Activation of a Turkish Blast Furnace Slag Using Alkalis

Sinan T. Erdo an¹, Ekin Altan²

¹Department of Civil Engineering, METU, Ankara, Turkey, sinante@metu.edu.tr ²Computational Mechanics of Materials and Structures Program, University of Stuttgart, Germany, ekin.altan@gmail.com.

Abstract

Alkali-activated ground, granulated blast furnace slag (AAS) systems are one of the better alternatives to Portland cement binders. The room temperature compressive strength development and heat evolution behavior of AAS pastes and mortars were studied. It was seen that, for room-temperature curing, liquid sodium silicate activator is ineffective. NaOH solution activation however, can result medium strength mortars, particularly for higher activator concentrations. Dual activation using both of the alkaline activators gave ultimate strengths comparable to or exceeding the strength of typical Portland cement (PC) mortars. However, early strength gain is lower than in PC mortars. The 7-day strength-to-28-day strength ratio was found to be lower than 60 % for all cases studied, even when activator concentration was quite high. Relations were developed between strength at 7 and 28 days and the cumulative heat evolved up to these ages. For dual-activator mixtures, strength and total Na2O present in the system appear to be linearly related. A better understanding of the relations between various properties of AAS systems can lead to the development of low-cost, sustainable binders.

Keywords: slag; alkali activation; ambient temperature; caustic soda; water glass.

1 Introduction

Increasing awareness about the environmental impact of construction materials used in large quantities (such as Portland cement concrete) has led researchers to seek alternative greener materials. Although various binding systems have been proposed to replace the hydration of Portland cement, a factory-made synthetic powder chemical with a large carbon footprint, all of these alternatives have some drawbacks, such as having high cost, having a low carbon footprint but very negative properties in other environmental respects, or simply (and often) being technically inferior to cement+water, in terms of mechanical property development, volume stability, etc.

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One alternative cementitious system which has been known for over 70 years (Purdon, 1940; Shi et al., 2006) and studied widely is the chemical (and sometimes thermal) activation of ground, granulated blast furnace slags (GGBFS) with concentrated alkaline solutions, referred to commonly as "alkali-activated slag" (AAS) systems. The hydration, mechanical properties, and durability of AAS have been studied extensively (Glukhovsky et al., 1980; Wang and Scrivener, 1995; Fernández-Jiménez et al., 1999; Puertas et al., 2002; Bakharev et al., 2003; Shi, 2003). Shi et al. (2006) present a detailed summary of such work, based on which it becomes clear that with sufficient knowledge about the properties of the particular slag being used, and proper choice of activating chemical and curing conditions, AAS mortars and concretes with mechanical properties and durability comparable to or better than those of PCC can be made. A recent study (Habert et al., 2011) in which the full environmental impacts (not only carbon footprint and related global warming potential) of various alkali-activated systems were compared using life cycle analysis with those of blended (pozzolan-containing) cements, shows that AAS systems are among the better alternatives to Portland-cement based systems.

Slags can show great variation in their chemical and physical properties since they are byproducts. Their glassy content which depends on rate and type of cooling, can significantly affect their potential for use in AAS systems. Heat evolution during blended cement hydration was found to be correlated to strength and useful as an indicator of the reactivity of a slag (Bougara et al., 2010). In addition, alkaline activators demonstrate selectivity i.e. the effect that an activator has on strength development may be different for slags of different origins (Shi and Day, 1996). For this reason, the use of AAS mortars and concretes in any region is closely tied to the level of experience with local slags.

This study puts forth some relations between the mechanical property development and heat evolution behavior of an AAS system incorporating a GGBFS from Turkey. The dependence of mechanical property development on alkaline activator type and concentration, and on curing temperature and duration were reported in Altan and Erdo an (2012). Since it was found that dual-activator mixtures containing both sodium silicate and sodium hydroxide solutions outperform single-activator mixtures, this study looks further into dual-activator, room-temperature-cured AAS pastes and mortars. Relations between various properties are proposed.

