

Lignopolymer Superplasticizers for Alternative Supplementary Cementitious Materials

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Abstract

Grafting hydrophilic polyacrylamide from a kraft lignin core results in a lignopolymer that effectively plasticizes portland cement paste. Here, the potential of this lignopolymer is examined for improving the workability of portland cement blended with two reactive, high surface area alternative supplementary cementitious materials (ASCMs): kaolin clay and the zeolite clinoptilolite. Both ASCMs are known to participate in hydration reactions and can significantly reduce workability when blended with portland cement, presenting a challenge when reducing the environmental impact of cement. Polyacrylamide-grafted kraft lignin was compared with a lignosulfonate developed for plasticizing portland cement and a commercial polycarboxylate ether. Compared to the other admixtures, the lignopolymer was found to adsorb strongly to both kaolin and clinoptilolite and resulted in the lowest yield stresses in pastes containing 25% ASCM and 75% Type I/II portland cement at both high (2.5 mg/mL) and low (0.25 mg/mL) admixture content. In contrast, the PCE had a low affinity for kaolin but was strongly bound to clinoptilolite, although the resulting tests of slump spread and viscosity were similar for these ASCMs. These results indicate that lignopolymers could be an effective superplasticizer for a broad range of high surface area, reactive ASCMs.

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I. INTRODUCTION

Portland cement is one of the most common synthetic materials, with an annual production of more than 4 trillion kilograms. The production process however is highly energy- and CO₂-intensive and accounts for an estimated 5-7% of the global CO₂ emissions each year. Because concrete is the largest consumer of cement, replacing a portion of the portland cement clinker in concrete with other constituents (i.e., supplementary cementitious materials, SCMs) can reduce this. Currently, fly ash, a by-product from coal-fired power generation, is commonly blended with portland cement, typically at rates of 20-40% by mass, although higher rates are also used. Since the 1940's it has been known that pozzolans or supplementary cementitious materials (SCMs), such as fly ash and slag, helps improve the concrete's durability and later age strength. Today, the additional improvements in sustainability associated with cement clinker fraction reduction in concrete are also well recognized. However with the growing environmental concerns about the sustainability of coal as an energy source and with higher costs and limited global availability of other traditional SCMs (e.g., slag, silica fume), there is a need to explore new SCM sources or alternative supplementary cementitious materials (ASCMs) [1].

A variety of finely divided, naturally occurring minerals such as kaolin, limestone, and zeolite, are abundant worldwide and could serve as potential ASCM sources. Given their range of compositions, these materials vary in their reactivity with cement, displaying a range of behavior from predominantly filler to some pozzolanic reactivity. As such, in addition to decreasing the cement clinker fraction in concrete, ASCMs have the potential to contribute to improved strength and decreased permeability through improvements in particle packing and the formation of secondary reaction products, which can densify the hydrated cement paste.

However, the decrease in concrete workability, and in particular flowability, associated with these ASCMs poses a serious hindrance to their implementation. In concrete, challenges with workability are typically overcome with the use of water reducing chemical admixtures, which commonly are long-chain polymers with anionic side groups. Water reducing admixtures improve workability by adsorbing onto the cement particle surface and, in some chemical architectures, by steric and/or electrostatic effects. Their net effect is to improve cement particle dispersion and ensure mix water is available for lubrication during early age mixing and placing. However, with ASCMs, even the addition of such water reducing chemical admixtures at recommended dosage rates does not produce a significant improvement in workability. This is due to the difference in the charge and surface area associated with these ASCMs compared to cement and traditional SCMs. The extremely

high surface area of ASCMs like kaolin and zeolite in particular leads to a high rate of admixture adsorption, and their low surface charge promotes aggregation. Using superplasticizing admixtures at higher than recommended dosage rates can offset some of the effects, but this increases the cost of concrete and the potential for unpredictable early age behavior (e.g., extended or abbreviated setting time, segregation or excessive bleeding). In addition, for superplasticizers derived from petrochemicals, there is an environmental cost associated with their use, which partially offsets the gains achieved through clinker fraction substitution with ASCMs. Hence, there is a need to identify or develop a superplasticizer that will improve the workability of these ASCM-containing concretes at lower dosages.

