hot well [1]. That is, it increases the thickening times for pumping the cement into place [12,20,21]. According to Magarini et al. [2]. The retardation process is not completely understood but it is known that retarders bind to calcium ions [22] and are able to inhibit the growth of ettringite crystals [23]. Besides extending the pumping time of cements, most retarders affect the viscosity to some degree. Retarders do not decrease the ultimate compressive strength of cement but do slow the rate of strength development [4,7]. Retarding effects of a retarder depends upon a number of factors including dosage of the additives, curing conditions among others. Therefore, Bottom Circulation Temperature (BHCT) should be carefully predicted so that the correct retarder concentration is used to avoid flash setting or very long setting up time due to over-retarded cement slurry [4]. Retarders are used at higher temperatures to allow time for mixing and placement of the cement slurry [6,24] and also when accelerating effect of another additive might dangerously reduce the time available for pumping the cement [12]. The most common retarders are natural lignosulfonates, cellulose and sugars derivatives [7,10]. The chemical nature of the retarder to be used is dependent on the cement phase [25]. Lignosulfonate and hydroxycarboxylic acids are retarders that are believed to perform well for oil well cements with low C_3A contents. Some admixtures act as retarders when used in small amounts but behave as accelerators when used in large amounts [26]. The newest retarders are made from various synthetic compounds [6]. Bentz et al. [26] reported on the use of carbohydrates such as sucrose as a retarder. According to Bentz et al. [26] the addition of carbohydrates such as sucrose can significantly extend thickening time or even prevent setting completely. However, they are not commonly used in oil and gas well cementing because of the sensitivity of the degree of retardation to small variations in concentration [25,27].

Lignosulfonate: Of the chemical compounds identified as retarders, lignosulfonates are the most widely used [1,4,7]. A lignosulfonate is a metallic sulfonate salt derived from the lignin recovered from processing wood waste. The resultant aqueous solution of lignosulfonic acid, simple sugars, starches, and natural gums is known as lignin liquor. The composition of the liquor is dependent on the wood source and the reaction conditions. Performance of the liquor as a retarder is dependent upon the proportioning of these compounds, their molecular weights, and the degree of sulfonation. As a result of processing, three grades of lignosulfonate are available for the retardation of cement slurries. Each grade is available as calcium/sodium or sodium salts. The three grades can be described as filtered, purified, and modified [7]. According to Adams and Charrier [13], the most common retarder among the three types may be calcium lignosulfonate. Its effectiveness is limited in temperatures above 200 °F. Concentrations of 0.1% bwoc - 1.0% bwoc are used in most slurry applications to give both predictable thickening times and compressive strengths. However, Bett [4] was of the view that calcium lignosulfonate concentration range of 0.1% bwoc - 0.5% bwoc is more preferred. Amounts above 1% bwoc do not add appreciably to slurry retardation. To Rike [10], lignosulfonate are the most commonly used retarders for squeeze cementing because they are consistent in quality and the dispersing effect makes smoother slurry of gel cements. Research conducted by Satiwariya et al.[19] on the effects of Lignosulfonate and temperature on compressive strength of class G type High Sulphate Resistant (HSR) cement revealed that Lignosulfonate with Q-Broxin type reached a maximum value with the addition of Lignosulfonate as much as 0.2% by weight of cement at temperatures ranging from 28 °C to 176 °F (80 °C). The addition of the Lignosulfonate additive at concentrations higher than 0.2% bwoc resulted in a decrease in the compressive strength of the cement.

Cellulose Derivatives: Hydroxyethyl cellulose (HEC) and carboxymethyl hydroxyethyl cellulose (CMHEC) are the two cellulose polymers used in well-cementing applications. HEC is commonly considered as a fluid-loss additive. Although as a possible option, it is worth noting that at Bottom Hole Circulating Temperature (BHCT) of 125 °F (52 °C) or less, the thickening time can be extended by approximately two hours in freshwater slurry. Traditionally, the only cellulose that is considered as a retarder is CMHEC. This is largely because it is functional as a retarder up to approximately 230 °F (110 °C) BHCT at the same concentrations as calcium Lignosulfonate, but it also provides good fluid-loss control [28]. To Adams and Charrier [13], Carboxymethyl hydroxyethyl cellulose (CMHEC) can be used to about 240°F (116 °C) BHCT.

