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# Influence of plasticizers on the rheology and early heat of hydration of blended cements with high content of fly ash

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ABSTRACT

The dispersing effectiveness of five commercial plasticizers; lignosulfonate (LS), naphthalene sulphonate–formaldehyde polycondensate (NSF) and three polycarboxylate ethers (PCEs) were quantitatively investigated in blended cements where ordinary portland cement (OPC) was partly replaced by fly ash (FA) up to 60%. The capacity of the plasticizers in FA blended cements mimics that in the OPC system. At low replacement amounts, FA acts mainly as filler and does not impart any significant effect on the plasticizers. From 40% FA loading, PCEs showed decreased performance compared to NSF and LS relative to that in OPC systems, attributing to higher affinity of the latter polymers for cement clinkers. Retardation by plasticizers is more pronounced at higher FA contents due to lower adsorption on FA than on cement grains. Performance of plasticizers in industrial FA blended cements mimics that in OPC due to its relative higher surface area to compensate otherwise lower early strength.



## 1. Introduction

The building sector is one of the most dominating industries globally due to the constant and growing demand of new construction materials in respond to the needs in the infrastructure business. Among materials utilized in a concrete, the cement is globally produced with an annual value of ~3.5 billion tons in 2011 [1,2]. Generally, production of one ton of OPC clinker emits an equivalence of about one ton of $CO_2$ when pulverized coal is used as a fuel, contributing to ~6% $CO_2$ emission annually worldwide, making the cement industry the third largest $CO_2$ emitter after housing and transport [3,4].

To reduce this, greener and more environmentally friendly binders are sought after. The aim is to reduce the level of $CO_2$ emissions by ~50% by 2050 as stated by the World Business Council for Sustainable Development. One of the many approaches in tackling this for the cement industry is to increase replacement of clinkers by supplementary cementing materials (SCMs). The advantage of such blended cement is a direct reduction in $CO_2$ emission, which is reflected in the percentage of substitution by the SCM if they don't have to account for any $CO_2$ emission, making them a popular choice in the cement industry. Generally, many natural, as well as synthetic SCMs can be utilized as suitable materials and these include industrial by-products such as granulated blast furnace slag (GBFS) from the steel industry and natural pozzolanic materials including calcined clays [5]. Among which, fly ash (FA) produced as a byproduct from coal power plants is one of the most commonly SCMs for blending cement in the world. Currently, FA replacement in cement is usually capped at around 20–30% by weight of binder (bwob). To further reduce $CO_2$ emission, a higher replacement percentage is thus desired, but must be balanced towards sufficient early strength demanded by the construction industry.

Incorporation of fly ash results in a change in the properties of these binders and thus compatibility with other additions could be potential challenges. Two such challenges are the impact on rheology and early hydration development of binders. In cement science, rheology of concrete and cement is commonly altered and improved by the addition of admixtures such as superplasticizers, retarders, etc. The introduction of admixtures improves not only the user friendliness of cementitious materials on site, but also increase and enable enhanced final properties and aesthetic of the composite or buildings. Significantly, the ease of working with concrete possessing improved rheological properties has created millions of savings and earnings, and optimization of labour forces for the construction industry. This demand of materials possessing ideal workability is expected to continue and grow with the rising usage of construction materials, such as in the area of self-

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consolidating concrete (SCC) to ease placement without the need of vibrators etc.

The largest group of rheology regulators among the admixtures is plasticizers, including superplasticizers which act by improving dispersion of particles in the early hydration ages of cement. They consist of a wide variety of chemicals, ranging from salts of carboxylic acids and modified lignosulfonates (natural products) to the naphthalene- and melamine-based polycondensates, and finally the largest group of polycarboxylates derivatives possessing a large extent of different functionalities [6]. With normal OPC, extensive research has been performed on these admixtures, both in determining their behaviours and effectiveness on rheology, and also the improvement of their additions on the final strengths and mechanical properties of concretes. The mechanisms underlying the effective dispersion of OPC by these admixtures as driven by electrostatic repulsion or steric hindrance have also been widely discussed. Their effectiveness is generally accounted for by the attributes of the clinker and hydrate phases [7,8], and the specific characteristics (both structural and chemical) of the admixtures added [9,10].

The basis of plasticizer in OPC based systems has been attempted to be applied as mechanistic assumptions in the studies of FA blended cements. However, with the deviation in chemical compositions of the blended cements from OPCs, differences in their interaction including colloidal chemistry, etc are possible and can generate many controversies in the direct application of this understanding. Some researches on the fundamentals of the colloidal interface of the polymer-inorganic materials have been performed in both isolated SCM systems [11,12] and selected blended cement systems [13]. Despite the extensive studies, more importantly, an actual understanding and quantification of the applied rheological effectiveness of these plasticizers is required to ensure optimal application of the admixtures in such system. Additionally, the influence of these admixtures on blended cements possessing higher replacement amounts of SCMs with the drive in creating a greener construction industry is also to be expected.

