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Improving local class A to Oil Well Cement using PET plastic waste

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IMPROVING LOCAL CLASS A TO OIL WELL CEMENT USING PET PLASTIC WASTE

MSc (50/50) Research Report

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ABSTRACT

Addition of polyethylene terephthalate (PET) waste plastic in cement mixtures mostly negatively affect cement matrix properties. Mainly, decreasing the compressive strength, while also affecting slurry properties of the cement mixtures. However, recent findings for concrete cement mixtures show that through prior pretreatment of the plastic waste material, via irradiation technique or through oxidizing solutions, the strength of cement mixtures is regained. Promoting sustainable practices, this work considered the utilization of local class A cement, improved into oil well cement, and then further investigates the prospect of using PET plastic waste in cementing oil and gas wells. Local class A was formulated into standard oil well cement utilizing chemical additives, whereby their compatibility and interactions were explored. A temperature of 38 ℃ and atmospheric pressure were utilized as bottom hole circulating conditions. Three unique PET derivatives as additives, counting pure PET fibres, irradiated PET fibres, and powder Bis(2-hydroxyethyl) Terephthalate (BHET) synthesized through PET glycolysis, were each then added in 0.2%, 1.0%, and 1.8% BWOC dosages. Varyingly, their addition increased the oil well cement compressive strengths, each optimally, by 22.05%, 19.34%, and 81.82%, respectively. Overall, plastic viscosities increased with increasing incorporation dosages, with slip effect resulting due to PET fibres incorporation. Addition of a superplasticizer among the additives is crucial in controlling rheological behavior and most importantly in improving compressive strength of PET plastic incorporated oil well cements. PET fibres have a potential to be used as reinforcements while BHET can be readily used as an oil well cement additive.

1. INTRODUCTION

The hydration reaction of oil well cement involves multiple physico-chemical mechanisms, covering diffusion, nucleation, growth, complexation, as well as adsorption mechanisms. A sequence of reactions takes place simultaneously and consecutively between water and cement constituents, with chemical additives in some cases, thereby leading to the setting and hardening of the oil well cement slurry. Strengths of hardened oil well cement mainly define the reliability and the ability to resist deformation when loads are applied. Deficiency in set cement's compressive strength (Huwel, 2014) signal increased chances of casing failure accompanied with a decrease in lifespan of a well, while according to Alp and Akin (2013) increased compressive strengths, additionally to increased durability, are further associated with decreased porosity. Aside from ensuring adequate mechanical properties of the set cement after the oil and gas well cementing operation, oil well cement additives also play a crucial role in controlling slurry properties including rheological behavior, thickening time, and fluid loss.

The utilization of polymer waste, counting rubbers (Ahmed et al., 2020) and plastics (Jassim, 2017), has been of interest lately, with researchers struggling to find widely applicable and sustainable alternative methods to handle this abundant non-biodegradable polymer waste. Nonetheless, several studies for application of these polymer wastes in cementing jobs have been carried out. Various studies show that Polyethylene Terephthalate (PET) plastic waste can be incorporated or added in concrete as aggregate, powder, or fibre. Further, these studies involving PET plastic incorporation in cement products have been a success to some extent. As fibres and coarse aggregates, PET in concrete has been reported to improve the workability of the concrete (Choi et al., 2005). Furthermore, it improves impact resistance, enhances cracking properties, and leads to increased flexural strength, especially in fibre forms as used in the studies by Kim et al. (2010); Koo et al. (2014); and Pelisser et al. (2012).

Hence, these studies further commonly reported that the compressive strength was reduced with the incorporation of PET waste. Additional effects apart from the slight decrease in density involve the decrease in elastic modulus with the increase in PET fibre incorporation volume reported by Kim et al. (2010), and the PET plastic's increased sensitivity to alkaline environments. Given the PET plastic's increased sensitivity to alkaline environments, the improvements brought about by adding recycled PET fibres in a study by Pelisser et al. (2012)

deteriorated after 150 days, accompanied by increasing porosity at about 365 days. Koo et al. (2014) together with Schaefer et al. (2017) further emphasised that the use of PET enhanced concrete under aggressive alkaline conditions must be thoroughly evaluated given the increased possibility of degrading durability perfomance under these conditions. Contrarily, the incorporation of PET waste in concrete as fine powder, as in the study of Umasabor and Daniel (2020), where PET plastic waste was pulverized into powder first, prior to mixing it with the concrete, reported varying results.

One remarkable study by Rai et al. (2012) set forth that the reductions in compressive strength and workability which resulted when different percentages by volume of plastic flakes partially replaced sand in concrete were minimal. Further, these reductions can be countered by adding a superplasticizer. Hence, the workability of the waste plastic mix concrete was reported to have increased by around $10 - 15\%$, while the compressive strength increased by approximately 5% following the addition of a superplasticizer to the cement mix.

Lee et al. (2019) discovered that chemically treating PET plastic before incorporation in concrete as the replacements of coarse aggregate, especially using the strong oxidizing calcium hypochlorite solution $(Ca(ClO)_2)$, yielded an improvement in bond strength between cementitious matrix and PET plastic aggregates with further reduction in the gap at the interfacial transition zone. As a result of such PET plastic pretreatment, the compressive strength of the concrete containing chemically oxidized PET plastic coarse substitute aggregates increased compared to the control PET aggregate which was treated with water while porosity and permeability decreased.

Major breakthroughs of using PET plastic waste to achieve notable improvements in cement related operations involved pretreatment of plastic before it is applied as a concrete additive, either in the form of aggregate or powder. Based on a number of different studies, the gamma irradiation of PET and its thermal depolymerization through glycolysis have emerged as leading techniques to be utilized for transforming the waste polyethylene terephthalate plastics for use in cement mixtures. Gamma irradiation results effects lead to direct changes in physical properties. Polyethylene terephthalate, like the many other polymers, undergoes major crosslinking and minor oxidative degradation on gamma radiation. However, with its sterilization through gamma radiation readily occurring in both film and fiber forms, withstanding at least 1000 kGy of

gamma radiation even though discoloration takes place at lower doses (Plester, 1973). Furthermore, both radiation-induced crosslinking and chain scission can result in improved PET plastic strength (Schaefer et al., 2017).

A study by Cota et al. (2007) reported that high density polyethylene (HDPE) mechanical strength properties improve with increasing gamma irradiation dose. Further, the application of radiation at lower dose rates led to effectively obtaining lower doses that necessarily provide a similar change in resistance parameters as high doses, meaning that gamma radiation affects HDPE in a more efficient way at lower dose rates.

In the case of irradiated PET as sand substitute in concrete, from the study of Martínez-Barrera et al. (2015) it was concluded that irradiated PET-enhanced concrete shows greater mechanical strength. It was reported that radiation-induced crosslinking improved the mechanical strength of PET enhanced concrete for doses up to 150 kGy, with greater compression strength exhibited by samples irradiated at a dose of 100 kGy.

Schaefer et al. (2017) also explored the effectiveness of gamma irradiated PET plastic when used as an additive in cement paste comprising of supplementary cementitious materials counting silica fume and Class F fly ash. This study of Schaefer et al. (2017) involved irradiation doses of 10 kGy for the low dose plastic additive and 100 kGy for the high dose plastic additive. It was then found that irradiating plastic at a high dose (100 kGy) was the best, recouparating strength lost due to the addition of plastic in cement paste. Furthermore, it was clarified that adding a high dose irradiated PET plastic rather than regular, non-irradiated or low dose irradiated PET plastic in various concretes caused an increase in compressive strength accompanied by a decrease in porosity.

Meanwhile, thermal depolymerization of polyethylene terephthalate through glycolysis to yield Bis(2-hydroxyethyl) Terephthalate (BHET) has been covered in numerous studies over the past decades. Recently, counting the studies by Bartolome et al. (2014) covering the recent developments; by Raheem et al. (2018) simulating the process of BHET and its recovery using two–stage evaporation systems; and by Lalhmangaihzuala et al. (2020) where the catalysis of PET depolymerization through glycolysis is significantly improved in an environmentally friendly way, hence the developed bio-derived solid heterogeneous orange peel ash catalyst.

In the study by Mendivil-Escalante et al. (2014), it was found that BHET synthesized through glycolysis from PET plastic waste has a great potential to be applied as a concrete mixture additive, although further research was recommended, particularly on resulting mechanical as well as durability performances.

In one remarkable study by Simsek (2020), it was found that cementitious composites of BHET have higher calcium hydroxide content and lower porosity together with water absorption percentages in comparison to cementitious composites of dioctyl terephthalate. It was reported that hydrogen bonds are formed in BHET cementitious composites, and those hydrogen bonds crucially prevent cement particles from agglomerating because of electrostatic attraction. They futher significantly contribute in healing cracks through formation of more hydrated products.

This project, unlike these previous studies, focuses on investigating the prospect of using waste PET plastics in cementing of oil and gas wells. Effects of the PET derived additives are investigated in significantly dispersed oil well cement slurries following highest amounts of the superplasticizer addition, hence its benefits to strength in PET containing concrete mixtures. PET was used in the form of pure fibres, irradiated fibres, and powdered BHET synthesized through its glycolysis (thermal depolymerization), while shallow oil well conditions were assumed.

Problem Statement:

Given the introduction of plastic waste without any pretreatment generally decreasing the quality of cement matrices, would the curing of PET containing cement mixtures at oil well temperature and pressure conditions have a unique effect, or would the proposed irradiation and depolymerization techniques for pretreatment of PET plastic waste before incorporation be able to effectively maintain or improve the slurry and matrix properties of the oil well cement.

The viscosity of polymer PET plastic waste at higher temperatures decreases, and polymer incorporation in oil well cement mix for utilization at increased temperatures, usually $> 110℃$, as of Abbas et al. (2013), could see cement slurry/matrix properties being consequently inadequate. Due to the lowering viscosity of the incorporated polymer additive, fluid loss together gas migration might occur during application. At this point should the issue of the polymer viscosity emerge, seemingly the option could be to rapidly increase the incorporation concentration of the polymer to encounter the problematic decreasing viscosity at high

temperatures (Abbas et al., 2013), or to settle for the lower temperature and pressure conditions where the PET incorporated oil well cement would probably function outstandingly. However, the leading solution could be adjustments in other blended cement additives dosages, which their compatibility with the incorporated PET plastic waste additive is also in question.

Aims and Objectives:

The aim of investigating the prospect of using PET plastic waste in cementing of shallow oil wells was carried out through the following objectives:

- Developing oil well cement slurry base design using local class A cement with oil well cement additives including a superplasticizer, retarder, expanding agent, fluid loss additive, and a defoamer at varying amounts; then assessing compatibility of these added additives, slurry mixability at a specified density, its settling and final strength.
- Incorporating PET plastic waste in fibre form on the oil well cement slurry to investigate the effects of PET plastic addition on the slurry's initial states and final hardened state.
- Pretreating PET plastic waste by gamma irradiation, to yield irradiated PET fibre additive, and by thermal depolymerization yielding BHET as the powdered additive, then investigate the effects of these PET plastic derived additives on the oil well cement slurry initial states and final hardened state.
- Cure oil well cement slurry samples at 38 ℃ and atmospheric pressure to correlate the curing conditions of prepared cement slurries to typical shallow oil well conditions.
- Prepare oil well cement slurries or samples varying by amount of PET plastic waste and/or additives added to roughly determine the optimum addition amounts.
- Thoroughly investigate the effects brought about by addition of BHET powder, irradiated, and non-irradiated PET plastic waste fibres on the oil well cement mixture by performing rheological measurements and failure parameter tests to determine each mixture's rheological properties (yield point and plastic viscosity) and compressive strength.

2. LITERATURE REVIEW

2.1. Fundamentals in Sustainable Manufacturing

A stepwise production of Portland clinker involves the crushing and grinding of raw materials, blending of the raw materials in the correct proportions, and burning the prepared mix in a kiln. Chemically, cement production begins with a calcination process where calcium carbonate is decomposed at a temperature of approximately 900 ℃, thereby leaving calcium oxide (burnt lime) while gaseous carbon dioxide is released, usually into the air. Thereafter, the clinkering process follows, clinker is produced, which consists of silicates, ferrites, and alumina of calcium that are given rise to by reacting calcium oxide from the calcination process with silica, alumina, and ferrous oxide at increased temperatures typically ranging between 1400 ℃ and 1500 ℃ (Nilsson et al., 2007).

The World Business Council for Sustainable Development (2014) reported that limestone, a source of calcium carbonate, is heated at a temperature of 1450 ℃ in a kiln containing small quantities of other raw materials including clay, sand and iron. As a result clinker is produced, with this process consuming large fuel amounts. Moreover, the produced clinker is just a hard intermediate product, it is further ground and milled at the same time with gypsum into fine powder, thereby the ordinary Portland cement is produced. However, more cement chemical additives other than the already mentioned gypsum can be added, and together with the produced clinker would be ground and milled to produce the unique desired oil well cement product.

2.1.1. Processing Routes

Main cement production processes involve the dry process, where raw materials are crushed and thereafter dried to raw meal as flowable powder, followed by feeding it into the kiln where it will be preheated or precalcined; the semi-dry process, where the dry raw meal is formed into pellets by combining it with water, followed by feeding those formed pellets into a grate preheater then into the kiln, alternatively straight to a long kiln equipped with crosses; the semi-wet process, where the slurry is initially dewatered in the filter presses, then the resulting filter cake is forced out into pellets followed by being fed either into a grate preheater, alternatively straight to a filter cake drier for raw meal production; and the wet processes, where raw materials, usually of high moisture levels, are crushed in water thereby forming a pumpable slurry which is either initially

fed to a slurry drier then into the kiln, or fed straight into the kiln (European Commission, 2001; Nilsson et al., 2007).

Given the environmental concerns including climate change and global warming together with the fact that the manufacturing of cement results to emission of carbon dioxide, a greenhouse gas regarded as the primary driver of global climate change, cement manufacturing industries can be advised to consider using more environmentally friendly cement production processes. According to Nilsson et al. (2007), approximately 5 % of the global carbon dioxide emissions back then came from cement production, with contributing factors counting the calcination process, a thermal treatment process in presence of air or oxygen in the kiln, and the immense demand and use of cement. Zhang et al. (2010) further reported that other deeply worrying emissions released during the manufacturing of cement include nitrogen oxides (NO_X) and sulphur dioxide (SO_2), which together with carbon dioxide are mainly emitted from the pre-calciner kiln system. Nonetheless, additional emissions like dust which is usually controlled using mechanical collectors or dust collectors, electrostatic precipitators, and fabric filters, was also highlighted as alarming. Furthermore, Nilsson et al. (2007) included the releases of carbon monoxides, volatile organic compounds, noise, together with dibenzofurans and polychlorinated dibenzodioxins as releases that pose relatively minor treats.

Taking into consideration a statement by Nilsson et al. (2007) which implied that the process route to manufacture cement is predominantly decided by whether the raw materials are dry or wet. One may be advised to use any manufacturing process that work best for their interests, either dry, semi-dry, semi-wet, or wet. However they would be strongly encouraged to employ a reasonable division of the combustion environment in the calciner since according to Zhang et al. (2010) a reasonable division of the combustion environment in the calciner can be regarded as the principal method to manage the formation of pollutant gases. In the contrary, one can be advised to specifically employ the use of a dry process route and add a reasonable division of the combustion environment in the calciner during cement production since according to both the European Commission (2001) and Zhang et al. (2010) the production of cement clinker via a dry process kiln with multi-stage suspension preheating and precalcination was then by far the best cement manufacturing method. Further demonstration was given by Zhang et al. (2010), where

the dry process cement production technology referred to as the pre-calcining technology indeed led to the reduction in the formation of heat loads and gas pollutants within the rotary kiln system, sorely by transferring of heavy raw material decomposition tasks to outside the kiln.

Moreover, with wet cement manufacturing process routes known for the increased energy consumption, one would indeed be greatly advised to employ the use of dry processing routes as much as they can to manufacture cement, thereby cutting in energy costs as the utilization of fuels will be lowered, and energy resources will consequently be reserved. According to European Commission (2001); Nilsson et al. (2007); and Zhang et al. (2010) cement manufacturing not only give emission and pollution issues, other underlying core issues involve the extreme high energy amounts consumed, with the energy costs usually ranging at about $30 - 40\%$ of production costs, and the enormous raw material amounts required for utilization, with a rough scale taken from Europe stating that about $1\ ton$ of clinker is produced by consuming raw materials with an average weight of $1.57\ tonnes$. Hence, the energy intensiveness and enormous raw material amounts consumed, one can clearly see that a proper choice of the manufacturing route alone is not enough to achieve a sustainable level. As a result, one may be encouraged to explore the use of alternative raw materials and fuels, together with more productive and environmentally friendly ways to produce clinker and cement as a whole.

2.1.2. Selection of Raw Materials

Cement manufacturing requires careful control when it comes to the chemistry of principal ingredients which are, namely, CaO, SiO_2, Fe_2O_3, and Al_2O_3, together with minor constituents including sulfites (SO_3), potassium oxide (K_2O), sodium oxide (Na_2O), titanium dioxide (TiO_2), and phosphorous pentoxide (P_2O_5) (Ghoroi and Suresh, 2007; Hıdıroğlu, 2017; Hokfors, 2014). The World Business Council for Sustainable Development (2014) wrote that the use of alternative waste raw materials and fuels, as natural raw materials and conventional fuels replacements, in optimum quantities with varyingly decreased proportions of natural raw materials or conventional fuels may also result in achieving the desired optimal balance of material composition in the clinker, although in a more sustainable way.

According to Oliveira et al. (2015) when calculations are done, prior the proportioning of raw materials, they must take into consideration the argillaceous or siliceous materials that might be contained in increased proportions within various limestones, as well as from the ash generated if coal is used to fire the kiln. Minor impurities in the raw material also must be taken into account, as they can have a significant effect on cement performance. Procter (2014) further wrote that during the course of selecting replacements for natural or conventional resources as raw materials or fuels to be used during cement production, it must be ensured that the alternative replacement fuels and raw materials fulfil the quality specifications equally as the natural raw materials and frequently used conventional resource fuels.

2.1.3. Raw Materials

Oil cements are the modifications of Portland cement, and Portland cement is produced by burning and grinding a mixture of calcareous and argillaceous materials (Morga, 1958). Calcareous materials act as a source of calcium carbonate, normally are natural occurring calcareous deposits, and they include the likes of limestone, marl, and chalk. On the other hand, several minerals and ores (argillaceous raw materials) including iron ore, shale, clay, and sand provide cement chemical necessities counting iron oxide, silica, and alumina (Morga, 1958; Nilsson et al., 2007).

Imbabi et al. (2013) with Snellings et al. (2012) reported that instead of the total usage of the above mentioned argillaceous natural raw materials including clay and shale, the partial use of process residues counting power station ash or fly ash, and blast furnace slag as partial natural raw materials replacements has been widely adopted. These process residues similarly contain significant quantities of clay-like components, resembling the partially replaced natural raw materials. According to Yi (2019) alkali waste usage as partial natural raw material replacement for calcareous materials is also possible. Moreover, Procter (2014) insisted that waste and by-products containing useful minerals including calcium, silica, alumina and iron may be utilized as natural raw material replacements in the cement kiln. Another remarkable study by Al Dhamri (2020) reported that oil based mud cuttings can be sucessfully recycled and reused as a natural raw materials replacement during the production of clinker as they contain silica, calcium and alumina.

The option of partially replacing natural cement raw materials with the resulting process residues comes with advantages including the cut in raw material costs, costs related to their pre-processing or mining if needed, which would come with a cut in energy costs too since preprocessing and mining are generally energy intensive operations. Given also the alarming negative climate changes worldwide, this option is encouraged as it comes with further benefits of saving energy through the use of process residues and waste materials as raw materials, while lowering the concerning consumption of natural resources (cement making natural raw materials), and possibly decreasing environmental impacts.

Also, the utilization of potential pozzolanic materials including rice husks, lime sludge, and broken bricks may significantly reduce cement manufacturing costs and further reduce the release of pollutants, hence these materials are self-calcining as they generally burn on their own.

2.1.4. Proportioning

Raw materials are first powdered, followed by mixing in specific proportions, and this raw material proportioning is key in obtaining a specific cement product with the required properties. Raw materials (also considering fuel waste) are proportioned accordingly in such a way that the cement's main mineral compositions including tricalcium aluminate, tetracalcium aluminoferrite, tricalcium silicate, and dicalcium silicate are uniquely combined to give rise to specific Portland clinker and further to certain specific class of oil cement (API cement). Hence, the compositions as displayed in Table 1 are different for each API cement class, and each cement class would further have unique fineness and varying water to cement ratio. Moreover, the difference in these API cement classes is motivated by the fact that they at least each would be exposed to different well conditions in the form of cement slurries, and those well conditions include varying high pressures and temperatures, as well as corrosive underground fluids and varying degrees of sulfate attacks (Hıdıroğlu, 2017).

Table 1: API Oil Well Cement Classes with Respective Typical Clinker Phase Compositions, Well Depth and Temperature Ranges, Together with Associated Degrees of Sulfate Resistance *(1. Pikłowska, 2017; 2. Mixhaux et al., 1989; 3. Teodoriu et al., 2019; 4. Nelson and Guillot, 2006, 5. Yi , 2019; 6. Hıdıroğlu, 2017)*

API CLASS	TYPICAL POTENTIAL PHASE COMPOSITION (%)				DEPTH (m)	TEMPERATURE (℃)	SULPHATE RESISTANCE
	C_3S	C_2S	C_3A	C_4AF			
A	50.33	25	9	8[1,2,6]	0 – 1830[1,3,5,6]	32.45 – 82.45[1,3,5]	Normal
B	46	31.67	5	12.33[1,2,6]	0 – 1830[1,3,5,6]	32.45 – 82.45[1,3,5]	Moderate & High
C	56.33	17	9	8.33[1,2,6]	0 – 1830[1,3,5,6]	32.45 – 82.45[1,3,5]	Normal, Moderate, & High
D	26.67	52.33	2.67	12[1,2,6]	1830 – 3050[1,3,5,6]	82.45 – 143.55[1,3,5]	Moderate & High
E	30	50.33	2.67	11[1,2,6]	1830 – 4270[1,6]	94 – 144[1]	Moderate & High
G	50	30	5	12[1,2,6]	0 – 2440[1,3,5]	44 – 111[1]	Moderate & High
H	50	30	5	12[1,2,6]	0 – 2440[1,3,5]	44 – 111[1]	Moderate & High

As displayed on Table 1 above, major constituent of the Portland clinker for every API cement grade is the silicate phases, and according to Nelson and Guillot (2006),- these phases generally account for about 80% of the total materials. Silicate phases found in oil well cements include tricalcium silicates ($3CaO \cdot SiO_2$), which is abbreviated as C_3S in Table 1, it is the major Portland clinker component as it produces more strength while also being behind the early bonding of cement, together with dicalcium silicate ($2CaO \cdot SiO_2$), which is abbreviated as C_2S, and it is responsible for late binding of cement, hence its slow hydration or medium activeness would have an effect on bonding time as well as on the final cement stone strength, consequently a small gradual gain in strength over a longer duration would be promoted.

Given the fact that increased tricalcium silicate amounts in cements provide even more heat required for cement hardening, as well as the exhibition of rapid strength and increased endurance build-ups, all because of the tricalcium silicate's high calorific value, thereby cements

with high tricalcium silicate amounts could further be distinguished by having increased hydration heat and shrinkage (Pikłowska, 2017). According to Mixhaux et al. (1989), magnesium and sulfates in downhole brines generally react with the hydration products of cement and consequently lead to loss of compressive strength. The development of cements having low amounts of tricalcium aluminate ($3CaO \cdot Al2O_3$), abbreviated as C_3A in Table 1, is key for oil well cements as such cements are less likely to experience sulfate attacks meaning the increased tricalcium aluminate amounts make cement more susceptible to sulfate attack (Mixhaux et al., 1989; Nelson and Guillot, 2006).

In Table 1**,** as the well depth goes deeper with increasing temperatures, the possibility of sulfate attacks also increases, thereby the ability to resist sulphate attacks (sulfate resistance) for that particular cement to be used in such depths and temperatures must also increase. Hence, API cement classes D and E are to be used in wells with greater well depth ranges and more extreme temperatures due to their low tricalcium aluminate contents. However, API cement classes D and E are not the only API cements with decreased tricalcium aluminate contents, API class B cements also, but they are used at the same well depth range of $0 - 1830$ m as API cement classes A and C with much higher tricalcium aluminate contents. This is because just like API cement classes A and C, API class B cements contain way more increased tricalcium silicate amounts which promote early strength, thereby it is not ideal or possible to use such cements in way more deeper wells due to early hydration and setting times, rather one may be strongly advised to use API class B cements in wells where formations contain extreme high sulfates contents, still between a $0 - 1830$ m well depth range.

Furthermore, tricalcium aluminate affects the bonding speed of a cement slurry, where it provides increased heat levels thereby accelerating bonding of a slurry (Nelson and Guillot, 2006). Tricalcium aluminate further has a power of corroding the installed casing, and it dissolves easily in water, particurlarly in sulphated water, making it to have limited contribution to high sulphate resistance cements (Pikłowska, 2017). On the other hand, tetracalcium aluminoferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$), abbreviated as C_4AF on Table 1, has an effect on strength over time, where during hydration it provides minor amounts of heat as it has a significant calorific value, thereby promoting low-heat hydration (Pikłowska, 2017).

Hence, rapid hydration, and early strength development promoted by tricalcium aluminate and tricalcium sulfate, respectively, thereby API cement classes D and E as displayed in Table 1 must have lowest concentrations of these rapid hydrating compounds. Reason being, because these API cements are to be specifically used in greater depths ($1830 - 3050$ m for API cement class D and $1830 - 4270$ m for API cement class E) with increased temperatures ($82.45 - 143.55$ ℃ for API cement class D and $94 - 144$ ℃ for API cement class E) which would result in unwanted extreme rapid hydration of the slurry and potentially make it impossible to pump or work with. Therefore, by having these compounds at such very low concentrations would extend the duration of hydration and further prolong time of pumping the slurry, thereby making it easier to use API cement classes D and E at these greater depths and higher temperatures.

API cement classes A, B, and D are manufactured for use in wells with depths below 1830 m. As displayed on Table 1, these cement classes have different compositions, thus each cement class function varyingly, with API class A cements used when no special necessities are required. API cement class B as briefly discussed above has low tricalcium aluminate amounts meaning it is more sulfate resistant, thereby it is to be specifically used in case where moderate to high sulfate resistance is needed, hence, more tricalcium aluminate in cement leads to sulfate attack susceptibility (Mixhaux et al., 1989; Nelson and Guillot, 2006; Teodoriu et al., 2019). Furthermore, API class C cements with significantly increased amounts of tricalcium silicate, and apparently being finely ground, they are specifically developed for use given a cement slurry with high early compressive strength is needed, hence, the significantly high tricalcium silicate amounts would mainly promote early rapid hydration (Pikłowska, 2017; Teodoriu et al., 2019).

