

**IMPLEMENTATION OF SUPERABSORBENT POLYMERS FOR
INTERNALLY CURED CONCRETE**

by

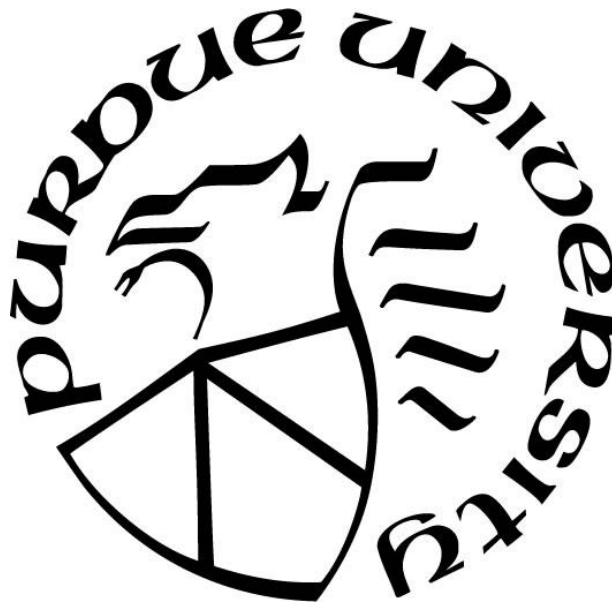
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*for Mom and Dad,
for Meg and Pompa,
for Grandma and Granddad,

but mostly, for me.*

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TABLE OF CONTENTS

LIST OF TABLES	12
LIST OF FIGURES	13
LIST OF ABBREVIATIONS AND SYMBOLS	16
ABSTRACT.....	17
1. INTRODUCTION	19
1.1 Motivation	19
1.2 Superabsorbent Polymers for Internally Cured Cement.....	20
1.3 Cement Hydration	21
2. EVALUATION OF BATCHING SEQUENCE AND VERIFICATION OF SAP IN CONCRETE	23
2.1 Overview	23
2.2 Materials and Methods	23
2.3 Results	24
2.3.1 Fresh Concrete Properties	24
2.3.2 Hardened Concrete Properties.....	24
2.3.3 Verification of SAP	25
2.4 Conclusions and Implications.....	27
3. EVALUATION OF MIX DESIGN STRATEGIES TO OPTIMIZE FLOW AND STRENGTH OF MORTAR INTERNALLY CURED WITH SUPERABSORBENT POLYMERS	28
3.1 Introduction	28
3.2 Materials and Methods	31
3.2.1 Characterization of Superabsorbent Polymers	31
3.2.2 Three Approaches used for Modifying Mixture Composition of Mortars	33
3.2.3 Mortar flow testing.....	36
3.2.4 Strength characterization	37
3.2.5 Microstructure of mortars.....	37
3.2.6 Statistical Analysis	38
3.3 Results and Discussion	38

3.3.1	Characterization of SAP absorption capacity.....	38
3.3.2	Results from Approach I: extra water – no HRWRA	40
3.3.3	Results from Approach II: HRWRA dosage varied to achieve target flow	46
3.3.4	Results from Approach III: HRWRA dosage set to achieve target flow of reference at given w/c.....	49
3.3.5	Microstructure of mortars.....	55
3.3.6	Discussion	57
3.4	Conclusions	58
3.5	Acknowledgments	59
4.	EFFECT OF BINDER CHARACTERISTICS ON WORKABILITY, HYDRATION, AND STRENGTH OF CEMENTITIOUS SYSTEMS WITH SUPERABSORBENT POLYMER ADMIXTURES	60
4.1	Introduction	60
4.2	Materials and Methods	62
4.2.1	Characterization of Superabsorbent Polymer.....	62
4.2.2	Preparation of Specimens.....	65
4.2.3	Mortar Flow Testing.....	68
4.2.4	Mortar Strength Characterization	68
4.2.5	Microstructure	68
4.2.6	Cement Hydration	69
4.2.7	Statistical Analysis	70
4.3	Results and Discussion	70
4.3.1	Type I Cements from Different Plants	70
4.3.2	Type III Cement	76
4.3.3	Type I Cement with 30% Slag Replacement by Weight.....	80
4.3.4	Overall Implications	83
4.4	Conclusions	84
4.5	Acknowledgments	85
5.	IMPACT OF SAP ON CRACKING TENDENCY OF MORTARS AND CONCRETE	86
5.1	Overview	86
5.2	Materials and Methods	86

5.3	Results	87
5.3.1	0.35 w/c Mortars Results	87
5.3.2	0.42 w/c Mortars Results	88
5.3.3	0.35 w/c Concretes Results	89
5.4	Conclusions and Implications.....	92
6.	CONCLUSIONS AND FUTURE DIRECTIONS	94
6.1	Conclusions	94
6.2	Future Directions	95
	APPENDIX.....	97
	REFERENCES	98

LIST OF TABLES

Table 3.1. Composition of the ordinary Type I Portland cement used in this study.	32
Table 3.2. Composition of mortar mixtures.....	34
Table 3.3. Percent of 28-day compressive and flexural strength of mortars attained by 7 days. .	45
Table 4.1. Properties of the ordinary portland cements and slag cement and the pH values of the simulated pore solutions used in this study.....	64
Table 4.2. Composition of 0.42 w/b cement paste and mortar mixtures with varying binder compositions.	66
Table 4.3. CH% (g/g) as determined by TGA of 7-day 0.42 w/c Type I cement pastes with and without SAP.	74
Table 4.4. CH% (g/g) as determined by TGA of 7-day 0.42 w/c Type III cement pastes with and without SAP with X-Type I pastes as references.....	79
Table 4.5. CH% (g/g) as determined by TGA of 7-day 0.42 w/c Type III cement pastes with and without SAP with X-Type I pastes as references.....	83
Table 5.1. Composition of 0.35 w/c concretes.....	86

LIST OF FIGURES

Figure 1.1. SEM, photo, and schematic images of SAP in dry and wet states.	20
Figure 1.2. Illustration of the cement hydration process with SAP internal curing in cement paste (a) immediately after mixing Portland cement, water, and SAP; (b) through final set; and (c) after several days curing. Figure from Erk and Bose. ³	21
Figure 2.1 SEM micrographs of 7-day 0.42 w/c concrete samples with: (a) LA-SAP added to cement and (b) LA-SAP added to aggregate. The remnants of the dehydrated LA-SAP particle were clearly visible as the grey film in the void shown in (a). The HA-SAP particle remnants were less visible, but still present in the void shown in (b).	25
Figure 2.2 SAP collected on a 0.063 mm sieve from fresh mortar samples for visual and tactile verification.	26
Figure 3.1. SEM images of the (a) LA and (b) HA dry SAP particles used in the experiments. .	31
Figure 3.2. Absorption capacity of SAP as a function of immersion time in: (a) RO water and (b) synthetic pore solution (inset displays the same data with a smaller-range vertical axis for greater detail).	39
Figure 3.3. Absorption capacity of SAP as a function of immersion time in synthetic pore solution with no HRWRA, a low dosage of HRWRA, and a high dosage of HRWRA for (a) LA-SAP and (b) HA-SAP.	40
Figure 3.4. (a) Percent flow over time of fresh mortar mixes, (b) compressive strength and (c) flexural strength of mortar containing extra water to offset SAP absorption. No HRWRA was added to these set of mixes. In Figures 4(b) and 4(c), bars with diagonal hatches represent mortars with w/c 0.42 prepared without extra water, bars with no hatches represent mortar mixes with 5% extra water and bars with horizontal dashes represent mortar mixes with extra water amount based on SAP's equilibrium absorption capacity in synthetic pore solution.	41
Figure 3.5. (a) Percent flow over time of fresh mortar mixes and (b) compressive strength, and (c) flexural strength of mortar samples with the addition of HRWRA and no extra water. HRWRA dosage was determined so as to achieve $110\% \pm 10\%$ flow of mortar at 10 minutes after the addition of water to the mix. In Figures (b) and (c), diagonal hatches indicate mortar with w/c 0.42 without extra water, consistent with representations of the types of mortar mixtures given in Figure 3.4.....	47
Figure 3.6. Percent flow of mortars over time with and without extra water and with the HRWRA dosage necessary to achieve at least $110\% \pm 10\%$ flow of No SAP mortars at the given total w/c at 10 minutes after the addition of water to the mix.	50
Figure 3.7. (a-c) Compressive strength and (d-f) flexural strength of mortar samples with the HRWRA dosage necessary to achieve at least $110\% \pm 10\%$ flow of No SAP mortar at the given total w/c at 10 minutes after the addition of water to the mix. Figures (a) and (d) show samples with no extra water. In Figures (b) and (e), 5% extra water has been used in each mix. In Figures	

(c) and (f), the amount of extra water was determined based on the equilibrium absorption capacity of the SAP used.....	52
Figure 3.8. Representative SEM images of 28-day mortar samples (<i>Approach III</i> ; w/c 0.42): (a) No SAP_0%_0.5%, (b) LA_0%_0.5% and (c) HA_0%_0.5%. The arrows in (a) indicate microcracks formed in the matrix of the mortar. The red outlines in in (b) and (c) indicate the outer edges of deswollen SAP particles.	56
Figure 3.9. SEM image of a SAP-related void in 28-day mortar sample HA_0%_0.5% (<i>Approach III</i> ; w/c 0.42): (a) with two spots highlighted for EDX analysis (1 and 2); (b) the SAP void outlined in red and the portlandite growth inside the void highlighted in cyan.....	57
Figure 4.1. (a) Absorption capacity of SAP as a function of immersion time in simulated Type I cement pore solutions from different manufacturing sources. (b) Change in percent flow of the mortar over time with the inclusion of SAP for each of Type I cements.	71
Figure 4.2. (a) Compressive and (b) flexural strength of Type I mortars with and without SAP through 28 days.....	72
Figure 4.3. Microstructure of 7-day 0.42 w/c pastes with and without SAP. X-Type I cement was used for (a) and (c), while Z-Type I cement was used for (b) and (d). One representative SAP void is outlined in red in each of (c) and (d) with the percent of that SAP void filled with hydration products reported.	73
Figure 4.4. Isothermal calorimetry analysis of 0.42 w/c cement paste showing the effect of different sources (and thus different chemistries) of Type I cement on (a) heat flow (24 hours) and (b) total heat (72 hours).	75
Figure 4.5. (a) Absorption capacity of SAP as a function of immersion time in simulated Type III cement pore solution with X-Type I pore solution as reference. (b) Change in percent flow of the mortar over with the inclusion of SAP for X-Type III and X-Type I cements.....	77
Figure 4.6. (a) Compressive and (b) flexural strength of X-Type III mortars with and without SAP through 28 days. X-Type I mortars are shown as references.....	78
Figure 4.7. Isothermal calorimetry analysis of 0.42 w/c cement paste showing the effect of Type I and Type III cement from the same source on (a) heat flow (24 hours) and (b) total heat (72 hours).	80
Figure 4.8. (a) Absorption capacity of SAP as a function of immersion time in simulated Type I with 30% slag replacement pore solution with X-Type I pore solution as reference. (b) Change in percent flow over time of mortar with the inclusion of SAP for X-Type I+Slag and X-Type I binders.....	80
Figure 4.9. (a) Compressive and (b) flexural strength of X-Type I mortars with 30% slag replacement with and without SAP through 28 days. X-Type I mortars without slag are shown as references.	82
Figure 4.10. Isothermal calorimetry analysis of 0.42 w/c cement paste showing the effect of 30% replacement of cement by slag on: (a) heat flow (24 hours) and (b) total heat (72 hours).	83

Figure 5.1. Steel ring strains over time for 0.35 w/c B Type I mortars with and without HA- and LA-SAPs.	88
Figure 5.2 Steel ring strain over time of 0.42 w/c B Type I mortars with and without HA- and LA-SAP.	89
Figure 5.3. Steel ring strain over time of 0.35 w/c Buzzi Type I Concretes with and without HA-SAP.	90
Figure 5.4. Photos of the No SAP concrete sample with red arrows pointing to the crack in the sample.	91
Figure 5.5. Photos of the 549-day HA-SAP concrete sample from angles comprising the full circumference of the sample.	91
Figure 5.6. Photo of the 549-day HA-SAP concrete sample with a red arrow indicating the superficial crack.	92

LIST OF ABBREVIATIONS AND SYMBOLS

°C	Degrees Celsius
A	Percent flow
AEA	Air entraining admixture
bwob	by weight of binder
bwoc	by weight of cement
C-S-H	calcium-silicate-hydrate
C ₃ S	tricalcium silicate
CH	calcium hydroxide
EDS	Energy dispersive x-ray spectroscopy
HA-SAP	High absorption SAP
HRWRA	High range water reducing admixture
IC	Isothermal calorimetry
kg	Kilogram
L	Liter
LA-SAP	Low absorption SAP
LWA	Lightweight aggregate
m ²	Square meters
mm	Millimeter
MPa	Megapascal
OPC	ordinary portland cement
PAA	Polyacrylic acid
PAM	Polyacrylamide
PCE	Polycarboxylate superplasticizer
psi	Pounds per square inch
Q	Absorption ratio
RO	Reverse osmosis
SAP	Superabsorbent polymer
SCM	Supplementary cementitious material
SEM	Scanning electron microscopy
SSD	Saturated surface dry
TGA	Thermogravimetric analysis
w/b	Water-binder ratio
w/c	Water-cement ratio
WRA	Water reducing admixture
μm	Micrometer

ABSTRACT

Hydrated portland cement provides the solid adhesive matrix necessary to bind aggregate (sand and gravel) into concrete. The hydration reaction requires water, however the products of the reaction limit further diffusion of water to unreacted cement. Superabsorbent polymer (SAP) hydrogel particles absorb mixing water, then subsequently desorb when the relative humidity drops, serving as internal water reservoirs within the cement matrix to shorten diffusion distances and promote the hydration reaction in a process called internal curing. Internally cured cementitious mixtures exhibit an increased degree of hydration and reduced shrinkage and cracking, which can increase concrete service life. Increased service life can, in turn, reduce overall demand for portland cement production, thereby lowering CO₂ emissions.

This dissertation addresses practical implementation questions key to the translation of SAP hydrogel internal curing technology to from the benchtop to the field in transportation applications, including: (1) What effects do mix design adjustments made to increase mixture flow when using SAP have on cementitious mixture properties? and (2) What effect do cementitious binder characteristics have on SAP performance?

The addition of SAP to a cementitious mixture changes the mixture's flow behavior. Flow behavior is an important aspect of concrete workability and sufficient flow is necessary to place well consolidated and molded samples. Often, additional water is added to mixtures using SAP to account for the absorbed water, however cementitious mixture workability is often tuned using high range water reducing admixtures (e.g., polycarboxylate ester-based dispersants). Fresh and hardened properties of mortars were characterized with respect to flow modification method (using the mortar flow table test; compressive strength at 3, 7, and 28 days; flexural strength at 7 and 28 days; and microstructural characterization of 28-day mortars). At typical doses, it was found that the addition of extra water lowers the resulting compressive and flexural strength, while high range water reducing admixtures administered at doses to achieve sufficient mortar flow did not compromise compressive or flexural strength.

The SAPs used in cement are generally poly(acrylamide-acrylic acid) hydrogels and are not chemically inert in high ionic-load environments, such as cement mixtures. The behavior of an industrial SAP formulation was characterized across five different cement binder compositions with respect to the cement hydration reaction (using isothermal calorimetry, thermogravimetric

analysis of hydration product fraction, and scanning electron microscopy (SEM)/energy dispersive x-ray spectroscopy (EDS) microstructural analysis), the absorption behavior of the SAP, and the fresh and hardened properties of SAP-cement composites (mortar flow and compressive and flexural strength). The change in properties induced by the addition of SAP was similar across ASTM Type I cements from three manufacturing sources, suggesting that SAP internal curing can be implemented predictably over time and geography. Excitingly, in analysis of cement systems meeting different ASTM standards (Type III and Type I with 30% replacement by mass with ground blast furnace slag), synergistic and mitigating reaction behaviors were observed, respectively, in Type III and slag cement, suggesting that further study of SAP with these cement systems could be of particular interest.

1. INTRODUCTION

1.1 Motivation

Better concrete for the remediation, repair, and expansion of infrastructure would lead to environmental and economic savings. Concrete is a valuable engineering material that combines affordability, good strength to weight ratio, and moldability.¹ By volume, concrete is the most widely used building material in the world. The ubiquity of concrete comes with significant greenhouse gas emissions, energy use, and natural resource consumption.² Globally, more than four billion tons of portland cement is produced annually.³ For every ton of Portland cement manufactured, about one ton of CO₂ gas is emitted, accounting for 8% of annual global CO₂ emissions.⁴

Improvements to durability and service life of concrete are one way to reduce the need for Portland cement production. Such concrete would reduce maintenance, increase return on investment, and decrease frequency of structure replacement, thus decreasing CO₂ emissions, energy usage, and natural resources depletion. In U.S. transportation applications from 1900 to 2015, a 10% increase in service life would have had the potential to decrease cement production by 2% over that same time frame.⁵

Hydrated portland cement provides the solid adhesive matrix necessary to bind aggregate (sand and gravel) into concrete.^{6,7} The hydration reaction requires water, however the products of the reaction limit further diffusion of water to unreacted cement.^{8,9} Superabsorbent polymer (SAP) hydrogel particles can serve as internal water reservoirs within the cement matrix to shorten diffusion distances and promote the hydration reaction in a process called internal curing.^{3,10–12} Internally cured cementitious mixtures exhibit an increased degree of hydration and reduced shrinkage and cracking, which can increase concrete service life.^{13,14}

This dissertation addresses practical implementation questions key to the translation of SAP hydrogel internal curing technology to from the benchtop to the field in transportation applications, including: (1) What effects do mix design adjustments made to increase mixture flow when using SAP have on cementitious mixture properties? and (2) What effect do cementitious binder characteristics have on SAP performance?

1.2 Superabsorbent Polymers for Internally Cured Cement

SAP hydrogels are covalently crosslinked polyelectrolyte networks that can be chemically and physically tuned to absorb 100 to 1000 times their mass in water ([Figure 1.1](#)). For cement internal curing applications, SAP used typically consists of sub-100 μm particles of poly(acrylic acid-acrylamide) (PAA-PAM),^{3,10,15} but other formulations suitable for cement applications, including bio-based SAP, have been studied.¹⁶ In laboratory settings, SAP can be custom synthesized to control properties including particle size, crosslinking, and charge densities.^{17–21} SAP can also be obtained commercially and could potentially be sustainably-sourced from recycled absorbent materials.^{22–24}

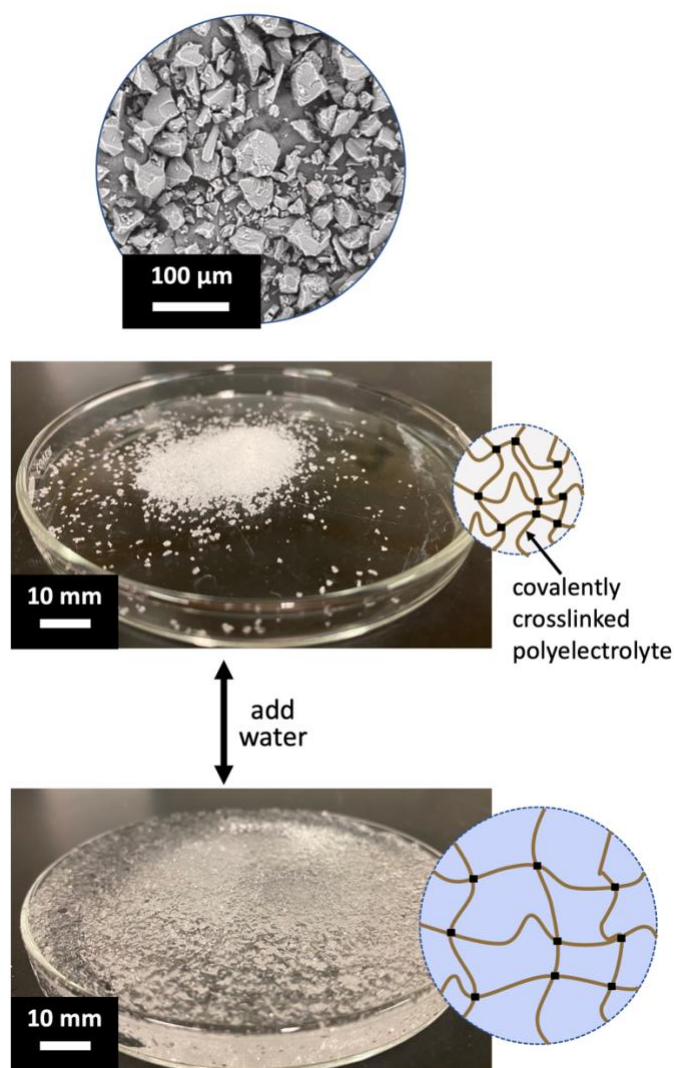


Figure 1.1. SEM, photo, and schematic images of SAP in dry and wet states.

SAP facilitates internal curing by first absorbing, then over time desorbing water within the cement paste matrix (Figure 1.2).³ Dry SAP particles are incorporated into cementitious mixtures before the addition of water to ensure even distribution of the particles throughout the mixture.²⁵ When water is added to the mixture, SAP absorbs a portion of the water due to an osmotic pressure gradient between the SAP and solution, and swells. As the cement hydration reaction progresses, the changing osmotic pressure gradient and relative humidity prompt deswelling of SAP, distributing water within the cement paste matrix for further cement hydration.^{3,10–12} The deswelled SAP remains within the discontinuous voids previously occupied by swollen SAP.^{18,26}

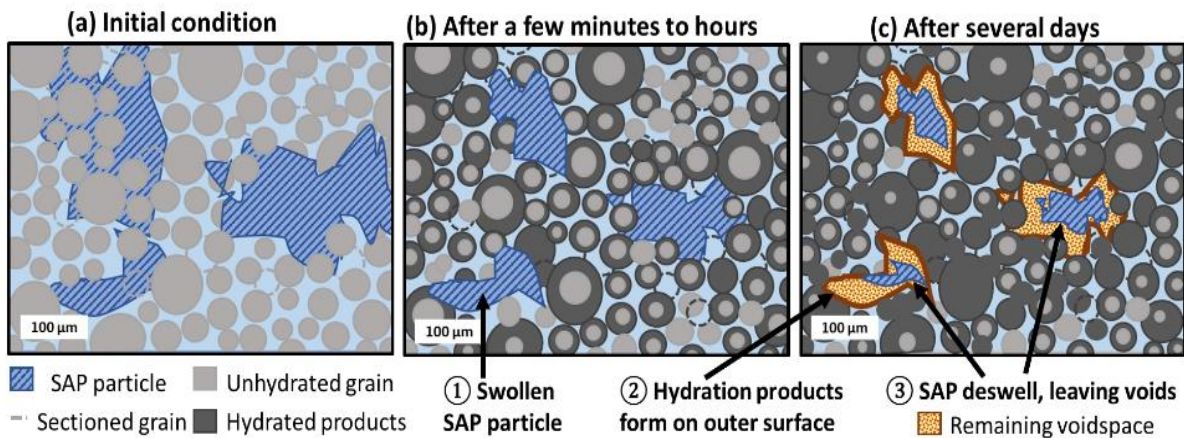
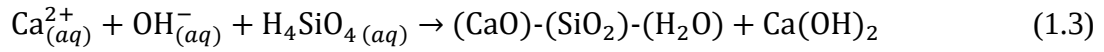
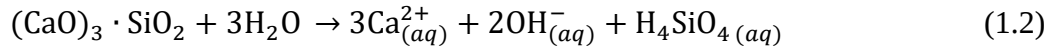


Figure 1.2. Illustration of the cement hydration process with SAP internal curing in cement paste (a) immediately after mixing Portland cement, water, and SAP; (b) through final set; and (c) after several days curing. Figure from Erk and Bose.³

1.3 Cement Hydration

Anhydrous ordinary portland cement (OPC) chemically reacts with water—hydrates—to become cement paste. Hydrated cement paste is an adhesive ceramic material that, when mixed with aggregate, forms the composite concrete.⁷ When OPC is mixed with water, its reactants dissolve into solution and, upon hydration, precipitate.⁸ Although reactants in OPC are generally impure, the hydration reactions can be represented by simplified (sometimes unbalanced) reactions such as the one for the hydration of tricalcium silicate (C_3S) in Equation 1.1, which is written in cement chemistry nomenclature.^{7,27} Alite, the impure form of C_3S present in OPC, accounts for 50-70% of OPC by mass and begins hydration within one hour of exposure to water.^{7,8,28,29} Equation 1.2 shows the dissolution of C_3S into calcium ions, hydroxide ions, and H_4SiO_4 , however

the solution contains a mix of the silicate species H_4SiO_4 , H_3SiO_4^- , and $\text{H}_2\text{SiO}_4^{2-}$. Equation 1.3 shows the precipitation of calcium-silicate-hydrate (C-S-H) and calcium hydroxide (CH).³⁰ C-S-H is a non-stoichiometric compound with a Ca/Si ratio ranging from around 1.2 to 2.1.³¹ As such, these representative hydration reaction equations are unbalanced and calcium silicate hydrate is represented as “C-S-H” or “(CaO)-(SiO₂)-(H₂O)” with dashes to signal the absence of a specific stoichiometry.²⁹



C-S-H is the majority cement hydration product, accounting for 50-60% of hydrated cement paste by volume, as well as the majority contributor to long-term strength and durability. Its strength can be attributed to its extremely high specific surface area of 100-1000 m²/g and corresponding extremely large van der Waals' forces.^{7,32} CH accounts for 20-25% of hydrated cement paste by volume. CH forms hexagonal platelets that have low specific surface area and can provide preferred cleavage sites, making it a secondary provider of strength.⁷ For the purposes of understanding SAP internal curing, the key significance of the cement hydration reaction is the fact that water is a necessary reactant in the formation of the hydration products provide cement, mortar, and concrete's strength and durability.

