Influence of Nucleation Seeding on the Compressive Strength of Ordinary Portland Cement and Alkali Activated Blast-Furnace Slag

M. Hubler, H. Jennings, and J. Thomas
Civil and Environmental Engineering, Northwestern University
Technological Institute 2145 Sheridan Rd.
Evanston, IL 60208

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A study is conducted to determine the effects on the early hydration kinetics and compressive strength by seeding of Portland cement and alkali-activated blast furnace slag with a pure form of calcium silicate hydrate (C-S-H). The effects of C-S-H seeding during the early nucleation and growth period of each type of cement, was measured with an isothermal calorimeter during the first day of hydration. The compressive strength was determined for 2” cylinders up to 28 days after mixing. It was found that C-S-H seeding results in an earlier and larger hydration heat development peak for both types of cement. The addition of C-S-H seed to the slag cement paste produced a significant increase in compressive strength only when cured in a sealed environment. For the Portland cement paste, the C-S-H seeding provides a slight increase in compressive strength when cured underwater. It was also found that careful dispersion of the C-S-H seed in the mix water further improves the early hydration heat development, but has no effect on the compressive strength. This work furthers the understanding of the early hydration behavior of slag paste and the effects of C-S-H seeding.

Introduction

Blast furnace slag is an industrial byproduct which has been effectively used as a constituent in Portland cement in response to growing concerns over the significant carbon footprint of the Portland cement manufacturing [1]. As a latent hydraulic material, slag forms hydration products and contributes to the strength of the blended cement [2]. The durability of various activated slag concrete mixes has been documented over 40 years and was found to be reliable [3]. An incomplete understanding of the hydration chemistry and physical products of slag cement are not well understood and the reaction of slag cement is slower than Portland cement. As a result, optimizing mix design of slag cements, predicting long term properties, and accelerating slag hydration are topics of interest in developing blast-furnace slag cement.

Blast furnace slag is activated by the high pH pore solution formed when blended with Portland cement. Similarly, it may be activated by the addition of alkalis to form alkali-activated slag paste to increase the rate of dissolution of the glassy phases in the slag. It is expected that C-S-H with a low Ca/Si ratio forms upon hydration of the slag since the Ca/Si ratio of slag is lower than that of Portland cement. The development of C-S-H in blended cement with ordinary Portland cement and pure slag paste were studied both during early hydration [4, 5], and in aged samples [6, 7]. These studies were able to conclude that the addition of blast-furnace slag reduces the Ca:Si ratio, increases the Al:Ca ratio, changes a strongly linear microstructural morphology to a fine foil-like morphology. The finer morpohology has been used to explain reduced diffusion rates through slag-based cements. Micrographs of slag-blended cements have confirmed that the primary reaction of slag grains is by dissolution-precipitation [8, 9], similar to that of ordinary Portland cement. Yet, none of these studies were able to determine the mechanism controlling the growth rate in pure slag. Experimental studies, such as the one presented here provide more insight into the mechanisms controlling slag hydration.

The reaction rate of slag cement can be adjusted to match the reaction rate of Portland cement by increasing the surface area of the slag cement [1, 10]. This can be achieved through grinding, which is not economical [11]. Seeding with a pure form of laboratory made C-S-H would have a similar effect. Adding this type of C-S-H to C_3S paste increased nucleation sites for hydration to occur [7]. The C-S-H seeds the formation of the C-S-H hydration product since the nucleation process, which governs C-S-H formation, is autocatalytic. When applied to a cement paste, the C-S-H seed would cause the hydration product to form within the pore spaces between particles while the typical hydration processes continue to occur. This paper presents experimental work investigating whether the concurrent formation of C-S-H causes an earlier and stronger hydration reaction that creates a denser microstructure with less capillary porosity. Compression tests are performed on cylinders of seeded cement pastes with the understanding that a dense microstructure should cause high compressive strength [12].

Gartner (1989) suggested that seeding the hydration reaction with C-S-H gel to accelerate hydration could shorten the induction period of C_3S paste [13]. However, Gartner did not provide data to support his hypothesis. In 1997 Taylor performed experiments from which he concluded that the method was ineffective or retarding [2]. More recently Thomas's experiments and modeling work showed that seeding with C-S-H was indeed effective and agreed with nucleation growth models in C_3S paste [7]. Although these studies have furthered the understanding of adding C-S-H gel as a seeding method for hydration, none have applied the method to commonly used cement. Here we present data showing effective C-S-H seeding of Portland cement and blast furnace slag for the first time.

Experimental Section

The method for creating the C-S-H seed material was similar to methods described by Thomas in 2009. Sodium silicate and calcium nitrate solutions were mixed to form a precipitate. The sodium silicate solution consisted of reagent-grade $Na_2SiO_3 \cdot 5H_2O$ powder dissolved in deionized water. Reagent-grade $Ca(NO_3) \cdot 4H_2O$ was used to make the calcium nitrate solution, also with deionized water. The two solutions were combined in a bottle and immediately formed C-S-H with a Ca/Si ratio of 1. After being shaken for 15 min, the precipitate was placed in a Buchner funnel to filter. Excess water was drawn out of the C-S-H after which it was rinsed with CaO solution. The concentration of lime in the rinse was selected to match that of the precipitated C-S-H. After completing filtration, the C-S-H gel was removed and stored in a sealed container.

