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Effects of Ferrous ion as Impurity in Mix-Water on the Setting Time of Oilwell Cement Slurry in High-Pressure, and High-Temperature Environment

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ABSTRACT

The effects of heavy metals in mix-water on the setting time of cement slurries have been investigated, to design acceptable ST of cement slurries; but, still there are reported cases of cement slurry ST failures. This may be as a result of the exclusion, of investigating the impact of ferrous ion in mix-water on setting time. Consequently, this research paper investigated the effects of ferrous ion as impurity in mix-water on the ST of slurries in high-pressure, and high-temperature environment. To accomplish this, sampled mix-water from the study area, Kolo Creek, were subjected to water analysis, using the American public health association drinking water test methods. The results revealed that, ferrous ion in high concentration was found presence in each of the mix-waters, when compared with the world health organisation threshold. These mix-waters were used to formulate slurries of 0.44 water-to-cement ratio. These slurries were subjected to ST tests using the CEMSET approach. In general, the results demonstrated that, high concentration of ferrous ion in mix-water, with the collaborating synergistic effects of HPHT *accelerated* the ST, which makes the cement slurry, to *set-faster.* This suggest that high concentration of ferrous ion induced the exothermic reaction of C_3A during hydration.

Keywords – Cement Slurry, CEMSET, Ferrous ion Concentration, Flash Set, Mix-Water, and Setting Time.

1. INTRODUCTION

Knowing the setting time (ST) property of Portland oilwell cement (POC) paste is very essential for planning the cementing of casing string during drilling and cementing operation. Mostly, after the cement slurry have been pumped into the wellbore, which is intended to keep the casing string in-place and isolate the movement of formation fluids from their respective zones to other zones. At this point, the well is left shut-in for a designed sufficient time to allow the cement to get set and harden, before resuming further drilling into deeper prospect towards the pay zone. Consequently, to avoid damage to the surface pumping equipment used to place the cement slurry, the cement slurry must continue, to be in a fluid state for a designed (thickening) time, while it is being pumped; to avoid wasting rig cost, and valuable rig time – downtime; hence, the cement paste should set shortly after being pumped and placed at the said desired depth. Thus, to understand the ST of oilwell cement slurries is of obvious considerable economic importance [1]. This have made many studies in the upstream petroleum industry, to have given many descriptions of the concept ‘setting time’ with the same meaning. Accordingly, Taylor [2] described this term as the stiffening of oilfield cement paste (Fig. 1; this was illustrated by the author of this research paper). In other words, Bullard [3] gave meaning to it as a change in cement slurry from a fluid state to a rigid state. Likewise, Zhang *et al.* [1] described ST, as the transformation of cement paste from a workable plastic grout into a rigid solid or cement sheath. Further on, Zhang *et al.* [1] opined that since ST occurred when the quantity of product is enough to cause the paste-particles to overlap, forming a continuous solid network, it can be termed as a percolation process. Based on this, ST can be described as a process that is consist of two stages, which include the initial setting time (IST) and final setting time (FST). The IST is the time which the cement paste begins the setting process, while the FST represents the beginning of hardening and gaining of strength by the cement sheath. In other words, Valic and Stepisnic [4] in a study, of cement hydration described ST as the length of time which cement slurry is in the plastic state that exhibits the beginning characteristics of binding. Further on, Valic and Stepisnic [4] explained that, ST is the interval of acceleration and deceleration periods, which cement slurry undergoes the most rapid hydration, to set.

Conversely, from the technical point of view, Rogers *et al.* [5]; Bahramian *et al.* [6]; Brooks *et al.* [7] reported that the ST of cement slurry is the period which gas or oil may migrate through the cement sheath or microannuli of the casing outer surface, which the resultant, if not controlled creates channels or microannuli. Mostly, when the slurry is poorly designed. In accordance to this premise, Gonzalo *et al.* [8] in an earlier study disclosed that 25% of primary cementing job catastrophes were caused by fluid migration. Though, other factors that militate against optimum ST of Portland oilwell cement slurry have been reported in many studies. These factors include chemical composition of the POC clinker, and ground particle size of the cement, if either or both are compromised during cement manufacturing; while bottomhole temperature and relative humidity, bottomhole pressure, fluid loss, water-to-cement ratio (w/c), mix-water quality, bottomhole contaminants, and improper use of additives ([9]; [10]; [11]; [12]; [2]). Accordingly, Boniface and Appah [13] opined that the optimal ST of POC slurry, during primary cementing job, is also a key factor for a successful zonal isolation and well integrity, because too much reactive cement slurry will result in a shorten ST, while an insufficiently reactive cement slurry used extended time to set. These reactive phases of cement slurry occur through hydration. During cement hydration the first two components to react, are tricalcium aluminate (C_3A) and tricalcium silicate (C_3S). The reaction of pure tricalcium aluminate (C_3A) with mix-water is very violet, and it leads to immediate stiffening of the cement paste, usually known as *flash set*. To prevent the flash setting properties of C_3A from happening, gypsum ($CaSO_4.2H_2O$) is always added to delay the formation of calcium aluminate hydrate (CAH); although it is C_3S that sets first. When pure tricalcium silicate (C_3S) is mixed with mix-water, it exhibits an initial set, but dicalcium Silicate (C_2S) stiffens in a more gradual manner. In practice, it is strictly not advisable to allow C_3A to set first, because it could cause the formation of porous calcium aluminate hydrate, if a hydrated cement paste is established by CAH. The remaining cement compounds would then hydrate within the porous network, and the strength characteristics of the cement paste would be adversely affected [14]. Therefore, the cement slurry must set, and develop sufficient strength to support the casing and seal off fluid movement behind the casing, before drilling further or completion activities can be resumed [15]. Nevertheless, POC are subjected to a wide range of pressure and temperature, which has a major effect on the time required for their setting and hardening. A premature setting can have disastrous consequences due to loss of circulation in the well, whereas too long ST can cause financial losses due to lost productivity. In addition, there may be possible segregation of the slurry or contamination by *in-situ* fluids. A slow setting behaviour can be achieved by adjusting the composition of the cement and/or by adding retarders. In terms of temperature, Neville [16] in a study, concluded that, the ST of cement slurry accelerated, as temperature was raised gradually to 85^0F, while at low temperatures the ST of cement slurry were retarded. Moreover, the reader should have in mind that, the scope of this paper is tailored on investigating the impact of ferrous ion concentration present in mix-water on the ST of cement slurry. Hence, previous studies that investigated the effects of heavy metals presence in mix-water on the ST of cement slurry were reviewed, to identified the research gap, "effects of ferrous ion in mix-water on ST of cement slurry".

