A REVIEW: THE STRENGTH INFLUENCE FACTORS OF SLAG AND FLY ASH BASED ALKALI ACTIVATED MATERIALS

Beibei Sun (1), Guang Ye (1), and Geert De Schutter (1)

(1) Ghent University, Department of Structural Engineering, Magnel Laboratory for Concrete Research, Technologiepark-Zwijnaarde 60, 9052 Ghent, Belgium

Abstract

Alkali-activated materials(AAM) are known to be environmentally friendly alternatives to cement-based materials because they can potentially reduce greenhouse gas emissions and reutilize industrial by-products. However, the application of AAM is still limited by the lack of mixture design regulation. Unlike cement, the very different chemical composition of the precusors and alkaline activators may result in a very fluctuating strength. In order to study the factors influencing the strength of slag and fly ash-based alkali-activated materials (BFS/FA-AAM), and clarify their reaction mechanism, this paper reviews current knowledge about the mechanical properties and the reaction mechanisms of BFS/FA-AAM. The control factors of strength are BFS/binder ratio, Na_2O/binder ratio, and SiO_2/Na_2O ratio. The ion concentrations, determined by these control factors, play a decisive role in the development of strength. Generally, the strength is proportional to the BFS/binder ratio. The best strength could be obtained at the optimum values of Na_2O/binder ratio, and SiO_2/Na_2O ratio. The optimum values of the SiO_2/binder ratio of BFS-AAM and FA-AAM are between 5.5%-8% and between 7-10%, respectively. The optimal values of the SiO_2/Na_2O ratio of BFS-AAM and FA-AAM are between 0.85-1.4 and between 0.6-1, respectively. For BFS/FA-AAM, the optimum ratio is still unknown. Further study is needed to investigate the effect of control factors on the mechanical properties of BFS/FA-AAM.

Keywords: slag and fly ash based alkali-activated materials, reaction mechanism, strength control factors

1. INTRODUCTION

It is known that cement production is associated with high energy consumption and the emission of a considerable amount of greenhouse gas[1]. For the sake of the environment protection, alkali-activated materials (AAM) have attracted attention as a potential replacement for ordinary Portland cement concrete (OPC)[2][3][4]. AAM possesses a lot of advantages, such as rapid strength gaining, low thermal conductivity, high volume stability, fire resistance, and chemical erosion resistance[5][6][7][8].

Typically, AAM is produced by the alkali activation of silica and alumina-rich materials using alkaline activators. The most popular precursors of AAM are blast furnace slag (BFS) and fly ash (FA). Blast furnace slag based alkali-activated materials (BFS-AAM) have poor workability and short setting time, while fly ash based alkali-activated materials (FA-AAM) characterizes with a slow strength development. Based on previous research, A good synergy between mechanical strength and durability could be obtained by adding BFS in FA-AAM[9][10][11][12] [13].

Although FA/BFS-AAM has good application prospects, the lack of mixture design regulation still limits the application of these materials. Currently, limited research has been conducted on mix design of FA/BFS-AAM[14][15][16][17]. The study of mix design mainly involves 3 difficulties. Firstly, the codes that are used for conventional concrete are not applicable for AAM. Secondly, the chemical composition and particle size of raw materials are not uniform. Thirdly, limited research has been conducted to study the mechanical properties of BFA/FA-AAM. Besides, a large number of them have focused on the effect of confusing factors, such as alkali activators/ precursor ratio, $NaOH/Na_2SiO_3$ ratio on mechanical properties of BFS/FA-AAM, which results in nonrepeatable mix proportion, because the modulus of Na_2SiO_3 varies a lot and the alkali concentration is unclear.

A literature study on the effect of the control factors on the strength and reaction process of BFS/FA-AAM has been looked though in this paper. The reaction product at different ages is closely related to the concentration of ions and the reaction mechanism in the system. In addition, any change of Na_2SiO_3 modulus and $NaOH/Na_2SiO_3$ ratio in mix design is indeed changing the control factors (the ion concentration). The main propose of this study is to understand the control factors influencing the strength of BFS/FA-AAM and to clarify their effect mechanism. Thus, it could provide a theoretical foundation for the mix design of BFS/FA-AAM.