Hydroxycarboxylic Acids: The hydroxycarboxylic acids are well known for their antioxidant and sequestering properties that benefit cement-slurry performance. The antioxidant property improves the temperature stability of soluble compounds such as fluid-loss additives. Commonly used hydroxycarboxylic acids and their derivatives are Citric acid, Tartaric acid, Gluconic acid, Glucoheptonate and Glucono-delta-lactone [28]. The commonly used hydroxycarboxylic acids are generally derived from naturally occurring sugars [14]. It has been found that sugar acts as a retarder of cement slurries when added in small concentrations and as an accelerator when added in high concentration of 0.2% to 1% by the weight of cement [24,25]. Hydroxycarboxylic acids are efficient to a temperature of 302 °F (150 °C). However, below 200 °F (93 °C) they can cause over retardation. One acid used is citric acid with an effective concentration of 0.1% - 0.3% bwoc [44].

Extenders

Many formations will not support long cement columns of high density slurries, these slurries weights need to be reduced to protect formations that have low fracture gradient or for economics purposes. To reduce the weight of cement slurries, extenders are used [29]. Extenders are also known as water adsorbing or lightweight inert materials [4,30,31]. They are broad class of materials that are used for reducing slurry density and increasing the yield of cement slurry. A reduction of slurry density reduces the hydrostatic pressure during cementing of weak and fragile formations or depleted reservoirs [30]. This helps prevent the breakdown of weak formation and loss circulation [12]. Extenders also reduce the amount of cement needed for cementing operation and because they are less expensive than cement, they bring considerable savings [1]. Extenders work by allowing the addition of more water to the slurry to lighten the mixture and to keep the solids from separating. These additives change the thickening times, compressive strengths and water loss [11]. In reducing slurry density, the ultimate compressive strength is reduced [4] and the thickening time is increased [31]. For example extenders such as bentonite, foamed cement and microspheres decrease the cement slurry density and final compressive strength at 100 °F (38 °C) after a 24-hour curing period [29]. Another behaviour of extenders was confirmed by an experiment conducted by Salam et al. [32] on the relationship between thickening time and extender. It was observed that increase in the percentage of extender from 5% to 15% resulted to corresponding increase in the thickening time. Three types of extender are normally used: water extender, gas and low-density aggregate [26]. Water is the cheapest and the commonest material that can be added to cement [6,31]. The more water that can be added to the slurry, the greater its volume or yield and the lower the slurry's density [26,29]. Normally a sack of cement (94 lb) will give about 1 ft^3 of slurry. Adding extra water can increase the volume to 3.0 ft^3/sk. The challenge is that the slurry will become too thin and the cement will settle and have free water. The disadvantage of adding the extra water is that the strength of the set cement is lessened by the dilution [6]. Adding water to the cement slurry increases its water-cement ratio (w/c) and this leads to a reduction in slurry viscosity and subsequently deposition of suspended solids in the slurry. Aside from this disadvantage, water prolongs thickening time of the slurry and dramatically reduces rock compression strength. In addition, water reduces concentration of chemical additives such as cement, and accelerators, retarders and fluid loss controllers and decreases their impact on the slurry. Therefore cement slurry diluting in order to lighten them is not permitted at all [33]. To prevent these problems, extenders such as bentonite or sodium silicate are added. Such extenders maintain homogeneous slurry, and prevent the development of excessive water [26,29]. Bentonite and sodium silicate are known as a physical (clay or organics) and chemical extender respectively [14]. If low density and higher strength are required, the density of the slurry can be reduced with gas extender. A stable foam cement will have discrete air bubbles that lower the density of the slurry but do not dilute the strength as much as water. Hollow ceramic spheres can be used for the same purpose [6]. Low-density aggregate is material that has density less than Portland cement. Therefore, the density of the cement slurry is reduced when significant quantities of such extenders are present [25]. It can be obtained from volcanic ash, diatomaceous earth and fly ash. Fly ash alone has a density slightly less than Portland cement, so it does not reduce slurry density very much. However, because fly ash is cheaper than cement, it can reduce the costs of the composition if the job is performed with half cements and half fly ash. Normally, some bentonite is added to a cement/pozzolan blend, which makes it possible to add more water [4,30]. The most common extender of oil well cement is bentonite (sodium montmorillonite) which is also the main constituent of the drilling fluids [32]. Other extenders of oil wells cement are: fly ash, diatomaceous earth, solid hydrocarbon (gilsonite), and expanded perlite [16,34].

