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Parameters Influencing the Initial Setting Time of Alkali-Activated Ground Granulated Blast furnace Slag Materials

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ABSTRACT

Various parameters influencing the initial setting time of alkali-activated slag materials have been investigated using the Vicat method. The alkali solutions used for the activation were liquid sodium silicate (water glass) of different moduli n (SiO_2/Na_2O ratio) and pH. The results indicate that the initial setting time is mainly influenced by two parameters; 1) the specific surface area of the slag and 2) the modulus of the solution. The results also suggest that the problem with controlling the initial setting time of alkali-activated slag can be solved by controlling the characteristics of the solvent used for the activation.

Keywords : alkali-activation, initial setting time, water glass modulus, sodium silicate solution, pH, specific surface area

1. INTRODUCTION

The increasing requirements for reduction of greenhouse gas emissions have led to the search for low CO_2 footprint cements that can be used as a complement or alternative to ordinary Portland cement (OPC). One such promising material is the industrial by-product ground granulated blast furnace slag (GGBS), which is known to have cementitious properties under alkali-activation [1]. When compared to OPC this type of materials also has the advantage of a different and finer pore structure that [1-3], for instance, result in lower water permeability as well as lower ion and molecular diffusivity. As a result, the material shows higher resistance to various aggressive media compared to OPC [1, 4]. The smaller pore size distribution and the addition of alkaline ions into the matrix also result in a depression of the water freezing temperature and, thus, an increase in the resistance against freeze-thaw damages [4, 5]. The higher strength, smaller pore size, lower permeability and higher resistance against chemical attacks etc., make them also to be possible alternatives for storage of radioactive waste and immobilization of toxic metals [6-9]. In addition, this type of cementitious materials shows even better fire resistance than OPC [1]. A recent review of this type of materials is given in [10].

However, a serious problem and also one of the limiting factors for extensive use of green alternatives to OPC is the difficulty in controlling the initial setting time [1, 11]. Despite extensive research on this type of materials, the initial reaction and hydration, which lead to the initial setting time, is not fully understood [1, 12-14] but it is generally accepted that parameters like the chemical composition of the cementitious material [1], the water content [15, 16], the viscosity of the initial mixture [17], the mixing time [18, 19] and the specific surface area (fineness) of the material [20] are of importance for the early reaction and the initial setting time. In addition, the initial setting time is highly dependent on the type of alkali used for the activation and, therefore, investigations are often focused on this parameter.

From the literature it is obvious that the most commonly used activators belong to the groups alkali-hydroxides and alkali-silicates, even if acid salts and aluminum containing compounds also can be used [1] for the alkali-activation of cementitious materials like GGBS. From studies on the influence of different types of alkali-hydroxides, see for instance [1, 17, 21-27], there are indications that some of them are more effective activators than others [21]. Whereas some accelerate the hydration process [25], other types of alkali-hydroxides have the opposite effect [17]. However, when the cementitious material contains a large amount of calcium oxide (CaO), as in the case of GGBS, the alkali-silicates are in general more effective activators than the alkali-hydroxides [1, 28] (and references therein).

The most commonly used type of alkali silicate activators is based on sodium silicates ($Na_2O \cdot nSiO_2$) of various moduli n. From investigations on the effect of sodium silicate solutions [15, 16, 24, 27], it has been suggested that the pH and the alkali modulus n are of less significance than the amount of activator, and that the content of SiO_2 is of higher importance than the content of Na_2O [16]. In addition, it has been suggested that the type of sodium silicate is of importance since it was shown that the setting time is much faster when dry (powder) sodium silicates is used for the activation than if liquid sodium silicate (commonly called water glass) is used [29].

From studies found in the literature it is thus obvious that many different factors are of importance for the early reaction and the initial setting of alkali-activated cementitious material. In this study we have used sodium silicate solutions (water glass) for the alkali activation of GGBS and examined some of the parameters that are suggested to have an influence on the initial setting time. The results show that the initial setting time of GGBS can be designed and controlled by controlling the characteristics of the activating solution.

2.   MATERIAL AND METHODS

2.1   GGBS materials

Two Swedish GGBS materials, Merit 5000 (*M*) and Hyttsand (*H*) from Merox AB, and one German product (*G*), from Tomas Concrete Group, have been used for this study. As shown in Table 1, the two Swedish products (*M* and *H*) have exactly the same chemical composition but they have different specific surface areas, whereas the German product (*G*) is different in both chemical composition and specific surface area compared to the *M* and *H* materials. It can be noted that the basicity coefficient Kb = $(CaO+MgO)/(SiO_2+Al_2O_3)$ [16] is about the same (around 1) for all three GGBS products whereas the hydration modulus HM = $(CaO+MgO+Al_2O_3)/SiO_2$ [16] differs somewhat (1.79 for *M* and *H*, and 1.89 for *G*). However,

for all the GGBS materials the value of HM is larger than 1.4, which is the minimum value to ensure sound hydration properties [16].