The goal of this study is to investigate a novel class of polymer-grafted lignins (lignopolymer) as superplasticizer to be used in blends of high surface area, reactive ASCMs and portland cement. Lignin, derived from plants where it serves to bind fibers or cells together, is a complex aromatic biopolymer that has a wide range of functional groups such as ether, hydroxyl and phenol. The major commercial use of lignin is lignosulfonate, which is derived from sulfite pulping of wood; these are used as a relatively low-cost chemical admixture, primarily for retarding hydration in portland cement concrete, but also exhibits moderate plasticization.

To enhance plasticizing capacity, polyacrylamide was grafted onto a kraft lignin core using controlled radical polymerization (CRP) following published methods [2], and the effects of this modified version of lignosulfonate on the workability of high surface area ASCMs kaolin, zeolite and portland cement blends are assessed by measurements of adsorption, zeta potential, rheological behavior, and hydration kinetics via isothermal calorimetry. The results are then compared to other commercially available superplasticizers.

II. MATERIALS AND METHODS

A. Materials

Reversible addition-fragmentation chain-transfer (RAFT) was used to synthesize polymer-grafted kraft lignin. BioChoice, a type of kraft lignin with low sulfur and ash content provided by Domtar, was used as the lignin source. The chemical structure of the various superplasticizers tested is shown in Figure 1. These were compared to two commercial admixtures: a lignosulfonate (Borresperse NA from Borregaard LignoTech) and a polycarboxylate ether (PCE) (ADVA 190, Grace Construction Chemicals), which were used as received.

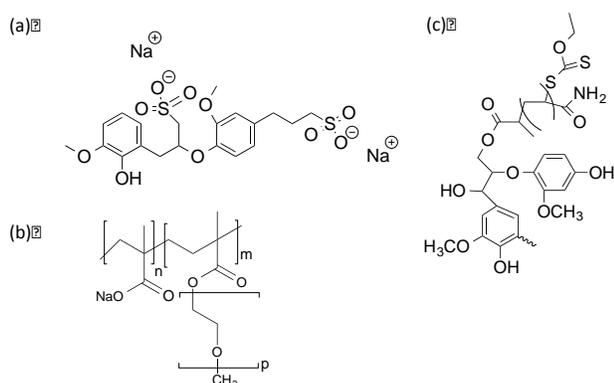


Figure 1. Admixtures used in this study.

Cement pastes were prepared using an ASTM C150 Type I ordinary portland cement whose composition is provided in Table 1 alone and in combination with four different ASCMs, each used at 25% replacement for cement by mass. The ASCMs examined were uncalcined kaolin (Sandersville, GA) and natural clinoptilolite zeolite (McKinney, TX).

Table 1. Mineral composition of portland cement used.

Component	%
Alite	60.58
Belite	19.37
Tricalcium aluminate	2.27
Periclase	5.83
Arcanite	0.50
Calcite	3.39
Brownmillerite	8.06

B. Heat of Hydration Measurements

Hydration was studied using isothermal calorimetry (Thermometric TAM Air). Cement pastes were prepared at a w/cm of 0.42 and an ASCM loading of 25% by mass of total cementitious materials, consistent with the sample preparation used for other testing reported here. Admixtures, when used, were added to the mixing water prior to adding the ASCMs and cement. The mixture was blended using a 6-speed hand mixer at low speed for 1 minute, then medium speed for 1 additional minute. Two replicate cement paste samples weighing 7.0 ± 0.5 g were prepared for each mixture. Hydration was monitored for 48 h at a constant temperature of 25 °C (77 °F).

C. Specific surface area and adsorption measurements

The nitrogen-accessible surface area of each ASCM was measured using the Brunauer-Emmett-Teller (BET) method using a Gemini VII Micrometric surface area analyzer. Each sample was dried for 24 hours at 150 °C prior to being analyzed.

Adsorption of the different superplasticizers onto each ASCM was determined using total organic carbon analysis. In this technique, the total amount of carbon left in the sample before and after adsorption is measured. Each superplasticizer was mixed with the ASCM at 5 different concentrations (0.25, 0.5, 1, 2 and 4 mg/mL) for 1 h to allow for adsorption. The sample was then centrifuged at 4400 rpm for 8 minutes. The supernatant obtained from centrifuging was subsequently diluted and the total organic carbon content was measured using a GE InnovOX TOC analyzer.