For each batch of C-S-H gel created, the percent of solid C-S-H was determined by measuring the weight of the gel before and after at 160ºC for 12h. The water/solid ratio initially ranged between 4-7%. By filtering smaller amounts of precipitate at a time a more consistent water/solid ratio could be obtained. The C-S-H gel used in the compression test experiments had an average ratio of 5.2% solids with a standard deviation of 0.4%.

A commercial ground slag product (NewCem, Lafarge) that was designed to be blended up to 50% with Portland cement was used in both the calorimetric studies and compression tests. Crystallized sodium silicate was added to the cement to activate the pure slag paste. Various studies have concluded that sodium silicate is an effective activator for slag cement in that it could attain equivalent compressive strengths to ordinary Portland cement over long periods of time [3, 13, 14]. C-S-H gel was added to the mix based on the ratio of solid C-S-H within the gel, to the weight of the pure slag. For shear mixed cylinders the required amount of seed was first mixed with deionized water until the selected w/c ratio for that mix was obtained. The C-S-H gel and water mixture exhibited a strong shear thickening behavior that persisted when mixed with the sodium silicate and dry slag. Similar viscosity of slag pastes was observed by Escalante-Garcia, *et al* [8]. High speed mixing was required to obtain a flowable paste. Mixing the seed into the water with a ¾” shear mixer for at least 5 min provided a better dispersion of C-S-H in the Portland cement paste. The gel and water mixture was stirred into the blended slag and sodium silicate activator for up to 10 min. Once a paste formed, the stirring rate was increased to prevent the C-S-H gel from gelling up.

An isothermal calorimeter (model 4200, Calorimetry Sciences Corporation, Linden, UT) was used to study the early hydration kinetics of the slag paste. The calorimeter was set to 20ºC with a time resolution of 1min. 1g of paste was sealed in a 1.3mL vial after mixing and placed in the instrument. Measurements were taken when the temperature of the sample and the calorimeter became consistent. The compression tests were performed on 2” cylinders that were filled with mixed paste in three lifts. After each lift, the cylinder was tapped to release bubbles. The last lift was rodded 10 times, tapped, and given a smooth finish. The cylinders were cured in two ways; either underwater or in sealed containers. The samples cured underwater were kept in a curing room with 100% humidity during the first 24 hours and then demolded before being placed in lime water. Samples that did not demold easily were removed with a small amount of air pressure through a hole in the form’s base or by cutting the mold from the cylinder. The compression tests were performed on a displacement driven concrete compression machine. The digital readout reported an initial value and the peak load reached during each compression test.

Results

Mix Design of Alkali activated - Slag - C-S-H paste. In order to compare strength tests on alkali-activated slag (AAS) paste with and without C-S-H seeding a range of mix design values that would work for both cases were considered. The goal of this step was to determine such a range of the mix components for cement consisting of slag, sodium silicate as the alkali activator, and C-S-H seed with approximately 0.05 solids content. A mix without C-S-H seeding was used to evaluate the maximum water-cement ratio (w/c) that would not bleed water at the top of the mix while setting. Using the range of w/c values which showed little to no bleeding, a slag mix with C-S-H seeding was then used to evaluate how much C-S-H seed could be added while allowing the paste to be workable. A workable paste was expected to flow on its own or when vibrated locally.

When the w/c ratio was kept below 0.45 at most a thin film of water was observed at the top of the sample. At a w/c ratio of 0.40 no bleeding occurred. In order for the mixture with a 0.40 w/c ratio to be workable with C-S-H seeding, the solids component of the C-S-H could be at most 1% of the mix solids. The amount of solid C-S-H from the seed can be increased to 1.5% of the amount of mix solids when the w/c ratio is increased to 0.43. When mixed within these proportions, a small quantity of the AAS paste forms a sticky paste after 5 min of mixing which does not flow unless vibrated locally.

The possibility of reducing the amount of silicate needed to activate the slag paste was also tested. Three different pastes were analyzed with the calorimeter consisting of slag paste with a 0.4 w/c ratio and a sodium silicate ratio to weight of slag of 0, 0.05, and 0.1. It was observed that a sodium silicate ratio to weight of slag of 0.1 resulted in more than a 50% increase in the hydration peak height of the slag paste, compared to a 0.05 ratio of sodium silicate. As a result a 0.1 sodium silicate ratio was adopted for all mixes with and without C-S-H seeding. Fig. 1 shows the results of this study both for AAS paste with and without C-S-H seed.