For this purpose, five different commercial plasticizers were selected to test for their dispersing effectiveness in fly ash blended cements. The selection included a high molecular weight Na-lignosulfonate (LS), a naphthalene sulphonate–formaldehyde condensate (NSF) and three different sets of polycarboxylate ether (PCEs) polymers possessing different side chain lengths. High amount of FA replacement, namely 20, 40 and 60% replacement of ordinary portland cement (OPC) by weight were investigated. A commercial FA cement (classified as CEM II/A-V in the European standard) containing 18.2% FA was also investigated in comparison to the manually blended FA/OPC binder system. Rheological analysis was performed employing the principles of a parallel plate rheometer, while the packing density and water demand were followed by the centrifugal consolidation method. Lastly, the impact of varying systems on the heat of hydration of the cement pastes was investigated by isothermal calorimetry and a correlation between this heat evolution profile and the rheological properties of the cement pastes was searched for.

## 2. Experiments and methods

### 2.1. Materials

An OPC, a standard fly ash cement (FA cement) and a fly ash (FA) were supplied by Norcem AS (Brevik, Norway). The main differences between the FA cement and the OPC were namely the presence of 18.2% FA in the former and their specific surface areas. The specific Blaine surfaces of OPC, FA cement and FA were 382, 454 and 357 $m^2/kg$ respectively. Table 1 displays the chemical compositions of the two cements and fly ash.

**Table 1**
Chemical compositions of OPC, FA cement and FA.

| | OPC | FA cement | FA |
|---|---|---|---|
| $SiO_2$ | 20.8 | 26.9 | 50.0 |
| $Al_2O_3$ | 4.6 | 8.1 | 23.9 |
| $Fe_2O_3$ | 3.5 | 4.2 | 6.0 |
| CaO | 61.6 | 51.5 | 6.3 |
| MgO | 2.4 | 2.2 | 2.1 |
| $P_2O_5$ | 0.2 | 0.2 | 1.1 |
| $K_2O$ | 1.0 | 1.0 | 1.4 |
| $Na_2O$ | 0.5 | 0.6 | 0.6 |
| $SO_3$ | 3.5 | 3.2 | 0.4 |
| Alkali | 1.1 | 1.2 | 1.6 |
| Total | 98.1 | 97.9 | 93.4 |

As dispersions, five commercial plasticizers were investigated, namely a purified sodium LS (Borregaard AS, Sarpsborg/Norway), a NSF (Sika AS, Sketten/Norway), and three sets of PCEs (Mapei Escon AS, Sagstua/Norway). The NSF has a solid content of 40 ± 0.5%. The LS possessed a high molecular weight and contained very low amount of sugar and organic acid. The three sets of PCEs are denoted SX, NRG and SRN. SX and SRN were both based on methacrylate based polycarboxylates. Industrially, SX is commonly employed in ready-mix systems and consists of one raw PCE possessing long side chains with low charge density. SRN on the other hand possesses intermediate workability and plasticizing effect, and only contains the methacrylate based PCE with short side chains and high charge density. NRG is made up of a combination of one methacrylate based PCE and an acrylate based PCE in the ratio of 1:9. The methacrylate based PCE possesses long side chains and low charge density and is similar to that in SX. The acrylate based PCE possesses very long side chains and very low charge density. NRG is commonly used in the precast industry and generally generates pastes with the shortest workability. A summary of the characteristics of the plasticizers listed here can be found in Table 2.

All materials were utilised as per obtained. For preparation of the blended cements, the OPC and FA were manually mixed in the ratio of 4:1, 3:2 and 2:3 to produce blended cements with FA content of 20, 40 and 60% by weight of total dry powder respectively. These blended cements were denoted as FA20, FA40 and FA60 respectively. Pure OPC and FA were investigated too. For the polymer, all samples were dissolved in deionised water to obtain solutions possessing solid contents of between 20 and 30% for increased accuracy of dosing. 4 different dosages were employed; 0.1, 0.2, 0.4 and 0.8% dry polymer bwob, respectively.

### 2.2. Experimental procedures

The cement pastes were prepared by adding the dry powder mix to water containing admixture to obtain water to cement + FA ratio (w/(c + FA)), or simply water to binder ratio (w/b) of 0.36. This low w/b of 0.36 was chosen to prevent bleeding or segregation at high FA replacement and plasticizers dosages to highlight the effectiveness of the plasticizers. The required dosage of plasticizers was added to the water and homogenized. The dry powder was then added to the homogenized solution over a period of 0.5 min before the mixture was blended under high shear for 1 min utilizing a kitchen blender (Philips, 600 W, capacity = 200 mL), let stand for 5 min and a final high shear mixing of 1 min to avoid false setting. The high shear mix was to mimic the high shear energy in a concrete partly imposed by coarse aggregate [14]. It should be noted here that high shear mixing in the current setup is only an attempt to mimic the shearing of paste in concrete test. For more actual