D. Mini-slump measurements

To gauge changes in workability and yield stress of the cement-ASCM pastes, mini-slump testing was performed on pastes of varying composition at a consistent water-to-cementitious materials ratio (w/c) of 0.42. The ASCM and OPC loading for each sample were 25 and 75 wt. % respectively. Samples were prepared at room temperature using a planetary (Hobart) mixer with a paddle fixture at a speed of 62 r/min using tap water in accordance with ASTM C305. The samples were agitated for 3 minutes.

Immediately after mixing, the samples were compacted into a 3-cm inner diameter and 5-cm high mini-slump cylinder (provided by BASF), and the cylinder was slowly lifted (5-11s) and diameters along the two orthogonal directions were immediately recorded. These values were used to calculate the slump spread and the relative flow area ratio relative to the original cylinder diameter.

III. RESULTS AND DISCUSSION

One of the major concerns with using a new admixture is to ensure that the formation of the various hydrated phases still takes place in the same time frame. It is necessary for the admixture to not affect the hydration curve significantly. In order to test the effects of LPAM on the ASCM cement blends isothermal calorimetry was performed. This technique is useful for better understanding how interactions between ASCMs, admixtures, and cement influence early cement hydration kinetics. The results for kaolin and zeolite cements are shown in Figure 2; results for the portland cement paste without admixtures or ASCMs are also plotted for comparison. The main exotherms around 6 h and 12 h, which can be attributed to the hydration of the alite or tricalcium silicate (C3S) and tricalcium aluminate (C3A) phases in the portland cement, respectively, are both significantly influenced by the presence of the ASCMs. The kaolin appeared to delay the onset of the initial C3S reaction by approximately 1.5 h, while increasing the heat released associated with the reaction of the aluminate phase by nearly 70% when no admixtures are used, compared to the portland cement alone. The zeolite, meanwhile, appeared to accelerate the C3S reaction by nearly 2 h, while increasing

the heat released by the aluminate reaction by approximately 40% when no admixtures were used. The increase in heat evolved by the aluminate reaction is consistent with the high aluminosilicate contents of both the kaolin and natural zeolite.

The admixtures had minimal effects on the hydration of both ASCMs, which is generally desirable since predictable behavior is preferred in practice. The exception observed was for the zeolite mixture at high admixture concentration, for which both admixtures increased the peak heat release observed 12 hours following addition of water. In particular, this peak (corresponding to the hydration of the C3A) shows an increase of approximately 20% and an acceleration of approximately 30 minutes relative to the zeolite paste without admixtures. The same peak in the kaolin mixtures, meanwhile, lacks this increase in height and, in fact, shows a slight deceleration of approximately 30 minutes when LPAM is used.

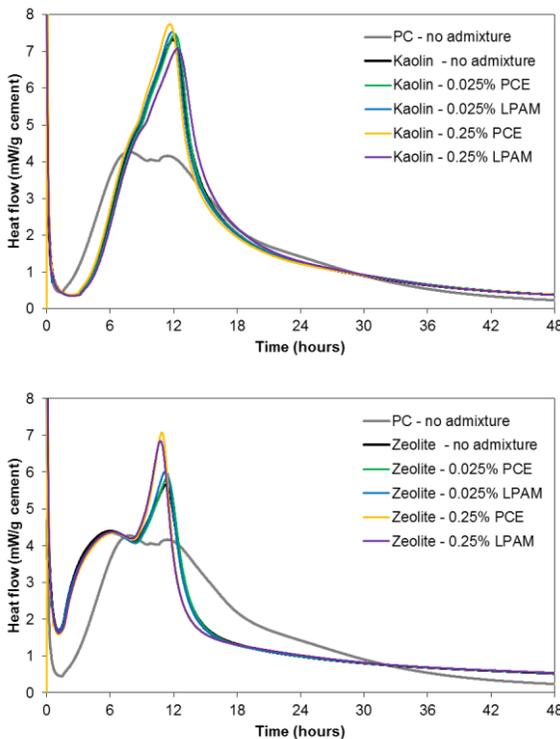


Figure 2. Calorimetry results for cement blends.