While API cement classes D and E as shown on Table 1, are to be specifically used where moderately high temperatures and pressures are experienced due to having decreased tricalcium silicate and tricalcium aluminate amounts, which are early strength development, and rapid hydration promoting principal compounds, respectively. Cement classes G and H on the other hand have strict manufacturing specifications as well as behaviours that are easily predicted, furthermore they can be used along with additional chemical additives, counting accelerators and retarders, thereby covering an even wider range of well depths and temperatures (even way more than the $0 - 2440$ m typical well depth range that these cement classes can cover without additional chemical additives). Even the entire wide range of well depth coverage is possible

using these API cement classes along with chemical cement additives (Pikłowska, 2017; Teodoriu et al., 2019). Moreover, as displayed on Table 1, API class G cements and API class H cements have similar composition, the only difference according to Nelson and Guillot (2006) is that API class H is coarser than API class G cement. Given the fact that the coarser grind lead to prolonged hydration, thereby API class G cements probably have more rapid hydration than the coarser API class H cements, given no chemical additives have been added on both cement classes.

2.1.5. Kiln Fuels Selection

Fuel burning taking place in the cement kiln system provides heat (thermal energy), thereby leading to the occurrence of a chemical reaction between the pre-blended raw materials and fuels' ash, and in turn this chemical reaction results into having clinker as a product (Ishak et al., 2016). However, when it comes to modern kilns, increased fuel amount is needed in the calciner compared to the kiln, since according to Hassold (2018) the calcination process consumes most energy apart from energy losses, thereby leading to about 60 -70 % of the fuel being burned in the precalciner. Furthermore, Hassold (2018) clarified that adequate energy density is required for the kiln fuel, and when that fuel with adequate energy density is fired it results to the partial melting of the feed (Typically at a temperature around 1450 ℃), while it further set about quality nodulized clinker, steady coating for long campaign life, and close contact reactants as well as their rapid reaction.

A range of fuels burned in cement making kilns include coal, historically the main fuel burned in cement making kilns; natural gas, which together with coal are burned or utilized in their natural forms; and other fossil fuels counting petroleum fuels, bituminous and shale sands. Well-known and frequently utilized fuels for the provision of increased temperatures in modern cement kilns include coal, natural gas, and petroleum fuels, moreover these fuels are not only fired in cement making kilns but they are also major sources of energy worldwide till to date (Youn et al., 2019). Hence, these widely consumed cement kiln fuels, one may be advised to use only coal and natural gas as primary fuels to fire the kiln.

This advice would be based on the fact that both coal and natural gas are used in their natural forms while petroleum fuels, bituminous sands, and shale sands need to be distilled and/or refined prior to their usage as fuels (Chinyama, 2011; Youn et al., 2019). With coal and natural

gas not requiring no prior distillation and/or refining before firing in the kiln, thereby no extra pre-processing costs are to be involved meaning decreased energy expenses. On the other hand, one may be advised to specifically use natural gas only among the previously mentioned kiln fuels, even though coal provides cheaper energy as well. This advice would sorely be based on the fact that when natural gas is burned to acquire energy, it results in fewer emissions of almost all forms of air pollutants, including carbon dioxide, compared to when coal or petroleum fuels are burned for the production of the same energy amount.

Considering the effects that come about due to the overuse of natural energy resources, counting the extinction of resources as they are mostly non-renewable as well as pollution of the environment briefly through emissions and associated acid rains together with global warming, the exploration and utilization of alternative fuels to fire the cement kilns has been receiving growing attention. Ptasinski et al. (2007) demonstrated in their study, referred to as the exergetic evaluation of biomass gasification, that fossil fuels can be successfully substituted by renewable fuels. There, they experimented with solid biofuels counting straw, untreated and treated wood, grass, and plants, together with liquid biofuels counting vegetable oil which were to be coal replacements as gasification feedstock.

According to Chinyama (2011), alternative fuels that can be fired to produce high temperatures during cement manufacturing include gaseous fuels counting pyrolysis gas, refinery waste gas, and landfill gas; the liquid fuels including wax suspensions, waste solvents, used oils and oil sludge, petrochemical waste, paint waste, distillation residues, chemical waste, as well as tar; and lastly the solid fuels which include, rice hulks, petroleum coke, refuse derived fuels, pulp and sewage sludges, paper waste, wood waste, plastic waste, rubber residues, used tyres, nut shells, battery cases, and domestic refuse.

When it comes to choosing fuels to be fired during cement production, one may surely be strongly advised to employ the use of alternative waste fuels as much as they can rather than the complete use of conventional fossil fuels, considering the facts that alternative waste fuels are relatively inexpensive, thereby cuts in energy costs. Moreover, the combustion of waste in cement kiln systems rather than in incinerators results in reduced carbon dioxide emissions, which is not only good for the environment but also good for the industry since there will be a reduction in carbon dioxide emission penalties (Chinyama, 2011).

A closer look into the burning of alternative waste fuels within the cement kiln systems. Given the combustion process in a calciner occurring at lower temperatures of around 900 ℃, coupled with the fact that lower grade heat of less than 18 MJ/kg is more appropriate for the calciner, thereby it would be advisable for one to use as much as they can of the low-grade alternative waste fuels to fire the calciner, hence more fuel is also needed in the calciner than in the kiln (Chinyama, 2011; Hassold, 2018). Moreover, on the account that the net energy requirement for calcination is much higher than the net energy requirement of producing clinker in the kiln, due to the exothermic formation reaction of tricalcium silicate (C_3S), one may indeed come to a solid conclusion that the burning of alternative waste fuels should mainly take place in the calciner.

According to Ptasinski et al. (2007) and Nørskov et al. (2012) there are diverse combinations of renewable biomass resources and various waste materials to produce waste derived fuels including refuse derived fuel and solid recovered fuel, which would obviously have comparatively higher calorific values (in comparison to individual waste fuels) depending on how they were synthesized. During the production of these waste derived fuels, there are variations in degree of waste size reduction as well as variations in the removal of organic and inert material. These production differences together with how refined and processed the final product is, mainly distinguish refuse derived fuels and solid recovered fuels (Psomopoulos, 2014). Moreover, solid recovered fuels are a biodegradable waste or residues fraction produced from various types of non-hazardous waste including municipal solid waste, industrial waste, and commercial waste, while the refuse derived fuels are crude materials mainly made from domestic non-hazardous waste. Although there usually are metals removal systems when waste derived fuels are produced, but pollutants including chlorine, sulphur and heavy metals remain significantly present in finished fuel products, however in minimized propotions (Nørskov et al., 2012).

Given one has to select a substitute waste fuel to be fired within the cement kiln system and they have to choose between untreated non-hazzardous waste as fuel and the refuse derived fuel, they would deffinitely be encouraged to employ the use of refuse derived fuel in this case. This advice is based on facts that refuse derived fuels generally contain relatively lower bulk density as well as lower content of ash, while having relatively higher heating value (Psomopoulos, 2014). On the other hand, the untreated non-hazardous waste not only has relatively lower calorific value,

meaning it would release a relatively lower energy amount per 1 kg of fuel burned, it also has a great potential to release increased amounts of pollutants counting heavy metals, sulphur, and chlorine due to not being pretreated.

According to Gawlik et al. (2007), solid recovered fuels unlike refuse derived fuels, meet a series of standards, environmentally and process-relevant standards, and those standards include the corroding capacity, biodegradable fraction as well as the required minimal contents of various critical trace elements counting mercury, thallium, and cadmium. Hence these standards which clearly display that refuse derived fuels are less refined than solid recovered fuels, coupled with the fact that refuse derived fuels generally are less efficient as kiln system's fuels when compared to solid recovered fuels which typically have a guaranteed quality average calorific value, thereby one may be encouraged to employ the use of solid recovered fuels rather than using refuse derived fuels. However, one would also be strongly advised to consider using these waste derived fuels correspondingly, for instance, given parts of the system or the whole system that require much higher energy amounts and refuse derived fuels do not contain that much of contaminants, although they are not refined, furthermore they have a satisfying calorific value, thereby in such a case refuse derived fuels can be utilized since they have would be having higher calorific values, thereby more efficient and economically viable in that particular system, while solid recovered fuels may then be burned in systems that require slightly decreased amounts of energy.

Note, the choice of opting for refuse derived fuels instead of solid recovered fuels in the previous case would only be based on extreme limited additional minor contaminants thereby minimal more emissions are to be released, in a sacrifice to save on refining or further waste preprocessing costs. Given solid recovered fuels and untreated non-hazardous waste as optional fuels in the cement kiln systems, one would be advised to use solid recovered fuels instead of untreated non-hazardous waste. This advice is based on facts that solid recovered fuels have relatively higher calorific values, they have a more homogeneous form which is tyically in pellets, and they have decreased content of moisture, thereby burning more efficiently than untreated nonhazardous waste (Gawlik et al., 2007).

Hence, with alternative waste fuels mainly being used as fuel in the calciners during the production of cement, moreover, with lower grade heat of less than or equal to 18 MJ/kg being

more appropriate for the calcination of raw materials, one would be greatly encouraged to employ the use of solid recovered fuels (since they have typical calorific values ranging around $16 - 22\ MJ/kg$), as a sustainable alternative to fossil fuel consumption during cement manufacturing rather than using untreated nonhazardous waste or refuse derived fuels (Chinyama, 2011; Hassold, 2018; Nasrullah et al., 2014). Furthermore, disregarding the limiting factors that come about when alternative waste fuels are utilized (limiting factors counting significant contents of heavy metals, chlorine, and sulfur pollutants present within these alternative waste fuels), the use of waste derived fuels is encouragable since by their utilization a sustainable alternative for waste material which could not be recycled because of their economic inefficiency is also achieved (Gawlik et al., 2007; Nasrullah et al., 2014).

2.2. Process Variables Management

According to Hokfors (2014), although the formation of intermediate products also releases certain amounts of heat, more heat is required for melting to produce final clinker product, specifically for evaporating water and for the decomposition of calcium carbonates, clays, as well as magnesium carbonates. Thereby, temperatures within the kiln form part of the process variables that need to be managed in order to produce quality clinker. Typical heat of reactions for the involved reactions of raw meal feed pyro-processing to produce cement clinker are also estimated and discussed as part of the crucial process variables. These change in enthalpies of the involved chemical reactions occurring at constant pressures are basically thermodynamic units of measurements that are key when it comes to calculations of each reaction's released or produced energy amounts per mole. With a positive value of a change in enthalpy (heat of reaction) indicating that products have greater enthalpy, and the reaction is thereby endothermic, meaning heat is required; and with a negative value of a change in enthalpy indicating that reactants have greater enthalpy, the reaction is thereby exothermic, meaning heat is produced. One last process variable included below is the flow of gases and solids within the cement kiln system, with heat transfer between these phases also being briefly highlighted.

In the following discussions, it is clear the main controlled variables in a cement manufacturing kiln system only include the raw meal pyro-processing temperatures and the temperature of the

exhaust gases, while the manipulated variables would include rates of fuel and kiln feed. Moreover, flow, the content of oxygen, as well as the pressure within the system are all usually controlled by occasionally adjusting the speed of fans.

2.2.1. Temperatures and Heat of Reactions

According to Hassold (2018); Manias (2004); and Nelson and Guillot (2006), the quickly rising and falling of the temperature within the kiln system promotes good formation of tricalcium silicate and dicalcium silicate crystals, with tricalcium silicate having to decompose during the cooling stage, and to counter the decrease of tricalcium silicate, cooling rates have to be increased. Hence, an increase in cooling rates brings about an increase in maintained tricalcium silicate amounts. Benefits of rapidly rising the temperatures within the kiln, followed by rapid cooling further include the formation of clinker that can be easily grinded meaning cement would have an increased milling capacity, which comes about because of the produced tiny but highly stressed crystals of tricalcium silicate. Hence, the highly reactive crystals of tricalcium silicate present in increased amounts due to rapid heating and cooling, thereby quality cement strength would be achieved since high tricalcium silicate amount produces more strength in cement products.

According to Wang (2006) depending on the temperature requirements needed for each cement clinker principal component to be formed, the preferred dry processing route applied to the modern rotary kiln system leads to the rotary kiln system being splitted into four kiln zones counting, the decomposition zone, transition zone, sintering zone, and the cooling zone. In addition to the different formation temperatures of cement clinker components, Table 2 further displays crucial raw meal feed pyroprocessing or clinker formation reactions as well as the associated typical heat of the chemical and mineralogical reactions (reaction enthalpies) occuring within the dry cement rotary kiln zones.

Table 2: Dry Cement Rotary Kiln Zones with Relative Reactions as well as Typical Reaction Conditions (Temperatures and Heat of Reactions) Required for the Formation of Quality Clinker Product. *(1. Wang et al., 2006; 2. Rodrigues et al., 2017; 3. Manias, 2004; 4. Benhelal et al., 2012; 5. Hokfors, 2014; 6. Ghoroi and Suresh, 2007)*

Kiln Zones	Clinker Formation Reactions & Reaction Conditions	
Decomposition Zone	Chemical Reactions	➢ $CaCO_3 \rightarrow CaO + CO_2$ ➢ $CaO + Al_2O_3 \rightarrow CaO \cdot Al_2O_3$ ➢ $CaO + Fe_2O_3 \rightarrow CaO \cdot Fe_2O_3$ ➢ $CaO + CaO \cdot Fe_2O_3 \rightarrow 2CaO \cdot Fe_2O_3$ ➢ $3(CaO \cdot Al_2O_3) + 2CaO \rightarrow 5CaO \cdot 3Al_2O_3$
	Main Reaction	$CaCO_3$ Decomposition
	Average Temperature (℃)	850 [1,2] or $550 - 960$ [4,5]
	Average rxn Heat (kJ/kg)	1750.19 [1,2,4,5]
Transition Zone	Chemical Reactions	➢ $2CaO + SiO_2 \rightarrow 2CaO \cdot SiO_2$
		➢ $3(2CaO \cdot Fe_2O_3) + 5CaO_3.3Al_2O_3 + CaO \rightarrow 3(4CaO \cdot Al_2O_3 \cdot Fe_2O_3)$
		➢ $5CaO \cdot 3Al_2O_3 + 4CaO \rightarrow 3(3CaO \cdot Al_2O_3)$
	Main Reaction	$2CaO \cdot SiO_2$ Formation
	Average Temperature Range (℃)	$800 - 1250$ [1,2,3,4,5]
	Average rxn Heat (kJ/kg)	-698.71 [1,2,4,5]
	Main Reaction	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ Formation
	Average Temperature Range (℃)	$999 - 1259$ [1,2,3,4]
	Average rxn Heat (kJ/kg)	-95.75 [1,2,4,5]
	Main Reaction	$3CaO \cdot Al_2O_3$ Formation
	Average Temperature Range (℃)	$999 - 1259$ [1,2,3,4]
	Average rxn Heat (kJ/kg)	-25.67 [1,2,5]
Sintering Zone	Chemical Reactions	➢ $2CaO \cdot SiO_2 + CaO \rightarrow 3CaO \cdot SiO_2$
	Main Reaction	$3CaO \cdot SiO_2$ Formation
	Average Temperature Range (℃)	$1305 - 1439$ [1,2,3,5]
	Average rxn Heat (kJ/kg)	-490.33 [1,2,5]
Cooling Zone	Main Reaction	Cooling of Clinker

Between the temperatures $550 - 960$ ℃ the decomposition of calcium carbonate as part of the raw meal feed takes place, starting from the preheaters, being intense in the precalciner, and completed in the kiln's decomposition zone. Additionally,-within this zone, besides this decalcination reaction, further formation of minor quantities of $CaO \cdot Al_2O_3$; $CaO \cdot Fe_2O_3$; $2CaO \cdot Fe_2O_3$; and $5CaO \cdot 3Al_2O_3$ compounds also take place (Benhelal et al., 2012; Hokfors, 2014). Within the transition zone, an exothermal zone and a zone of rapidly increased temperatures, typically at temperatures ranging from 800 ℃ to 1250 ℃, dicalcium silicate components form, followed by tetracalcium aluminoferrite formation at temperatures ranging from 999 ℃ to 1259 ℃, and lastly, the formation of tricalcium aluminate also at temperatures ranging from 999 ℃ to 1259 ℃. These formation reactions within the transition zone strictly take place in the kiln.

Before reaching the cooling zone, the material undergoing pyroprocessing reaches the rotary kiln's sintering zone where it is further subjected to even higher temperatures ranging from about 1305 ℃ to approximately 1439 ℃, thereby leading to the formation of tricalcium silicate components (Benhelal et al., 2012; Hokfors, 2014; Manias, 2004; Rodrigues et al., 2017; Wang, 2006). In the transition zone, a zone further known for liquid phase formation, the significantly increased reaction heat amounts (-698.71 kJ/kg) are released with an aim of elevating the feed material's temperature from about 960 ℃ to approximately 1259 ℃. Moreover, tricalcium silicate formation from dicalcium silicate and calcium oxide in the sintering zone is an exothermic reaction (-490.33 kJ/kg), meaning it mainly occurred at a temperature greater than 1430 ℃, roughly at a temperature ranging between1430 ℃ and 1439 ℃. Hence, according to (Jons, 1980), this tricalcium silicate formation reaction is exothermic under temperatures greater than 1430 ℃ and endothermic under temperatures below 1430 ℃.

After all these reactions, at any temperature of more than 1259 ℃, the solid clinker would then melt and consequently a perfectly nodulized clinker mixture would be produced. Following the leaving of the produced clinker from the high temperature transition zone, the produced clinker proceeds to the cooling zone and to the air cooler where it is cooled. The cooling of clinker mainly takes place in the air cooler than in the dry rotary kiln's cooling zone, thereby the cooling zone in the dry rotary kiln would be extremely short (Wang, 2006).

2.2.2. Clinker Quality Parameters

According to Fadayini et al. (2020) and Winter (2005), the chemical parameters are based on the oxide composition, and they are crucial in detailing the characteristics of finished clinker product.

First, is the Lime Saturation Factor (LSF), a ratio of calcium oxide to other main oxides, particularly estimates the ratio of $3CaO \cdot SiO_2$ to $2CaO \cdot SiO_2$ in the clinker. With clinker having increased LSF expected to be comprised of increased $3CaO \cdot SiO_2$ to $2CaO \cdot SiO_2$ proportion in comparison to clinker with lower LSF. On the other hand, LSF values exceeding 1.0 would be signaling an increased possibility of having unreacted lime within the clinker.

$$LSF = \frac{CaO}{2.8SiO_2 + 1.2Al_2O_3 + 0.65Fe_2O_3} \qquad Equation\ 1$$

This LSF calculation is also applicable to ordinary Portland cement (comprised of only clinker and gypsum) with a modification of subtracting $(0.7 \times SO_3)$ from the CaO content. However, this calculation still does not account for fine limestone in cement, even slag together with fly ash given they are used as substitute raw materials are left unaccounted for, therefore the presence of these fine raw materials would require a more complicated calculation of LSF. According to Winter (2005), by estimating the amount of carbon dioxide and further accordingly adjusting the formula, limestone could be quantified. However, the presence of either or both fly ash and slag as substitute raw materials may see this clinker LSF calculation being highly inconvenient, practically.

Following, is the Silica Ratio or Silica Modulus abbreviated as SR, with its' increase signaling that the clinker is comprised of increased amounts of calcium silicates and low amounts of ferrites and aluminates. The typical silica ratio ranges from 2.0 to 3.0 (Fadayini et al., 2020 and Winter, 2005).

$$SR = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \qquad Equation\ 2$$

Lastly, is the alumina ratios abbreviated as AR, a measure of aluminate and ferrite phases in the clinker. In Portland clinker it typically ranges from 1.0 to 4.0, with clinker products having a

higher AR values signaling proportionally increased aluminate together with decreased ferrite contents (Fadayini et al., 2020 and Winter, 2005).

$$AR = \frac{Al_2O_3}{Fe_2O_3} \qquad Equation\ 3$$

The fourth and unpopular parameter as detailed by Winter (2005) is the Lime Combination Factor abbreviated as LCF. It resembles the LSF parameter however with a subtraction of free lime content from the whole CaO amount. Moreover, given its' value is 1.0 for instance, that would mean the greatest silica portion is in the form of $3CaO \cdot SiO_2$.

2.3. Energy Efficient Processing

During the production of cement, particularly in the pyro-processing stage, cement kilns play a very critical part, and their improvements towards sustainability and optimum manufacturing technologies have since been the centre of attention. Dating back in 1930's, when the Germans made attempts of redesigning the kiln system with an aim of reducing fuel amounts that were being wasted, and consequently coming up with remarkable grate preheater and gas suspension preheater technological developments.

According to Manias (2004), main types of cement kilns include the rotary kilns as well as the vertical cement kilns. Amongst these cement kiln types only rotary kilns are widely used for clinker production as of late, and therefore the following discussions will be based on productions via rotary kilns. Hence, with the dry processing routes being more preferrable and with modern cement plants rapidly adopting the use of them, the discussions in this paper will be more focusing on a dry method of processing.

The success of the rotary kiln in the cement industry came about due to the decreased kiln size while the kiln dimensions remained unchanged, and the increased production capacity which resulted in operational costs reductions accompanied by a break-through in efficient energy consumptions due to modern preheating and precalcining installations according to Telschow (2012). With the cement kilns being the hearts of the cement production processes, the rotary kilns which are known for the continuous production of large cement or clinker quantities while maintaining uniform and high-quality products, have to further fulfil their other purpose of

maintaining low operating costs with clinker production at its maximum rate. However, saving on costs is not only the area of focus. Given the looming resource depletion and climate crises, technologies including efficient coolers, precalcination, together with proper modeling of the kiln and successful search for accurate heat transfer phenomena may prove to be even more useful in saving energy, broadening and increasing sustainable alternative fuel types that can be utilized, as well as reducing the associated greenhouse gas emissions.

2.4. Additives Management

The manufacturing of oil well cements undergo in a way that they must meet the desired physical and chemical standards, standards that will enable this manufactured cement to be successfully applied on a certain type of well formation. In most cases, additional or corrective components must be added to produce optimal compositions. Moreover, in relation to the application of that particular cement, multiple cement additives may be included. Joel (2009) and Fink (2015) reported that these cement additives are the blended chemicals and materials, blended into the base cement slurries where they enhance cement performance. They are added under normal conditions in the manufactured clinker after its thorough grinding and milling, thereby leading to the production of a cement product with optimal compositions (Nilsson et al., 2007).

When these cement additives are added into the cement formulations, they are added with regards to various aspects (Fink, 2015). Depending on each type of cement additive, cement additives are generally added for the following reasons; dispersing cement particles, modifying cement setting time while facing a challenge of the wells' extreme temperature and pressure conditions, controlling filtration loss of the liquid from the cement slurry, indemnifying for shrinkage of the cement while it undergoes setting and hardening, ensuring improvements of interfacial bonding between the cement and casing, and for controlling the formation fluids inflow into the cement column as the oil cement sets.

While formulating the appropriate cement slurry for any cementing operation, appropriate selection of chemical additives and their optimum quantity is a must. Types of cement additives include retarders, accelerators, extenders, fluid loss additives, lost circulation material, dispersants, special additives such as antifoams, and weighting agents. Given that they are developed to allow the use of Portland based cement in diversified oil and gas well applications,

each cement additive major type also has different types of chemical additives which perform nearly the same function when designing cement slurry, and in this part few of the best in each category are going to be reviewed (Anaele and Otaraku, 2020; Fink, 2015; and Oliveira et al., 2015).

Loss of circulation issue when applying primary cementing would later lead to the requirement of remedial cementing, however with proper utilization of lost circulation additives, loss of whole fluids before and during a cementing job would be prevented. The addition of antifoams in cement slurries on the other hand would be aimed at reducing foaming as well as minimising air entrainment during mixing. While expansion additives would be added with an aim of improving the cement to pipe and formation bond by causing the exterior dimensions of cement that is setting to grow slowly when the cement is exposed to down-hole fluids, weighting agents are added with an aim of increasing the density of the cement slurry, and light weight additives are added with an aim of lowering hydrostatic pressure as well as improving slurry economy (Mixhaux et al., 1989; Nelson and Guillot, 2006).

Fluid loss control additives on the other hand reduce the rate at which cement slurry filtrate is lost to a permeable formation given a cement slurry is being applied across a permeable formation, especially under pressure. They viscosify the mix water or plug the pore throat in the filter cake with long polymer chains (Nelson and Guillot, 2006). Given that failure to control fluid loss of the cement would result to early slurry dehydration thereby early cement hardening and further secondary cementing might be required since the speedy escape of fluid from cement would form holes, therefore one may indeed be advised to make use of fluid loss additives (Broni et al., 2015).

Friction reducers, commonly known as dispersants, act on the surface of cement grains making cement slurries less viscous thereby they would be mixed and pumped easily. Considering the fact that dispersants not only decrease the rate of turbulent flow but also often exhibit secondary retardation and further improve fluid loss control, thereby it is also advisable for one to make use of them accordingly with quality understanding of the end results (Nelson and Guillot, 2006).

Extenders reduce slurry density thereby also reducing the hydrostatic pressure during cementing operation and avoiding lost circulation that may come about due to breakdown of weak formations. In the meantime, they may also increase slurry yield where the cement quantity

needed for production of a targeted volume of set product would be reduced (Nelson and Guillot, 2006). Given the facts that extenders not only lighten cement slurries to protect weak formations, but they also have a possibility of being used to increase slurry yields, thereby one may indeed be advised to consider using them where necessary since the increased slurry yields would lead to reduction in costs and further to cuts in budgets while also it would mean less cement was used thereby less clinker amounts utilized and consequently less concerning pollutant emissions would have been released during the production of reduced clinker amounts.

2.4.1. Accelerators

Accelerators as cement additives are added with an aim of cutting down the time it takes for cement to set, generally by speeding up the reaction rate between water and cement, in some cases also increasing early strength development (Myrdal, 2007). This means the cements' thickening time shortens given the accelerated compressive strength development of cement, thereby the costly operating oil rig times consequently shorten as a result the rigs operating costs are also reduced. According to Myrdal (2007), with some accelerators accelerating either setting or hardening and some accelerating both setting and hardening, actually the starting point or the initial action of the accelerator takes place in the plastic state of the cement paste, and in the latter stage the accelerator mainly take action in the hardened state. Even though accelerators function differently and incompatibly, Myrdal (2007) implied that a significant number of accelerators have an effect on both the setting and hardening of cement, occasionally based on the amount of the accelerator put.

Types of accelerators include soluble inorganic salts and soluble organic salts as well as compounds, with most accelerators on the market being the mixtures of compounds from both soluble organic and inorganic salts. Soluble organic salts and compounds include a group of alkanolamines, and a group of carboxylic and hydroxycarboxylic acids as well as their salts. Moreover, triethanolamine, and calcium formate, respectively, are the most commonly used accelerators among their groups (Myrdal, 2007). One can be encouraged to use triethanolamine when they have it readily available and need to accelerate the hydration of aluminate-containing phases, particularly tricalcium aluminate hydration kinetics, while retarding the hydration of tricalcium silicate. Moreover, the addition of triethanolamine as an accelerator might result into it reacting with the ferrite phase of Portland cement, thus resulting into having a chelating effect,

and the chelating effect of triethanolamine with ferrite ions either accelerates or retards the hydration of cement depending on the applied dosage (Myrdal, 2007; Yohannes et al., 2017).