Bentonite: Bentonite is by far the most common type of additive used to lower cement slurry density [4,10,11,32]. Bentonite is used to prevent solids separation, reduce free water, reduce fluid loss, and increase slurry yield. Bentonite can be added to any API class of cement and is commonly used with other extenders [7]. This type of clay (sodium montmorillonite) is the same additive used extensively for building drilling fluid viscosity. However, it must be noted that bentonite marketed for use in drilling fluid formulation is sometimes treated with organic polymer that is undesirable for cement slurries formulation since it tends to increase slurry viscosity [16]. The addition of bentonite lowers the slurry density because of its lower specific gravity and because its ability to hydrate permits the use of much higher water concentrations. According to Bett [4], bentonite concentrations of 2 to 16% by weight of cement (bwoc) have been used in cement design. It is able to hold water which is 16 times its volume and it therefore also ensures no free water evolves during cement set up. However, concentrations as high as 25% by weight of cement have been used [16]. The bentonite usually is blended dry with the cement before mixing with water, but it can be pre-hydrated in the mixing water. Much higher increases in water content can be obtained for each percent bentonite added when the bentonite is pre-hydrated in the mixing water. The ratio of bentonite dry blended to bentonite pre-hydrated is about 3.6: 1 for comparable slurry properties. In addition to lowering slurry density, the addition of bentonite lowers slurry cost. However, a high percentage of bentonite in cement also will cause a reduction in cement strength and thickening time. Also, the higher water content lowers the resistance to sulphate attack and increases the permeability of the set cement. At temperatures above 230 °F (110 °C), the use of bentonite promotes retrogression of strength in cements with time [16].

Sodium Silicate: Sodium silicate is the most commonly used chemical extender for cement slurries. It is five to six times effective as bentonite on equivalent concentration basis. It is available in both dry and liquid forms, making it readily adaptable to onshore and offshore applications. The solid form is sodium metasilicate (Na_2SiO_3) [14]. It is typically dry-blended with the cement and used in temperatures up to 200 °F (93 °C) with concentrations normally ranging from 0.1% to 4% bwoc [35]. Solid sodium silicate is not as effective if dissolved directly in the mixwater unless calcium chloride is dissolved in the water first. The liquid sodium silicate is normally used in seawater application at a concentration of 0.1 to 0.8 gal/sk of cement densities of 14.2 to 11.5 lbm/gal [14].

Heavy Weight Agents

The main purpose of heavy weight additives is to restrain high formation pressures. The main requirements for heavy weight agent (weighting agents) are that, they have specific gravity greater than the cement, consistent particle size distribution and low water requirement. Chemically weighting agents are inert in the cement slurry and do not interfere with logging tools [36]. When high pore pressures, unstable wellbores, and deformable/plastic formations are encountered, high weight muds of over 18 ppg may be used and correspondingly cement slurries of equal weight must be used [2]. The most obvious way of increasing cement density is to reduce the amount of water in the cement slurry [1]. However, slurries with densities greater than 17.5 lb/gal would be too thick to mix and pump without weighting agents [6]. This would therefore require dispersants to maintain pumpability [2]. When weights higher than 17.5 lb/gal are required, materials with high specific gravities are added. To Lake and Mitchell [14], heavy weight agents are normally required at densities greater than 17 lb/gal where dispersants or silica is no longer effective. The most common weighting agents are Hematite, Ilmenite and Barite [2]. Other weighting agents are heavy particulate material such as salt, Ottawa sand or titanium oxide [35,37].

