Prediction of the compressive strength of one-part geopolymers
Previsão da resistência de geopolímeros monofásicos

Abdollahnejad, Z. Nazari, A. Pacheco-Torgal, F. Sanjayan, J.G. Barroso de Ag - torgal@civil.uminho.pt
University of Minho

Abstract

The discovery of one-part geopolymers is considered a key event on the evolution of geopolymer technology because emulates one of the most important properties of Portland cement, the just add water concept. This materials are not associated with the known problems of two part geopolymers, namely the use of caustic solutions that have poor workability and make the handling and application of geopolymers difficult and the fact that alkaline or soluble silicates are not consumed during geopolymerization leading to severe efflorescence phenomena. However, so far very few investigations were published on this field and some report low mechanical strength. This paper discloses results regarding the numerical modelling of one part-geopolymers compressive strength.

Resumo

A descoberta dos geopolímeros monofásicos é considerado um importante acontecimento no âmbito da tecnologia dos geopolímeros porque mimetizam uma das mais importantes propriedades do cimento Portland, o conceito relativo à simples adição de água. Estes materiais não estão associados aos conhecidos problemas dos geopolímeros correntes nomeadamente a utilização de soluções cáusticas, baixa trabalhabilidade que dificultam a sua colocação e o facto das espécies alcalinas e silicatos solúveis não reagirem na sua totalidade durante a reacção de geopolímerização originando o aparecimento de elevada quantidade de eflorescências. Contudo muito poucas investigações foram publicadas neste domínio e algumas apresentam baixa resistência mecânica. Este artigo apresenta resultados relativos à modelação numérica da resistência à compressão de geopolímeros monofásicos.

Keywords

Geopolymer; one part-geopolymers; durability; efflorescences; numerical modelling; compressive strength

Palavras-chave

Geopolímeros monofásicos; durabilidade; modelação numérica; resistência à compressão

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1.Introduction

Ordinary Portland cement (OPC) is the dominant binder in the construction industry with an annual production of almost 3 Gt [1]. Additionally, the production of one tonne of OPC generates 0.55 tonnes of chemical CO_2 and requires an additional 0.39 tonnes of CO_2 in fuel emissions for the baking and grinding activities, resulting in a total of 0.94 tonnes of CO_2. In 2000, the cement industry emitted, on average, 0.87 kg of CO_2 for every 1 kg of cement produced [2]. As a consequence, this industry contributes to about 7% of the total worldwide CO_2 emissions [3]. It is also expected that the global demand of OPC will have a twofold increase by the year 2050, reaching a total of 6 Gt/year. The urge to reduce carbon dioxide emissions, and also, the fact that OPC structures built a few decades ago are still facing disintegration problems points out the handicaps of OPC. Additionally, Portland cement based concrete presents higher permeability, allowing water and other aggressive media to enter, further leading to carbonation and corrosion issues. The early deterioration of reinforced concrete structures based on OPC is a current phenomenon of significant consequences, both in terms of the cost for the rehabilitation of these structures and as a result of the environmental impacts associated with these operations. Investigations [4-8] carried out so far in the development of geopolymers showed that much has already been investigated, and also, that an environmentally friendly alternative to OPC is rising. According to Davidovits [9], geopolymer production generates just 0.184 tons of CO_2 per ton of binder. These findings, however, were not confirmed by Duxon *et al*. [10]. These authors stated that, although the CO_2 emissions generated during the production of Na_2O are very high, the production of geopolymers is still associated with a level of carbon dioxide emissions lower than the emissions generated in the production of OPC. Meanwhile, an independent study made by Zeobond Pty LtD concluded that the former was responsible for 80 % lower CO_2 emissions [11]. Weil *et al*. [12] compared Portland cement concrete to geopolymeric concrete possessing similar durability reporting that the latter implies 70% lower CO_2 emissions, all of which confirming the aforementioned reductions. McLellan et al. [13], in turn, reported a 44 to 64 % reduction in greenhouse gas emissions of geopolymers when compared to OPC. Habert et al. [14] confirmed that they are responsible for lower impacts on global warming when compared to OPC but, on the other hand, demonstrate higher environmental impacts regarding other impact categories. Lower CO_2 emissions geopolymers are therefore needed. Nevertheless, the durability of geopolymers is still the subject of some controversy [15, 16]. Juenger et al. [1] argue that "*The key unsolved question in the development and application of alkali activation technology is the issue of durability*", and more recently, Van Deventer et al. [17] recognized that "*whether geopolymer concretes are durable remains the major obstacle to recognition in standards for structural concrete*". Efflorescences are an important drawback of two part geopolymers and, so far, have received very little attention. According to Skvara et al. [18], the bond between the sodium ions (Na^+) and the aluminosilicate structure is weak, thus explaining the leaching behaviour. These results are very important because they constitute a step back in the development of geopolymers. For one, the use of hydrothermal curing implies serious limitations for on-site concrete placement operations. Alternatively, the use of calcium based mixtures reduces the acid resistance and raises the chances of ASR occurrence. The discovery of one-part geopolymers is considered a key event on the evolution of low carbon geopolymer technology in the "just add water" concept. In 2007 some authors [19] disclosed results on sodium silicate free geopolymers. However they were associated with very low compressive strength. However, their related mechanical performance around 1 MPa was simply too small for construction purposes. According to those authors an increase in the compressive strength to 4MPa would require 24 h hydrothermal treatment at 100 ºC. The

