Topic of research: Oil Well Cement

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DEDICATION

This research is dedicated to my cousin SiSi, who has been nicely my supporter until my research was fully finished, and my beloved mother who, for months past, has encouraged me attentively with her fullest and truest attention to accomplish my work with truthful self-confidence.

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Your student,
Abdelrhman Medhat

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Abstract

The productivity of an oil well is significantly affected by the quality of cementing between the well casing and the surrounding strata. Cement slurry flowability and stability are major requirements for successful oil well cementing. The properties of oil well cement slurries depend on its mixture design and the quality of its components. Because the cement is the most active component of the slurry and usually has the greatest unit cost, its selection and proper use are important in obtaining an effective, yet economical material meeting the expected service life performance of the well.

Type I/II ordinary portland cements can provide adequate strength and durability for common applications. However, some demanding applications may require the use of other cements to meet specific performance criteria. For instance, the need for high-early strength cements in pavement repairs, the use of blended cements with aggregates susceptible to alkali-aggregate reactions, and the use of oil well cements in the exploration and production of oil and gas in onshore as well as offshore wells are examples of such applications. Although slightly modified Type I, II and III portland cements can be used for cementing around the steel casing of gas and oil wells having depths not exceeding 1800 m (6000 ft), deeper wells usually require special oil well cements.

LIST OF ABBREVIATIONS

OWCs	Oil well cement
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
MSR	Moderate Sulphate Resistance
HSR	High Sulphate Resistance
C_3S	Tricalcium Silicate
C_2S	Dicalcium Silicate
C_3A	Tricalcium Aluminate
C_4AF	Tetracalcium Alumino Ferrite
Bwoc	By Weight of Concrete
w/c	water to cement ratio

1. Introduction

Oil well cementing is the process of placing a cement slurry in the annulus space between the well casing and the geological formations surrounding to the well bore. When a certain section of the depth of an oil or gas well has been drilled successfully, the drilling fluid cannot permanently prevent the well bore from collapsing.

In addition to their exposure to severe temperature and pressure, oil well cements (OWCs) are often designed to overcome weak or porous formations, corrosive fluids, and over-pressured formations. The appropriate cement slurry design for well cementing is a function of various parameters," including the well bore geometry, casing hardware, drilling mud characteristics" The rheological behavior of OWC slurries must be optimized to achieve effective well cementing operation. Strict control of the hardened cement mechanical properties and durability during the service life of the well are very important criteria, especially under such severe environments. Thus, a special class of cements called oil well cements (OWCs), has emerged and is specified by the American Petroleum Institute (API Specification 10A, 2002). A number of additives have also been used to alter the chemical and physical properties of the OWC slurries as required for the flowability, and stability of the slurry and long-term performance of wells. We will discuss the basic concepts involved in oil well cementing, the different types of OWCs, and their chemical and physical properties. An insight into the additives that can modify the behavior of the OWC systems and allow successful slurry placement between the casing and the formation, rapid compressive strength development.

2. Definition of oil well cement

Oil-well cement is defined by the API for Classes A – H as the product obtained by grinding clinker, consisting essentially of hydraulic calcium silicates, to which no additions other than set-modifying agents have been blended during manufacture

Oil well cement, also known as plugging cement, is a kind of special cement used in the cementing engineering of oil well or gas well. It consists of Portland cement or blended cement, plus additives. Its performance is consistently stable in well cementing applications at extremes of depth, temperature, and pressure. **[2]**

In the exploitation process of petroleum and natural gas, when the drilling depth reaches the design requirements, we usually put a steel casing into the borehole and pump cement slurry into the borehole around the casing to cement the casing with the surrounding formation. This process not only blocks the oil, gas, and water layers but also forms an isolated channel from the oil or gas layer to the surface. **[2]**

Therefore, oil well cementing was introduced in the late 1920s (Joshi and Lohita, 1997) with a number of objectives:

- protecting oil producing zones from salt water flow,
- protecting the well casing from collapse under pressure,
- protecting well casings from corrosion,
- reducing the risk of ground water contamination by oil, gas or salt water,
- bonding and supporting the casing, and
- providing zonal isolation of different subterranean formations in order to prevent exchange of gas or fluids among different geological formations.

