Petroleum and Coal

**Article** **Open Access**

# Hybrid Modification of Eco-Friendly Biodegradable Polymeric Films by Humic Substances from Low-Grade Metamorphism Coal

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Received October 15, 2021, Accepted March 16, 2022

**Abstract**

The devastating effect of the operational failure of a cementing job is enormous. Additives used for cement slurry recipe contribute substantially to the total cause of an operational failure. Therefore, it is imperative that a paradigm shift that addresses the challenges of cementing failure be considered. A comparative analyses were performed with imported polymer (Hydroxyethylcellulose) as against local polymers (cassava starch) for cement slurry design to determine fluid loss. Polymer's concentration of 0.1% by weight of cement was used for the cement slurry design, in order to characterize their fluid loss. Experimental study of cement slurry density of 14ppg and 15.8ppg at temperatures of 80ºF (29ºC) and 190ºF (88ºC) and the result of the local-based polymers (cassava starch), namely; 96/1632 (PG1); 98/0505 (PG2) and 92/0057 (PG3) were ascertained; for 96/1632 (PG1) as temperature increased then decreased in fluid loss, 289 to 95 cc/30min; for 98/0505 (PG2) the fluid loss decrease from 293 to 98 cc/30min; for 92/0057 (PG3) it decreases from 346 to 105 cc/30min and HEC decreased from 247 to 91 cc/30min. A cement slurry density of 15.8ppg of the same concentration and temperatures, results showed that for 96/1632 (PG1) as temperature increased there was a corresponding decreased in fluid loss from 103 to 43 cc/30min; for 98/0505 (PG2) the fluid loss decreased from 121 to 53 cc/30min; for 92/0057 (PG3) the fluid loss decreased from 136 to 61cc/30min and for HEC the fluid loss decreased from 151 to 69 cc/30min.

***Keywords**: Cement-slurry; Fluid-loss; Hydroxyethylcellulose; Green chemistry; Cassava starch.*

## 1. Introduction

Separating different producing zones is usually done through cementing operations to protect the well from harsh underground conditions. Zonal isolation depends on a set of parameters generally classified into four. The first group is concerned with cement sheath properties which directly affect well productivity. The second group describe design parameters needed for ensuring consistency in cement physical and chemical properties. The third considers special cementing operations for intervening in various situations like squeeze cementing etc. The last group entails job evaluations that comes after cement slurry is placed.

Given that the first two categories determine largely the nature of cement design and cement-reservoir interactions, they are frequently considered as hugely important in oil and gas drilling. This explains why after a successful drilling, various producing zones are sealed off from communicating. This practice is very good both from a reservoir and cement points of view. This is because zonal isolation preserves reservoir conditions around the wellbore while also stopping fluid migrations which is detrimental to well integrity. The durability of oil or gas well is dependent on the absolute binding of the cement structures and ought to deliver its intended service [2]. The authors further stated economy, safety, and environmental factors as factors affecting durability. "The restriction of fluid movement between zones and protection of casing from corrosion as well as closing non-productive well could be achieved by the used of cement in drilling operations [3].

Fluid influx has short term consequences like loss of composition, and it can also cause longer term problems including gas migration [4]. Hence, many well currently are facing these problems of gas leakages and persistent casing pressures. Some of these problems have proven difficulty in tackling in the past. Because of complex conditions downhole, several chemicals referred to as additives are usually needed in the design of optimum cement slurries to improve desired American Petroleum Institute (API) properties. At different temperature conditions of oil or gas well, firm and absolute placement of cement slurries are required along the wellbore and an even filled with the annular volume. However, fluid loss additives are needed to prevent water encroachment in or out the formation, while free water additive is a key ingredient of cement slurry design towards achieving zero percent free water at formation temperature.

The property of slurries that should be reduced to be bearest minimum when cement set its free water content [5]. Other vital properties include plastic viscosity, gel strength, yield point, fluid loss and dynamic settling properties. The right slurry design should at least possess the ability to prevent particle settling and still possess enough rheological properties to prevent free water incidence. This is because presence of free water is usually a sign of improper design which adversely affects topsides when cement set. The loss of integrity following this phenomenon can lead to other challenges like gas migration as proper sealing ability cannot be guaranteed using this kind of slurries. It can also increase the incidence of corrosion due to infiltration of formation water.