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use of a much more intensive treatment (140 ºC) would increase compressive strength to 12-20 MPa. However, such treatment conditions not only are difficult to implement in the construction industry but more important constitute a setback in terms of energy and carbon footprint when compared to traditional two part geopolymers. Recent investigations also confirm this low comrpressive strength [20]. Some authors even report a compressive strength decrease with time for one-part geopolymers based on calcined red mud and sodium hydroxide blends [21]. Abdollahnejad et al. [22] recently investigated one-part geopolymers having obtained relevant compressive strength by using fly ash and minor amounts of OPC. Since supply chain risks can limit geopolymer technology wider adoption the use of minor volumes of OPC can help overcome this problem. Previous works used the Johnson–Mehl–Avrami–Kolmogorov (JMAK) model concerning the kinetics of crystallization in amorphous materials [23]. This paper discloses results regarding the modelling the compressive strength of one part-geopolymers with the JMAK model.

2.EXPERIMENTAL WORK

2.1Materials, mix design and testing

The composition of one part geopolymers include kaolin, fly ash, ordinary Portland cement (OPC), sodium hydroxide, calcium hydroxide (Ca(OH)$_2$), water and superplasticizer. The OPC is of class I 42,5 R type, containing between 95% to 100% of clinker content, a specific weight of 3.15 g/cm^3 and a Blaine fineness of 3842 cm^2/g.The superplasticizer (SP) used was SIKA 3002 HE. The referred SP was used to maintain a uniform consistency throughout the different mixes. The chemical composition of the fly ash complies with the minimum requirements indicated in EN-450-1 [24] for use as a partial replacement of cement in concrete. Based on this standard, the fly ash was categorized as class B and group N for the loss of ignition and fineness, respectively. Also, the material in question has a specific weight of 2.42 g/cm^3 and a chemical composition as shown in Table 2.The kaolin has a BET surface area of 21 m^2/g and its particle size is shown in Fig 1, this is crucial information as this parameter influences the dehydroxylation temperature of kaolin. The DTA/TGA curves for kaolin are presented in Fig 1. A well-defined endothermic DTA peak and sharp weight loss in the TGA curve appears between 550 ºC and 600 ºC. This loss results from the transition to the amorphous and more reactive metakaolin phase. A mixture of kaolin and sodium hydroxide was calcined in a furnace at 650 ºC during 140 minutes as described in the international patent WO 2007/109862 A1 authored by Zheng et al. [25]. The cooled mixture was then ground into powder. Table 1 and shows the compositions of the one parte geopolymer mixtures used in the present study. After demoulding the specimens were submitted for a thermal treatment during 24 h at different temperatures (40ºC, 60ºC and 80ºC) The specimens were also placed in the chamber room, with relative humidity of 58 %, during the curing time. Compressive strength tests were performed on 50×50×50 mm^3 concrete specimens, according to NP EN 206-1[26]. The compressive strength, for each mixture, was obtained from an average of the results of 3 cubic specimens.