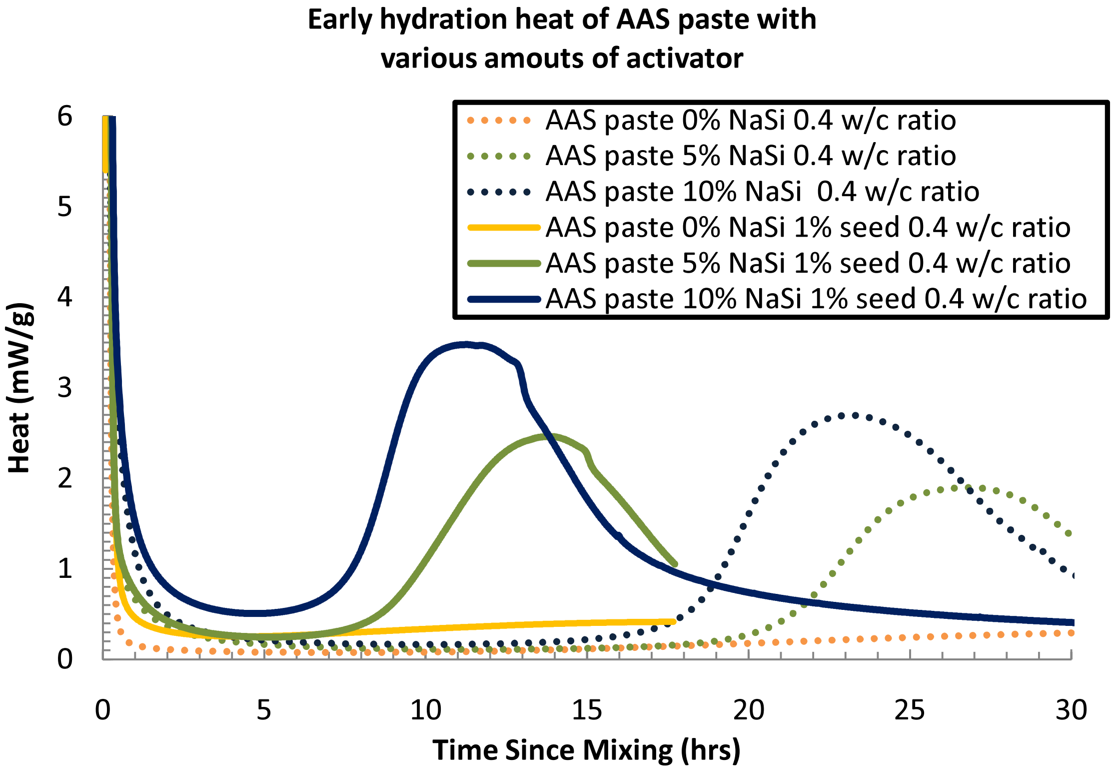

Fig. 1. The heat evolution of activated slag paste with C-S-H seed and either 0%, 5%, and 10% activation by sodium silicate is plotted. The dotted lines indicate the same results for activated slag paste without C-S-H seed.

Early Hydration of Activated Slag Paste with C-S-H seed. The early hydration kinetics of various slag mixes within the previously selected range of workable mixes, were studied in an isothermal calorimeter. As the amount of seed was increased the w/c ratio was also increased linearly to allow for a mixable paste. Once a well mixed paste was obtained, the peak of the early hydration heat rate curve was expected to occur earlier and at a higher value as the amount of seed was increased. These trends were observed in Fig. 2, but with a slight dip around 1% seed.