The trends seen in the hydration data can be related to the adsorption of the admixtures to the ASCM phases. The affinity of the admixtures for the different ASCMs was determined by measuring the supernatant decanted from the samples after centrifuging using TOC. These measurements were then normalized against the ASCM's nitrogen accessible surface area and are reported in Figure 3. For kaolin, LPAM had the highest adsorption, followed by LS

and then PCE. PCE appeared to plateau at 0.02 m²/g whereas the mass adsorbed for LPAM increased monotonically with concentration with a highest recorded value of 0.25 m²/g. This was not the case for zeolite for which adsorption of both LPAM and PCE increased with concentration while LS had the lowest overall adsorption. It is interesting to note that there were no significant differences in concentration-dependent adsorption for LS for both kaolin and zeolite, suggesting a lack of specific interactions between these mineral surfaces and LS.

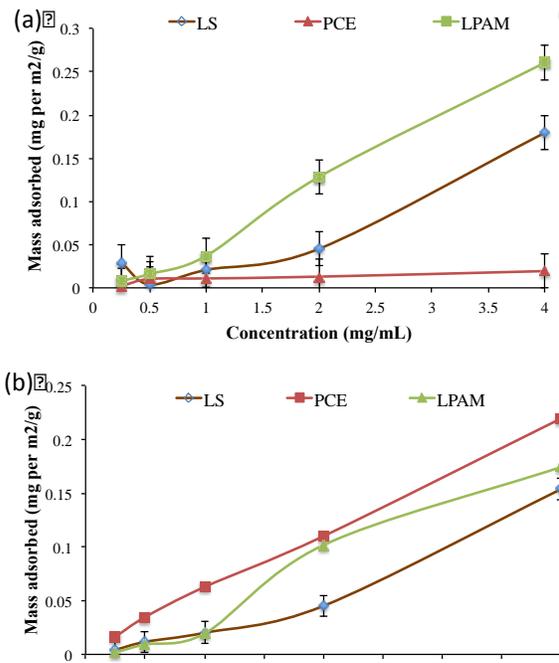


Figure 3. Adsorption isotherms onto the ASCMs: (a) kaolin, (b) zeolite.

For both the lignin-based samples, LPAM and LS, a plateau value was not observed in the TOC data, which suggests that the surface of the ASCM continues adsorbing the admixture or that the lignin is capable of aggregating or accumulating, perhaps in layers, on the ASCM surface. The LPAM adsorbed significantly more than the LS which indicates that the grafting promotes admixture binding, which is due to the reduction in aggregation in the grafted samples compared to lignin itself. This suggests that the preferential adsorption to these ASCM surfaces of LPAM is due to the kraft lignin core, which is rich in carboxylate groups but has few sulfonate groups, but direct comparisons will be required to establish this given the contributions of the polyacrylamide grafts to the interactions with cementitious particle surfaces.

In contrast, the PCE only appeared to reach a plateau for kaolin and continually adsorbed on the zeolite surface,

which can be attributed to the porous structure of zeolite. The hydration data for zeolite in Figure 2 (b) show an initial increase in the early time points, which represents fast wetting of the porous structure. As a result, the admixtures continue adsorbing to the surface monotonically with concentration. This explains the difference in adsorption trends of PCE on zeolite and kaolin.

As seen from the hydration data in Figure 2 (a) there is a delay on the onset of the hydration peaks for kaolin, which can possibly explain the different adsorption behaviors. For this ASCM, it is possible that at a low concentration of PCE the entire surface is saturated and no further adsorption is possible due to the repulsion between the individual polymers. In contrast, the low grafting density on the lignin core in LPAM could allow further lignin-lignin interactions creating a thick layer of this superplasticizer, which provided improved steric repulsion.

In order to relate the particle-particle interactions with hydration effects, the effects of these admixtures on workability of the cement paste was considered. The workability of ASCM-containing cement pastes was measured using mini-slump spread tests that were performed at admixture concentrations of 0.25 mg/mL and 2.5 mg/mL. The slump spread values were converted to yield stress, τ_0 , by measuring the spread radius (R) using equation 1:

$$\tau_0 = \frac{225\rho gV^2}{128\pi^2 R^5}$$

where ρ is the paste density, g is the gravitational constant and V is the volume.