Table 1- Composition of one part geopolymer mixes

Mix	OPC (%)	Fly ash (%)	Ca(OH)$_2$ (%)	Calcined stuff (%)	Sand (%)	SP (%)	
OPC 30-FL 58.3-CH 7.7-CS 4	30	58.3	7.7	4			
OPC 26-FL 58.3-CH 7.7-CS 8	26	58.3	7.7	8	0.8	0.8	0.35
OPC 18-FL 58.3-CH 7.7-CS 16	18	58.3	7.7	16			

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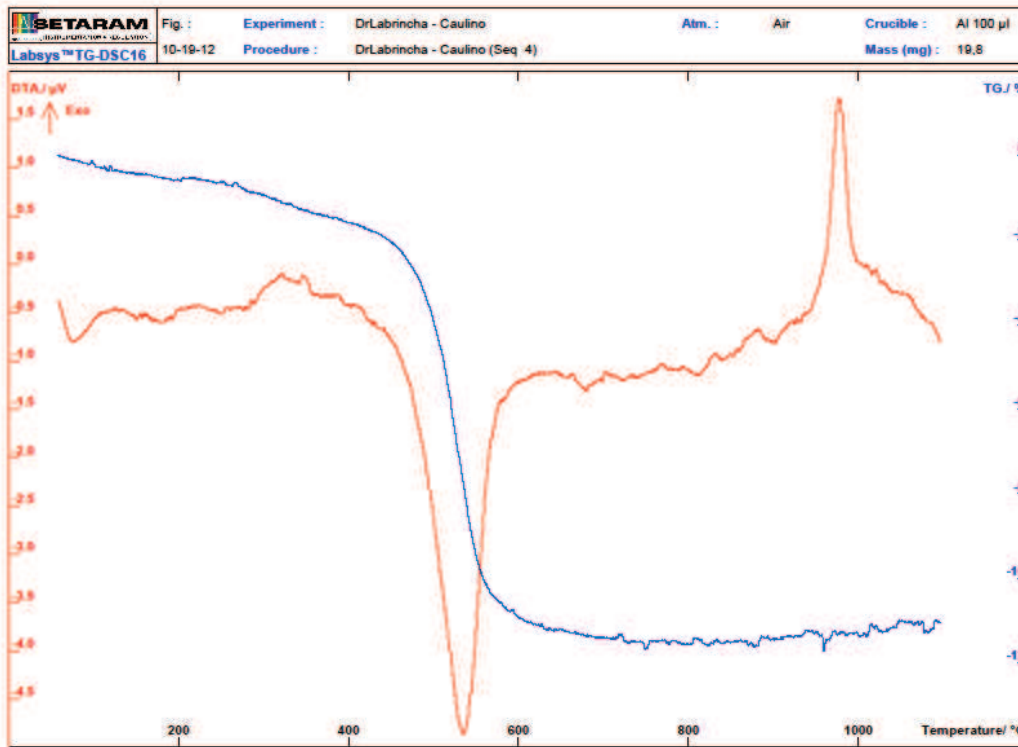
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Figure 1 – DTA/TGA curves for kaolin