2. EVALUATION OF BATCHING SEQUENCE AND VERIFICATION OF SAP IN CONCRETE

Text and figures in the following chapter have been adapted with permission from³³ **Adams, C. J.**; Bose, B.; Mann, E.; Erk, K. A.; Behnood, A.; Castillo, A.; Rodriguez, F. B.; Wang, Y.; Olek, J. Superabsorbent Polymers for Internally Cured Concrete. *JTRP Tech. Reports* **2022**. <https://doi.org/10.5703/1288284317366>.

2.1 Overview

This section describes the research results obtained during the investigation of batching sequence and verification of SAP's presence when using SAP. The objective of this study was to determine the effects of the order of addition of SAP during the concrete batching sequence on the resultant concrete properties as well as to determine methods for verification of the presence of SAP particles in fresh concrete. This objective was accomplished first by evaluating two batching sequences with respect to the effect on slump, air content, compressive strength, and microstructure of concrete, and second by participation in a RILEM TC 260-RSC interlaboratory study on SAP verification in as-delivered concrete. The primary finding from the batching sequence study was that previously mentioned concrete properties were insensitive to the point of addition of SAP (i.e., it did not matter whether SAP was added to the cement or to the aggregate in batching sequence). The primary finding from the SAP presence verification study was that qualitative assessment could be performed on-site in minutes via sieving, while quantitative assessment required lab-scale testing.

2.2 Materials and Methods

Two approaches to adding dry SAP particles during the concrete mixture batching sequence were evaluated: (1) SAP-to-cement and (2) SAP-to-aggregate. Both sequences were prepared in a Lancaster low shear mixer (Lebanon, PA) using oven-dried aggregates with additional water added to bring the aggregates to saturated surface dry conditions (SSD). In both sequences, fine and coarse aggregate were mixed first for two minutes. This was followed by addition of cement and then followed by addition of water, HRWRA, and AEA. Type I cement (13.6 kg), #23 fine aggregate (9.6 kg), #8 coarse aggregate (13.6 kg), tap water (2.5 kg) MasterGlenium 7511 (1.0%

bwoc), MasterAir AE 200 (0.3% bwoc), and an anionic SAP (termed “LA-SAP” in [Chapter 3](#) of this dissertation) were used. All components were mixed for another two minutes before testing. Typical lab procedure for batching sequence is SAP-to-cement where dry SAP particles are stirred into cement to promote distribution of the SAP particles throughout the mix before the addition of water. To evaluate sensitivity of properties to batching, a SAP-to-aggregate method was tested, concrete was batched starting by mixing dry fine and coarse aggregate with SAP before the addition of cement, water, HRWRA, and AEA.

Air content of fresh concrete was measured using ASTM C231.³⁴ Slump³⁵ was measured immediately and at 30 minutes after the addition of water to the mix. Concrete was cast into 4x8” cylinders for compression testing at 7 and 28 days.³⁶ Three specimens were cast for each mix order for testing at each age. Microstructure samples were cut from purpose-cast cylinders at 7 days and hydration halted with isopropanol for backscattered SEM analysis.

Qualitative and quantitative verification of SAP in fresh mortar were tested using two acrylate SAPs of unknown composition with a different maximum particle sizes, referred to here as “large” and “small.” High aggregate load mortar (cement:fine aggregate of 1:5.5) at 0.40 w/c with 0.15% SAP bwoc and 0.8% HRWRA was used for testing.

2.3 Results

2.3.1 Fresh Concrete Properties

The SAP-to-cement sequence resulted in concrete with air content of 5.8%, an initial slump of 6.6 inches, which increased to 6.8 inches at thirty minutes. The SAP-to-aggregate sequence produced concrete with a lower air content of 4.4% and lower slump of 4.5 inches, which fell to 3.7 inches at thirty minutes. The targets established with the input of the study advisory committee for air content and slump were 5-8% and 5-8 inches, respectively. The SAP-to-cement concrete fell within these ranges, while the SAP-to-aggregate was slightly under in both air content and slump.

2.3.2 Hardened Concrete Properties

SAP-to-cement and SAP-to-aggregate orders of addition displayed comparable compressive strength at 7 days (6440 psi and 6270 psi, respectively; p-value = 0.22, all t-tests were

two-tailed hypothesis tests conducted at the 5% significance level). At 28 days, SAP-to-cement (7212 psi) displayed increased strength over SAP-to-aggregate (6945 psi). While this difference in compressive strength is statistically significant (p -value = 0.04), it only amounts to a 4% improvement in compressive strength.

SEM analysis showed similar microstructure and SAP distribution between the two orders of addition ([Figure 2.1](#)). Prior to analysis, SAP distribution in the SAP-to-aggregate sample was of particular interest—would the SAP particles stick or otherwise concentrate around the aggregates, potentially disrupting the interfacial transition zone? No evidence of this behavior was observed in either batching method.

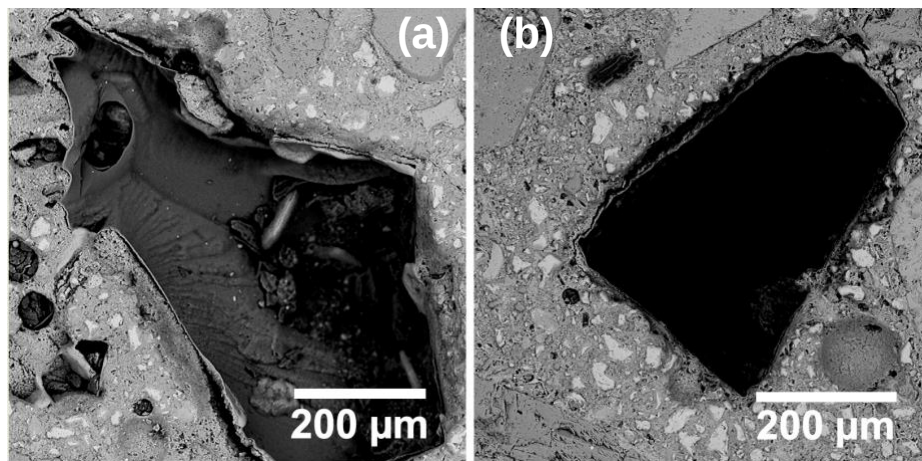


Figure 2.1 SEM micrographs of 7-day 0.42 w/c concrete samples with: (a) LA-SAP added to cement and (b) LA-SAP added to aggregate. The remnants of the dehydrated LA-SAP particle were clearly visible as the grey film in the void shown in (a). The HA-SAP particle remnants were less visible, but still present in the void shown in (b).

2.3.3 Verification of SAP

Qualitative verification of SAP was performed via sequential sieving of approximately 0.2 kg of the prepared mortar. First, mortar was rinsed through a 2 mm (#10) sieve with tap water to remove aggregates. The remaining slurry was then rinsed through a 0.063 mm (#230) sieve with tap water to collect SAP particles. At this time, positive or negative verification of the presence of SAP in the original mortar was possible via visual observation and tactile inspection of the soft wet SAP particles ([Figure 2.2](#)). The entire procedure was completed in less than 10 minutes. Similar magnitude sieves of a different mesh sizes could be used to similar effect.



SAP A: large particles



SAP B: small particles

Figure 2.2 SAP collected on a 0.063 mm sieve from fresh mortar samples for visual and tactile verification.

Quantitative verification of SAP required careful collection of all SAP from a known quantity of mortar. To promote complete separation of SAP from higher density aggregates and cement, approximately 2 L of mortar was massed and placed in a five-gallon bucket along with an excess of tap water (approximately 10 L). The contents of the bucket were swirled into a whirlpool for one minute and then allowed to settle. SAP is less dense than water and did not settle with the aggregates and the majority of the cement. All liquid and floating solids (including SAP) were poured off through a 0.125 mm sieve. Contents of the sieve were examined for qualitative verification of SAP and collected. The collected sample was dried to constant mass, then oven-heated to 500°C for three hours, to burn off the SAP fraction of the sample without degrading any mineral content. The sample was then massed again to find the mass of SAP burned off, which was compared to the expected mass of SAP in the starting mortar sample. The percent error in experimental measurement of SAP was higher (14%) for the small SAP particles than for the large SAP particles (9%) due to difficulty in reclaiming the sample from the 0.125 mm sieve. Sample collection was performed in approximately 10 minutes, with a total experimentation time of three days. A similar magnitude sieve of a different mesh size could be used.

2.4 Conclusions and Implications

The following conclusions resulted from this batching sequence study:

- The slump and air content of SAP-to-cement fell within the target ranges for concrete in this study, while the slump and air content of SAP-to-aggregate fell slightly below the target ranges for concrete in this study.
- The batching sequence of SAP-to-cement concrete yielded comparable or minorly improved strength at both 7 and 28 days compared to SAP-to-aggregate concrete.
- SAP showed no signs of interference with the interfacial transition zone, “sticking” or concentrating around the aggregates, or agglomeration within the cement matrix in the SEM analysis of either order of addition.
- Qualitative verification of the presence of SAP in fresh mortar was performed in minutes using field-ready equipment.
- Quantitative verification of the amount of SAP in fresh mortar was performed at lab-scale with 9-14% error.

A number of implications resulted from this study. First, for the same AEA and HRWRA dosage and conventional SAP dosages, addition of SAP-to-cement yielded higher air content and slump values, suggesting that this order of addition would require lower admixture dosages than that of SAP-to-aggregate to achieve the same target air content and slump values. Second, SAP distribution within the mixture was insensitive to the order of addition. Seven-day compressive strength of concrete was also insensitive to the order of addition of SAP and the increased strength gain at 28 days displayed in SAP-to-cement concrete was minimal. Combined, these results indicate that in terms of hardened properties, concrete internally cured with SAP yields similar properties regardless of order of addition of SAP, meaning that the order of addition could be selected to optimize processing workflow without sacrificing material properties. Furthermore, verification of SAP in as-delivered concrete could be performed in minutes on-site, with follow-up quantitative lab-scale testing of delivered SAP dosage possible within days.

3. EVALUATION OF MIX DESIGN STRATEGIES TO OPTIMIZE FLOW AND STRENGTH OF MORTAR INTERNALLY CURED WITH SUPERABSORBENT POLYMERS

Text and figures in the following chapter have been adapted with permission from³⁷ **Adams, C. J.**; Bose, B.; Olek, J.; Erk, K. A. Evaluation of Mix Design Strategies to Optimize Flow and Strength of Mortar Internally Cured with Superabsorbent Polymers. *Constr. Build. Mater.* **2022**, 324, 126664. <https://doi.org/10.1016/J.CONBUILDMAT.2022.126664>.

3.1 Introduction

Use of more durable concrete for the remediation, repair, and expansion of infrastructure would lead to environmental and economic savings. For every ton of portland cement manufactured, about 1 ton of CO₂ gas is emitted, accounting for 8% of annual global CO₂ emissions.⁴ The cement industry ranks third in industrial energy consumption, accounting for 7% of global usage.³⁸ One promising strategy to reduce the environmental impact of global production and utilization of concrete is to focus on its durability and service life. Usage of more durable concrete would reduce maintenance costs, increase return on investment, and decrease frequency of replacement of existing structures, thus decreasing CO₂ emissions and energy consumption.

Compared to traditional concrete, internally cured concrete has been reported to achieve higher degrees of hydration while also attaining reduced shrinkage and cracking potentials.¹⁴ These attributes make internally cured concrete a viable material for improving durability and service life of concrete infrastructure. However, for these benefits to be realized, practical implementation strategies are needed to facilitate the transition of bench science technology to application at scale.

Internal curing of concrete is achieved by entrainment of water in some sort of reservoir that can deliver additional water to the hydration reaction within the cement matrix deeper than the limit of water diffusion from external surfaces as described by Jensen and Hansen in 2001 and 2002.^{11,39} One of the most common methods of internal curing of concrete involves the use of lightweight aggregate (LWA). While demonstrated to be a successful strategy in the past (e.g., when used in high performance concrete bridge decks),⁴⁰ LWA has some drawbacks when it comes to field implementation, the biggest of which is the need for prewetting before incorporation into the concrete mixture.⁴¹ Prewetting is typically achieved by applying a soaker hose or sprinkler to

a pile of LWA before use. The exact length of prewetting time varies depending on the specific LWA used and can take 24-48 hours.^{40,42} In general, the process of LWA prewetting is vulnerable to inconsistencies in implementation, leading to unpredictable values of the total water to binder ratios (w/b).⁴¹ Additionally, in order to be effective as an internal curing agent, the LWA needs to replace at least 20% of the fine aggregate in a given mixture.⁴⁰ More recently, the use of superabsorbent polymers (SAP) has gained increased interest, as evidenced by the 2021 updated RILEM state-of-the-art report and a 2022 review of recent advances in SAP for concrete.^{10,43}

The degree of hydration, strength, durability,^{44,45} resistance to cracking,³⁹ and freeze-thaw resistance^{46,47} of cementitious mixtures can also be increased through internal curing with very low dosages (0.2% by weight of binder) of SAP particles. These SAP particles consist of covalently crosslinked polyelectrolyte networks that can be chemically and physically tuned to absorb 100 to 1000 times their mass in water, which allows SAP to function as a water entraining material within the cement matrix.³ For applications involving internal curing of concrete, SAP is typically composed of poly(acrylic acid-acrylamide)^{17,48} which can be either obtained commercially or custom synthesized (for control of its chemistry). The size of SAP particles can be controlled through synthesis method or mechanical grinding.⁴⁹⁻⁵¹ When used as an internal curing agent, the SAP is added to cementitious mixtures in the form of dry particles.

SAP facilitates internal curing by first absorbing, then desorbing (over time) water within the cement paste matrix.^{3,52,53} A portion of the mixing water used in preparation of the concrete mixture is absorbed by SAP particles causing them to swell. As the cement hydration reaction progresses, the osmotic pressure gradient prompts deswelling of SAP. As the water desorbs from SAP particles, it is distributed within the cement paste matrix and becomes available for further cement hydration.^{11,54-58} The remnants of deswelled SAP remain within the discontinuous voids previously occupied by swollen SAP particles.^{18,26,53}

Since, as previously mentioned, SAP is added to the cementitious mixture in its dry state, the water it absorbs comes from the mixing water. By absorbing a portion of the mixing water, SAP effectively renders that water unavailable for cement hydration until it begins to desorb. This uptake of water reduces the effective water-cement ratio and decreases the workability of the fresh mixture.⁵⁹ In some studies, presoaking of SAP prior to mixing with other raw materials reduced the effect of SAP on workability.⁶⁰ In cases where SAP is added in dry state, the workability of cementitious mixtures can be increased through the addition of extra water, use of high-range water

reducing admixture (HRWRA), or both.^{46,61,62} Although presoaking of SAP can yield better workability, addition of SAP in dry state ensures better dispersion of the SAP particles in the cementitious matrix.^{63,64}

The amount of extra water added when using SAP is typically determined by one of three approaches: (1) extra water is added until the flow of a mixture containing SAP matches that of an equivalent mixture without SAP,⁵⁷ (2) 5% extra water by weight of binder is added when using SAP of any type,⁵⁹ or (3) extra water is added according to the equilibrium absorption capacity of the SAP being used.⁶⁵ Equilibrium absorption capacity of the SAP is the mass of liquid absorbed per mass of dry SAP when the absorption process has reached its equilibrium.⁵⁰ This value is determined by *ex situ* immersion measurements, such as gravimetric tea bag or filtration tests, with equilibrium corresponding to mass stabilization. The mass stabilization generally requires relatively long periods of time (typically greater than 60 minutes).⁶⁶ In the third approach for determination of the extra water needed in the mixture, the equilibrium absorption capacity of the SAP is assumed to be equivalent to the amount of water sequestered from the mixture by the SAP through the process of absorption. In either the second or third approach, extra HRWRA is typically added according to the HRWRA dosage required to maintain workability of the mix.⁶⁷ The first approach addresses initial flow effects of SAP usage but does not account for additional liquid absorption by SAP prior to desorption. Unfortunately, there are no established guidelines as to which of these approaches optimizes workability while minimizing the impact on strength development. That gap in knowledge is one of the factors limiting the use of SAP in large-scale projects.

Another reason for the limited use of SAP in large-scale applications is the fact that most studies involving SAP only investigated concrete mixtures with a low (0.15 to 0.35) water-cement ratio (w/c) values.^{26,48,54,62} This is because SAP has been found to be efficient in mitigating autogenous shrinkage,^{11,61,68,69} which is most prevalent in water-starved concrete systems. Few studies have focused on the use of SAP in mixtures with w/c of 0.42 or higher.⁴⁵

This study aims to directly measure the effects of adding extra water, HRWRA, or both to SAP-containing mortars with initial w/c value of 0.42 to determine whether these approaches can be implemented to maintain the flow. The compressive and flexural strengths of mortar samples were also measured to provide guidance as to which of the above-mentioned strategies ensure a

preservation (or enhancement) of strength while providing sufficient workability of the fresh mortar mixture.

3.2 Materials and Methods

3.2.1 Characterization of Superabsorbent Polymers

Two acrylic acid-based SAPs from industrial sources were used in as-received form. For the purposes of this paper, these two SAPs are identified as “LA” (low absorption) and “HA” (high absorption), indicating their relative absorption capacity as determined through gravimetric swelling tests. Results of the gravimetric swelling tests that led to this nomenclature are detailed in [Section 3.3.1](#).

Scanning electron microscopy (SEM) images of dry SAP particles are shown in [Figure 3.1](#). Here, the expression “dry SAP particles” refers to the state of SAP as received and stored in a sealed container at room temperature until testing. Both SAPs were composed of particles with irregular shapes. The dry particle size of the LA- and HA-SAP were calculated to be $116.0 \pm 70.0 \mu\text{m}$ and $48.9 \pm 21.9 \mu\text{m}$, respectively. These average sizes were obtained by analyzing the SEM images of about 100 particles using ImageJ software.

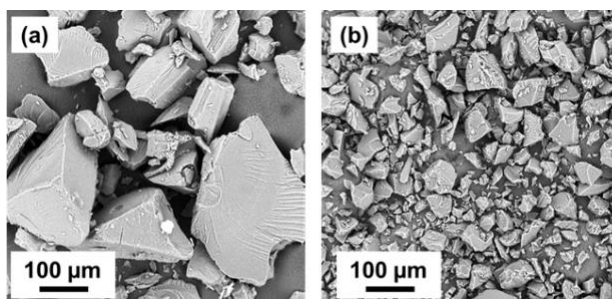


Figure 3.1. SEM images of the (a) LA and (b) HA dry SAP particles used in the experiments.

The absorption capacity of the SAP particles was measured using gravimetric absorption tests in both reverse osmosis (RO) water and cementitious pore solution.^{66,70} Synthetic or extracted pore solution is a well-established method for characterizing swelling behavior and absorption capacity of SAP.^{20,71} These *ex-situ* absorption tests typically yield an overestimation of the amount of water that would be absorbed by SAP particles in real applications as the ion concentration of the immersion solutions does not change over time as it does in actual hydrating mixtures.^{50,55,72}

Nonetheless, this method provides a simple and practical way of estimating absorption capacity of SAP particles.

The synthetic pore solution was prepared by adding tap water to cement at a 1:10 ratio by weight and mixing these two materials for 30 seconds. The solution was then allowed to settle for 1 minute before decanting. Fresh pore solution was prepared for each batch of gravimetric absorption tests. Ordinary Type I portland cement (OPC) in compliance with ASTM C150⁷³ was obtained from Buzzi Unicem (Greencastle, IN) and used to prepare all pore solutions. This cement was used throughout this study and its composition (as per its mill certificate) is shown in [Table 3.1](#).

Table 3.1. Composition of the ordinary Type I Portland cement used in this study.

Oxide Composition	wt. (%)	Phase Composition	wt. (%)
SiO ₂	19.50	C ₃ S	60.2
Al ₂ O ₃	5.20	C ₂ S	9.0
Fe ₂ O ₃	2.73	C ₃ A	8.9
CaO	63.42	C ₄ AF	8.1
MgO	2.32		
SO ₃	3.25		

For both the RO water and pore solution measurements, 200 mL of liquid was added to a beaker and a teabag was fully immersed into the solution for 30 seconds. The teabag was allowed to drip dry and was then weighed to obtain the wet mass of the bag (m_{bag}). Then, 0.2 g of dry SAP particles (m_{dry}) were added to the wet teabag. The teabag was then immersed into the solution and removed at specific time intervals of 0.5, 1, 3, 5, 15, 30, 60, 120 minutes for weighing (m_{wet}). In the case of pore solution, the beakers were covered with aluminum foil in between measurements to minimize the potential for carbonation. Gravimetric absorption tests were conducted in triplicate and averaged. The absorption ratio, Q (grams of absorbed fluid per grams of dry SAP particles), was calculated using [Equation 3.1](#).

$$Q = \frac{m_{wet} - m_{bag} - m_{dry}}{m_{dry}} \quad (3.1)$$

To investigate whether the addition of the HRWRA had an effect on the absorption capacities and kinetics of the SAP at low and high admixture dosages, another set of gravimetric absorption tests was carried out in pore solution that contained varying dosages of a Type A/F admixture (ASTM C494/C494M).⁷⁴ The HRWRA used was MasterGlenium 7511 (BASF, Ohio, USA), a polycarboxylate-based aqueous solution. To prepare these absorption solutions, a predetermined amount of HRWRA was added to 200 mL of decanted pore solution and the resulting mixture was stirred for 30 seconds.

The amount of HRWRA added to the pore solution depended on the objective of the test. When examining the effects of a low dosage of HRWRA on SAP absorption capacity, the admixture dosage incorporated in the pore solution was 0.7% by weight of cement. However, the mortar samples described in *Approach II*, below, utilized approximately twice the dosages of HRWRA. To address this issue, SAP absorption was also tested in pore solution containing 1.4% HRWRA by weight of cement.

3.2.2 Three Approaches used for Modifying Mixture Composition of Mortars

The compositions of the mortar mixtures used in the study are reported in Table 3.2. The samples are identified as X_A%_B% where X represents the type of SAP used (if any), A is the % of extra water added to offset SAP absorption and B is the % of HRWRA used to maintain flow. As reported in this paper, the dosages of extra water and HRWRA are always given as percent by weight of cement (% bwoc). As an example, HA_5%_0.3% signifies that the mortar was internally cured with HA-SAP particles, and that it contained, respectively, 5% bwoc of extra water (to offset SAP absorption), and 0.3% bwoc of HRWRA (to control the flow). Three approaches for modifying mortar mixture designs were selected to evaluate changes in workability and other properties when using SAP. These included: *Approach I*, where only extra water was added to offset SAP absorption and no HRWRA was used; *Approach II*, where only HRWRA was used; and *Approach III*, where both extra water and HRWRA were added. The amount of extra water added was determined using two common methods: (1) addition of a fixed (i.e., 5%) amount and, (2) addition of an amount determined by measuring the pore solution equilibrium absorption capacity of the specific SAP.^{67,69,72} More details are provided below.

Table 3.2. Composition of mortar mixtures.

Mix Design	Approach Number	Sample	Cement (g)	Sand (g)	Water (g)	SAP (g) / (% bwoc)	HRWRA (mL) / (% bwoc)	(w/c) _{total}	Extra Water (% bwoc)	Initial % Flow (at 10 min)‡
1	I	No SAP_0%_0%	3500	9625	1610	0 / 0%	0 / 0%	0.42	0%	66%
2*	I	LA_0%_0%	3500	9625	1610	7 / 0.2%	0 / 0%	0.42	0%	21%
3*	I	HA_0%_0%	3500	9625	1610	7 / 0.2%	0 / 0%	0.42	0%	31%
4	I	No SAP_5%_0%	3500	9625	1786	0 / 0%	0 / 0%	0.47	5%	100%
5	I	LA_5%_0%	3500	9625	1786	7 / 0.2%	0 / 0%	0.47	5%	49%
6	I	HA_5%_0%	3500	9625	1786	7 / 0.2%	0 / 0%	0.47	5%	64%
7	I	No SAP_7%_0%	3500	9625	1852	0 / 0%	0 / 0%	0.49	7%†	102%
8	I	LA_7%_0%	3500	9625	1852	7 / 0.2%	0 / 0%	0.49	7%†	62%
9	I	No SAP_10%_0%	3500	9625	1954	0 / 0%	0 / 0%	0.52	10%†	124%
10	I	HA_10%_0%	3500	9625	1954	7 / 0.2%	0 / 0%	0.52	10%†	100%
11§	II, III	No SAP_0%_0.5%	3500	9625	1610	0 / 0%	17.5 / 0.5%	0.42	0%	113%
12	II	LA_0%_1.45%	3500	9625	1610	7 / 0.2%	50.8 / 1.45%	0.42	0%	104%
13	II	HA_0%_1.15%	3500	9625	1610	7 / 0.2%	40.3 / 1.15%	0.42	0%	120%
14	III	LA_0%_0.5%	3500	9625	1610	7 / 0.2%	17.5 / 0.5%	0.42	0%	57%
15	III	HA_0%_0.5%	3500	9625	1610	7 / 0.2%	17.5 / 0.5%	0.42	0%	93%
16	III	No SAP_5%_0.3%	3500	9625	1786	0 / 0%	10.5 / 0.3%	0.47	5%	120%
17	III	LA_5%_0.3%	3500	9625	1786	7 / 0.2%	10.5 / 0.3%	0.47	5%	63%
18	III	HA_5%_0.3%	3500	9625	1786	7 / 0.2%	10.5 / 0.3%	0.47	5%	91%
19	III	No SAP_7%_0.27%	3500	9625	1852	0 / 0%	9.5 / 0.27%	0.49	7%†	124%
20	III	LA_7%_0.27%	3500	9625	1852	7 / 0.2%	9.5 / 0.27%	0.49	7%†	83%
21	III	No SAP_10%_0.13%	3500	9625	1954	0 / 0%	4.4 / 0.13%	0.52	10%†	135%
22	III	HA_10%_0.13%	3500	9625	1954	7 / 0.2%	4.4 / 0.13%	0.52	10%†	98%

*Mix was not cast due to insufficient workability (flow at 10 minutes was less than 45%).