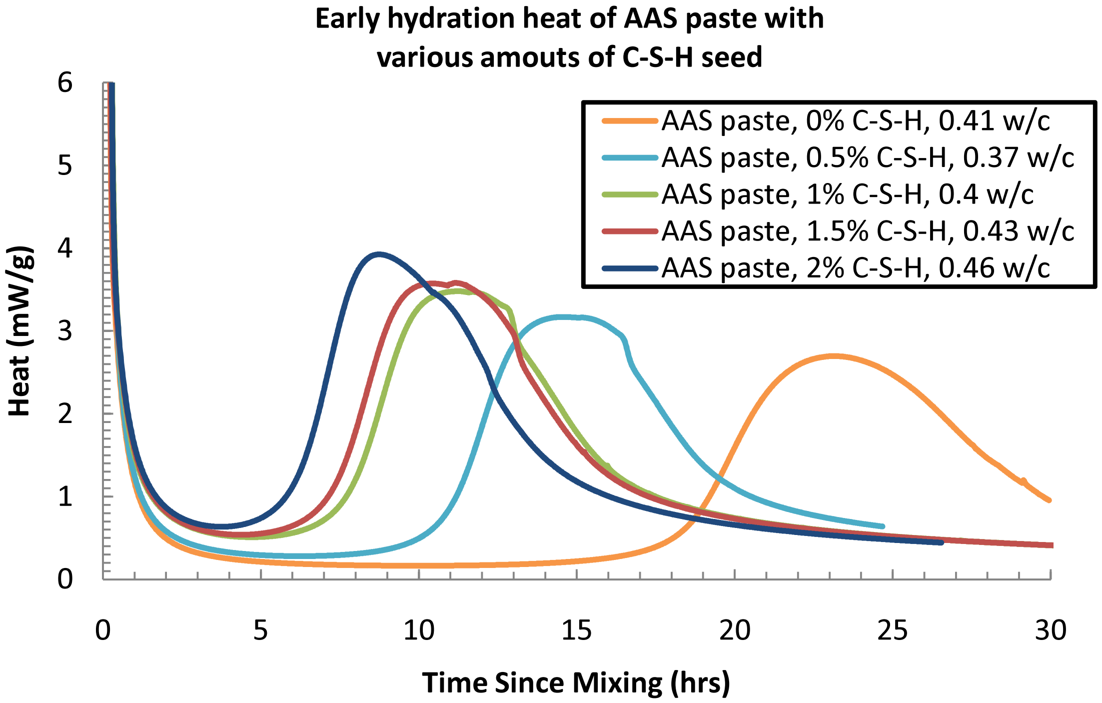

Fig. 2. Calorimetry results for the hydration kinetics for activated slag paste with increasing amounts of added C-S-H seed. The w/c ratio was increased to allow for workability of the paste as more gel was added to the mix. The slight changes in w/c ratio had much smaller effects on the hydration curves than those observed due to the addition of the seed.

Activated blast-furnace slag paste with C-S-H mixing study. Preliminary compression tests of activated slag paste with C-S-H gel displayed a much more pronounced increase in compressive strength when there were no observable white specks of C-S-H in the cured cylinders. These specks were related to the mixing procedure for combining the dry and wet ingredients. The C-S-H gel needed to be well mixed with water before dispersal in the slag paste could be accomplished. A ¾” shear mixer was used to dissolve the C-S-H gel in the water to create a gel of a lower solids percent. The mixing time for the combination of gel and water was studied for 10g of gel. A minimum of 5 min of mixing the gel and water with the shear mixer ensured no visible specks in 1.5”x0.75” tall test cylinder vials. When mixing the C-S-H gel and water mixture into the dry paste, an effect on pore size in the cured sample was observed. After the 5 min of shear mixing required for dispersal of the C-S-H gel in the water, additional mixing by hand or slow mixing machine in excess of 10 min caused large pores to form. These two effects were considered in defining a mixing procedure of an initial 5 min shear mixing of water and C-S-H gel followed by less than 10 min paddle or rod mixing the combined paste. Voids were still observed when mixing larger batches of paste. These could occasionally be reduced by placing the fresh cylinders on a vibration table.

Using the improved mixing procedure to reduce the white flecks and pores, the early heat evolution study was repeated. Fig. 5 illustrates the difference observed with the shear mixed activated slag paste with C-S-H seeding, and with the previously used rod mixing. The shift in the peak of the heat evolution is not only higher, but also earlier. This change is similar to that seen in the C_3A heat evolution peak of the ordinary Portland cement results.

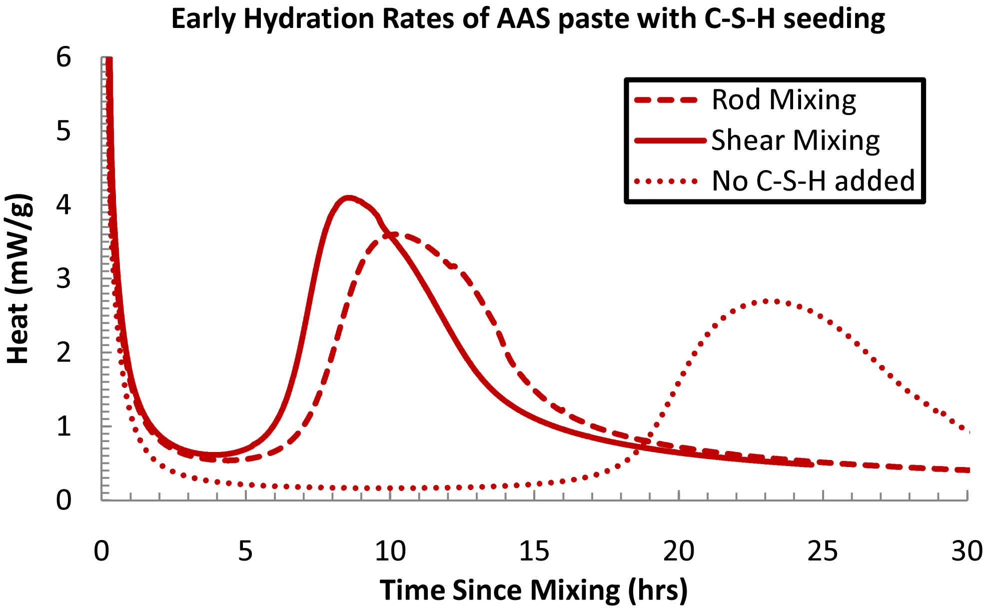

Fig. 3. A study of the effect of shear mixing the C-S-H seed before adding it to an activated slag mix with 1.33% C-S-H seed and a 0.42w/c ratio. An increased and sooner heat development peak results from shear mixing.