Field experience has shown that cement behavior remains very difficult to predict and extensive design and testing is required to adjust and optimize almost each and every job. Sometimes, variability can be so dramatic that some additives performance can be completely lost in some cement grades [1]. Thus, there is usually dramatic effects in fluid loss at any slight temperature increase. Cement response to additives is closely monitored at every stage of a job implementation [6]. Fluid loss is essential to allow an even placement of cement and ensure acceptable cement hydration. It is advocated that once the cement is placed, the water to cement ratio is kept within acceptable limits and cement hydration, for instance, consolidation will take place as designed and that mechanical properties will develop as scheduled.

The focus of this study is on fluid loss control during placement; cement, in this case, is at the very early stages of its hydration and within the induction period. Pre-induction period, fast dissolution and precipitation processes occur and modify the surfaces of all mineral phases present in the cement [7]. Of course, most times the pre-induction period lasts a few minutes. It was observed that a very limited reaction activity of very slightly hydrated cement enters the induction period. Cement is pumped downhole and placed against the formation during this induction phase. For high-temperature application, retarders are added in order to maintain cement in the induction phase throughout the pumping time [1]. Conventional copolymers generally comprises 2-Acrylamido-2-methyl propane sulfonic acid [8]. Study on the mechanism of action of these polymers has equally been carried out [9-10,12]. And it was discovered that the performance is directly linked to adsorption of the polymer on the cement surface. Again this adsorption is electro-statically driven, anionic sulfonate groups from the "AMPS" monomeric units adsorbs onto the cationic sites on the cement [11-12].

The objective of this study is to evaluate the effectiveness of storage amylose/amylopectin based polymer such as cassava starch as cementing additive to control fluid loss and compare it with the structural cellulose-based polymer such as hydroxyethylcellulose-HEC). The benefit of the storage polymer is that it promotes the principle of green chemistry, however, the benefits are not only health and environment-related, but also economical, as the costs of storage, regulation and protecting workers and the public from exposure to hazardous chemicals are reduced.

## 2. Material and methods

Raw samples were collected from the South-East geopolitical zone of Nigeria. Preparation of the raw samples was done in accordance with the Food and Agricultural Organization procedures. Thereafter, laboratory analyses were conducted to ascertain American Petroleum Institute, standard to ensure it meets specifications prior to usage.

### 2.1. Cement slurry design

The main aim of slurry design should be to produce slurries that can withstand the rigours of field application. In achieving that proper mixing using standard equipments, proper placing and thickening time is needed. While the stability of the slurry is equally critical during the whole process. Most time, optimization is carried out to ensure proper design for a good cementing job.

Dry samples of three cultivars were used for the experiments. Two different cement slurry densities; 14 and 15.8ppg were prepared with 0.10% BWOC polymer concentration as shown in Table 2. Samples were weighed and then blended uniformly before added to the mixing fluids. Standard CTC constant speed mixer (Model-7000) of 1.2L capacity was used to an obtained homogenous mixture. The mixer motor was turned on and maintained at (4000±200 rpm) according to API RP10-2B procedure. Water and liquid additives were turned to thoroughly disperse before cement addition. Cement and solid additives were blended for about 15 seconds. After all addition, mixing speed was increased to 12000±500 rpm for 35 seconds. Cement and solid additives and water temperature were kept at 23±1.1°C before mixing.

#### *2.1.1. API fluid loss test*

Static fluid loss experiments were performed and conditioned for 20 minutes at temperatures ranging from 80°F (29°C) to 190°F (88°C) using atmospheric consistometer according to API standard [13]. A standard 175ml filtration cell fitted with a 45µm (325) mesh screen supplied by OFI Testing equipment (Houston, USA) was used. The operating procedure and test conditions are detailed in API 10-B norm [14]. The conditioned slurry was placed in the preheated fluid loss cell (the fluid loss cell was heated in the heating jacket prior to conditioning). Nitrogen was used to apply 1000psi (60 bars) on top of the cell. The test started when the bottom outlet was opened to atmospheric pressure. The filtrate was collected, measured and plotted against time. It was ensured that filtration lasted for 30minutes without nitrogen breakthrough.