2. REACTION MECHANISM OF BFS/FA-AAM
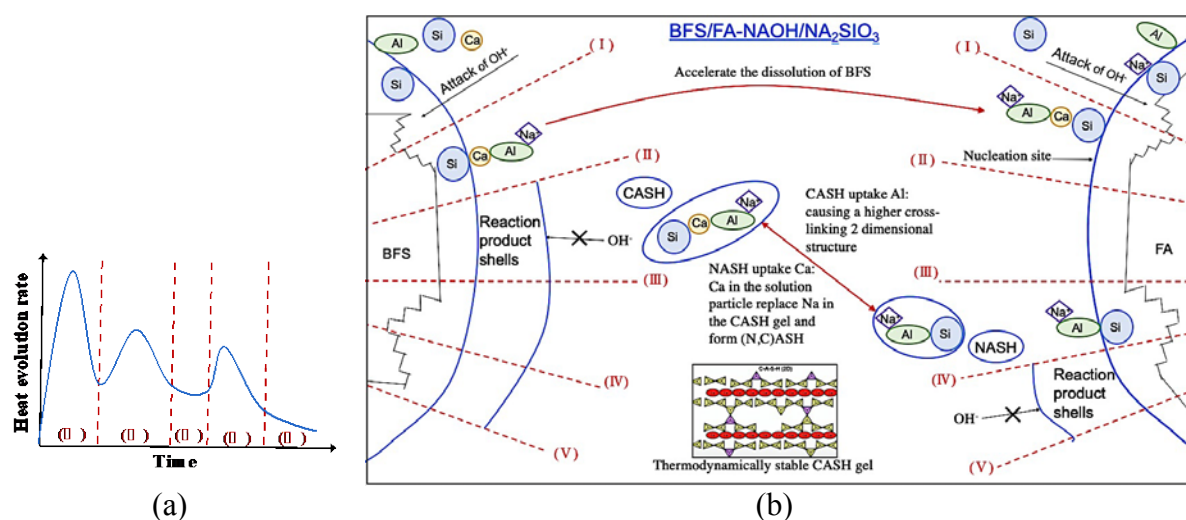
2.1 Reaction process

A theoretical heat evolution rate curve is shown in Fig. 1(a). The reaction mechanism of BFS and FA alkali-activated by NaOH and Na_2SiO_3 could be divided into 5 stages based on isothermal calorimetry study[18][19][20], as shown in Fig. 1(b). In literature, the optimum value and occurrence time vary, and different stages may emerge, appearing as another type of curve. This is due to the effect of control factors on the reaction process, which will be discussed later.

In the initial stage, the undersaturation degree of modifying elements is very large, So a large amount of reaction elements is released. Previous research has shown that among the reaction ions, the Si-O-Si bonds are stronger than Si-O-Al, the bonds between network forming species and network modifying species are the weakest[21][22][23]. Because BFS contains a more substantial amount of Ca and Mg and less Al than FA. Therefore, the dissolution of BFS is faster than that of FA. The first heat evolution rate is mainly caused by the dissolution of BFS.

In the second stage, the formation of CASH is characterized by the second heat evolution peak. During the dissolution, the FA particles could act as nuclea sites, capturing the reaction ions released by BFS. Therefore, CASH gel is not only formed on the surface of BFS, but also on the surface of FA. The formation of CASH gel consumes ions, leading to a rapid increase of the undersaturation degree and promoting the release of reaction ions before a Si layer could be created on the surface of BFS. In the third stage, a period of reduced heat production rate occurs.

The accumulation of reaction products on the surface of BFS forms shells and prevents the further reaction of unreacted BFS. The dissolution of BFS is gradually stopped. In the meantime, the FA particle is still mainly under the destruction period. The reaction ions releasing rate is faster than the reaction products forming rate, because of its relatively lower reactivity and the amber curing temperature.

After the induction periods, sufficiently high content of reaction ions exist in the solution around FA particles in the fourth stage, leading to the polycondensation of a large amount of NASH gels. The generated NASH and CASH gels have different structures than those in a single precursor system, because they do not develop separately but interact with each other in the further reaction process[21]. An exchange of Al and Ca ions proceeds in the restructuration of CASH and NASH gels. In the fifth stage, the reaction produces shell gradually formed on the surface of the FA particle, and the dissolution is therefore ceased. A thermodynamically stable CASH gel will be created if time is long enough[21].