3. Compressive strength modelling

Figure 3 show compressive strengths of one part geopolymers according to curing time. It also includes the predicted values according to the JMAK model. The equation of this model is as follows:
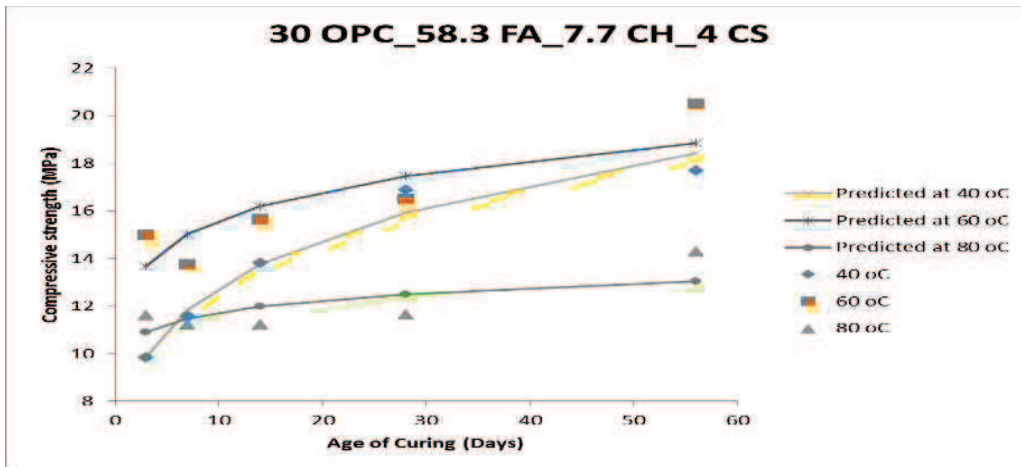
$$f(t) = 1 - exp(-kt^n) \qquad (1)$$

Where f(t) is degree of reaction, t is time of reaction, k is a constant and n is the exponent. According to Fig. 3 the degree of reaction in cementitious systems is related directly to compressive strength. Therefore, Eq. (1) can be adopted for compressive strength of geopolymers as follows:
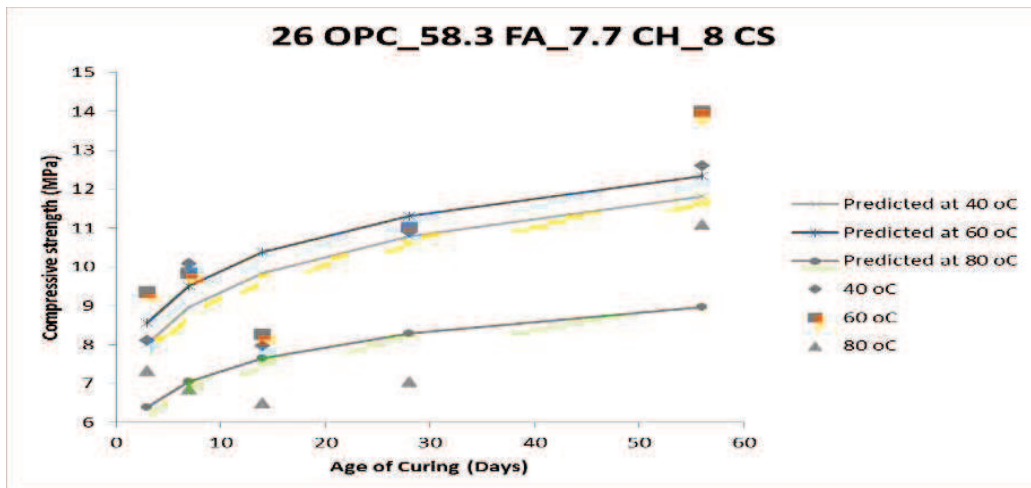
$$f_c = \alpha[1 - \exp(-kt^n)] \qquad (2)$$