Calcium formate functions as expected for an accelerator, it decreases the setting times, while increasing the compressive strength. Moreover, according to Heikal (2004) it decreases total porosity and initiate the unloosening of calcium hydroxide. Lower porosity, also given that there is sufficient binding material content, means the cement has higher strength. Furthermore, the unloosened calcium hydroxide, which is one of the major constituents of hydrated Portland cement is a good indication for evolution of cement hydration reactions. Another recommendation would be that of combining both triethanolamine and calcium formate to use their mixture for accelerating cement hydration process, hence according to Myrdal (2007) the combination of these two accelerators results into a synergistic effect, meaning their mixture accelerates cement hydration at an even greater rate compared to these individual accelerators.

Soluble inorganic salts include alkali and alkali earth metals salts of hydroxide, chloride, bromide, fluoride, nitrite and nitrate, carbonate, thiocyanate, sulphate, thiosulphate, perchlorate, silicate, and aluminate (Myrdal, 2007). When it comes to participating in accelerating the reaction rate, both the ions of the anion and the metal's cation take part. According to both Myrdal (2007) and Tamas (1966), calcium chloride is the most effective and widely utilized accelerator, in such a way that nearly all manufactured accelerators that are in the market are comprised of calcium chloride. Looking at the possibilities of an accelerator reacting with the ferrite phase of Portland cement, according to Tamas (1966) such hypotheses were raised and ruled out. These hypotheses referred to calcium chloride accelerating the cement hydration process by chemically reacting with the aluminate and/or the cement's ferrite phases or with calcium hydroxide formed during hydration, while leaving the silicate phases unaffected. Tamas (1966) further clarified that it is highly unlikely that these processes or reactions are needed during the action of calcium chloride, given that aluminates and ferrites are only a minor part of commercial Portland cement and their hydration products not only are small in absolute amount but also have specific surfaces that are negligible in comparison with the hydration products of the silicate phases.

On the contrary of using the best of soluble organic salts and compounds as accelerators, particularly the mixture of triethanolamine and calcium formate, one may instead be encouraged to use calcium chloride to accelerate the process of cement hydration. Reasons for this recommendation is the lower costs of calcium chloride meaning saving in costs, calcium chloride's readily availability meaning it can be acquired easily, and lastly but not least calcium chloride has the predictable performance characteristics as it has spent decades being used and studied as an accelerator (Myrdal, 2007; Tamas, 1966).

2.4.2. Retarders

Retarders as cement chemical additives are added with an objective of decreasing the speed of cement hydration, by slowing down the setting time of the resulting cement slurry. Given the fact that most of the time oil cements utilized in wells of different formations generally lack extended fluid life for operating at bottom hole circulating temperatures of more than 38 ℃ which means decreased thickening time, thereby the retarders play a role of hydration inhibition and delaying the setting, consequently providing enough duration for slurry to be properly placed in deeper and higher temperature wells, meaning the thickening time of pumping the cement slurry in place would be increased (Anaele and Otaraku, 2020). Furthermore, the effectiveness of a retarder in delaying cement hydration is dependent on the dosage of the additive as well as on curing conditions, as a result the prediction of the Bottom Circulation Temperature (BHCT) must also be accurate in order for the correct concentration of the retarder to be used, thereby avoiding fast setting while also avoiding over retardation.

Even though the mechanism for cement retardation through the use of retarders is still controversial, according to Nelson and Guillot (2006) existing theories, which are not fully descriptive on their own, include the adsorption theory, where the retarder is believed to be adsorbing onto the hydration product surfaces and as a result hindering contact with water; the precipitation theory, where the retarder is believed to be reacting with ions of calcium, hydroxyl, or both in the aqueous phase, and leading to the formation of a layer that is insoluble and impermeable surrounding grains of cement; the nucleation theory, where the retarder is believed to be adsorbing onto the hydration products' nuclei and inhibiting the upcoming growth; as well as the complexation theory, where the retarder is believed to act as a chelating agent, chelating the ions of calcium and hinder the formation of nuclei. Factors counting the cement product

phase (either aluminate or silicate phase) where the retarder shall be acting upon, as well as the retaders' chemical nature, are the main factors that must also be closely considered (Nelson and Guillot, 2006).

Some of the most utilized chemical additives as the oil well cement retarders include lignosulphonates which are the readily available cement retarders extracted from wood pulp and as an aqueous solution they are known as the lignin liquor coming in a form of calcium and sodium salts of lignosulphonic acids, several saccharides and natural gums; as well as cellulose extracts counting carboxymethyl hydroxyethyl cellulose and hydroxyethyl cellulose (Mixhaux et al., 1989; Nelson and Guillot, 2006).

The addition of lignosulphonate retarders in concentrations of about $0.1 - 1.5\%$ by weight of cement generally lead to the retardation process in cement slurries being effective until temperatures of about $122\ ℃$ are reached (Mixhaux et al., 1989; Nelson and Guillot, 2006). Given one has to choose a cement retarder to be used at much greater depths of temperatures higher than $122\ ℃$ and they only have lignosulphonates, they would be greatly encouraged to use those lignosulphonates and further treat them with borax, hence according to Anaele and Otaraku (2020), lignosulphonates mixed with chemicals including borax can be utilized at well temperatures adding up to $315\ ℃$. Calcium lignosulfonate is regarded as the best lignosulphonate retarder and it has guaranteed effectiveness at temperatures above $93\ ℃$ according to Bediako and Joel (2016).

Between the mentioned cellulose extracts or derivatives which are for use in well cementing jobs as retarders, one may be advised to specifically utilize hydroxyethyl cellulose when they further want to ensure constant maintenance of water/solid ratio in cement slurries downhole, hence hydroxyethyl cellulose is also used as fluid loss additive (Nelson and Guillot, 2006). Hydroxyethyl cellulose as a fluid loss additive would be controlling the rate of water that could be lost to adjacent permeable zones through suitable viscosification by simply making the cement slurry avoid losing water by filtration into permeable zones (Broni et al., 2015). However, one may be advised to rather choose using carboxymethyl hydroxyethyl cellulose instead of hydroxyethyl cellulose given the facts that carboxymethyl hydroxyethyl cellulose is more effective as a retarder at temperatures of about up to $110\ ℃$ BHCT while hydroxyethyl cellulose is only effective as a retarder at temperatures of about up to $52\ ℃$ BHCT where the

thickening duration in freshwater slurry would only be increased by roughly two hours (Anaele and Otaraku, 2020). Given that the cement thickening time must be equal to mixing, pumping and displacing cement job time plus another $1-2$ hours duration as a reasonable safety factor, and according to Lake (2006) most cementing jobs (mixing, pumping and displacing) are completed in a duration of about 90 minutes or less (which is seemingly too much time given only two hours extension is provided by hydroxyethyl cellulose as a retarder in freshwater slurries), therefore one may indeed be advised to rather make use of carboxymethyl hydroxyethyl cellulose as a retarder, especially in wells with greater depths as it seemingly guarantees longer retardation periods even at higher bottom hole circulation temperatures.

One may still doubt the use of carboxymethyl hydroxyethyl cellulose instead of hydroxyethyl cellulose, arguing that hydroxyethyl cellulose would be a better fit for their intended applications as it would also guarantee that there would be no fluid losses. Nonetheless, they would still be advised to choose carboxymethyl hydroxyethyl cellulose as a cellulose derivative retarder appropriate for use since carboxymethyl hydroxyethyl cellulose also provide quality fluid loss control while they also have been utilized for decades as the only cellulose derivative retarder, meaning greater exposure on its ups and lows as well as more developed experiences in its usage as retarders.

Given the review by Bediako and Joel (2016) that carboxymethyl hydroxyethyl cellulose as a retarder, still at temperatures $\geq 110\ ℃$ BHCT and at equal concentrations as calcium lignosulphonate retarder, these two retarders function the same, therefore should one have them both readily available the only advice would be to choose either. However, they should consider using calcium lignosulphonate in squeeze cementing since according to Rike (1973) lignosulphonates used as retarders in squeeze cementing is more appropriate given they provide consistent quality while the resulting dispersing effect also produces a more even slurry of gel cements.

2.5. Proposed Sustainable Production Processes

Below is Figure 1, a separate line preheater precalciner kiln system employing a dry clinker/cement production process with an installed waste heat recovery system, showing the proposed cement production process. The proposed dry processing route to produce cement clinker utilizes a rotary kiln equipped with a single precalciner, four cyclone preheaters in each of the two cyclone preheater towers, tertiary air duct, bypass system, as well as specifically low NO_x burners to fire the kiln system and the grate cooler for quality cooling of the produced clinker product. Furthermore, waste heat recovery system is also installed for the recovery of waste heat from the hot exhaust gases and convert it into electricity to be utilized in powering the plants necessities including operating equipment counting induced draft fans (ID fans) among them. Also, there is a proposed use of at least 60% waste derived fuels (refuse derived fuels or solid recovered fuels) as precalciner fuel while raw materials would also be diversely utilized accordingly.

The installed waste heat recovery power generation system utilizes the heat from the rotary kiln released through the two preheater towers in the form of hot kiln exhaust gases as well as the heat from the grate clinker cooler also in the form of hot exhaust air. The recovery of heat from the preheater towers goes through the preheater boiler while from the clinker cooler it goes through the clinker cooler boiler. Each boiler then release heat in the form of steam, followed by the combining of those released steam streams into one stream of high-pressure steam before it reaches the steam turbine generator which will then generate electricity simply by extracting thermal energy from the pressurized steam then utilize it to carry out mechanical work on a rotating output shaft. Given that the generation of electricity via the installed waste heat recovery system comes about without any additional fuels in the kiln or in the precalciner, thereby it is clear that this recovery system may have a significant impact on saving the plant's energy costs.

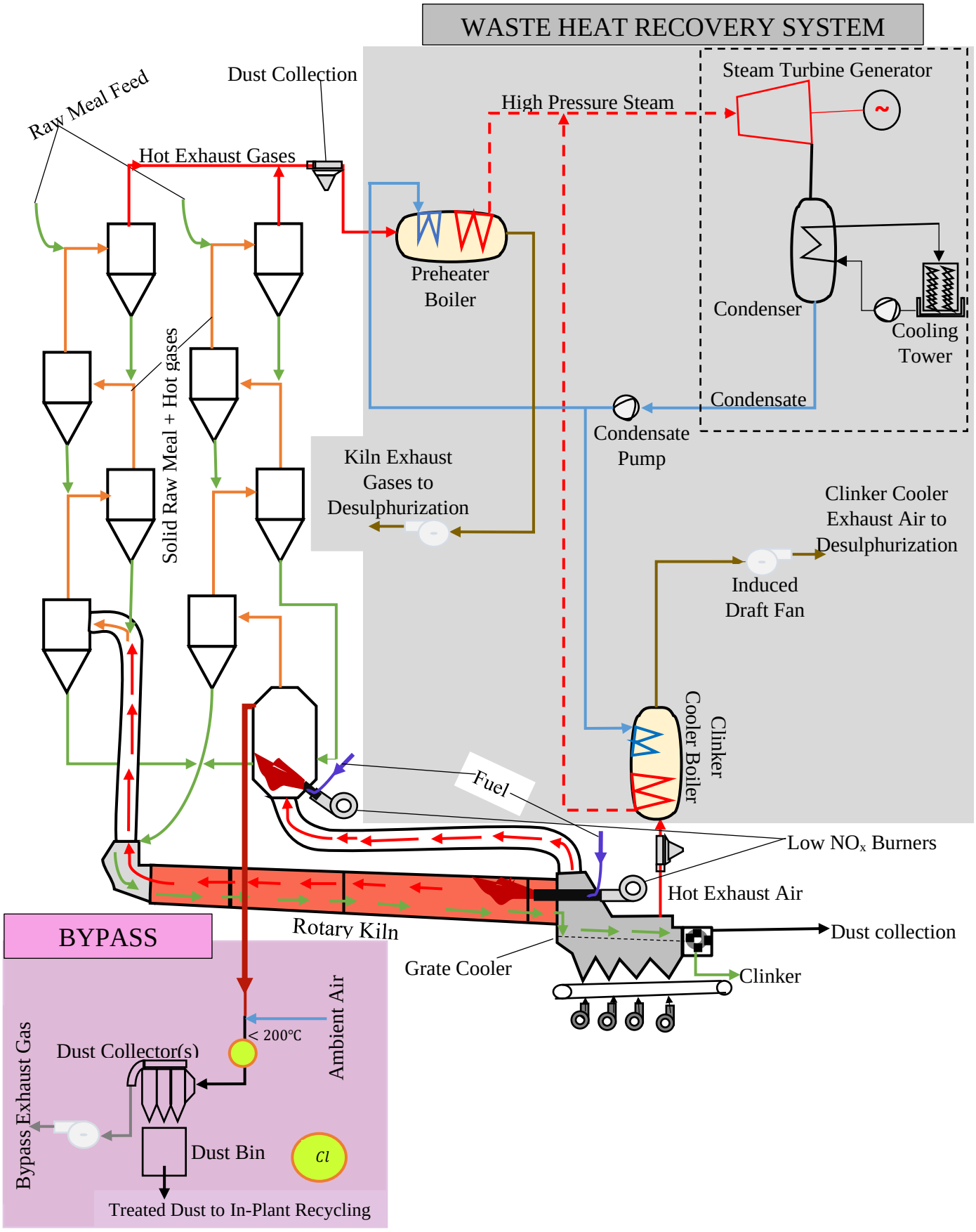
WASTE HEAT RECOVERY SYSTEM
Raw Meal Feed
Dust Collection
Hot Exhaust Gases
High Pressure Steam
Steam Turbine Generator
Preheater Boiler
Condenser
Cooling Tower
Condensate
Condensate Pump
Solid Raw Meal + Hot gases
Kiln Exhaust Gases to Desulphurization
Clinker Cooler Exhaust Air to Desulphurization
Induced Draft Fan
Clinker Cooler Boiler
Fuel
Low NOx Burners
Hot Exhaust Air
Rotary Kiln
Dust collection
Grate Cooler
Clinker
BYPASS
Ambient Air
< 200°C
Dust Collector(s)
Bypass Exhaust Gas
Dust Bin
Cl
Treated Dust to In-Plant Recycling

Figure 1: A Separate Line Preheater Precalciner Rotary Kiln System Employing a Dry Clinker/Cement Production Process as well as the Waste Heat Recovery System *(Sourced from (Atmaca and Yumrutaş, 2015; Bayuaji et al., 2016; Harder, 2002; Huang et al., 2005; Tsamatsoulis, 2016).*

In the grate cooler, as the cooling air would be flowing through the grate plate which moves from the zone of effective cooling to the zone of recuperating heat, it is important that these zones within a grate cooler are separated enough and they are individually optimized, thereby improving heat transfer while at the same time ensuring quality clinker cooling.

Considering that the performance of the grate cooler can also play a significant role in waste heat recovery, where it recovers heat from the hot clinker exiting the kiln, thereby the transfer of heat within it would also be managed accordingly for the optimum recovery of waste heat as well as for quality cement clinker formation conditions. Improved heat transfer within the grate cooler would result to improved waste heat recovery. Hence, the grate cooler's speed would then be lowered thereby increasing the thickness of the cement clinker bed on the grate, particularly on the zone of heat recovery that is separated from the zone of effective cooling within the grate cooler, as a result the transfer of heat in the grate cooler would be further improved. The grate plate for the installed grate clinker cooler would further have air outlets positioned horizontally together with an increased pressure drop, thereby improving the transfer of heat within the grate cooler even more and consequently improving the recovery of waste heat (Radwan, 2012).

The recovery of waste heat energy in this proposed cement production process would further be ensured by the reduction of primary air entering the kiln system through the low NO_X burners, while ensuring the increase of secondary air and tertiary air from the grate cooler. The use of low NO_X burners would specifically contribute to the lowering of pollutant NO_X emissions since the proposed separate line preheater precalciner rotary kiln system tend to release an increased amount of nitrogen oxide pollutants due to having much higher peak temperatures at times (Hassold, 2018).

This proposed rotary kiln system equipped with waste heat recovery system is also expected to generate waste cement kiln dust in increased amounts, and the increased dust amounts would

specifically pose an issue on the waste heat recovery system and to the performance of the kiln, mainly in preheaters. Moreover, due to high chances that a considerable amount of heat can be lost through the rotary kiln's shell, fuel amounts would be reduced in the main kiln burner while they are increased in the precalciner. However, this way of reducing the rotary kiln's thermal load may possibly lead to the formation of cement kiln dust that cannot be recycled for reuse in the process since more alternative or substitute waste fuels (especially refuse derived fuels) are intended to be used to fire the precalciner, and the resulting cement kiln dust would be composed of increased chlorine metal contents. Hence, the use of more and more of waste derived fuels increases the amounts of chlorine metals in the system's generated dust and gases. As a result, the bypass system is introduced, and its' installation is indeed necessary although it would contribute to loss of considerable heat amounts as some of the precalciner/kiln hot exhaust gases would exit along with the hot removed dust, meaning the preheater systems' thermal efficiency would also be reduced by the reduction of internal circulating dust in the preheater system.

Also, given that dust from the grate cooler dust is usually hard and abrasive, while the dust from the kiln is usually sticky and fine powdered, thereby the introduced bypass system from the precalciner is mainly installed to recover fine powdered and obviously high alkaline cement kiln dust, hence waste derived fuels would mainly be fired in the precalciner. The bypassed chlorine concentrated dust would then be treated where the expected high chlorine amounts would be removed, and thereafter the treated dust would be recycled to the raw mixture for reuse as a raw material for the same cement production process. Moreover, this bypass system would be ensuring that chlorine build-up in the to be released exhaust gases is minimised as much as possible. In addition, the efficiency of cyclone preheaters when it comes to separation would be optimized if it needs be (possibly by pressure drop). Also, the dust removers are already installed for constant removal of dust in the hot exhaust gases leaving the grate cooler and the preheater towers hence large amounts of dust are expected to come along. Furthermore, to control the effect of dust that might enter the installed waste heat recovery system with hot exhaust gases, the boilers could be further equipped with a cleaning device (Radwan, 2012).

Quality pyro-processing of the raw materials would be inevitable given a more effective combustion environment within the proposed separate line preheater precalciner rotary kiln system. To ensure higher enough degree of raw meal calcination for the production of good

quality cement clinker, the raw meal's residence time in the kiln system would be mainly controlled by the installed kiln inlet seals which also minimize the induced false that may negatively affect the performance of the kiln and the recovery of heat energy in the grate cooler. Further with effective solid gas separation, efficient circulation of dust, as well as the quality precalcined raw materials due to proper modeling of the kiln system coupled with easily regulated kinetic behavior, a higher enough degree of calcination would surely be obtained (Manias, 2004).

Although an exhaust gas heat exchanger is not included in the proposed cement clinker production process, its' installation is highly recommended. It would be installed between the boiler and the exit point of exhaust gases coming from the boiler, while being connected to pure cycle unit and further to the already existing cooling tower. The exhaust gas heat exchanger would lead to reduction in maintenance costs, since with its installation the costs of dismantling the entire waste heat recovery system to replace the boilers would also be eliminated.

The exhaust gas heat exchanger would be using water to recover heat, thereby additional to heat recovery it would serve to filter sizeable portions of pollutants out of the exhaust gases, especially carbon dioxide pollutant gases. This would further decrease the strain on the filter systems that are also highly recommended for installation in this proposed production process. However, the installation and operation of the installed bypass duct (leading to the chlorine/dust bypass system) together with the operation of the recommended exhaust gas heat exchanger or the already installed waste heat recovery system would individually bring an increase in the system's pressure. As a result, induced draft fans are installed to maintain minimal pressure (pressure drop) across both the heat recovery and bypass systems, and the more the pressure in the system the more fan power would be required.

Furthermore, the released exhaust gases, especially the exhaust gases from the preheater systems, they would be desulphurized via the dry lime scrubbing technique, where lime would be injected directly into the exhaust gas for the removal of not only sulphur dioxides but also acidic gases of hydrochloric acid. The rest of the pollutant gases including carbon dioxide, nitrogen oxides as well as the unrecycled dust would further be managed sustainably.

3. EXPERIMENTAL PROCEDURE

Experimental work carried out for this project involved prior analysis of the local class A cement, preparations of the PET/PET plastic waste based additives, and the base design. Preparations of oil well cement slurries blended with the prepared PET/PET based additive(s) followed, accompanied by the determination of relative compressive strengths and rheological behaviours.

Composition of the used local class A cement was determined through XRF analysis using the X-ray Florescence (XRF) spectroscopy.

3.1. Materials

The under investigation local class A cement (42.5R AfriSam high strength cement) shown in Figure 2 was provided by AfriSam South Africa. It is for use under normal conditions, when there are no particular properties specified for any other type are required (For general use).

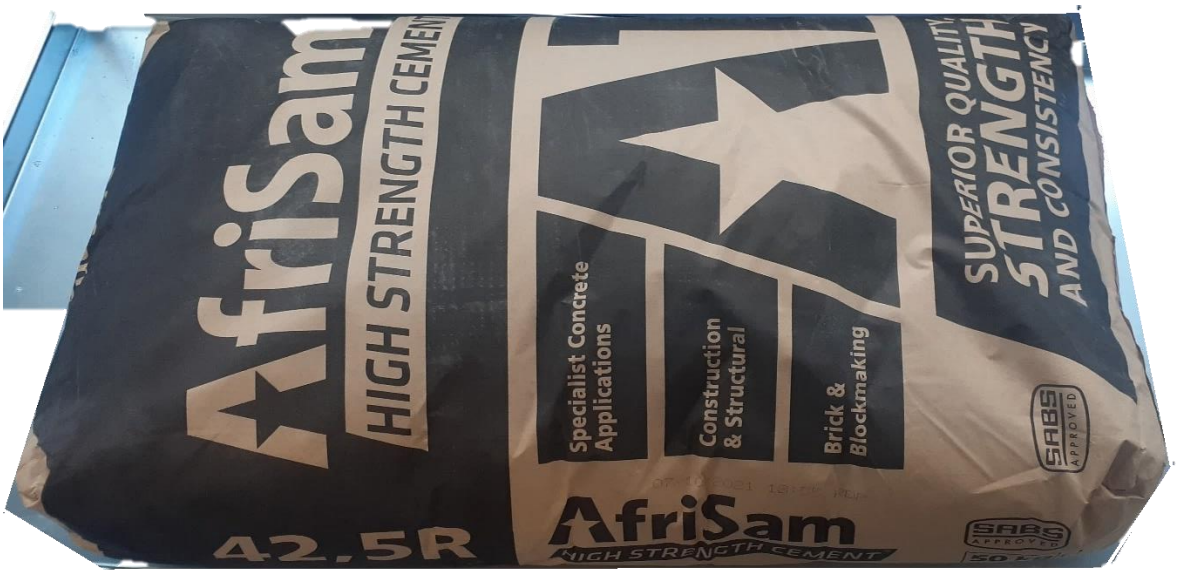

Figure 2: Picture of the Utilized Local Class A Cement.

Utilized oil well cement additives included the polycarboxylate based superplasticizer (PCE) provided by Sika South Africa, citric acid as a retarder, calcium oxide as an expanding agent, polyvinyl alcohol as a fluid loss additive, and polyethylene glycol (PEG 6000) as a defoamer.

Calcium oxide, polyvinyl alcohol, and polyethylene glycol (PEG 6000), and citric acid were all sourced from Sigma Aldrich, together with lead acetate (used as a catalyst during PET depolymerisation) and ethylene glycol (≥ 99.5%). Also used as a solvent in depolymerisation of PET to yield the BHET additive. These chemicals did not undergo any further processing or purification; they were used in their original sourced state.

Polyethylene Terephthalate (PET) was sourced from waste PET plastic bottles, which were washed and dried before they were processed accordingly.

3.2. PET Additives Preparations

Waste PET plastic bottles were washed using tap water, dried, and cut into flakes with dimensions of about 1 cm × 1 cm, with the harder top and bottom parts of the bottles being left out. Thereafter, the flakes were uniquely prepared or processed as explained and shown below to yield the respective PET derived additives.

3.2.1. Additive I- Pure PET Fibres

After the cut PET plastic flakes with dimensions of about 1 cm × 1 cm were obtained, they were further cut into short and thin sized PET fibres using a scissor. Final length of the fibres was limited to 1 cm while the thickness was limited to less than 1180 μm, with the help of sieve analysis the fibres that did not pass through the sieve of 1180 μm by size were eliminated or cut further as represented in Figure 3.

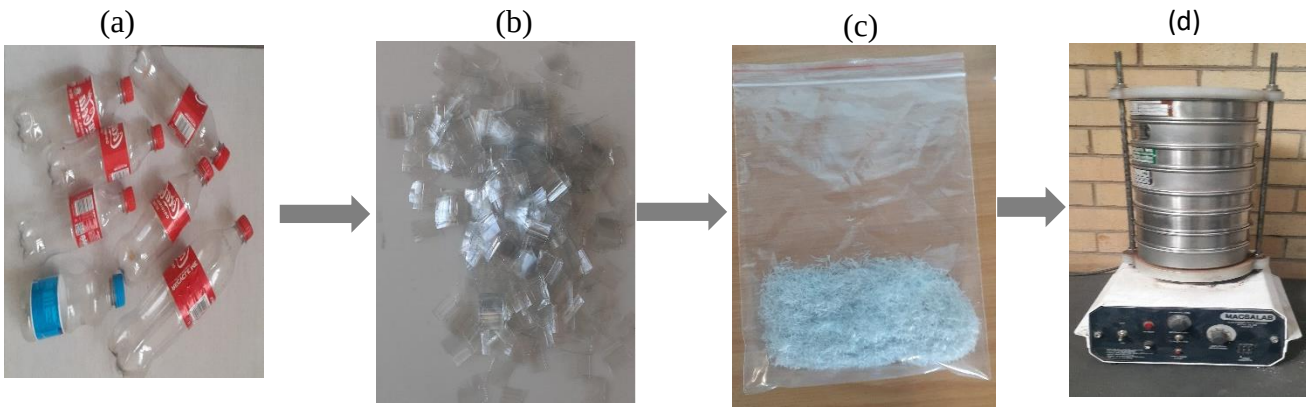

Figure 3: (a) Waste PET Plastic Bottles (b) Cut PET Plastic Flakes (c) Prepared PET Fibre Additive (d) Sieve Through to Eliminate Thicker Fibres.

3.2.2. Additive II-Irradiated PET Fibres

Washed (using tap water), dried, and cut waste PET plastics with dimensions of about 1 cm × 1 cm were sent to an irradiation facility where they were irradiated at radiation doses of 5.8 Gy/ min up to a total dose of 10 kGy using a cobalt-60 gamma irradiator.

Irradiated PET plastic flakes were then further cut into short and thin sized PET fibres using a scissor. Final length of the fibres was limited to 1 cm while the thickness was limited to less than 1180 µm, with the help of sieve analysis the fibres that did not pass through the sieve of 1180 µm by size were eliminated or cut further.