Figure 1: (a) A theoretical heat evolution rate curve of BFS/FA-AAM; (b) Reaction process of BFS/FA-AAM

2.2 Reaction products

Both micro and nanostructure research has shown that a complex mix of amorphous CASH and NASH gels are formed at an early age (28d) [5][25]. The results from NMR analysis show that the higher content of FA is associated with higher polymerization. More Q^4 and Q^3 units are detected when the BFS/binder ratio was 10% (binder refers to the sum of the mass of BFS and FA). While reaction products with Q^1 and Q^2 units, but without Q^3 and Q^4 units were observed when the BFS/binder ratio was 30-50%[26].

When the pH is higher than 12, CASH gels are preferentially formed instead of NASH gels. As time goes by, the Ca in the solution gradually distorts the Si-O-Al bonds and create new Si-O-Ca bonds, because of the polarizing effect. Therefore, higher Ca content and lower Al content is gradually found in the structure. As a result, NASH turns into (N,C)ASH gel with a more depolymerized structure. On the other hand, the released Al form NASH is taken up by CASH in bridge positions to build a 2-dimensional structure with higher cross-linking. Ultimately, a single CASH gel (most thermodynamically stable) could be formed[27]. A series of secondary products with crystalline phase are accompanied, such as hydrotalcite, tetracalcium aluminate

hydrate, katoite, stratlingite and zeolitic phase (including hydroxysodalite, zeolite P, Na-chabazite, zeolite Y and faujasite)[28][29][30][31][32][33].

3. CONTROL FACTORS AND MECHANISMS

3.1 BFS/binder ratio

As shown in Fig. 2(a), There is a strong linear relationship between the BFS/b ratio and 28 d strength[34][35][36][37]. The results indicate that the higher the content of BFS, the higher the strength. It seems that FA has little help on the development of strength. This is probably because of the low reactivity of FA. As discussed in the reaction mechanism, the formation of NASH gels is later than the formation of CASH gels. In this age, the hollow sphere particle of FA create lots of pore in the materials, since the time is insufficient for the precipitate of reaction products to fill the hollow space. The pores created by FA cause stress concentrations in the material and thus result in a decrease of strength. 90d of curing age is suggested for BFS/FA-AAM.

The effect of the BFS/binder ratio on the reaction process is shown in Fig. 2(b). The increase of the content of BFS is associated with an increase of Ca and a decrease of Al in the reaction system. Since the Ca-O-Si bonds are weaker than Al-O-Si bonds. It may lead to faster dissolution and a higher value of the first peak. As the reaction process advances, an induction period may occur before the second peak, because the number of nuclei sites is reduced, and the Si layer may form on the surface of BFS, which hinders the further dissolution of reaction ions. The induction period between the second and the third peak may be shortened or may even disappear. Because less NASH is formed, the value of the third peak may decrease.
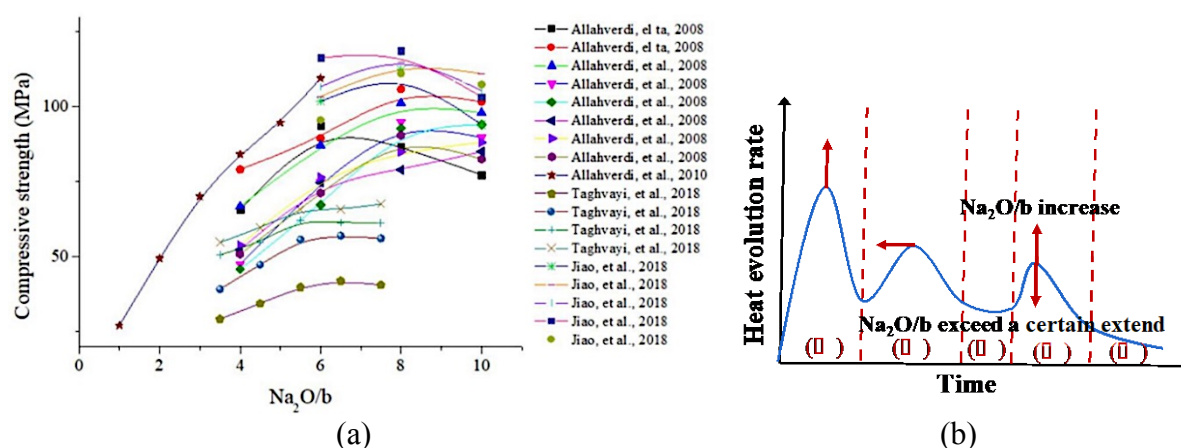