Table 1 – Chemical compositions (in wt%) and physical properties of the GGBS materials used in this study (as given by the suppliers)

Chemical composition and physical properties	*M* Merit 5000	*H* Hyttsand	*G* German
CaO	31	31	40
SiO_2	34	34	35
Al_2O_3	13	13	12
Fe_2O_3	0.4	0.4	
SO_3	0.25	0.25	≤ 0.2
Alkalinity (Na_2Oeq)	0.9	0.9	1.2
MgO	17	17	7
TO_2	2.4	2.4	≤ 1.2
Mn_2O_3	0.8	0.8	≤ 0.6
Cl^-			≤ 0.05
S^{2-}	1.3	1.3	
Specific surface area, SSA (cm^2/g)	5000	3500	4200
Glass content (%)	99	99	≥ 90

2.2   Alkali solutions

For the alkali-activation, sodium silicate solutions (commonly called water glass) of various moduli were used. The solutions were prepared by adding dissolved sodium hydroxide (NaOH, Fisher Scientific) to a commercial available water glass from Sibleco Nordic. The latter contains 27.6 wt% of SiO_2 and has the molar modulus $n = 3.35$. In order to allow for thermal equilibrium, each specific alkali-solution (i.e. sodium silicate and sodium hydroxide) was prepared more than one day prior to the use in the sample preparations.

2.3   Sample proportions

For all samples, the amounts of the commercial water glass and GGBS material were 20 g and 50 g, respectively, and the water-to-GGBS (dry material) ratio was kept constant at w/s = 0.5. Thus, only the water glass modulus was varied, which in turn influences the pH of the prepared solution, as shown in Table 2. In this table it is furthermore shown how the Na_2O/CaO and $Na_2O/GGBS$ ratios and pH vary for the different *M*-samples (i.e. GGBS material, sodium silicate solution and sodium hydroxide). The samples are hereafter denoted by the added NaOH solution concentration (ranging from 5 to 35 wt%) together with the specific water glass modulus n of the activating solution given in a parenthesis.

2.5   pH measurement of the alkali-activated samples

In order to measure the pH values of the alkali-activated GGBS samples, the following steps were taken. First, the GGBS material was mixed with the prepared water glass solution of a specific modulus. Secondly, a specific volume of the sample was taken into a vial and thereafter diluted. Third, the slurry was subsequently centrifuged for quick sedimentation. Finally, the measurements were done on the solution on top of the sediment and then recalculated to take the dilution into account.

It should be noted that in some cases the measured pH values of the samples were > 14 and they are not included in Table 2. The reason for this is that a sodium ion error generally occurs at higher pH values, i.e. where the hydrogen ion concentration is very low compared to the sodium ion concentration, which results in a lower value of the pH than the actual one [30].

Table 2 – Sample compositions and relevant initial parameters (pH > 14)*

Sample	NaOH (wt% in water)	pH (water glass)	pH (in mixture)	SiO_2/Na_2O (molar modulus n)	Na_2O:CaO (mole %)	Na_2O:Slag (wt %)
Merit 5000						
M5	5	11.82	12.56	2.59	11.3	4.2
M7	7	12.11	12.78	2.36	12.3	4.6
M8	8	12.24	12.88	2.25	12.8	4.8
M9	9	12.42	13.02	2.16	13.3	5.0
M10	10	12.6	13.13	2.07	13.8	5.2
M12	12	13.02	13.36	1.90	14.9	5.6
M15	15	13.31	13.61	1.69	16.4	6.3
M20	20	13.59	13.86	1.40	19.2	7.5
M25	25	13.81	----*	1.17	22.1	8.8
M30	30	13.90	----*	0.99	25.2	10.3
M35	35	13.98	----*	0.84	28.4	12.0
TCG / German						
G5	5	11.82		2.59	9.0	4.2
G10	10	12.6		2.07	11.1	5.2
G15	15	13.31		1.69	13.2	6.3
G25	25	13.81		1.17	18	8.8

2.4   Vicat test method

The initial setting time, i.e. the time when the material loses its plasticity, was measured by a standard Vicat equipment (Toni Technik) with a calibrated weight of 300 g and a cylindrical needle with a flat tip area of 1 mm^2. Each sample composition was measured in certain time intervals, somewhat dependent on the concentration, and in triplicate to ensure repeatability and to obtain an average value of the initial setting time.

2.6   Ion chromatography

A Dionex ion chromatography (IC) system (Dionex ICS series) was used to quantify the amount of dissolved calcium ions for some of the sample compositions. For these measurements we used the same solution extraction methodology as for the pH determination (as previously described).

