Investigation of the Thermal Stability of Extracted Lignin - Based Oil - Well Cement

Antony Fundia Simbiri1, Ogbonna F. Joel1, Emmanuel E. Okoro2, Daniel O. Oyoo4

1World Bank Africa Center of Excellence, Center for Oilfield Chemicals Research, University of Port Harcourt, Port Harcourt, Nigeria
2Department of Petroleum Engineering, 1World Bank Africa Center of Excellence, Center for Oilfield Chemicals Research, University of Port Harcourt, Port Harcourt, Nigeria
3Department of Gas and Petroleum Engineering, Kenyatta University, Nairobi, Kenya

Abstract: For the use of polymeric materials in the various, continuously expanding industrial applications, thermal stability is essential. It is crucial to have a thorough grasp of thermal stability and the kinetic mechanisms at play when designing materials for a particular application. The aim of this work was to establish the thermal stability of lignin-based oil-well cement. First, the thermal stability of lignin extracted from SCB was evaluated. The initial weight-loss temperature (Td) of the lignin-based cement sample which takes place when there is 5% loss of its weight, was at 78.5°C. Due to the production of highly condensed aromatic structures, more than 50% of the lignin cement sample was still un-volatilized by 600°C. Additionally, by 623°C, 85.5% of the lignin-based cement sample was still un-volatilized. The initial weight-loss temperature (Td) of the sodium lignosulfonate-based cement sample, was at 73°C. By 600°C the sodium lignosulfonate cement sample had lost up to 21% of its mass, which is higher than the 13.5% recorded for the lignin-based cement sample. This suggests that the thermal stability of sodium lignosulfonate-based cement is lower than the lignin-based cement slurry in high temperature zones. Consequently, the thermal stability of oil-well cements, especially in HPHT environments can be enhanced by the addition of SCB-based lignin into the cement slurry.

Keywords: Degradation, initial weight - loss temperature, thermal stability, lignin, thermogravimetric analysis, sodium lignosulfonate

1. Introduction

For the use of polymeric materials in the various, continuously expanding industrial applications, thermal stability is essential. It is crucial to have a thorough grasp of thermal stability and the kinetic mechanisms at play when designing materials for a particular application [1], [2]. The impact of this parameter on the various polymers that make up a mix is quite crucial. The thermal stability of the blends is significantly influenced by the compatibility of specific polymers [3], [4].

It has been discovered that, in addition to heat, there are other variables that contribute to the thermal degradation of polymers, [3]. The mechanism of heat degradation of different polymers or their mixtures varies as a result. It appears that variances can arise even within the same type of polymer. Therefore, environmental conditions, the composition of the polymer, blending effectiveness, other current chemicals, etc. are the main elements that significantly influence the degradation of polymer blends.

The study's analysis of the thermal characteristics of SCB-reinforced cement composites showed that, in comparison to cement composites formed of alkaline bagasse, the addition of SCB to cement lowers the cement composites' thermal conductivity and produces a weaker specific heat [5]. The findings also showed that the cement composite got lighter and had a lower thermal conductivity the more SCB fibers were added to the cement. Similar to these studies, [6] conducted on the effects of high temperatures on self-compacting concrete with high levels of metakaolin and sugarcane bagasse ash (SCBA) found that these materials are less sensitive to high temperatures than room temperature, exhibiting less cracking and strength losses.

For example, a multilayer array of ligno-cellulosic materials positioned in the midst of two precast panels was designed to address thermal stability. The findings showed that the introduction of coconut fibers reduces the concrete's heat conductivity [7]. This implies that additional research into the qualities of thermal stability for particular ligno-cellulosic materials under various conditions is necessary.

The usage of nanoparticles is one method that researchers have adopted to solve the problem of the thermal stability of ligno-cellulosic materials at high temperatures. The oil and gas business has been predicted to benefit from nanotechnology. There have also been some quite intriguing discoveries related to the application of nanotechnology in cement slurry additives. Several academics have been working hard in this area [8], [9]. Given the requirement for the inclusion of various components in the cement-like plasticizers, it has been demonstrated that the addition of nanoparticles to cement slurry can reduce the workability [10]. Cement pastes were shown to have quicker initial and final setting times, proving that silica fume and nanosilica improved cement hydration [11]. Nanosilica further improves fluid loss control, final compressive strength, early strength development, and the potential for a broad temperature application [12].

In fact, research into nanotechnology is gaining significant momentum. And this is quite energizing. But even cutting-edge nanotechnology has its limitations. The development of
nanotechnology is expensive. The cost of nanoparticles is high [13]. Compared to bulk materials, the production of nanoparticles requires a significant increase in energy consumption per mass [14]. The lack of commercially available nanoparticles for the oil and gas industry is a risky barrier. This is despite the enormous sums of money that several significant oil service companies have invested in nanotechnology.