where f c is the compressive strength and α is a constant. Eq. (1) is solved for degree of reaction varying between 0 and 1. In Eq. (2), f c is greater than1and hence for our case where strengths are below100MPa, we divide the strengths by 100.This normalised number can be included in the constant α. For specimens with higher strengths, one can divide them by a reference number. To determine k and n, Eq. (2) can be written in the following form:
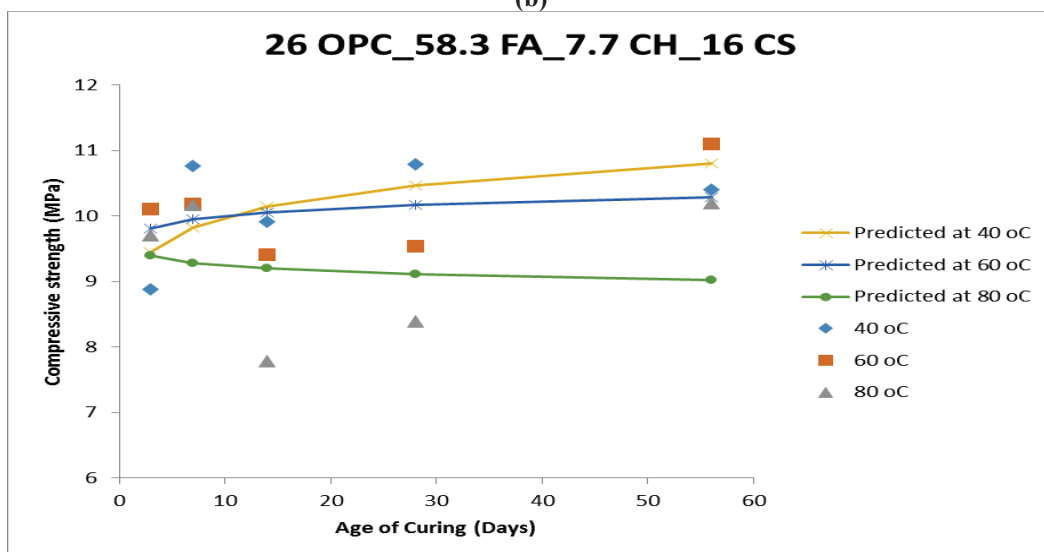
$$\ln(-\ln(1-f_c)) = \ln k + n \ln t \qquad (3)$$

k and n can be easily found from intercept and slope of the line plotted in the form of ln (1-ln(1-f_c)) versus ln t respectively. These lines for the whole considered geopolymeric systems considered in this study have been plotted in Fig. 4. Calculated k and n and their corresponding equations have been given in Table 2. The predicted compressive strengths for one part geopolymeric mixtures was presented in Fig. 3. The results are influenced not only by the one part geopolymer mixture but also by the temperature treatment.

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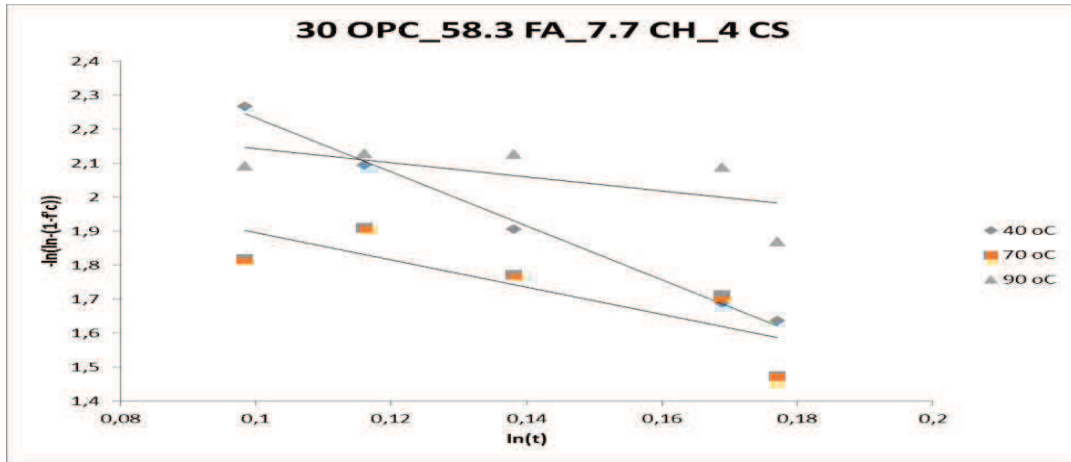Conference on Engineering
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(a)

(b)