2 Experimental

2.1 Materials

The slag used was received, from Kardemir Iron and Steel Plant, in Karabük, Turkey, in powder form. The as received oxide composition and physical properties of the slag are given in Table 1.

Table 1. Oxide analysis of the slag used.



39.90
11.13
0.26
34.56
9.37
0.09
1.18
0.35
4228
3.06

The alkaline activators used were laboratory-grade > 97 % pure NaOH pellets, and liquid sodium silicate. The pellets were dissolved in water to obtain the various molarity mixtures used for the different activation attempts. The sodium silicate, Na₂O.*x*SiO₂.*n*H₂O, where *x* represents the degree of polymerization and *n* represents the moles of water, was a 40°-42° Baume solution with a solids content of 37.5 % (thus containing 62.5 % water) and a SiO₂/Na₂O weight ratio of 3.2. From here on, water glass (WG) is used to refer to the sodium silicate solution. The activators were mixed together and allowed to cool to room temperature prior to mixing with the slag. After an initial mixing of the slag with the activator solution mixture, CEN standard sand was added, the mixture mixed again, diluted water added to adjust flowability, and the whole mixture mixed once again.

2.1 Methods

2.1.1 Measurement of Strength

The mixing and preparation of the specimens used to investigate strength development was done according to EN 196-1 (2005) with the exception that the water-to-binder ratio was not 0.50 but slightly lower. The total water content of the mixtures was selected to give AAS mortars with similar flow properties as a typical EN 196-1 portland cement (PC) mortar. 4x4x16 cm³ prism specimens were cast. The specimens were left at room temperature for the whole curing time, demolding taking place after 24 hours. All samples were tested up to age ~10 weeks. Table 2 summarizes the different activation and curing scenarios studied for strength development.

Table 2. Summary of mixture proportions of mortars used to evaluate rates and amounts of strength
development.

	Ambient temperature cured samples
Slag content (kg / m ³)	~ 225
Concentration of NaOH [*] solution (M)	0 to 16
MOH solution / Waterglass	2.5
Amount of MOH solids (wt. % of slag)	0 to 4.46
Waterglass / Slag	0 or 0.25
Total water / Slag	~ 0.46
Total water / Total solids	~ 0.41

2.1.1 Measurement of Heat Evolution

An eight channel isothermal micro calorimeter was used to monitor the heat of reaction. ~5 g paste samples with slag-to-activator ratios identical to the paste phase of the chosen mortar samples were used. Table 3 lists these mixtures. A measured amount of dry, ground slag calculated to have a specific heat capacity approximately equal to that of the paste was used as the heat reference. The activator solutions were mixed by hand with the slag and the pastes were immediately placed in the calorimeter. The heat evolution of the pastes at 23 °C was tested until the heat signature appeared nearly stable for each mixture. Since the sample size was quite small, the measurements were done twice for each mixture to check that the pastes were adequately mixed. The two heat signatures were nearly identical for each paste.

Paste Number	1	2	3	4	7	8
Slag content (kg / m ³)	~ 225	~ 225	~ 225	~ 225	~ 225	~ 225
Molarity of NaOH solution [*]	2	5	8	16	0	8
NaOH solution / Waterglass	2.5	2.5	2.5	2.5	0	-
Waterglass / Slag	0.25	0.25	0.25	0.25	0.25	0
Total water / slag	~ 0.46	~ 0.46	~ 0.46	~ 0.46	~ 0.46	~ 0.46
Total water / total solids	~ 0.41	~ 0.41	~ 0.41	~ 0.41	~ 0.41	~ 0.41

Table 3. Pastes tested using isothermal calorimetry.

3 Results and Discussion

The influence of increasing the amount of water glass, and increasing the concentration of the NaOH solution used to activate the slag, on strength development of mortar mixtures is given in Figure 1.