†Extra water percent was determined by the equilibrium absorption capacity in pore solution of the relevant SAP (7% for LA-SAP and 10% for HA-SAP.) Full equilibrium absorption capacity results are reported in [Section 2.3.1](#).

‡Full analyses of “percent flow” results are presented in [Sections 3.3.2, 3.3.3, and 3.3.4](#).

§ Mix 11 met the design specifications of both Approach II and Approach III. Mix 11 was a 0.42 w/c mortar without any extra water with HRWRA dosed such that the mortar demonstrated an initial flow of $110 \pm 10\%$, which met the requirements of Approach II. Additionally, Mix 11 did not contain any SAP, which in combination with its HRWRA dosage determination, met the requirements of a 0.42 w/c, No SAP mortar within the specifications of Approach III.

The proportion of cement to sand in all mortar mixtures was 1:2.75 by weight. The cement used was the same as that used for absorption capacity tests. Locally available natural siliceous sand was used to prepare mortars. Prior to usage, the sand was oven dried and sieved to pass through a No. 4 (4.75 mm) sieve. The HRWRA, when used for mortar mixes, was the same one as that used for absorption capacity tests. The admixture was completely pre-dissolved in the mixing water prior to addition to the mixer.

The mortars were prepared in a 20 L capacity mortar mixer (Hobart HL200, Ohio, USA). Sand and water in the amount needed to bring previously oven-dried sand to SSD condition (ASTM C128-15)⁷⁵ were placed in the mixing bowl and stirred for ten seconds, then mixed at medium speed for 1 minute and 50 seconds. The mixer was then stopped and dry cement (as well as dry SAP particles, when used) was added to the bowl, followed by the mixing water. The materials in the bowl were then stirred by the mixer for 10 seconds and mixed for 1 minute 50 seconds at medium speed. Once the mixing cycle was completed, the mixing bowl was removed from the mixer and a metal spoon was used to hand stir the mortar three times.

Approach I: Extra water – no HRWRA

In this set of tests (Mix Designs 1-10 in [Table 3.2](#)), only water was used to improve workability and no HRWRA was added to any of the mixes. LA- and HA-SAP mortar mixes were tested both with and without extra water. Reference mixes without SAP were made at each resulting w/c. When extra water calculations were based on the pore solution absorption capacity of the SAP, then the amount of extra water required for SAP absorption was calculated by multiplying the equilibrium absorption capacity of the SAP (g pore solution/g SAP) by the total mass of dry SAP added to the mix. This resulted in the addition of 7% bwoc extra water for the LA-SAP and 10% bwoc extra water for the HA-SAP.

Approach II: HRWRA dosage varied to achieve target flow

Small test batches of mortars were produced at w/c of 0.42 and various dosages of HRWRA to find the dosage required to achieve a target flow of $110\% \pm 10\%$ at 10 minutes after the addition of water to cement. [Section 3.2.3](#) details both the small batch mixing and flow testing procedures

used on these test batches. For more details regarding mix design proportions, see [Table 3.2](#) (Mix Designs 11-13).

Approach III: HRWRA dosage set to achieve target flow of reference at a given w/c value.

Approach III was developed to facilitate the collection of a complete set of compressive and flexural strength data for all w/c of interest. In *Approach I*, the SAP-containing mortars with total w/c value of 0.42 were too stiff to be cast in the molds (50 mm cubes and 40 x 40 x 160 mm prisms) used for preparation of specimens for, respectively, compressive and flexural strength determination. As such, it was not possible to collect a complete set of mechanical strength data for the specimens prepared using *Approach I*. For *Approach III*, all samples contained some dosage of HRWRA to provide uniformity of mix design while also ensuring that even the lowest w/c samples were sufficiently workable for casting. For each reference (i.e., no SAP) mixture with w/c represented in the mixes prepared using *Approach I*, the HRWRA dosage necessary to achieve at least $110\% \pm 10\%$ flow of mortar for the reference mortar without SAP was determined using test batches as in *Approach II*. The resulting HRWRA dosage was then used in all mixes, including mixtures with SAP, at that w/c. This allowed mechanical testing specimens to be cast for all mixes in this set. The amount of extra water required for SAP absorption was calculated the same way as described for *Approach I*, [above](#). For more details regarding mixture proportions, see [Table 3.2](#) (Mix Designs 11 and 14-22).

3.2.3 Mortar flow testing

Small batches (about 1 liter, prepared using $1/8^{\text{th}}$ of the mass of those mixed for specimen casting detailed in [Table 3.2](#)) of each mortar were mixed using a 5 L capacity mortar mixer (Hobart N50, Ohio, USA) following the same mixing sequence and duration as that described in [Section 3.2.2](#). Percentage flow of mortar was measured over time using ASTM C1437-20⁷⁶ with the following modifications: each layer of mortar placed in the mold was tamped 25 (rather than 20) times for better consolidation and, after dropping the table, the diameter of the spread mortar was measured six (rather than four) times for improved accuracy. The spread values were measured at 10, 30, 60, 90, and 120 minutes after water was added to the mortar mix in order to capture the

change in flow values through initial set time (92 minutes as reported in the cement's mill certificate).

3.2.4 Strength characterization

Compressive strength and flexural strength values were determined for all mortar samples according ASTM C109/C109M-20b⁷⁷ and ASTM C348-20,⁷⁸ respectively. All specimens were both hand-tamped and placed on a vibrating table for thirty seconds to promote consolidation. Compressive strength of the mortar specimens was measured at 3, 7, and 28 days while flexural strength was determined at 7 and 28 days. All specimens were cured at $23 \pm 0.1^\circ\text{C}$ and $50 \pm 0.1\%$ relative humidity (RH) until the time of testing. This curing regime is different from that stated in ASTM C109⁷⁷ and was implemented to eliminate potential external curing.

3.2.5 Microstructure of mortars

Mortar specimens prepared using the method described in [Section 3.2.2](#) were used for SEM imaging. Only select 28-days old samples were used for microstructure analysis. After 28 days of curing at $23 \pm 0.1^\circ\text{C}$ and $50 \pm 0.1\%$ RH, the specimens were immersed in isopropanol for 48 hours to stop hydration, cut into manageable pieces with a glycol-cooled diamond saw, vacuum dried for 48 hours at $23 \pm 5^\circ\text{C}$, and then vacuum impregnated with epoxy. The epoxy embedded mortar samples were then dried at $60 \pm 5^\circ\text{C}$ for 24 hours. Then, a fresh section of each epoxy coated sample was exposed by cutting with a diamond saw and polished. The samples were then carbon coated and imaged (in the backscattered mode) using a NanoScience Instruments Phenom Desktop SEM (Arizona, USA). For the mortar samples containing SAP particles, at least 30 random SAP voids were imaged and further analyzed using ImageJ software to quantify size of the voids. The analysis of the size of the voids involved measuring their diameter in several directions using ImageJ and then reporting the largest diameter of that particular void to compare the average size of SAP voids in select mortar samples following the methodology described in Bose, et al.¹⁸

3.2.6 Statistical Analysis

All error bars reported represent $\pm$ one standard deviation. When significance is stated, a two-sample, two-tailed hypothesis “t-test” was conducted at the 95% confidence level and the p-value is reported.

3.3 Results and Discussion

3.3.1 Characterization of SAP absorption capacity

The absorption capacities of the low absorption (LA) and high absorption (HA) SAP types in RO water and in synthetic pore solution are shown in [Figure 3.2](#). The absorption capacities of both SAP compositions immersed in synthetic pore solution ([Figure 3.2b](#)) were reduced compared to their absorption capacities when immersed in RO water ([Figure 3.2a](#)). This is because the ions present in pore solution reduced the osmotic pressure that drives the process of water absorption.⁶⁶ After the first 30 minutes of exposure to the synthetic pore solution ([Figure 3.2b](#)), the LA-SAP particles had a significantly (~30%) lower absorption capacity compared to HA-SAP particles. While SAP compositions are unknown, it has been demonstrated previously that either an increase in anionicity²⁰ or increase in crosslinking density will decrease the equilibrium absorption capacity of SAP.^{17,21} In addition, plots presented in [Figure 3.2a](#) indicate that the LA-SAP particles absorbed RO water more rapidly than the HA-SAP particles even though the HA-SAP particles were of smaller average size. While insights into this phenomenon is not fully possible without information regarding SAP composition, it has been seen in the past that smaller particles generally absorb more quickly.²¹ However, it is also possible that the smaller average size of the HA-SAP particles gave rise to a phenomenon known as “gel blocking” where the flow of water into the teabag is physically blocked as the small particles aggregate and swell.⁷⁹

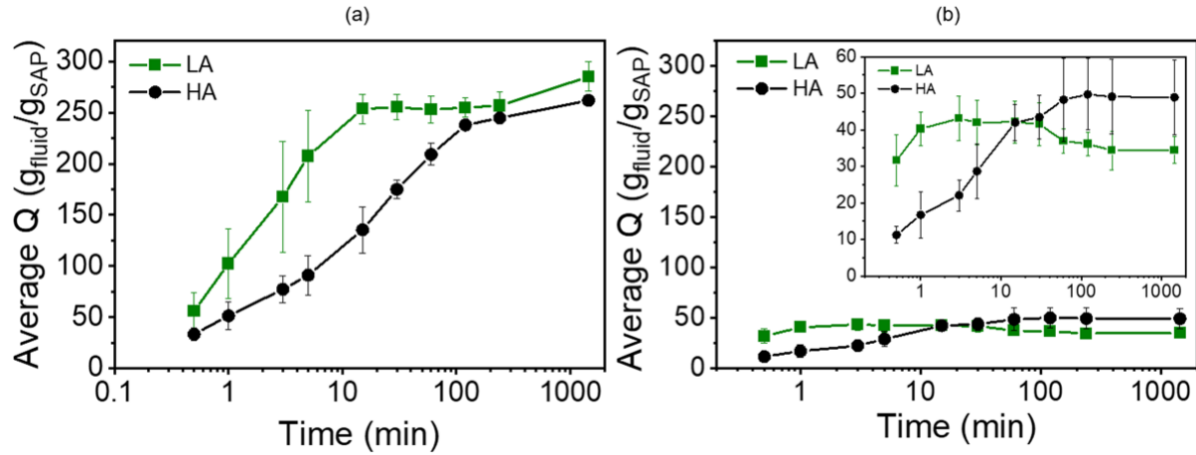


Figure 3.2. Absorption capacity of SAP as a function of immersion time in: (a) RO water and (b) synthetic pore solution (inset displays the same data with a smaller-range vertical axis for greater detail).

Results shown in [Figure 3.3](#) compare the absorption capacity of SAP in pore solution formulated with or without HRWRA. These gravimetric swelling tests with HRWRA were conducted to determine if HRWRA influences the absorption kinetics of the SAP types used in this study. The maximum HRWRA dosage tested for each SAP corresponds to the HRWRA dosage required in *Approach II* for SAP-containing mortar mixes a constant w/c of 0.42 to achieve the target flow of $110\% \pm 10\%$ at 10 minutes after the addition of water. There was no significant difference in pore solution absorption capacity of the SAP in presence of the HRWRA when compared to absorption capacity in the absence of HRWRA.

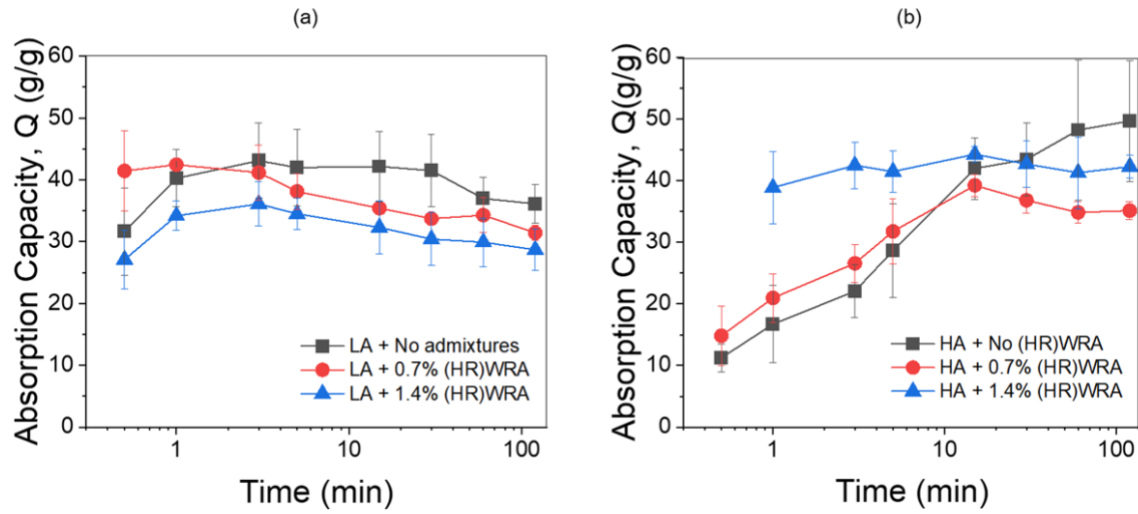


Figure 3.3. Absorption capacity of SAP as a function of immersion time in synthetic pore solution with no HRWRA, a low dosage of HRWRA, and a high dosage of HRWRA for (a) LA-SAP and (b) HA-SAP.

3.3.2 Results from Approach I: extra water – no HRWRA

In *Approach I*, all mortar mixes consisted of only cement, sand, water, and SAP (refer to [Table 3.2](#), Mix Designs 1-10). This allowed for quantification of the effects of SAP on flow of mortar without any potential interactions from HRWRA. Flow, compressive strength, and flexural strength or mortars results are displayed in [Figure 3.4](#).

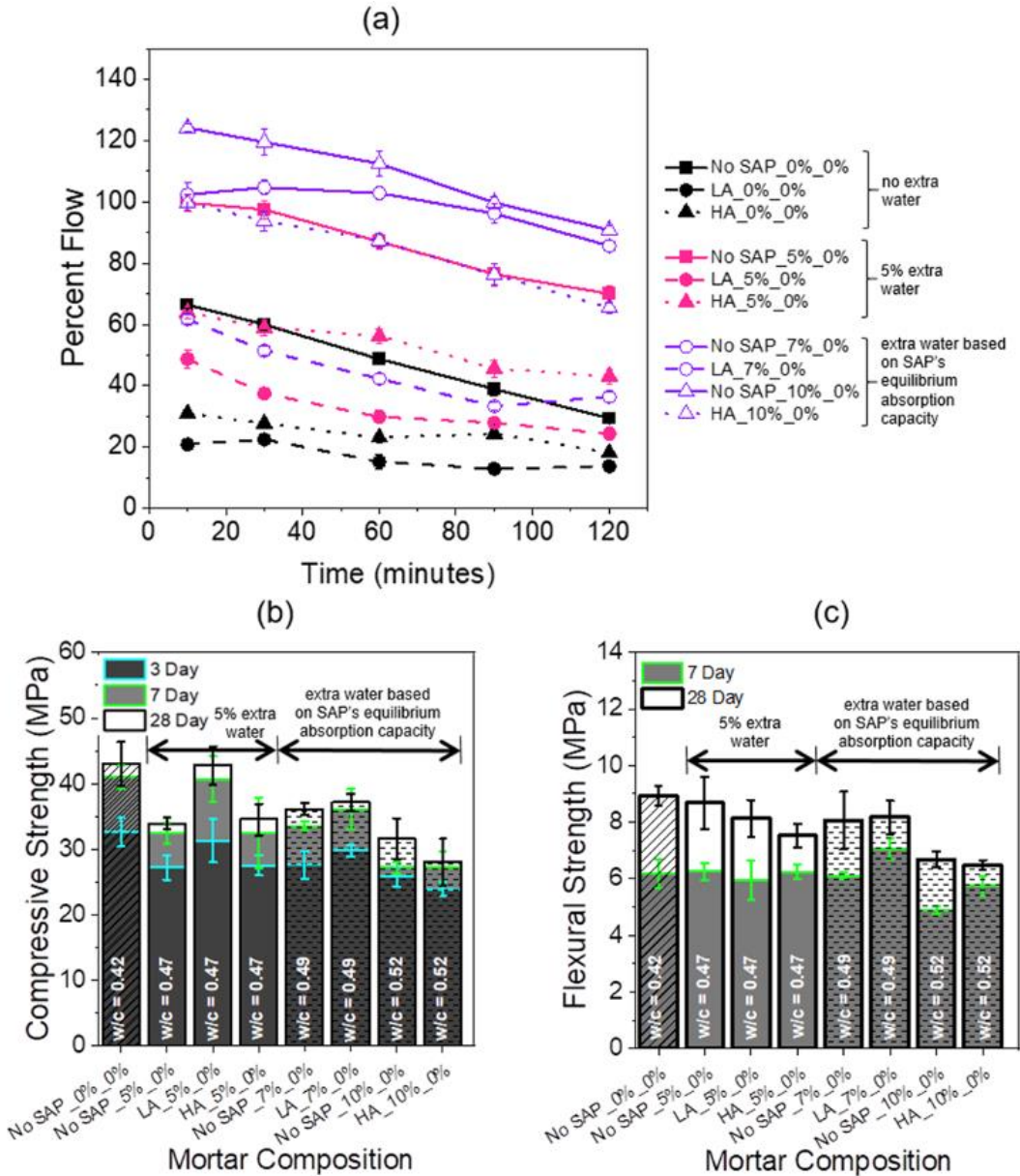


Figure 3.4. (a) Percent flow over time of fresh mortar mixes, (b) compressive strength and (c) flexural strength of mortar containing extra water to offset SAP absorption. No HRWRA was added to these set of mixes. In Figures 4(b) and 4(c), bars with diagonal hatches represent mortars with w/c 0.42 prepared without extra water, bars with no hatches represent mortar mixes with 5% extra water and bars with horizontal dashes represent mortar mixes with extra water amount based on SAP's equilibrium absorption capacity in synthetic pore solution.

Flow behavior of mortars (Approach I)

The percent flow of mortars with and without extra water over time is shown in [Figure 3.4a](#). For each w/c, samples containing SAP had a lower percent flow than the reference sample

without SAP. For example, No SAP_0%_0% had an initial percent flow of 66%, while LA_0%_0% had an initial percent flow of 21% and HA_0%_0% had an initial percent flow of 31%. When present, SAP absorbed mixing water and, as expected, the percent flow of the mortar decreased.⁵⁹

Interestingly, the addition of LA-SAP resulted in a 10-16 percentage points greater drop in percent flow of mortar than the addition of HA-SAP, despite the fact that at equilibrium, HA-SAP had a higher absorption capacity for synthetic pore solution than LA-SAP (Figure 3.2b). For example, samples with 5% extra water, No SAP_5%_0% had an initial percent flow of 100%, while LA_5%_0% had an initial percent flow of 49% and HA_5%_0% had an initial percent flow of 64%. Thus, while equilibrium absorption capacity was useful for characterizing SAPs of different compositions, it did not logically predict the relative effect of SAP composition on percent flow of mortar. Among possible explanations for this disconnect are the impact of time-varying differences between *in situ* pore solution and the *ex situ* synthetic pore solution used for gravimetric absorption tests and differences in SAP absorption kinetics. *Ex situ* pore solution was decanted to use as pore solution in gravimetric absorption tests. The total concentration and types of cementitious ions present in experimental system was constant. *In situ*, the concentration and types of ions present in pore solution changes as additional cement dissolves and hydrates. Over time, the difference between the *ex situ* pore solution and the *in situ* pore solution would reasonably be expected to vary. Along with this variation would come a variation in the difference between *ex situ* and *in situ* absorption kinetics of the SAPs as influenced by the type of ions and their concentration. Relative SAP absorption kinetics could also play a role in the deviation from expected relative effect on mortar flow of the two SAPs. As previously noted, LA-SAP displayed a higher absorption capacity than HA-SAP for the first 30 minutes of gravimetric absorption tests in synthetic pore solution (Figure 3.2b). That higher initial absorption capacity could dominate the effect on mortar flow.

As expected, the addition of extra water to mortar increased the percent flow in both the samples with and without SAP, with the addition of higher amounts of extra water resulting in a greater increase in percent flow. For example, No SAP_10%_0% had a higher percent flow than No SAP_5%_0%, which had higher percent flow than No SAP_0%_0%. Similarly, HA_10%_0% had a higher percent flow than HA_5%_0%, which had a higher percent flow than HA_0%_0%. This confirms that the use of SAP does not alter the fundamental behavior of mortars, namely that the flow of similar mixtures increases as the w/c increases.⁷

Based on laboratory observations, mortars with an initial flow of less than 45% had insufficient workability to be cast into viable specimens. Attempts at casting such mortars resulted in poorly consolidated specimens with externally visible honeycombs and voids, despite the use of a combination of two consolidation techniques (hand tamping and vibration for thirty seconds on a vibrating table) to promote consolidation. As such, mortars with initial flow of less than 45% were not used to cast specimens for mechanical testing. The flow of mortars containing SAP without extra water ([Table 3.2](#), Mix Designs 2 and 3) was significantly less than 45%, confirming the need for attention to mix design when using SAP. All other mortars displayed an initial flow of >45% and were therefore used to cast specimens for mechanical testing ([Table 3.2](#), Mix Designs 1, 4-22).

While the addition of 5% extra water to cementitious mixtures containing SAP is a common approach,^{67,72} it did not result in mortars with sufficient workability for both SAP compositions used in this study. For the HA_5%_0% sample, the initial percent flow was 64%, which had fallen to 59% by 30 minutes, providing sufficient workability for casting. However, for the LA_5%_0% sample, the addition of 5% extra water produced an initial percent flow of 49% which had fallen to 38% by 30 minutes and was thus insufficient for casting. As such, the addition of 5% extra water to SAP-containing mixtures does not universally guarantee sufficient workability for all mixing and placement timescales.

Strength of reference mortars (Approach I)

[Figure 3.4b](#) shows the compressive strength of mortar samples at 3, 7, and 28 days. [Figure 3.4c](#) shows their flexural strength at 7 and 28 days. While analyzing these results, it is first useful to inspect the suite of SAP-free, reference mortars to confirm the observation of expected trends. As expected, the references with w/c of 0.47 (No SAP_5%_0%), 0.49 (No SAP_7%_0%), and 0.52 (No SAP_10%_0%) showed decreased compressive strength compared to the 0.42 w/c reference (No SAP_0%_0%). Only the 0.52 w/c reference showed statistically significant reduced flexural strength compared to the 0.42 reference (p-value = 0.001, all t-tests were two-sample, two-tailed hypothesis tests conducted at the 5% significance level). However, flexural tests have increased sensitivity to single flaws, which means it is not surprising that the 0.47 and 0.49 w/c references would display comparable flexural strength to the 0.42 w/c reference. Importantly,

reference mixtures prepared at a higher w/c behaved as expected compared to the lower w/c references.

Strength of mortars with 5% extra water (0.47 w/c) (Approach I)

SAP-containing mortar samples with 5% extra water (LA_5%_0% and HA_5%_0%) showed comparable or improved compressive strength and comparable flexural strength when compared to the reference of the same w/c (No SAP_5%_0%). In fact, LA_5%_0% not only showed significantly increased compressive strength compared to the same (i.e., 0.47) w/c reference (p-value = 0.007) but displayed compressive strength comparable to the 0.42 w/c reference (p-value of 0.925), despite the fact that it had the higher w/c value by ~12%.

As SAP is an internal curing agent, it is useful consider the indicators of hydration kinetics in evaluating its effects. In [Figure 3.4b and c](#), it is visible that the relative strength gains at 7 days were not always the same between a reference at a certain w/c and a SAP-containing sample at the same w/c. To quantify that difference, the percent of 28-day strength attained by 7 days by a specific sample (% 28-day strength) was calculated for both compressive and flexural strength using [Equation 3.2](#):

$$\% \text{ 28 day strength} = \frac{(\text{strength at 7 days})_n}{(\text{strength at 28 days})_n} \times 100, \text{ where } n \text{ is the mix design} \quad (3.2)$$

This metric serves as an indicator of relative strength development and is shown for all *Approach I* samples in [Table 3.3](#). Both SAP-containing samples with 5% extra water displayed similar percent of 28-day compressive strength attained by 7 days to the reference (96%, 95%, and 94% for, respectively, mix designs 4 (reference), 5, and 6). Interestingly, HA_5%_0% showed a higher percent of 28-day flexural strength attained by 7 days (83%) than that observed for either LA_5%_0% or their reference No SAP_5%_0% (73% and 72%, respectively).

Table 3.3. Percent of 28-day compressive and flexural strength of mortars attained by 7 days.

Mix Design	Sample	% of 28-Day Compressive Strength attained by 7 Days	% of 28-Day Flexural Strength attained by 7 Days
1	No SAP_0%_0%	95%	69%
4	No SAP_5%_0%	96%	72%
5	LA_5%_0%	95%	73%
6	HA_5%_0%	94%	83%
7	No SAP_7%_0%	93%	76%
8	LA_7%_0%	97%	87%
9	No SAP_10%_0%	86%	73%
10	HA_10%_0%	97%	89%

Strength of mortars with extra water based on the equilibrium absorption capacity of SAP (7% and 10% or 0.49 and 0.52 w/c) (Approach I)

Mix designs 7, 8, 9, and 10 contained extra water in the amounts determined from the equilibrium absorption capacity data for LA-SAP (mix designs 7 and 8) and HA-SAP (mix designs 9 and 10). Both the LA- and HA-samples displayed compressive and flexural strength values comparable to those obtained from reference mortar with the same w/c value. The results of the t-tests (comparing each sample to its associated reference) resulted in the following: $p = 0.33$ and $p = 0.85$ for 7% extra water compressive and flexural strength values, respectively; and $p = 0.25$ and $p = 0.38$ for 10% extra water compressive and flexural strength values, respectively. These similar strength values suggest that the addition of SAP may not decrease compressive or flexural strength at a given total w/c.