Additionally, nano - particles' efficacy is still lacking. It is incredibly rare for academics and oil professionals to work closely together to validate and test nanomaterials in actual field settings after conducting benchwork in world - class laboratories. Few oil corporations are willing to take a chance on everything for a technology that is still mired in debate, despite the fact that the application, initiation, and acceptance of new technologies traditionally require time, energy, and resources. In reality, very few field tests involving nanoparticles have been conducted [15]. Finally, the production of these nanoparticles is typically risky, harmful to the environment, and poisonous [16]. Due to their small size and high surface - to - area ratio, nanoparticles have a high likelihood of being absorbed through the skin or even inhaled [17]. In fact, there is yet no clear response to the question of the ecological index of spent drilling mud using nanomaterials as additives or even in the oil well cementing.

As can be seen, there is still a long way to go in nanotechnology. Yet the oil and gas business must deal with the problem of shrinkage at high temperatures right away rather than waiting. Thus, the need for searching for affordable, non - toxic, environmentally friendly alternatives remains. We aim to show that ligno - cellulosic materials are the way forward in this effort. In an attempt to warrant the use of lignocellulosic materials, we sought to establish how lignin would behave in high temperatures and thus proceeded in evaluating the thermal stability of lignin in cementing operations. Thermogravimetric analysis (TGA) was conducted on lignin, 0.4% lignin - based cement and 0.04% sodium - lignosulfonate based cement. In our view, such an assessment of the thermal stability of SCB extracted lignin - based cement remains a virgin research zone.

2. Methodology

The first test was on lignin sample.5.972 mg of the extracted lignin was weighed on a 13mg pan and analyzed. The device used is a TGA50 Shimadzu using detector TA - 60WS. The inert gas nitrogen flow rate was 50ml/minute. The sample pan was lowered into the furnace and heating was done at intervals of 10°C under inert condition of nitrogen gas. The sample was heated until it reached a temperature of 600°C and the weight loss was recorded. The same procedure was conducted for lignin - based cement sample and sodium lignosulfonate - based cement sample.

3. Results and Discussion

Thermo - Gravimetric Analysis of Extracted Lignin

The result is shown in Figure 1. Three stages of lignin breakdown take place, (the light blue lines indicate the changes). In the first phase, the thermogram shows a gradual decrease from 33.39°C to 64.62°C. There is a weight loss of 1.271%. This is followed by a wide and flat endothermic peak that gently slopes. The initial weight - loss temperature (Ti) of the extracted lignin, was at 312°C. From 263.02°C, the thermogram shows a sharp exothermic rate in degradation, with a recorded weight loss of 18.87% until 367.78°C.

![Figure 1: TGA curve for extracted lignin. (Source: Author 2023)](image-url)
Thermo - Gravimetric Analysis of Lignin - Based Cement Slurry

To supplement the above information on the thermal stability of the extracted lignin, we sought to comprehend the thermal stability of lignin - based cement slurry. The procedure of analysis was similar to the above - described method. The results and consequent investigation of its effect is elucidated below. The cement slurry was prepared using cement Class G with a density of 16ppg, with various additives including anti - foam additive, fluid loss additive, dispersant additive and retarder additive. The concentration of lignin in the cement slurry was 0.4% (bwoc). Deionized water was used in mixing the slurry.

Figure 2 shows the thermal degradation of 0.4% lignin - containing cement slurry. The outcomes demonstrated that heat degradation of lignin - containing cement slurry may be separated into four stages (the red lines show point of change). Initially, the first stage was seen at 23 to 123 °C because the lignin sample was losing moisture [18]. The initial weight - loss temperature (T$_l$) of the lignin - based cement sample which takes place when there is 5% loss of its weight, was at 78.3°C. At temperatures of between 123 and 423°C, the second stage, was seen. The third stage, which was seen to occur in the temperature range between 423 and 473°C. In the final stage, the degradation of lignin occurred above 473°C. In this phase, the degradation plot bears a nearly plateau form.

Thermo - Gravimetric Analysis of Sodium Lignosulfonate Based Cement

As reported earlier by previous scholars [19], lignosulfonates have a strong impact on the evolution of hydration. A revelation on the profile of this hydration under heat is vital since some of the BHCT are very high. Figure 3 shows the thermal degradation of 0.04% Sodium lignosulfonate containing cement slurry. The outcome reveals a similar degradation in comparison with the lignin containing cement slurry. The degradation may be grouped into four stages. However, a significant change in degradation takes place at 473°C (the green colored line). The plot becomes turbulent. A significant drop in mass of approximately 7% is recorded, with the residue at 600°C making up to 21% of the initial mass.
Figure 3: TGA curve for 0.04% Sodium Lignosulfonate - based cement slurry. (Source: Author 2023)

Thermodynamic mechanisms that include mass and heat transfer typically affect how the extracted lignin degrades thermally, [20], due to the multiple oxygen functional groups in its structure having varied thermal stabilities, and their scission taking place at different temperatures, occurring throughout a wide temperature range. In the first phase, the thermogram shows a gradual decrease (Figure 1). The lack of moisture is to blame for this weight loss [21] and low molecular compounds. This is followed by a wide and flat endothermic peak that gently slopes. This is associated with the primary lignin pyrolysis [22]. As a result of this degradation, inter-unit connections are broken, releasing monomeric phenols into the vapour phase [23], and this precipitates the drastic degradation process that follows. The second stage is linked to the breakdown of lignin's carbohydrate components, which are transformed into volatile gases like CO, CO₂, and CH₄ [24]. The initial weight - loss temperature (Tᵢ) of the extracted lignin, this is the degree at which the sample weighs 5% less, was also recorded. The degradation process may be connected to the gradual breakdown of certain aromatic rings in lignin above 367.78°C [25]. By 600°C, more than 50% of the lignin sample was still un-volatilized due to the formation of highly condensed aromatic structures [23].