(a)   (b)
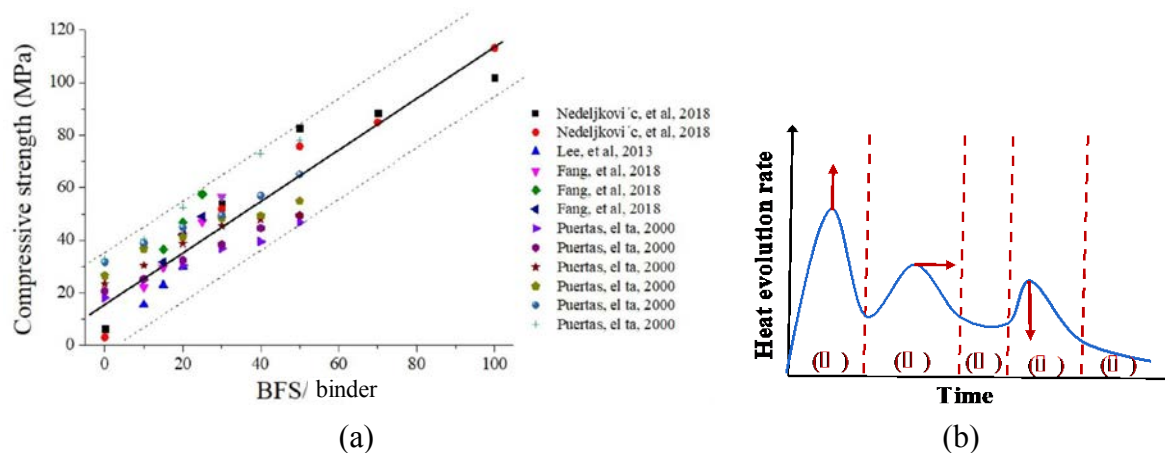
Figure 2: Effect of BFS/binder ratio on BFS/FA-AAM: (a) effect on strength; (b) effect on reaction process

3.2 Na₂O/binder ratio

The effect of Na_2O/binder ratio on BFS/FA-AAM is shown in Fig. 3[38][39][40]. The strength first increases and then decreases with the Na_2O/binder ratio. Higher content of OH^- increases the dissolution of BFS and FA, associated with a higher value of the first peak. At the same time, a higher amount of free ions and a high amount of catalyzer (Na^+) improve the formation rate of CSH gels. The second peak may be advanced or may even merge with the first peak.

The destruction coagulation period of NASH is accelerated since the higher content of released monomers has a higher tendency to be connected. To a certain extent, the third peak may increase with the Na_2O/binder ratio.

However, when the Na_2O/binder ratio exceeds a specific value, the third peak may begin to decrease. When the concentration of OH^- is high, the dissolution of $Ca(OH)_2$ is reduced, and a thin layer of $Ca(OH)_2$ is formed on the surface of BFS particles. So Ca is less capable of reacting with Al and Si and forming the CASH gels. What is more, excess OH^- causes Al-Si gel precipitation at the very early stage on the surface of the FA particles, so the subsequent polymerization is hindered, and the strength is therefore decreased. Excess Na may also cause efflorescence and reduce the strength to some extent. To obtain the highest strength, the optimum value of Na_2O/binder ratio in BFS-AAM and FA-AAM is 5.5%-8% and 7%-10%, respectively, while the optimum value of Na_2O/binder ratio in BFS/FA-AAM is still unknown.
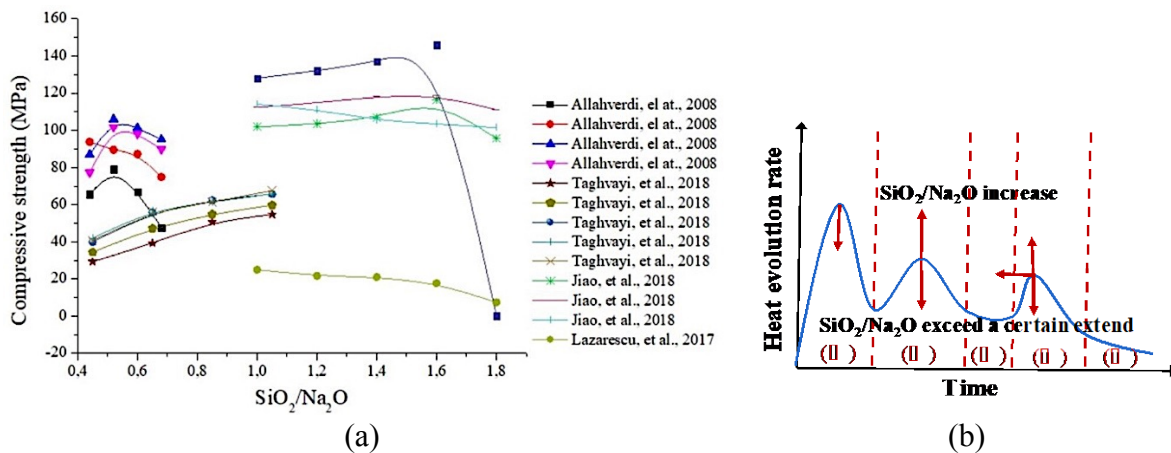