C-S-H activated blast-furnace slag paste compression tests. C-S-H activated blast-furnace slag paste showed sensitivity to mixing and curing procedures. Effects of mixing the activated slag paste with a commercial mixing machine and by hand were studied independent of the addition of C-S-H to the paste. This provided an understanding of the significance of the type of mixing independent of the shear-stiffening effects the additional C-S-H gel introduces. The commercial mixer provided less control over the mixing speed, the shape of the implement, or the volume being mixed. The mixing procedures were comparable in mixing time, mix proportions, and environmental conditions. Hand mixing showed a consistent 50% improvement in compressive strength as illustrated in Fig. 4. As a result, all other mixes produced for these studies were mixed by hand.

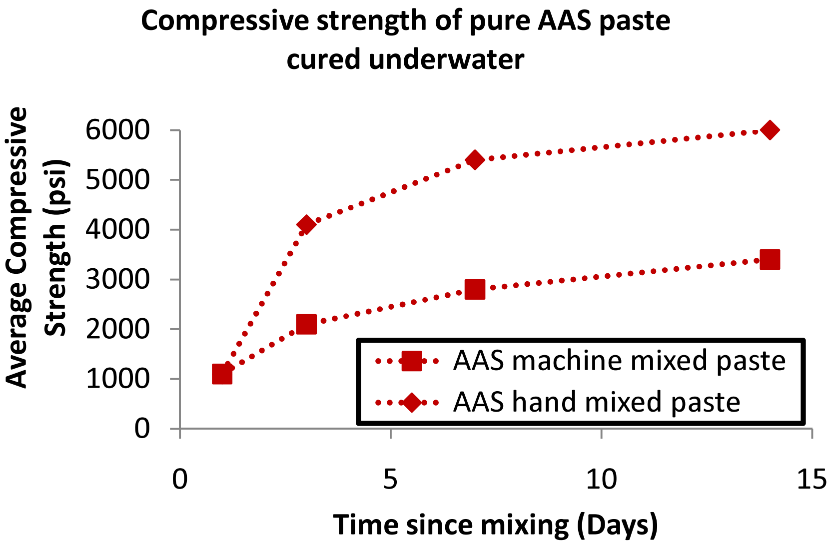

Fig. 4. A study of the compressive strength of alkali activated slag paste when mixed with an industrial mixing machine and by hand. The mixes contained blast-furnace slag, 10% NaSi activator, and a 0.42 w/c by weight of slag. Both mixes were cured in a sealed environment.

To investigate curing effects on the compressive strength of activated blast-furnace slag paste with C-S-H gel, similar hand mixed cylinders were placed in sealed and underwater conditions. The samples placed underwater needed to be demolded after one day of storage in a 100% humidity curing room in order to be placed underwater. The demolding process caused no visible damage to the soft cylinders. The addition of C-S-H gel typically allowed the green cylinders to simply slide out of the mold. The compressive strength results presented in Fig. 5 show not only an increase in strength for cylinders cured in a sealed condition, but also a reverse trend of increasing strength compared to the decreasing strength observed in the underwater cured samples. During curing, the samples kept underwater developed fine crack lines along the outside of the cylinder, along which they later broke during testing. The fracture surfaces of these underwater cured samples were curved and very smooth. The cracks were not observed when cured sealed, and the fracture surfaces resembled the rough surfaces of the cured paste without C-S-H seed. The effect is clearly a result of the added C-S-H as only a slight increase in strength, and no change in the trend of strength development was observed for the pure activated slag samples. In view of these results, all further compression tests for activated slag paste with and without C-S-H seed were performed on cylinders that were cured in a sealed environment.