3.2.3. Additive III- Depolymerized PET Plastic Powder Additive

PET plastic was depolymerized through glycolysis to form Bis(2-Hydroxyethyl) terephthalate (BHET) as follows.

PET plastic flakes weighing 20.132 grams and 80 mL of ethylene glycol (a solvent) were introduced into a 250 mL round bottom flask, followed by the addition of 0.406 g of lead acetate as a catalyst for this chemical depolymerization of PET reaction. The prepared mixture was then refluxed at a temperature of 190 ℃ in a closed system for 90 minutes, using a glass condenser and continously running tap water for cooling. As the reaction continued under reflux, the mixture changed from being clear with visible continously dissolving flakes of PET to being

uniform, viscous and grayish liquid, which further turned into an opaque gray coloured semi-solid when cooled to room temperature.

After the mixture was heated under reflux and allowed to cool, unreacted ethylene glycol was separated from the refluxed mixture by adding 40 mL volume of distilled water to dissolve it, followed by heating the resulting mixture while stirring using a magnetic stirrer hot plate. The mixture was then allowed to cool to room temperature and as it was cooling the development of white crystals, the resulting BHET, could be seen. Vacuum filtration of the mixture using a buchner funnel, vacuum flask, filter paper and a vacuum pump then followed, thereafter the recovered crystalline residual BHET was further dried in an oven at a temperature of 65 ℃ and weighed.

The above steps for synthesis of BHET(displayed in Figure 4 below) were repeated for the second time to acquire enough BHET amount to be used as an oil well cement additive.

The prepared BHET powder, to be used as an oil well cement additive, then underwent IR analysis using a PE IR Subtech Spectrum ASCII PEDS 4.00,_scanning from $450\ cm^{-1}$ to $4000\ cm^{-1}$.

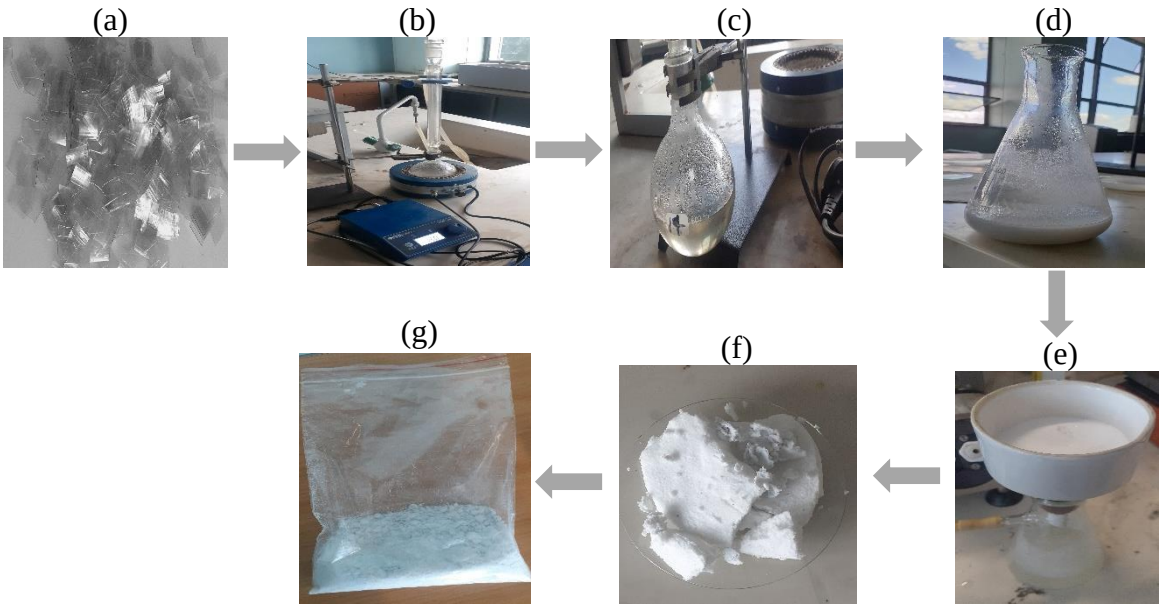

Figure 4: (a) PET Plastic Flakes (b) Mixture Under Reflux (c) Resulting Homogeneous Mixture After Reflux (d) Mixture After Dissolving the Excess Solvent (e) Vacuum Filtration of the Mixture (f) Resulting Residue/BHET (g) Dried and Packed BHET.

3.3. Oil Well Cement Slurry Formulations and Sample Preparations

Designing an oil well cement slurry included the slurry base design where the focus was on determining standard mix water ratio first, then assessing compatibility and influence of the polycarboxylate based superplasticizer together with the rest of the additives, mainly citric acid as a retarder and calcium oxide as an expanding agent. Mixabilities and settling of the base slurries was also closely monitored as part of the base design. Effects of PET and PET derived additives were then investigated after standard base mix design(s) were successfully formulated.

Preparations of oil well cement slurry and specimens employed the API recommended practices outlined in API Recommended Practice 10A (2002), with cement sieved though 850 μm sieve prior to being utilized, and slurries puddled in layers as they were being placed in moulds containing a releasing agent and a sealant.

3.3.1. Slurry Base Design

The following properties and qualities were assessed or closely observed as detailed below for standardization of oil well cement slurry/slurries base design(s).

3.3.1.1. Slurry Density and Water Requirement

Oil well cement slurries, including base cement slurries shown in Table 3, were formulated to have resulting theoretical slurry densities falling within a range of 15.8 ∓ 0.05 ppg (1.89 ∓ 0.005 g/mL), in reference to the usually desired density of class A oil well cement slurries for cementing light formations. The desired slurry density/specific gravity (of 1.89 g/mL) was then used to determine the water requirements by calculation as shown in subsection 4.3.1., with the following expression of determining each blended materials' volume in each mix container used for the calculations.

$$\text{Volume} = \frac{\text{Weight of the material}}{\text{Specific gravity of the material} \times \text{Density of deionized water}}$$

Utilized specific gravities of each blended material/additive are shown in the appendix as Table 1A.

Table 3: Oil Well Cement Slurry Samples with Varying Concentrations of Additives Prepared as Part of the Base Design.

Base Slurry	Cement	CaO	PVA	Citric Acid	PEG	PCE
Base Slurry 1	530	–	–	–	–	–
Base Slurry 2	530	5.3	2.65	0.795	0.109	1.06
Base Slurry 3	530	5.3	2.65	0.795	0.109	1.59
Base Slurry 4	530	5.3	2.65	0.795	0.109	2.12
Base Slurry 5	530	5.3	2.65	0.53	0.109	1.59
Base Slurry 6	530	2.65	2.65	0.53	0.109	1.59
Base Slurry 7	530	10.6	2.65	0.53	0.109	2.12
Base Slurry 8	530	5.3	2.65	0.53	0.109	2.12

3.3.1.2. Mixability

Beginning at the mixing point of liquid part (deionized water and blended additives) with the solid part to the end of the mixing process. The capability of the under-development oil well cement slurry to form a homogeneous dispersed mixture, without agglomerating, separating or changing due to chemical interactions was closely observed.

Mixability of each oil well cement base slurry was then rated using the following criteria:

- Poor → Oil well cement slurry agglomerated during mixing and/or formed paste immediately at the end of the mixing process.
- Satisfactory → Oil well cement slurry was easy to mix and formed a homogeneous dispersed mixture.

3.3.1.3. Settling of the Slurry

During settling of the oil well cement slurries they were closely observed whether water came out of the thickening oil well cement matrix.

Settling of each oil well cement base slurry was then rated as follows:

- Poor → Considerable amount of water came out of the thickening oil well cement matrix.
- Satisfactory → Minimal or no water came out of the thickening oil well cement matrix.

3.3.2. Preparations of Sample Slurries/Specimens

Owing to the base mix design, the base slurry 7 from Table 3 was used as the control given its impressive properties, counting compressive strength, mixability, and settling, while its rheology was later included in the results. To assess the effect of the prepared PET, irradiated PET fibres, and BHET additive in cementing of oil and gas shallow wells. These additives were added in concentrations of 0.2%, 1.0%, and 1.8% BWOC as shown in section 3.4. for each property test.

3.4. Assessing PET Additives

To discover the effects of adding the prepared PET plastic based additives in oil well cements, the resulting compressive strengths together with rheological behaviors were used.

3.4.1. Failure Parameter Tests

Compressive strength tests were performed to indicate the ability of each prepared oil well cement sheath in withstanding differential oil and gas well pressures.

3.4.1.1. Compressive Strength Tests

Prepared oil well cement slurry samples were transferred into $50\,\text{mm} \times 50\,\text{mm}$ cubical steel moulds that were lightly coated with grease as a releasing agent and as a sealant in between the moulds, followed by covering the top of the moulds with a flat metal sheet as a cover plate. Thereafter, the moulds and their contents were completely immersed in a preheated atmospheric curing water bath for a period of $24\,\text{hours}$, thereby allowing for curing of the prepared oil well cement slurries at prescribed curing conditions of $38\,℃$ and $\text{atmospheric pressure}$, the corresponding bottom-hole circulating temperature and pressures as per API Recommended Practices 10A (2002) and ANSI/API Specifications 10A (2009). To further ensure waterproofness, a plastic was used to collectively cover the immersed contents. After the curing period at $\sim 24\,\text{hours}$, the cured specimens were removed and cooled by being temporarily submerged in water with temperature maintained at $27\,℃ \pm 3℃$. Following cooling, they were wiped using a paper towel and they would be ready for compressive strength tests.

Using destructive testing method, the set oil well cement cubical specimens were crushed using a hydraulic press, then the maximum compression load each specimen could withstand was recorded in kiloNewtons. A minimum of three specimens for each uniquely prepared slurry were casted as in Table 4 to assess effects of adding pure PET fibres, irradiated PET fibres, and synthesized BHET Additive(s) on Compressive Strength. During testing the average maximum compression load was determined and used to calculate the respective compressive strength in MPa.

Table 4: Showing Oil Well Cement Mix Design Utilized.

Sample Number	Additives (g)								
	Cement	CaO	PVA	Citric Acid	PEG	PCE	PURE PET Fibres	Irradiated PET Fibres	BHET Additive
Control Sample	180.3	3.61	0.90	0.18	0.037	0.72	–	–	–
Sample 1	180.3	3.61	0.90	0.18	0.037	0.72	0.36	–	–
Sample 2	180.3	3.61	0.90	0.18	0.037	0.72	–	0.36	–
Sample 3	180.3	3.61	0.90	0.18	0.037	0.72	–	–	0.36
Sample 4	180.3	3.61	0.90	0.18	0.037	0.72	1.80	–	–
Sample 5	180.3	3.61	0.90	0.18	0.037	0.72	–	1.80	–
Sample 6	180.3	3.61	0.90	0.18	0.037	0.72	–	–	1.80
Sample 7	180.3	3.61	0.90	0.18	0.037	0.72	3.25	–	–
Sample 8	180.3	3.61	0.90	0.18	0.037	0.72	–	3.25	–
Sample 9	180.3	3.61	0.90	0.18	0.037	0.72	–	–	3.25

3.4.2. Rheological Property Tests

An MCR 101 conventional rotational and non-pressurized rheometer equipped with a viscotherm and a computerized software for displaying and analysing results was used to measure the rheological properties of the prepared sample oil well cement slurries. Measurements started at shear rates of $\sim 5\, s^{-1}$. Following some of API Recommended Practice 10B-2 (2013) recommendations, measurements started at low speeds of about 3 rpm (shear rates of $\sim 5\ \mathrm{s}^{-1}$ as per the used rheometer) , and limited to a maximum speed of 300 rpm which was equivalent to the maximum shear rate of $\sim 392.7\ \mathrm{s}^{-1}$. Disqualification of readings obtained at rotational

speeds greater than 300 rpm was because of respective high solid content which could result to erroneous results due to being affected by centrifuge forces.

Rheological property tests were then all conducted under atmospheric pressure coupled with a temperature of 38℃, simulating the bottom hole circulating temperature or conditions. The scaled down mix design used to assess the effects of pure PET, irradiated PET, and synthesized BHET additives on the oil well cement rheology is displayed in Table 5. Resulting plastic viscosity values for each uniquely prepared oil well cement slurry were thereafter calculated and generated by the software, with the Bingham I model and the Herschel buckley models further utilized to identify yield point values in these dispersant concentrated oil well cement slurries. Detailed instrument information and measurement system (spindel type and measurement gap or distance between the spindel and the surface) was as shown below except for samples incorporated with 1.8% BWOC of the prepared PET derived additives. Where the concentrated fibres prevented the spindel to reach the surface, while the BHET additive at the same dosage completely changed the nature of the slurry thereby a $CP50-1SN23441$ Spindel with its measuring system had to be used:

Application: $RHEOPLUS/32\ V3.40\ 21005258-33024$

Device: $MCR101\ SN80866381;\ FW3.40D090210$

Measuring System: $CC27/HR-SN23758;\ d=0\ mm$

Accessories: $TU1=C-PTD200-SN80862123$; DevCOM1=Physica VT 2

Table 5: Displaying the Preparations of Oil Well Cement Slurries.

Sample Number	Additives (g)								
	Cement	CaO	PVA	Citric Acid	PEG	PCE	PURE PET Fibres	Irradiated PET Fibres	BHET Additive
Control Sample	30	0.60	0.15	0.03	0.0062	0.12	–	–	–
Sample 1	30	0.60	0.15	0.03	0.0062	0.12	0.060	–	–
Sample 2	30	0.60	0.15	0.03	0.0062	0.12	–	0.060	–
Sample 3	30	0.60	0.15	0.03	0.0062	0.12	–	–	0.060
Sample 4	30	0.60	0.15	0.03	0.0062	0.12	0.30	–	–
Sample 5	30	0.60	0.15	0.03	0.0062	0.12	–	0.30	–
Sample 6	30	0.60	0.15	0.03	0.0062	0.12	–	–	0.30
Sample 7	30	0.60	0.15	0.03	0.0062	0.12	0.54	–	–
Sample 8	30	0.60	0.15	0.03	0.0062	0.12	–	0.54	–
Sample 9	30	0.60	0.15	0.03	0.0062	0.12	–	–	0.54

4. RESULTS AND DISCUSSIONS

The prospect of using polyethylene terephthalate plastic waste in cementing atmospheric pressured and elevated temperature oil and gas wells was investigated following the formulation of local class A cement into oil well cement. PET plastic was prepared into varingly two forms intended to be used as additives, namely fibres and powder. Fibre forms of PET additives counted simply cut PET fibres as well as cut then irradiated PET fibres, while the powder form included chemically depolymerized PET into bis(2-hydroxyethyl) terephthalate through glycolysis.

4.1. Local Class A Cement Composition

Major composition of the local class A cement and the trace elemental compositions, determined through XRF analysis, are presented in Table 6 and Table 7 respectively.

Table 6: Showing Major Composition of the Local Class A Cement.

Composition	Weight Percentage (%)
SiO_2	22.11
Al_2O_3	6.50
Fe_2O_3	2.70
MnO	0.09
MgO	2.13
CaO	57.94
Na_2O	0.02
K_2O	0.38
TiO_2	0.47
P_2O_5	0.12
Cr_2O_3	0.03
NiO	0.00
Loss on ignition	4.12
Total	96.61

Table 7: Trace Elemental Composition of the Utilized Local Class A Cement.

Composition	Concentration (ppm)
Sc	59.22
V	86.74
Cr	87.5
Co	10.18
Ni	27.28
Cu	64.83
Zn	19.17
Ga	8.21
Rb	29.24
Sr	287.78
Y	20.57
Zr	145
Nb	6.52
Mo	1.28
Ba	268.18
Pb	13.88
Th	Dl
U	Dl

The major composition of the local class A cement as determined by X-Ray fluorescence (Table 6) is relatable to some extent to that of the API certified Class A oil well cements, citing literature compositions detailed in Table 1B of the appendices. Calcium oxide content is abundant, with a ratio of 57.94 wt% as determined by X-ray fluorescence. Hence, it is part of all the crucial Portland cement clinker mineral phases, namely the dicalcium silicate phase, tetracalcium aluminoferrite phase, tricalcium aluminate phase and the tricalcium silicate phase (Formation of these Portland cement clinker phases is detailed in Table 2B of appendix B, assuming the production is carried out using a standard dry cement rotary kiln).

Aluminium oxide, which is mainly part of the tetracalcium aluminoferrite and tricalcium aluminate clinker phases, was found to be present at a ratio of 6.50 wt%. Signaling that the under investigation local class A cement has significantly lower contents of tetracalcium aluminoferrite and tricalcium aluminate phases. Iron oxide was then found to be present at a ratio of 2.70 wt%, thereby signaling that this local class A cement comprises of the lowest tetracalcium aluminoferrite phase out of all the other three mineral phases, hence, it is the only clinker phase mainly comprised of the iron oxide compound. Determined silicon oxide's ratio of 22.11 wt% on the other hand indicates that this local class A cement has abundant silicate phases (dicalcium silicate and tricalcium silicate). Thereby, this local class A cement was obtained by grinding clinker consisting essentially of hydraulic calcium silicates, and it is classified as ordinary type I cement considering it is also for general use.

4.1.1. Mineral Composition Calculations

Mineral composition of the utilized class A cement was determined as follows, utilizing the compositions presented in Tables 6 and 7:

Given $\frac{w_{Al_2O_3}}{w_{Fe_2O_3}} = \frac{6.50}{2.70} = 2.41$ (with w being the percentage mass fraction of a compound written as a subscript)

$$Hence, \frac{w_{Al_2O_3}}{w_{Fe_2O_3}} > 0.64,$$

thereby the quantities of the following compounds are calculated follows:

- $3CaO \cdot Al_2O_3 = 2.65\, w_{Al_2O_3} - 1.69\, w_{Fe_2O_3}$

  $= 2.65\,(6.50) - 1.69\,(2.70)$

  $= 12.66$

∴ The percentage of tricalcium aluminate $(3CaO \cdot Al_2O_3)$ in the under investigation local class A cement is equal to 12.66%.

- $4CaO \cdot Al_2O_3 \cdot Fe_2O_3 = 3.04\, w_{Fe_2O_3}$

$$= 3.04\ (2.70)$$
$$= 8.21$$

∴ The Tetracalcium aluminoferrite $(4CaO \cdot Al_2O_3 \cdot Fe_2O_3)$ content of the under investigation local class A cement is equal to 8.21%.

- $3CaO \cdot SiO_2 = 4.07\ w_{CaO} - 7.60\ w_{SiO_2} - 6.72\ w_{Al_2O_3} - 1.43\ w_{Fe_2O_3} - 2.85\ w_{SO_3}$
$= 4.07\ (57.94) - 7.60\ (22.11) - 6.72\ (6.50) - 1.43\ (2.70) - 2.85\ (0)$
$= 20.24$

∴ Tricalcium silicate $(3CaO \cdot SiO_2)$ content of the under investigation local class A cement is equal to 20.24%.

- $2CaO \cdot SiO_2 = -3.07\ w_{CaO} + 8.60\ w_{SiO_2} + 5.07\ w_{Al_2O_3} + 1.08\ w_{Fe_2O_3}$
$= -3.07\ (57.94) + 8.60\ (22.11) + 5.07\ (6.50) + 1.08\ (2.70)$
$= 48.14$

∴ Dicalcium silicate $(2CaO \cdot SiO_2)$ content of the under investigation local class A cement is equal to 48.14%.

The main compounds, dicalcium silicate, tricalcium silicate, tetracalcium aluminoferrite, and tricalcium aluminate, as determined, constituted for 89.25% of the total local class A cement weight, with the determined tetracalcium aluminoferrite content not significantly differing from the contents of the API certified class A oil well cements presented in Table 1B of appendices. The tetracalcium aluminoferrite content is 8.21 wt%, which would be considerable the same as the literature tetracalcium aluminoferrite content of approximately 8 wt% by average. The present tricalcium aluminate content, although also not specified by ANSI/API Specifications 10A (2009), was found to be 12.66 wt%, which is slightly higher than the determined literature average (in Table 1B of the appendices) of approximately 9 wt% tricalcium aluminate ratio. Due to this higher tricalcium aluminate amounts than the determined literature average, the local class A cement is more likely to experience sulfate attacks, hence, according to Nelson and Guillot (2006) the increased tricalcium aluminate amounts make cement more susceptible to sulfate attacks.

Although tricalcium silicate and dicalcium silicate contents combined formed a big portion of the cement's major composition, they were determined to have each notable differences when compared to the average literature values in 1B of the appendices, where they were determined to be approximately 50.33 wt% and 25 wt%, respectively. Seemingly interchanged for the under investigation local class A cement, it was found to have a tricalcium silicate content of 20.24 wt% while the dicalcium silicate content was determined to be 48.14 wt%. Hence the determined higher dicalcium silicate content, which is responsible for slow hydration and late binding of cement. Local class A cement originally had a relatively significant but small gradual gain in strength over a longer duration compared to the typical API certified class A oil well cements. Furthermore, due to relatively lower tricalcium

silicate content, which is responsible for more strength while also being behind the early bonding of cement, thereby this local class A cement originally had lower early rapid hydration when compared to the typical API class A oil well cements. Given this lower tricalcium silicate amount it had lower hydration heat and shrinkage (Pikłowska, 2017).

A loss on ignition of 4.12% resulted when this under investigation local class A cement was heated up to 1000 ℃, see Table 6. In Comparison to that of API certified class A oil well cements as per ANSI/API Specifications 10A (2009) specifying an acceptable maximum of 3% loss on ignition, this local class A cement has considerably greater loss on ignition. This according to the Portland Cement Association (1988), could be attributed to inadequate storing and extended storage periods including adulteration. However, this was not the case as the purity, storage times and location were ensured to be adequate. Given this higher loss on ignition of its nature, thereby there would be higher chances of pre-hydration and/or carbonation during the cementing operation when using this local class A cement. Meeting requirements for API class A oil well cements as per ANSI/API Specifications 10A (2009), this local class A cement was determined to have magnesium oxide content of 2.13 wt%, which is well below the specified maximum of 6 wt%.

4.2. Preparation of Bis(2-Hydroxyethyl) Terephthalate

The synthesis of BHET from PET through catalyzed glycolysis is presented as a reaction mechanism in Figure 5, with the balanced chemical reaction shown in section 4.2.1.

4.2.1. Balanced Reaction

$$\mathrm{PET} + 2\mathrm{EG} \rightarrow \mathrm{BHET}$$

$$(\mathrm{C_{10}H_8O_4})_n + \mathrm{C_2H_6O_2} \rightarrow \mathrm{C_{12}H_{14}O_6}$$

4.2.2. BHET Synthesis Reaction Mechanism

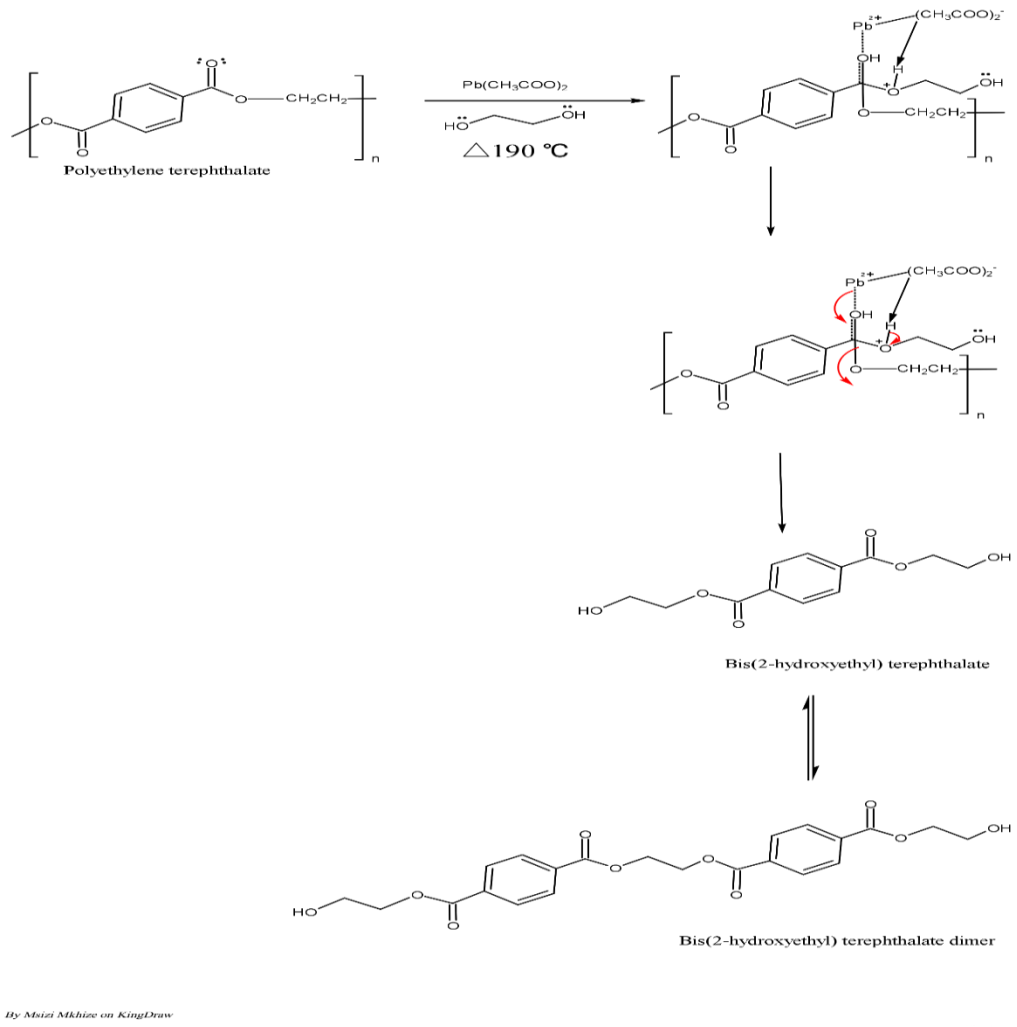

Figure 5: Reaction Mechanism for the Synthesis of Bis(2-Hydroxyethyl) Terephthalate Through Catalyzed Glycolysis.

During the formation of BHET as shown in its formation reaction mechanism labeled as Figure 5, the lead acetate catalyst provided a pathway with a lower free energy of activation, where lead formed a complex with the carbonyl group thereby resulting to the facilitation of ethylene glycol's attack on PET. Hence, the reaction rate of PET glycolysis was effectively increased at a reaction temperature of 190 ℃. A lone pair on the oxygen atom of ethylene glycol then began the attack on the PET's carbonyl carbon of the ester. Thereafter, a bond between the ethylene glycol's hydroxyethyl group and the carbonyl carbon of the polyester formed, thereby breaking the long chain into short chain oligomers and finally BHET.

4.2.3. BHET Percentage Yield

The yield of BHET synthesized from PET through catalyzed glycolysis was determined to be as follows for the two consecutive production runs:

- First Run

$\text{Initial Mass of PET} = 20.132\ \text{g}$ $\text{BHET Recovered} = 15.967\ \text{g}$

$$\text{Percentage Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\%$$

$$= \frac{15.967\ \text{g}}{20.132\ \text{g}} \times 100\%$$

$$= 79.31\%$$

- Second Run

$\text{Initial Mass of PET} = 20.082\ \text{g}$ $\text{BHET Recovered} = 15.902\ \text{g}$

$$\text{Percentage Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\%$$

$$= \frac{15.902\ \text{g}}{20.082\ \text{g}} \times 100\%$$

$$= 79.19\%$$

BHET's percentage yields of averaged 79.25%, signaling great recovery rate from the PET through thermal depolymerization via catalysed glycolysis.