Calculation of fluid loss: if however, filtration proceeds for 30minutes without nitrogen breakthrough, then; $V_{API} = 2V(t_{30})$. In the case of nitrogen blowout, the test was stopped and reported API volume was calculated as: $V_{API} = 2V_{(breakthrough)}\sqrt{\frac{30}{t_{breakthrough}}}$.

### 2.2. Materials

#### *2.2.1. Cement and additives*

The cement grade used for the study is the certified HSR class G cement and corresponds to AOI specifications (API 10 A), derivatized imported polymer HEC) and local polymers (cassava starch), antifoam (FP-30L) and freshwater

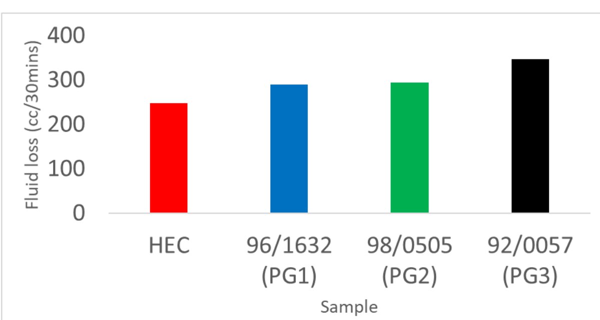


Figure 1. Fluid loss of different samples of polymers at 80°F (29°C) of 14ppg cement slurry

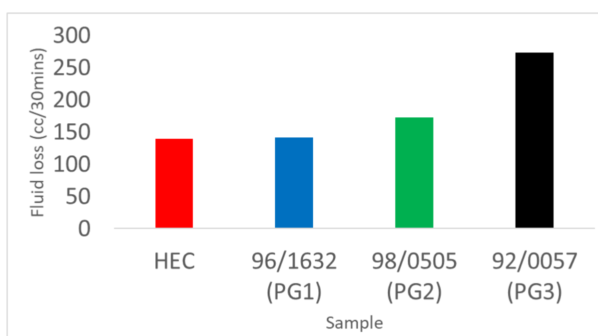


Figure 2. Fluid loss of different samples of polymers at 120°F (49°C) of 14ppg cement slurry

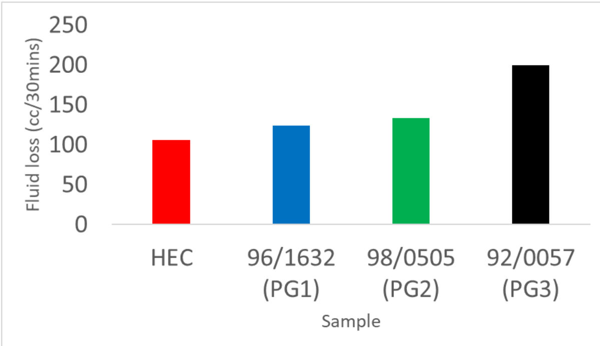


Figure 3. Fluid loss of different samples of polymers at 150°F (66°C) of 14ppg cement slurry

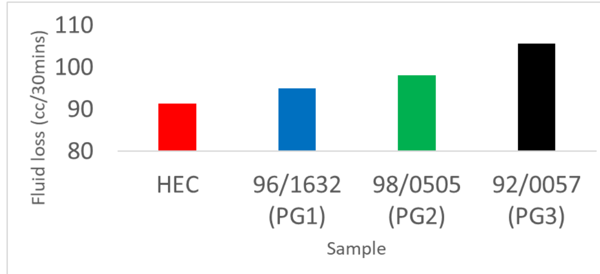


Figure 4. Fluid loss of different samples of polymers at 190°F (88°C) of 14ppg cement slurry