3. Classification of Oil Well Cements

Both American Petroleum Institute and Indian Standards have given nine classes of oil well cement from A to H & J. But the specification of cement falling under a particular class is different in both the standards

The temperature and pressure in the oil well usually rise with the increase of well depth. For every 100m depth, the temperature increases by about 3℃ and the pressure increases by 1.0~ 2.0mpa. Under high temperature and pressure, various properties of oil well cement will be greatly influenced. Therefore, different grades of oil well cement should be used in wells with different depths. According to the US API specification, oil well cement can be classified into nine grades. Each grade is further divided into **ordinary** type (O, $C_3A < 15\%$), **moderate sulfate** resistant type (MSR, $C_3A \leq 8\%$, $SO_2 \leq 3\%$), and **high sulfate resistant** type (HSR, $C_3A \leq 8\%$). **[1]**

Grades of Oil Well Cement – (Based on sulphate resistance)

The three grades are-

Grade O: Ordinary Cement

Grade MSR: Moderate Sulphate Resistance

Grade HSR: High Sulphate Resistance

Class A	Intended for use from surface to a depth of 6,000 ft when special properties are not required. Available only in Ordinary type (**similar to ASTM C150, Type I cement class**). **[3]**
Class B	Intended for use from surface to a depth of 6,000 ft when conditions require moderate to high sulfate resistance. Available in both Moderate type (**similar to ASTM C150, Type II**) and High Sulfate Resistant types. And has a lower C_3A content than class A **[3]**
Class C	Intended for use from surface to a depth of 6,000 ft when conditions require high early strength. Available in all three degrees of sulfate resistance (Ordinary type and in Moderate and High Sulfate Resistant types). This class is roughly equivalent to ASTM Type III. The C_3S content and the surface area are relatively high **[3]**
Class D	This API cement class is intended for use at depths from 6,000 to 10,000 ft and at moderately high temperatures and pressures. Available in both Moderate and High Sulfate Resistant types. (no longer used) **[3]**
Class E	Intended for use at depths from 10,000 to 14,000 ft and at high temperatures and pressures. Available in both Moderate and High Sulfate Resistant Types. (no longer used) **[3]**
Class F	Intended for use at depths from 10,000 to 16,000 ft and at extremely high temperatures and pressures. Available in High Sulfate Resistant types. (no longer used) **[3]**
Class G	Intended for use as a basic cement from the surface to a depth of 8,000 ft as manufactured. With accelerators and retarders, it can be used at a wide range of depths and temperatures. It is specified that no additions except calcium sulfate or water, or both, shall be blended with the clinker during the manufacture of Class 'G' cement. Available in Moderate and High Sulfate Resistant types. It can be used with accelerators and retarders to cover a wide range of well depths and temperatures **[3]**
Class H	This API cement class is intended for use as a basic cement from the surface to a depth of 8,000 ft as manufactured. This cement can be used with accelerators and retarders at a wide range of depths and temperatures. It is specified that no additions except calcium sulfate or water, or both, shall be blended with the clinker **[3]**

	manufacture of class H cement. **Available only in Moderate Sulfate Resistant** type. It can be used with accelerators and retarders to cover a wide range of well depths and temperatures. **[3]**
Class j	Class J cement has been officially deleted from the API classification, because it is rarely used. This cement is **not a true Portland cement**, but is based upon a β-dicalcium silicate–silica composition in approximate proportions 60:40, respectively. Class J cement was designed for cementing wells above 110°C, where hydrothermal hydration takes place. The rate of hydration is slow compared with Portland-based oil-well cements, because of the lack of tricalcium silicate. **[4]**

API Class	C_3S%	C_2S%	C_3A%	C_4AF%	Property
A	53	24	8+	8	High Early Strength
B	47	32	5-	12	Better retardation
C	58	16	8	8	Low heat of hydration
D&E	26	54	2	12	Resistance to sulfate attack
G&H	50	30	5	12	

Typical Composition and Properties of API Classes of Portland Cement [3]

4. Sulphate Attack

Sulfate attack is one of the degradation mechanisms of cementitious materials. This phenomenon has been and continues to be the subject of many investigations, as it may cause the premature failure of civil and highway concrete infrastructure. **[6]**

The process of sulfate attack

The hydrated calcium trisulfoaluminate ($C_3S.C_3A.H_{32}$), commonly known as ettringite, is a crystalline meta-stable hydration product of Portland cement. During the first 24 hours of hydration, the tricalcium aluminate (C_3A) reacts with gypsum ($CaSO_4.2H_2O$), added to the clinker to regulate the C_3A rate of hydration, to form what is known as primary **ettringite** **[6]**

$$3CaO.Al_2O_3 + 3\,(CaSO_4.2H_2O) \rightarrow Ca_6[Al(OH)_6]_2.(SO_4)_3.26H_2O$$