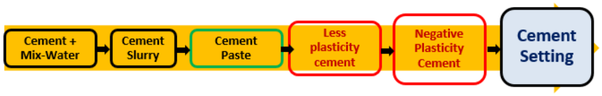


Fig. 1 Stiffening of POC slurry.

Previous works conducted on the effects of quantity of mix-water on the ST of oilwell cement are as follows: Valic and Stepisnic [4] in a study of hydration of cement pastes by reflection of ultrasonic shear waves employed a novel nondestructive method. The method used was based on the reflection of ultrasonic shear waves through different cement pastes, to determine early hydration process of pastes in selected hydraulic environments during setting. In the work, gypsum cement pastes were prepared by thoroughly mixing corresponding powders with an adequate amount of distilled water. In the study, gypsum cement pastes of three different water/gypsum ratios (w/g) of 0.5, 0.4 and 0.6 w/g were prepared; though, from the study 0.5 w/g ratio was recommended by the cement manufacturer for practical purposes. Practically, during the experimental tests, 2g of each of the prepared slurries were collected and subjected to the ultrasonic reflection tests. The ultrasonic reflection coefficient measurements of the gypsum cement pastes of three different pastes of water-to-gypsum ratio (w/g) of 0.5, 0.4 and 0.6, were conducted, and the results of these ratios were represented as a, b, and c, respectively, in

Fig. 2. In Fig. 2, the early-stage shapes of these curves show a short induction period followed by a fast rate of change (Δr_0), which both strongly dependent on the w/g. The results showed that all samples indicated an apparent decrease in hardness at retarded time, in which the Δr_0 became smaller with the increasing w/g. Explicitly, the curve corresponding to the cement paste with 0.5 ratio (or sample a) indicated that the start of intensive hydration and the hardness maximum in the sample with higher w/g shift to longer time of hardness. In addition, the curve showed that the hardness maximum, decreased with increasing w/g. On the other hand, sample (b) with 0.4 w/g was smaller than the manufacturer's recommended 0.5 w/g, but the start of the intensive hydration was somewhat prolonged and the hardness maximum to a certain degree was reduced compared to the recommended w/g = 0.5, and when observed, the rate of the Δr_0 decreased after hydration was much faster, which finally resulted in a break. In Fig. 2, this was evidenced with a sudden drop at time, t = 22 minutes. In another observation, the sample (b) with 0.6 w/g started to harden almost immediately after mixing. This was observed after 3 minutes of being mixed, and eventually unpumpable after 5 minutes. Similarly, the sample (a) with 0.5 w/g began to harden after 2 minutes of being mixed, and became harden after 8 minutes. Therefore, the study of Valic and Stepisnic [4] in parts concluded that high quantity of mix-water in water-to-cement ratio above the manufacturer's recommended ratio prolongs the cement slurry ST during cement hydration reaction. In another developmental study, Zhang *et al.* [1] studied the early hydration reaction and ST of oilwell cement. The oilfield cementing ST tests were conducted on Class H cement slurry, to determine the rate of hydration at a particular ST with-respect-to w/c. In this study, Zhang *et al.* [1] prepared various cement slurries of 0.25, 0.3, 0.35, 0.4, and 4.5 w/c; and, these samples were subjected to the Vicat setting tests. The results obtained from the tests are presented in Fig. 3, and it showed that, a linear relationship does not only exist between w/c and hydration at setting; but showed that, the higher w/c requires more ST.

Conversely, from a critical point of view, the mix-water quality used to mix POC into slurry, and how these qualities affect the ST of cement slurry are of importance. Though, this aspect has frequently been overlooked by many studies, when tried to improve the ST of cement slurry in different well applications at the slurry design stage ([17]; [18]). Consequently, the characterisation, pretreatment, treatment of mix-water, to eliminate its impurities becomes imperative. Hence, it is not surprising that poor quality of mix-water is culpable of affecting the ST of cement slurry; mostly, with the presence of heavy metals in the mix-water used in the formulation of cement slurry.

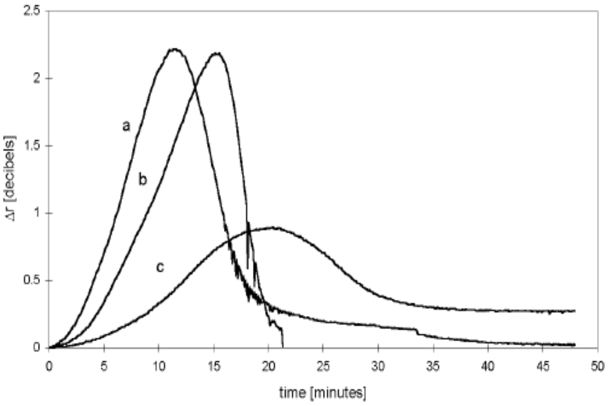


Fig. 2 Hardening of gypsum pastes with three different w/g ratios: a) 0.5, b) 0.4, and c) 0.6 [4].

In this context, Nygaard *et al.* [19]; Kiran, *et al.* [20] reported that, when the chemistry of mix-water is changed, the whole hydration reaction of the cement slurry-sheath system is impacted negatively. In addition, many studies have disclosed that mix-water hardness, temperature, and pH are the major factors that militates against cement slurry ST ([21]; [22]; [23]). This in return affects the cement sheath integrity, which includes the durability, compressive and tensile strengths, and permeability. These mix-water were usually collected at rig site from groundwater sources without water reticulation, due to the high cost of transporting potable mix-water to rig site [24].

