INTERNAL STRUCTURE CHARACTERIZATIONS OF HARDENED CEMENT PASTE CONTAINING SHRINKAGE REDUCING ADMIXTURE USING NANOINDENTATION AND SEM TECHNIQUES

CHUN LIU[1,2] * , DENG CHEN[3]
[1] Architectural Engineering Institute, Zhejiang Guangsha College of Applied Construction Technology, Jinhua 322100, China
[2] College of Information and Mechanical and Electrical Engineering, Ningde Normal University, Ningde 352000, China
[3] College of Civil Engineering, Suzhou University of Science and Technology, Suzhou 215011, China

The internal structure has an important role in determining the properties of cementitious materials. Shrinkage reducing admixture (SRA) is often applied in concrete for reducing shrinkage, but there is little systematic work on the internal structure especially form the nano-scale. The internal structure characterizations of hardened cement paste containing SRA have experimental been investigated by the combined use of nanoindentation and SEM techniques. The results indicate that the utilization of SRA increases the volume fractions of porosity and unhydrated particles of hardened cement paste, but reduces the volume fractions of hydration products at 3 days, and however, with the increase of curing age to 28 days, the effect of SRA is reversed, and importantly, the utilization of SRA also increases the ratio of HD C-S-H to LD C-S-H. In addition, the internal microstructure is also improved due to the utilization of SRA.

Keywords: *shrinkage reducing admixture, internal structure, hardened cement paste, nanoindentation, SEM, C-S-H*

1. Introduction

In general, the crack of cementitious materials is hard to avert as its nature. With the increase of various shrinkages, the crack is further aggravated, which affects the safety and durability of practical concrete engineering. In order to reduce the shrinkage and cracking sensitivity of cementitious materials, some useful materials are selected to manufacture concrete from the perspective of optimal mix proportion such as fiber [1] and expansive agent [2]. However, the usages of fiber and expansive agent increase the cost of concrete production, and have great or degraded effect on other properties of concrete during reducing shrinkages. And especially, the useful effect of one type of fiber or expansive agent reducing shrinkage is limited to one or two type of shrinkages, which hinders their applications. At present, shrinkage reducing admixture (SRA) as one chemical admixture can effectively reduce various shrinkages of cementitious materials to lead to its widespread application [3]. SRA delays the hydration reaction of cement to result in the reduced early strengths, but improves the later hydration [4]. In addition, SRA can improve the durability of concrete such as permeability of chloride and resistance to freeze-thaw. Some degraded properties of concrete with SRA can be compensated by many approaches such as the combined utilization of SRA and other admixtures as well as different curing method [5, 6]. However, the mechanism of SRA on the concrete properties is not fully and systematically understood, which hinders its larger applications.

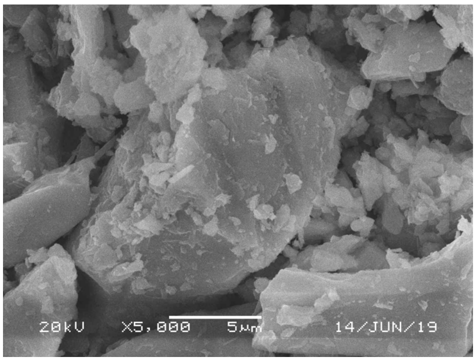
In general, the microstructure evolution plays an important role in determining the macroscopic properties of concrete [7]. In recent years, some mechanism of concrete properties is revealed from the perspective of the nanostructure variation by means of nanoindentation which further contributes to the guidance of cementitious material design [8]. The hardened cement paste mainly consists of unhydrated particles, porosity, calcium silicate hydrate (C-S-H), calcium hydroxide (CH) and other small amounts of hydration products. Each phase has its own nanomechanical properties which are not changed regardless of mix proportion, curing method and water-binder ratio [9]. Based on the different ranges of nanomechanical properties, C-S-H can be divided into high density C-S-H (HD C-S-H) and low density C-S-H (LD C-S-H). In addition, some results indicated that the third type of C-S-H was found, ultra high density C-S-H (UHD C-S-H) [10]. UHD C-S-H was mainly from cementitious materials at low water-binder ratio whose nanomechanical properties were similar with those of CH. However, there were also other reports which manifest that UHD C-S-H was false phase, only the composite of HD C-S-H and CH at low water-binder ratio, rather than a pure phase [11]. The different constituent phases have a great