As cement hydration takes place the amount of gypsum decreases and part of the ettringite is transformed into calcium monosulfo-aluminate hydrate

$$Ca_6[Al(OH)_6]_2(SO_4)_3.26H_2O + 2\,(CaO.Al_2O_3) + 4H_2O \rightarrow 3\,(3CaO.Al_2O_3.CaSO_4.12H_2O)$$

This reaction also depends on several factors as the ratio between $\frac{SO4}{C3A}$, the pore solution alkalinity, the water to cement ratio (w/c) and the environment temperature. When hydrated cement is placed in an environment containing high sulfate concentrations, as could be the case of many formations, the calcium monosulfo-aluminate hydrate and the calcium hydroxide present in the cement paste will react with the sulfate ions coming from the environment to form what is known as secondary or delayed **ettringite** **[6,7]**

$$3CaO.Al_2O_3.CaSO_4.12H_2O + 2(CaSO_4.2H_2O) + 16H_2O \rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O$$

As indicated in the previous equations, **ettringite** is a crystalline compound that contains **32 water molecules**. Therefore, the formation of ettringite involves considerable expansion and weight growth. As the reaction takes place, the expansive product (mainly ettringite) will start filling the cement paste pores and once these are complete, will start building up internal pressure that causes cement cracking and strength loss. This phenomenon is known as sulfate attack. There are several aspects that differentiate the service performance of oil well cements from those found in concrete used in the building construction industry. These are most likely related to the service conditions, primarily temperature, pressure, degree of hydrated cement, water saturation and permeability. These differences provide a comparatively less aggressive environment for oil well cements sulfate attack as compared to concrete used for building construction **[6,7]**

5. Cementing Additives Types

Additives are chemical compounds, which added in small quantities to change the physical properties of cement slurry and/or of the set cement. Most cementing chemical additives are available either in solid or liquid form. Most of the cement additives available at present have been developed by specialized cementing Companies, although increasingly products from independent chemical manufacturers are offered to the oil and gas Industry. **[5]**

5.1 Dosing Cementing Chemical

Additives can be dosed in three essentially different ways:

- Dry blending with cement. The mixing of a relatively small quantity of a powdery product, typically **1%** into a large matrix is rather problematic and easily can result in a poor, inhomogeneous distribution. This method therefore is not recommended.

- Dosing of the additives in the mix water affords a good control over the actual rates applied and ensures a consistent treatment. Waste is incurred, because, as a contingency, the volume of mix water prepared is usually larger than actually needed for the job. The simplicity of the operation and the accurate dosing however make this the preferred route.

- Metering of additives in liquid form into the mix water tanks of the cement unit when filling up. This avoids the waste of the mix water dosing but requires a reliable, often complicated, metering system able to stand the rigours of a cementing operation. This method therefore can be recommended only for advanced and integrated operations. **[5]**

5.2 Cementing Accelerators Chemicals

Products to shorten the thickening time of the cement slurry and to accelerate strength development in situations where low temperatures would lead to excessive waiting-on-cement times. The most commonly used accelerators are **calcium and sodium chloride** in dosages of 2%-4% and 5%-10% by weight of cement (bwoc) respectively, dissolved in the mix water.

Aluminum sulphate is a very effective accelerator, which needs to be moderated by adding ferrous sulphate. However, its thixotropic effect makes it less attractive for most applications as this will adversely affect displacement and leads to unacceptably high ECD in Drilling, potentially inducing circulation losses or fracturing. **[5]**

Cementing Retarders Additives

These products are applied to achieve the opposite effect of accelerators, increasing thickening time to a level required by the temperature/pressure, adequate for the job. Quite a large number of different types of retarders are available, from cement Contractors and chemical manufacturers alike. Most retarders are characterized by an exponential response in the thickening time of the cement slurry, that is at low dosage rates the effect is rather small, increasing exponentially with a further chemical addition. Therefore, these products should only be used over a certain concentration range.

The different types comprise:

- Sodium chloride at concentrations above 18% by weight of water
- Cellulose and sugar derivatives
- Polyhydroxy organic acids
- Organo phosphonates

Typical dosage rates are in the range of 0.25%-0.75% bwoc. the retarding effect is temperature-dependent and most commercial products can be used only in a given temperature range. **A common side-effect of a retarder is the reduction of slurry viscosity and yield point. [5]**

5.3 Cement Extenders Additives

Cement extenders are routinely used to achieve one or both of the following.

- Reduce slurry density: A reduction of slurry density reduces the hydrostatic pressure during cementing. This helps to prevent induced lost circulation because of the breakdown of weak formations. In addition, the number of stages required to cement any oil & gas well may be reduced.

