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# The effect of superplasticizers on rheology and early hydration kinetics of rice husk ash-blended cementitious systems

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## HIGHLIGHTS

- RHA in a blended system is experimented with three types of superplasticizers.
- The effect of PCE to RHA blended systems significantly lowers the yield stress.
- The workability of RHA in a blended system performs better with lignosulphonates especially over time.
- More precipitation of ettringite in RHA blended systems is observed with PCE.
- Further C-S-H growth in RHA blended systems is observed with lignosulphonate.

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## ABSTRACT

Superplasticizers (SPs) have been employed in concrete technology for decades to improve the workability of concrete in its fresh state. The addition of SPs in cement-based systems affects the early properties. Although the interaction of the cement particles with various SPs has been extensively researched, there still exists limited research on the interaction of SPs with supplementary cementitious materials such as rice husk ash (RHA). This paper investigates the rheological properties and early hydration kinetics of RHA-blended systems with three types of SPs, a polycarboxylate ether (PCE) and two lignosulphonates (LS-acc and LS-ret). In rheological properties, the addition of SP causes an initial improvement of workability as the yield stress is significantly reduced. The pastes with PCE and LS-acc show a slight increase of yield stress over time whereas pastes with LS-ret tend to lower the yield stress slightly over time, further improving the workability. Without SP, pastes with RHA show a lower yield stress but an increase in plastic viscosity as cement is further replaced with RHA. The addition of the LS SPs is observed to lower the plastic viscosity but remains constant with further replacement of cement with RHA. This indicates that LS SPs further adsorbs on RHA particles and hydration products produced causing dispersion of the particles within the system. In early hydration kinetics, pastes with PCE retard hydration and the degree of retardation is further increased with LS SPs. In the presence of RHA, the retardation of LS SP systems is significantly reduced. The pastes with PCE show more ettringite in the SEM micrographs, but is observed to be shorter needles. This indicates an initial good workability for PCE. However, C-S-H and CH were observed to be low in quantity, whereby the pastes with LS show more nucleation sites for C-S-H and CH. The ettringite needles in the LS systems were similar in quantity and more elongated in some cases but not abundant as in the PCE systems.

## 1. Introduction

The building industry is one of the most important sectors in the world due to the increasing demand for infrastructure development. Among other building materials, concrete construction is largely opted for the development of infrastructure mainly due to its outstanding strength and durability properties. One of the most important components of concrete is cement, which is currently estimated to be produced at 4.6 billion tonnes annually [1]. The amount of pollution resulting from cement production is significantly high. For every tonne of cement produced within

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the cement production industry, 842 kg of $CO_2$ is emitted [2]. Currently, the annual $CO_2$ emission amounts to approximately 5% of the total worldwide emissions [1]. With the increasing demand for cement especially in developing countries within the coming years, sustainable solutions are required to limit pollution. The reduction of $CO_2$ is mostly achieved by replacement of clinker with supplementary cementitious materials (SCMs). Majority of the SCMs are by-products of industries, and their utilisation in concrete not only minimises the environmental pollution as well as reduces $CO_2$ emission from the clinker process but also may enhance the strength properties of concrete [3] as well as its durability [4]. Common SCMs such as fly ash (FA) and slag (GGBS) have acquired extensive research, and thus standards for their respective uses and feasible replacement ratios of these SCMs in blended systems are already incorporated in European standards [5]. Despite their dominance in the concrete industry, such SCMs are not commonly available worldwide. Rojas and De Rojas Gómez [6] report that such SCM production in recent years has declined due to changes related to technology and industrial processes. Therefore, recently more focus has been put on alternative and more sustainable SCMs such as rice husk ash (RHA).

RHA is a by-product from rice, which is available in hot and moist climates that can be found for example in many regions in Africa. Most countries in Africa lack the availability of FA and GGBS primarily due to the lack of industries in the region. RHA is produced through combustion of rice husks yielding approximately 20–25% by weight of the husks [7,8]. The pozzolanic reactivity of the ash primarily depends on the combustion process and temperature [9]. Better reactivity is also favoured by the fineness of the material, which is achieved with a mean particle size of 5–10 μm [10,11], and the reactive silica formed during combustion. The high amorphous silica (ranging from 85 to 95%) is apparent when the rice husks are incinerated at temperatures between 600and 650 °C [7,12]. This makes it suitable for use as a SCM and rather environmentally sustainable due to its low energy and low-tech requirements for processing. Many researchers have reported that the reactivity of RHA tends to improve mechanical properties of concrete especially at later ages [12–15]. There has been extensive research on the hardened properties of blended systems incorporating RHA but limited research is focussed on the fresh properties, including its interaction with superplasticizers (SPs) and its effects in the early stages of the concrete processing. Due to the large surface area of RHA particles, they tend to have a high demand for water, which decreases the workability of concrete [13,16]. The use of SPs improves the workability without the need to increase the water to cement ratio (w/c), thus enhancing the mechanical performance and durability of the concrete [17–19]. Generally, SPs added to cementitious systems causes complexation of ions in the system, adsorption of the SP polymers on the surface of cement grains and poisoning of the nucleation and/or growth of the main hydrates [20]. The addition of SPs to cementitious systems with SCMs is known to alter the hydration and rheological behaviour of concrete [21]. Therefore, rheology of concrete depends on many parameters such as the properties of the SCMs, the interaction of the SCM with the cement particles as well as the type of SP used, among others.