For both LA_7%_0% and HA_10%_0%, there was an accelerated strength gain through 7 days for the SAP-containing samples compared to their No SAP references (see [Table 3.3](#)). The difference in percentage strength gained between the two samples can be interpreted as a difference in the rate of strength development. LA_7%_0% showed 4 percentage points accelerated compressive strength gain and 11 percentage points accelerated flexural strength gain over No SAP_7%_0%. HA_10%_0% displayed more aggressive accelerated strength gain of 11 percentage points for compressive strength gain and 16 percentage points accelerated flexural strength gain over No SAP_10%_0%. This increase in percentage of 28-day compressive strength attained by 7 days for higher w/c mortars suggests that high-w/c mortars internally cured with SAP may hydrate

more rapidly (and develop higher early-age strength) than similar mortars without SAP, while attaining comparable 28-day strengths.

In summary, when following *Approach I*, it was observed that the introduction of SAP resulted in the need for extra water in order to produce mortar with sufficient flow to cast compressive and flexural test specimens. However, the addition of 5% extra water, as is sometimes recommended,⁶⁷ proved to be insufficient to guarantee mortar with sufficient flow to be cast. At a given w/c, the addition of SAP resulted in comparable or improved values of compressive and flexural strengths. At w/c ≥ 0.49 the strength development was accelerated when using SAP, suggesting that the addition of SAP could benefit high w/c mixes which are not typically considered as candidates for internal curing.

3.3.3 Results from Approach II: HRWRA dosage varied to achieve target flow

As stated in the previous section, following the methods of *Approach I* required the addition of extra water in order to produce castable mortars containing SAP. That addition of extra water resulted, in some cases, in a reduction of mechanical properties. To alleviate this problem, in *Approach II*, various dosages of HRWRA were used in place of extra water to achieve a target flow of mortars. Flow, compressive strength, and flexural strength of mortars results are displayed in Figure 3.5.

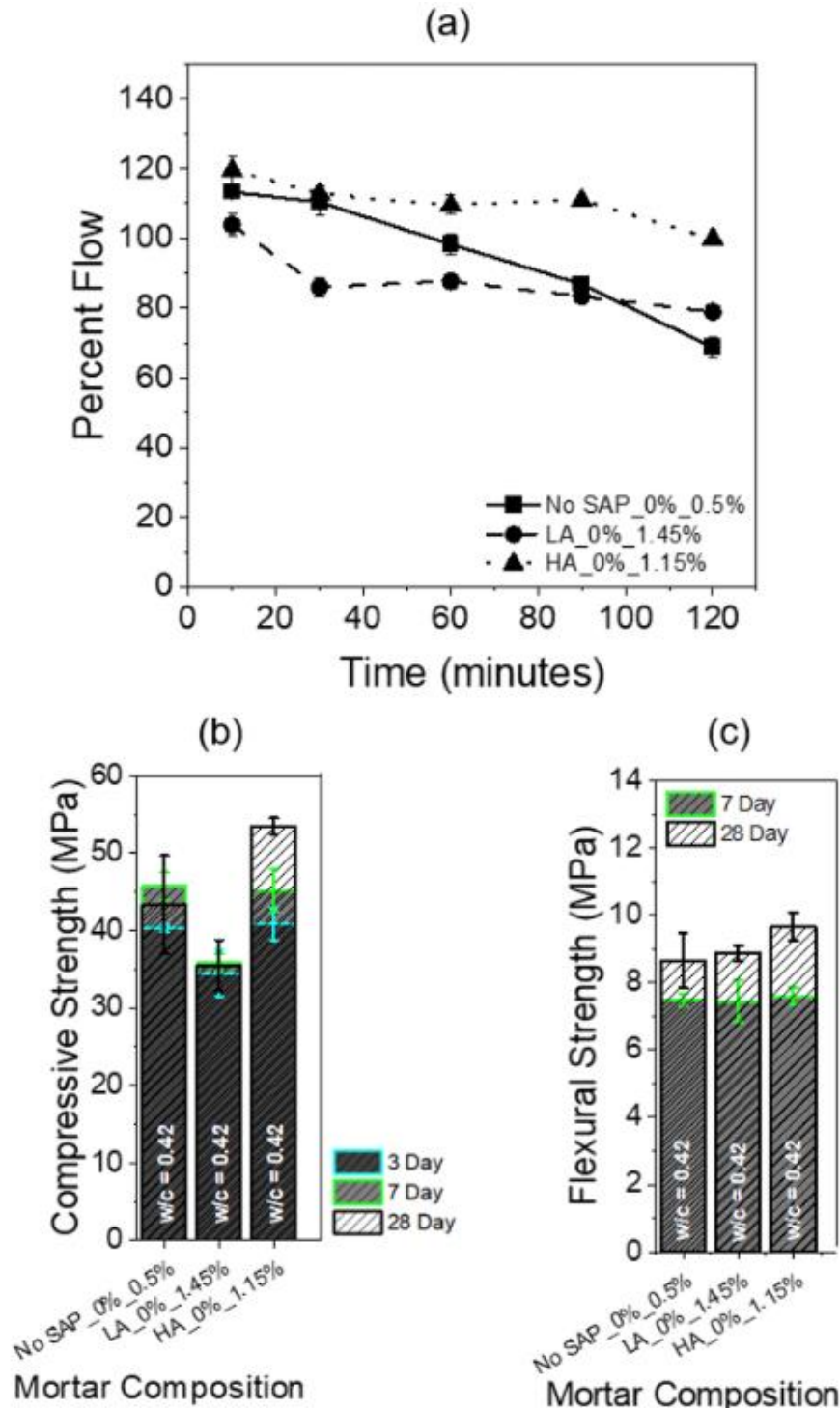


Figure 3.5. (a) Percent flow over time of fresh mortar mixes and (b) compressive strength, and (c) flexural strength of mortar samples with the addition of HRWRA and no extra water. HRWRA dosage was determined so as to achieve $110\% \pm 10\%$ flow of mortar at 10 minutes after the addition of water to the mix. In Figures (b) and (c), diagonal hatches indicate mortar with w/c 0.42 without extra water, consistent with representations of the types of mortar mixtures given in [Figure 3.4](#).

Flow behavior of mortars (Approach II)

Figure 3.5a shows the percent flow graphs of mortars with HRWRA dosage to achieve $110\% \pm 10\%$ flow at 10 minutes after the addition of water. The target flow was achieved for both the HA- and LA-SAPs, however the required HRWRA dosage exceeded the manufacturer-recommended dosage of 0.975%.⁸⁰ Counter to what might be expected, the LA-mortar mix required a higher (1.45%) dosage of HRWRA to achieve the target flow than what was required for the HA-mortar mix (1.15%). The LA-mortar mix was expected to have more free water due to the lower equilibrium absorption capacity of LA-SAP in pore solution compared to HA-SAP (Figure 3.2b). This deviation from expectation may be attributable to the different absorption kinetics of the two SAP types in pore solution. As shown most clearly in the inset of Figure 3.2b, the LA-SAP displayed a larger absorption capacity than HA-SAP during the first ten minutes of gravimetric swelling in pore solution. Thus, at very short times, less free water was likely present in mortars containing LA-SAP, resulting in greater required HRWRA dosages to achieve the target flow at 10 minutes. These results further reinforce the thesis that equilibrium absorption capacity alone does not fully characterize the effect of SAP on the flow of mortar; absorption kinetics must also be considered.

Strength of mortars (Approach II)

The compressive strength at 3, 7, and 28 days of all *Approach II* samples is shown in Figure 3.5b. The HA_0%_1.15% sample exhibited comparable 3-, 7-, and 28-day compressive strength to the No SAP_0%_0.5% reference ($p = 0.64, 0.78$, and 0.052 , respectively, at the 5% significance level). However, the LA_0%_1.45% sample exhibited reduced compressive strength at 3- and 7-days and comparable compressive strength at 28-days compared to the No SAP_0%_0.5% reference ($p = 0.03, 0.001$, and 0.13 respectively) which may be attributable to the very high HRWRA dosage of 1.45% that resulted in retardation of early compressive strength development. When using higher HRWRA dosages, it is important to consider the effect of the dosage on mechanical properties. Other studies have reported a reduction in compressive strength when exceeding a certain dosage of polycarboxylate superplasticizers due to the onset of segregation.^{81,82} The higher HRWRA dosages used with SAP in *Approach II* exceeded the manufacturer recommendation, but no segregation was observed in the mortars with SAP. This suggests that

early and long-term strength can be maintained for SAP-cured mortars if a HRWRA dosage needed to achieve target flow is below the onset of segregation.

The flexural strength at 7 and 28 days of all *Approach II* samples is shown in [Figure 3.5c](#). When percent flow of the internally cured samples was reached by the addition of HRWRA without addition of extra water, the flexural strength of the samples was comparable to the same w/c reference mortars at both 7- and 28-days ($p = 0.92$ and 0.58 , respectively, for LA; $p = 0.64$ and 0.13 , respectively, for HA). Without extra water, the presence of SAP reduced the effective w/c. This effect, in addition to the enhanced hydration provided by SAP, ensured that the SAP-containing samples were of comparable strength to the reference sample. These results also imply that the presence of SAP will not detrimentally impact flexural strength, provided that HRWRA is used to achieve the level of workability needed for proper consolidation.

To summarize the findings related to *Approach II*, the HRWRA dosage required to achieve a set target flow did not correspond to the relative equilibrium absorption capacities of the low- and high-absorption SAPs. Specifically, the mortar containing LA-SAP required a higher HRWRA dosage than the mortar containing HA-SAP to achieve the target flow, indicating that absorption capacity is not the only property of SAP that affects the flow of mortar. Compressive and flexural strength of SAP-containing mortars were maintained at all ages tested except when the HRWRA dosage exceeded a critical value. This suggests that in situations where sufficient flow of SAP-mortar can be achieved with the application of HRWRA alone, there are strength benefits to modifying workability without the use of extra water.

3.3.4 Results from Approach III: HRWRA dosage set to achieve target flow of reference at given w/c

In *Approach I*, the mortars containing SAP without extra water did not flow sufficiently to be cast. This result inspired *Approach III*. The HRWRA dosage required to achieve a target flow of reference mortars without SAP at each w/c of interest was determined and used for all mixes at that w/c.

Flow behavior of mortars (Approach III)

[Figure 3.6](#) shows the flow behavior of mortar samples prepared following *Approach III*. All samples tested had an initial percent flow of at least 45% (as required for casting), suggesting

that this mix design method has the potential to ensure a viable workability when using SAP. This result is of particular interest because of its practicality—if a mortar mix design flows at least 110% $\pm$ 10% without SAP, there may not be a need for any mix design adjustments in order to incorporate SAP.

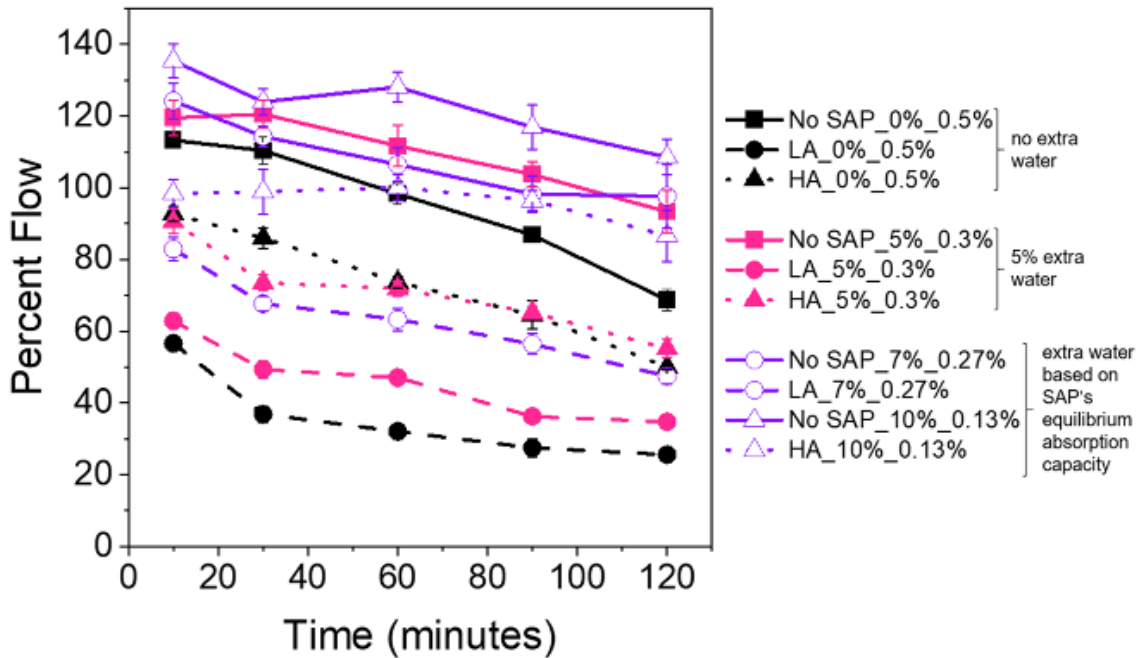


Figure 3.6. Percent flow of mortars over time with and without extra water and with the HRWRA dosage necessary to achieve at least 110% $\pm$ 10% flow of No SAP mortars at the given total w/c at 10 minutes after the addition of water to the mix.

The addition of HRWRA did not change the overall trends previously observed in *Approach I* (Figure 3.4a). The addition of extra water increased percent flow. The addition of SAP decreased percent flow relative to samples with the same total w/c but not containing SAP. As in *Approach I*, at each w/c, the LA-SAP samples have lower percent flow than the HA-SAP samples, likely due to the difference in absorption kinetics between the two SAP types. Given that HRWRA did not significantly affect SAP absorption behavior in *ex situ* tests (see Section 3.3.1), these results were not surprising, but still important to confirm.

In both *Approach I* and *II*, equilibrium absorption capacity was not predictive of the SAP's effect on the percent flow of mortar. Here, no sample containing SAP exhibited comparable short-time flow to the 0.42 w/c reference with 0.5% HRWRA (No SAP_0%_0.5%), even when using a combination of HRWRA and extra water according to the equilibrium absorption capacity of the

specific SAP. This further reinforces the notion that SAP equilibrium absorption capacity in pore solution alone cannot be used to determine the water dosage necessary to negate SAP's effect on percent flow of mortar.

Strength of mortars (Approach III)

Figure 3.7 shows the compressive and flexural strength of all *Approach III* specimens.

Figure 3.7. (a-c) Compressive strength and (d-f) flexural strength of mortar samples with the HRWRA dosage necessary to achieve at least $110\% \pm 10\%$ flow of No SAP mortar at the given total w/c at 10 minutes after the addition of water to the mix. Figures (a) and (d) show samples with no extra water. In Figures (b) and (e), 5% extra water has been used in each mix. In Figures (c) and (f), the amount of extra water was determined based on the equilibrium absorption capacity of the SAP used.

Bars with hatches and dashes are consistent with representations of types of mortar mixtures given in Figure 3.4.

Figure 3.7 continued

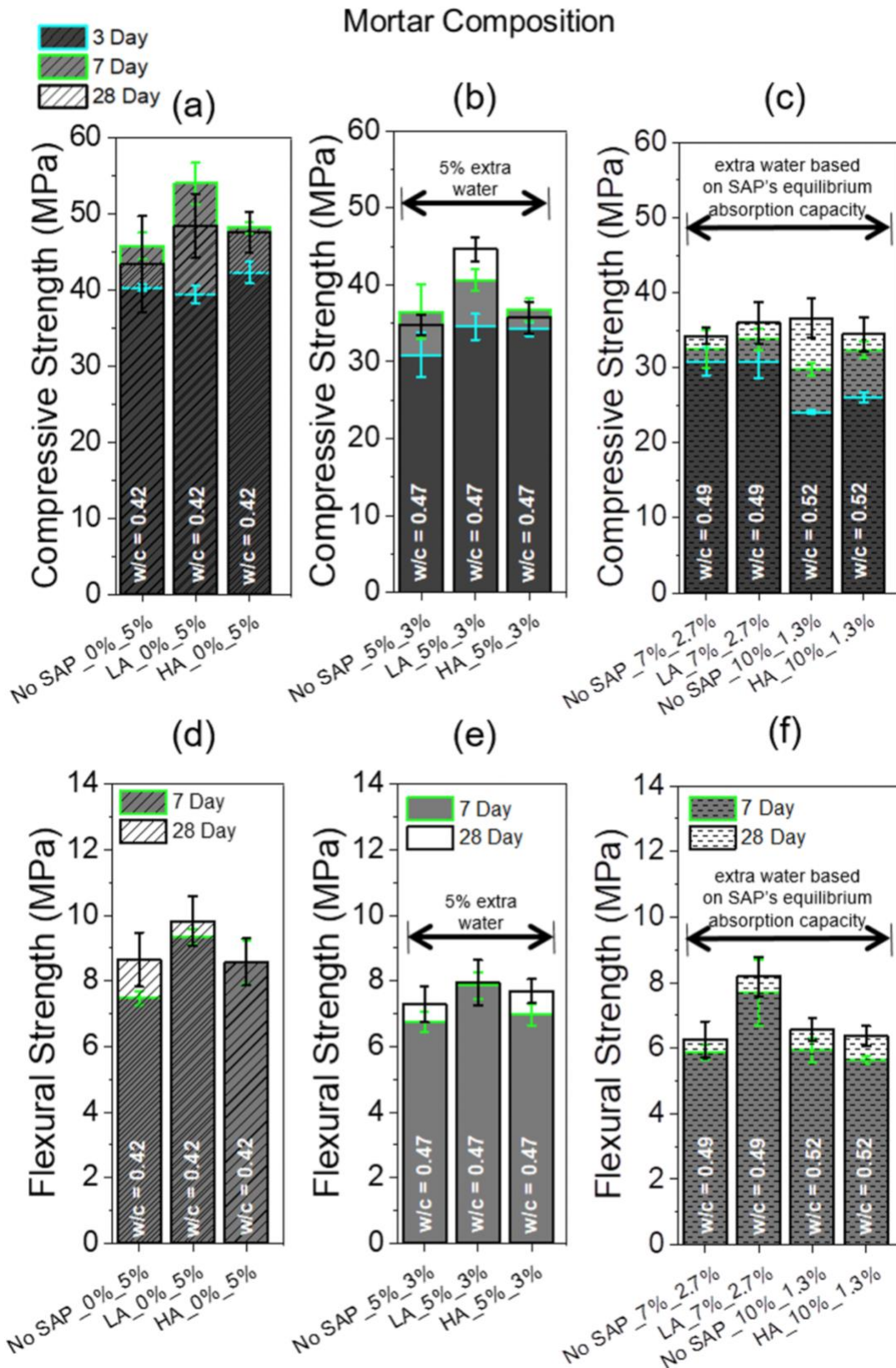


Figure 3.7a-c shows the compressive strength of all *Approach III* specimens. For each given total w/c, presence of SAP either preserved or increased compressive strength relative to the corresponding No SAP reference (compare No SAP_0%_0.5%, No SAP_5%_0.3%, No SAP_7%_0.27%, and No SAP_10%_0.13%) at all ages. This result reinforces what was observed at 7 and 28 days in *Approach I*: specimens, i.e., that the presence of SAP itself does not have a detrimental effect on compressive strength. Any decrease in compressive strength compared to the 0.42 w/c reference (No SAP_0%_0.5% in Figure 3.7a) could be attributed to the increased total w/c. Thus, minimizing the amount of extra water employed when using SAP minimizes the reduction in compressive strength. This follows conventional understanding of the effects of w/c on strength, namely that an increase in w/c leads to a decrease in compressive strength.⁷

Figure 3.7d-f shows the flexural strength of all *Approach III* specimens. With no extra water addition and a 0.5% dosage of HRWRA, presence of SAP improved or maintained 28-day flexural strength (Figure 3.7d). This again reinforces the finding that the reduction of the effective w/c, in conjunction with higher degree of hydration due to the presence SAP, plays a more important role in determining flexural strength than the presence of SAP-related voids. Figure 3.7d also shows that without the addition of extra water, LA- and HA-SAP can be used with 0.5% HRWRA without compromising flexural strength compared to the No SAP_0%_0.5% reference. When 5% extra water was added to partially offset mixing water absorbed by SAP (in conjunction with 0.3% HRWRA), the flexural strength of SAP-containing samples at all ages was comparable to the No SAP_0%_0.5% reference (Figure 3.7d and e). When extra water (along with HRWRA) was added in an amount based on equilibrium absorption capacity in pore solution for each of the SAP (7% for LA-SAP and 10% for HA-SAP mixtures), the internally cured mortars displayed comparable or improved 28-day flexural strength values when compared to their respective reference mortars (Figure 3.7f).

For the HA_10%_0.13% SAP-containing specimens with w/c of 0.52 there was a 13-percentage-point accelerated compressive strength gain through 7 days compared to No SAP_10%_0.13% specimens, as calculated using Equation 2.2, above. There was no similar accelerated strength gain for the 0.49 w/c SAP-containing specimen, i.e., LA_7%_0.27%. In *Approach I*, the SAP-containing samples at both 0.49 and 0.52 w/c displayed accelerated strength gain with greater acceleration associated with the higher w/c values (above). In *Approach III*, the accelerated strength gain due to the addition of SAP to 0.52 and 0.49 w/c mixtures may have been

partially or completely counteracted by the addition of the polycarboxylate-based HRWRA as polycarboxylate-based admixtures have been shown to retard hydration and strength development.⁸³ When using HRWRA, a higher w/c (0.52) was necessary before any accelerated strength gain due to SAP was observed.

Approach III, where HRWRA dosage was set such that a mortar without SAP at the given w/c flowed at least $110\% \pm 10\%$, produced mortar with sufficient flow for casting for all mixes tested, suggesting that this method may represent a viable general approach when employing SAP for internal curing purposes. The general trends in compressive and flexural strength previously observed in *Approach I* were also observed in *Approach III*. Specifically, at a given w/c, compressive and flexural strengths were either preserved or improved when using SAP. As such, in order to maximize compressive and flexural strength values, no extra water should be added when using SAP if sufficient flow can be achieved with the use of the HRWRA.

3.3.5 Microstructure of mortars

SEM micrographs of select w/c 0.42 mortars (Mix Designs 11, 14 and 15, see [Table 3.2](#)) are shown in [Figure 3.8](#). In the No SAP_0%_0.5% sample ([Figure 3.8a](#)), microcracks were clearly visible throughout the cement paste matrix of the mortar. Microcracks were notably absent in the matrices of the corresponding SAP-containing samples ([Figure 3.8b and c](#)). The lack of microcracks in these SAP-containing samples may have potentially helped them to achieve the later-age levels of compressive and flexural strengths that were either comparable to or improved compared to the levels of strengths observed in the reference specimens (see [Figure 3.7a and d](#)). Analysis of the average diameter of the SAP-related voids in mortars with SAP particles revealed that their average sizes were 302 μm and 127 μm , in samples containing LA- and HA-SAP particles respectively. This relative size relationship was expected as the average dry particle size of the LA-SAP particles was larger than that of the HA-SAP particles (see [Section 3.2.1](#)). Although the average size of SAP-related voids was larger for the LA-SAP-cured samples, both the 28-days compressive and flexural strengths of the LA_0%_0.5% sample were comparable to those of the HA_0%_0.5% sample ([Figure 3.7a and d](#)). These results seem to indicate that the presence of larger SAP-related voids does not necessarily mean that mechanical strength will be compromised. Other factors, such as SAP absorption and desorption kinetics governing the subsequent release of

water during hydration of cement might also play a role in determining the values of mechanical strength.^{84,85}

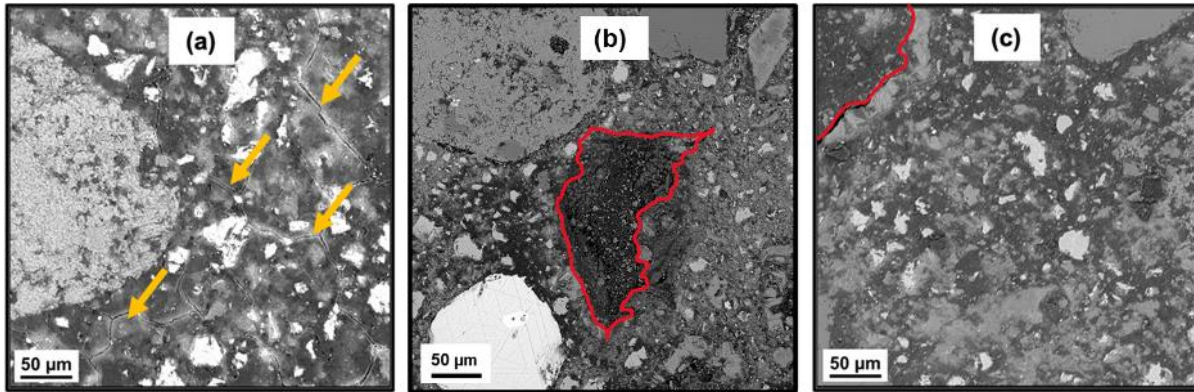


Figure 3.8. Representative SEM images of 28-day mortar samples (*Approach III*; w/c 0.42): (a) No SAP_0%_0.5%, (b) LA_0%_0.5% and (c) HA_0%_0.5%. The arrows in (a) indicate microcracks formed in the matrix of the mortar. The red outlines in (b) and (c) indicate the outer edges of deswollen SAP particles.