4.2.4. Synthesized BHET Composition

4.2.4.1. FTIR Analysis

The synthesized BHET after analysis through FTIR spectroscopy generated the spectrum presented as Figure 6.

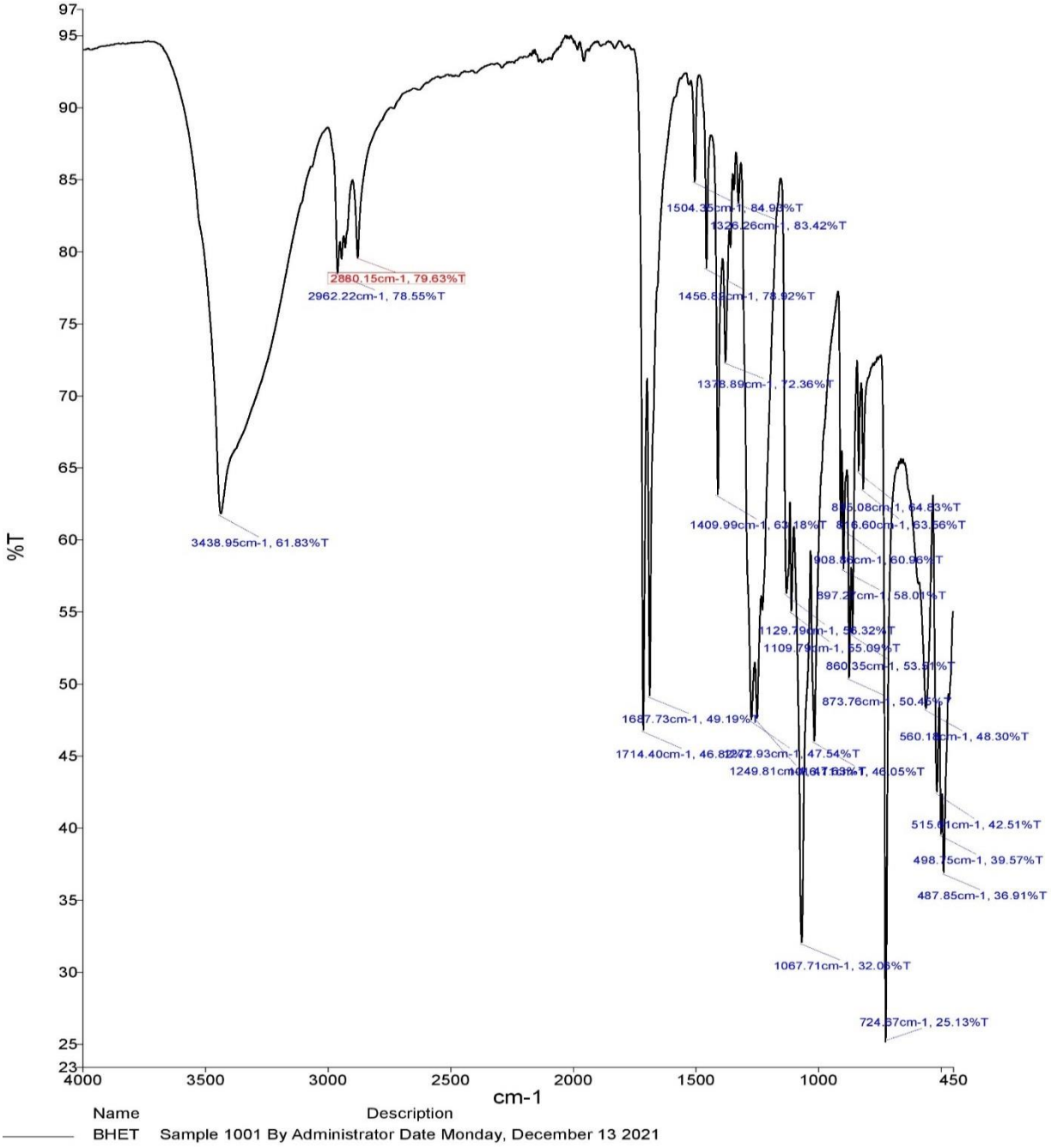

Figure 6: FTIR Analysis of the Prepared BHET to be Used as an Oil Well Cement Additive.

The IR spectrum of the prepared Bis(2-hydroxyethyl) Terephthalate to be used as an additive is displayed as Figure 6. In this spectrum, various prominent peaks were observed. The first strong and broad peak at a frequency of $3438.95\ cm^{-1}$ shows the OH band; at a frequency of $2962.22\ cm^{-1}$ a peak for alkyl $-CH$ is observed, while at $1714.40\ cm^{-1}$ frequency $C=O$ stretching is also seen. The presence of an aryl group is represented by a peak at a frequency of $1504.35\ cm^{-1}$; with the two $C-O$ peaks at $1249.81\ cm^{-1}$ and $1067.71\ cm^{-1}$ frequencies being for the aromatic ester and the primary alcohol, respectively; and then the $-CH_2$stretching is observed at a frequency of $724.67\ cm^{-1}$; thereby confirming all the functional groups present in BHET.

4.2.4.2. X-ray fluorescence (XRF) Analysis

Analysis through XRF spectroscopy, where the synthesized BHET was heated up to a temperature of 1000 ℃, only yielded the trace elements shown in Table 8 as the BHET greatly evaporated during the analysis.

Table 8: Trace Elemental Composition of the Synthesized BHET.

Composition	Concentration (ppm)
Sc	Dl
V	137.34
Cr	8.38
Co	1.49
Ni	Dl
Cu	Dl
Zn	2.9
Ga	8.43
Rb	Dl
Sr	0.83
Y	11.65
Zr	25.79

Nb	Dl
Mo	Dl
Ba	Dl
Pb	18086.96
Th	Dl
U	Dl

Through X-Ray Fluorescence analysis, where this BHET was heated up to a temperature of 1000 ℃, only the trace elements could be identified as shown in Table 8. Trace concentration of lead was found to be the highest accounting for approximately 98.92% of the determined trace elements, while the other trace elements were each determined to be less then 1%. Failure to characterize any major elements is due to high evaporating rate of this BHET, thereby at high temperatures and pressures of oil and gas wells, BHET usage as an oil well cement additive could not be beneficial as its viscosity at increased temperatures decreases.

Its utilization at increased temperatures could see cement slurry/matrix properties being consequently inadequate. Due to BHET's lowering viscosity, fluid loss together with gas migration would readily occur during application (Abbas et al., 2013). Nonetheless, its recovery rate, the percentage yields of approximately 79%, signals it could be readily used once its viable applications are determined. Irradiation of PET to yield irradiated PET fibres on the other hand changed the clear colour of PET flakes into being dull.

4.3. Outcomes of Oil Well Cement Slurry Formulations and Sample Preparations

4.3.1. Control Slurry Density and Mix Water Requirement Calculation

Base design of the oil well cement slurries was first formulated based on the desired oil well cement slurry density, thereby requiring each component's weight and volume to be calculated as shown in table 9. Further, calculations of the required mix water ratio followed as detailed after Table 9.

Table 9: Showing Each Oil Well Cement Slurry Component with Respective Mix Design Quantities.

Material	Weight (g/mix container)	Volume (ml/mix container)
Class A oil well cement	530	$\frac{530}{2.96 \times 0.9998} = 179.09$
Calcium oxide (1% BWOC)	$\frac{2}{100} \times 530 = 10.6$	$\frac{10.6}{3.34 \times 0.9998} = 3.17$
Polyvinyl alcohol (0.5% BWOC)	$\frac{0.5}{100} \times 530 = 2.65$	$\frac{2.65}{1.329 \times 0.9998} = 1.99$
Citric Acid (0.15% BWOC)	$\frac{0.1}{100} \times 530 = 0.53$	$\frac{0.53}{1.665 \times 0.9998} = 0.32$
Polycarboxylate based superplasticizer (0.2% BWOC)	$\frac{0.2}{100} \times 530 = 2.12$	$\frac{2.12}{1.07 \times 0.9998} = 1.98$
Polyethylene glycol (0.05% BWOW)	$\frac{0.05}{100} \times \mathbf{P} = 5 \times 10^{-4}\mathbf{P}$	$\frac{5 \times 10^{-4}\mathbf{P}}{1.13 \times 0.9998} = 4.43 \times 10^{-4}\mathbf{P}$
Mix Water	$0.9998 \times \mathbf{P} = 0.9998\mathbf{P}$	$\mathbf{P}$
Total	$530 + 10.6 + 2.65 + 0.53 + 2.12 + 5 \times 10^{-4}\mathbf{P} + 0.9998\mathbf{P} = \mathbf{545.90 + 1.0003P}$	$179.09 + 3.17 + 1.99 + 0.32 + 1.98 + 4.43 \times 10^{-4}\mathbf{P} + \mathbf{P} = \mathbf{186.55 + 1.0004P}$

Where; BWOC is an abbreviation of by weight of cement, BWOW is an abbreviation of by weight of water, and **P** is the unknown variable that must be solved.

Total weight per mix container = $545.90 + 1.0003\mathbf{P}$

Total volume of cement slurry per sack of cement = $186.55 + 1.0004\mathbf{P}$

$$\text{Desired Oil Well Cement Slurry Density} = \frac{\text{Total weight per mix container}}{\text{Total oil well cement slurry volume}}$$

$$1.89 = \frac{545.90+1.0003\mathbf{P}}{\mathbf{186.55+1.0004P}}$$

$$1.89 \times (186.55 + 1.0004\mathbf{P}) = 545.90 + 1.0003\mathbf{P}$$

$$352.5795 + 1.890756\mathbf{P} = 545.90 + 1.0003\mathbf{P}$$

$$0.890456\mathbf{P} = 193.3205$$

$$\mathbf{P} = 217.10$$

$$\rightarrow \text{Volume of mix water required in each mix container} = \mathbf{P} = 217.10 \text{ ml}$$

$$\rightarrow \text{Weight of mix water in each mix container} = 0.9998\mathbf{P} = 0.9998\ (217.10) = 217.06 \text{ g}$$

$$\therefore \text{Mix water ratio} = \frac{217.06}{530} = 0.4096 = 40.96\% \text{ BWOC} = 41\% \text{ BWOC}$$

Mix water ratio required to yield oil well cement slurries of density approximated 1.89 g/mL as calculated is 41% BWOC.

4.3.2. Base Slurries' Resulting Compressive Strengths

Utilizing the determined water ratio requirements to formulate the oil well cement slurry design, maximum compression loads each of the designed base slurries or samples could withstand is shown in Table 10.

Table 10: Showing Maximum Compression Loads Each of the Prepared Base Specimens Could Withstand.

Base Slurry Number	1	2	3	4	5	6	7
1st Maximum Load (kN)	68.0	20.45	20.4	20.3	36.8	37.8	38.5
2nd Maximum Load (kN)	67.8	21.0	20.42	19.3	36.6	35.1	38.5
3rd Maximum Load (kN)	68.0	20.6	20.36	19.1	35.6	38.0	39.3
Average Maximum Load (kN)	67.93	20.68	20.39	19.57	36.33	36.97	38.77
Standard Deviation ($\pm$kN)	0.1155	0.2843	0.0306	0.6429	0.6429	0.1528	0.4619

Sample calculation of compressive strength in MPa for $50\,\text{mm} \times 50\,\text{mm}$ prepared oil well cement cube specimens of base slurry number 1, using the average resulting maximum compression load determined in Table 10.

$$\text{Compressive strength (MPa)} = \frac{\text{Average Maximum load (N)}}{\text{Cross Sectional Area of the cube (mm}^2\text{)}}$$

$$= \frac{\text{Average Maximum load (N)}}{\text{L}^2}$$

$$= \frac{(67.93 \times 1000)\text{N}}{(50\text{mm})^2}$$

$$= \frac{67930\ \text{N}}{2500\ \text{mm}^2}$$

$$= 27.17\ \text{N/mm}^2 = 27.17\ \text{MPa}$$

Similar calculations, using the relevant average resulting maximum compression loads shown in Table 10, were then done for the rest of the base oil well cement specimens, yielding compressive strengths included in Table 11. Mixabilities and settling of the oil well cement slurries are also recorded in this table.

Table 11: Mixabilities, Settling, and Compressive Strengths of the Prepared Base Design Oil Well Cement Slurries.

Base Slurry	Base Mix Design Additives (g)						Mixability	Settling	Compressive Strength (MPa)	Standard Deviation (±MPa)
	Cement	CaO	PVA	Citric Acid	PEG	PCE				
Base Slurry 1	530	–	–	–	–	–	Poor	Satisfactory	27.17	0.05
Base Slurry 2	530	5.3	2.65	0.795	0.109	1.06	Satisfactory	Satisfactory	8.27	0.11
Base Slurry 3	530	5.3	2.65	0.795	0.109	1.59	Satisfactory	Satisfactory	8.16	0.01
Base Slurry 4	530	5.3	2.65	0.795	0.109	2.12	Satisfactory	Satisfactory	7.83	0.26
Base Slurry 5	530	2.65	2.65	0.53	0.109	1.59	Satisfactory	Satisfactory	14.53	0.26
Base Slurry 6	530	5.3	2.65	0.53	0.109	2.12	Satisfactory	Satisfactory	14.79	0.06
Base Slurry 7	530	10.6	2.65	0.53	0.109	2.12	Satisfactory	Satisfactory	15.51	0.18

Mixability Rating: Poor → Oil well cement slurry agglomerated during mixing and/or formed paste immediately at the end of the mixing process.

Satisfactory → Oil well cement slurry was easy to mix and formed a homogeneous dispersed mixture.

Settling Rating: Poor → Considerable amount of water came out of the thickening oil well cement matrix.

Satisfactory → Minimal or no water came out of the thickening oil well cement matrix.

Over the period of 24 hours, the under investigation local class A cement, in its pure form/without any additives while designed to have a slurry density of ~1.89 g/mL, reached a

maximum compressive strength of 27.17 MPa, see Table 11, after curing at a temperature of 38 ℃ and atmospheric pressure. This reached compressive strength significantly exceeds the API specified minimum compressive strength of 12.4 MPa under similar curing conditions and period (ANSI/API Specifications 10A, 2009). Hence, great potential of successfully formulating the oil well cement for cementing shallow oil and gas wells using this local class A cement could be foreseen, given that the compressive strength would most probably be slightly negatively affected by the addition of additives as the standard workable oil well cement slurry is developed.

The addition of additives to develop the workable and standard oil well cement slurry and matrix from the local class A cement had diverse effects, overall, significantly decreasing the compressive strength while mixability/workability was enhanced. The addition of citric acid as a retarder proved to be extremely effective. Certainly, overcoming the pre-hydration and/or carbonation signaled by the cement's higher loss on ignition, while its retarding activity was further coupled with the slower hydration nature of this cement, hence, significantly higher dicalcium silicate with significantly lower tricalcium silicate contents. Its addition at a concentration of 0.15% BWOC, in the presence of the other additives, significantly decreased compressive strength to between 7.83 MPa and 8.27 MPa, which is below the recommended minimum compressive strength of 12.4 MPa as per ANSI/API Specifications 10A (2009). When its dosage was decreased to 0.1% BWOC, the compressive strength increased to above the recommended minimum of 12.4 MPa.

Addition of a polycarboxylate based superplasticizer (PCE), see Table 11, at concentrations of 0.2%, 0.3%, and 0.4% BWOC while the added concentration of citric acid was 0.15% BWOC, with concentrations of the rest of the additives remaining unchanged, yielded decreasing compressive strengths with increasing concentrations or dosages, respectively, 8.27 MPa, 8.16 MPa, and 7.83 MPa. In the contrary, with decreased concentration of the citric acid retarder to 0.1% BWOC, the addition of a PCE superplasticizer at concentrations 0.3% and 0.4% BWOC, respectively yielded 12.56 MPa and 14.79 MPa. Contrarily leading to an increase in compressive strength with an increase in dosage of the PCE superplasticizer. Thereby signs of incompatibility between the added citric acid as a retarder and the PCE superplasticizer were observed.

According to Plank and Winter (2008), this incompatibility between citric acid and the PCE superplasticizer is caused by competitive adsorption of citrate onto the particle surface of cement resulting to the displacement of PCE, thereby flowability of the resulting oil well cement slurry would be reduced. Further, following the study of Bessaaies-Bey et al. (2016), it was reported that there are different concentration regimes for this competitive additive adsorption. Therefore, in this case when citric acid was added at a concentration of 0.1% BWOC, there were enough free adsorption sites on cement grains, causing the retarder to not compete with PCE for adsorption onto the cement surface. However, when the concentration of the citric acid, which has a strong retarding action, was increased to 0.15% BWOC, a competition for adsorption into the cement surface occurred, with the citrate preferentially occupying the few available sites, hence, citric acid was the strongest surface binding additive in this case. This then further resulted to a decrease in compressive strength as evident in Table 11.

Calcium oxide addition as an expanding agent on the other hand functioned outstandingly along with the PCE superplasticizer and the rest of the additives. There was an increase in compressive strength of the set specimens as its concentration was increased hand in hand with that of the PCE superplasticizer, see Table 11. Furthermore, no cracks were observed on the set oil well cement specimens, meaning calcium oxide successfully overcame any possible cracking tendencies as the oil well cement slurry was setting.

4.4. Outcomes of Assessing PET Additives

4.4.1. Failure Parameter Tests (Compressive Strength Tests)

Effects of the waste derived PET additives, counting the pure PET fibres, irradiated PET fibres, as well as the synthesized BHET additive, on compressive strength of the prepared class A identified and improved oil well cement was investigated and outcomes are detailed in Tables 12, 13, and plotted in Figure 7.

The oil well cement specimens each blended with either 0.2%, 1.0%, and/or 1.8% BWOC concentrations of the PET derived additives when subjected to compression loads withstood the maximum compression loads as shown in Table 12.

Table 12: Maximum Compressive Loads Each of the Specimens Blended with Varying Quantities of Prepared Additives Could Withstand.

Sample Number	1	2	3	4	5	6	7	8	9
1st Maximum Load (kN)	44.6	34.6	55.45	49.3	41.8	71.3	48.6	48.8	66.6
2nd Maximum Load (kN)	39.6	41.2	54.8	46.8	46.9	70.2	47.8	45.6	66
3rd Maximum Load (kN)	38.2	36.4	55.2	43	43.8	70	45.6	44.4	66.1
Average Resulting Maximum Load (kN)	40.80	37.40	55.15	46.37	44.17	70.50	47.33	46.27	66.23
Standard Deviation($\pm$kN)	3.37	3.41	0.33	3.17	2.57	0.30	2.53	2.28	0.32

Sample calculation of compressive strength using sample number 1.

$$\text{Compressive strength (MPa)} = \frac{\text{Average Maximum load (N)}}{\text{Cross Sectional Area of the cube (mm}^2\text{)}}$$

$$= \frac{\text{Average Maximum load (N)}}{\text{L}^2}$$

$$= \frac{(40.8 \times 1000)\text{N}}{(50\ \text{mm})^2}$$

$$= \frac{40800\ \text{N}}{2500\ \text{mm}^2}$$

$$= 16.32\ \mathrm{N/mm^2} = 16.32\ \mathrm{MPa}$$

Similar calculations, using the relevant average resulting maximum compression loads shown in Table 12, were then done for the rest of the sample oil well cement specimens, yielding compressive strengths displayed in Table 13.

Table 13: Displaying Resulting Compressive Strengths of Each Oil Well Cement Samples Containing Pure PET Fibres, Irradiated PET Fibres, and/or Synthesized BHET Additive.

Sample Number	Additives (g)									Compressive Strength (MPa)	Standard Deviation (±MPa)
	Cement	CaO	PVA	Citric Acid	PEG	PCE	PURE PET Fibres	Irrad PET Fibres	BHET		
Ctrl Sample	180.3	3.61	0.90	0.18	0.037	0.72	–	–	–	15.51	0.18
Sample 1	180.3	3.61	0.90	0.18	0.037	0.72	0.36	–	–	16.32	1.35
Sample 2	180.3	3.61	0.90	0.18	0.037	0.72	–	0.36	–	14.96	1.36
Sample 3	180.3	3.61	0.90	0.18	0.037	0.72	–	–	0.36	22.06	0.13
Sample 4	180.3	3.61	0.90	0.18	0.037	0.72	1.80	–	–	18.55	1.27
Sample 5	180.3	3.61	0.90	0.18	0.037	0.72	–	1.80	–	17.67	1.03
Sample 6	180.3	3.61	0.90	0.18	0.037	0.72	–	–	1.80	28.2	0.12
Sample 7	180.3	3.61	0.90	0.18	0.037	0.72	3.25	–	–	18.93	1.01
Sample 8	180.3	3.61	0.90	0.18	0.037	0.72	–	3.25	–	18.51	0.91
Sample 9	180.3	3.61	0.90	0.18	0.037	0.72	–	–	3.25	26.48	0.13

Utilizing the outcomes detailed in Table 13, a plot relating the resulting compressive strengths and the percentages of PET derived additives incorporated in the oil well cement was produced and presented as Figure 7.

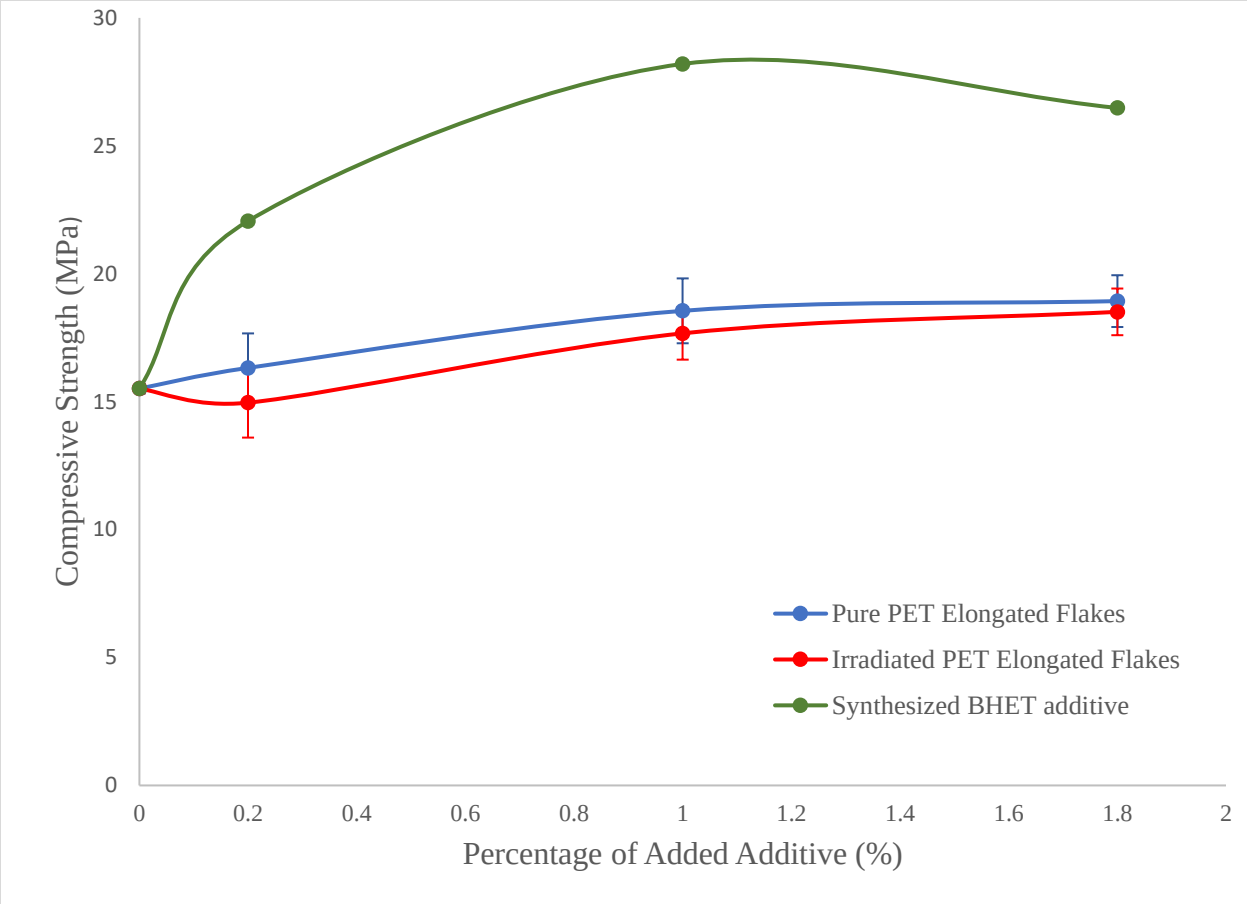

Figure 7: Graph of Resulting Compressive Strengths Per Added Percentage of Waste PET Derived Additives.

Compressive strengths of pure PET fibre additive containing class A identified oil well cement increased from 15.51 MPa of the reference to 16.32 MPa, 18.55 MPa, and 18.93 MPa, per respective pure PET fibre dosages of 0.2%, 1.0%, and 1.8% bowc, see Table 13 and Figure 7. These are respectively, 5.22%, 19.60%, and 22.05% increases in compressive strength when compared to the reference found to have a compressive strength of 15.51 MPa after being cured under the same conditions and for the same period. These PET fibres as additives played a reinforcing role, reinforcing the oil well cement, thereby leading to increased strength.

Meanwhile, the addition of irradiated PET fibres at concentrations of 0.2%, 1.0%, and 1.8% BWOC, led to 14.96 MPa, 17.67 MPa, and 18.51 MPa, respectively, as the resulting compressive strengths. These are respectively, a 3.5% decrease in compressive strength, then 13.93%, and 19.34% increases in compressive strength(s) compared to the reference's

compressive strength of 15.51 MPa. Reinforcing capabilities of the irradiated PET fibres were observed through the increases in compressive strength with increased incorporation concentration of at most 1.8% BWOC, however, they are relatively lower compared to those brought about by addition of the pure untreated PET fibres at similar concentrations. These relatively lower reinforcing capabilities of irradiated PET fibres are due to the pretreatment with a total irradiation dose of 10 kGy.

The applied irradiation weakened the strength of the PET film flakes, however, not enough as to becoming brittle so it can easily be ground into powder. This weakening of PET film flakes consequently yielded weaker PET fibres when cut, thereby breaking relatively easier when reinforcing. The increased compressive strength although not significant, according to Schaefer et al. (2017) could further be attributed to $C-A-S-H$ gels formation together with secondary $C-S-H$ throughout the processes of hydration, although most certainly after high radiation doses. Hence, even the smallest sized fibres, close to being powederd form, were incorporated. Further, increased PET plastic crystallinity after being irradiated could also potentially be a contributer towards increased strengths acquired in cement mixes containing irradiated PET plastics (Schaefer et al., 2017).