3.   RESULTS

3.1   Initial setting time as a function of water glass modulus

Fig. 1 shows the setting time profiles for some of the measured *M*-samples. It can be observed that the initial setting time displays a minimum for the sample *M10* (n = 2.07) and that it is longer for both the *M7* and *M20* samples (n = 2.36 and 1.40, respectively). It should be noted that these latter samples contain either lower or higher concentration of sodium (activated with water glass of higher or lower moduli, respectively) compared to the sample *M10* (n = 2.07). The sample *M20* (n = 1.40) shows, furthermore, a faster initial setting time than *M7* (n = 2.36). From this figure it can also be observed that the sample made of Hyttsand (*H*) did not show any initial setting after two hours. In fact, independent on the moduli of the water glass used for the activation, the initial setting was so slow that sedimentation of the GGBS particles occurred, and no initial setting was obtained even after 24 hours. This material is therefore considered as
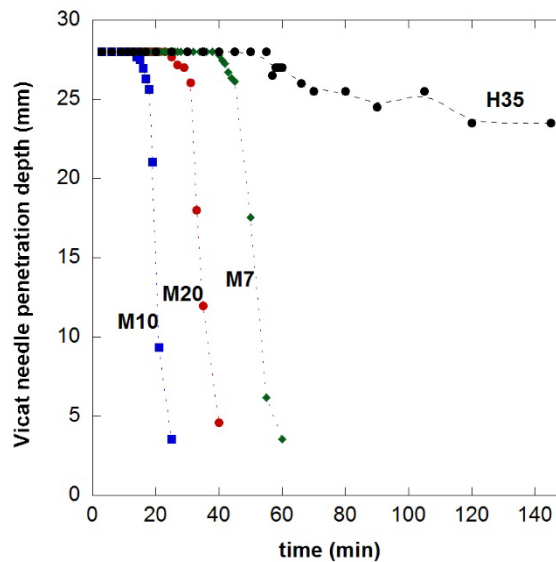

Figure 1 – Typical setting time profiles (an average based on three different measurements) for three of the M-samples and one of the H-samples.

inactive in the time interval of interest for this study.

In Fig. 2 the initial setting times obtained for the entire series of **M**-samples, i.e. **M5** ($n = 2.59$) to **M35** ($n = 0.84$) are shown by solid circles. As indicated already in Fig. 1, the initial setting time is fastest for the sample **M10** ($n = 2.07$) and becomes longer at both higher and lower sodium content (lower and higher water glass moduli). From the Fig. 2 it can also be observed that the initial setting time seems to show two different moduli dependences. For samples activated with water glass of moduli higher than $n = 2.07$ (**M10**), a rapid decay with increasing sodium content (decreasing modulus) is shown whereas at higher concentrations (lower moduli)
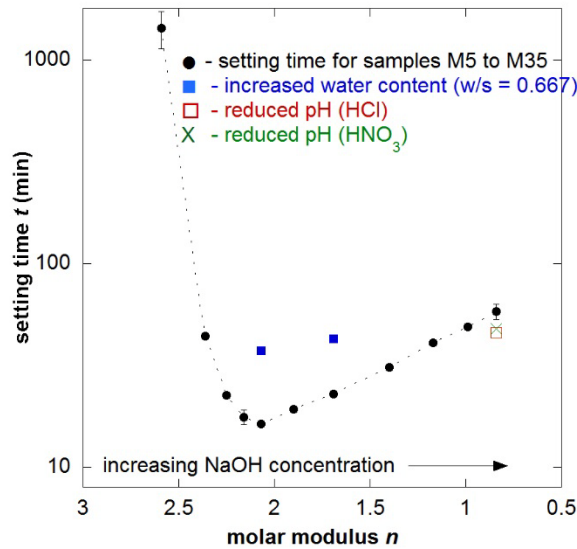

*Figure 2 – The initial setting times (in minutes) for the series of **M**-samples as a function of modulus. n of the water glass used for the alkali-activation.*

the initial setting times are more smoothly increased. The reason for a minimum in the setting time curve is not obvious and one possible explanation, which will be discussed in section 4 below, is that the water glass used for the alkali-activation has different effect on the GGBS material in the different concentration (moduli) regions.

3.2 Initial setting time as a function of particle size

By use of the GGBS material **G** instead of the material **M**, the specific surface area is reduced from 5000 cm^2/g to 4200 cm^2/g (Table 1). In Fig. 3 the obtained initial setting times for the samples **G10** ($n = 2.07$), **G15** ($n = 1.69$), and **G25** ($n = 1.17$) and the corresponding **M**-samples are shown. These results clearly indicate that the initial setting time is dependent on the specific surface area since it is increased for the **G**-material, which contains larger particles.

However, for the **G** material not only the specific surface area but also the chemical composition is different compared with the **M** material. As shown in Table 1, the main differences are the MgO, CaO and the glass contents. Especially the Mg content might be of importance since it previously was shown to have an influence on the initial rate of reaction [31, 32]. In addition, the content of Mg, and then particularly the ratio Mg/Si, influences the structure development in the early stage of the hydration [33]. It is thus not obvious if the increased initial setting time of the **G**-samples is caused by the larger specific surface area or the difference in chemical composition. However, since a lower MgO content should result in a faster initial reaction [32]

the longer initial setting time of the *G*-samples indicates that the specific surface area is more important than the chemical composition.