Hematite (Fe_2O_3): This is the most commonly used heavy weighting additive. Hematite is a brick-red, naturally occurring mineral with a dull metallic luster. It contains approximately 70% iron. The specific gravity of hematite ranges from 4.9 to 5.3, depending on purity. It can be used to overcome many shortcomings of barite [35,38]. The high specific gravity of hematite can be used to raise slurry densities to 22 ppg. However, dispersants are often used to prevent excessive hematite slurry viscosity. Hematite significantly reduces the pumpability of slurries and therefore friction reducing additives may be required when using hematite.

Ilmenite (FeO TiO_2): Ilmenite (Iron Titanium Oxide) is not as commonly used as hematite, although it has some advantages over hematite. Ilmenite is a black to dark brownish-black, naturally occurring mineral with a submetallic luster that contains approximately 37% iron. It resembles magnetite in appearance but has only a slightly magnetic character. The specific gravity ranges from 4.5 to 5, depending on the purity [35]. Although ilmenite has a slightly lower specific gravity than hematite, it requires no additional water and provides about the same slurry density increase as hematite at comparable concentrations. Like hematite, ilmenite has little effect on thickening time or compressive strength [16].

Barite ($BaSO_4$): Barite is not normally used in cementing as a weighting agent because of its high surface area and high water demand. It is a soft, light gray, naturally occurring non-metallic material. The specific gravity ranges from approximately 4.0 to 4.5, depending on purity [6]. Barite can be used to attain slurry densities of up to 18 ppg. It also causes a reduction in strength and pumpability [31].

Fluid Loss Additives (FLA)

Fluid loss additive is also known as permeability plugging additive. Fluid loss additives are commonly employed in field cementing operations reduce the rate at which water from cement is forced into permeable formations when a positive differential pressure exits into the permeable formation [6]. That is, it prevents dehydration of cement slurry [4]. In the presence of differential pressure, filtrate loss to permeable strata can dramatically alter the physical properties of oilwell cements. Thickening time, rheology, and mud displacement efficiency are all impacted by the changes in the water-cement (w/c) ratio brought on by the loss of cement filtrate. As the liquid phase of the cement passes into the formation, filter cake is formed on the formation face. Fluid loss additives function primarily by promoting the deposition of a low permeability filter cake, thereby limiting the rate of filtrate loss to permeable strata [39]. Restricting fluid loss protects water-sensitive formations [39]. It also minimises formation damage, improves bonding and squeeze type cementing [13]. Too much fluid loss may provide space for the gas to get into the cement slurry in the annulus [37]. Therefore fluid loss additives are to reduce gas migration [13,40]. The uncontrolled loss of filtrate during the cementing operation can result in job failure due to dehydration of the cement into an unpumpable state, high equivalent circulating densities; an increased likelihood of annular gas migration and unsuccessful squeeze operations [38]. Fluid loss additives are normally polymers such as cellulose, polyvinyl alcohol, polyalkanolamines, polymers of polyacrylamides, and liquid latex such as styrene butadiene latex. These materials are classified as water-insoluble and water-soluble FLAs. Most fluid loss additives increase the slurry viscosity, although some retard it to some degree [6]. According to Adams and Charrier [13] cellulose derivatives are the most common fluid loss additives and normal concentration vary from 0.3 to 3.0% by weight of the cement. Higher percentages of FLA produce excessive viscosities and therefore making it difficult to mix in field operations [13].

Hydroxyethyl cellulose (HEC): This is a white, powdered, water-soluble polymer. Manufactured in wide range of grades, these principally differ in molecular weight. HEC-based materials are used to enhance the fluid loss control properties of various cement systems and are effective over a broad range of well conditions [34]. It is commonly used at temperatures up to approximately 180 °F (82 °C) for fluid loss control and may be used at temperatures up to approximately 230 °F (110 °C) Bottom Hole Circulating Temperature (BHCT), depending on the co-additives used and the slurry viscosity limitations [14].