Figure 3: Effect of Na_2O/b ratio on BFS/FA-AAM: (a) effect on strength; (b) effect on reaction process

3.3 SiO_2/Na_2O ratio

The effect of the SiO_2/Na_2O ratio on BFS/FA-AAM is shown in Fig. 4[38][39][40][41]. With the increase of SiO_2/Na_2O, the strength first increases, then decreases. The first peak may decrease because the undersaturation degree of Si is lower in the solution, and the dissolution of Si is hindered. The second peak may increase because with more structure-forming element (Si) available in the solution, the reaction products could not only form on the surface of BFS particles, but also in the solution. Therefore, a denser microstructure could be generated. The third peak may be advanced because the dissolved Al is absorbed by Si in the solution, instead of being precipitated on the surface of FA particles. The dissolution of reaction ions is accelerated, and the formation of NASH gels advanced with more monomers for polymerization. More Si-O-Si bonds are formed, which are stronger than Si-O-Al bonds, leading to a higher degree of polymerization.

However, when the SiO_2/Na_2O ratio exceeds a particular value, the strength begins to decrease. Excess SiO_2/Na_2O could hinder the further dissolution of reaction ions since the Si layer may form on the surface of the precursor particles. Less dissolution of reaction ions eventually prevents the formation of CASH. On the other hand, excess SiO_2 species could form polymerized SiO_4 and precipitation, which may depress the precipitation of zeolite crystals and hinder the polymerization of FA in the subsequent process. To obtain the highest strength, the

optimum value of SiO_2/Na_2O ratio in BFS-AAM and FA-AAM is 0.85-1.4 and 0.6-1, respectively, while the optimum value of SiO_2/Na_2O ratio in BFS/FA-AAM is still unknown.


Figure 4: Effect of SiO_2/Na_2O ratio on BFS/FA-AAM: (a) effect on strength; (b) effect on reaction process

3.4 Other factors

The relationship between the l/b ratio (the mass ratio of alkaline activated solution and binder) and the compressive strength and workability is shown in Fig. 5[34][36][42][43]. The study indicates that l/b has little effect on the strength of AAM. One significant difference between OPC and AAM is that the formation of reaction products requires no water. Water nearly reacts during the creation of CASH. In FA-AAM, water is consumed in the dissolution stage while release again in the polymerization process. Obviously, water is not chemically bound to the structure of the matrix[44]. From the reaction mechanism point of view, less water leads to a slightly higher compressive strength. But its effect is negligible, compared with the effect of control factors on the strength.