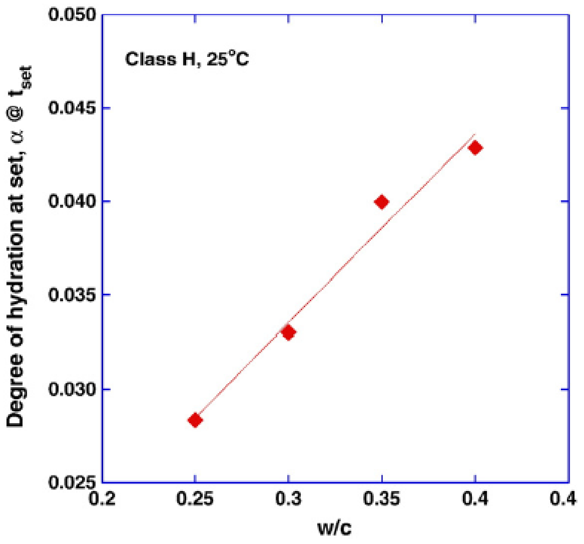


Fig. 3 Class H cement hydration performance at ST versus w/c [1].

Hence, in onshore operations freshwater is used as mix-water for the preparation of cement slurry. Further on, for inland operations, mostly in the estuaries, brackish water is used as the mix-water; while in offshore operations seawater is used as the mix-water. Although, each of these types of mix-waters had its shortcomings on the ST of cement slurry. Fresh (natural) water is suitable for oilwell cementing, provided it is found in adequate quantity; but natural water that are slightly acidic and harmless. This water which contained deleterious organic acids adversely affected the ST [16]. Accordingly, in a study, Engineering Feed [25] reported that freshwater was superlative when used to prepare cement slurry, since it had the ability to accelerate the ST of cement paste. This characteristic exhibited by freshwater was due to the low concentration of sodium chloride (NaCl) found in the freshwater. Hence, McCoy [26] suggested that any naturally occurring water (fresh water) which is suitable for drinking purposes can be fundamentally used as mix-water for cement slurry and concrete. In contrast, Ullman [27] stated that not all less saline (fresh water) is appropriate for making cement. Also, Ullman [27] pointed out that saline water (seawater) is an accelerator when the composition of sodium chloride (NaCl) is in low concentrations, and this can shorten the ST of cement slurries, or accelerate the cement setting [14]. Also, Abrams [28] suggested that seawater has a total salinity of approximately 3.5 percent (78 percent of dissolved solids being NaCl and 15 percent $MgCl_2$ and 7 percent of $MgSO_4$), and produces a slightly higher early strength, but a lower long-term strength. The loss of strength according to Abrams [28] is usually no more than 15 percent, and should often be tolerated. Some tests suggested that seawater slightly accelerates the ST of cement; also, Thomas [29] showed that, an extensive reduction in the IST; but, not unavoidably in the final set; because of the modern development of offshore fields, seawater has significantly become very widely used for cementing operations. Therefore, seawater, like most inorganic salt brines, slightly accelerates the ST of cement. The sodium, magnesium and calcium chlorides concentrations in the seawater all act as cement accelerators; while with the use of brackish water, which has more salinity than freshwater, but not as much as seawater should be contemplated. It can also be referred as the primary waste product of the salinity incline power. Brackish water is believed to increase the ST of cement paste when it does not contain deleterious substances. In agreement to this, an experimental investigation by Mbadike and Elinwa [30] showed that brackish water, when used as the mix-water increases the ST of the concrete produced. Consequently, the use of brackish water as mix-water in oilwell cementing can be detrimental. High salt contents found in brackish water, especially calcium chloride ($CaCl_2$) may retard the cement ST. Composition of organic contaminants in brackish water may severely affect the cement slurry just that, it may slow the cement ST [11]. According to Tchobanoglous *et al.* [31] brackish water contains chlorides and sulfates. In relation to this, the study by Gao and Song [32] investigated the influence of chemical impurity on cement ST, and compressive strength by adding Stannous Sulphate, and the results showed that, stannous sulphates increase the ST of the POC with an increase of the 8-additive percentage. Fundamentally, cement slurries ST will tremendously be enhanced if all these factors reviewed are adequately and properly checkmate. Hence, the poor quality of mix-water would always impact negatively on the cement ST.

In summary, the aforementioned reviewed studies have showed that, temperature and pressure, w/c, and chemical impurities in mix-water accelerates the ST of cement slurry. Nevertheless, these studies never gave account on the effects of ferrous ion presence in mix-water on the ST performance of cement slurry in HPHT environment. To achieve this research gap, this paper aimed at examining the effects of the different known concentrations of ferrous ion present in mix-water, on the ST performance of cement slurry. The objectives of this paper involved: a random and robust collection of mix-water samples from eight (8) boreholes of depths approximately below 60ft., at different locations of the study area, Kolo Creek, Nigeria. With regards to this, the mix-water samples were collected between November, 2018 – March, 2019; these sampled mix-waters were subjected to water analysis, to classify the physicochemical properties of the mix-waters; formulated Class G oilwell cement slurries; to test the ST using the CEMSET approach; to drew inferences based on the analysed results.

1.1. Study Area

This study opted for Kolo Creek (Latitude 04^0 24′26.893″ and 04^0 59′05.094″ North and longitude 06^0 14′59.190″ and $06^0 20′47.701″$ East) as study area, because of its high activities of oil exploration and production [33]. The map of Kolo Creek is presented in Fig. 4. The exploration and production company, had since began in 1964, which an international oil company (IOC) had been the sole operator of the oil mining leases (OMLs) of between 35 and 36 [33]. Also, the area is associated with high content of ferrous iron in the groundwater ([34]; [35]; [36]). Conversely, the water quality index (WQI) of Kolo Creek, as presented in Fig. 5, shows that the groundwater is classified as good, but not potable [35].