Fig. 1. The effect of: a) increasing the waterglass activator content, and b) increasing the concentration of NaOH solution, on compressive strength development.

From Fig. 1a, it is clear that waterglass alone does not lead to a mortar of reasonable strength, reaching only about 3 MPa at 28 days. The mortar containing an 8M NaOH solution does gain some strength, although a low 15 MPa, in the absence of waterglass. From this figure, it appears that NaOH is a more effective activator at room temperature than waterglass. Mortars containing both activators, however, can gain substantial strength, up to and above 80 MPa at 28 days, as seen in Fig. 1b. Comparing the strength gain curves of the mortar activated with 8M NaOH and waterglass (in Fig. 1b), and that of the one activated with the 8M NaOH solution only (in Fig. 1a), it is understood that the use of both activators produces the highest strengths and that sodium silicate is ineffective only when alone. Figure 2 shows the change in the rate of heat evolution of the pastes activated using both NaOH solutions of different concentrations and a fixed amount of water glass.



Fig. 2. Rate of heat evolution of double-activator AAS pastes over time.

The area under the curves in Fig. 2 can be integrated to calculate the total amount of heat evolved up to any time. It is seen that as the NaOH concentration increases, the height of the heat evolution rate peak increases. The peak also tends to shift towards earlier ages. Both of these changes indicate an increase in the total amount of heat evolved at early ages. As the concentration of the NaOH solution surpasses a critical value, somewhere between 5M and 8M for these pastes, the increase in peak height becomes more pronounced. The rate of strength gain (slope of the curves in Fig. 1b) at early ages also increases more noticeably beyond 8M concentration. This signals a possible relation between the heat of reaction and compressive strength of AAS systems, similar to the relation which roughly holds for Portland cement pastes and mortars.

The existence of such a relation can be tested by plotting the compressive strength of the AAS mixtures at a certain age (such as 7 or 28 days) against the heat evolved up to that age, as shown in Figure 3.



Fig. 3. Compressive strength at vs. specific heat evolved up to: a) 7 days; b) 28 days.

It is seen that a relatively strong relation exists between the amount of evolved reaction heat and compressive strength achieved. Using relations such as these, it may be possible to make predictions about the strength of AAS mortars and concrete, using heat measurements, similar to maturity methods used for Portland cement concrete (Carino, 2004).

Since dual-activator mortars appear to gain higher strengths, another relation worth investigating is that between the total Na2O content contributed by the two activators and the compressive strength achieved at a certain age, shown in Figure 4.



Fig. 4. a) 7-day compressive strength; and b) 28-day compressive strength, vs. total Na₂O in the dual-activator system.

The compressive strength of the AAS mortars appears to increase nearly linearly with increasing total percentage of Na_2O present in the system. This would explain how adding water to such a mortar would decrease strength significantly (Altan and Erdo an, 2012) not by increasing the average spacing between the slag particles and resulting a less dense microstructure but also by diluting the chemical activators.

One other relation to investigate is that between the 7-day and 28-day compressive strengths of these mortars, shown in Figure 5.



Fig. 5. Dependence of 7-day strength-to-28-day strength ratio on total Na₂O from activators.

The 7-day/28-day strength ratio is about 75 % for Portland cement based systems. The ratio can vary slightly from this value depending on the type and amount of cement used, the water-to-cement ratio etc. In these AAS mortars, this ratio is significantly lower, indicating that strength gain is slow at early ages and greater at late ages. Mortars with higher amounts and/or concentrations of activator (thus with higher total Na₂O) yield a higher ratio, approaching ~60 % which is still slower than Portland cement systems but reasonable.

It should be noted that the relations shown in Figs 3 through 5 are for dual activator systems using the given slag and sodium silicate solution. A sodium silicate solution with a different modulus, or simply the use of a different GGBFS with substantially different reactivity than the one used in this study could result in changes in the strength development rate and ultimate amount, as well as rate and amount of evolved heat.