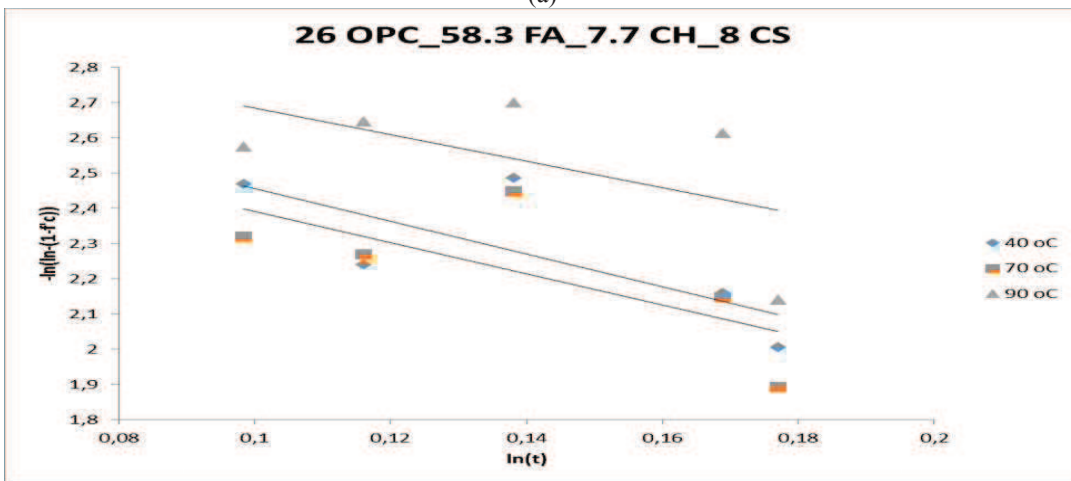**(c)**

Figure 2 – Experimental and predicted compressive strength of mixtures a) 30 OPC_58.3 FA_7.7 CH_4 CS,
b) 26 OPC_58.3 FA_7.7 CH_8 CS and c) 18 OPC_58.3 FA_7.7 CH_16CS

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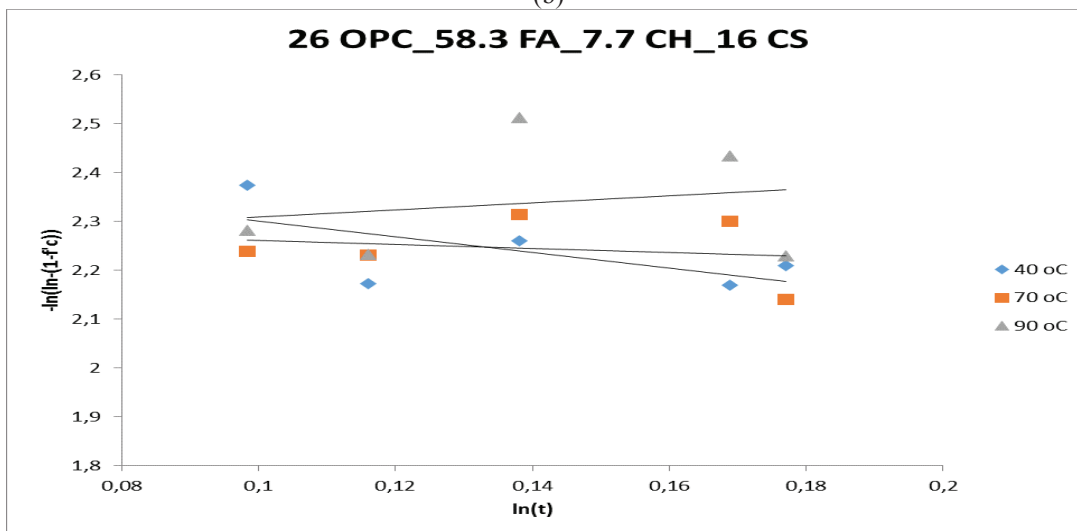Faculty of Engineering   Covilhã | Portugal

(a)

(b)

(c)

Figure 3 – Plots for determining *k* and *n* in a) 30 OPC_58.3 FA_7.7 CH_4 CS, b) 26 OPC_58.3 FA_7.7 CH_8 CS and c) 18 OPC_58.3 FA_7.7 CH_16CS

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Table 2- Constant, exponent and equation of compressive strength evolution for one part geopolymers