Furthermore, based on private interviews with several Community Leaders at Kolo Creek (Otuasaga, Oruma, Imiringi, Amurukani, Kolo 1, Kolo 2, Kolo 3, Emeyal 1, Emeyal 2, etc.) communities and staff of the IOC, it was revealed that, remedial cementing jobs on some of the production wells were conducted always, to reduce oil migration. Therefore, this study is very important. Thus, this paper is expected, to yield supportable outcomes and solutions that, would make the cementing of similar oilwells economically viable, and safer in the study area.

2. MATERIAL AND METHOD

2.1. Material

The materials used for the investigations were Class G cement, eight (8) sampled ferrous mix-water, de-ionised water, and 36 formulated cement slurries; while the major equipment were weighing balance, thermocouple and Chandler model 7322 HPHT pressurised consistometer, and cement mixer.

2.1.1 Deionised Mix-water

The deionized water is a product of Roshan industries. The deionized water is of high grade de-ionized, and it is branded as ultra-violet treated and premium water quality. A 20-litre plastic-can was purchased from an industrial chemical dealer in Yenagoa, Bayelsa State, Nigeria. The deionised mix-water was used, to formulate the neat cement slurries. These slurries were used as the control cement slurries for the ST tests.

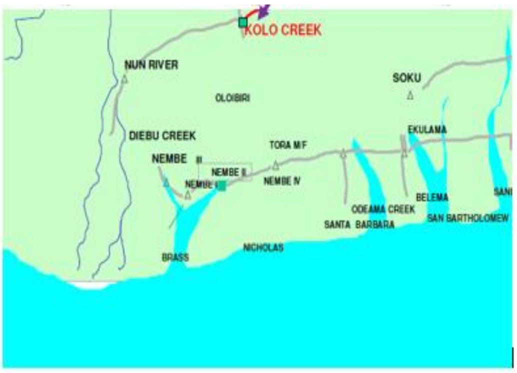


Fig. 4 Kolo Creek in red-like color; modified from Creek [37] and Adesuyi [33].

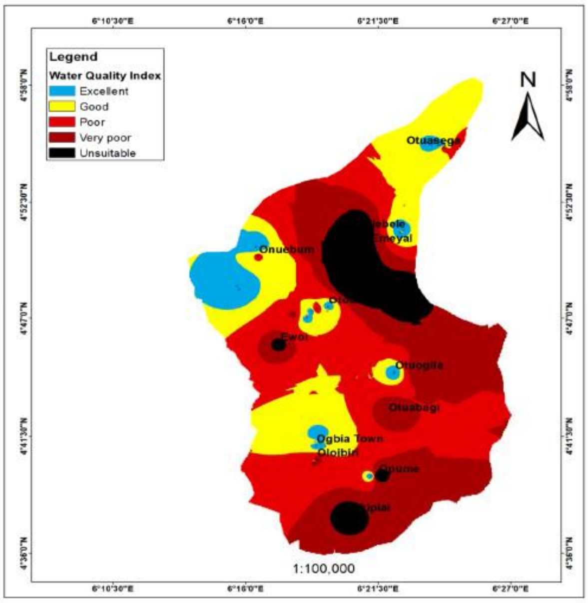


Fig. 5 Water Quality Index map for Kolo Creek [35].

2.1.2 Sampling and collection of mix-water

Table 1 shows the locations in Kolo Creek, where the eight (8) mix-water samples were collected; each of these samples were collected from 8 different boreholes, at the depth approximately below 60ft. These samples were collected between the months of November, 2018 – March, 2019. Before these samples were collected from each borehole, the *in-situ* mix-water in the borehole were hovered for 20 minutes. This was done with the aid of a submersible pump, at the flow rate (Q) of 20 litres/minutes. This was aimed at collecting uncontaminated mix-water in each the boreholes. These samples were collected into a rinsed 4-litre empty plastic container from each of these boreholes. The containers were closed hermetically, to avoid the appearance of air bubbles, and rapid self-oxidation. These containers were labeled; each of the label on the containers indicated the date, time, and location of the sample collected. Then, the mix-water samples were transported to Niger Delta University chemistry laboratory for water chemistry analysis.

Table 1 Sampled mix-water location.

S/No	Water Samples	Location	GPS Location
1	WS1	Deionised Water	Nil
2	WS2	Kolo 2 Izogbo	$4^{0}48'20''N\ 6^{0}22'33''E$
3	WS3	Otuasege Otumisou	$4^{0}55'2''N\ 6^{0}23'33''E$
4	WS4	Kolo 2 Otu-ogele	$4^{0}48'23''N\ 6^{0}22'32''E$
5	WS5	Otuasege Otuwododo	$4^{0}55'5''N\ 6^{0}23'39''E$
6	WS6	Kolo 1 Emelala	$4^{0}48'23''N\ 6^{0}22'32''E$
7	WS7	Otuasege winners	$4^{0}54'51''N\ 6^{0}23'7''E$
8	WS8	Oruma Ebifro	$4^{0}55'2''N\ 6^{0}24'11''E$
9	WS9	Kolo 2 Angala	$4^{0}48'22''N\ 6^{0}22'32''E$