Some of the SAP-related voids in the sample with HA-SAP-particles contained growths of identifiable hydration products. [Figure 3.9a](#) shows a SAP-related void in a HA_0%_0.5% specimen with two spots (1 and 2) where energy-dispersive x-ray (EDX) analysis was conducted. In instances where there was substantial growth of hydration products around the vicinity of the SAP-related voids, the perimeter of the SAP particle in the hardened matrix was difficult to distinguish as the significant growth of hydration product partially obscured the original dimensions of the swollen SAP particles. [Figure 3.9b](#) illustrates the relevant features of the SAP void: original perimeter of the SAP particle at the time of final set outlined in red and hydration product growth highlighted in cyan. Remnants of the dehydrated SAP, along with other intermixed hydration products were also present (region inside the SAP void that is not highlighted in [Figure 3.9b](#)). The EDX analysis of the locations shown in [Figure 3.9a](#) yielded the following atomic percentages (Ca: $27.4 \pm 0.1\%$, O: $66 \pm 1\%$, others (Na, Si, K, Al, Mg, S, Na): $6 \pm 1\%$). Based on the EDX analysis and the morphology of the growth inside the SAP-related voids it is postulated that it is most likely a portlandite. Previous studies have also found portlandite in SAP-related voids.^{18,53} The growth of hydration products inside the SAP-related voids was not observed in the LA-SAP-cured samples.

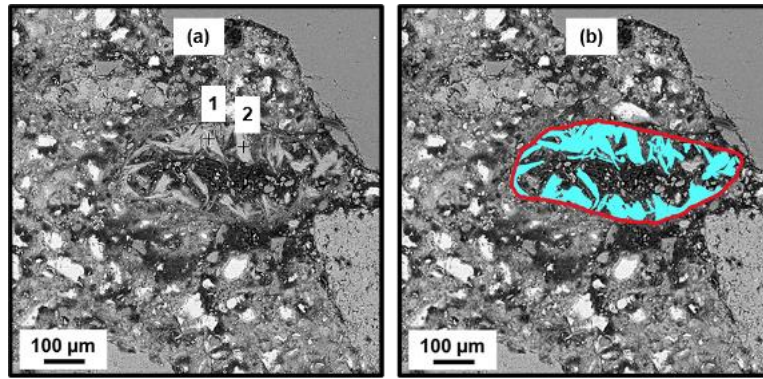


Figure 3.9. SEM image of a SAP-related void in 28-day mortar sample HA_0%_0.5% (*Approach III*; w/c 0.42): (a) with two spots highlighted for EDX analysis (1 and 2); (b) the SAP void outlined in red and the portlandite growth inside the void highlighted in cyan.

3.3.6 Discussion

The results of this study have implications for both further laboratory research and field implementation of SAP-based internal curing technology.

While the addition of a fixed 5% of extra water is a simple, and thus common, strategy for improving flow when using SAP, it does not universally guarantee that any SAP-containing mortar will develop a flow $>45\%$. Such flow is needed to produce well-consolidated samples with the use of a vibrating table. When relying only on the addition of extra water to increase the flow, the equilibrium absorption capacity of the SAP used may be a more appropriate and reliable method. However, if the aim is to increase the flow without sacrificing strength, the use of extra water should be avoided and a reasonable amount of HRWRA should be added instead.

This study utilized SAPs from two industrial sources. Despite differences in their chemical formulations, both SAPs produced mortars with comparable mechanical properties. Both formulations were crosslinked poly(acrylic acid-acrylamide) type SAP, but their exact chemical composition was not known, including a lack of information on the relative amount of covalent crosslinking and the ratio of acrylic acid to acrylamide in the internal polymer network. It can be assumed that the two SAP types used had different formulations based on their differing absorption behavior in [Figure 3.2](#). Yet, both SAP types resulted in mortars with comparable mechanical properties and both eliminated microcracks in 0.42 w/c mortars, demonstrating their utility as internal curing agents.

For research methods relying on the absorption properties of SAP, and for any SAP applications prioritizing the maximization of percent flow, it may be important to characterize absorption kinetics over time as well as at equilibrium. As seen in [Figure 3.2](#), for the first 15 minutes of testing in pore solution, the LA-SAP had a higher absorption capacity than the HA-SAP. However, the LA-SAP had a lower equilibrium absorption capacity than the HA-SAP at long times. When conducting mortar flow table testing, it was evident that absorption kinetics influenced flow properties. Despite having the lower equilibrium absorption capacity, LA-SAP samples consistently exhibited lower percentage flow than HA-SAP samples at any given w/c ([Figure 3.4](#) and [Figure 3.6](#)). Given that both SAP types resulted in mortars with similar mechanical properties, SAP formulation for a specific application could be selected based on absorption kinetics and desired flow properties without sacrificing strength.

As both SAP and HRWRA are chemical admixtures, it is prudent to examine the interaction of the two. Both SAP types exhibited similar absorption behavior in absence of HRWRA as well as in the presence of low and high dosages of HRWRA, indicating that neither SAP type was negatively affected by the presence of HRWRA. Furthermore, SAP-containing mortars with HRWRA had greater percent flow than SAP-containing mortars at the same w/c without HRWRA, indicating that the use of SAP does not disrupt the performance of HRWRA.

For field applications, *Approach III* appears to be able to provide a practical template for producing SAP-containing mixtures with sufficient flow for casting and obtainment of good mechanical properties without requiring the characterization of SAP absorption properties. Mortars with HRWRA dosage sufficient to produce high enough flow ($110\% \pm 10\%$ at $w/c \geq 0.42$) can be modified by addition of SAP at a typical dosage (0.2% by weight of cement). In this study, all such mortars developed a flow $>45\%$ and either preserved or improved compressive and flexural strength values compared to SAP-free mortars prepared at the same w/c. While such properties as SAP absorption, particle size, and shape were characterized as part of this study, those results were not actually needed for a successful implementation of *Approach III*.

3.4 Conclusions

Mix design adjustments were required when SAP was added to a 0.42 w/c Type I OPC mortar with a cement:sand ratio of 1:2.75. Without the addition of extra water and/or HRWRA, the resultant SAP-containing mixtures were too stiff to make properly consolidated specimens.

Three approaches to modify percent flow of mortars through mix design were investigated: extra water alone (*Approach I*), HRWRA alone (*Approach II*), and extra water and HRWRA together (*Approach III*).

The combination of extra water and HRWRA used in *Approach III* demonstrated a potential “rule of thumb” for a simplified batching process for SAP-containing mortars based on the behavior of mortar mixes with equal w/c without SAP. Specifically, it was found that mortar mixtures with $w/c \geq 0.42$ and sufficient HRWRA dosage to produce a flow of $110\% \pm 10\%$ could be modified by addition of a typical SAP dosage (0.2% by weight of cement) and still develop a flow of at least 45%, which would be sufficient for casting of adequate quality specimens. The implications of this approach are important from a practical point of view as it allows for easy modification of mixtures by the addition of SAP without the need for specific characterization of its absorption capacity.

In all mix designs tested, when w/c was held constant, the addition of SAP preserved or increased compressive and flexural strength through 28-days. In other words, the addition of SAP alone did not decrease compressive or flexural strengths. In high w/c (≥ 0.49) mixtures, the addition of SAP accelerated compressive and flexural strength development in samples without HRWRA (*Approach I*) and accelerated compressive strength development in samples with $w/c=0.52$ and HRWRA (*Approach III*). Additionally, microstructural refinement typically associated with SAP internal curing of lower w/c mixtures, namely the absence of microcracks compared to SAP-free samples, was observed at a w/c of 0.42.

3.5 Acknowledgments

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4. EFFECT OF BINDER CHARACTERISTICS ON WORKABILITY, HYDRATION, AND STRENGTH OF CEMENTITIOUS SYSTEMS WITH SUPERABSORBENT POLYMER ADMIXTURES

Text and figures in the following chapter have been adapted with permission from **Adams, C. J.**; Bose, B.; Mann, E.; Olek, J.; Erk, K. A. Effect of binder characteristics on workability, hydration, and strength of cementitious systems with superabsorbent polymer admixtures. Submitted March 2023.

4.1 Introduction

Superabsorbent polymers (SAP) used for internal curing are hydrogel particles that initially absorb and subsequently release internal water throughout the cement matrix to fuel the hydration reaction.^{11,86} These hydrogels are typically networked poly(acrylamide-acrylic acid) copolymers.^{3,10} In general, the key performance characteristic of SAP particles is their absorption capacity, which depends on the particles' composition and size as well as the composition of the absorbed fluid and, in particular, the concentration and identity of cations present in solution.^{3,21,54,57} This has clear implications for the use of SAP particles in cementitious mixtures in which the concentration and composition of ions present in pore fluid change as a function of time and chemical characteristics of cement and cementitious binders.⁵⁵

Multivalent cations, including those found in cementitious pore solution (such as Ca^{2+} and Al^{3+}), are able to form temporary and permanent ionic crosslinks within poly(acrylamide-acrylic acid) hydrogels which directly impact SAP absorption capacity.^{19,21,87} Previous work by Lee et al. established that poly(acrylamide-acrylic acid) SAP absorption behavior in model solutions and in cement paste depends on an interplay of alkalinity, Ca^{2+} concentration, and ionic exchange rates.⁵⁷ While exploration of ion exchange as part of cation-polymer interactions is an important basic research area, insight into SAP behavior that hinges on pore solution analysis is a potential barrier to implementation of SAP internal curing at scale. As such, additional cement characteristics as reported on mill certificates were looked to for the purpose of this study for their potential effects on pore solution chemistry and thus SAP absorption behavior.

Dissolution kinetics play a role in pore solution composition. The ratio of surface area to mass of binder, as measured by Blaine fineness (m^2/kg), affects the extent of dissolution of the binder powder. Dissolution can be simply considered as the reverse process of nucleation and

growth, occurring only at the surface of a material.^{88,89} As such, binders with a smaller surface area to mass ratio (lower Blaine fineness) dissolve more slowly than binders with similar composition but larger surface area to mass ratio (i.e., higher Blaine fineness). Many commercially available cements meet the ASTM C150⁹⁰ compositional requirements of both, Type I and Type III binders, with the key difference between the two Types being early age strength as measured by ASTM C109⁷⁷ (e.g., minimum 1-day strength of 12.0 MPa for Type III, minimum 3-day strength of 12.0 MPa for Type I). The accelerated rate of strength development of Type III cement of the same composition as Type I cement is the result of increased Blaine fineness and with it, dissolution speed and reactivity.⁹¹

The composition of a binder also controls the possible ionic concentration of a pore solution. Of particular interest in this study was equivalent alkalinity, which is a weighted measure of the concentration (weight %) of sodium oxide (Na_2O) and potassium oxide (K_2O) in ordinary portland cement.⁹⁰ Immediately after mixing of cement with water the sodium (Na^+) and potassium (K^+) ions (typically present in the form of highly soluble alkali sulfates) are released into pore solution and contribute to the increase of the alkalinity (OH^- ion concentration) of the liquid phase. Therefore, the alkalinity of a binder system directly impacts the ionic concentration of the pore fluid. Furthermore, increased concentration of sodium and potassium ions has been shown to inhibit, or even reverse, divalent ionic crosslinking in poly(acrylic acid) through ion exchange.^{57,92} As such, increased alkalinity (i.e., pH) of pore solution could increase the absorption capacity of SAP exposed to such liquid phase.

This study builds on the previously published work by the authors on using SAP to optimize properties of mortars and concretes intended for transportation infrastructure applications.^{33,37} In such applications, the choice of binder system depends on many factors, including (but not limited to) design constraints, field conditions, project type, local cement availability cost, and specification limits on allowed amounts of supplementary cementitious materials (SCMs). Due to different chemical makeups and/or particle sizes, Type III cement provides a different chemical environment than Type I cement, which provides a different chemical environment than Type I cement with partial replacement by SCMs. Among Type I cements, chemistry varies from manufacturer to manufacturer and across batches, as routinely evidenced in mill certificates. As such, there is a need to improve understanding of SAP behavior and performance across various binder systems. While use of SAP for internal curing has been

extensively studied with Type I cement,^{17,18,26,33,37,54,55,61,70,72,93,94} and increasingly in cementitious systems containing SCMs, including slag,^{45,61,95} there is limited literature on the use of SAP for internal curing in cementitious systems with Type III cement⁹⁶ and on interaction of SAP with different Type I cement compositions (e.g. representing different sources).⁹⁷

This study aims to examine the effects of binder source and type on the performance of pastes and mortars internally cured with SAP in order to develop information that could help with the implementation of this curing method. The study was conducted on three experimental matrices each representing a different mode in which binders could vary depending on application: (1) cement manufacture source, (2) cement type, and (3) cement blend. In each experimental matrix, the binder system served as the variable in SAP-containing cement pastes and mortars. To examine the effect of cement source, Type I cements from three different manufacturers, located in the US states of Indiana and Michigan were selected. To examine the effect of cement type, a Type I and a Type III cements from the same manufacturer were used. To examine the effect of cement blend, a binder system based on Type I cement was compared to a binder system consisting of 70% of the same Type I cement and 30% (by mass of total cementitious binder) of the ASTM C989⁹⁸ grade 100 slag cement. The effectiveness of SAP as internal curing agent in these different types of experimental matrices was evaluated as by monitoring the rate and the extent of hydration, pore fluid absorption by SAP particles, microstructure of cement pastes, flow of fresh mortars, and compressive and flexural strength of mortars.

4.2 Materials and Methods

4.2.1 Characterization of Superabsorbent Polymer

A polyacrylate-based SAP formulation was industrially sourced and used as-received. The SAP was stored in an airtight container before use. The absorption capacity of the SAP used here (termed “HA-SAP” in [Chapter 3](#) of this dissertation) was sensitive to the composition of the simulated pore fluid.^{33,37} This SAP was chosen for further study based on the assumption that any changes in SAP internal curing performance associated with changes in binder chemistry would be maximized by use of SAP formulation that previously displayed different absorption behavior when exposed to pore fluids of variable composition.

As previously mentioned, the goal of this study was to characterize the influence of binder characteristics on the performance of SAP as an internal curing agent in order to aid with SAP selection for internal curing purposes. As such, the SAP was first characterized with respect to its absorption behavior in the presence of simulated pore solution representing different binder chemistries. The following binder systems were used: three sources of Type I ordinary portland cement with varying alkalinities and finesses (termed X-Type I, Y-Type I, and Z-Type I), one Type III ordinary portland cement (X-Type III), and one X-Type I ordinary portland cement with 30% slag replacement by weight of binder (bwob).^{90,98} The slag used was grade 100. X-Type I cement was the same cement used in the authors' previous study.³⁷ The compositions of the binders used in this study, as reported in their respective mill certificates, are presented in Table 4.1.

The pH of simulated pore solutions for each of the binder systems was also measured. Simulated pore solutions were prepared by mixing tap water and binder at a water-binder (w/b) ratio of 10. Since tap water from the same tap was used for all simulated pore solutions, it was assumed that the compositional contribution of tap water to the solutions was constant across all solutions. As such, the observed compositional differences across simulated pore solutions were attributed to binder system alone. The solutions were hand stirred for 30 seconds then allowed to settle for one minute, followed by decanting for pH testing (Oakton Acorn series pH 5+, Cole-Parmer, Illinois, USA). The measured pH values are reported in Table 4.1.

Table 4.1. Properties of the ordinary portland cements and slag cement and the pH values of the simulated pore solutions used in this study

		X-Type I (wt. %)	Y-Type I (wt. %)	Z-Type I (wt. %)	X-Type III (wt. %)	Grade 100 Slag (wt. %)
Oxide Composition	SiO ₂	19.5	19.8	19.7	19.62	34.57
	Al ₂ O ₃	5.2	5.3	4.9	5.3	10.2
	Fe ₂ O ₃	2.73	2.07	3.01	2.63	0.73
	CaO	63.42	62.7	62.3	63.58	40..69
	MgO	2.32	2.8	3.2	1.94	10.76
	Na ₂ O	0.65*	0.12	0.13	0.65*	0.56†
	K ₂ O	--	0.11	0.96	--	--
	SO ₃	3.25	2.62	4.03	4.06	1.75
Phase Composition	C ₃ S	60.2	50.8	52	58.8	--
	C ₂ S	9	17.2	17	11.9	--
	C ₃ A	8.9	10.3	8	9.6	--
	C ₄ AF	8.1	6.1	9	8	--
Blaine Fineness (m²/kg)	--	412	418	376	593	5337
Measured pH of Simulated Pore Solutions	--	12.27	12.32	12.37	12.16	12.15‡

*Reported as Na₂O equivalent in the mill certificate.

†Reported as equivalent alkalis in the mill certificate.

‡X-Type I with 30% slag replacement by total mass of binder.

Gravimetric absorption “tea-bag” tests were used to quantify the absorption capacity of the SAP in simulated pore solution of each binder system of interest.^{70,99} Simulated pore solution was prepared in the same manner as that used for pH testing. The simulated pore solution was kept in covered beakers throughout the two hours of testing to minimize carbonation. The absorption capacity, *Q* (grams of absorbed fluid per grams of dry SAP), of SAP was calculated using [Equation 3.1](#) for immersion times of 0.5, 1, 3, 5, 15, 30, 60, 120 minutes.

While the tea-bag method has been shown to overestimate the amount of fluid absorbed by SAP in typical cement mixtures where pore fluid ion concentration changes over time and SAP

particles are subject to confinement, it still remains a useful characterization tool for simply and reproducibly estimating the absorption capacity of SAP.^{10,50,72}

Dry SAP was stored as received in a sealed container at room temperature from receipt until testing. The SAP consisted of irregularly shaped particles with sizes calculated to be about $48.9 \pm 29.9 \mu\text{m}$. Average particle size was found by analyzing SEM images of about 100 particles using ImageJ software.

4.2.2 Preparation of Specimens

Cement paste and mortar specimens were made using each of the binder systems listed in Section 4.2.1. Cement paste specimens were used for microstructural analysis and evaluation of cement hydration. Mortar specimens were used for evaluating the flow behavior and compressive and flexural strength values at different ages. The mixture proportions for all specimens are reported in Table 4.2. Mix designs P-1 through P-10 indicate the cement paste mixtures, while mix designs M-1 through M-10 indicate the corresponding mortar mixtures. Sample names reflect the binder identity and the presence or absence of SAP. For example, “X-Type I” refers to a cement paste or mortar made with X-Type I cement without SAP, while “X-Type I_SAP” refers to a cement paste or mortar made with X-Type I cement with SAP.

In both cement pastes and mortars, SAP was added at a dosage of 0.2% bwob when used. The total w/b of the pastes and mortars was held constant at 0.42 for all mixes—both those containing SAP and those without SAP. No additional “mixing” or “curing” water was added to account for water absorbed by SAP. Previous findings showed that such additions lower mechanical strength and are unnecessary if high range water reducing admixture (HRWRA) is used to adjust mixture workability.^{33,37} Type A/F polycarboxylate-based aqueous HRWRA (MasterGlenium 7511, BASF, Ohio, USA) was used to modify workability while maintaining a constant total w/b across samples.⁷⁴

Table 4.2. Composition of 0.42 w/b cement paste and mortar mixtures with varying binder compositions.

Mix Design	Sample	Cement (g)	Slag (g)	Water (g)	SAP (g) / (% bwob)	HRWRA (mL) / (% bwob)	Sand (g)	Initial % Flow of Mortar (at 10 min)
P-1	X-Type I	100	0	42	0 / 0%	0.7 / 0.7%	-	-
P-2	X-Type I_SAP	100	0	42	0.2 / 0.2%	0.7 / 0.7%	-	-
P-3	Y-Type I	100	0	42	0 / 0%	0.7 / 0.7%	-	-
P-4	Y-Type I_SAP	100	0	42	0.2 / 0.2%	0.7 / 0.7%	-	-
P-5	Z-Type I	100	0	42	0 / 0%	0.7 / 0.7%	-	-
P-6	Z-Type I_SAP	100	0	42	0.2 / 0.2%	0.7 / 0.7%	-	-
P-7	X-Type III	100	0	42	0 / 0%	0.7 / 0.7%	-	-
P-8	X-Type III_SAP	100	0	42	0.2 / 0.2%	0.7 / 0.7%	-	-
P-9	X-Type I + Slag	70	30	42	0 / 0%	0.7 / 0.7%	-	-
P-10	X-Type I + Slag_SAP	70	30	42	0.2 / 0.2%	0.7 / 0.7%	-	-
M-1	X-Type I	3500	0	1610	0 / 0%	17.5 / 0.5%	9625	113%
M-2	X-Type I_SAP	3500	0	1610	7 / 0.2%	17.5 / 0.5%	9625	93%
M-3	Y-Type I	3500	0	1610	0 / 0%	14 / 0.4%	9625	107%
M-4	Y-Type I_SAP	3500	0	1610	7 / 0.2%	14 / 0.4%	9625	66%
M-5	Z-Type I	3500	0	1610	0 / 0%	17.5 / 0.5%	9625	120%
M-6	Z-Type I_SAP	3500	0	1610	7 / 0.2%	17.5 / 0.5%	9625	88%
M-7	X-Type III	3500	0	1610	0 / 0%	31.5 / 0.9%	9625	110%
M-8	X-Type III_SAP	3500	0	1610	7 / 0.2%	31.5 / 0.9%	9625	56%
M-9	X-Type I + Slag	2450	1050	1610	0 / 0%	10.5 / 0.3%	9625	104%
M-10	X-Type I + Slag_SAP	2450	1050	1610	7 / 0.2%	10.5 / 0.3%	9625	32%

Note: Total binder amounts were fixed at 100g for all cement pastes and 3500g for all mortars.

Cement pastes were made using deionized (DI) water and a 0.7% HRWRA dosage. DI water was used for the preparation of pastes because pastes for isothermal calorimetry and for thermogravimetric analysis were prepared in different laboratories with potentially different tap water. Mortar specimens were made using tap water from a single tap and the dosage of HRWRA was held constant within a given binder system (e.g., mix designs M-3 and M-4 show that 0.4% HRWRA bwob was used for both Y-Type I and Y-Type I_SAP mortar specimens). The HRWRA dosage for each binder system was determined experimentally based on the flow behavior of its reference mortar (without SAP). The mortar flow testing procedure, detailed in [Section 4.2.3](#), was used with reference mortars to identify the HRWRA dosage required to achieve a target flow of $110\% \pm 10\%$ at 10 minutes after the addition of water to binder. The HRWRA dosages established with the SAP-free reference mortars ranged from 0.3% to 0.9% bwob. These dosages fall within the manufacturer-recommended dosage range of 0.195% to 0.975% bwob. This HRWRA dosing method allowed control of HRWRA dose within each system and prevented any variation in hydration kinetics due to variation in HRWRA dose within the system.^{37,100} All mortars, including those with SAP, displayed sufficient flow to be cast into well-consolidated specimens.

Mortars specimens were prepared using locally available natural siliceous sand. The sand was oven dried and sieved to pass through a No. 4 (4.75 mm) sieve and used at a ratio of 1:2.75 binder-to-sand by weight. Prior to mixing, sufficient water was added to the oven-dried sand to bring it to the saturated surface dry (SSD) condition.⁷⁵

For the mixing of cement pastes, dry binder and dry SAP particles (when used) were hand mixed for 30 seconds. Water with pre-dissolved HRWRA was added next and the mixture was mixed at 400 rpm using a Renfert Twister vacuum mixer (St. Charles, IL, USA) for 60 seconds, scraped from the sides of the container, and allowed to rest for 30 seconds. The paste was then mixed in the vacuum mixer for another 60 seconds. For preparation of microstructural analysis and thermogravimetric analysis (TGA) specimens, paste was cast into 1"x2" cylindrical molds. Once cast, pastes specimens were kept in sealed molds and stored in an environmental chamber at 23 ± 0.1 °C and $50 \pm 0.1\%$ relative humidity for 24 hours. Specimens were then demolded and stored in the same environmental chamber until testing. For isothermal calorimetry, cement pastes were transferred to ampoules for testing immediately after mixing.

Mortars were mixed in a 20 L capacity mortar mixer (Hobart HL200, Ohio, USA). Sand and the water required to bring the oven-dried sand to SSD condition were first placed in the

mixing bowl and stirred for 10 seconds, then mixed at medium speed for 1 minute and 50 seconds. Dry binder and dry SAP (when used) were added to the mixing bowl, followed by the mixing water and pre-dissolved HRWRA. The contents of the bowl were then stirred for 10 seconds, followed by mixing at medium speed for 1 minute and 50 seconds. Upon completion of machine mixing, the bowl was removed from the mixer and hand stirred with a metal spoon three times. Handling of mortars after mixing varied by characterization method and is detailed in [Sections 3.3 and 3.4](#).

4.2.3 Mortar Flow Testing

For mortar flow testing, small batches (about 1L, prepared using 1/8th the masses reported for mortars in [Table 4.2](#)) were mixed in a 5L capacity mortar mixer (Hobart N50, Ohio, USA) following the same mixing sequence described in [Section 4.2.2](#). ASTM C1437-20⁷⁶ was followed with the following modifications to improve consolidation and accuracy: each layer of mortar in the mold was tamped 25 (rather than 20) times and the diameter of the spread mortar was measured six (rather than 4) times. Mortar flow was tested at 10, 30, 90, and 120 minutes after the addition of water to binder to determine the percent flow of mortar over time.