Figure 4 shows the effect of these admixtures on Portland cement paste without any ASCM present. We can see that LS and KL have some impact on the yield stress, but PCE and LPAM seem to have much more significant impacts. The reduction of yield stress observed with LPAM suggests that this grafted nanoparticle architecture can be effective in improving flowability. LPAM induced the lowest yield stress at lower concentrations and had a similar effect at high concentrations.

When portland cement was blended with ASCMs, similar trends were observed but with lower reductions in yield stress. At 0.25 mg/mL, LPAM produced the lowest yield stress for both kaolin and zeolite as seen in Figure 5 (a) and (b). LPAM adsorbed strongly to both surfaces at both concentrations, which correlates with the increases in slump spread and reductions in calculated yield stress. As seen in Figure 3 PCE had a slightly higher adsorption than LPAM for most of the concentration range for zeolites, this explains the slightly lower yield stress observed for PCE in Figure 5(b). This validates the fact the higher adsorption of the admixture to the ASCM results in more dispersion power. The significant decrease in yield stress with LPAM dosage

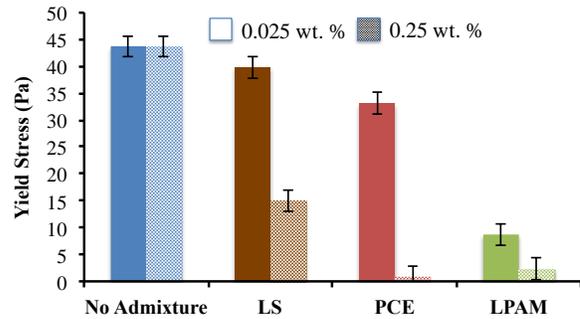


Figure 4. Yield stress values of portland cement.

observed above suggests that there are strong steric interactions taking place between the particles, which is not observed in the case of lignin. Polyacrylamide-grafting of kraft lignin increased its effects on the workability of ASCM-blended cement. These observations are corroborated with previously published studies that suggest side chains are necessary for improved workability due to their steric interactions. Otherwise the admixture needs to be added above saturation level, which may result in some non-adsorbed floating particles that may increase workability. We believe this is the case for lignosulfonates in zeolite-cement blend. In conclusion, this shows that LPAM provides reductions in yield stress at ten-times lower dosage than the recommended dosage for current superplasticizers.

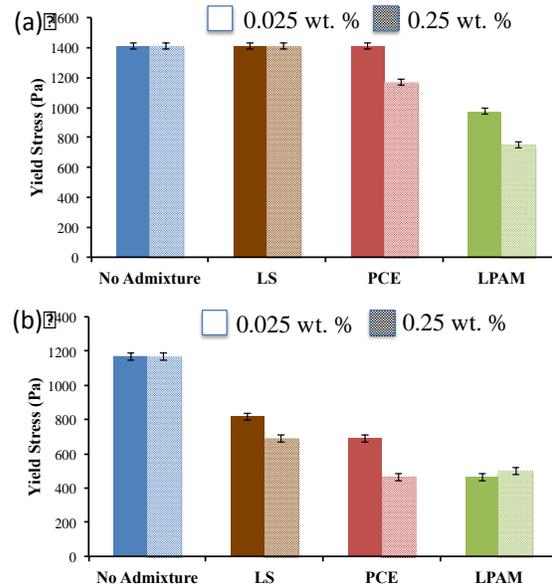


Figure 5. Yield stress values of cement with ASCMs: (a) kaolin, (b) zeolite.

IV. CONCLUSION

High surface area ASCMs such as kaolin and zeolite can significantly reduce workability when blended with portland cement. In this study, we demonstrated that a novel polyacrylamide-grafted kraft lignin nanoparticle LPAM can be used to improve both ASCM formulations. LPAM had significantly better performance than lignosulfonates as shown in the study and the grafting of a small amount of hydrophilic polymer present results in improved dispersant properties. Also, isothermal calorimetry and TOC suggested that PCE and LPAM work in a different manner, which allows LPAM to have significant effects on the workability of these blends at ten-times lower dosage than currently commercially used admixtures. In conclusion our study indicates that LPAM can be used as an effective admixture for reactive, high surface area ASCMs.

V. ACKNOWLEDGMENTS

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VI. REFERENCES

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