2.1.3 Mix-water and Its Physicochemical Properties

At the Chemistry Laboratory, Niger Delta University, Nigeria, water analyses were conducted on the mix-water samples, to identify the presence of heavy metals and other physical parameters. The investigated heavy metals were in no any particular order limited to: arsenic (As), chlorine (Cl), cadmium (Cd), chromium (Cr), magnesium (Mg), calcium (Ca), mercury (Hg), and zinc (Zn), copper (Cu), iron (Fe), lead (Pb); while the physical properties of the mix-water samples were examined onsite, which includes: pH, turbidity, total dissolved solids (TDS), and electrical conductivity. These water analyses were conducted using the American Public Health Association drinking water test methods (APHA, 1998 [38]). Explicitly, the presence of heavy metals in the mix-water samples were determined by the Atomic Absorption Spectrophotometer (AAS); while the anion, and cation of the heavy metals were measured and determined using standard titrimetric and spectrophotometric methods. Subsequently, the physicochemical results obtained were benchmarked with the World Health Organisation, and Nigeria Standard Drinking Water Quality standards values ([39]; [40]). The water analysis results show that, in each of the tested samples for the physicochemical parameters, the ferrous ion (Fe^{2+}) concentration was higher (0.52 to 6.82mg/L); which is greater than 0.3mg/L (Table 2). This was the only heavy metal that is strongly in dispute with the WHO's and NSDWQ's Drinking Water Quality standards. However, groundwater from this study area, have been declared previously as good water, but not as potable water [35]. The aforementioned water analyses method employed in this paper, to determine the suitability of mix-water as potable water, have also been used and reported by many studies ([41]; [42]; [35]; [43]). Hence, its application in this paper.

2.1.4 Class G oilwell cement

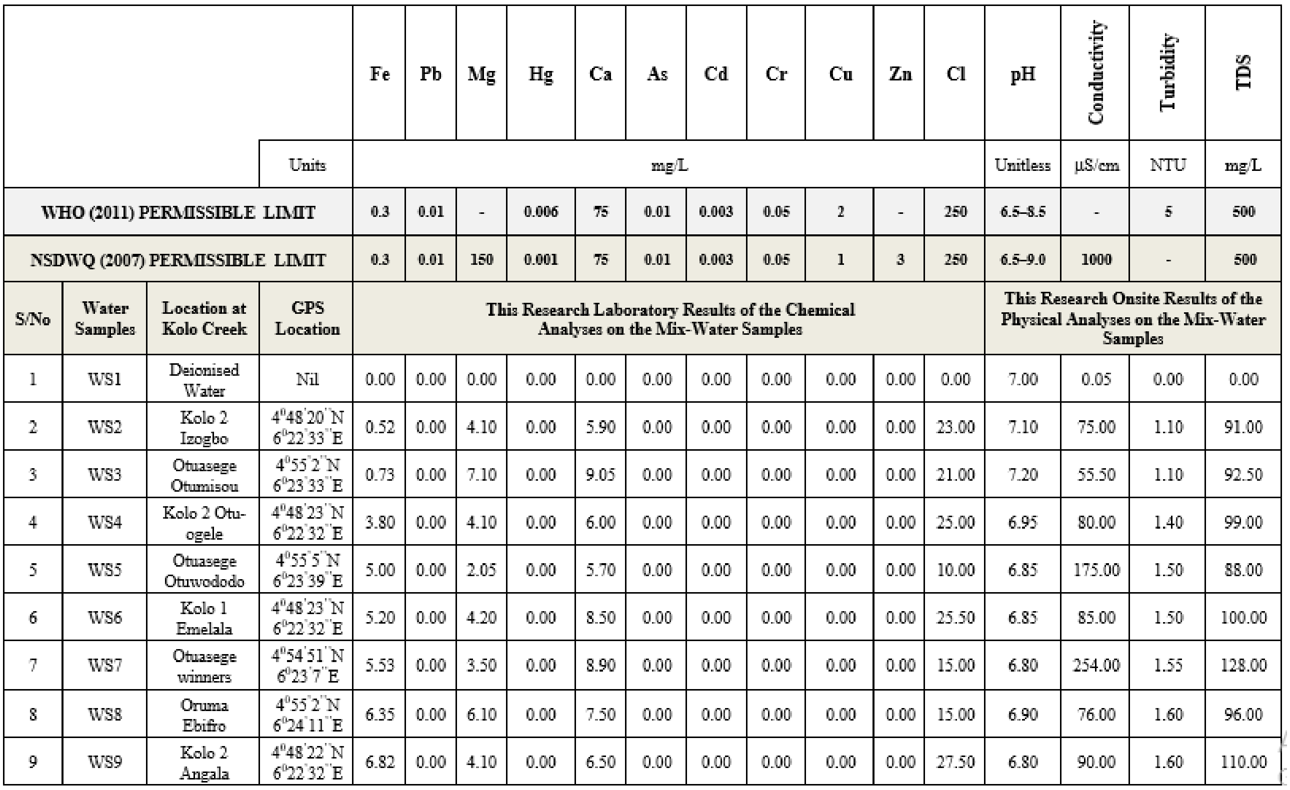
Class G oilwell cement was used as one of the experimental materials. This Class G oilwell cement was provided by a Vendor to the petroleum engineering laboratory, Niger Delta University, Nigeria. Class G oilwell cement (OWC) is envisioned for use as oil and gas basic cement. More information about the Class G cement specifications is presented in Tables 4 and 5.