4.2.4 Mortar Strength Characterization

Compressive and flexural strength was determined for all mortars in triplicate according to ASTM C109/C109M-20b⁷⁷ and ASTM C348-20⁷⁸, respectively. Specimens were both hand-tamped and placed on a vibrating table for 30 seconds to promote consolidation. Specimens were stored before and after demolding (at 24 hours) in an environmental chamber at 23 ± 0.1 °C and relative humidity of $50 \pm 0.1\%$ until the time of testing. This change in curing regimen from the moist room required by ASTM C109 was implemented to ensure no external curing occurred in this internal curing study. Compressive strength was measured at 3, 7, and 28 days, while flexural strength was measured at 7 and 28 days.

4.2.5 Microstructure

Several 7-day paste samples were selected for backscattered SEM imaging. Specimens were immersed in isopropanol for 48 hours to stop hydration via solvent exchange. Specimens

were then cut to size with a propylene glycol-cooled diamond saw to expose the interior surface. Cut samples were vacuum dried for 48 hours at 23 ± 5 °C, vacuum impregnated with epoxy, and dried at 60 ± 5 °C for 24 hours. The epoxy-mounted specimens were then cut with a diamond saw and polished to expose a fresh cement paste surface before carbon coating. An FEI Quanta 650 FEG (Hillsboro, Oregon, USA) was used for backscattered imaging at 15 kV. Thirty random SAP voids were imaged and analyzed using ImageJ software to quantify the void size and area fraction of hydration product infilling following the procedure detailed in Bose et al.¹⁸

4.2.6 Cement Hydration

Thermogravimetric Analysis

TGA was conducted on cement paste samples with and without SAP to quantify the calcium hydroxide (CH) content. At 7 days, samples were removed from the environmental chamber and immersed in isopropanol for 24 hours to halt hydration. Samples were then ground into a powder using a mortar and pestle with care taken to ensure powder collected for TGA originated from the interior of the original cement paste specimens. After grinding, the powdered paste was sieved through a 75 μm sieve and dried in a vacuum oven at 23 °C until constant mass was obtained (3 days) to remove free water. TGA was performed with a 2050 Thermogravimetric Analyzer (TA Instruments, New Castle, Delaware, USA) using platinum crucibles. Samples were heated from 23 °C to 1000 °C at a rate of 10 °C per minute in a nitrogen gas atmosphere.

Isothermal Calorimetry

Hydration kinetics were measured using a TA Instruments TAM Air isothermal calorimeter (New Castle, Delaware, USA). Paste samples were mixed outside of the calorimeter, so initial aluminate phase dissolution reactions were not recorded. Following mixing, 12 ± 3 mg of paste was added to glass ampoules, which were sealed, weighed, and placed in the calorimeter for testing for 72 hours. The calorimeter maintained a constant temperature of 23 ± 0.02 °C. All samples were tested in triplicate and the average results are reported.

4.2.7 Statistical Analysis

All error bars reported represent $\pm$ one standard deviation. When significance is stated, a two-sample, two-tailed hypothesis “t-test” was conducted at the 95% confidence level and the p-value is reported.

4.3 Results and Discussion

4.3.1 Type I Cements from Different Plants

Characterization of SAP Absorption Capacity and Mortar Flow

The absorption capacities (Q) of SAP over a period of 120 minutes in simulated pore solutions from each of the three Type I cements are shown in [Figure 4.1a](#). The delta percent mortar flow with the inclusion of SAP in Type I cements is shown in [Figure 4.1b](#). Delta percent mortar flow (ΔA) was calculated according to [Equation 4.1](#).

$$\Delta \text{Percent Flow}(\Delta A) = A_{SAP} - A \quad (4.1)$$

where A was the percent flow (at the specified time) of the mortar without SAP and A_{SAP} was the percent flow of the mortar at the specified time with SAP. The resulting difference shows the change in percent flow of the mortar due to the inclusion of SAP. As expected, these values were all negative, indicating that the mortar flow decreased due to the absorption of fluid from the mixture by SAP.

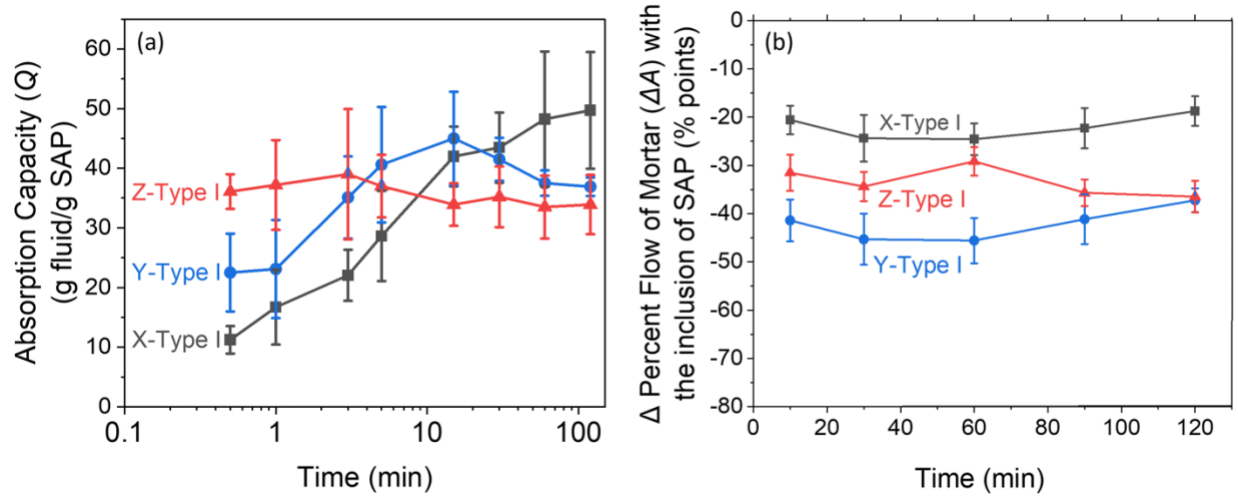


Figure 4.1. (a) Absorption capacity of SAP as a function of immersion time in simulated Type I cement pore solutions from different manufacturing sources. (b) Change in percent flow of the mortar over time with the inclusion of SAP for each of Type I cements.

Figure 4.1a shows that SAP absorption capacity, Q , was influenced by slight differences in composition of the same type of cement (in this case, Type I OPC) due to the fact that these materials were sourced from different cement plants. The values of Q varied with changes in cement composition, particularly within the first minute of immersion, when at 30 seconds, all three pore solutions yielded significantly different Q , ranging from 11.2 ± 2.3 to 36.1 ± 2.9 g fluid/g SAP. On the other hand, at equilibrium (Q_{eq} , 120 minutes), the relative magnitudes of Q were comparable across the three Type I simulated pore solutions (p-values of 0.117 and 0.087, respectively when comparing the absorption capacity in Y-Type I and Z-Type I simulated pore solutions with that in X-Type I simulated pore solution).

As seen in Figure 4.1b, the inclusion of SAP in a Type I mortar mix decreased the percent flow of the mortar at all times through initial set. However, the values of Q_{eq} did not correlate with values of ΔA . In fact, there was no time at which Q was significantly different across cement types and directly correlated with the value of ΔA .

While gravimetric absorption “tea bag” tests can be useful for characterization of SAP behavior, their limitations in predicting *in situ* absorption behavior in actual cement pastes, mortars, and concretes have been documented.^{66,101,102} The lack of correlation between Q and ΔA at any time indicates that gravimetric absorption tests in simulated pore solution cannot reliably predict cement mixture workability when using SAP. For this study, comparing Q and ΔA was a useful

mode of analysis of the effect of cement chemistry on the behavior of the SAP-containing mortar. However, if a specific percent mortar flow is desired for an application, such as 3D printing, HRWRA dosage can be modified to meet a flow target without compromising strength.^{33,37}

Compressive and Flexural Strengths

The compressive and flexural strengths of Type I mortars with and without SAP are shown in Figure 4.2. At all ages tested, within a Type I cement source, the No SAP and SAP-containing mortars displayed comparable strength in both compression and flexure. For example, the mean values of the 7-day flexural strengths of X-Type I and X-Type I_SAP were comparable (p-value = 0.054). This finding agrees with previous work performed by the authors which showed that the addition of SAP to mortars based on Type I cement did not decrease compressive or flexural strength as long as the w/c remained constant.³⁷ In short, despite the difference in flow behavior of different Type I mortars with SAP (Figure 4.1b), all three of these mortars had a comparable strength values.

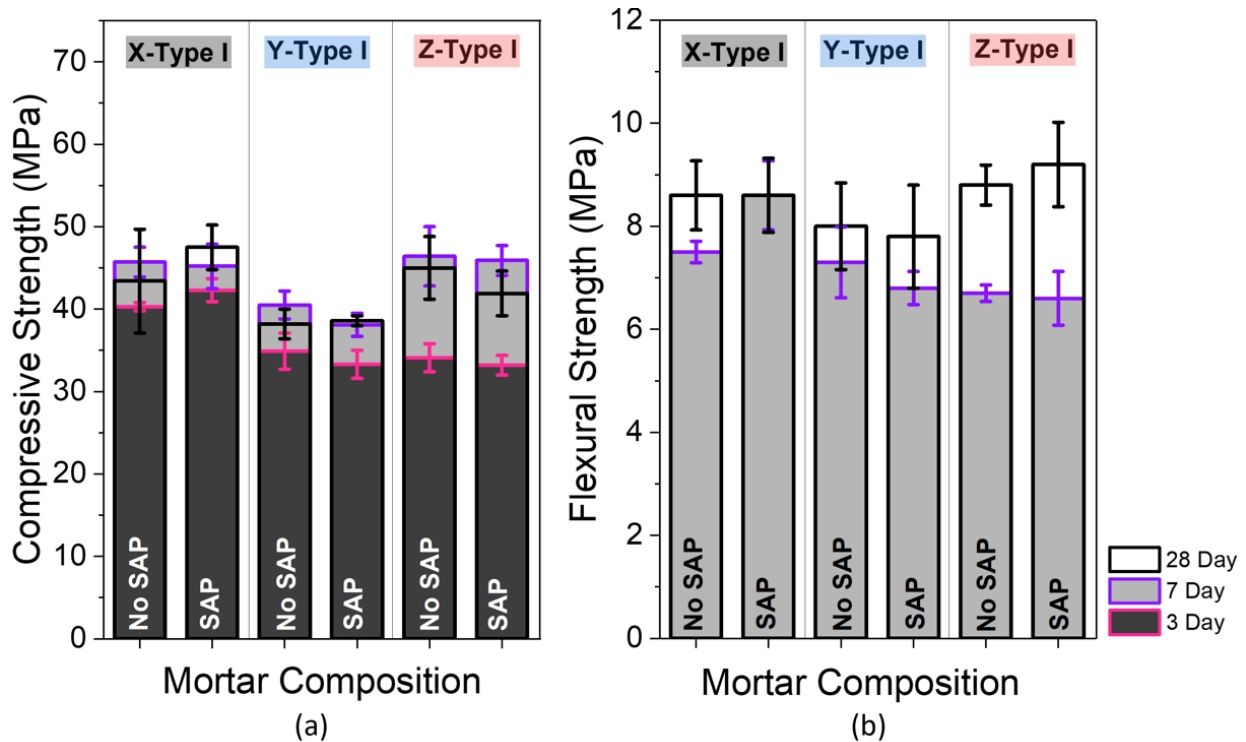


Figure 4.2. (a) Compressive and (b) flexural strength of Type I mortars with and without SAP through 28 days.

Microstructural Analysis

Scanning electron micrographs of reference and internally cured cement pastes are shown in [Figure 4.3](#). For each internally cured paste sample, the amounts of hydration product observed within the SAP voids were measured ([Figure 4.3](#)) in order to determine the effects of SAP particles and cement source on the cement paste microstructure. Microstructural analysis was performed on cement pastes consisting of X-Type I and X-Type Z with and without SAP. These two cement sources were chosen due to the fact that they displayed the most different absorption behavior in gravimetric absorption tests ([Figure 4.1a](#)).

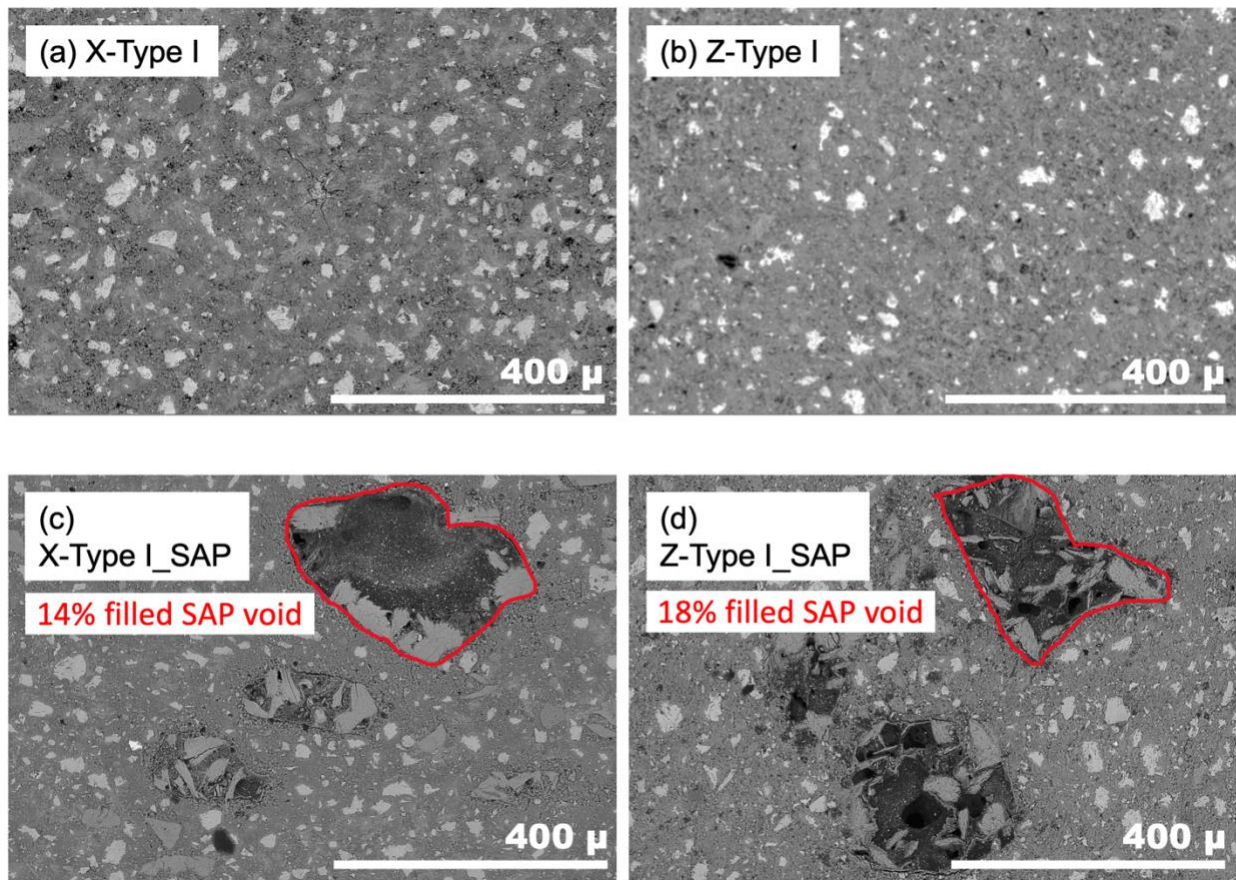


Figure 4.3. Microstructure of 7-day 0.42 w/c pastes with and without SAP. X-Type I cement was used for (a) and (c), while Z-Type I cement was used for (b) and (d). One representative SAP void is outlined in red in each of (c) and (d) with the percent of that SAP void filled with hydration products reported.

As seen in the micrographs shown in [Figures 4.3c and 4.3d](#), one of the observed features of the cement microstructures was the “infilling” of the SAP voids with hydration product. Based

on elemental analysis previously reported by the authors for X-Type I mortars containing SAP,^{33,37} the hydration products are believed to be mostly CH with some amount of intermixed C-S-H.

To determine how cement chemistry affected the observed infilling of SAP-induced voids, the amounts (by area fraction) of hydration product observed within the SAP voids were quantified for each of the internally cured paste. Of the 31 hydrogel voids analyzed for each paste containing SAP particles, the following numbers of voids were more than 50% filled: 24 voids in X-Type I_SAP and 22 voids in Z-Type I_SAP (See [Appendix](#)). Despite the different absorption behavior and mortar flow behavior of SAP in the two Type I cements, the relative degree of SAP void-filling was comparable, which could be a contributing factor to the similar insignificant change in mechanical strength at 7 days with the addition of SAP in both Type I cements observed in [Figure 4.2](#).

Cement Paste Hydration Characterization

The amounts of calcium hydroxide (CH%) present in hydrated cement pastes determined using the TGA method are listed in [Table 4.3](#). As CH is a by-product of the cement hydration reaction, increased CH% serves as an indicator of increased degree of hydration. All Type I cement pastes containing SAP showed increased CH% over the reference (same Type I source but without SAP). As reported [above](#), the hydration products formed in the SAP-related voids were predominantly CH, which would moderately contribute to increased CH% in SAP-containing pastes. However, due to the small relative volume fraction of SAP voids compared to the cement matrix as a whole, the increased CH is more likely due to the increased cement hydration caused by SAP, rather than by infilling of the SAP-related voids.

Table 4.3. CH% (g/g) as determined by TGA of 7-day 0.42 w/c Type I cement pastes with and without SAP.

Cement	CH (% g/g cement paste) Reference	CH (% g/g cement paste) With SAP
X-Type I	10.46	11.90
Y-Type I	10.87	12.97
Z-Type I	11.44	13.96

[Figure 4.4](#) shows the effect of different sources of Type I cement on the isothermal calorimetry analysis of internally cured cement pastes. Based on the slopes and positions of heat

flow curves and the relative total heats, the presence of SAP particles in pastes from all three cement sources increased the rate of hydration and resulted in comparable or higher total hydration in pastes when compared to its own reference to varying degrees.

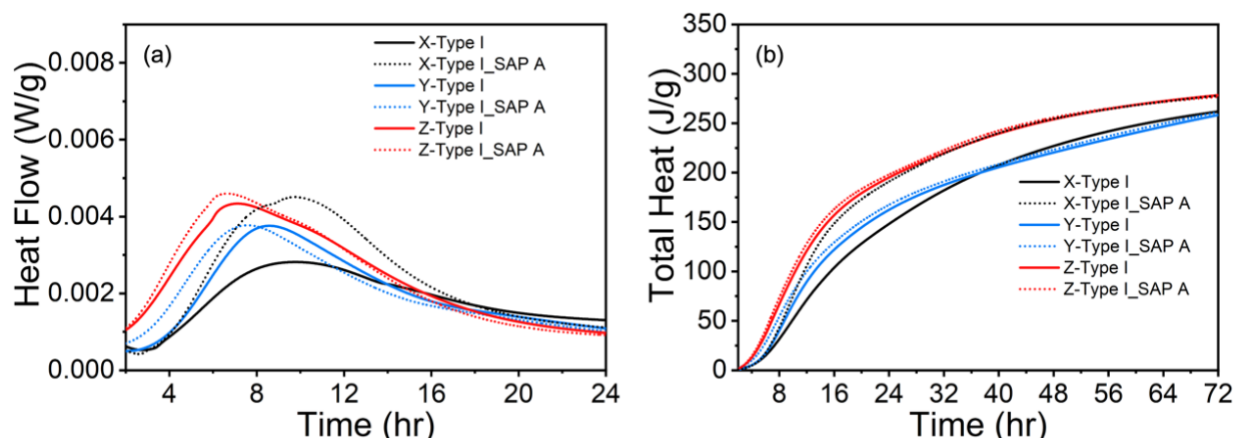


Figure 4.4. Isothermal calorimetry analysis of 0.42 w/c cement paste showing the effect of different sources (and thus different chemistries) of Type I cement on (a) heat flow (24 hours) and (b) total heat (72 hours).

Regardless of the source of cement, the SAP containing pastes increased the rate of hydration (as indicated by the steeper slope of the curve of [Figure 4.4a](#)) during the acceleration period when compared to the corresponding reference paste without SAP. In these pastes, this acceleration in hydration corresponds to an increase in total hydration (total heat over 72 hours) as seen in [Figure 4.4b](#), where the pastes containing SAP displayed greater total hydration compared to the reference paste with the same Type I cement without SAP. This behavior of increased hydration during acceleration is indicative of increased strength development reactions, which may explain how Type I mortars containing SAP achieved comparable strength to mortars without SAP ([Figure 4.2](#)) despite the presence of SAP-induced macrovoids ([Figures 4.3c and d](#)).

The presence of SAP particles significantly increased both, the height of main hydration peak (between 4 and 16 hours) and total heat generated in X-Type I cement paste, when compared to X-Type I without SAP. The dramatic increase in height of main peak is an indication of the increase in the effective w/c.¹⁰³ This implies that majority of the SAP particles released their stored water by the end of the acceleration period (i.e., by 16 hrs.), thus facilitating hydration reactions of C_3S . For both Y-Type I and Z-Type I cement pastes with SAP, the main hydration peaks and total heat curves were more similar to those of the corresponding pastes without SAP. This may

indicate that in these mixes, the release of water from SAP was more gradual and did not have a strong effect on the rate of hydration reaction within the acceleration period.

The Z-Type I cement pastes displayed earlier setting time when compared to X-Type I and Y-Type I cement pastes, which follows the trend expected based on the initial setting time reported in the mill certificates of the three cements (92, 113, and 87 minutes for X-, Y-, and Z-Type I cements, respectively). The Z-Type I_SAP paste indicated a faster attainment of the acceleration period, along with a slightly higher main hydration peak, when compared to Z-Type I without SAP. This could be due to SAP displaying a relatively high absorption capacity in Z-Type I pore solution ([Figure 4.1a](#)) and thus the release of the retained water from the SAP after the induction period caused a quicker rate of heat development during the acceleration period and higher main hydration peak.

Among the reference pastes without SAP, Z-Type I displayed the highest total heat, and thus highest total hydration. This could be due to the fact that of the three cement sources studied, Z-Type I had the highest total amount of alkali oxide content ([Table 4.1](#)). This would result in dissolution of the greater amount of alkali ions in the pore solution and contribute towards earlier attainment of higher hydration.

4.3.2 Type III Cement

Characterization of SAP Absorption Capacity and Mortar Flow

The absorption capacities (Q) of SAP over a period of 120 minutes in simulated pore solutions from X-Type I and X-Type III cements are shown in [Figure 4.5a](#). The delta percent mortar flow (ΔA) with the inclusion of SAP is shown in [Figure 4.5b](#) (calculated using [Equation 4.1](#)).

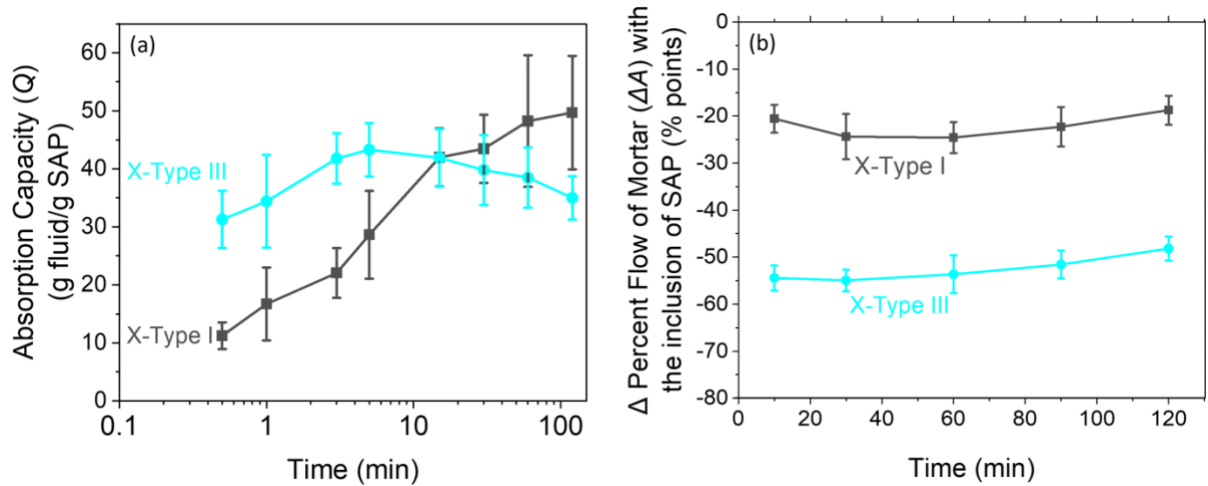


Figure 4.5. (a) Absorption capacity of SAP as a function of immersion time in simulated Type III cement pore solution with X-Type I pore solution as reference. (b) Change in percent flow of the mortar over with the inclusion of SAP for X-Type III and X-Type I cements.

Figure 4.5a shows that the values of Q were affected by the type of cement used to prepare the pore solutions. As in the experiments with different Type I cement sources ([above](#)), this effect was particularly notable within the first minute of immersion, when at 30 seconds, the two pore solution types yielded significantly different absorption capacities in the SAP. SAP in X-Type I simulated pore solution displayed a Q value of 11.2 ± 2.3 , while SAP in X-Type III displayed a higher Q value of 31.3 ± 4.9 g fluid/g SAP. Again, at 120 minutes, the relative magnitudes of the Q values were comparable ($p = 0.094$) in both X-Type I and X-Type III simulated pore solutions.

Figure 4.5b shows that the inclusion of SAP in X-Type III mortar resulted in greater magnitude values of ΔA at all times through initial set more so than was observed in X-Type I mortar. This could be seen to correlate with the increase in Q values displayed in X-Type III simulated pore solution compared to X-Type I simulated pore solution, but it would not be appropriate to generalize given that no similar trend was observed in Type I mortars across cement sources ([above](#)).