On the other hand, lignin - based cement slurry had slightly differing results (Figure 2). The outcomes demonstrate that heat degradation of lignin - containing cement slurry may be separated into four stages (the red lines show point of change). Initially, the first stage the lignin sample was losing moisture, a coincidence with the previous work of [18]. The initial weight - loss temperature (Tᵢ) of the lignin - based cement sample, was at 78.3°C. This is significantly lower than the initial weight - loss temperature (Tᵢ) of the extracted lignin. This was expected since a large percentage of the lignin - based cement sample was water. And therefore, as the temperature rose, so did the evaporation. When hydrated materials are put through thermal tests, the temperature range at which chemically bonded water is lost varies depending on a number of factors, including the weight - to - cement ratio, the age of the cement, and the amount of polymer used [26].

Later the second stage is recorded, which displays the breakdown of volatile compounds (such as CO, CO₂, CH₄, and β - O - 4’ linkages due to the cleaving of the side chains), which is agreement with previous studies [27], [28]. The loss of chemically coupled water with every hydrated phase present in the slurry, including hydrated calcium silicate and ettringite, is what causes any further dehydration at this stage, [26]. Given that it is known that tiny anions can replace sulfate anions in ettringite, the creation of ettringite is apparently a consequence of the lignosulfonates' templating potential [29]. But since the weight loss is significantly low, then hydrated complexes are significantly stable. This modest loss brought on by hydration products is consistent with findings from past investigations [30]. The third stage of the lignin - based cement sample saw the dissolution of the aromatic rings and the cleavage of the C - C connections and 5 - 5’ linkages [31]. The breakdown of the aromatic ring and condensation process took place above 473°C in the last step. In this phase, the degradation plot bears a nearly plateau form. It is vital to note that at this temperature of 473°C, the weight loss of the lignin - based cement slurry is approximately 13.5%. There is a slight increment of around 1% in the weight loss up to 623°C. Cumulatively, this implies that 85.5% of the lignin - based cement sample was still un-volatilized.

It was shown that the thermal stability of lignin - based cement slurry was much higher than that of pure lignin when compared to the TGA of lignin. This is most likely a result of extremely condensed aromatic structures forming after adhering to the C - S - H complex, [23].
On the other hand, sodium lignosulfonate - based cement slurry had slightly differing outcome (Figure 3). The results reveal that heat degradation of sodium lignosulfonate containing cement slurry may be separated into three stages (the green line show point of change). The initial weight loss temperature (T1) of the sodium lignosulfonate - based cement sample lost 5% of its weight, was at 73°C. This is significantly lower than the initial weight loss temperature (Ti) of the lignin - based cement sample. This might be explained by the cement slurry sample's residual moisture having been removed. However, the sodium lignosulfonate cement sample shows a similar degradation profile as that of the lignin - based cement sample, up to 473°C. Whereas the lignin - based cement sample retains a steady gradual degradation, the sodium lignosulfonate demonstrates a sharp change.

The sudden intense turbulent change observed in the thermogram of Sodium lignosulfonate containing cement is attributed to the deteriorative effect of sulfonyl groups on thermal properties of polymer materials. Adding organic sulfonates to hydrated calcium aluminates results in lamellar formations [32]. These are large anionic templates that form around the calcium aluminate columns. This is in agreement with the observations earlier on recorded [33]. Furthermore, the dehydration shown on the thermogram at 473°C is characteristic of Ca (OH)2 dehydration in cement slurry, while its intensity shows the magnitude of hydration of the C3S component of cement [34]. Therefore, sodium lignosulfonate - based cement depicted complete decomposition after 473°C. By 600°C the sodium lignosulfonate cement sample had lost up to 21% of its mass, which is higher than the 13.5% recorded for the lignin - based cement sample.

4. Conclusion

The thermal stability of sodium lignosulfonate - based cement is lower than the lignin - based cement slurry in high temperature zones. Consequently, the thermal stability of oil - well cements, especially in HPHT environments can be enhanced by the addition of SCB based lignin into the slurry.

Acknowledgements

The authors wish to express their deep gratitude to RUFUROM, the World Bank Africa Center of Excellence, Center for Oilfield Chemicals Research, University of Port Harcourt, United States International University, Nairobi, Pharmaceutical Sciences Department for the TGA Machine.

CRediT Author Statement

Antony Fundia Simbiri: Conceptualization, Methodology, Testing, Writing - Original draft preparation, reviewing and editing. Joel F. Ogbonna, Emmanuel E. Okoro, Daniel O. Oyoo: Supervision.

Conflict of Interest

The authors declare that they have no competing interests.

References


Volume 12 Issue 7, July 2023
www.ijsr.net
Licensed Under Creative Commons Attribution CC BY