2.2. Methods

2.2.1. Measurement of Setting Time

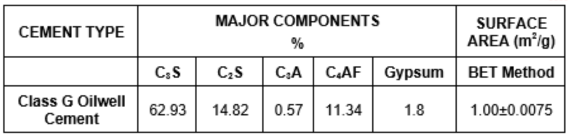
The Vicat equipment is used, to measure the ST of oilwell cement slurry, at static and atmospheric conditions only ([44]; [45]; [46]; [47]). Alternatively, the CEMSET device is used, to estimate the ST of oilwell cement slurry, at semi-dynamic state, under simulated low shear (low pump rate or large casing size), high shear (high pump rate or small casing size), pressure (15 to 7,493psi), and temperature (32 to 180^{0}F) conditions; but not at continuous vigorous shear, and HPHT conditions ([48]; [49]). For this reason, to measure the ST of cement slurry, at simulated continuous vigorous high shear (high pump rates, or small casing sizes), and HPHT environments, a customised API thickening time test device was used. The API thickening time test device used was the Chandler model 7322 HPHT pressurised consistometer with an additional thermocouple feature ([49]; [50]; [51]). Since, this research is intended to measure the initial and final ST performances of cement slurry, at continuous vigorous high shear at HPHT conditions; then, at this point, it is obvious that, the Vicat, and no-shear-, and pre-shear-CEMSET tests were not applicable, in testing the ST of the investigated cement slurries, due to their deficiencies, to test the ST of cement slurry, at continuous vigorous high shear at HPHT conditions. As a result, the Chandler model 7322 HPHT pressurised consistometer with an additional customised thermocouple feature, were used for the tests, to measure the initial ST, and final ST of the investigated cement slurries. During the tests the potentiometer with the paddle assembly was replaced with the thermocouple probe. Therefore, the initial, and final ST were not measured based on the slurry's consistency at $30B_c$, $70B_c$ and $100B_c$; but, based on the initial exothermic reaction or increase in temperature of initial hydration, and the just to declined temperature of the final hydration, which respectively, correlated well to the initial, and final ST. The thermocouple measures, were graphically displayed as temperature curve, in which the initial, and final ST were respectively, recorded as the initial temperature increase, and the about decline temperature, with respect to time.

Table 2 Physicochemical properties of the mix-water samples, at Kolo Creek.



				Fe	Pb	Mg	Hg	Ca	As	Cd	Cr	Cu	Zn	Cl	pH	Conductivity	Turbidity	TDS
			Units	mg/L											Unitless	µS/cm	NTU	mg/L
WHO (2011) PERMISSIBLE LIMIT				**0.3**	**0.01**	**-**	**0.006**	**75**	**0.01**	**0.003**	**0.05**	**2**	**-**	**250**	**6.5–8.5**	**-**	**5**	**500**
NSDWQ (2007) PERMISSIBLE LIMIT				**0.3**	**0.01**	**150**	**0.001**	**75**	**0.01**	**0.003**	**0.05**	**1**	**3**	**250**	**6.5–9.0**	**1000**	**-**	**500**
S/No	**Water Samples**	**Location at Kolo Creek**	**GPS Location**	**This Research Laboratory Results of the Chemical Analyses on the Mix-Water Samples**											**This Research Onsite Results of the Physical Analyses on the Mix-Water Samples**			
1	WS1	Deionised Water	Nil	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.00	0.05	0.00	0.00
2	WS2	Kolo 2 Izogbo	$4^{0}48'20''$N $6^{0}22'33''$E	0.52	0.00	4.10	0.00	5.90	0.00	0.00	0.00	0.00	0.00	23.00	7.10	75.00	1.10	91.00
3	WS3	Otuasege Otumisou	$4^{0}55'2''$N $6^{0}23'33''$E	0.73	0.00	7.10	0.00	9.05	0.00	0.00	0.00	0.00	0.00	21.00	7.20	55.50	1.10	92.50
4	WS4	Kolo 2 Otu-ogele	$4^{0}48'23''$N $6^{0}22'32''$E	3.80	0.00	4.10	0.00	6.00	0.00	0.00	0.00	0.00	0.00	25.00	6.95	80.00	1.40	99.00
5	WS5	Otuasege Otuwododo	$4^{0}55'5''$N $6^{0}23'39''$E	5.00	0.00	2.05	0.00	5.70	0.00	0.00	0.00	0.00	0.00	10.00	6.85	175.00	1.50	88.00
6	WS6	Kolo 1 Emelala	$4^{0}48'23''$N $6^{0}22'32''$E	5.20	0.00	4.20	0.00	8.50	0.00	0.00	0.00	0.00	0.00	25.50	6.85	85.00	1.50	100.00
7	WS7	Otuasege winners	$4^{0}54'51''$N $6^{0}23'7''$E	5.53	0.00	3.50	0.00	8.90	0.00	0.00	0.00	0.00	0.00	15.00	6.80	254.00	1.55	128.00
8	WS8	Oruma Ebifiro	$4^{0}55'2''$N $6^{0}24'11''$E	6.35	0.00	6.10	0.00	7.50	0.00	0.00	0.00	0.00	0.00	15.00	6.90	76.00	1.60	96.00
9	WS9	Kolo 2 Angala	$4^{0}48'22''$N $6^{0}22'32''$E	6.82	0.00	4.10	0.00	6.50	0.00	0.00	0.00	0.00	0.00	27.50	6.80	90.00	1.60	110.00

Table 3 Class G cement: clinker and surface area.



CEMENT TYPE	MAJOR COMPONENTS %					SURFACE AREA (m^2/g)
	C_3S	C_2S	C_3A	C_4AF	Gypsum	BET Method
Class G Oilwell Cement	62.93	14.82	0.57	11.34	1.8	1.00±0.0075

Table 4 Class G cement: major chemical properties

S/No.	Parameter/Unit	Value
1.	Loss on ignition, %	0.80
2.	Insoluble residue, %	0.42
3.	MgO, %	2.0
4.	C_3S, %	63
5.	C_2S, %	14.80
6.	C_3A, %	2.2
7.	$C_4AF + 2C_3A$, %	18
8.	Gypsum, %	< 1.8
9.	Alkali content expressed as Na_2O, %	0.66
10.	SO_3, %	1.65
11.	Al_2O_3 to Fe_2O_3	> 0.64

Table 5 Class G cement: physical properties.