Lost Circulation Additives

Lost circulation additive is also known as macro plugging materials. Lost-circulation additives are used to plug zones that have a tendency to draw in fluid because they are unconsolidated or weak. Large particulates can be placed in the cement slurry to prevent fracturing or to bridge existing fractures. These particles should have a broad particle size distribution, should not accelerate or retard excessively, should have sufficient strength to keep a fracture bridged, and should be inexpensive and non-toxic [6]. Organic Lost Circulation Materials (LCM), traditionally utilised in drilling fluid formulations, should not be used in cement slurry. Although they achieve the objective of sealing the permeable zones, after the well has been completed, the organic material is carbonised, leaving high porosity within the loss zones, thus providing a flow path for possibly corrosive formation fluids [4]. The most common materials are ground coal, ground gilsonite, and ground walnut hull. A research conducted by Slagle and Carter [41] revealed gilsonite as an additive that has yielded excellent results in areas of incompetent formations as well as in other types of lost circulation zones. The field results examined generally showed that fill-up of 80% to 90% can be obtained in areas where only 50% to 60% fill-up was possible with other types of slurries. Fibrous and flake materials are also used as lost circulation materials. Fibrous materials are normally inert polymers such as nylon, and the flake materials are cellophane or similar materials [1].

Gilsonite: Gilsonite is a naturally occurring, solid carbonaceous material that is classified as an asphaltite. It is a relatively pure hydrocarbon without significant amounts of mineral impurities [42]. Its particle size varies between 4 and 100 mesh. It is effective at bottomhole temperatures between 60 °F (16 °C) and 230 °F (110 °C). A typical additive concentration range from 5 to 50 lb/sk of cement. Gilsonite additive's low specific gravity helps improve its ability to control lost circulation. However, this feature can also cause the additive to separate to the top of thin slurries and slurries containing dispersant. Adding 2% or more bentonite to the slurry will prevent separation. Gilsonite to oil well cement reduces slurry weight without loss of compressive strength and also acts as effective bridging and plugging agent to seal fractures in weak formation while cementing [8].

Expansion Additives

Expansion additives cause the exterior dimensions of set cement to grow slowly when the cement is in the presence of down-hole fluids. This minor growth of the exterior dimensions of the slurry causes the cement to bond better to pipe and formation. The most common additives for this use are based on calcium sulphoaluminate and calcium oxide [6]. Rubiandini et al. [43] reported CaO and MgO as two of the most effective additives to create excellent expanding cement which they used to find the effect of adding up burnt pure CaO and MgO on the value of compressive strength and shear bond strength of API class G cement in high pressure and high temperature condition. The method that was used for the research was an evaluation of the data from a simulator that simulated within temperature range of 212 °F - 482 °F (100 °C - 250 °C) and pressure of 2 000 psi. The conclusion that was drawn from the analysis of the results was that addition of burnt pure CaO and MgO increase shear bond strength and compressive strength at a temperature up to 200 °C. The optimum concentration of the additives used was from 3% - 5% bwoc. According to Rubiandini et al. [43], addition of burnt pure CaO and MgO won't be effective for a temperature of 482 °F (250 °C).

Dispersants

Dispersants also known as friction reducing additives are added to improve upon the flow properties of cement slurry [4,31]. In particular, they are used to offset overly-high viscosity and some slurries tendency to gel [12]. Dispersants assist in providing fluid loss control for high density slurries [13]. They also help establish turbulent flow at low pumping rate when needed [4,12,13]. Dispersant allow the water content of the cement to be lowered without making it difficult to pump. At right concentration, dispersants improve cement homogeneity and lower its permeability. However, an overdose of dispersant can produce phase separation in the cement slurry that results in cement particles settling out of solution and the development of free fluid. The most common dispersant is the sodium salt of Polynapthalene Sulfonate (PNS) which is also referred as Polysulfonated Napthalene (PNS) [1,5,6].

Polynapthalene Sulfonate (PNS): Polynapthalene Sulfonates (PNS) are the most widely used materials for dispersing cement particles in slurries [5]. It is available as a calcium and/or sodium salt, and can be obtained in both solid and liquid form. The commercial liquid form typically has a solids content of approximately 40%. The benefit of using PNS is that improved rheological properties can be obtained, and slurries can be pumped with reduced frictional pressures. PNS can also allow higher solids-to-water ratio slurries to be designed with improved properties. PNS materials are polymeric with molecular weights ranging between about 3,000 and 20,000 [5,6,44].