Curing temperature (°C)	30 OPC_58.3 FA_7.7 CH_4 CS			26 OPC_58.3 FA_7.7 CH_8 CS			26 OPC_58.3 FA_7.7 CH_16 CS		
	k	n	Equation	k	n	Equation	k	n	Equation
40	0.08	0.23	$f_c = 100\left[1-e^{-0.0805\,t^{0.07}}\right]$	0.13		$f_c = 100\left[1-e^{-0.0717\,t^{0.09}}\right]$	0.04		$f_c = 100\left[1-e^{-0.0942\,t^{0.0491}}\right]$
60	0.12	0.11	$f_c = 100\left[1-e^{-0.1258\,t^{0.07}}\right]$	0.13		$f_c = 100\left[1-e^{-0.0772\,t^{0.10}}\right]$	0.01		$f_c = 100\left[1-e^{-0.1014\,t^{0.01}}\right]$
80	0.10	0.06	$f_c = 100\left[1-e^{-0.1078\,t^{0.05}}\right]$	0.12		$f_c = 100\left[1-e^{-0.0854\,t^{0.10}}\right]$	0.01		$f_c = 100\left[1-e^{-0.1002\,t^{-0.0145}}\right]$

4. Conclusions

The JMAK equation was used as a basic formulation for predicting compressive strength of one part geopolymers. The degree of reaction of geopolymers was supposed to be related directly to compressive strength and then Avrami constants and exponents were found for all geopolymers. It was shown that compressive strength evolution of some one part geopolymers can be found by the proposed equations.

References

[1] Juenger, M.; Winnefeld, F.; Provis, J.; Ideker, J.: "Advances in alternative cementitious binders". *Cement and Concrete Research* Vol. 41, (2011), ISSN 0008-8846, pp.1232-1243.

[2] Damtoft, J.; Lukasik, J.; Herfort, D.; Sorrentino, D.; Gartner, E.: "Sustainable development and climate change initiatives". *Cement and Concrete Research* Vol.38, (2008), ISSN 0008-8846, pp.115-127 (2008)

[3] Pacheco-Torgal, F.: "Introduction". In "Eco-efficient concrete". Eds. Pacheco-Torgal, F., Jalali, S., Labrincha, J., John, V. Woodhead Publishing Limited Abington Hall, Cambridge, UK, 2012

[4] Pacheco-Torgal, F.; Castro-Gomes, J.; Jalali, S.: "Alkali – activated binders: a review Part 1 Historical background, terminology, reaction mechanisms and hydration products". *Construction and Building Materials* Vol.22, (2008), ISSN 0926-3373, pp.1305-1314.

[5] Pacheco-Torgal, F.; Castro-Gomes, J.; Jalali, S.: "Alkali – activated binders: a review Part 2 About materials and binders manufacture". *Construction and Building Materials* Vol.22, (2008), ISSN 0926-3373, pp.1315-1322.

[6] Li, C.; Sun, H.; Li, L.: "A review: The comparison between alkali-activated slag (Si+Ca) and metakaolin (Si+Al) cements", *Cement and Concrete Research* Vol.40, (2010), ISSN 0008-8846, pp.1341-1349.

[7] F. Pacheco-Torgal, Z. Abdollahnejad, S. Miraldo, S. Baklouti and Y.Ding, "An overview on the potential of geopolymers for concrete infrastructure rehabilitation". *Construction and Building Materials* Vol.36, (2012), ISSN 0008-8846, pp.1053-1058 (2012).

[8] Pacheco-Torgal, F.; Ding, Y.; Miraldo, S.; Abdollahnejad, Z.; Labrincha, J.:"Are geopolymers more suitable than Portland cement to produce high volume recycled aggregates HPC ?". *Construction and Building Materials* Vol.32, (2012), ISSN 0008-8846, pp.1048-1052.

[9] Davidovits, J.; Comrie, D.; Paterson, J.; Ritcey, D.: "Geopolymeric concretes for environmental protection". *ACI Concrete International* Vol.12, (1990) pp.30-40.

ICEUBI2015 - INTERNATIONAL CONFERENCE ON ENGINEERING 2015 – 2-4 Dec 2015 – University of Beira Interior – Covilhã, Portugal

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[10] Duxson, P.; Provis, J.; Luckey, G.; Van Deventer, J.: "The role of inorganic polymer technology in the development of "Green Concrete". *Cement and Concrete Research* Vol.37 (2007), ISSN 0008-8846, pp.1590-1597.