Nevertheless, water content is still an important factor in considering the workability of BFS/FA-AAM. With the increase of the l/b ratio, the dimensional flowability is increased. Water demand is affected by several factors, including particle size and shape distribution and specific surface area[45]. It is recommended to use the w/b ratio (the mass ratio of water and binder) instead of the l/b ratio to obtain more precise results for further study.
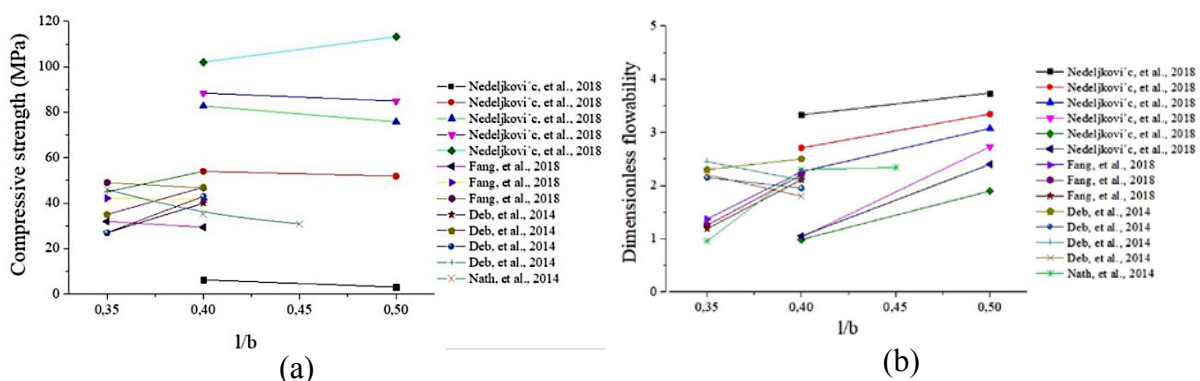
Figure 5: Effect of l/b ratio on BFS/FA-AAM: (a) effect on strength; (b) effect on flowablity

4. CONCLUSIONS

In this paper, a theoretical foundation of the strength development of BFS/FA-AAM is built. The demonstration of the effect of control factors on the strength and reaction process could provide some guidance for the mix design of BFS/FA-AAM. For further study of mix design, a quantitative relationship between these factors and strength is required.

ACKNOWLEDGEMENTS

REFERENCES

[1]. Davidovits, J. 'Geopolymer cements to minimize carbon-dioxide greenhouse warming'. Conference: Proceedings of the Advances in Cement and Concrete, eds M.W. Grutzeck & S. L. Sarkar, Durham,1994.

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

[3]. Turner, L.K, Collins, F.G. 'Carbon dioxide equivalent (CO_2-e) emissions: a comparison between geopolymer and OPC cement concrete'. Construction and Building Materials.43(2013)125-130.

[4]. Jannie, S.J. van Deventer, Provis. J.L, Duxson. P, Brice. D.G. 'Chemical Research and climate change as drivers in the commercial adoption of alkali activated materials'. Waste Biomass Valorization.1(2010)145-155.

[5]. Fernandez-Jimenez. A.M, Palomo, A., Lopez-Hombrados, C. 'Engineering properties of alkali-activated FA concrete' ACI Materials Journal.103 (2)(2006)106-112.

[6]. Sofi, M., Jannie, S.J. 'Engineering properties of inorganic polymer concretes (IPCs)'. Cement and Concrete Composites.37(2007)251-257.

[7]. Rashad, A.M, 'A comprehensive overview about the influence of different admixtures and additives on the properties of alkali-activated FA', Material Design.53(2014)1005-1025.

[8]. Yusuf, M.O., Johari, M.A.M, Ahmad, Z.A., Maslehuddin, M. 'Evolution of alkali activated ground blast furnace slag-ultrafine palm oil fuel ash based concrete'. Material Design.55(2014)387-393.

[9]. Nedeljković, M., Arbi, K., Zuo, Y.B., Ye, G. 'Microstructure and mineralogical analysis of alkali activated FA-slag pastes'. Conference: the 3nd International RILEM Conference on Microstructure Related Durability of Cementitious Composites, Nanjing, China, 2016.

[10]. Nedeljković, M., Arbi, K., Zuo, Y.B., Ye, G. 'Physical properties and pore solution analysis of alkali activated FA-slag paste'. Conference: International RILEM Conference on Materials, Systems and Structures in Civil Engineering, August 2016

[11]. Nedeljković, M., Zuo, Y.B., Arbi, K, Ye, G. 'Natural carbonation of alkali-activated FA and slag pastes'. Conference: Fib Symposium 2017 (high tech concrete): Where technology and engineering meet!), At Maastrich, the Netherlands, June 2017.