Antifoam Agents

Many additives cause foaming problems, but if slurry foams excessively, during mixing, centrifugal pump will air lock, and mixing must be stopped [12]. Therefore antifoams are introduced in cement slurries to decrease foaming and minimise air entrainment during mixing [14]. Excessive foaming can also result in an underestimation of the density downhole and cavitation of the mixing system. The additives modify the surface tension in the cement slurry so that foaming is prevented or the foam breaks up. The concentration required to be effective is very small, typically less than 0.1% by weight of water (BWOW) [4]. Antifoam agents consist primarily of polyglycol or silicones or a mixture of both, and may also include additional surfactants [14]. The cheapest and the most commonly used antifoam agents are Polypropylene glycols, [14] though Polyethylene glycols are also used [1]. To work properly, it is mixed with the water before slurry preparation. Defoamers or foam breakers such as silicones are sometimes used because they can break and prevent foam [6,14].

Conclusions

From the review the following conclusions are made:

(i) Calcium Chloride and Sodium Chloride are the most commonly used accelerators to speed up the normal rate of reaction between cement and water. However, Calcium Chloride ($CaCl_2$) is undoubtedly the most efficient and economical accelerator used effectively at temperatures between 40 °F and 120 °F (4°C and 49°C) in concentrations of 2% to 4% bwoc. Averagely, Calcium Chloride concentration range of 1.5% bwoc to 3. 7% bwoc is often used based on the various concentrations reviewed.

(ii) Of the chemical compounds identified as retarders to decrease the speed of cement hydration, calcium lignosulfonates are the most widely used. Its effectiveness is limited in temperatures above 200 °F. Concentrations of 0.1% bwoc - 1.0% bwoc are used in most slurry applications to give both predictable thickening times and compressive strengths. However, concentrations range of 0.1% - 0.5% is also used.

(iii) Extenders are materials that are used for reducing slurry density and increasing the yield of cement slurry. Of the material (extenders) used in oil well cementing, bentonite appeared to be the most common type. Bentonite can be added to any API class of cement and is commonly used with other extenders. Bentonite concentrations of 2 to 16% by weight of cement (bwoc) have been used in cement design. However, concentrations as high as 25% by weight of cement have also been used in cementing operations.

(iv) The main purpose of heavy weight additives is to restrain high formation pressures. Heavy weight agents are normally required at densities greater than 17 lb/gal where dispersants or silica is no longer effective. Though there are common types like Ilmenite and Barite, they are less used as compared to Hematite in oil well cementing operations.

(v) Fluid Loss Additives (FLAs) are employed to reduce the rate at which water from cement is forced into permeable formation. There are several materials that are effective as FLAs which are grouped as water-insoluble and water-soluble. Cellulose derivatives such as HEC appeared to be one of the common FLAs used at a concentration of 0.3-3.0% bwoc and at temperatures up to approximately 180 °F (82 °C).

(vi) The common Lost Circulation Materials (LCM) identified includes ground coal, ground gilsonite, and ground walnut hull. Gilsonite is an additive that has yielded excellent results (about 80% - 90% fill-up) in areas of incompetent formations as well as in other types of lost circulation zones. Gilsonite is effective at bottomhole temperatures between 60 °F (16 °C) and 230 °F (110 °C). A typical additive concentration range from 5 to 50 lb/sk of cement.

(vii) Expansion additives are used to cause the exterior dimensions of set cement to grow slowly when the cement is in the presence of down-hole fluids. CaO and MgO are two of the most effective additives to create excellent expanding cement.

(viii) Though there are various advantages of using dispersants in cements slurries, it is primarily used to lower the frictional pressures of cement slurries. Commonly used dispersant is identified as PNS which is available as a calcium and/or sodium salt.

(ix) Antifoams are introduced in cement slurries to decrease foaming and minimise air entrainment during mixing. Concentration required to be effective is very small, typically less than 0.1% by weight of water (bwow). The cheapest and the most commonly used antifoam agents are Polypropylene glycols, though Polyethylene glycols are also used.

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