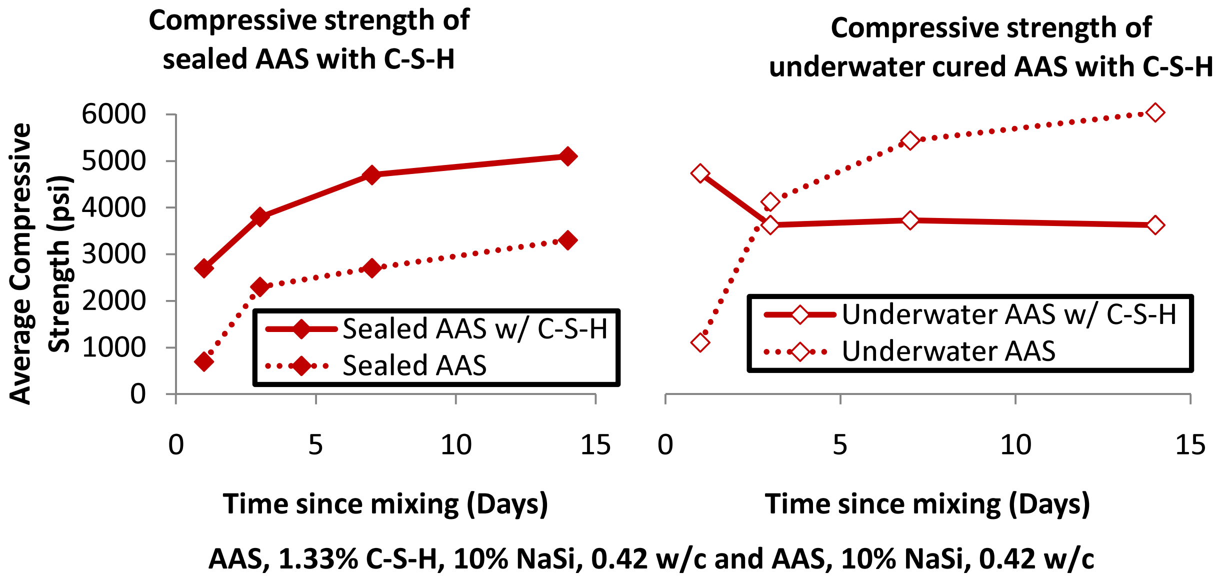

Fig. 5. A study of the effect of curing conditions on the compression strength of NaSi activated slag cylinders with 0.43 w/c and added C-S-H seed. The C-S-H seed was shear mixed with the mix water before being added or simply added to the paste without mixing. Two cement mixes were mixed by hand and cured in a sealed container until tested. The other two cement mixes were mixed by hand and cured in 100% humidity for 1 day, after which they were demolded and cured in lime water until tested.

The final set of compressive strength tests presented in Fig. 6 was conducted on activated slag paste cylinders that were hand mixed and cured in a sealed environment with and without C-S-H seed. The added C-S-H gel was shear mixed with the mix water to facilitate mixing. The results indicate that C-S-H seeding has a significant effect on the compressive strength. Within 1 day of mixing the compressive strength is 5.5 times greater and continues to develop at approximately 2 times higher compressive strength during the first 28 days.

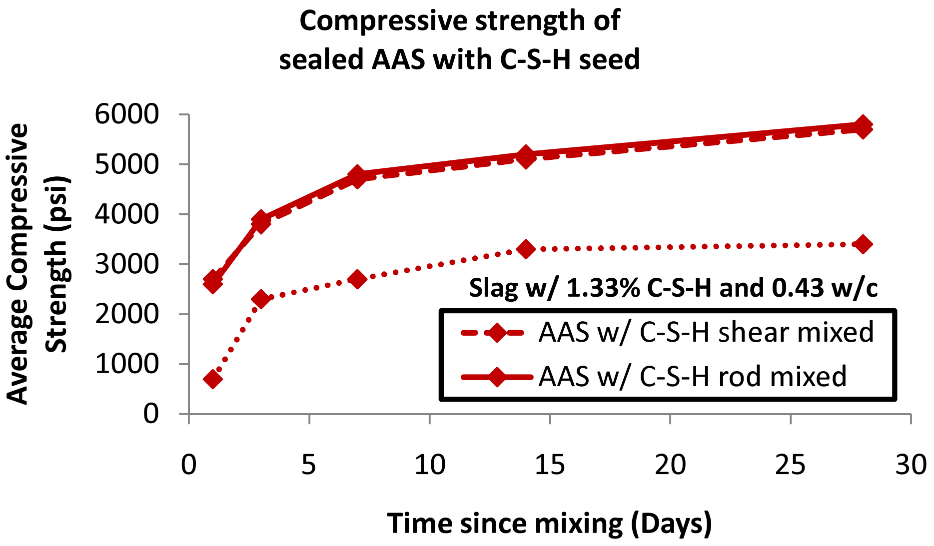

Fig. 6. A comparison of compression test results of NaSi activated slag cylinders with 0.43 w/c, both with and without added C-S-H seed. The C-S-H seed was shear mixed or not shear mixed with the mix water before being added. All three cement mixes were mixed by hand and cured in a sealed container until tested.

Early hydration of OPC with C-S-H seeding. Initial tests of C-S-H seeding of OPC paste were done with 1% C-S-H by weight of cement and a 0.4 w/c ratio to allow for workability while minimizing bleeding in an unseeded control paste. Seeding with C-S-H gel resulted in a earlier and wider peak in early hydration. When the C-S-H seed was dispersed in the water required for the mix with a small shear mixer, before being added to the Portland cement, an even higher peak in the hydration curve was observed. The greater effect is seen in the second hydration peak, which is typically associated with C_3A hydration.

Note that for each mix calculations were done to consistently consider 10g of OPC with a 0.4w/c ratio. The % solids of the C-S-H gel, as determined from oven-drying, were used to calculate the amount of gel required. The water from the computed amount of gel was subtracted from the water to be added to the mixture to ensure the 0.4 w/c ratio.