[12]. Arbi, K., Nedeljković, M., Zuo, Y.B., Ye, G. 'Durability of alkali-activated FA and slag concrete'. Conference: 9th International Concrete Conference 2016 Environment, Efficiency and Economic Challenges for Concrete, At Dundee, Scotland, UK, July 2016.

[13].　Ma, Y.J., Hu, J., Ye, G. 'The effect of activating solution on the mechanical strength, reaction rate, mineralogy, and microstructure of alkali-activated FA'. Journal of Materials Science.47(11)(2012)4568-4578.

[14].　Anuradha, R., Sreevidya, V., Venkatasubramani, R., Rangan, B.V. 'Modified guidelines for geopolymer concrete mix design using Indian Standard'. Asian Journal of Civil Engineering and Building House.13 (3)(2012)353-364.

[15].　Ferdous, M.W., Kayali, O., Khennane, A. 'A detailed procedure of mix design for FA based geopolymer concrete'. In: Fourth Asia-Pacific Conference on FRP in Structures, Australia. 2013, 11-13.

[16].　Lloyd, N.A., Rangan, B.V. 'Geopolymer concrete with FA'. In: Second International Conference on Sustainable Construction Materials and Technologies, Ancona, Italy. 2010.

[17].　Ferdous, M.W., Kayali, O., Khennane, A. 'A detailed procedure of mix design for FA based geopolymer concrete'. Fourth Asia-Pacific Conference on FRP in Structures, Australia. 2013,11-13.

[18].　Zuo, Y.B. Experimental Study and Numerical Simulation of the Reaction Process and Microstructure Formation of Alkali activated Materials. Ph.D. Thesis, Delft: Delft University Press, 2018, 42-59.

[19].　Chithiraputhiran, S., Neithalath, N. 'Isothermal reaction kinetics and temperature dependence of alkali activation of slag, fly ash and their blends'. Construction and Building Materials. 45 (2013) 233-242.

[20].　Gao, X., Yu, Q., Brouwers, H. 'Reaction kinetics, gel character and strength of ambient temperature cured alkali activated slag–fly ash blends, Constr. Build. Mater., 80 (2015) 105-115.

[21].　Hamilton J. P., Brantley S. L., Pantano C. G., etc, ''Dissolution ofNepheline, Jadeite and Albite Glasses: Toward Better Models for Aluminosilicate Dissolution,'' Geochim. Cosmochim. Acta, 65 [21] 3683–702 (2001).

[22].　Blum A. E., Lasaga A. C., ''The Role of Surface Speciation in the Dissolution of Albite,'' Geochim. Cosmochim. Acta, 55 [8] 2193–201 (1991).

[23].　Oelkers E. H., Gislason S. R., ''The Mechanism, Rates and Consequences of Basaltic Glass Dissolution: I. An Experimental Study of the Dissolution Rates of Basaltic Glass as a Function of Aqueous Al, Si and Oxalic Acid Concentration at 251Cand pH53 and 11,'' Geochim. Cosmochim. Acta, 65 [21] 3671– 81 (2001).

[24].　Garcia-Lodeiro, I., Palomo, A., Fernández-Jiménez, A. 'Crucial insights on the mix design of alkali-activated cement-based binders'. Handbook of Alkali-Activated Cements, Mortars and Concretes, Oxford: Woodhead Publishing, 2015, 49-73.

[25].　Yip C.K., Lukey G.C., Deventer J.S.J. 'The coexistence of geopolymeric gels and calcium silicate hydrate at the early stage of alkaline activation'. Cement and Concrete Research 35 (2005) 1688-1697.

[26].　Lee N.K., Lee H.K. 'Reactivity and reaction products of alkali-activated, FA/slag paste'. Construction and Building Materials. 2015, 81:303-312.

[27].　Garcia-Lodeiro I., Palomo A., Fernández-Jiménez A., Macphee D.E. 'Compatibility studies between N-A-S-H and C-A-S-H gelss. Study in the ternary diagram Na2O–CaO–Al2O3–SiO2–H2O'. Cement and Concrete Research 41 (2011) 923-931.

[28].　Wang, S.D. and Scrivener, K. L., 'Hydration products of alkali activated slag cement', Cem. Concr. Res. 25 (3) (1995) 561-571.