- Increase slurry yield: Extenders reduce the amount of cement required to produce a given volume of set product. This results in a greater economy. **[5]**

Extenders Categories

Extenders can be classified into one of three categories, depending upon the mechanism of density reduction and/or yield increase. Often more than one type of extender is used in the same slurry.

• Water extenders: Clays and various water viscosifying agents allow the addition of more water to achieve slurry extension. Such extenders maintain a homogeneous slurry and prevent the development of excessive free water.

• Low-density aggregates: This varied category consists of materials with densities lower than that of Portland cement (3.20 g/cm3). The slurry density is reduced when significant quantities of such extenders are present.

• Gaseous extenders: Nitrogen or air can be used to prepare foamed cement with exceptionally low densities yet sufficient compressive strength.**[5]**

Extender	Range of Slurry Slurry Densities Obtainable (lbm/gal) 6 – 11 – 16	Performance Features and Other Benefits
Bentonite	11.5 – 15	Assists fluid-loss control
Fly ashes	13.1 – 14.1	Resist corrosive fluids
Sodium silicates	11.1 – 14.5	Available in solid or liquid form; effective at low concentrations; ideal when mixing slurry with seawater
Microspheres	8.5 – 15	Good compressive strength, low permeability, thermal stability, and insulating properties
Foamed cement	6 – 15	Good compressive strength and low permeability

5.4 Cement Expanding agents Additives

The purpose of these agents is to reduce shrinkage of setting cement Two types of expanding additives are available:

Chemical or crystal growth expanders. **Calcium sulphate hemihydrate and calcined magnesium oxides** are the most prominent compounds. They produce their expanding effect well after the cement has set.

Gas-generating expanders. (Hydrogen) gas is generated in-situ during the gelling stage of the cement slurry. The expansion takes place as a consequence of reduced hydrostatic pressure in this stage where the weight of the cement column is progressively carried by the gel structure. The most common material used for this purpose is **aluminum powder.** An added advantage of this system is the good bonding of cement to casing providing an effective gas-tight seal. The safety aspects of hydrogen however should not be overlooked, where explosive limits ofH_2/air mixtures are between 1.5 and 98% v.

The use of chemical expanding agents in combination with surfactants in general is not recommended. The latter reduce the volumetric reduction of cement slurry in the hydration stage, which is more effective for improving sealing than expansion in a later stage by these agents. **[5]**

Strengthening agents Additives

Fibrous materials additives are available that, when added to any oil & gas well cements in concentrations between 0.15% and 0.5% BWOC, increase the cement's resistance to the stresses associated with perforating, hydraulic fracturing, and formation movement. Such materials transmit localized stresses more evenly throughout the cement matrix. **Nylon fibers**, with fiber lengths up to 1 in., are commonly used.**[5]**

5.5 Cement Weighting Agents Chemicals

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. The most common cement weighting agents are as following **[8]**

- Ilmenite
- Hematite
- Barite
- Manganese tetraoxide.

Cement Dispersants Additives

Treatment with a dispersant aims to reduce the viscosity of the cement slurry, thereby promoting turbulent flow at lower pump rates. As a side effect, dispersants also cause retardation **[5]**

Three different types are available;

- Synthetic polymers such as **polyacrylates**
- Lignosulphonate or lignin derivatives
- Organic acids.

5.6 Fluid Loss Additives

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. That is, it prevents dehydration of cement slurry. In the presence of differential pressure, filtrate loss to permeable strata can dramatically alter the physical properties of OWC. Thickening time, rheology, and mud displacement efficiency are all impacted by the changes in (w/c) ratio brought on by the loss of cement filtrate. 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. Restricting fluid loss protects water-sensitive formations. It also minimizes formation damage, improves bonding and squeeze type cementing. Fluid loss additives are normally polymers are classified as water-insoluble and water-soluble Fluid loss additive such as **[8]**

- polyvinyl alcohol,
- polyalkanolamines,
- polymers of polyacrylamides
- styrene and butadiene latex

6. Conclusions

A successful oil well cementing should satisfy two basic criteria: (a) it should be easily pumpable for a sufficient time to allow proper placement of the slurry in the well bore subjected to extreme levels of temperature and pressure, and (b) the cement slurry should develop and maintain sufficient mechanical strength to support and protect the casing, and must have low permeability and adequate durability to ensure the long-term isolation of the producing formation. Chemical admixtures and mineral additives play an important role by altering the chemical and physical properties of the oil/gas well cement slurry and maintaining the proper rheology necessary for the placement of the cement slurry in typically deep well bores.

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