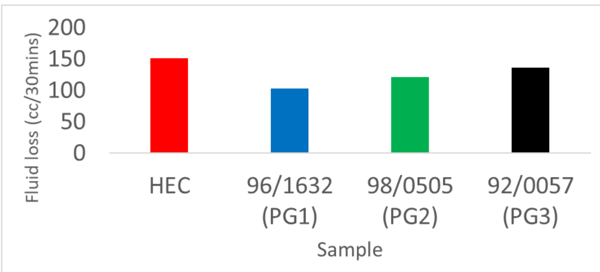


Figure 5. Fluid loss of different samples of polymers at 80°F (29°C) of 15.8ppg cement slurry

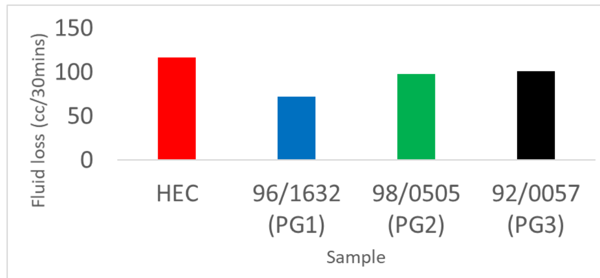


Figure 6. Fluid loss of different samples of polymers at 120°F (49°C) of 15.8ppg cement slurry

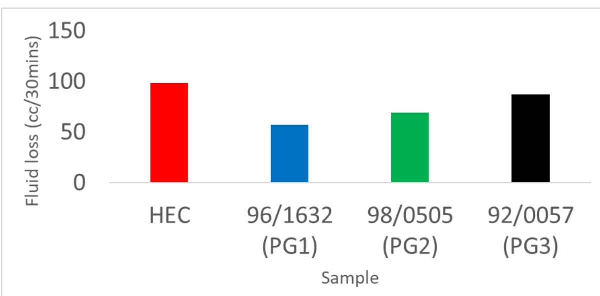


Figure 7. Fluid loss of different samples of polymers at 150°F (66°C) of 15.8ppg cement slurry

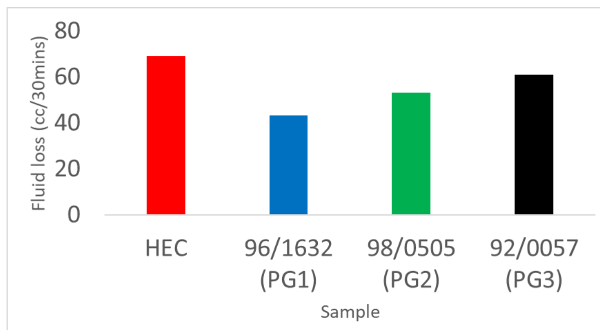


Figure 8. Fluid loss of different samples of polymers at 190°F (88°C) of 15.8ppg cement slurry

### 2.3. Impact of imported and local polymers on cement slurries fluid loss

Fluid loss control is essential for cementing to prevent fluid migration and segregation. Performance of three local-based polymers 96/1632 (PG1); 98/0505 (PG2) and 92/0057 (PG3) were studied and compared with HEC based polymer to determine effectiveness in preventing fluid loss as depicted in Figures 2.1 to 2.8. For cement slurry density of 14ppg, at temperatures of 80°F (29°C) to 190°F, results showed that for 96/1632 (PG1) as temperature increased there was a corresponding decreased in fluid loss from 289 to 95 cc/30min; for 98/0505 (PG2) the fluid loss decrease from 293 to 98 cc/30min; for 92/0057 (PG3) it decreases from 346 to 105 cc/30min and HEC decreased from 247 to 91 cc/30min. A cement slurry density of 15.8ppg of the same concentration and temperatures, results showed that for 96/1632 (PG1) as temperature increased there was a corresponding decreased in fluid loss from 103 to 43 cc/30min; for 98/0505 (PG2) the fluid loss decreased from 121 to 53 cc/30min; for 92/0057 (PG3) the fluid loss decreased from 136 to 61cc/30min and for HEC the fluid loss decreased from 151 to 69 cc/30min.