In order to further investigate the specific surface area dependence on the initial setting time, the weight fractions of the two chemically identical GGBS materials *M* and *H* was (see Table 1) systematically varied. For these measurements the water glass of modulus $n = 1.69$ was used as the activator. The results, as a function of the specific surface area after replacement of *H* (wt%), are shown in Fig. 4 (solid circles). From this figure it is clear that the specific surface area has a distinct influence on the initial setting time since the smaller the specific surface area, the longer initial setting time is obtained.
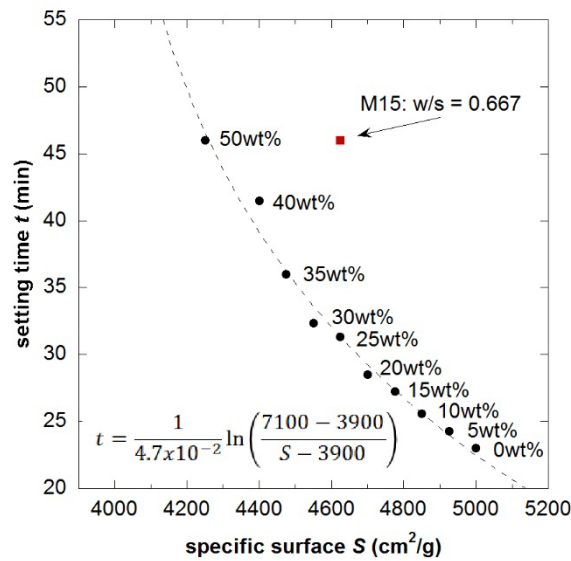

*Figure 4 – The initial setting times as a function of the specific surface area (obtained by replacing **M** with different weight fractions of **H** as given in the figure). The dotted line displays the curve fitting by equation 1 (also given in the figure). T = 20°C.*

4.   Discussion

4.1   pH dependence

Even if the hydration mechanism is poorly understood [1], it is generally believed that the hydration process of GGBS materials occurs in several steps and starts with the wetting and (partly) dissolution of slag particles. At this stage of the process there is a destruction of slag bonds, such as Ca-O, Mg-O, Si-O-Si, Al-O-Al and Al-O-Si, and the dissolved ions migrate out of the slag material into the liquid phase surrounding the particles [33]. Thereafter a Si-Al layer is formed on the surface of the slag particles and subsequently the C-S-H gel is developed [34]. During this so-called dissolution phase, the bond breaking and the following diffusion of ions should be highly dependent on their solubility (and consequently on the pH [35]). A higher solubility would thus result in a higher content of dissolved and diffusing ions.

For alkali-activated GGBS materials the solubility of different ions, as a function of pH, was previously studied by investigating the pore solution as a function of hydration time. It was found that the solubility of Si, Ca, Al and Mg is strongly dependent on the pH [36] at all times during the hydration process. In Ref [36] it was furthermore shown that for pH values higher

than 11.5 the concentrations of Si and Al are increasing whereas the concentrations of Ca and Mg are decreasing. Since both the silica content [37] and pH [36] affect the formation of C-S-H, it was suggested that the solubility of silica, and then consequently the pH, is the most important factor for alkali-activation of GGBS [36].

The pH seems thus to be a possible candidate for determining the initial stage and setting time of alkali-activated GGBS materials. If so, keeping water, sodium and silica contents, (and thereby the water glass modulus n) of the alkali-activating solution unchanged, but reducing pH, should have a noticeable influence on the initial setting time. Therefore, two pH adjusted water glass solutions were prepared and used for the activation. For this experiment the water glass used for the activation of the *M35* ($n = 0.84$, pH 13.98) sample was pH adjusted, by hydrochloric acid (HCl) or nitric acid (HNO$_3$), to about the same value as the pH of the solution used for activating the *M15* sample ($n = 1.69$, pH 13.3). Thus, the value of the modulus was kept at $n = 0.84$ but the pH was adjusted to 13.3. If the pH is the main determining parameter, the initial setting time of these samples should be the same as for the sample activated by the solution of the higher modulus (n=1.69). However, as can be observed in Fig 2, where the initial setting times for the HCl and HNO$_3$ adjusted samples are shown by an open square and a cross, respectively, this seems not to be the case. Even if the initial setting times are somewhat reduced for samples activated by the pH adjusted solutions, they are still far from that of the *M15* sample. Thus, even if the pH of the alkali-activating solution has a large influence on the solubility of ions it seems not to be the main responsible parameter, at least not the only decisive factor, for the initial setting time. It should be noted that the addition of chloride ions Cl$^-$ (from the addition of HCl) might induce structural changes of the water glass [38]. However, since similar initial setting times are obtained for both samples, independent on the type of acid used for the pH adjustment, this seems to be a minor problem. It should also be noted that for ordinary Portland cement (OPC), both chloride and nitrate ions may accelerate the hydration process [33, 34] but as shown from this study, for alkali-activated GGBS materials this acceleration effect appears not to be significant compared to the effect of the water glass modulus.

Another explanation for the different behaviors of the initial setting time for samples activated with water glass of various moduli could be that the change of modulus, by the addition of NaOH, not only affects the pH of the solution (and the dissolution phase), but also the microstructure of the solution itself. The structure of water glass is known to be strongly dependent on, for instance, the pH and the silica content [39]. Increased pH results in smaller particles sizes with decreased number of Si-O-Si bridges, with an increased viscosity as a consequence. Thus, for water glass of higher pH there are indications that larger silica particles/aggregates break up into smaller units [39], which most likely influences how fast slag ions can interact with the silicate units, i.e. the silicate anions.

4.2   Water glass modulus (n) dependence

The addition of NaOH to water glass does not only change the pH but also the modulus n, and the structure and viscosity of water glass solutions. In a previous investigation [38], it was shown that the viscosity of water glass is extremely dependent on the modulus. Of interest for this study is that the viscosity increases as the solution is either more siliceous or more alkaline, i.e. at both lower and higher moduli. Thus, at a certain value of the modulus, a viscosity minimum of the water glass was found. Interestingly, the value obtained for the minimum was $n = 1.8$ [38], which is close to the value where the pH shows an inflection point, as shown in Fig.