S/No.	Parameter/Unit	Value
1.	Specific Gravity, unitless	3.14
2.	Surface Area, m^2/g	1.00
3.	Bulk Weight, lbs./ft^3	3.14
4.	Water for standard consistency [(Water (g)/Cement (g)* %]	0.44
5.	Initial Setting Time at atmospheric condition, minutes	30
6.	Final Setting at atmospheric condition, minutes	600
7.	Minimum Thickening Time, minutes	90
8.	Maximum Thickening Time, minutes	120
9.	Thickening Time + Additives to enable placement in HT, ^{0}F	550
10.	Maximum Consistency Between 15 – 30 minutes, Bearden (B_c)	30
11.	Minimum Compressive Strength at curing: time (8hrs), temperature (100^{0}F), and Atmos. pressure, psi	300
12.	Maximum Compressive Strength at curing: time (8hrs), temperature (140^{0}F), and Atmos. pressure, psi	1,500
13.	Depth Usage as Neat Cement Slurry, ft.	≈ 8,000
14.	Depth Usage when mixed with Additives, ft.	> 8000
15.	Response to Retarders, unitless	Excellent
16.	Free water content, mL	4.3
17.	Soundness, %	0.08

3. RESULTS AND DISCUSSION

ST is an important response variable for designing a successful primary cement job. If a designed cement slurry remains flowing state, over a prolonged period of time and functions as a solid when it stops flowing, in a reasonable period of time as desired; then, it is suitable for that particular cement job [52]. Therefore, Figs. 6 to 9 illustrate the results, of the effects of the different ferrous ion concentration present in mix-water on the initial setting time (IST), and final setting time (FST) of cement slurry in high-pressure, and high temperature environment. ST is an important response variable for designing a successful primary cement job. If a designed cement slurry remains in a flowing state, over a prolonged period of time, and functions as a solid; when it stops flowing, in a reasonable period of time as desired; then, it is suitable for that particular cement job [52].

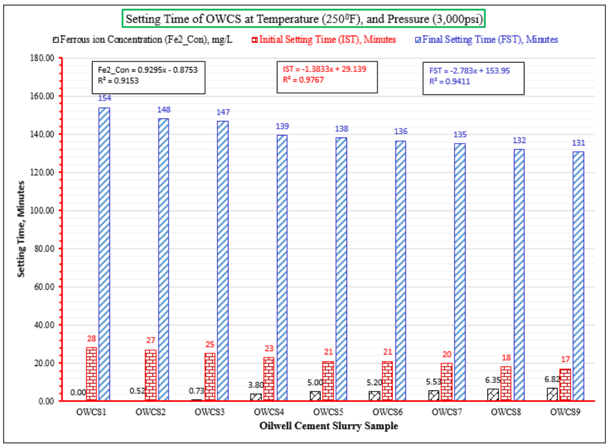


Fig. 6 The ST of the investigated ferrous cement slurry systems, when w/c, temperature, and pressure, were kept constant at about 0.44, 250^{0}F, and 3,000psi, respectively.

In view of that, Fig. 6 shows the results of the IST and FST of the investigated ferrous cement slurry systems and the reference deionised oilwell cement slurry (OWCS1); when w/c, temperature, and pressure, were kept constant at about 0.44, 250^{0}F, and 3,000psi, respectively. Additionally, the results in Fig. 6 indicates that, as the ferrous ion concentration increases at the rate of 0.93mg/L, the IST and FST respectively decrease at the rate of -1.38 and -2.78 minutes, which is the fastest accelerated ST. From this results of Fig. 6, it is observed that, the increase of ferrous ion concentration in mix-water, accelerates the ST of cement slurry.

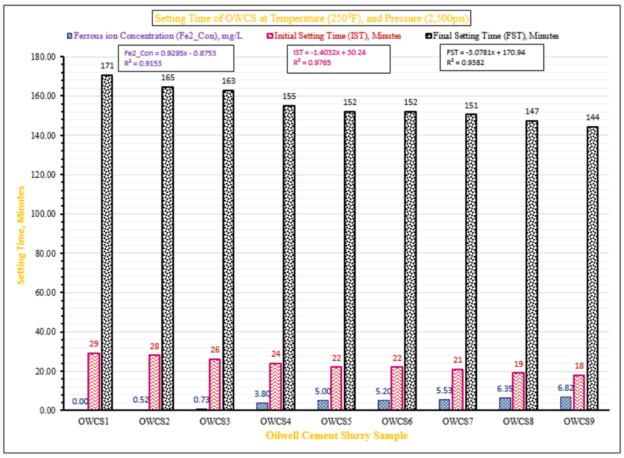


Fig. 7 the ST of the investigated ferrous cement slurry systems, when w/c (0.44), temperature (250^{0}F), and pressure (2,500psi).

Similarly, Fig. 7 shows results obtained from the ST of the investigated ferrous cement slurry systems, and the reference deionised OWCS1, when the experimental condition was conducted at w/c (0.44), temperature (250^{0}F), and pressure (2,500psi). This results in Fig. 7 illustrates that, as the ferrous ion concentration increases at the rate of 0.93mg/L, the IST and FST decreases at the rate of -1.40 and -3.08 minutes, respectively, which is the second-fastest accelerated ST. This explained that, the presence of ferrous ion in high concentration shortened the ST of cement slurry.

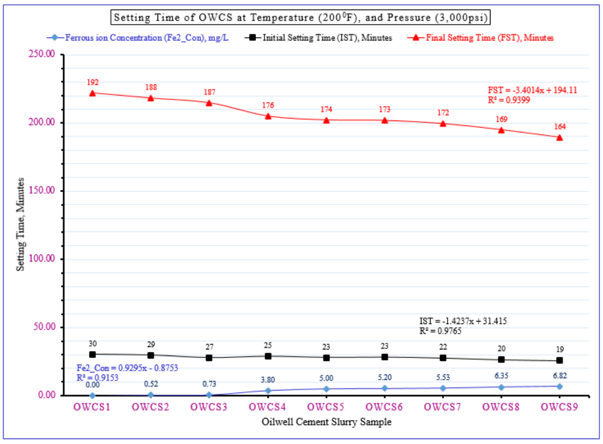


Fig. 8 The ST of the investigated ferrous cement slurry systems, when w/c, temperature, and pressure, were respectively held constant at approximately 0.44, 200^{0}F, and 3,000psi.