Compressive and Flexural Strength

The compressive and flexural strengths of X-Type III mortars with and without SAP are shown in [Figure 4.6](#) with X-Type I mortars as reference. For X-Type III mortars, the addition of SAP resulted in a 22% increase in 3-day compressive strength over that of its SAP-free reference—

60.3 MPa versus 49.5 MPa ($p = 0.038$)—while yielding comparable 7- and 28-day compressive and flexural strengths ($p = 0.631$ and $p = 0.852$, respectively). Furthermore, the elevated 3-day compressive strength of X-Type III_SAP matched the compressive strength at 7 days of the X-Type III without SAP (both 60.3 MPa, $p = 1.0$). This suggests that SAP could be used with Type III cement to significantly decrease the time to service post-casting.

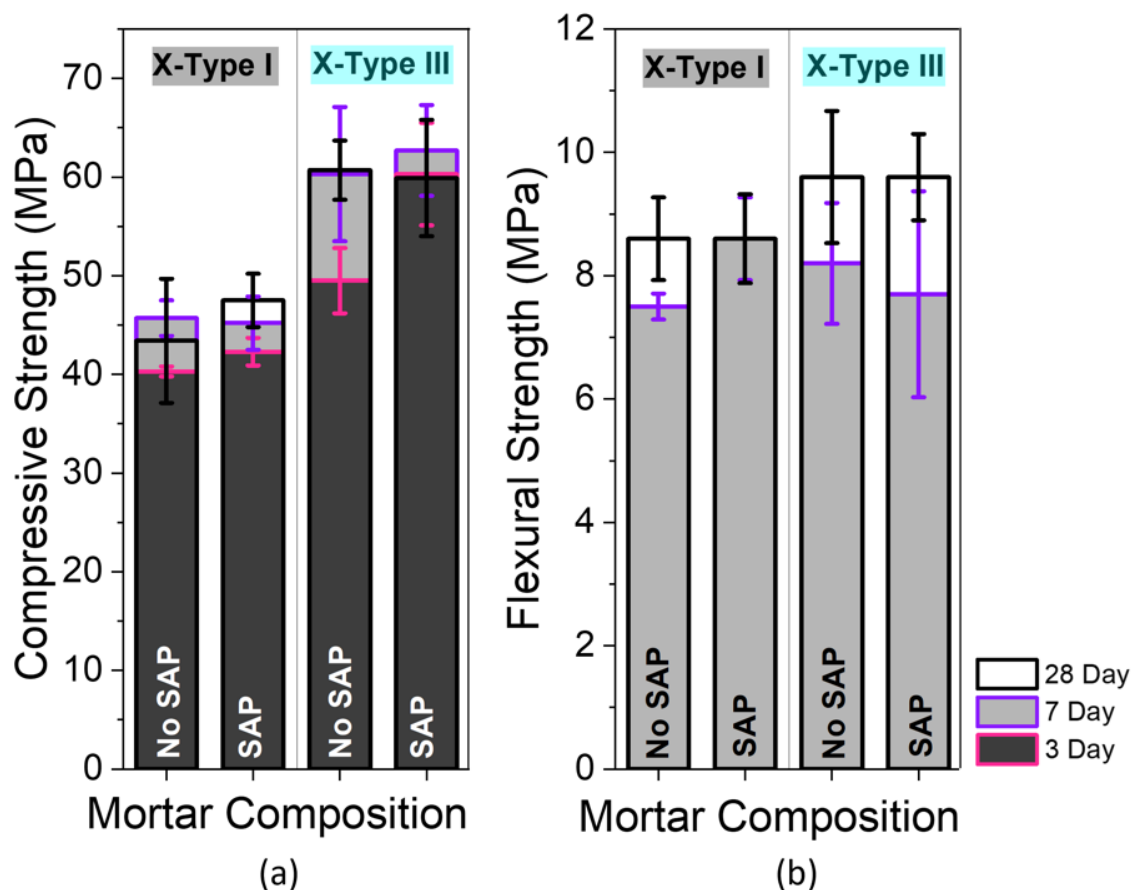


Figure 4.6. (a) Compressive and (b) flexural strength of X-Type III mortars with and without SAP through 28 days. X-Type I mortars are shown as references.

Cement Paste Hydration Characterization

Table 4.4 lists the amounts of calcium hydroxide (CH%) present in 7-day cement pastes determined using TGA. As seen in the Type I cement pastes containing SAP (Table 4.3), X-Type III with SAP showed increased CH% over the Type III reference without SAP, indicating increased

hydration. When comparing each X-Type III sample to its X-Type I counterpart, the X-Type III sample showed increased CH% at 7 days, which agrees with the increased compressive strength observed across both X-Type III samples compared to their X-Type I counterparts in [Figure 4.6a](#).

Table 4.4. CH% (g/g) as determined by TGA of 7-day 0.42 w/c Type III cement pastes with and without SAP with X-Type I pastes as references.

Cement	CH (% g/g cement paste) Reference	CH (% g/g cement paste) With SAP
X-Type I	10.46	11.90
X-Type III	11.57	14.61

[Figure 4.7](#) shows the isothermal calorimetry data for cement paste with two different types of cement from the same source (X-Type I and X-Type III). Presence of SAP caused an increase in total heat in both Type I and Type III pastes, which is an indication of greater amount of hydration when compared to the respective Type I and Type III pastes without SAP.

For the pastes with Type III cement, faster early-strength development was observed when compared to Type I cement pastes, as expected ([Figure 4.7a](#)). Of particular note, the main hydration peak of the X-Type III_SAP paste was noticeably shifted to the left (earlier in time) compared to the X-Type III reference paste. While the peak heights were comparable in both cases, the left-shift of the hydration peak with SAP indicates accelerated hydration. In combination, accelerated hydration and increased total heat at 72 hours of the X-Type III pastes with SAP supports the significant increase in compressive strength observed in 3-day X-Type III_SAP samples in [Figure 4.6a](#). This suggests a synergistic accelerating effect when using SAP and Type III cement in combination.

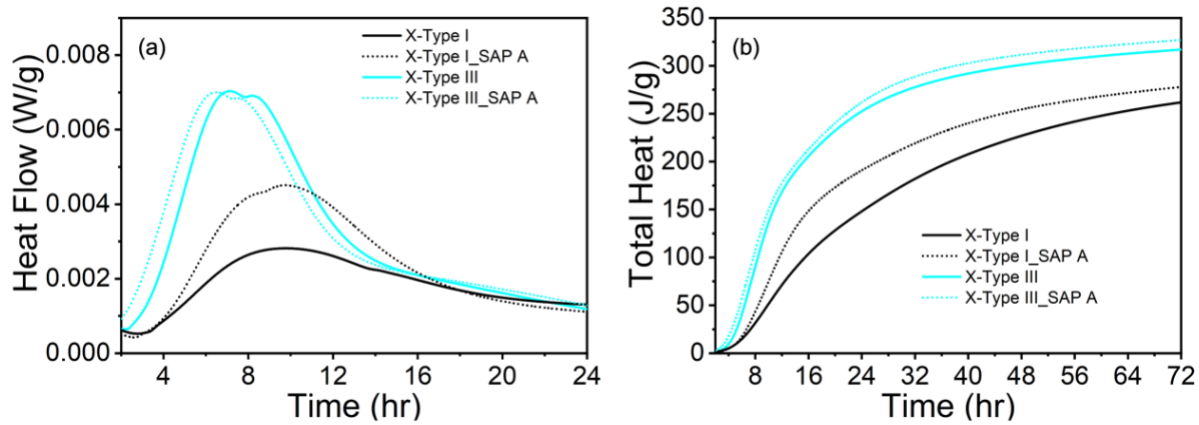


Figure 4.7. Isothermal calorimetry analysis of 0.42 w/c cement paste showing the effect of Type I and Type III cement from the same source on (a) heat flow (24 hours) and (b) total heat (72 hours).

4.3.3 Type I Cement with 30% Slag Replacement by Weight

Characterization of SAP Absorption Capacity and Mortar Flow

The absorption capacities (Q) of SAP over a period of 120 minutes in simulated pore solutions from X-Type I and X-Type I + Slag cements are shown in [Figure 4.8a](#). Delta percent mortar flow (ΔA) with the inclusion of SAP is shown in [Figure 4.8b](#) (calculated using [Equation 4.1](#)).

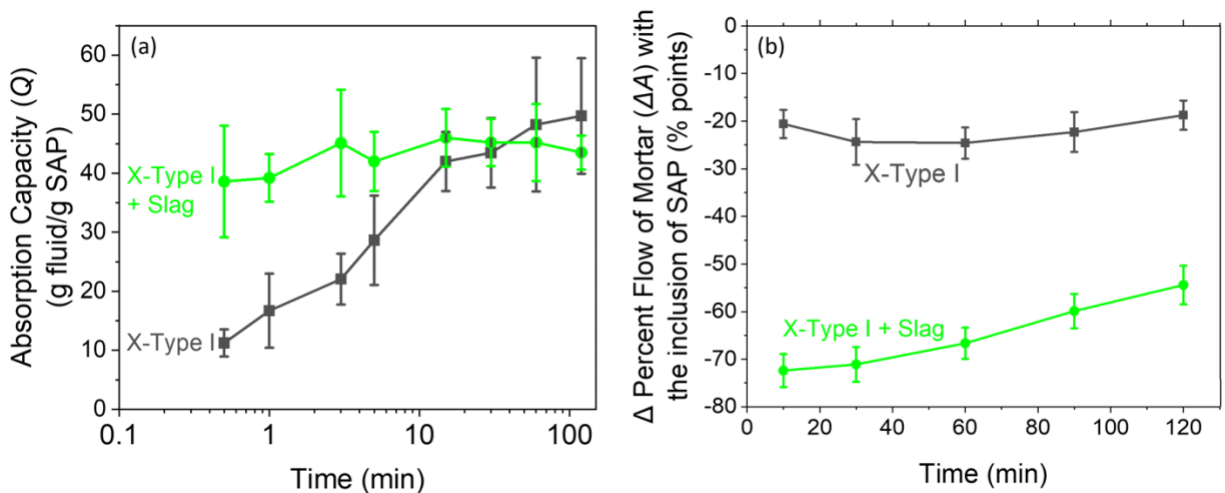


Figure 4.8. (a) Absorption capacity of SAP as a function of immersion time in simulated Type I with 30% slag replacement pore solution with X-Type I pore solution as reference. (b) Change in percent flow over time of mortar with the inclusion of SAP for X-Type I+Slag and X-Type I binders.

Figure 4.8a shows that SAP absorption capacity, Q , was affected by the cement type of the simulated pore solution. As in all previous experiments (Figures 4.1a and 4.5a), this effect was particularly notable within the first minute of immersion, when at 30 seconds, the two simulated pore solution types yielded significantly different absorption capacities in the SAP. SAP in X-Type I simulated pore solution displayed a Q value of 11.2 ± 2.3 , while SAP in the binary binder simulated pore solution displayed a higher absorption capacity of 38.6 ± 9.5 g fluid/g SAP. Again, at 120 minutes, the relative magnitudes of Q were comparable ($p = 0.365$) in both X-Type I and X-Type I + Slag simulated pore solutions.

Figure 4.8b shows that the inclusion of SAP in X-Type I+Slag mortar resulted in a greater magnitude ΔA value at all times through initial set. This increase in magnitude of ΔA was greater in the binary mortar than in X-Type I mortar. This could be seen to correlate with the increase in Q value displayed in X-Type III simulated pore solution compared to X-Type I simulated pore solution, but it would not be appropriate to generalize given that no similar trend was observed in Type I mortars across cement sources (Figure 4.1b).

Compressive and Flexural Strength

The compressive and flexural strengths of X-Type I mortars with 30% slag replacement with and without SAP are shown in Figure 4.9 with X-Type I mortars as reference. The addition of SAP to X-Type I mortar with 30% slag replacement resulted in an increase in the mean values of both 3- and 28-day compressive strength ($p = 0.007$ and $p = 0.015$, respectively). The increase in 3-day compressive strength is of particular interest given the significant reduction in early age compressive strength when using slag replacement compared to straight Type I cement (22.0 MPa for X-Type I + Slag versus 40.3 MPa for X-Type I). Flexural strength values were comparable in slag replacement mortars with and without SAP at all ages. Measured flexural strength is strongly a measure of largest flaw size in a specimen. As such, the presence of SAP-induced macrovoids may dominate flexural behavior over any increased strength due to SAP in these systems that was displayed in the compressive strength results.

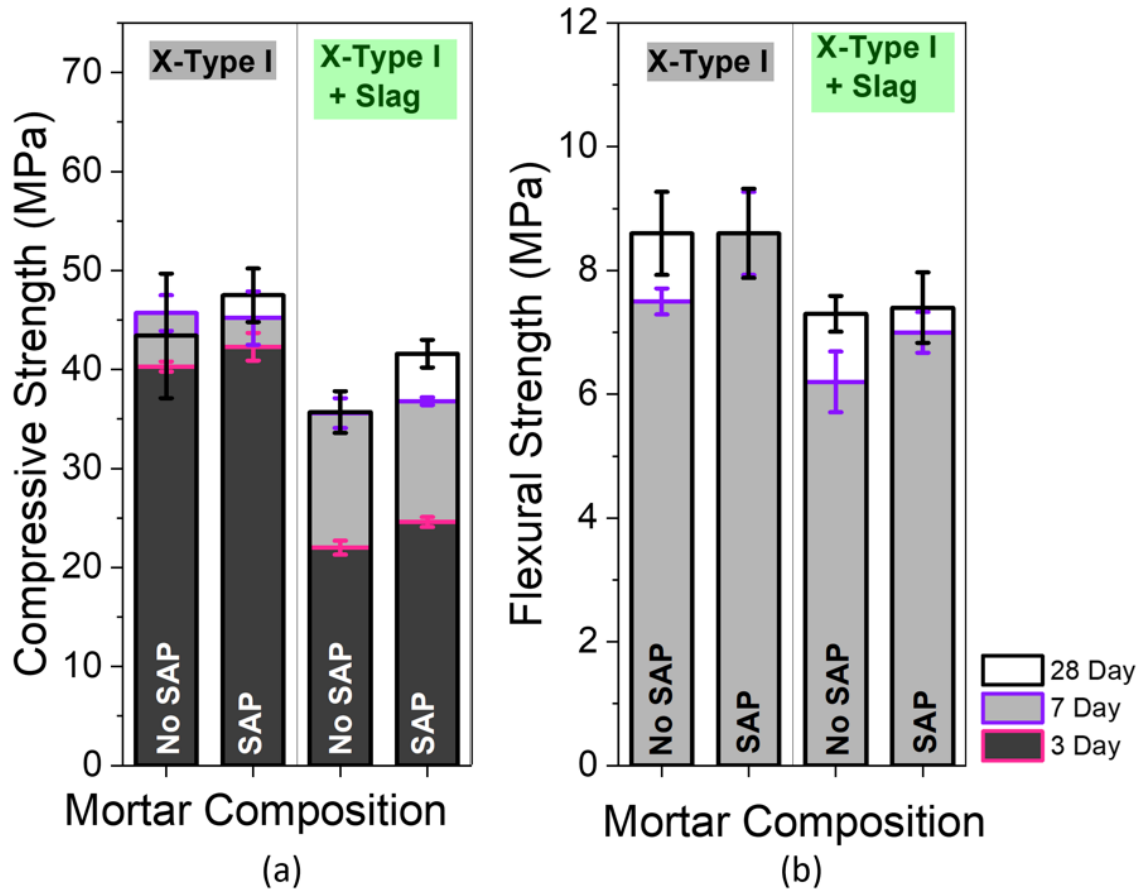


Figure 4.9. (a) Compressive and (b) flexural strength of X-Type I mortars with 30% slag replacement with and without SAP through 28 days. X-Type I mortars without slag are shown as references.

Cement Paste Hydration Characterization

Table 4.5 lists the amounts of calcium hydroxide (CH%) present in 7-day cement pastes determined using TGA. For X-Type I with 30% slag replacement pastes, the sample with SAP showed slightly increased CH% over the reference without SAP, which suggests SAP increased hydration at 7 days.

Table 4.5. CH% (g/g) as determined by TGA of 7-day 0.42 w/c Type III cement pastes with and without SAP with X-Type I pastes as references.

Cement	CH (% g/g cement paste) Reference	CH (% g/g cement paste) With SAP
X-Type I	10.46	11.90
X-Type I + Slag	10.70	11.49

Figure 4.10 shows the effect of partial replacement of cement with slag on the isothermal calorimetry analysis of internally cured pastes. As indicated by the total heat curve (Figure 4.10b), total hydration was reduced for both pastes containing slag. This was expected due to the presence of slag in the binder system, and has been reported by previous researchers.^{104,105} Furthermore, the increased heat flow observed in the first 12 hours has been previously observed through the first 10 hours in mixtures with as little as 10% slag replacement.¹⁰⁵ The addition of SAP did not significantly affect the heat flow or total heat curves within the 72 hours of testing. To understand the full extent of the benefit of internal curing in slag-containing mixtures, a longer duration of isothermal calorimetry analysis may be beneficial.

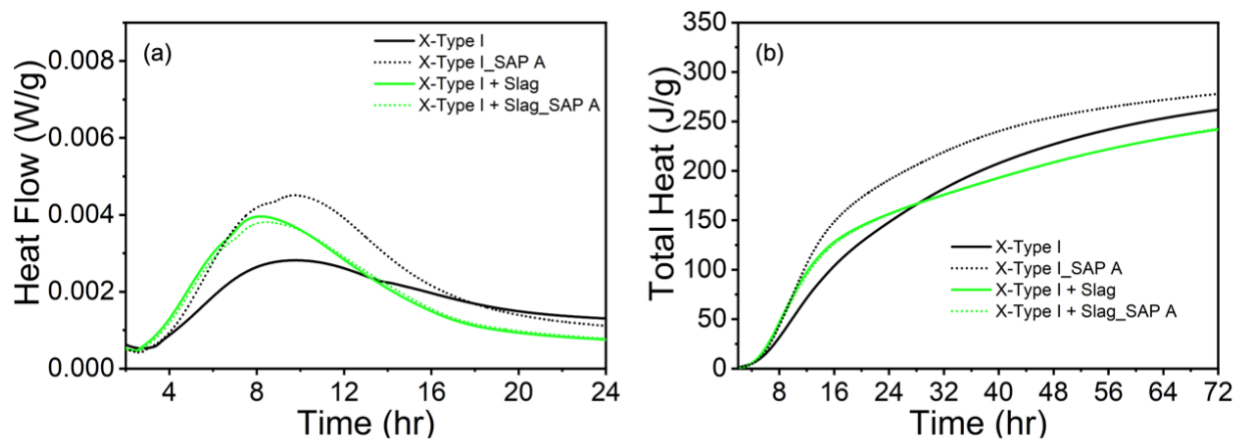


Figure 4.10. Isothermal calorimetry analysis of 0.42 w/c cement paste showing the effect of 30% replacement of cement by slag on: (a) heat flow (24 hours) and (b) total heat (72 hours).

4.3.4 Overall Implications

An exciting additive effect between Type III cement and SAP emerged in the isothermal calorimetry and compressive strength results of this study. Type III cement is intended for applications where early age strength is desired. Comparing the heat flow and total heat curves of X-Type I and X-Type III cement pastes evidenced this with the earlier hydration peak time, increased hydration peak height and increased total heat through 72 hours for X-Type III. The

addition of SAP to X-Type III cement paste enhanced all three of these effects desired in Type III cement. Furthermore, X-Type III_SAP displayed the same compressive strength at 3 days as X-Type III without SAP displayed at 7 days. The combined strength development acceleration of Type III cement and SAP has great implications for field applications where speed to reopening and extended construction seasons can have economic and quality of life impacts.

While not as dramatic a result as that found for Type III cement, it is nonetheless important that the addition of SAP to each of the Type I cement sources tested resulted in similar mechanical property changes and increases in CH% at 7 days. The predictability of the effect of SAP on Type I cement strength development in this study suggests that mechanical properties observed when using SAP in one Type I system can reasonably be expected to be observed in other Type I systems as well.

However, SAP did decrease mortar flow of different Type I mortars by significantly different amounts. As such, for field and other applications where workability of mixtures must fall within certain targets, mix design adjustments to address flow and workability of mixtures containing SAP would need to be determined for the specific system. As previously found, workability losses due to the use of SAP could be mitigated with HRWRA without compromising strength.^{33,37}

The results presented here begin to inform SAP internal curing behavior in binder systems beyond Type I, but there is still much room for continued study. As the question of how to decrease the environmental impact of concrete use continues to be attacked from all possible facets of concrete production, SAP internal curing should be evaluated particularly with respect to strategies that affect the chemistry of fresh cementitious mixtures. Examples of such systems include, but are not limited to, Type II cements and blended cements including supplementary cementitious materials beyond ground blast furnace slag.

4.4 Conclusions

The interaction of binder chemistry and SAP internal curing was studied using five binder systems (three Type I cement systems, one Type III system, and one binary Type I system with 30% slag replacement).

When comparing all five binder systems investigated, SAP absorption capacity and percent flow of mortar were both impacted by changes in binder characteristics, including binder chemistry

and fineness. As such, in contexts where properties prior to initial set are of particular concern, attention should be paid to the impact of binder characteristics on SAP behavior.

Hardened properties of Type I cement pastes and mortars, including compressive strength at 3, 7, and 28 days; flexural strength at 7 and 28 days; and CH% at 7 days were comparably impacted by the inclusion of SAP regardless of the cement source and thus cement chemistry. With respect to hardened properties, this study suggests that SAP could be used in any Type I system with similar expectations of impact on material properties.

In Type III mortar systems, those with SAP displayed nearly identical compressive strength at 3 days as those without SAP displayed at 7 days. Combined with the accelerated hydration and increased total hydration observed through isothermal calorimetry, this result strongly suggests that Type III cement and SAP behave synergistically to accelerate curing and strength development. This suggests that SAP internal curing could be particularly well-suited to applications where Type III cement is already preferred.

SAP-containing binary Type I mortars with 30% slag replacement showed increased compressive strength at 3 and 28 days and increased CH% at 7 days. Yet no significant increase in hydration through 72 hours was observed via isothermal calorimetry with SAP, suggesting that further study is needed to understand the performance of SAP in slag cements.

In future work on SAP internal curing, the results from this study suggest that SAP can be used predictably in Type I cements (with the need for extra care in mix design when fresh properties are of primary interest). Most excitingly, this study suggests that non-Type I binder systems should be the subject of further study for SAP internal curing based on the synergistic and mitigating effects, respectively, of SAP in Type III and binary Type I with 30% slag replacement systems studied here.

4.5 Acknowledgments

The authors thank Edwin Valez-Calez, and Jonathan Kline for their assistance in conducting the SAP absorption tests.

5. IMPACT OF SAP ON CRACKING TENDENCY OF MORTARS AND CONCRETE

Text and figures in the following chapter have been adapted with permission from³³ **Adams, C. J.**; Bose, B.; Mann, E.; Erk, K. A.; Behnood, A.; Castillo, A.; Rodriguez, F. B.; Wang, Y.; Olek, J. Superabsorbent Polymers for Internally Cured Concrete. *JTRP Tech. Reports* **2022**. <https://doi.org/10.5703/1288284317366>.

5.1 Overview

This section describes the research results obtained during the investigation of cracking tendency of SAP-containing mortar and concrete under conditions of restrained shrinkage. The objective of this study was to determine the impact of SAP on the cracking tendency of mortar at 0.35 and 0.42 w/c and concrete at 0.35 w/c. This objective was accomplished by conducting the ring test on mortars with and without SAP and both values of w/c. The primary finding was that the addition of SAP increased time to cracking and reduced average stress rate in Type I mortars at both w/c values and in Type I concrete.

5.2 Materials and Methods

Mortars were prepared as described in [Section 3.2.2](#). The Type I mortars with w/c of 0.42 had the same relative composition as Mix Designs 11, 12, and 13 from [Table 3.2](#). The Type I mortars with w/c of 0.35 were batched using the same three mix designs with the amount of water lowered to yield w/c of 0.35. Concretes with a w/c of 0.35 were prepared following the SAP-to-cement method described in [Section 2.2](#), using the same materials and the proportions listed in [Table 5.1](#).

Table 5.1. Composition of 0.35 w/c concretes.

	No SAP	HA-SAP
Cement (kg)	5.0000	5.0000
Sand (kg)	9.13793	9.13793
Coarse Aggregate (kg)	12.93103	12.93103
Water (kg)	2.40669	2.40669
HRWRA (mL / %bwoc)	25.0 / 0.05%	57.5 / 0.12%
AEA (mL / %bwoc)	6.9 / 0.01%	6.9 / 0.01%
HA-SAP (g / %bwoc)	0.0 / 0%	10.0 / 0.2%

After batching, mortars and concretes were cast into a ring mold according to ASTM C1581/C1581M with a properly sized cardboard tube serving as the outer ring and four strain gauges distributed evenly inside the inner steel ring.¹⁰⁶ One day after casting, the outer cardboard ring was removed and the top surface of the specimen was sealed with self-adhesive aluminum tape to restrict drying to the circumference surface of the ring. Strain gauge measurements were collected until the sample cracked. The ring had four strain gauges placed at regular intervals. The diametrically opposed strain gauge measurements were averaged for data analysis.

5.3 Results

5.3.1 0.35 w/c Mortars Results

Strains generated in the steel ring supporting the $w/c = 0.35$ mortars are shown in [Figure 5.1](#). The No-SAP mortar served as a reference. This mortar cracked at an age of 4.25 days. The time- to-cracking values increased for both mortars containing SAPs and were, respectively, 5.25 days for LA-SAP and 5.0 days for HA-SAP. These higher time-to-cracking values represented 24% and an 18% increase for LA-SAP and HA-SAP mortars, respectively, over the values observed for No SAP reference mortar.