5. Since this is also the concentration where the fastest initial setting time of our series of *M*-samples, i.e. *M10* (*n* = 2.07) is obtained (see Figure 2), one might speculate that the initial setting time to a large extent is dependent on the viscosity of the solution used for the activation [40].
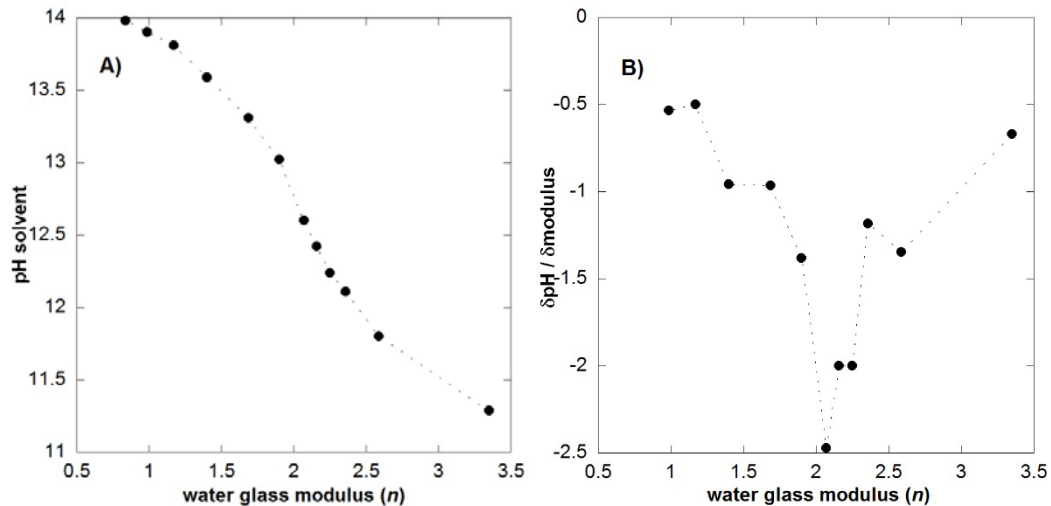

Figure 5 – A) pH values of the solutions used for the sample preparations and the pH value of the as received solution (n = 3.35). B) The inflection point in pH is found at n = 2.07, as shown by the derivative curve.

In Fig. 6 the concentration of dissolved calcium ions for some of the investigated samples, as determined by ion chromatography (IC), is shown. It can be observed that the largest fraction of these ions is found in the same sample composition as the one for which the fastest initial setting time is obtained, i.e. the sample *M10* (*n* = 2.07). Thus, in the sample *M10*, the highest amount of calcium ions are available for the structure development of the hydration product. Since the solubility of alkali-hydroxides decreases with increased pH [35], this behavior should mainly be dependent on how easy (and fast) dissolved ions are transported out from the solid particle surface into the surrounding liquid. Accordingly, the amount of dissolved calcium ions in the solution should be highly dependent on the viscosity of the solution, which in turn, should have an influence on the initial setting time. This suggestion would then be in agreement with previous studies that have shown that the viscosity of the activating solution has a large influence on the initial setting time and hydration process of alkali-activated GGBS [17, 29, 41]. More specific, the early reaction of alkali-activated mineral materials is diffusion controlled [29, 41], and therefore also dependent on the viscosity of the initial mixture [17].

A similar modulus dependence of the initial setting time was previously observed [42] for GGBS activated by water glass of three different moduli (*n* = 1.6, 2.0 and 2.4). In agreement with the results from this study, the fastest initial setting time was also in that study obtained for the sample activated by water glass of modulus *n* = 2.0 whereas both lower (*n* = 1.6) and higher (*n* = 2.4) moduli resulted in longer initial setting times. In that study [42] isothermal calorimetric scans were combined with results obtained by the Vical method and it was shown that both the initial and final setting times, as well as the heat evolution during the hydration, were influenced by the modulus of the activator. Since alkali-activation is known to be highly dependent on both

the chemical composition of the binder material and the activator concentration, the results from Ref [42], in combination with the present findings, imply that the setting time of GGBS must be extremely dependent on the water glass solution used for the activation. Actually, a similar conclusion was previously drawn from a study in which it was shown that the initial stage of the gelation process of alkali-activated materials is determined by the structure of the water glass used for the activation [43]. However, since the structure of water glass is dependent on the pH of the solutions [39], more detailed measurement on the molecular arrangement in such liquids are needed to elucidate if it is the structure or the pH of the liquid that is the most important parameter for the initial setting time of alkali-activated materials.
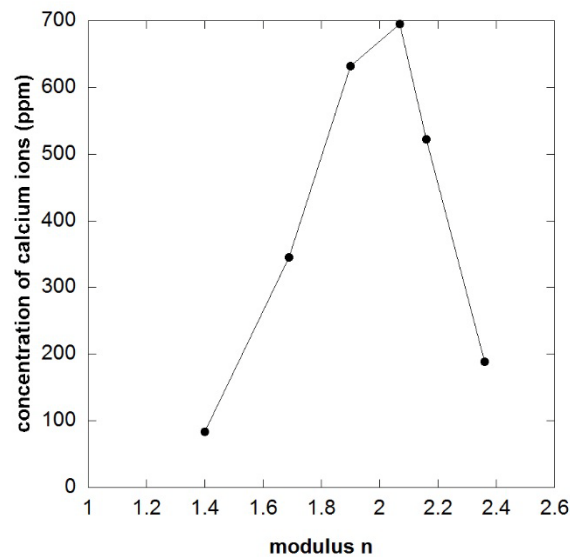