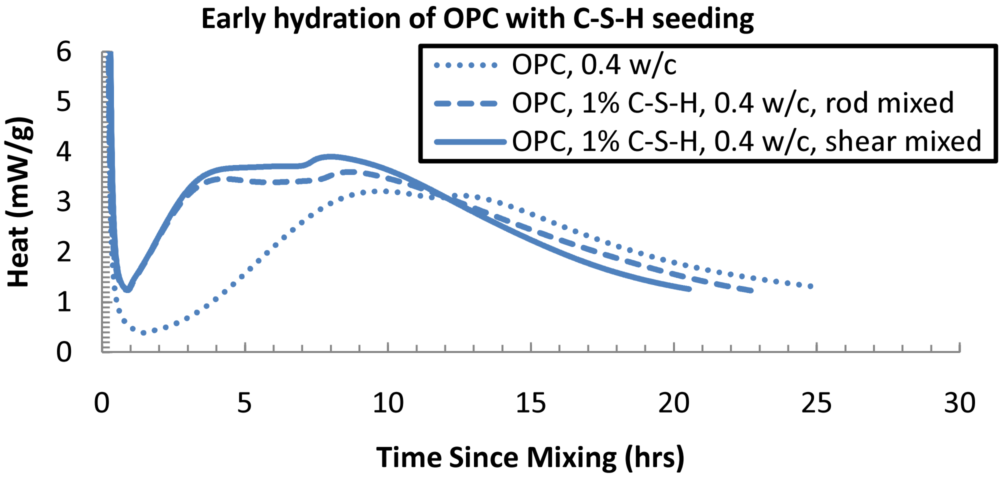

Fig. 7. The heat output of ordinary Portland cement paste with C-S-H seeding during the first 24 hours of hydration.

Compression Tests of OPC with C-S-H seeding. The compression tests of the 2" cylinders of seeded OPC paste and unseeded OPC paste are shown in Fig. 2. Each data point is an average of at least three test results. All of the OPC cylinders were mixed by hand and the C-S-H was mixed into the water with a hand-held shear mixer. The cylinders were cured for one day in a curing room, after which they were demolded and placed in lime water until the day of testing. All the samples broke in a similar fracture pattern with a jagged fracture surface, breaking down the center of the cylinder or in shear.

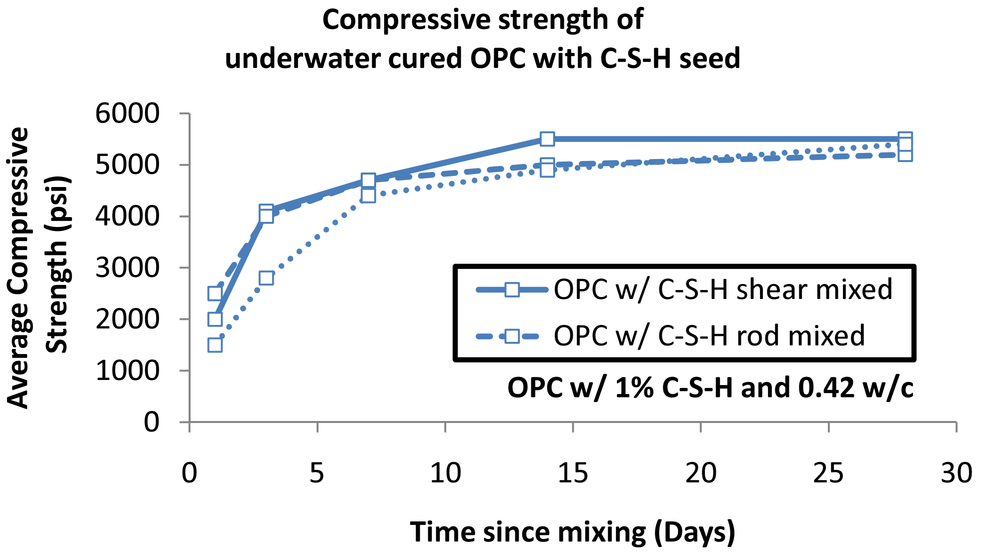

Fig. 8. A comparison of compression test results of ordinary Portland cement cylinders with 0.42 w/c, both with and without added C-S-H seed. The C-S-H seed was shear mixed or not shear mixed with the mix water before being added.

All three cement mixes were mixed by hand and cured in 100% humidity for 1 day, after which they were demolded and cured in lime water until tested.

Discussion

Addition of the same type of laboratory-made C-S-H is shown to have a similar effect on the early hydration behavior of ordinary Portland cement and the activated slag paste, even with this difference in Ca/Si ratio. The similarity of the response of activated slag and ordinary cement to the C-S-H seed suggests that the same nucleation and growth process of hydration products occurs in both. This result provides supporting evidence that slag paste may be modeled using existing models and simulations for ordinary Portland cement. A model of the reaction occurring in slag pastes has been developed by Chen and coworkers in 2007 [15]. With the understanding that the slag reaction is governed by the same nucleation and growth as in ordinary Portland cement, such a model can now be combined with boundary-nucleation methods developed for Portland cement [16].