[29]. Myers, R.J., Lothenbach, B., Bernal, S.A. and Provis, J.L., 'Thermodynamic modelling of alkali-activated slag cements', Appl. Geochem. 61 (2015) 233-247.

[30]. Richardson, I.G., Brough, A. R., Groves, G.W. and Dobson, C.M., 'The Characterization of Hardened Alkali-Activated Blast-Furnace Slag Pastes and the Nature of the Calcium Silicate Hydrate (C-S-H) Phase', Cem. Concr. Res. 24 (5) (1994) 813-829.

[31]. Palomo, A., Grutzeck, M. W. and Blanco, M. T., 'Alkali-activated FAes - A cement for the future', Cem. Concr. Res. 29 (8) (1999) 1323-1329.

[32]. Duxson, P., Fernández-Jiménez, A., Provis, J., Lukey, G., Palomo, A. and Van Deventer, J., 'Geopolymer technology: the current state of the art', J. Mater. Sci. 42 (9) (2007) 2917-2933.

[33]. Criado, M., Fernández-Jiménez, A., Palomo, A., Sobrados, I. and Sanz, J., 'Effect of theSiO2/Na2O ratio on the alkali activation of FA. Part II: 29Si MAS-NMR Survey', Micropor Mesopor Mat.109 (1–3) (2008) 525-534.

[34]. Nedeljkovi´c, M., Li, Z.M. and Ye, G. 'Setting, Strength, and Autogenous Shrinkage of Alkali-Activated Fly Ash and Slag Pastes: Effect of Slag Content'. Materials.11(2018) 2121

[35]. Lee, N.K., Lee, H.K., 'Setting and mechanical properties of alkali-activated fly ash/slag concrete manufactured at room temperature'. Construction and Building Materials 47 (2013) 1201-1209.

[36]. Fang, G.H., Ho, W.K., Tu, W.L., Zhang, M.Z. 'Workability and mechanical properties of alkali-activated fly ash-slag concrete cured at ambient temperature'. Construction and Building Materials 172 (2018) 476- 487.

[37]. Puertas, F., MartõÂnez-RamõÂrez, S., Alonso, S., VaÂzquez, T. 'Alkali-activated fly ash/slag cement Strength behaviour and hydration products'. Cement and Concrete Research 30 (2000) 1625-1632

[38]. Allahverdi, A., Najafi Kani, E., Esmaeilpoor, S. 'Effects of Silica Modulus and Alkali Acttivated Concentration on Activation of Blast-Furnace Slag'. Iranian Journal of Materials Science and Engineering, 5(2)(2008) 32-35

[39]. Taghvayi, H., Behfarnia, K., Mohammadbagher, K. 'The Effect of Alkali Concentration and Sodium Silicate Modulus on the Properties of Alkali-Activated Slag Concrete' Journal of Advanced Concrete Technology. 16(2018) 293-305.

[40]. Jiao, Z.Z., Wang, Y., Zheng, W.Z., Huang, W.X. 'Effect of Dosage of Alkaline Activator on the Properties of Alkali-Activated Slag Pastes'. Advances in Materials Science and Engineering. (2018) 1-12.

[41]. Lăzărescu, A. V., Szilagyi, H., Baeră, C., Ioani, A.' The Effect of Alkaline Activator Ratio on the Compressive Strength of Fly Ash-Based Geopolymer Paste'. IOP Conf. Ser.: Mater. Sci. Eng. 2017.

[42]. Deb, P.S., Pradip, N., Sarker, P.K. 'The effects of ground granulated blast-furnace slag blending with fly ash and activator content on the workability and strength properties of geopolymer concrete cured at ambient temperature'. Materials and Design 62 (2014) 32-9.

[43]. Pradip, N., Sarker, P.K. 'Effect of GGBFS on setting, workability and early strength properties of fly ash geopolymer concrete cured in ambient condition'. Construction and Building Materials 66 (2014) 163-171.

[44]. Xu, H., Deventer, J.S.J., Jannie, S.J. 'The effect of alkali metals on theformation of geopolymeric gelss from alkali-feldspars'. Colloid Surf.216(2003)27-44.

[45]. Hewlett, P., Lea's Chemistry of Cement and Concrete, Butterworth-Heinemann, Oxford, 2003.