[11] Duxson, P.; Van Deventer, J. "Geopolymers, Structure, Processing, Properties and Applications", Ed. J. Provis & J. Van Deventer, Woodhead Publishing Limited Abington Hall, Cambridge, UK (2009).

[12] Weil, M.; Dombrowski, K.; Buchawald, A. "Life-cycle analysis of geopolymers", In Geopolymers, Structure, Processing, Properties and Applications, Ed. J. Provis & J. Van Deventer, pp.194-210, Woodhead Publishing Limited Abington Hall, Cambridge, UK (2009).

[13] McLellan, B.; Williams, R.; Lay, J.; Van Riessen, A.; Corder, G.: "Costs and carbon emissions for geopolymer pastes in comparison to ordinary Portland cement". *Journal of Cleaner Production* Vol.19, (2011), ISNN pp.0959-6526, pp.1080-1090.

[14] Habert, G.; de Lacaillerie, J.; Roussel, N.: "An environmental evaluation of geopolymer based concrete production: reviewing current research trends". *Journal of Cleaner Production* Vol.11, (2011), ISNN pp.0959-6526, pp.1229-1238.

[15] Pacheco-Torgal, F.; Abdollahnejad, Z.; Camões, A.; Jamshidi, M.; Ding, Y.:" Durability of alkali-activated binders. A clear advantage over Portland cement or an unproven issue ?". *Construction and Building Materials* Vol.30, (2012), ISSN 0008-8846, pp.400-405 (2012)

[16] Provis, J.; Muntingh, Y.; Lloyd, R.; Xu, H.; Keyte, L.; Lorenzen, L.; Krivenko, P.; Van Deventer, J.: "Will geopolymers stand the test of time?". Ceramic Engineering and Science Proceedings Vol.28, (2008) pp.235-248.

[17] Van Deventer, J.; Provis, J.; Duxson, P.: "Technical and commercial progress in the adoption of geopolymer cement". *Minerals Engineering* Vol. 29, (2012), ISSN 0892-6875, pp.89-104).

[18] Škvára, F.; Šmilauer, V.; Hlaváček, P.; Kopecký, L.; Cílová, Z.: "A weak alkali bond in (N, K)–A–S–H gels: evidence from leaching and modelling". *Ceramics – Silikáty* Vol. 56 (4) (2012) ISSN 0862-5468, pp. 374-382.

[19] Kolousek, D.; Brus, J.; Urbanova, M.; Andertova, J.; Hulinsky, V.; Vorel, J.: "Preparation, structure and hydrothermal stability of alternative (sodium silicate-free) geopolymers". *Journal of Materials Science* Vol. 42 (2007), ISSN 0022-2461, pp. 9267-9275.

[20] Peng, M.-X.; Wan, Z.-H.; Shen, S.H.; Xiao, Q.G.: "Synthesis, characterization and mechanisms of one-part geopolymeric cement by calcining low-quality kaolin with alkali". *Materials and Structures* 48 (2014), ISSN 1359-5997, pp. 699-708.

[21] Ke, X.; Bernal, S.; Ye, N.; Provis, J.; Yang, J.: "One-part geopolymers based on thermally treated red mud/NaOh blends". *Journal of American Ceramic Society* Vol. 98, (2015), ISSN 1551-2916, pp.5-11.
[22] Abdollahnejad, Z.; Hlavacek, P.; Miraldo, S.; Pacheco-Torgal, F.; Aguiar, A.: "Compressive strength, microstructure and hydration products of hybrid alkaline cements". *Materials Research* 17 (2014), ISSN 1980-5373, p.10.

[23] Arshad, M.; Maaroufi, A.: "Relationship between Johnson–Mehl–Avrami and Šesták–Berggren models in the kinetics of crystallization in amorphous materials". *Journal of Non-Crystalline Solids* Vol.413, (2015), ISSN 0022-3093, pp.53–58.

[24] NP EN 450-1, Fly ash for concrete – Part 1: Definition, specifications and conformity

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criteria

[25] Zheng, D.; Van Deventer, J.S.L.; Duxson, P.: The dry mix cement composition, methods and systems involving same. International Patent WO 2007/109862 A1, 2007.

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