Figure 6 – The concentration of dissolved calcium ions during the first stage in the hydration process, i.e. in the dissolution phase.

4.3   Particle size dependence

Fig. 3 gives an indication on that the initial setting time is dependent on the specific surface area. Although the calcium content in the *G*-samples is higher than in the *M*-samples (see Table 1), the smaller specific surface area of the *G*-material most likely limits the availability, and thereby also the dissolution, of calcium ions from the solid material, which is necessary for building up the initial network of hydration products. As a consequence, a smaller specific surface results in a longer initial setting time.

From the results shown in Fig. 3 it can also be observed that the difference in initial setting times between the *M* and *G*-samples decreases with decreasing moduli of the activating solution. For samples activated with water glass of moduli $n = 2.07$, 1.69 and 1.17, the initial setting time differs by a factor of 2.6, 1.8 and 1.4, respectively. For alkali-activated cementitious materials it has previously been shown that a larger specific surface needs more hydration water [5] and a possible explanation for the reduced difference might then be that the finer slag particles (i.e. the larger specific surface area) in the *M*-samples can absorb more water on the surfaces. The larger amount of absorbed water should, in turn, result in that the fraction of free water, in the solution, is decreased for these samples. Since characteristics, such as structure and viscosity, of water glass are known to be dependent on the water content [38], the fraction of

water in the solution should also have an influence on the initial stage of the alkali-activation. Thus, with decreasing water glass modulus, the viscosity of the *M*-samples most likely increases faster compared to that of the *G*-samples. Since the initial stage of the hydration process, and the subsequent development of hydration products, is dependent on the diffusion of ions, an increased viscosity would result in a slower diffusion. This should, in turn, result in a longer initial setting time. As a consequence, the faster increase in the initial setting time of the *M*-samples should reduce its difference from that of the *G*-samples.

By keeping the solution at a constant modulus and successively increasing the particle size by replacing parts of the *M*-material with the *H*-material, it is obvious that the increased particle size results in an increasing initial setting time, as shown in Fig. 4. This behavior is expected since the initial setting time should be related to the initial flow, that previously has been shown to be dependent on the fineness of the material [20]. In that previous study it was shown that an increase in fineness of the slag particles leads to a decreased initial flow, which most likely has an effect on the rate of chemical reactions [44] during the initial stage of the hydration process.

The initial setting time is found at the point at which the material loses its plasticity during the initial stage of the hydration. This time, here denoted *t*, is related to the development of a specific quantity of hydration products, which in turn is dependent on the reaction rate when the volume is constant [44]. Since the initial setting time also is dependent on the rate of dissolution of ions from the GGBS material, and how fast calcium ions can react with anions (or groups of anions) from the activator [33], the initial setting time and the solubility of GGBS ions should be interrelated. Consequently, it is reasonable to assume that the amount of dissolved calcium ions from the dissolution of GGBS particles, and thereby the concentration of calcium ions in the mixing solution, is a function of the specific surface *S* of the slag.

Considering a chemical reaction that takes into account both a lower and a higher limit for an initial setting time, we can derive the following relationship between *t* and *S*:

$$t = \frac{1}{k}\ln\left(\frac{A-B}{S-B}\right) \tag{1}$$

where *k* is the kinetic coefficient of the chemical reaction and *A* and *B* are the constants describing the higher and lower limit of the specific surface area, respectively . By curve fitting the present results (see Fig. 4), it is found that $k = 4.7 \times 10^{-2}$ min^{-1}, $A = 7100$ m^2/g and $B = 3900$ m^2/g. This indicates that, for this specific chemical composition of the GGBS material, no initial setting time occurs for specific surface areas below 3900 m^2/g whereas for specific surface areas above approximately 7100 m^2/g, the initial setting time will occur almost instantaneous. It should be noted that the particle size, and thereby the specific surface area, is changed during the dissolution process. This effect is not taken into account in this relatively simple relationship.

4.4   Water content dependence

During the hydration process, GGBS particles are gradually dissolved, hydration products nucleate on the particle surfaces and particles are bound together in clusters. Subsequently, a network is formed throughout the material and the material changes from a viscous liquid, in which particles are dissolved, to an interconnected solid phase. In analogy with the hydration process of ordinary Portland cement [45], this point can be considered as a solid percolation

threshold at which the initial setting occurs. For alkali-activated cementitious materials it has previously been shown that a larger specific surface is more reactive and needs more hydration water [13]. This can most likely be explained by the water-to-binder ratio having an influence on the amount of hydration product that is needed for the formation of the percolating solid network in a similar way as previously has been described for cement [45]. In Ref [45] it was furthermore shown that for cement of higher water-to-binder ratios, larger amounts of the hydration product is needed for formulation of the percolating solid network directly related to the initial setting time.