This overall positive effect of both these PET fibre additives on compressive strength of oil well cement would also be attributed to the added PCE superplasticizer. This PCE superplasticizer, with its proven effectiveness, further had a more significant influence in enhancing the strength of the oil well cement containing the PET fibres. Theoretically, it stimulated adhesive strength between the incorporated waste PET plastic fibres and the oil well cement (Rai et al., 2012). However, despite these positive effects on compressive strength brought about by these waste PET derived fibre additives, their addition still pose a serious challenge. A challenge of fibres being unevenly distributed as they are too light weight, thereby mostly moving and occupying the top part of the wet and dispersed oil well cement slurry until it starts setting. Their uneven distribution causes the set oil well cement to have enormous difference in the resulting beneficial reinforcements, see Figure 8.



Figure 8: Set Oil Well Cement Specimen Incorporated with Short PET Fibres After a Destructive Compressive Strength Test.

Hence, the high standard deviations ranging from 0.91 MPa up to 1.36 MPa, as displayed in Table 13 and Figure 7, are results of inconsistencies caused by the added waste PET derived fibre additive being unevenly distributed within parts of the oil well cement.

BHET addition to the oil well cement led to an increase in compressive strength by 42.23%, 81.82%, and 70.73% per respective dosages of 0.2%, 1.0%, and 1.8% BWOC. The resulting increase in compressive strength, with optimum addition concentration of 1.0% BWOC BHET additive, could be due to BHET's hydrophilic hydroxyl groups granting increased chances of cement water hydration, as in the study of cementitious composites by Simsek (2020), thereby resulting to closely packed oil well cement. It would further be attributed to the fine powdered nature of BHET, which made its addition effects outperform the ones brought about by the PET reinforcing fibre additives. Hence, according to Ávila-Córdoba et al. (2013) an increase in particle size of incorporated PET leads to a decrease in compressive strength.

Referring to the respective standard deviations displayed in Table 13 and Figure 7, all being 0.13 MPa or less, thereby signaling improved precision, the use of BHET as an oil well cement additive for enhancing compressive strength when cementing shallow oil and gas wells therefore would be a great success. Further, considering the significance of resulting early

strength developments of the oil well cement at these low dosages, thereby BHET synthesized through glycolysis of PET can be successfully used as an accelerator.

4.4.2. Rheological Property Tests

Frictional pressures that would occur during the pumping of the designed oil well cement slurries in the well were predicted through determining their rheological properties at ambient conditions and at temperature of 38 ℃, assuming the bottom hole circulating temperature. The outcomes of each slurry as designed in Table 5 are presented as Figure 9 for the reference slurry; Figure 10 for the slurries incorporated with 0.2% and 1.0% BWOC dosages of the pure PET fibre additive; Figure 11 for the slurry incorporated with 1.8% BWOC dosage of the pure PET fibre additive; Figure 12 for the slurries incorporated with 0.2% and 1.0% BWOC dosages of irradiated PET fibre additive; Figure 13 for the slurry incorporated with 1.8% BWOC dosage of irradiated PET fibre additive; Figure 14 for the slurries incorporated with 0.2% and 1.0% BWOC dosages of the synthesized BHET additive; and Figure 15 for the slurry incorporated with 1.8% BWOC dosage of the synthesized BHET additive.

Summarized measurement results of the plots presented in these figures are found on Table 1C, while data of the plots is also detailed in appendix C.

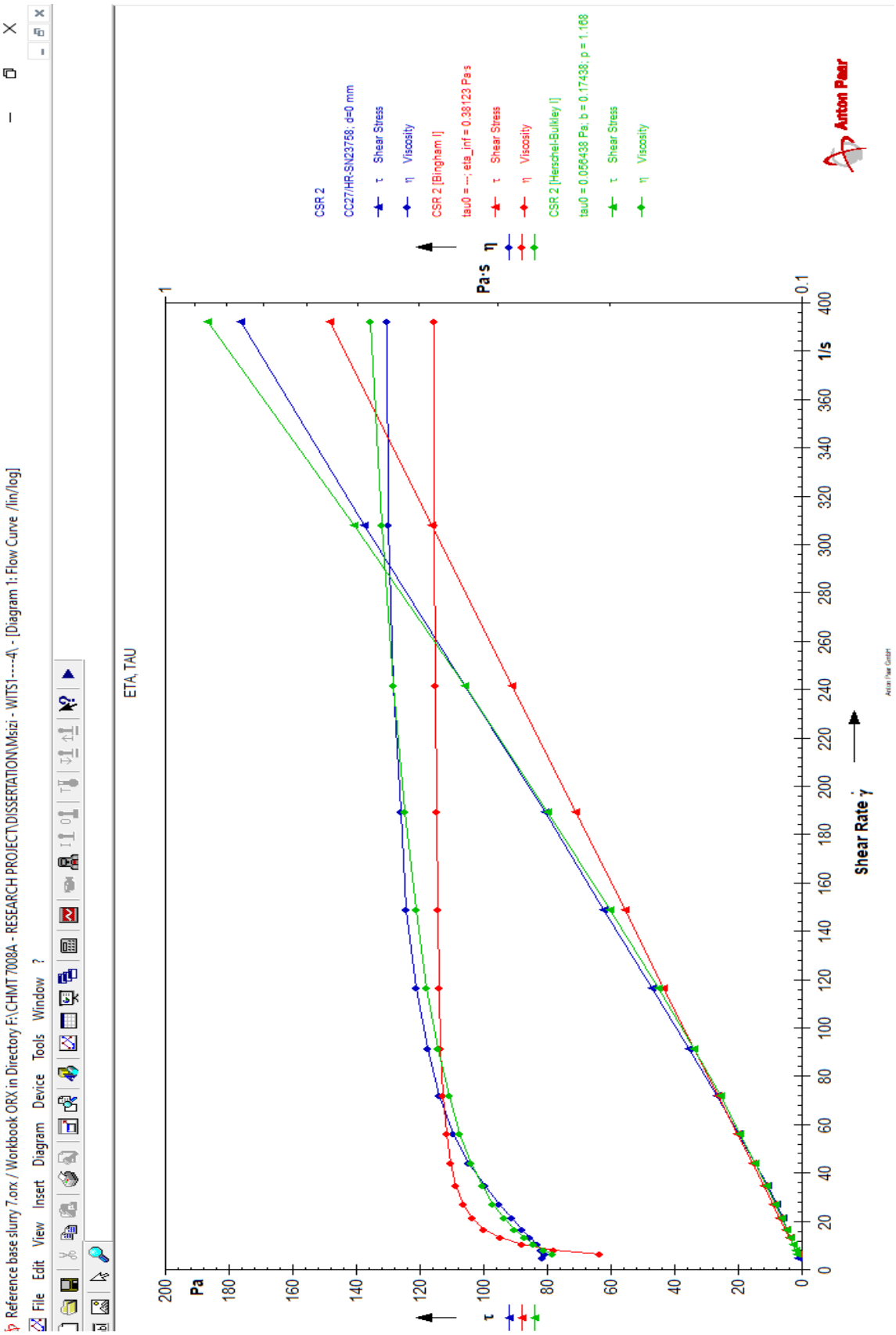

Figure 9: Shear Rate vs Shear Stress and Shear Rate vs Apparent Plastic Viscosity Plots for the Reference Oil Well Cement Slurry.

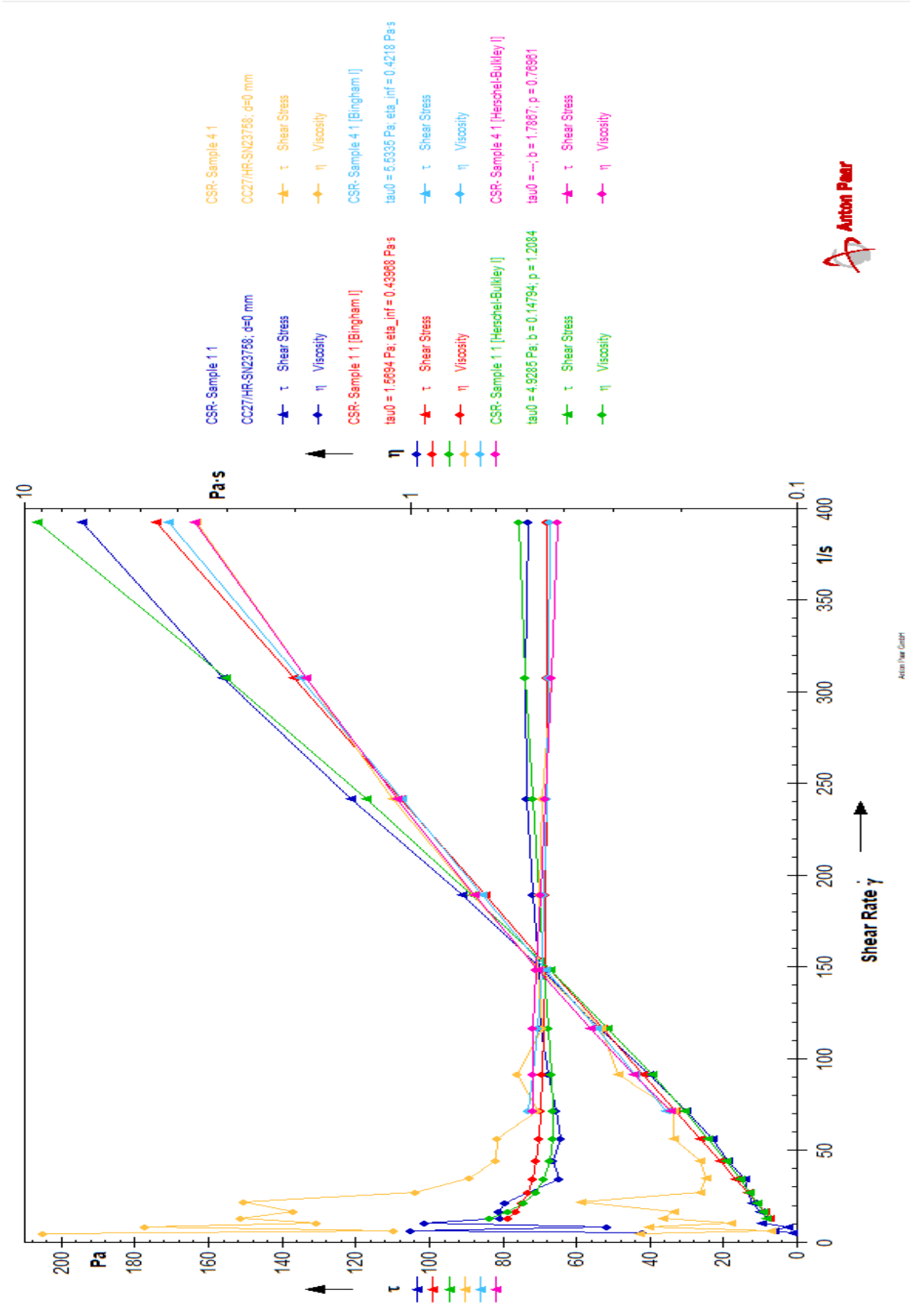

Figure 10: Shear Rate vs Shear Stress and Shear Rate vs Viscosity Plots for Samples 1 and 4, Oil Well Cement Slurries Containing 0.2% BWOC and 1.0% BWOC Pure PET Fibre Additive Concentrations, Respectively.

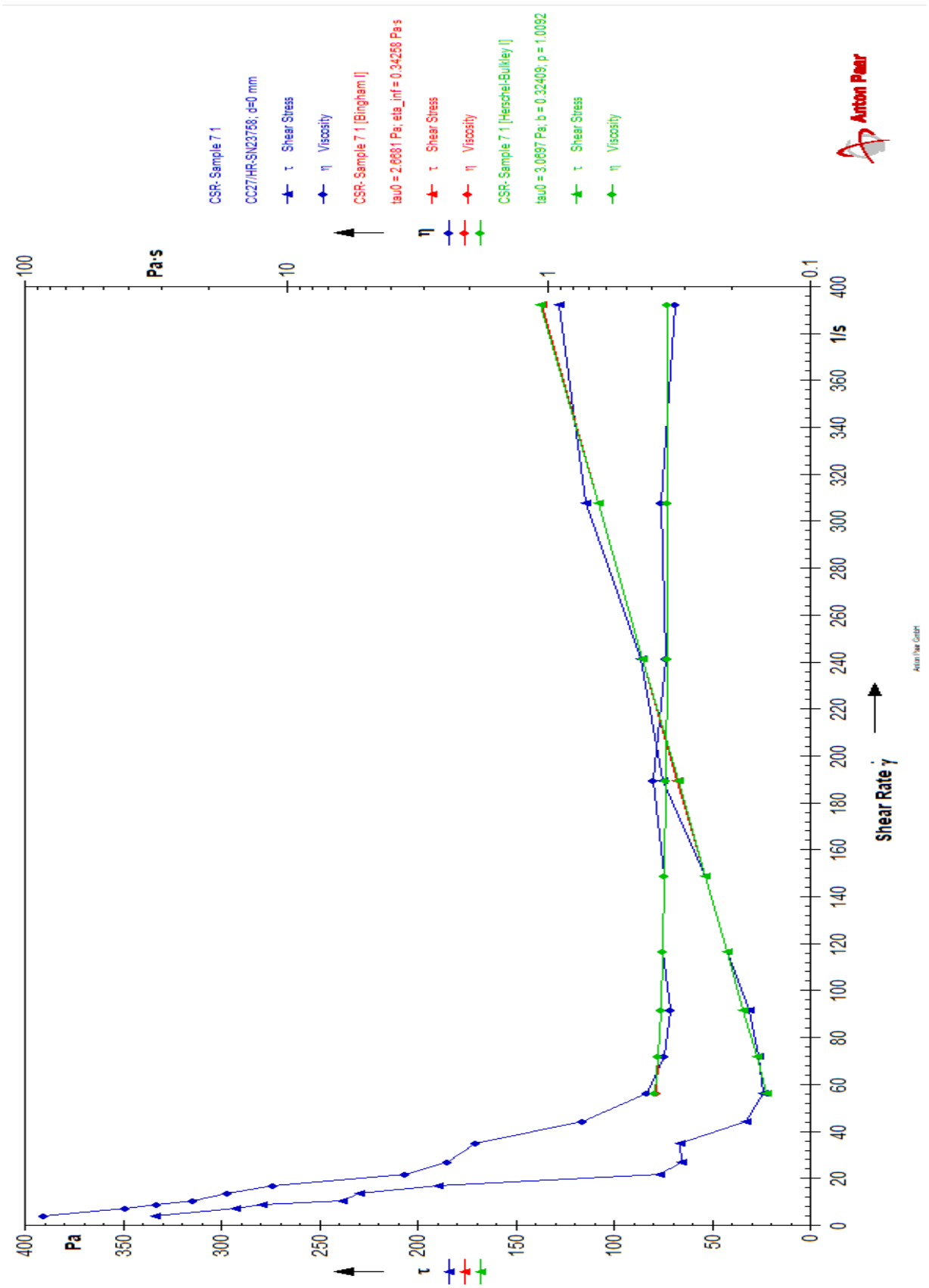

Figure 11: Shear Rate vs Shear Stress and Shear Rate vs Viscosity Plots for Sample 7, the Oil Well Cement Slurry Containing 1.8% BWOC Pure PET Fibre Additive Concentration.

PCE superplasticizer workability enhancement abilities on oil well cement slurries proved to be extremely effective. The formulated base oil well cement slurry containing the maximum recommended plasticizer/dispersant concentration of 0.4% BWOC displayed to have a plastic viscosity of 381.23 cP after being subjected to shear rates ranging from ~3 rpm up to ~300 rpm. Looking at Figure 9, displaying the rheological behavior of the reference oil well cement slurry, a significantly dispersed oil well cement slurry was formulated. This significant dispersion of the prepared oil well cement slurry could be enhanced by the secondary dispersion action of the incorporated citric acid retarder, which has been determined to have incompatibilities resulting to competitive adsorption with the PCE superplasticizer. Hence, in this case mostly at concentrations of 0.15% BWOC citric acid and between 0.2% − 0.4% BWOC for the PCE superplasticizer.

Aside from enhanced mixabilities, well dispersed oil well cement slurries are known for efficiently displacing drilling fluid and being efficiently pumpable even at higher densities (Al Didi, 2022; Foroushan et al., 2021). Effects of pure PET fibres, irradiated PET fibres, and the synthesized BHET additive on rheological properties of the oil well cement are summarized in Table 1C, with respective calculations and measurement results further detailed in Appendix C.
The incorporation of 0.2% and 1.0% BWOC pure PET fibres in the oil well cement resulted to respective increases in plastic viscosity from 381.23 cP of the reference oil well cement slurry to 439.68 cP and 421.8 cP, which are 15.33% and 10.64% plastic viscosity increases, respectively. The lower plastic viscosity increase after addition of 1.0% BWOC pure PET fibres could be largely influenced by the slip effect, as seen in Figure 10, which saw the measurements being taken from a much higher shear rate of 71.882 s^{-1}. Further given the yield strength that is 252.59% higher than that of the oil well cement incorporated with 0.2% BWOC pure PET fibres, thereby the plastic viscosity of 1.0% BWOC pure PET fibres containing oil well cement slurry is more likely to be relatively higher.

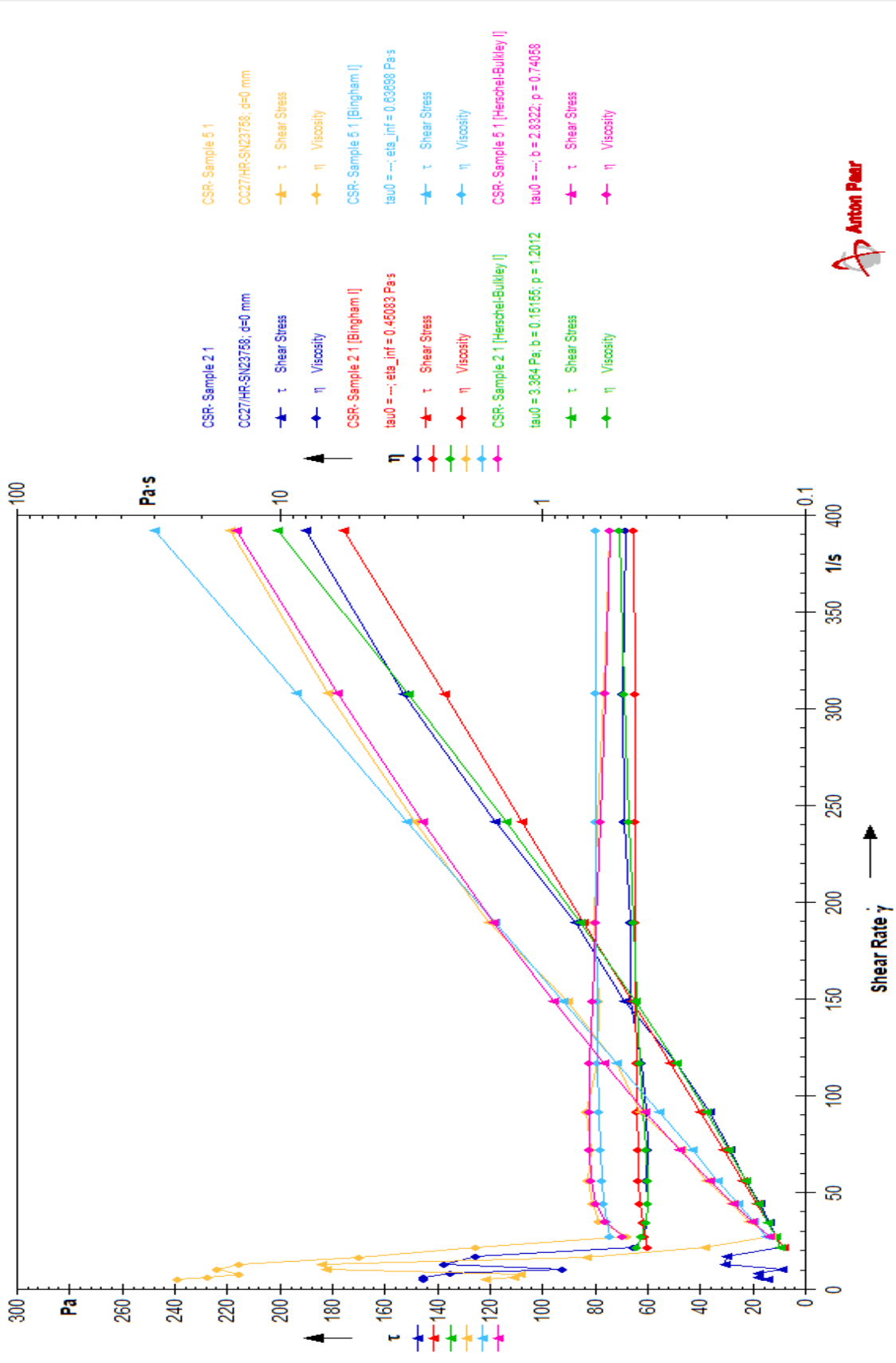

Figure 12: Shear Rate vs Shear Stress and Shear Rate vs Viscosity Plots for Samples 2 and 5, Oil Well Cement Slurries Containing 0.2% BWOC and 1.0% BWOC Irradiated PET Fibre Additive Concentrations, Respectively.

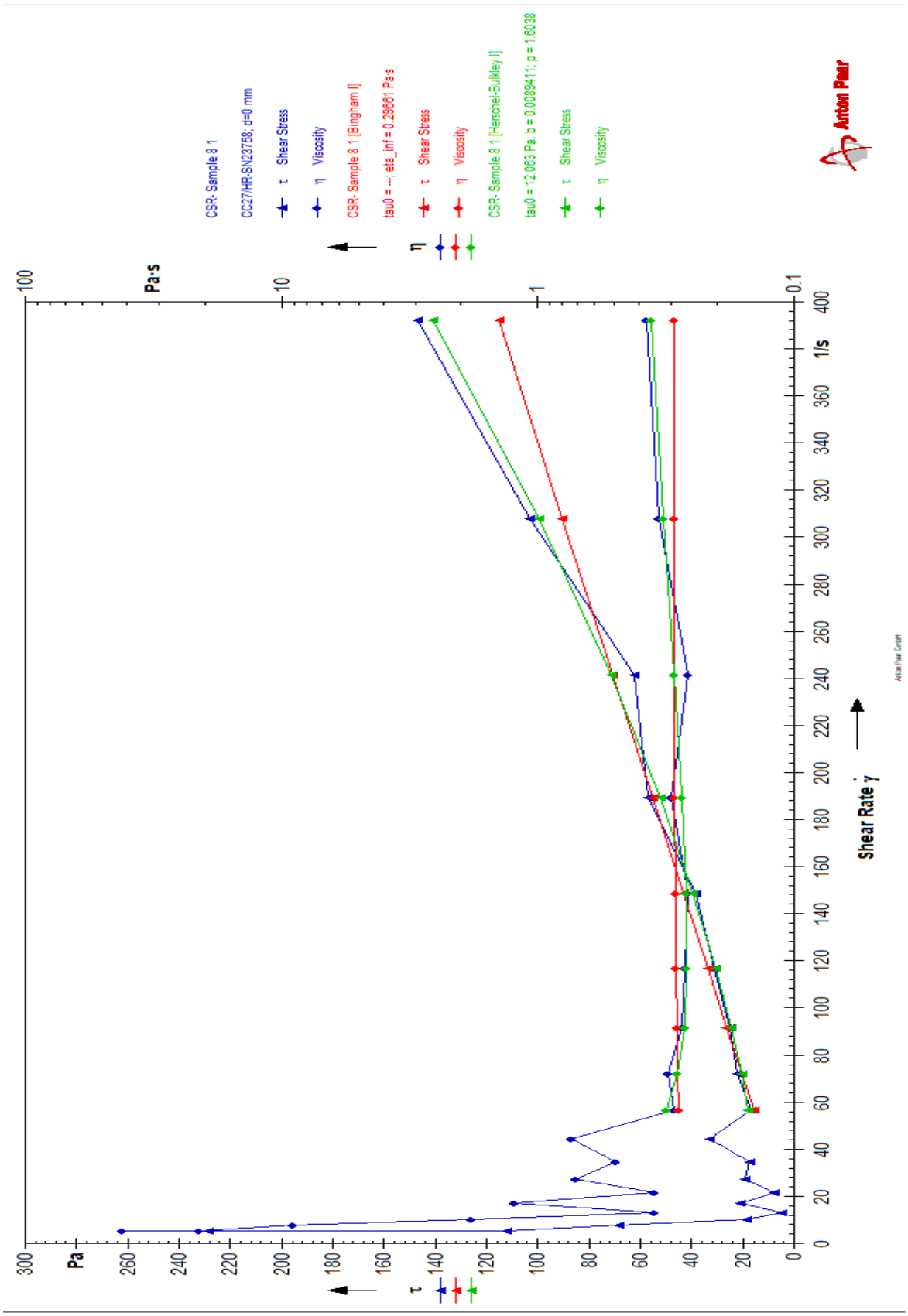

Figure 13: Shear Rate vs Shear Stress and Shear Rate vs Viscosity Plots for Sample 8, the Oil Well Cement Slurry Containing 1.8% BWOC Irradiated PET Fibre Additive Concentration.

Irradiated PET fibre additive added at a concentration of 0.2% BWOC (Figure 12) increased the slurry's plastic viscosity by 18.26% (from 381.23 cP of the reference oil well cement slurry to 450.83 cP), while its addition at a concentration of 1.0% BWOC (Figure 12) increased the plastic viscosity by 67.09%, from the reference slurry's 381.23 cP to 636.98 cP. These resulting increases in plastic viscosity are comparatively significant when the irradiated PET fibres are added rather than the pure PET fibres. Meaning irradiation of PET fibres had a negative effect on plastic viscosity of the oil well cement slurry, hence lower plastic viscosities are desired for the slurry to remain pumpable. Further, it had no notable impact in reducing or enhancing the slip effects as shown in Figures 12 and 13.