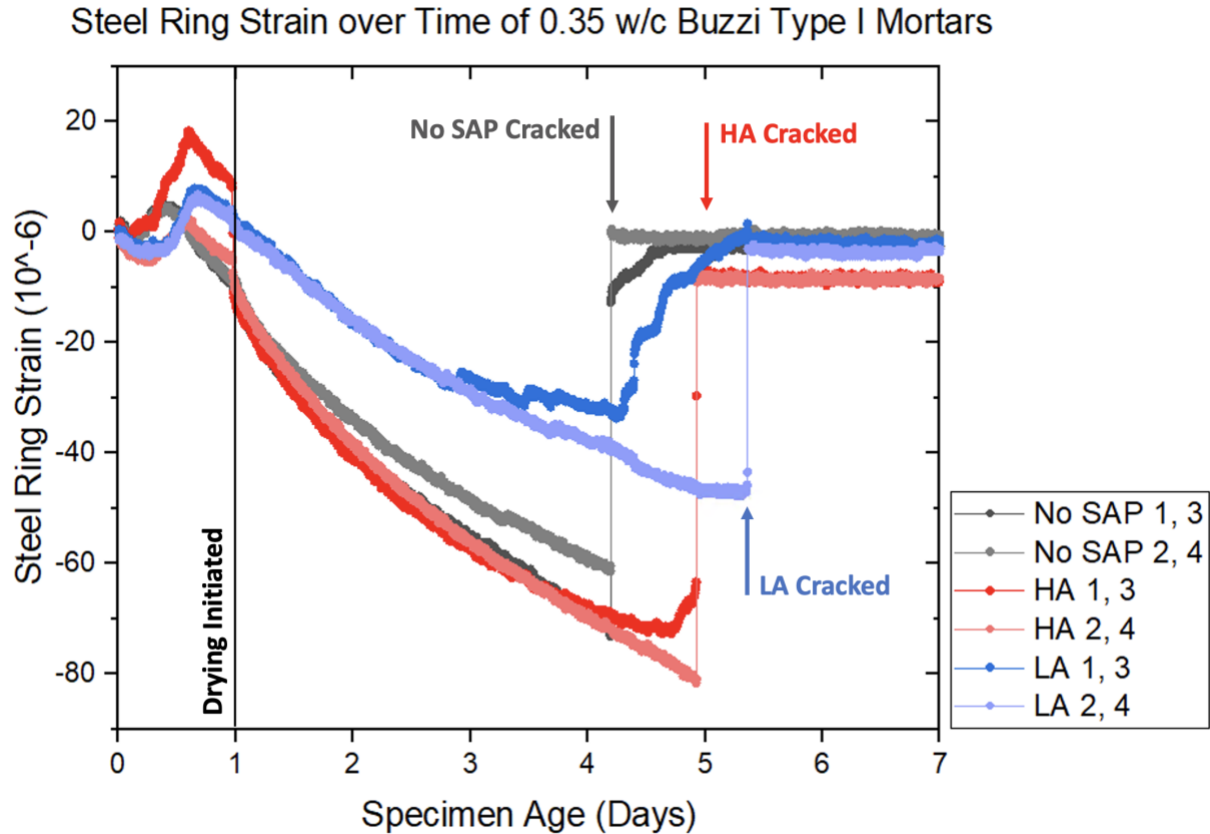


Figure 5.1. Steel ring strains over time for 0.35 w/c B Type I mortars with and without HA- and LA-SAPs.

5.3.2 0.42 w/c Mortars Results

Strains generated in the steel ring supporting the 0.42 w/c mortars are shown in [Figure 5.2](#). The No SAP mortar served as a reference. This mortar cracked at an age of 4.5 days. The time-to-cracking values increased for both mortars containing SAPs and they were, respectively, 5.0 days for LA-SAP and 6.0 days for HA-SAP. These higher time-to-cracking values represent 11% and 33% increases for 0.42 w/c LA-SAP and HA-SAP mortars, respectively, over the 0.42 w/c No SAP reference mortar. Of additional note, the time-to-cracking of 4.5 days for the 0.42 w/c No SAP mortar was exceeded not only by the 0.42 w/c mortars containing SAP, but also by both 0.35 w/c mortars containing SAP, despite their reduced values of the water-to-cement ratio.

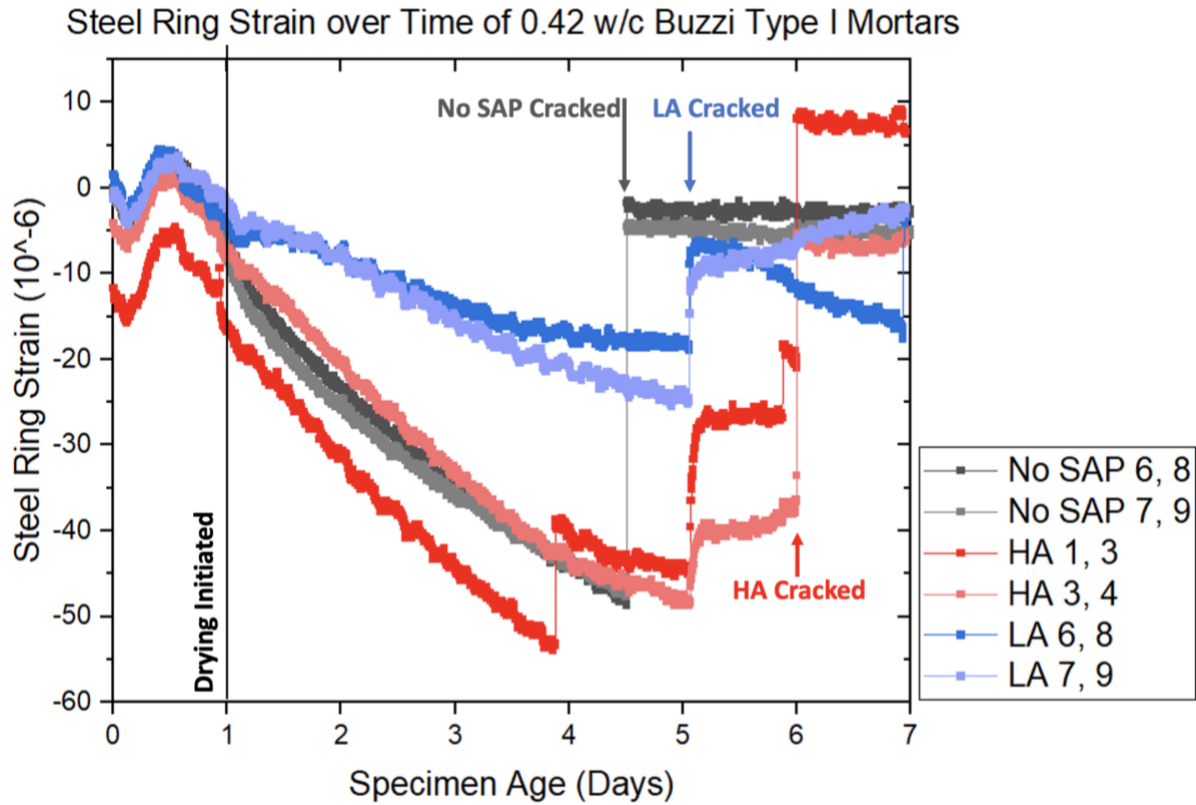


Figure 5.2 Steel ring strain over time of 0.42 w/c B Type I mortars with and without HA- and LA-SAP.

5.3.3 0.35 w/c Concretes Results

Strains generated in the steel ring supporting the 0.35 w/c concretes are shown in [Figure 5.3](#). The No SAP concrete served as a reference and cracked at an age of 12 days.

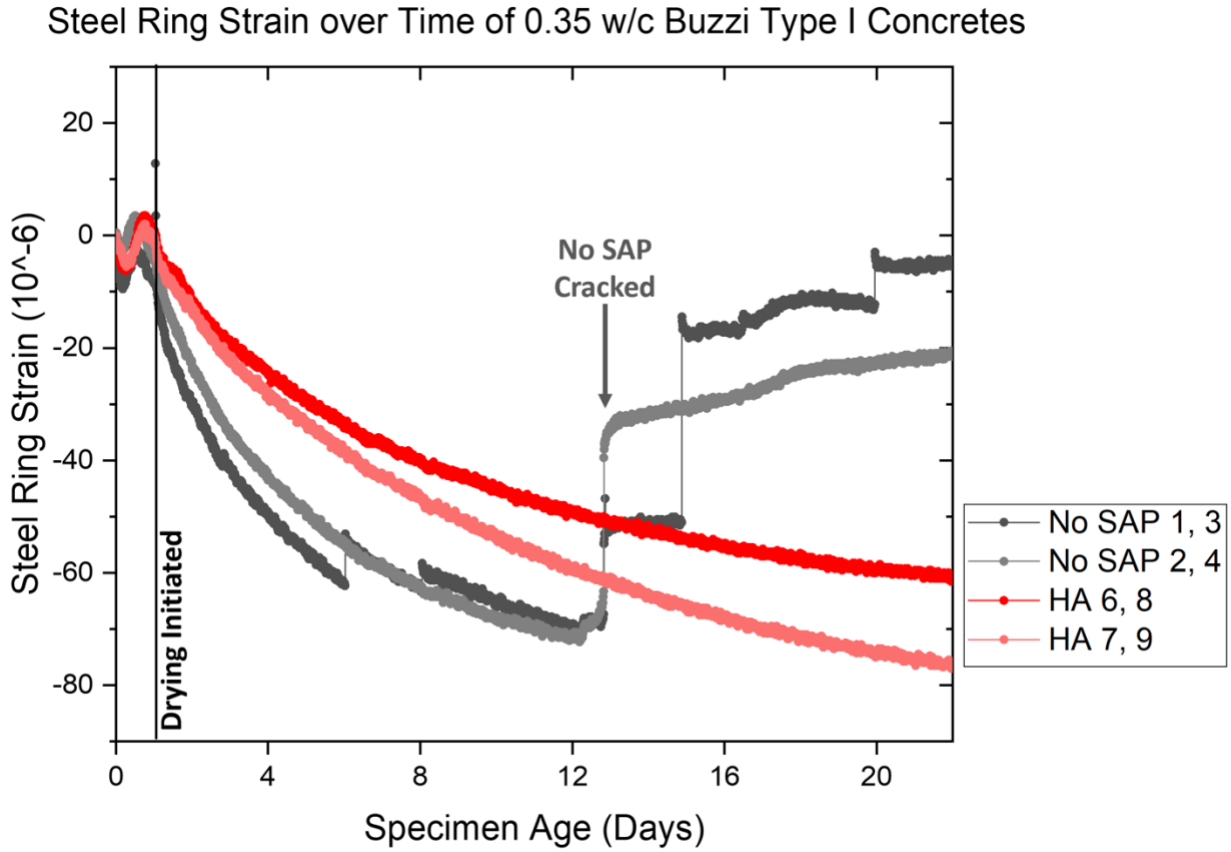


Figure 5.3. Steel ring strain over time of 0.35 w/c Buzzi Type I Concretes with and without HA-SAP.

Quantitative data collection of the steel ring strains was interrupted at 22 days, however, periodic visual inspection for cracks in the HA-SAP concrete continued through 549 days at which time there was no evidence of significant cracking in the HA-SAP concrete. This represents at least a 4500% increase in time to cracking when using HA-SAP in 0.35 w/c concrete compared to the reference concrete without SAP.

Figures 5.4 and 5.5 show photographs taken at 549 days of the two concrete rings. Figure 5.4 shows pictures of the No SAP concrete ring with red arrows pointing to the crack passing through the full height and radial cross-section of the sample. The photos were taken on day 549, but the crack was visible starting at 12 days. Figure 5.5 shows images of the full 360° circumference of the HA-SAP concrete with no visible significant cracking. A superficial crack following an imperfection in the original mold is visible at the top of the sample in Figure 5.5e,

but as is shown in [Figure 5.6](#), the crack did not propagate through a radial cross-section of the sample.

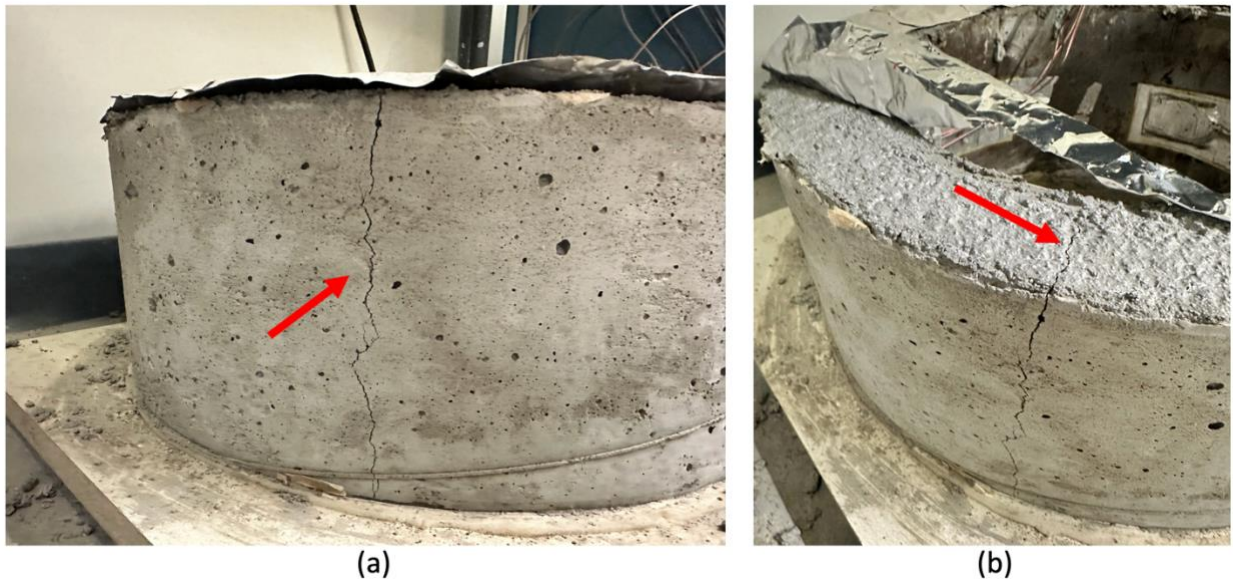


Figure 5.4. Photos of the No SAP concrete sample with red arrows pointing to the crack in the sample.

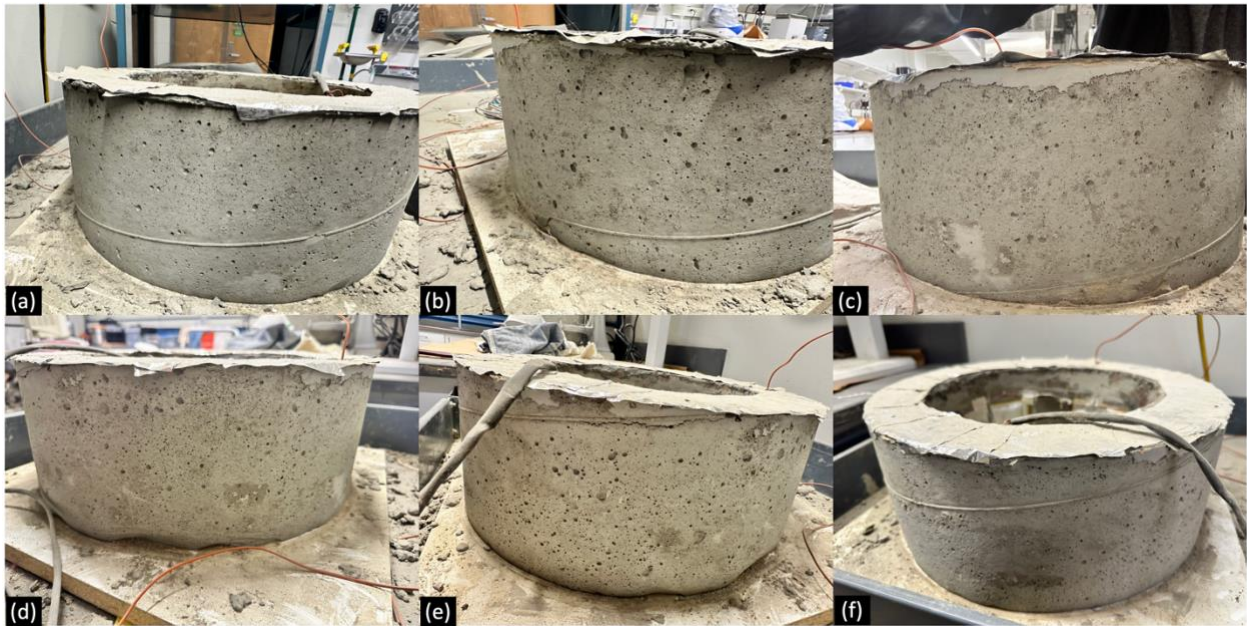


Figure 5.5. Photos of the 549-day HA-SAP concrete sample from angles comprising the full circumference of the sample.



Figure 5.6. Photo of the 549-day HA-SAP concrete sample with a red arrow indicating the superficial crack.

5.4 Conclusions and Implications

The following conclusions resulted from this cracking tendency study:

- SAP-containing mortars at both 0.35 and 0.42 w/c cracked at later ages than reference mortars without SAP.
- SAP-containing mortars at 0.35 w/c cracked at later ages than 0.42 w/c mortars without SAP, despite having a lower w/c.
- SAP-containing concrete at 0.35 w/c did not crack for over 1.5 years, while the No SAP concrete cracked after only 12 days.

A number of implications resulted from this study. First, SAP can be used to decrease cracking tendency of both high and low w/c mixes. Second, 0.35 w/c mortars with SAP have longer time-to-cracking than 0.42 w/c mortars without SAP, meaning SAP can be used assure the high performance of lower w/c mixes as it decreases their cracking tendency. Third, the 4500%+ increase in time to cracking in SAP-containing 0.35 w/c concrete indicates that decrease in cracking tendency caused by the inclusion of SAP is of a scale to significantly improve the performance of concrete in field-scale applications. A limitation of this study is the lack of replicates. Further validation is warranted. This could include replication studies as well as stress

rate and maximum strain analysis, particularly in concrete samples. For SAP-containing samples, it would likely be advantageous to combine the ASTM C1581 standard with some sort of accelerated aging study (e.g., freeze-thaw cycling) to allow for further differentiation among samples that reach equilibrium without cracking.

6. CONCLUSIONS AND FUTURE DIRECTIONS

6.1 Conclusions

This dissertation sought to address practical implementation questions key to the translation of SAP hydrogel internal curing technology to from the benchtop to the field in transportation applications, including: (1) What effects do mix design adjustments made to increase mixture flow when using SAP have on cementitious mixture properties? and (2) What effect do cementitious binder characteristics have on SAP performance?

SAP was well-distributed throughout concrete mixtures when added before water in all batching sequences studied and resulted in comparable compressive strengths at 7 and 28 days. As such, batching sequence can be chosen to optimize processing workflow without sacrificing long-term material properties. Furthermore, there was no sign of agglomeration of SAP within the cement matrix nor of any disruption of the interfacial transition zone around fine or coarse aggregate caused by the introduction of SAP to any of the mortars or concretes in this dissertation. (Chapter 2 and Section 3.3.5)

Verification of SAP in as-delivered concrete was performed in minutes using methods suitable for on-site testing, with follow-up quantitative lab-scale testing of delivered SAP dosage completed within days. (Section 2.3.3)

SAP-containing mortars and concretes displayed significantly increased times to cracking under restrained shrinkage with a particularly exciting increase in time to cracking in SAP-containing 0.35 w/c concrete of over 4500%. At the time of this writing, 1.5 years after casting, the SAP-containing concrete ring is still intact. (Chapter 5)

Mix design adjustments were required to maintain sufficient flow to cast well-consolidated samples when using SAP in all 0.42 w/c cementitious mortars studied. Often, additional water is added to mixtures using SAP to account for the absorbed water, however, in this study, it was evident that this practice lowers the resulting compressive and flexural strength. Thus, in situations where strength is an important design criterion, no extra water should be added to account for SAP absorption. Instead, HRWRA at range of dosages could be used in lieu of extra water to increase mixture flow when using SAP without compromising compressive and flexural strengths. Modest HRWRA dosages (sufficient to achieve 110% flow of SAP-free mortars) resulted in SAP-

containing mortars suitable for casting consolidated samples. Higher HRWRA dosages (sufficient to achieve 110% flow of SAP-containing mortars) were also used without compromising 28-day strength. ([Chapter 3](#))

When comparing SAP behavior across binder systems (Type I OPC from three different sources, Type III OPC, and a binary Type I/slag system), it was evident that SAP and fresh mortar properties were impacted by differences in binder characteristics. As such, in contexts where properties prior to initial set are of particular concern, attention should be paid to the impact of binder composition on SAP behavior. This would likely include additional flow or slump testing and subsequent modifications to HRWRA dosage. ([Chapter 4](#))

In Type I OPC systems, the addition of SAP affected the hardened properties (e.g., strength, CH%) comparably for all three cement sources tested, suggesting that SAP could be used in any Type I system with similar expectations of impact on post-initial set material properties. This result has valuable implications for the feasibility of utilizing SAP in project design. ([Chapter 4](#))

SAP-containing binary Type I mortars with 30% slag replacement showed increased compressive strength at 3 and 28 days and increased CH% at 7 days. Yet no significant increase in hydration through 72 hours was observed via isothermal calorimetry with SAP, suggesting that further study is needed to understand the performance of SAP in slag cements. ([Chapter 4](#))

Excitingly, in Type III mortar systems, SAP-containing mortars displayed nearly identical compressive strength at only 3 days as SAP-free mortars displayed at 7 days. Combined with the accelerated hydration and increased total hydration observed through isothermal calorimetry, this result strongly suggests that Type III cement and SAP behave synergistically to accelerate curing and strength development. This suggests that SAP internal curing could be particularly well-suited to applications where Type III cement is already preferred. ([Chapter 4](#))

6.2 Future Directions

The work represented here suggests three overarching paths for future work: (1) a continuation of research into the interaction of SAP with various binder systems, (2) additional research into applied implementation strategies for SAP, and (3) the other an exploration of basic behavior of superabsorbent polymers in cementitious environments.

Based on the synergistic effects of SAP observed in Type III and binary Type I/slag cement systems in this dissertation and on the continued push for cement alternatives, all binder systems

relying on a hydration reaction to achieve cementing behavior (e.g., all portland cement-based systems, limestone calcined clay cements,¹⁰⁷ aluminosilicate geopolymers,¹⁰⁸ and magnesium-based cements¹⁰⁹) are ripe for study with SAP.

For widespread implementation, the delivery method of SAP into a given cementitious mixture needs further development. How can SAP be dosed and added to a concrete mixer at scale in a way that ensures adequate dispersion within the mixture and without loss of material? Possibilities include packaging in dissolvable bags, pre-mixing with another particulate component (e.g., cement, SCM, or dry sand), but all delivery methods need field trials to determine their suitability across the dimensions of implementation ease and technical results.

The industrial SAPs used in this study and the majority of SAP produced are not necessarily designed for cement applications. Rather, they are formulations borrowed from the large existing SAP applications of absorbent hygiene products and water treatment.¹⁰ There is still room for design of SAPs tailored to cementitious applications. Work is already being done in this area (e.g., the development of pozzolan-containing SAP),^{18,26,110} but there are significant opportunities for further exploration and development of new SAP formulations based on research in the realms of aqueous, cement, and polymer chemistry as well as in biomineralization. Such work not only has the potential to add to understanding of cement-polymer systems, but also to provide insights into polymer-inorganic systems more broadly.

APPENDIX

Supplemental Information for Chapter 3 “Effect of binder characteristics on workability, hydration, and strength of cementitious systems with superabsorbent polymer admixtures”

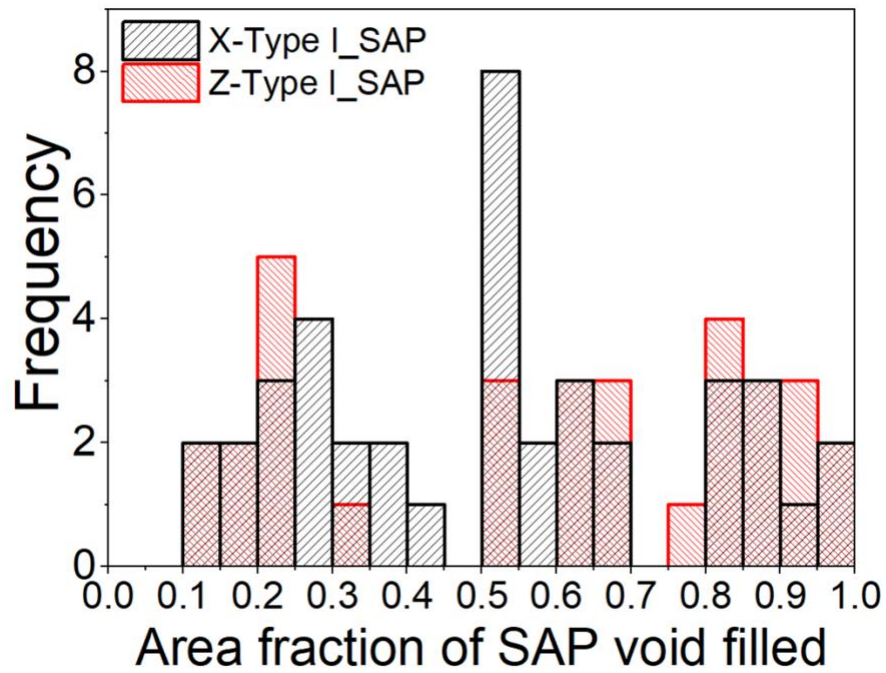


Figure A.1. Results of microstructural analysis of 0.42 w/c pastes with SAP A. Area fraction of SAP particle voids filled with hydration products for each sample is shown.

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