There exist many models that describe the rheology of materials however, complex materials such as pastes, mortar and concrete mostly conform to the Bingham model (Eq. (1)) or in other cases to the Herschel-Bulkley model (Eq. (2)) [21].

$$\tau = \tau_o + \eta_{pl} \cdot \dot{\gamma} \tag{1}$$

$$\tau = \tau_o + \mathrm{K} \cdot \dot{\gamma}^n \tag{2}$$

In the above equations, $\tau$. represents the shear stress (Pa); $\tau_o$ the yield stress (Pa), which is identified as the minimum stress required for the system to start flowing; $\eta_{pl}$ represents the plastic viscosity (Pa·s); and $\dot{\gamma}$ represents the shear rate ($s^{-1}$). K denotes the consistency index, whereas, $n$ denotes the flow index. Both parameters are related to the properties of the material. Depending on the value of $n$, the flow of the paste can behave as shear thinning i.e. when $n < 1$, or as shear thickening i.e. when $n > 1$. The shear stress and shear rate can be derived from the torque and rotational speed respectively, obtained from a rheometer. Towards the evolution of concrete with the most commonly used SCMs and addition of SPs, there is still a need to understand the rheological behaviour of such cementitious systems.

In literature, most studies focus on the impact of RHA on strength development when combined with SP [22–24] but limited research deals with the fresh properties of such systems. The novelty of this paper is to clarify the effect of three different types of SPs on the early hydration kinetics and rheological properties of RHA-blended pastes. The SPs used for the present work are polycarboxylate ether (PCE) with low charge density and two types of lignosulphonates (LS). The SPs were selected due to their improvement in workability especially for hot climatic conditions such as those experienced in Africa, where there exist significant quantities of RHA to be incorporated in cementitious materials. PCEs in general have a higher dispersing effect in cement pastes compared to other SPs [25]. In particular, the low charge density of PCE-based SPs exhibits good workability retention tendencies at temperatures between 20 – 30 °C. Lignosulphonates also have good dispersing effects, hence improving the fresh properties of concrete over time [26,27].

## 2. Materials and mixtures

### 2.1. Materials

The mineral powders used in this research were CEM I 42.5 R, RHA, and limestone filler (LSF). The addition of LSF was limited to 10% for all mixtures. LSF acts as a filler material, which contributes to the particle packing [28,29] of the pastes, as well as provides a further reduction of clinker, therefore enhancing $CO_2$ reduction. The chemical composition of the binders was determined according to DIN EN 196-2:2005. The physical properties included particle size distribution (PSD) determined by laser granulometry, bulk density determined by He-pycnometry and surface area (Blaine) measured according to EN 196-6:2010. These properties are listed in Table 1, and the PSD curves are shown in Fig. 1. The cement and limestone originated from Rüdersdorf-Germany and Medenbach-Germany, respectively. The RHA was purchased and processed at Mbeya University of Science and Technology in Tanzania. The processing of the RHA powder included incineration of the husks in a furnace at 600 °C at a rate of 100 °C per hour. After burning, the coarse ash was left to cool naturally for 24 h. The coarse ash was then ground in a disc mill for approximately 1 min.

The three types of chemical admixtures used in this research were obtained from commercial manufacturers – PCE, and two LS products – a liquid-based SP characterised with retarding effects (LS-ret) and a powder-based LS characterised with accelerating effects (LS-acc). The solid content of the PCE and LS-ret were

**Table 1**
Chemical and physical properties of the binders used.

| Property | CEM I 42.5 R | RHA | LSF |
|---|---|---|---|
| $SiO_2$ (%) | 20.56 | 88.84 | 1.47 |
| $Al_2O_3$ (%) | 4.36 | 0.80 | 0.46 |
| $Fe_2O_3$ (%) | 2.27 | 0.39 | 0.40 |
| $TiO_2$ (%) | 0.20 | 0.04 | 0.05 |
| CaO (%) | 62.80 | 1.78 | 90.68 |
| MgO (%) | 2.14 | 0.92 | 0.61 |
| $Na_2O$ (%) | 0.28 | 1.10 | 3.27 |
| $K_2O$ (%) | 0.95 | 2.80 | 0.54 |
| $SO_3$ (%) | 3.45 | 0.35 | 0.34 |
| $P_2O_3$ (%) | 0.00 | 0.61 | 2.19 |
| LOI (%) | 2.40 | 2.02 | – |
| $d_{50}$ (μm) | 11.75 | 8.30 | 7.38 |
| Density ($g/cm^3$) | 3.12 | 2.31 | 2.74 |
| Blaine ($cm^2/g$) | 4110.00 | 9040.00 | 5130.00 |