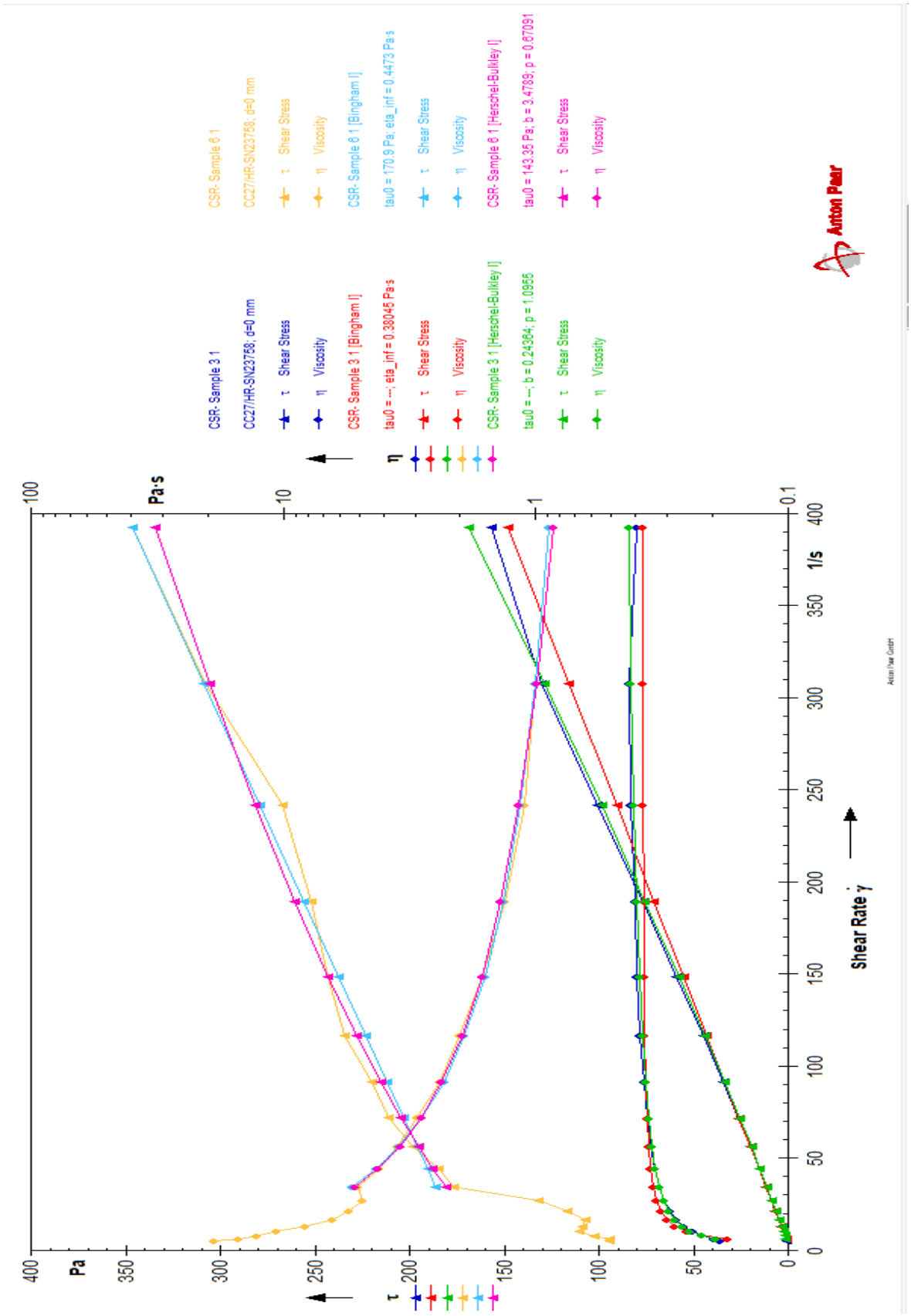

Figure 14: Shear Rate vs Shear Stress and Shear Rate vs Viscosity Plots for Samples 3 and 6, Oil Well Cement Slurries Containing 0.2% BWOC and 1.0% BWOC of Synthesized BHET Additive Concentrations, Respectively.

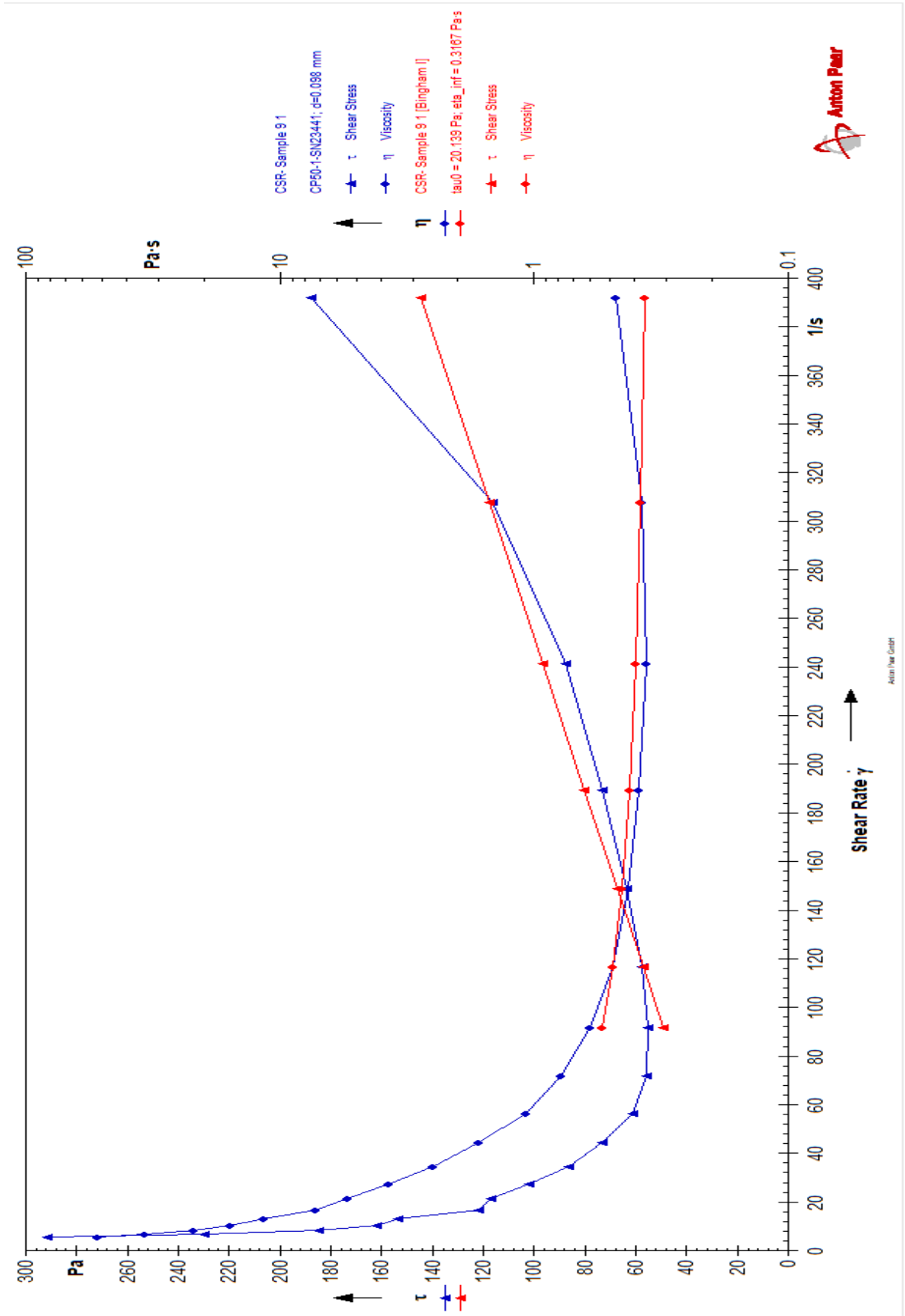

Figure 15: Shear Rate vs Shear Stress and Shear Rate vs Viscosity Plots for Sample 9, the Oil Well Cement Slurry Containing 1.8% BWOC Synthesized BHET Additive Concentration.

The oil well cement slurry containing 0.2% BWOC of the synthesized BHET additive had a plastic viscosity of 380.45 cP, which is a slight 0.21% plastic viscosity decrease from the reference oil well cement slurry with a plastic viscosity of 381.23 cP. An increase in incorporation concentration to 1.0% BWOC synthesized BHET additive then significantly affected the oil well cement slurry viscosity, increasing it to 447.3 cP, which is a 17.33% increase in plastic viscosity compared to that of the reference oil well cement slurry. This slight influence of BHET on plastic viscosity and/or rheological behavior of oil well cement, especially at low concentrations of around 0.2% BWOC, would further promote its application as an accelerator additive, improving early compressive strength developments, hence its strength stimulating capabilities at these lower incorporation dosages as shown in Figure 7. See also the resemblance in rheological behaviors of the reference oil well cement slurry and 0.2% BWOC BHET containing oil well cement slurries in Figures 9 and 14, respectively.

At higher concentrations, however, BHET would result to poor rheology for oil well cement slurries, given the further associated and/or resulting significantly higher and rising with an increase in added BHET concentration yield strengths, as displayed in Figures 14 and 15. Hence, the nature of the slurry also completely turned into paste with 1.8% BWOC BHET addition concentration. Meanwhile, the incorporation of both the pure PET fibres and irradiated PET fibres significantly results to more and more slip effects with increasing incorporation concentrations, making the oil well cement slurry rheology hard to adequately redefine and/or measure. On the positive side, the observed resulting yield strengths for these oil well cement slurries incorporated with the prepared PET derived fibre additives, both the PET fibres displayed to result to much relatively lower increases in yield strengths compared to the BHET additive.

5. CONCLUSIONS

The local class A, type I identified, cement was successfully utilized with the addition of additives, to yield the oil well cement for cementing normal, shallow oil and gas wells. PCE superplasticizer displayed incompatibilities with citric acid retarder at certain addition concentrations. Meanwhile, addition of a superplasticizer among the additives at reasonable dosages per given slurry design was found to be crucial in PET plastic incorporated oil well cements. It enabled enhancements in compressive strengths by increasing adhesive strength between PET fibres and cement mixture. Oil well cement reinforcements through PET fibres, rarely irradiated and pure, have a potential to be used in oil well cementing. However, these PET fibres unevenly reinforce different parts of the cement matrix. Irradiation of PET to be incorporated in oil well cements results to significantly increased plastic viscosities, increasing with an increase in dosage. BHET synthesized through glycolysis of PET can be readily used as an accelerator, especially at concentrations of about 0.2% BWOC where it barely affects oil well cement slurry rheological behaviors while significantly increasing early compressive strength. BHET utilization in HPHT oil and gas wells have to be reconsidered given its rapidly decreasing viscosity nature under high temperatures. Further investigations focusing on the influence of completely powdered and irradiated at varying radiation doses PET plastics are suggested, while more studies on utilization and further influence of BHET in oil well cements are recommended.

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7. APPENDICES

APPENDIX A

Table 1A: Materials Utilized in formulation of the Oil Well Cement Slurry Mixtures and Their Respective Specific Gravities

Material	Specific Gravity
Class A oil well cement	2.96
Calcium oxide	3.34
Polyvinyl alcohol	1.329
Citric Acid	1.665
Polycarboxylate based superplasticizer (PCE)	1.07
Polyethylene glycol	1.1254

APPENDIX B

Table 1B: Typical Compositions of API Certified Class A Oil Well Cements from Literature.

API Class	Typical Clinker Phase Percent Composition (%)			
	$3CaO \cdot SiO_2$	$2CaO \cdot SiO_2$	$3CaO \cdot Al_2O_3$	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$
A	53	24	8	8[1]
	53	24	8	8[2]
	45	27	11	8[3]
Average	50.33	25	9	8[1,2,3]

1. Pikłowska, 2017
2. Mixhaux, Nelson, and Vidick, 1989
3. Hıdıroğlu, 2017

Table 2B: Dry cement rotary kiln zones together with involved reactions as well as typical reaction conditions (temperature and heat of reactions) required for the formation of quality clinker as a product.

Kiln Zones	**Clinker Formation Reactions & Reaction Conditions**	
Decomposition Zone	Chemical Reactions	➢ $CaCO_3 \rightarrow CaO + CO_2$ ➢ $CaO + Al_2O_3 \rightarrow CaO \cdot Al_2O_3$ ➢ $CaO + Fe_2O_3 \rightarrow CaO \cdot Fe_2O_3$ ➢ $CaO + CaO \cdot Fe_2O_3 \rightarrow 2CaO \cdot Fe_2O_3$ ➢ $3(CaO \cdot Al_2O_3) + 2CaO \rightarrow 5CaO \cdot 3Al_2O_3$
	Main Reaction	$CaCO_3$ Decomposition
	Average Temperature (℃)	850 [1,2] or $550 - 960$ [4,5]
	Average rxn Heat (kJ/kg)	1750.19 [1,2,4,5]
	Chemical Reactions	➢ $2CaO + SiO_2 \rightarrow 2CaO \cdot SiO_2$
		➢ $3(2CaO \cdot Fe_2O_3) + 5CaO_3.3Al_2O_3 + CaO \rightarrow 3(4CaO \cdot Al_2O_3 \cdot Fe_2O_3)$
		➢ $5CaO \cdot 3Al_2O_3 + 4CaO \rightarrow 3(3CaO \cdot Al_2O_3)$

Transition Zone	Main Reaction	$2CaO \cdot SiO_2$ Formation
	Average Temperature Range (℃)	$800 - 1250$ [1,2,3,4,5]
	Average rxn Heat (kJ/kg)	-698.71 [1,2,4,5]
	Main Reaction	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ Formation
	Average Temperature Range (℃)	$999 - 1259$ [1,2,3,4]
	Average rxn Heat (kJ/kg)	-95.75 [1,2,4,5]
	Main Reaction	$3CaO \cdot Al_2O_3$ Formation
	Average Temperature Range (℃)	$999 - 1259$ [1,2,3,4]
	Average rxn Heat (kJ/kg)	-25.67 [1,2,5]
Sintering Zone	Chemical Reactions	➢ $2CaO \cdot SiO_2 + CaO \rightarrow 3CaO \cdot SiO_2$
	Main Reaction	$3CaO \cdot SiO_2$ Formation
	Average Temperature Range (℃)	$1305 - 1439$ [1,2,3,5]
	Average rxn Heat (kJ/kg)	-490.33 [1,2,5]
Cooling Zone	Main Reaction	Cooling of Clinker

1. Wang, Lu, Li, Li, and Hu, 2006

2. Rodrigues, Soares Junior, Costa Junior, and Costa, 2017

3. Manias, 2004

4. Benhelal, Zahedi, Shamsaei, and Bahadori, 2012

5. Hokfors, 2014

6. Ghoroi and Suresh, 2007

APPENDIX C

Table 1C: Summarized Results for Rheology Measurements Displayed in Figures 9, 10, 11, 12, 13, 14, and 15.

Sample	Gap (mm)	Defined minimum shear rate (1/s) for calculations	Plastic Viscosity (cP)	Yield Strength (Pa)	
				Bingham I	Herschel-Bulkley
Reference	0	5	381.23	–	0.056438
1	0	13.184229	439.68	1.5694	4.9285
2	0	21.407793	450.83	–	3.364
3	0	5	380.45	–	–
4	0	71.881866	421.8	5.5335	–
5	0	27.282644	636.98	–	–
6	0	34.775451	447.3	170.9	143.35
7	1.107	56.466754	342.58	2.6681	3.0697
8	3.860	56.477222	296.61	–	12.063
9	0.098 (Using CP50 – 1SN23441 Spindel)	91.661071	316.7	20.139	53.781

Rheological Properties Measurements and Calculations

Reference- Base Slurry 7

Data Series Information

Name: CSR 2

Sample: Reference - Base slurry 7

Table 2C: Rheological Properties Measurements of the Reference Slurry.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	5	1.28	0.256	******	******
2	6.37	1.61	0.253	******	******
3	8.12	2.08	0.256	******	******
4	10.3	2.7	0.261	******	******
5	13.2	3.53	0.268	******	******
6	16.8	4.63	0.276	******	******
7	21.4	6.11	0.286	******	******
8	27.3	8.16	0.299	******	******
9	34.8	11	0.315	******	******
10	44.3	14.8	0.334	******	******
11	56.4	19.9	0.352	******	******
12	71.9	26.7	0.372	******	******
13	91.7	35.4	0.387	******	******
14	117	47.1	0.403	******	******
15	149	62.4	0.419	******	******
16	190	80.9	0.426	******	******
17	242	106	0.439	******	******
18	308	137	0.446	******	******
19	392	176	0.449	******	******
*** 20 ***	500	214	0.428	******	******

Data Series Information

Name: CSR 2 [Bingham I]

Sample: Reference - Base slurry 7

Table 3C: Rheological Properties Measurements and Calculations of the Reference Slurry Through the Bingham Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	6.37	1.33	0.208	-1.1	0.381
2	8.12	1.99	0.246	-1.1	0.381
3	10.3	2.84	0.275	-1.1	0.381
4	13.2	3.92	0.298	-1.1	0.381
5	16.8	5.3	0.316	-1.1	0.381
6	21.4	7.06	0.33	-1.1	0.381
7	27.3	9.3	0.341	-1.1	0.381
8	34.8	12.2	0.35	-1.1	0.381
9	44.3	15.8	0.356	-1.1	0.381
10	56.4	20.4	0.362	-1.1	0.381
11	71.9	26.3	0.366	-1.1	0.381
12	91.7	33.8	0.369	-1.1	0.381
13	117	43.4	0.372	-1.1	0.381
14	149	55.6	0.374	-1.1	0.381
15	190	71.2	0.375	-1.1	0.381
16	242	91	0.377	-1.1	0.381
17	308	116	0.378	-1.1	0.381
18	392	148	0.378	-1.1	0.381

Data Series Information

Name: CSR 2 [Herschel-Bulkley I]

Sample: Reference - Base slurry 7

Table 4C: Rheological Properties Measurements and Calculations of the Reference Slurry Through the Herschel-Bulkley Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	6.37	1.57	0.247	0.0564	******
2	8.12	2.07	0.255	0.0564	******
3	10.3	2.73	0.264	0.0564	******
4	13.2	3.6	0.273	0.0564	******
5	16.8	4.76	0.283	0.0564	******
6	21.4	6.3	0.294	0.0564	******
7	27.3	8.35	0.306	0.0564	******
8	34.8	11.1	0.318	0.0564	******
9	44.3	14.7	0.331	0.0564	******
10	56.4	19.4	0.344	0.0564	******
11	71.9	25.8	0.358	0.0564	******
12	91.7	34.2	0.373	0.0564	******
13	117	45.4	0.388	0.0564	******
14	149	60.2	0.405	0.0564	******
15	190	79.9	0.421	0.0564	******
16	242	106	0.439	0.0564	******
17	308	141	0.457	0.0564	******
18	392	187	0.476	0.0564	******

Samples 1 & 4

Data Series Information

Name: CSR- Sample 1 1

Sample: Sample 1 - 0.2% BWOC PET

Table 5C: Rheological Properties Measurements of Sample 1 (Oil Well Cement Slurry with 0.2% BWOC PET).

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	5	1.26	0.252	******	******
2	6.37	6.36	0.999	******	******
3	8.12	2.53	0.312	******	******
4	10.3	9.48	0.917	******	******
5	13.2	7.74	0.587	******	******
6	16.8	9.98	0.594	******	******
7	21.4	12.3	0.573	******	******
8	27.3	13.5	0.495	******	******
9	34.8	14.4	0.413	******	******
10	44.3	18.9	0.427	******	******
11	56.4	23	0.408	******	******
12	71.9	30.1	0.419	******	******
13	91.6	40.5	0.442	******	******
14	117	53.9	0.461	******	******
15	149	69.2	0.465	******	******
16	190	91.3	0.481	******	******
17	242	121	0.502	******	******
18	308	156	0.508	******	******
19	392	194	0.495	******	******
*** 20 ***	500	231	0.461	******	******

Data Series Information

Name: CSR- Sample 1 1 [Bingham I]

Sample: Sample 1 - 0.2% BWOC PET

Table 6C: Rheological Properties Measurements and Calculations of Sample 1 (Oil Well Cement Slurry with 0.2% BWOC PET) Through the Bingham I Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	13.2	7.37	0.559	1.57	0.44
2	16.8	8.96	0.533	1.57	0.44
3	21.4	11	0.513	1.57	0.44
4	27.3	13.6	0.497	1.57	0.44
5	34.8	16.9	0.485	1.57	0.44
6	44.3	21	0.475	1.57	0.44
7	56.4	26.4	0.467	1.57	0.44
8	71.9	33.2	0.461	1.57	0.44
9	91.6	41.9	0.457	1.57	0.44
10	117	52.9	0.453	1.57	0.44
11	149	67	0.45	1.57	0.44
12	190	84.9	0.448	1.57	0.44
13	242	108	0.446	1.57	0.44
14	308	137	0.445	1.57	0.44
15	392	174	0.444	1.57	0.44

Data Series Information

Name: CSR- Sample 1 1 [Herschel-Bulkley I]

Sample: Sample 1 - 0.2% BWOC PET

Table 7C: Rheological Properties Measurements and Calculations of Sample 1 (Oil Well Cement Slurry with 0.2% BWOC PET) Through the Herschel-Bulkley Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	13.2	8.27	0.627	4.93	******
2	16.8	9.4	0.56	4.93	******
3	21.4	10.9	0.51	4.93	******
4	27.3	13	0.475	4.93	******
5	34.8	15.7	0.452	4.93	******
6	44.3	19.4	0.437	4.93	******
7	56.4	24.3	0.43	4.93	******
8	71.9	30.9	0.429	4.93	******
9	91.6	39.7	0.433	4.93	******
10	117	51.5	0.441	4.93	******
11	149	67.4	0.453	4.93	******
12	190	88.6	0.467	4.93	******
13	242	117	0.485	4.93	******
14	308	155	0.504	4.93	******
15	392	206	0.526	4.93	******

Data Series Information

Name: CSR- Sample 4 1

Sample: Sample 4 – 1.0% BWOC PET

Table 8C: Rheological Properties Measurements of Sample 4 (Oil Well Cement Slurry with 1.0% BWOC PET).

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	4.77	42.9	8.99	******	******
2	6.39	7.08	1.11	******	******
3	8.23	40.1	4.88	******	******
4	10.3	18.1	1.76	******	******
5	13.2	36.4	2.76	******	******
6	16.7	33.6	2.01	******	******
7	21.8	58.9	2.7	******	******
8	27.3	26.6	0.973	******	******
9	34.9	24.6	0.706	******	******
10	44.3	26.6	0.601	******	******
11	56.4	33.8	0.598	******	******
12	71.9	33.7	0.469	******	******
13	91.6	48.6	0.531	******	******
14	117	53.4	0.457	******	******
15	149	70	0.471	******	******
16	190	88	0.464	******	******
17	242	110	0.456	******	******
18	308	134	0.434	******	******
19	392	163	0.416	******	******
*** 20 ***	500	200	0.4	******	******

Data Series Information

Name: CSR- Sample 4 1 [Bingham I]

Sample: Sample 4 - 1.0% BWOC PET

Table 9C: Rheological Properties Measurements and Calculations of Sample 4 (Oil Well Cement Slurry with 1.0% BWOC PET) Through the Bingham I Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	71.9	35.9	0.499	5.53	0.422
2	91.6	44.2	0.482	5.53	0.422
3	117	54.8	0.469	5.53	0.422
4	149	68.3	0.459	5.53	0.422
5	190	85.5	0.451	5.53	0.422
6	242	107	0.445	5.53	0.422
7	308	135	0.44	5.53	0.422
8	392	171	0.436	5.53	0.422

Data Series Information

Name: CSR- Sample 4 1 [Herschel-Bulkley I]

Sample: Sample 4 - 1.0% BWOC PET

Table 10C: Rheological Properties Measurements and Calculations of Sample 4 (Oil Well Cement Slurry with 1.0% BWOC PET) Through the Herschel-Bulkley Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	71.9	34.6	0.481	-13.4	******
2	91.6	44.4	0.485	-13.4	******
3	117	56.3	0.482	-13.4	******
4	149	70.6	0.474	-13.4	******
5	190	87.8	0.463	-13.4	******
6	242	109	0.449	-13.4	******
7	308	134	0.434	-13.4	******
8	392	164	0.417	-13.4	******

Sample 7

Data Series Information

Name: CSR- Sample 7 1

Sample: Sample 7 - 1.8% BWOC PET

Table 11C: Rheological Properties Measurements of Sample 7 (Oil Well Cement Slurry with 1.8% BWOC PET).

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	3.93	334	84.8	******	******
2	7.14	293	41.1	******	******
3	8.88	279	31.4	******	******
4	10.5	239	22.8	******	******
5	13.6	229	16.8	******	******
6	16.7	190	11.3	******	******
7	21.8	76.8	3.52	******	******
8	26.9	65.6	2.44	******	******
9	35.2	66.7	1.9	******	******
10	44.3	32.9	0.743	******	******
11	56.5	23.8	0.422	******	******
12	71.9	26.1	0.363	******	******
13	91.7	31.4	0.343	******	******
14	117	42.6	0.365	******	******
15	149	53.4	0.359	******	******
16	190	75.5	0.398	******	******
17	242	86	0.356	******	******
18	308	114	0.372	******	******
19	392	128	0.326	******	******
*** 20 ***	500	158	0.316	******	******

Data Series Information

Name: CSR- Sample 7 1 [Bingham I]

Sample: Sample 7 - 1.8% BWOC PET

Table 12C: Rheological Properties Measurements and Calculations of Sample 7 (Oil Well Cement Slurry with 1.8% BWOC PET) Through the Bingham I Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	56.5	22	0.39	2.67	0.343
2	71.9	27.3	0.38	2.67	0.343
3	91.7	34.1	0.372	2.67	0.343
4	117	42.6	0.365	2.67	0.343
5	149	53.6	0.361	2.67	0.343
6	190	67.7	0.357	2.67	0.343
7	242	85.4	0.354	2.67	0.343
8	308	108	0.351	2.67	0.343
9	392	137	0.349	2.67	0.343

Data Series Information

Name: CSR- Sample 7 1 [Herschel-Bulkley I]

Sample: Sample 7 - 1.8% BWOC PET

Table 13C: Rheological Properties Measurements and Calculations of Sample 7 (Oil Well Cement Slurry with 1.8% BWOC PET) Through the Herschel-Bulkley Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	56.5	22.1	0.391	3.07	******
2	71.9	27.3	0.38	3.07	******
3	91.7	34	0.371	3.07	******
4	117	42.6	0.365	3.07	******
5	149	53.6	0.36	3.07	******
6	190	67.6	0.356	3.07	******
7	242	85.4	0.354	3.07	******
8	308	108	0.352	3.07	******
9	392	137	0.35	3.07	******

Samples 2 & 5

Data Series Information
Name: CSR- Sample 2 1
Sample: Sample 2 - 0.2% BWOC Irradiated PET
Number of Intervals: 3
Application: RHEOPLUS/32 V3.40 21005258-33024
Device: MCR101 SN80866381; FW3.40D090210; Slot3
Measuring Date/Time: 3/15/2022; 11:12 AM
Measuring System: CC27/HR-SN23758; d=0 mm
Accessories: TU1=C-PTD200-SN80862123; DevCOM1=Physica VT 2

Interval: 1
Number of Data Points: 0

Time Setting: 1 Meas. Pts., Reject
Meas. Pt. Duration 0.5 min
Measuring Profile:
Shear Rate d(gamma)/dt = 5 1/s

Interval: 2
Number of Data Points: 0

Time Setting: 1 Meas. Pts., Reject
Meas. Pt. Duration 1 s
Measuring Profile:

Interval: 3
Number of Data Points: 20

Time Setting: 20 Meas. Pts., Reset Strain
Meas. Pt. Duration 10 s
Measuring Profile:
Shear Rate d(gamma)/dt = 5 ... 500 1/s log

Table 14C: Rheological Properties Measurements of Sample 2 (Oil Well Cement Slurry with 0.2% BWOC Irradiated PET).