Experimental results here have shown that cassava starch compared favourably with hydroxyethylcellulose. It should be noted that, field experience in a number of application shows that most operators accept fluid loss values below 200 to 250 cc/30min. However, for casing or narrow annulus liner jobs in permeable zones, below 50 or even 15 are needed. A 15.8 ppg slurry without fluid-loss additives will have values higher than 1500 ml./30 min [1]. Therefore, the result of this work proves that cassava starch could be a good substitute as fluid loss reducers for cement slurry design. The local-based cement slurry polymer cassava starch (96/1632 (PG1) performed favorably with the imported based cement slurry polymer HEC, with local based cement slurry polymers 98/0505 (PG2) and 92/0057 (PG3) having better fluid loss control. The study revealed that local polymers (cassava starch) reduced fluid loss in cement slurry density of 14ppg and 15.8ppg. However, 0.1% by weight of cement of cassava starch reduced fluid loss with increase in temperature.

### 2.4. Analysis of variance of fluid loss of imported and local based cement slurry polymers

Table 2.1 result showed that for cement slurry design of 14 ppg, the average fluid loss of HEC was 145.93 (SD = 70.25), while the average of PG1, PG2, and PG3 were 162.63 (SD = 86.71), 174.48 (SD = 85.22) and 231.38 (SD = 103.04) respectively. Thus indicating no significant difference between the fluid loss of the four different polymers used as viscosifier. This result pretty indicates that PG1, PG2, and PG3 polymer can be used as a substitute for HEC. Results from a further investigation using SPSS 22 software showed that for fluid loss there was no significant difference among the polymers. Similar results were also noticed for cement slurry design for 15.8 ppg, with no significant difference.

Table 2. Analysis of Variance for Fluid loss

| Polymer | Cement slurry design for 14ppg Fluid loss (cc/30min) | Cement slurry design for 15.8ppg Fluid loss (cc/30min) |
|---|---|---|
| HEC | 145.93$^{a}$ | 108.9$^{a}$ |
| PG1 | 162.63$^{a}$ | 68.78$^{a}$ |
| PG2 | 174.48$^{a}$ | 85.25$^{a}$ |
| PG3 | 231.38$^{a}$ | 96.25$^{a}$ |

## 3. Conclusions

A fluid loss in cement slurry was minimized with Local cassava starch (96/1632 (PG1) when compared with imported HEC polymer. Also, cassava starches 98/0505 (PG2) and 92/0057 (PG3) minimized the fluid loss in cement slurry but little below when compared with an imported polymer. As the temperature increased from 80°F to 190°F there was a corresponding decrease in fluid loss. Local cassava starch exhibited excellent fluid loss at cement slurry density of 15.8ppg because it was below 200 cc/30mins which is in line with field acceptable value stated by other investigators and researchers. However, for critical jobs like narrow annulus liner or casing job across permeable hydrocarbon zones, values below are required for fluid loss. Also, at cement slurry density of 14ppg, the fluid loss was minimized at temperatures of 120°F to 190°F.

Statistical analysis obtained revealed that there was no significant difference between the imported HEC polymer and local polymers (cassava starches). Local cassava starch 98/0505 (PG2) had the highest mean plastic viscosity at 14ppg. This shows that local cassava starch PG2 was slightly better than imported polymer hydroxyethylcellulose. This product is unique in that apart from its ability to reduce fluid loss with an increase in temperature, it is self-active, and also supports the principle of green chemistry due to its environmental friendliness.

***Acknowledgments***

*Authors wish to acknowledge World Bank Africa Centre of Excellence in Oilfield Chemicals Research (ACE-CEFOR), University of Port Harcourt Nigeria for support. Thanks to Baker Hughes Incorporated, Nigeria and Pollution Control and Environmental Management (POCEMA) Limited, Port Harcourt, where experimental work was conducted. This study was supported by National Root Crop Research Institute (NRCRI), Umudike.*

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