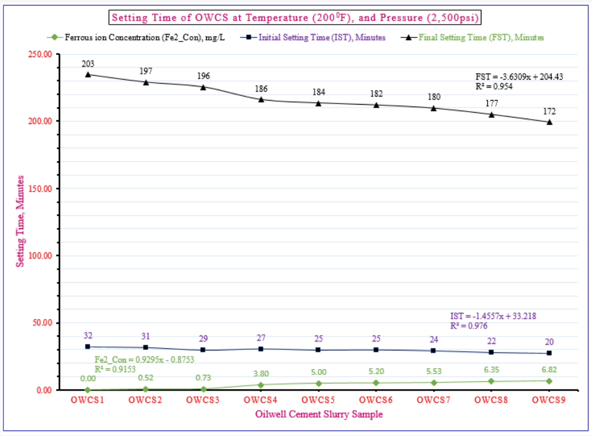


Fig. 9 the ST of the investigated ferrous cement slurry systems, when w/c, temperature, and pressure, were respectively held constant at approximately 0.44, 200^0F, and 2,500psi.

Furthermore, the results presented in Figs. 8, and 9 show similar trend as those in Figs. 6, and 7; despites, the respective different experimental conditions of w/c (0.44), temperature (200^0F), and pressure (3,000psi) as indicated in Fig. 8; and w/c (0.44), temperature (200^0F), and pressure (2,500psi) in Fig. 9. Explicitly, Fig. 8 illustrates that, the IST and FST individually declines at the rate of -1.42 and -3.40 minutes, which is observed as the third-fastest accelerated ST; while that of Fig. 9 reveals that, the IST and FST of the cement slurry system declines at the rate of -1.42 and -3.40 minutes, respectively. This is the observed as the least-fastest accelerated ST.

Generally, using the bottom-top approach to analysis the results in terms of ferrous ion concentration, temperature and pressure; it was observed that in Fig. 9, with the simulated experimental condition of temperature (200^0F) and pressure (2500psi), the average IST, and FST were recorded at 26, and 186 minutes, respectively. Conversely, in Fig. 8, when the temperature was held at 200^0F, while pressure was increased to 3000psi, the average IST, and FST were respectively, measured at 24, and 177 minutes. Whereas, the results in Fig. 7 shows that, when the temperature was increased from 200 to 250^0F, and pressure was rather reduced from 3000 to 2500psi; the average IST was estimated as 23 minutes, while the average FST was estimated as 156 minutes. Furthermore, in Fig. 6, when the experimental condition was changed to an approximate temperature, and pressure of 250^0F, and 3000psi; the average IST was estimated as 22 minutes, while the average FST was estimated as 140 minutes. Therefore, the overall results of this study revealed that, as temperature, pressure, and concentration of ferrous ion continued to increase, it resulted in more accelerated ST.

Technically, these results explained that, the ST of the ferrous cement slurry systems were accelerated (or shortened), as the ferrous ion concentration, temperature, and pressure were increased. Therefore, this study evidenced that, there exist a strong inverse-proportional linear relationship between the dependent variable, ST (IST and FST), and the independent variables, ferrous ion concentration, temperature, and pressure in the investigated cement slurry. This is shown statistically by the *coefficient of determination* (R^2). The R^2 values are expressed in Figs. 6 to 9. These values on the average, are approximately above 90%. Vividly, this explains that, about 98, and 94% of the variation in each of the IST, and FST responses, respectively, of the investigated cement slurry systems were explained by the presence of high ferrous ion concentration in the sampled mix-water, in regards with the prevailing simulated HPHT experimental conditions.

Critically, the overall results suggested that, the faster ST or flash set is attributed to tricalcium aluminate (C_3A) in the hydration reaction. Since, C_3A clinker has a faster rate of reaction during hydration in a high-pressure and high-temperature oilwell. Therefore, more concentrations of retarders would be needed to bring up the ST results [51]. Moreover, Madhusudana *et. al.* [53]; Patil *et al.* [21]; Minocha and Goyal [54]; Nikhil *et al.* [22]; Kucche *et al.* [23] separately opined that, the presence of chemical impurities in mix-water can strongly partake in the hydration reaction of cement slurry, and negatively impact on the ST of cement slurry. Hence, in this study, the presence of ferrous ion concentration in mix-water above the WHO [40] limit of 0.3mg/L, can be classified as chemical impurity in cementing of oilwells; which has been demonstrated by this study that, the ST of the ferrous cement slurry systems were accelerated (or shortened), as the ferrous ion concentration, temperature, and pressure were increased.

4. CONCLUSION

In this study, the results obtained, have demonstrated that, high concentration of ferrous ion in the mix-water resulted in accelerated setting time of the ferrous cement slurry in a HPHT environment. The outcomes of the experimental results are summarised and presented as follows:

- The presence of ferrous ion concentration in mix-water above the WHO limit of 0.3mg/L, is classified as chemical impurity in cementing of oilwells.

- The R^2 values vividly disclosed that, about 98% of the variation in the IST response; and 94% of the variation in the FST response, of the investigated cement slurry systems were explained by the presence of high ferrous ion concentration in the sampled mix-water. With regards, to the exposed prevailing simulated HPHT experimental conditions.

- At the simulated HP of 2500psi, and HT 200^0F the IST, and FST were approximately measured at the rate -1.47, and -3.63 minutes, with an R^2 values of 98, and 95%, respectively. This was declared as the least accelerated setting time; whereas the fastest accelerated setting time was observed, when the HP was held at 3000psi, and HT at 250^0F, which resulted in an IST of -1.38 minutes, and a FST of -2.78 minutes, with an R^2 values of 98, and 94%, respectively. These evidenced that, at increasing HPHT, the ferrous cement slurry setting time accelerated.

- The overall results explained that, the ST of the cement slurry systems were accelerated (or shortened), as the ferrous ion concentration, temperature, and pressure were increased.

Finally, the implication of the overall results of this study revealed that, mix-water with high concentration of ferrous ion is only suitable for cementing surface casings, and shallow oilwells. Therefore, retarders shall be needed, to bring up the setting time of ferrous cement slurry; if the need arises to drill and cement deeper oilwells.

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