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Speed [1/min]	Torque [µNm]	Status []
1	5.03	14.2	2.83	3.9	684	Dy_accu
2	6.37	18	2.83	4.94	864	Dy_accu
3	8.1	18.1	2.24	6.28	871	Dy_accu
4	10.4	8.75	0.84	8.08	420	Dy_accu
5	13	30.7	2.35	10.1	1,470	Dy_accu
6	16.8	30	1.79	13	1,440	Dy_accu
7	21.4	9.65	0.451	16.6	463	Dy_accu
8	27.3	11.2	0.41	21.1	536	Dy_accu
9	34.8	14.1	0.405	27	675	Dy_accu
10	44.3	17.6	0.397	34.3	843	Dy_accu
11	56.4	22.6	0.401	43.7	1,090	Dy_accu
12	71.9	28.6	0.398	55.8	1,370	Dy_accu
13	91.7	36.9	0.402	71.1	1,770	Dy_accu
14	117	49.1	0.42	90.5	2,360	Dy_accu
15	149	69	0.464	115	3,310	Dy_accu
16	190	87.5	0.461	147	4,200	Dy_accu
17	242	118	0.488	187	5,660	Dy_accu
18	308	153	0.497	239	7,350	Dy_accu
19	392	190	0.485	304	9,140	Dy_accu
*** 20 ***	500	229	0.457	388	11,000	Dy_accu

Data Series Information
Name: CSR- Sample 2 1 [Bingham I]
Sample: Sample 2 - 0.2% BWOC Irradiated PET
Number of Intervals: 1
Application: RHEOPLUS/32 V3.40 21005258-33024
Analysis Method: Bingham I
Analysis Result: tau0 = ---; eta_inf = 0.45083 Pa·s

Interval: 1
Number of Data Points: 13

Table 15C: Rheological Properties Measurements and Calculations of Sample 2 (Oil Well Cement Slurry with 0.2% BWOC Irradiated PET) Through the Bingham I Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Speed [1/min]	Torque [µNm]	Status []
1	21.4	8.48	0.396	******	******	******
2	27.3	11.1	0.408	******	******	******
3	34.8	14.5	0.417	******	******	******
4	44.3	18.8	0.424	******	******	******
5	56.4	24.3	0.43	******	******	******
6	71.9	31.3	0.435	******	******	******
7	91.7	40.1	0.438	******	******	******
8	117	51.5	0.441	******	******	******
9	149	65.9	0.443	******	******	******
10	190	84.3	0.445	******	******	******
11	242	108	0.446	******	******	******
12	308	138	0.447	******	******	******
13	392	176	0.448	******	******	******

Data Series Information
Name: CSR- Sample 2 1 [Herschel-Bulkley I]
Sample: Sample 2 - 0.2% BWOC Irradiated PET
Number of Intervals: 1
Application: RHEOPLUS/32 V3.40 21005258-33024
Analysis Method: Herschel-Bulkley I
Analysis Result: tau0 = 3.364 Pa; b = 0.15155; p = 1.2012

Interval: 1
Number of Data Points: 13

Table 16C: Rheological Properties Measurements and Calculations of Sample 2 (Oil Well Cement Slurry with 0.2% BWOC Irradiated PET) Through the Herschel-Bulkley Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Speed [1/min]	Torque [µNm]	Status []
1	21.4	9.37	0.438	******	******	******
2	27.3	11.4	0.418	******	******	******
3	34.8	14.1	0.406	******	******	******
4	44.3	17.7	0.401	******	******	******
5	56.4	22.6	0.401	******	******	******
6	71.9	29.1	0.405	******	******	******
7	91.7	37.8	0.413	******	******	******
8	117	49.5	0.424	******	******	******
9	149	65.1	0.437	******	******	******
10	190	85.9	0.453	******	******	******
11	242	114	0.471	******	******	******
12	308	151	0.491	******	******	******
13	392	201	0.512	******	******	******

Data Series Information
Name: CSR- Sample 5 1
Sample: Sample 5 - 1.0% BWOC Irradiated PET
Number of Intervals: 3
Application: RHEOPLUS/32 V3.40 21005258-33024
Device: MCR101 SN80866381; FW3.40D090210; Slot3
Measuring Date/Time: 3/15/2022; 11:54 AM
Measuring System: CC27/HR-SN23758; d=0 mm
Accessories: TU1=C-PTD200-SN80862123; DevCOM1=Physica VT 2

Interval: 1
Number of Data Points: 0

Time Setting: 1 Meas. Pts., Reject
Meas. Pt. Duration 0.5 min
Measuring Profile:
Shear Rate d(gamma)/dt = 5 1/s

Interval: 2
Number of Data Points: 0

Time Setting: 1 Meas. Pts., Reject
Meas. Pt. Duration 1 s
Measuring Profile:

Interval: 3
Number of Data Points: 20
Time Setting: 20 Meas. Pts., Reset Strain
Meas. Pt. Duration 10 s
Measuring Profile:
Shear Rate d(gamma)/dt = 5 ... 500 1/s log

Table 17C: Rheological Properties Measurements of Sample 5 (Oil Well Cement Slurry with 1.0% BWOC Irradiated PET).

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Speed [1/min]	Torque [µNm]	Status []
1	4.98	122	24.4	3.86	5,840	Dy_accu
2	5.93	111	18.7	4.6	5,330	Dy_accu
3	7.63	109	14.2	5.92	5,210	Dy_accu
4	10.5	182	17.4	8.13	8,740	Dy_accu
5	12.9	184	14.3	10	8,840	Dy_accu
6	16.7	83.3	4.98	13	4,000	Dy_accu
7	21.6	38.7	1.79	16.7	1,860	Dy_accu
8	27.3	13.1	0.479	21.2	628	Dy_accu
9	34.8	21.4	0.613	27	1,030	Dy_accu
10	44.3	28.5	0.642	34.4	1,370	Dy_accu
11	56	37.6	0.672	43.4	1,810	Dy_accu
12	71.9	47.2	0.657	55.8	2,270	Dy_accu
13	91.6	62.8	0.685	71.1	3,010	Dy_accu
14	117	72.3	0.619	90.5	3,470	Dy_accu
15	149	90.4	0.607	115	4,340	Dy_accu
16	190	121	0.638	147	5,800	Dy_accu
17	242	149	0.616	187	7,140	Dy_accu
18	308	182	0.59	239	8,720	Dy_accu
19	392	219	0.558	304	10,500	Dy_accu
*** 20 ***	500	253	0.506	388	12,200	Dy_accu

Data Series Information
Name: CSR- Sample 5 1 [Bingham I]
Sample: Sample 5 - 1.0% BWOC Irradiated PET
Number of Intervals: 1
Application: RHEOPLUS/32 V3.40 21005258-33024
Analysis Method: Bingham I
Analysis Result: tau0 = ---; eta_inf = 0.63698 Pa·s

Interval: 1
Number of Data Points: 12

Table 18C: Rheological Properties Measurements and Calculations of Sample 5 (Oil Well Cement Slurry with 1.0% BWOC Irradiated PET) Through the Bingham I Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Speed [1/min]	Torque [µNm]	Status []
1	27.3	15.1	0.552	******	******	******
2	34.8	19.9	0.571	******	******	******
3	44.3	25.9	0.585	******	******	******
4	56	33.3	0.596	******	******	******
5	71.9	43.5	0.605	******	******	******
6	91.6	56.1	0.612	******	******	******
7	117	72.1	0.617	******	******	******
8	149	92.5	0.621	******	******	******
9	190	118	0.625	******	******	******
10	242	152	0.627	******	******	******
11	308	194	0.629	******	******	******
12	392	248	0.631	******	******	******

Data Series Information
Name: CSR- Sample 5 1 [Herschel-Bulkley I]
Sample: Sample 5 - 1.0% BWOC Irradiated PET
Number of Intervals: 1
Application: RHEOPLUS/32 V3.40 21005258-33024
Analysis Method: Herschel-Bulkley I
Analysis Result: tau0 = ---; b = 2.8322; p = 0.74058
Interval: 1
Number of Data Points: 12

Table 19C: Rheological Properties Measurements and Calculations of Sample 5 (Oil Well Cement Slurry with 1.0% BWOC Irradiated PET) Through the Herschel-Bulkley Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Speed [1/min]	Torque [µNm]	Status []
1	27.3	13.6	0.499	******	******	******
2	34.8	20.1	0.577	******	******	******
3	44.3	27.8	0.627	******	******	******
4	56	36.6	0.655	******	******	******
5	71.9	48	0.668	******	******	******
6	91.6	61.2	0.668	******	******	******
7	117	77	0.66	******	******	******
8	149	96	0.645	******	******	******
9	190	119	0.625	******	******	******
10	242	146	0.603	******	******	******
11	308	178	0.578	******	******	******
12	392	217	0.553	******	******	******

Sample 8

Data Series Information
Name: CSR- Sample 8 1
Sample: Sample 8 - 1.8% BWOC Irradiated PET

Table 20C: Rheological Properties Measurements of Sample 8 (Oil Well Cement Slurry with 1.8% BWOC Irradiated PET).

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	5.46	229	41.9	******	******
2	5.33	112	21	******	******
3	7.55	68.2	9.04	******	******
4	10.3	18.9	1.83	******	******
5	13.2	4.62	0.35	******	******
6	17.2	21.1	1.23	******	******
7	21.4	7.53	0.352	******	******
8	27.3	19.3	0.71	******	******
9	34.8	17.3	0.497	******	******
10	44.6	33	0.74	******	******
11	56.5	16.7	0.296	******	******
12	72	22.5	0.312	******	******
13	91.6	25	0.273	******	******
14	117	31	0.266	******	******
15	149	38.4	0.258	******	******
16	190	57	0.301	******	******
17	242	62.7	0.259	******	******
18	308	103	0.336	******	******
19	392	147	0.375	******	******
*** 20 ***	500	158	0.315	******	******

Data Series Information
Name: CSR- Sample 8 1 [Bingham I]
Sample: Sample 8 - 1.8% BWOC Irradiated PET

Table 21C: Rheological Properties Measurements and Calculations of Sample 8 (Oil Well Cement Slurry with 1.8% BWOC Irradiated PET) Through the Bingham I Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	56.5	15.9	0.281	-0.898	0.297
2	72	20.4	0.284	-0.898	0.297
3	91.6	26.3	0.287	-0.898	0.297
4	117	33.7	0.289	-0.898	0.297
5	149	43.2	0.291	-0.898	0.297
6	190	55.3	0.292	-0.898	0.297
7	242	70.8	0.293	-0.898	0.297
8	308	90.4	0.294	-0.898	0.297
9	392	115	0.294	-0.898	0.297

Data Series Information
Name: CSR- Sample 8 1 [Herschel-Bulkley I]
Sample: Sample 8 - 1.8% BWOC Irradiated PET

Table 22C: Rheological Properties Measurements and Calculations of Sample 8 (Oil Well Cement Slurry with 1.8% BWOC Irradiated PET) Through the Herschel-Bulkley Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	56.5	17.8	0.316	12.1	******
2	72	20.6	0.286	12.1	******
3	91.6	24.6	0.268	12.1	******
4	117	30.6	0.262	12.1	******
5	149	39.4	0.264	12.1	******
6	190	52.3	0.276	12.1	******
7	242	71.4	0.296	12.1	******
8	308	99.6	0.324	12.1	******
9	392	141	0.36	12.1	******

Samples 3 & 6

Data Series Information
Name: CSR- Sample 3 1
Sample: Sample 3 - 0.2% BWOC BHET
Number of Intervals: 3
Application: RHEOPLUS/32 V3.40 21005258-33024
Device: MCR101 SN80866381; FW3.40D090210; Slot3
Measuring Date/Time: 3/15/2022; 11:24 AM
Measuring System: CC27/HR-SN23758; d=0 mm
Accessories: TU1=C-PTD200-SN80862123; DevCOM1=Physica VT 2

Interval: 1
Number of Data Points: 0

Time Setting: 1 Meas. Pts., Reject
Meas. Pt. Duration 0.5 min
Measuring Profile:
Shear Rate d(gamma)/dt = 5 1/s

Interval: 2
Number of Data Points: 0

Time Setting: 1 Meas. Pts., Reject
Meas. Pt. Duration 1 s
Measuring Profile:

Interval: 3
Number of Data Points: 20

Time Setting: 20 Meas. Pts., Reset Strain
Meas. Pt. Duration 10 s
Measuring Profile:
Shear Rate d(gamma)/dt = 5 ... 500 1/s log

Table 23C: Rheological Properties Measurements of Sample 3 (Oil Well Cement Slurry with 0.2% BWOC BHET).

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Speed [1/min]	Torque [µNm]	Status []
1	5	0.927	0.185	3.88	44.5	Dy_accu
2	6.37	1.25	0.197	4.94	60.2	Dy_accu
3	8.12	1.79	0.22	6.29	85.9	Dy_accu
4	10.3	2.49	0.24	8.02	119	Dy_accu
5	13.2	3.42	0.259	10.2	164	Dy_accu
6	16.8	4.65	0.277	13	223	Dy_accu
7	21.4	6.27	0.293	16.6	301	Dy_accu
8	27.3	8.46	0.31	21.1	406	Dy_accu
9	34.8	11.3	0.325	27	542	Dy_accu
10	44.3	15	0.339	34.3	720	Dy_accu
11	56.4	19.8	0.351	43.8	950	Dy_accu
12	71.9	26.1	0.363	55.8	1,250	Dy_accu
13	91.7	34.3	0.374	71.1	1,650	Dy_accu
14	117	45.1	0.386	90.5	2,160	Dy_accu
15	149	59.1	0.397	115	2,840	Dy_accu
16	190	76.6	0.404	147	3,670	Dy_accu
17	242	101	0.419	187	4,860	Dy_accu
18	308	131	0.424	239	6,270	Dy_accu
19	392	156	0.399	304	7,510	Dy_accu
*** 20 ***	500	180	0.359	388	8,620	Dy_accu

Data Series Information
Name: CSR- Sample 3 1 [Bingham I]
Sample: Sample 3 - 0.2% BWOC BHET
Number of Intervals: 1
Application: RHEOPLUS/32 V3.40 21005258-33024
Analysis Method: Bingham I
Analysis Result: tau0 = ---; eta_inf = 0.38045 Pa·s

Interval: 1
Number of Data Points: 18

Time Setting: -

Table 24C: Rheological Properties Measurements and Calculations of Sample 3 (Oil Well Cement Slurry with 0.2% BWOC BHET) Through the Bingham I Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Speed [1/min]	Torque [µNm]	Status []
1	6.37	1.11	0.175	******	******	******
2	8.12	1.78	0.219	******	******	******
3	10.3	2.63	0.254	******	******	******
4	13.2	3.71	0.281	******	******	******
5	16.8	5.08	0.302	******	******	******
6	21.4	6.83	0.319	******	******	******
7	27.3	9.07	0.332	******	******	******
8	34.8	11.9	0.343	******	******	******
9	44.3	15.5	0.351	******	******	******
10	56.4	20.2	0.357	******	******	******
11	71.9	26.1	0.362	******	******	******
12	91.7	33.6	0.366	******	******	******
13	117	43.1	0.369	******	******	******
14	149	55.3	0.372	******	******	******
15	190	70.8	0.374	******	******	******
16	242	90.6	0.375	******	******	******
17	308	116	0.376	******	******	******
18	392	148	0.377	******	******	******

Data Series Information
Name: CSR- Sample 3 1 [Herschel-Bulkley I]
Sample: Sample 3 - 0.2% BWOC BHET
Number of Intervals: 1
Application: RHEOPLUS/32 V3.40 21005258-33024
Analysis Method: Herschel-Bulkley I
Analysis Result: tau0 = ---; b = 0.24364; p = 1.0955

Interval: 1
Number of Data Points: 18

Time Setting: -

Table 25C: Rheological Properties Measurements and Calculations of Sample 3 (Oil Well Cement Slurry with 0.2% BWOC BHET) Through the Herschel-Bulkley Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Speed [1/min]	Torque [µNm]	Status []
1	6.37	1.23	0.193	******	******	******
2	8.12	1.79	0.221	******	******	******
3	10.3	2.53	0.244	******	******	******
4	13.2	3.48	0.264	******	******	******
5	16.8	4.73	0.282	******	******	******
6	21.4	6.36	0.297	******	******	******
7	27.3	8.49	0.311	******	******	******
8	34.8	11.3	0.324	******	******	******
9	44.3	14.9	0.336	******	******	******
10	56.4	19.6	0.347	******	******	******
11	71.9	25.7	0.358	******	******	******
12	91.7	33.7	0.368	******	******	******
13	117	44.2	0.378	******	******	******
14	149	57.8	0.389	******	******	******
15	190	75.6	0.399	******	******	******
16	242	98.8	0.409	******	******	******
17	308	129	0.419	******	******	******
18	392	168	0.429	******	******	******

Data Series Information
Name: CSR- Sample 6 1
Sample: Sample 6 - 1.0% BWOC BHET
Number of Intervals: 3
Application: RHEOPLUS/32 V3.40 21005258-33024
Device: MCR101 SN80866381; FW3.40D090210; Slot3
Measuring Date/Time: 3/15/2022; 12:08 PM
Measuring System: CC27/HR-SN23758; d=0 mm
Accessories: TU1=C-PTD200-SN80862123; DevCOM1=Physica VT 2

Interval: 1
Number of Data Points: 0

Time Setting: 1 Meas. Pts., Reject
Meas. Pt. Duration 0.5 min
Measuring Profile:
Shear Rate d(gamma)/dt = 5 1/s

Interval: 2
Number of Data Points: 0

Time Setting: 1 Meas. Pts., Reject
Meas. Pt. Duration 1 s
Measuring Profile:

Interval: 3
Number of Data Points: 20

Time Setting: 20 Meas. Pts., Reset Strain
Meas. Pt. Duration 10 s
Measuring Profile:
Shear Rate d(gamma)/dt = 5 ... 500 1/s log

Table 26C: Rheological Properties Measurements of Sample 6 (Oil Well Cement Slurry with 1.0% BWOC BHET).

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Speed [1/min]	Torque [µNm]	Status []
1	5.02	94.5	18.8	3.89	4,530	Dy_accu
2	6.31	94.8	15	4.89	4,550	Dy_accu
3	8.07	103	12.7	6.26	4,920	Dy_accu
4	10.4	110	10.6	8.04	5,290	Dy_accu
5	13.2	108	8.2	10.3	5,210	Dy_accu
6	16.8	107	6.39	13	5,160	Dy_accu
7	21.4	117	5.47	16.6	5,620	Dy_accu
8	27.3	132	4.85	21.1	6,340	Dy_accu
9	34.8	177	5.09	27	8,490	Dy_accu
10	44.3	185	4.16	34.4	8,860	Dy_accu
11	56.6	199	3.51	43.9	9,540	Dy_accu
12	72	211	2.94	55.8	10,100	Dy_accu
13	91.7	220	2.4	71.1	10,600	Dy_accu
14	117	234	2	90.6	11,200	Dy_accu
15	149	243	1.63	115	11,700	Dy_accu
16	190	252	1.33	147	12,100	Dy_accu
17	242	267	1.11	187	12,800	Dy_accu
18	308	308	1	239	14,800	Dy_accu
19	392	346	0.882	304	16,600	Dy_accu
*** 20 ***	500	386	0.772	388	18,500	Dy_accu

Data Series Information
Name: CSR- Sample 6 1 [Bingham I]
Sample: Sample 6 - 1.0% BWOC BHET
Number of Intervals: 1
Application: RHEOPLUS/32 V3.40 21005258-33024
Analysis Method: Bingham I
Analysis Result: tau0 = 170.9 Pa; eta_inf = 0.4473 Pa·s

Interval: 1
Number of Data Points: 11

Time Setting: -

Table 27C: Rheological Properties Measurements and Calculations of Sample 6 (Oil Well Cement Slurry with 1.0% BWOC BHET) Through the Bingham I Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Speed [1/min]	Torque [µNm]	Status []
1	34.8	186	5.36	******	******	******
2	44.3	191	4.3	******	******	******
3	56.6	196	3.47	******	******	******
4	72	203	2.82	******	******	******
5	91.7	212	2.31	******	******	******
6	117	223	1.91	******	******	******
7	149	237	1.6	******	******	******
8	190	256	1.35	******	******	******
9	242	279	1.15	******	******	******
10	308	309	1	******	******	******
11	392	346	0.883	******	******	******

Data Series Information
Name: CSR- Sample 6 1 [Herschel-Bulkley I]
Sample: Sample 6 - 1.0% BWOC BHET
Number of Intervals: 1
Application: RHEOPLUS/32 V3.40 21005258-33024
Analysis Method: Herschel-Bulkley I
Analysis Result: tau0 = 143.35 Pa; b = 3.4789; p = 0.67091

Interval: 1
Number of Data Points: 11

Time Setting: -

Table 28C: Rheological Properties Measurements and Calculations of Sample 6 (Oil Well Cement Slurry with 1.0% BWOC BHET) Through the Herschel-Bulkley Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Speed [1/min]	Torque [µNm]	Status []
1	34.8	181	5.2	******	******	******
2	44.3	188	4.23	******	******	******
3	56.6	196	3.46	******	******	******
4	72	205	2.84	******	******	******
5	91.7	215	2.35	******	******	******
6	117	228	1.95	******	******	******
7	149	243	1.63	******	******	******
8	190	261	1.37	******	******	******
9	242	282	1.16	******	******	******
10	308	306	0.993	******	******	******
11	392	335	0.853	******	******	******

Sample 9

Data Series Information

Name: CSR- Sample 9 1

Sample: Sample 9 - 1.8% BWOC BHET

Table 29C: Rheological Properties Measurements of Sample 9 (Oil Well Cement Slurry with 1.8% BWOC BHET).

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	5.55	292	52.6	******	******
2	6.73	230	34.2	******	******
3	8.42	185	21.9	******	******
4	10.4	162	15.6	******	******
5	13.3	153	11.5	******	******
6	16.9	122	7.23	******	******
7	21.6	117	5.4	******	******
8	27.2	102	3.76	******	******
9	34.7	86.7	2.49	******	******
10	44.4	73.1	1.65	******	******
11	56.6	61.3	1.08	******	******
12	72	56	0.779	******	******
13	91.7	55.5	0.605	******	******
14	117	57.4	0.492	******	******
15	149	63.9	0.429	******	******
16	190	73.5	0.387	******	******
17	242	87.5	0.362	******	******
18	308	116	0.377	******	******
19	392	188	0.479	******	******
*** 20 ***	500	168	0.336	******	******

Data Series Information

Name: CSR- Sample 9 1 [Bingham I]

Sample: Sample 9 - 1.8% BWOC BHET

Table 30C: Rheological Properties Measurements and Calculations of Sample 9 (Oil Well Cement Slurry with 1.8% BWOC BHET) Through the Bingham I Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	91.7	49.2	0.536	20.1	0.317
2	117	57.1	0.489	20.1	0.317
3	149	67.3	0.452	20.1	0.317
4	190	80.2	0.423	20.1	0.317
5	242	96.6	0.4	20.1	0.317
6	308	118	0.382	20.1	0.317
7	392	144	0.368	20.1	0.317

Data Series Information

Name: CSR- Sample 9 1 [Herschel-Bulkley I]

Sample: Sample 9 - 1.8% BWOC BHET

Table 31C: Rheological Properties Measurements and Calculations of Sample 9 (Oil Well Cement Slurry with 1.8% BWOC BHET) Through the Herschel-Bulkley Model.

Meas. Pts.	Shear Rate [1/s]	Shear Stress [Pa]	Viscosity [Pa·s]	Yield Stress [Pa]	Infinite Shear Viscosity [Pa·s]
1	91.7	56.1	0.612	53.8	******
2	117	58.3	0.499	53.8	******
3	149	62.7	0.421	53.8	******
4	190	71.2	0.375	53.8	******
5	242	87.8	0.364	53.8	******
6	308	120	0.391	53.8	******
7	392	184	0.469	53.8	******

APPENDIX D

Table 1D: API Cement Classes with Respective Typical Clinker Phase Compisitions, Well Depth and Temperature Ranges for Application, as well as Degrees of Sulfate Resistance

API CLASS	TYPICAL POTENTIAL PHASE COMPOSITION (%)				DEPTH (km)	TEMPERATURE (℃)	SULPHATE RESISTANCE
	C3S	C2S	C3A	C3AF			
A	53	24	8	8[1]	0-1830[1]	44–94[1]	Normal
	53	24	8	8[2]	0-1830[5]	26.67 – 76.67[3]	
	45	27	11	8[6]	0-1830[3]	26.67 – 76.67[5]	
	–	–	–	–	0-1830[6]		
AVERAGE	50.33	25	9	8[1,2,6]	0-1830[1,3,5,6]	32.45–82.45[1,3,5]	
B	47	32	5	12[1]	0-1.83[1]	44–94[1]	Moderate & High
	47	32	5	12[2]	0-1.83[3]	26.67 – 76.67[3]	
	44	31	5	13[6]	0-1.83[5]	26.67 – 76.67[5]	
	–	–	–	–	0-1.83[6]	–	
AVERAGE	46	31.67	5	12.33[1,2,6]	0-1.83[1,3,5,6]	32.45–82.45[1,3,5]	
C	58	16	8	8[1]	0-1.83[1]	44–94[1]	Normal, Moderate, & High
	58	16	8	8[2]	0-1.83[3]	26.67 – 76.67[3]	
	53	19	11	9[6]	0-1.83[5]	26.67 – 76.67[5]	
	–	–	–	–	0-1.83[6]	–	
AVERAGE	56.33	17	9	8.33[1,2,6]	0-1.83[1,3,5,6]	32.45–82.45[1,3,5]	
D	26	54	2	12[1]	1.83-3.05[1]	94–144[1]	Moderate & High
	26	54	2	12[2]	1.83-3.05[3]	76.67-143.33[3]	
	28	49	4	12[6]	1.83-3.05[5]	76.67-143.33[5]	
	–	–	–	–	1.83-3.05[6]	–	
AVERAGE	26.67	52.33	2.67	12[1,2,6]	1.83-3.05[1,3,5,6]	82.45–143.55[1,3,5]	
E	26	54	2	12[1]	1.83-4.27[1]	94-144[1]	Moderate & High
	26	54	2	12[2]	1.83-4.27[6]		
	38	43	4	9[6]	–		
	–	–	–	–	–		

AVERAGE	30	50.33	2.67	11[1,2,6]	1.83–4.27[1,6]	94-144[1]	
G	50	30	5	12[1]	0-2.44[1]	44-111[1]	Moderate & High
	50	30	5	12[2]	0-2.44[3]		
	50	30	5	12[6]	0-2.44[5]		
AVERAGE	50	30	5	12[1,2,6]	0-2.44	44-111[1]	
H	50	30	5	12[1]	0-2.44[1]	44-111[1]	Moderate & High
	50	30	5	12[2]	0-2.44[3]		
	50	30	5	12[6]	0-2.44[5]		
AVERAGE	50	30	5	12[1,2,6]	0-2.44[1,3,5]	44-111[1]	

1. Pikłowska (2017)
2. Mixhaux, Nelson, and Vidick, (1989)
3. Teodoriu, Yi, and Salehi (2019)
4. Nelson and Guillot (2006)
5. Yi (2019)
6. Hıdıroğlu (2017)