The effect of C-S-H seeding on the alkali activated slag paste is quantitatively almost twice that of the effect on the Portland cement paste. Integration of the area under the early hydration heat curve during the first 24 hours in Fig. 2 and 7 gives a measure of the degree of hydration for the first day. This value goes from 20 mJ/g, for pure activated slag paste, to 38 mJ/g with activated slag paste with C-S-H seeding. The compressive strength for one day of curing changes to 139 psi with the addition of the C-S-H seed. In summary, for every 1% of C-S-H seed which is added there is a 17 mJ/g increase in early heat output and a 4600 psi increase in compressive strength after the first day. The same considerations for the ordinary Portland cement paste shows that for every 1% of C-S-H seed added to the paste there is a 9 mJ/g increase in early heat output and an 1100 psi increase in compressive strength. C-S-H seeding methods are much more effective for activated slag paste than ordinary Portland cement pastes. As such, further research into using these methods is directly correlated and useful for advancing high-percentage slag cements.

As illustrated in Fig. 5, the blast-furnace slag paste shows a great sensitivity to curing conditions if the C-S-H gel is added to the composition. This sensitivity is not well explained with our current understanding of hydration based on the behavior of ordinary Portland cement. Hydration of cement cannot proceed when the relative humidity within the capillary pores drops below 80% [17, 18]. As was illustrated by Price in 1951 [19], the reduction of the moist curing period directly reduces the compressive strength of concrete even if it contains an adequately high w/c ratio to allow for full hydration. The cement mixes used for this study started with a w/c ratio below 0.5, for which self-desiccation is expected to occur during sealed curing [20]. As a result, the observed increase in compressive strength only under sealed curing conditions is unexpected. The explanation must lie in the properties of blast-furnace slag paste and how the addition of C-S-H seed affects the early microstructure development since it was only observed in the seeded slag paste and correlated to a change in the fracture surface when broken. A key difference in ordinary Portland cement and blast-furnace slag paste is the fineness and shape of the particles. The added C-S-H gel may interact differently with the geometry particles in the paste in addition to the differences in the hydration reaction in the case of blast-furnace slag and ordinary Portland cement. Further investigations of water diffusion rates and the hydration structure of slag paste containing C-S-H gel could provide insight into the effects of curing on the compressive strength.

With the observed improvements in the early compressive strengths and the shortened induction period for pure blast-furnace slag paste, its use may be compared with that of ordinary Portland cement. With the addition of 2% C-S-H seed to the activated slag paste and careful sealed curing the start of the hydration kinetics peak occurs after 8.6 hours this is exactly the same point at which the hydration kinetics starts to peak for the underwater cured pure Portland cement paste. The shape of the hydration kinetics curve is still a double peak for the Portland cement paste, which clearly indicates different mechanisms of hydration occurring than in the single peak of the pure slag paste, the compressive strengths are also comparable. After one week the difference in the compressive strength of the activated slag paste with C-S-H seeding and the pure Portland cement paste is 6.45%, after two weeks 2.56%, and after four weeks ….. After a month the compressive response of the two materials approaches each other. Even after a month there are still clear differences in other properties which were not documented here. For example, the cylinders made of ordinary Portland cement showed longitudinal shrinkage as they cured, while the slag based cylinders with added C-S-H gel displayed more volumetric shrinkage behavior.

Conclusions

The addition of laboratory-made C-S-H gel has been proposed as a potential method for accelerating the early hydration rate of cements and its effectiveness for C_3S paste in experiments performed in 2009 [7]. Here experiments have been done that show the effective acceleration of early hydration through the addition of C-S-H gel to ordinary Portland cement and alkali activated blast-furnace slag paste. The acceleration of early hydration is much more pronounced for the slag paste, creating a response during early hydration similar to that of ordinary Cement paste without additional C-S-H gel. The early hydration rate of ordinary Portland cement was more accelerated when the C-S-H gel was shear mixed in to the paste. Visually the shear mixing reduced the amount of C-S-H gel clumps in the hydrated compression cylinder sample for ordinary Portland cement paste.

An increase in compressive strength accompanies the development of a denser, less porous, microstructure for cement materials. With the understanding developed in previous work [7], in that C-S-H gel acts as a seed for nucleation sites for further C-S-H growth, an increase in compressive strength would reinforce this observation. This work demonstrates that with specific curing procedures the addition of C-S-H gel does increase the compressive strength of both ordinary Portland cement and activated slag paste. Activated slag paste is traditionally a material with a slow gain of strength. These results demonstrate a method to allow it to develop strength as quickly as ordinary Portland cement paste.

Initial results indicated a decrease in compressive strength when C-S-H gel was added to the activated slag paste. This decrease was accompanied with the development of cracks and smooth fracture surfaces during testing after three days of curing. Although the specific cause of cracking was not isolated, it could be avoided through sealed curing. Sealed curing of the activated blast-furnace slag with added C-S-H gel does not show the development of cracks and results in a higher compressive strength for the paste throughout the first month. Further studies of the hydration and microstructure development of blast-furnace slag are needed to clarify mechanisms that would explain these results. A better understanding of this system would allow for modeling, prediction of properties, and effective use of laboratory C-S-H gel as an accelerant in blast-furnace slag paste.

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