By the replacement of the *M*-material with larger particles, as in the *H* material, the effective water content is changed. For instance, the effective water concentration of the sample with 25 wt% replacement of *M* with *H* can be approximated by 0.5/0.75 = 0.667, where 0.5 is the water-to-binder ratio. Figs. 2 and 4 (closed squares) show that the increased initial water content has a relatively large effect on the initial setting time. In addition, it can be observed that the initial setting time cannot completely be explained by the increase in effective water content. Thus, the *H* fraction dependent increase of the initial setting time is not entirely due to the increased effective water content. Rather it has to be explained by the decrease in total specific surface.

5.   CONCLUSIONS

The results from this study show that the initial setting time of GGBS, alkali-activated by water glass of various moduli, is dependent on the particle size of the GGBS material and the specific modulus of the water glass, which are both parameters that have an influence on the viscosity of the activated mixture.

- The pH may not be a decisive parameter for the initial setting time but just a consequence of the addition of sodium hydroxide, which, in turn, determines the modulus of the water glass and the dissolution of ions from the slag. The amounts of ions are important for the structure and strength development.
- The modulus of water glass has a strong influence on the hydration rate, i.e. the rate for building up the gelation network. This is probably due to its effect on the viscosity of the water glass, which is also dependent on the portion of free water in the mixture.
- The particle size determines the concentration of dissolved calcium ions necessary for the development of the hydration product, and the fraction of free water in the solution. The latter also affects the viscosity of the initial mixture.

REFERENCES

1.   Shi C, Krivenko PV, Roy D. Alkali-activated cement and concretes 2006: Taylor and Frances Group, London and New York.
2.   Lecomte I, Henrist C, Liegeois M, Maseri F, Rulmont A, Cloots R. (micro)-structural comparison between geopolymers, alkali-activated slag cement and portland cement. J. Eur. Ceram. Soc. 2006;26(16):3789-3797.

3. Chen W, Brouwers HJH. The hydration of slag, part 1: Reaction models for alkali-activated slag. J. Mater. Sci. 2007;42(2):428-443.
4. Bai Y, Collier NC, Milestone NB, Yang CH. The potential for using slags activated with near neutral salts as immobilisation matrices for nuclear wastes containing reactive metals. J. Nucl. Mater. 2011;413(3):183-192.
5. Fu YW, Cai LC, Wu YG. Freeze-thaw cycle test and damage mechanics models of alkali-activated slag concrete. Constr. Build. Materi. 2011;25(7):3144-3148.
6. Cho JW, Ioku K, Goto S. Effect of Pb^{II} and Cr^{VI} ions on the hydration of slag alkaline cement and the immobilization of these heavy metal ions. Adv. Cem. Res. 1999;11(3):111-118.
7. Deja J. Immobilization of Cr^{6+}, Cd^{2+}, Zn^{2+} and Pb^{2+} in alkali-activated slag binders. Cem. Concr. Res. 2002;32(12):1971-1979.
8. Qian G, Sun DD, Tay JH. Characterization of mercury- and zinc-doped alkali-activated slag matrix - part I. Mercury. Cem. Concr. Res. 2003;33(8):1251-1256.
9. Qian GR, Sun DD, Tay JH. Characterization of mercury- and zinc-doped alkali-activated slag matrix - part II. Zinc. Cem. Concr. Res. 2003;33(8):1257-1262.
10. Rakhimova NR., Rakhimov RZ. A review on alkali-activated slag cements incorporated with supplementary materials. J. Sustain. Cem-based Mater. 2014;3(1):61-74.
11. Peter Domone, Illston J, eds. Construction materials - their nature and behaviour. 4th ed. 2010, Spon Press: London and New York.
12. Pacheco-Torgal F, Castro-Gomes J, Jalali S. Alkali-activated binders: A review - part 1. Historical background, terminology, reaction mechanisms and hydration products. Constr. Build. Mater. 2008;22(7):1305-1314.
13. Pacheco-Torgal F, Castro-Gomes J, Jalali S. Alkali-activated binders: A review. Part 2. About materials and binders manufacture. Constr. Build. Mater. 2008;22(7):1315-1322.
14. Roy D. Alkali-activated cements - opportunities and challenges. Cem. Concr. Res. 1999;29(2):249-254.
15. Yang K-H, Mun J-H, Sim J-I, Song J-K. Effect of water content on the properties of lightweight alkali-activated slag concrete. J. Mater. Civ. Eng. 2011;23(6):886-894.
16. Chang JJ. A study on the setting characteristics of sodium silicate-activated slag pastes. Cem. Concr. Res. 2003;33(7):1005-1011.
17. Cheng TW, Chiu JP. Fire-resistant geopolymer produced by granulated blast furnace slag. Miner. Eng. 2003;16(3):205-210.
18. Palacios M, Banfill PFG, Puertas F. Rheology and setting of alkali-activated slag pastes and mortars: Effect of organ admixture. ACI Mater. J. 2008;105(2):140-148.
19. Palacios M, Puertas F. Effectiveness of mixing time on hardened properties of waterglass-activated slag pastes and mortars. ACI Mater. J. 2011;108(1):73-78.
20. Yang K-H, Song J-K. Workability loss and compressive strength development of cementless mortars activated by combination of sodium silicate and sodium hydroxide. J. Mater. Civ. Eng. 2009;21(3):119-127.
21. Altan E, Erdogan ST. Alkali activation of a slag at ambient and elevated temperatures. Cem. Concr. Compos. 2012;34(2):131-139.
22. Fernandez-Jimenez A, Puertas F. The alkali-silica reaction in alkali-activated granulated slag mortars with reactive aggregate. Cem. Concr. Res. 2002;32(7):1019-1024.
23. Collins F, Sanjayan JG. Early age strength and workability of slag pastes activated by NaOH and Na_2CO_3. Cem. Concr. Res. 1998;28(5):655-664.
24. Shi CJ, Day RL. Some factors affecting early hydration of alkali-slag cements. Cem. Concr. Res. 1996;26(3):439-447.
25. Naceri A, Bouglada MS, Grosseau P. Mineral activator and physical characteristics of slag cement at anhydrous and hydrated states. World Acad. Sci. Eng. Tech. 2009;56:137-139.
26. Yang K-H, Sim J-I, Nam S-H. Enhancement of reactivity of calcium hydroxide-activated slag mortars by the addition of barium hydroxide. Constr. Build. Mater. 2010;24(3):241-251.
27. Burciaga-Diaz O., Magallanes-Rivera RX., Escalante-Garcia JI. Alkali-activated slag-metakaolin pastes: Strength, structural, and microstructural characterization. J. Sustain. Cem-based Mater. 2013;2(2):111-127.