4 Conclusions

This study investigated relations between the heat evolved by AAS pastes (containing GGBFS as its sole powder binder) and the strength gain of AAS mortars, activated using a constant amount of water glass and a constant amount of NaOH solutions with varying concentrations. The following conclusions were drawn:

- a) NaOH solution is more beneficial to strength gain than water glass solution for mortars cured at room temperature. Concentration of NaOH solution directly influences rate of strength gain and ultimate strength for room temperature-cured mixtures since it affects slag dissolution amount and rate.
- b) At room temperature, mixtures containing only NaOH solution as the alkaline activator give earlier rate of heat evolution vs. time peaks. Mixtures with only water glass activator give much later peaks. Mixtures using both activators show intermediate heat evolution rate peaks but achieve much greater compressive strength than either single-activator mixture.
- c) Strong relations exist between the total amount of heat evolved up to a chosen age and the compressive strength of the mortar at that age.
- d) The 7-day and 28-day strengths of the dual-activator mortars are nearly linearly related to the total amount of Na2O contributed by the chemical activators.
- e) The 7-day strength to 28-day strength ratio is much lower than in Portland cement binders, as development of mechanical properties is slow at early ages.

References

Purdon AO. (1940) The action of alkalis on blast furnace slag, *Journal of the Society of Chemical Industry* 59: 191-202.

Shi C, Krivenko PV, Roy D. (2006) Alkali-Activated Cements and Concretes, London: Taylor and Francis.

Glukhovsky VD, Rostovskaja GS, Rumyna GV. (1980). High strength slag-alkaline cements. In: *7th international congress on the chemistry of cement*. Paris: Editions Septima, 164–168.

Wang SD, Scrivener K. (1995). Hydration products of alkali activated slag. *Cement and Concrete Research* 25(3): 561–571.

Fernández-Jiménez A, Palomo JG, Puertas F. (1999). Alkali-activated slag mortars: mechanical strength behaviour. *Cement and Concrete Research* 29(8): 1313-1321.

Puertas F, de Gutierrez R, Fernández-Jiménez A, Delvasto S, Maldonado J. (2002) Alkaline cement mortars.

Chemical resistance to sulphate and seawater attack. Materiales de Construcción 52 (267): 55-71.

Bakharev T, Sanjayan JG, Cheng Y-B. (2003) Resistance of alkali-activated slag concrete to acid attack, *Cement and Concrete Research* 33(10): 1607-1611.

Shi C. (2003). Corrosion resistance of alkali-activated slag cement, *Advances in Cement Research* 2003; 15(2): 77-81.

Habert, G., d'Espinose de Lacaillerie, J.B., Roussel, N. (2011) An environmental evaluation of geopolymer based concrete production: reviewing current research trends. *Journal of Cleaner Production* 19 (11), 1229-1238.

Bougara A, Lynsdale C, Milestone NB. (2010) Reactivity and performance of blastfurnace slags of differing origin, *Cement and Concrete Composites* 32(4): 319-324.

Shi C, Day RL. (1996) Selectivity of Alkaline Activators for the Activation of Slags. *Cement, Concrete and Aggregate* 18(1): 8-14.

Altan, E., Erdo an, S.T. (2012), Alkali activation of a slag at ambient and elevated temperatures. *Cement and Concrete Composites* 34(2), 131-139.

EN 196-1. (2005) *Methods of testing cement - Part 1: Determination of strength*. European Norm 196-1. Brussels: European Committee for Standardization.

Rangan BV. (2008) Fly-Ash Based Geopolymer Concrete. Research Report. Curtin University of Technology,

Faculty of Engineering and Computing, 2008.

Carino, N. J. (2004) "The Maturity Method," Chapter 5 in *Handbook on Non Destructive Testing of Concrete*, 2nd Edition, V. M. Malhotra and N. J. Carino, Eds., CRC Press, Boca Raton, Florida.