28. Shi C, He F. On the state and roles of anion or anion group of activators during activation of slag. Proceeding of the 1st International conference on advances in chemically-activated materials, CAM'2010. 2010. China.
29. Ravikumar D, Neithalath N. Reaction kinetics in sodium silicate powder and liquid activated slag binders evaluated using isothermal calorimetry. Thermochim. Acta. 2012;546:32-43.
30. Personal communication with a product specialist at WWR International AB.
31. Ben Haha M, Lothenbach B, Le Saout G, Winnefeld F. Influence of slag chemistry on the hydration of alkali-activated blast-furnace slag - part I: Effect of MgO. Cem. Concr. Res. 2011;41(9):955-963.
32. Bernal SA, Nicolas RS, Myers RJ, de Gutierrez RM, Puertas F, van Deventer JSJ, Provis JL. Mgo content of slag controls phase evolution and structural changes induced by accelerated carbonation in alkali-activated binders. Cem. Concr. Res. 2014;57:33-43.
33. Brough AR, Atkinson A. Sodium silicate-based, alkali-activated slag mortars part i. Strength, hydration and microstructure. Cem. Concr. Res. 2002;32(6):865-879.
34. Krizan D, Zivanovic B. Effects of dosage and modulus of water glass on early hydration of alkali-slag cements. Cem. Concr. Res. 2002;32(8):1181-1188.
35. Zumdahl SS. Chemical principles 4th ed 2002.
36. Song SJ, Jennings HM. Pore solution chemistry of alkali-activated ground granulated blast-furnace slag. Cem. Concr. Res. 1999;29(2):159-170.
37. Greenberg SA, Chang TN. Investigation of colloidal hydrated calcium silicates .2. Solubility relationships in calcium oxide-silica-water system at 25 degrees. J. Phys. Chem. 1965;69(1):182-188.
38. Yang X, Zhu W, Yang Q. The viscosity properties of sodium silicate solutions. J. Solution Chem. 2008;37(1):73-83.
39. Nordstrom J, Nilsson E, Jarvol P, Nayeri M, Palmqvist A, Bergenholtz J, Matic A. Concentration- and Ph-dependence of highly alkaline sodium silicate solutions. J. Colloid Interface Sci. 2011;356(1):37-45.
40. Jansson H, Tang L. The initial setting time of ground granulated blastfurnace slag ggbs and its relation to the modulus of the alkali-activating solution. Proceeding of the XXII Nordic concrete research symposium. 2014. Reykjavik, Iceland
41. FernandezJimenez A, Puertas F. Alkali-activated slag cements: Kinetic studies. Cem. Concr. Res. 1997;27(3):359-368.
42. Bernal SA, Provis JL, Rose V, Mejia de Gutierrez R. Evolution of binder structure in sodium silicate-activated slag-metakaolin blends. Cem. Concr. Compos. 2011;33(1):46-54.
43. Criado M, Fernandez-Jimenez A, Palomo A, Sobrados I, Sanz J. Effect of the SiO_2/Na_2O ratio on the alkali activation of fly ash. Part II: ^{29}Si MAS-NMR survey. Micropor. Mesopor. Mater. 2008;109(1-3):525-534.
44. Beltram P. Rates of chemical reactions: Their measurement and mathematical expressions, in Fundamentals of chemistry 2009.
45 Zhang J, Weissinger EA, Peethamparan S, Scherer GW. Early hydration and setting of oil well cement. Cem. Concr. Res. 2010;40(7):1023-1033.