---

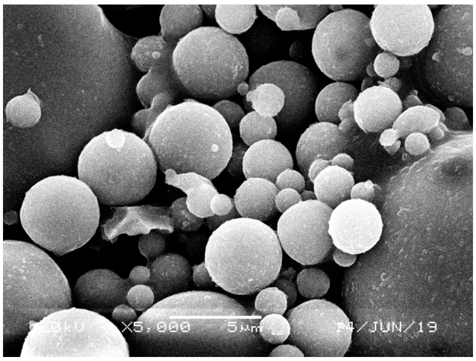
* Autor corespondent/*Corresponding author*,
E-mail: liuchun917@126.com

effect on the macroscopic properties of hardened cement paste. Raw materials used to prepare concrete especially mineral and chemical admixtures may cause the variation of constituent phases to lead to the change of properties of cementitious materials. Barbhuiya et al. [12] found that metakaolin transformed portlandite into C-S-H and changed the relative proportions of various C-S-H phases, which helped the understanding of mechanism of metakaolin on the properties. He et al. [13, 14] stated that lithium slag and rice husk ash increased the volume fraction of HD C-S-H. However, up to now, there is little information about the nanostructure of hardened cement paste containing SRA, which hinders the reveal of mechanism of SRA to further promote its application.

Based on the above discussion, in this work, the effect of SRA on nanostructure evolutions of hardened cement paste was investigated by using nanoindentation, and its microstructure variation was also determined through scanning electron microscope (SEM) technique. The results will contribute to understanding the mechanism of SRA on the properties of cementitious materials.



(a) Cement



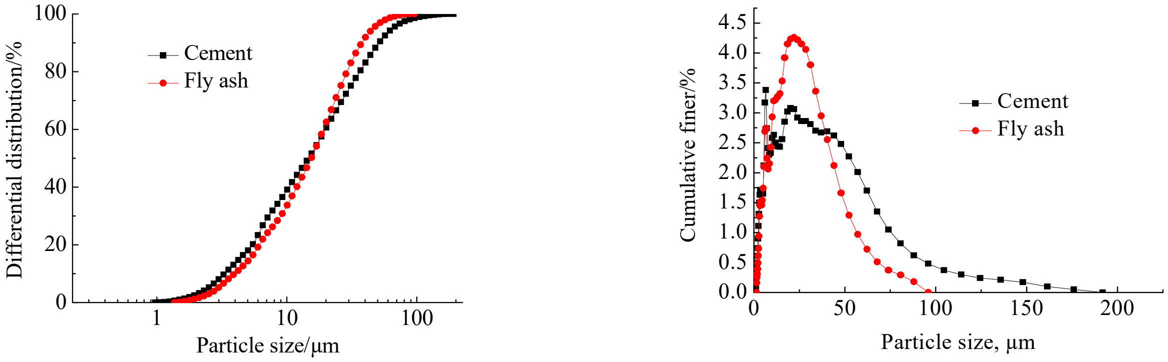
(b) Fly ash

Fig. 1 - SEM images of cement and fly ash.

Table 1

Chemical compositions of cement and fly ash (wt. %)

Type	SO_3	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2
Cement	2.33	22.32	3.17	4.85	62.56	1.23	0.35	0.07	0.31
Fly ash	0.62	50.77	6.23	27.32	8.01	1.45	1.31	0.42	1.32



(a) Grading curves

(b) Particle size distributions.

Fig.2 - Fineness of fly ash and cement.

2. Experimental

2.1 Materials

Cement used in this investigation was Portland cement which had the strength grade of P·O42.5 agreeing with Chinese standard GB 175-2007. Fly ash was from the thermal power plant as supplementary cementious material. The chemical compositions of cement and fly ash are obtained in Table 1. Their SEM images with the magnifications of 5000× are presented in Fig. 1. The shape of fly ash is smooth and globular, which can improve the workability of concrete, and however, the shape of cement is angular, which hinders the increase of fluidity. Meanwhile, the fineness of fly ash and cement is determined, shown in Fig. 2. As for the mean sizes, fly ash particles have smaller sizes than cement particles. Hence, fly ash used to replace cement in concrete can present micro filler effect due to the smaller sizes. SRA was from Jiangsu Bote Advanced Materials Co., Ltd in China, whose color was light yellow and surface tension was about 40mN/m.

2.2 Mix proportions

Two types of cement paste with fly ash were prepared. Fly ash was used to replace cement, and the content of fly ash was 20%. The water-binder ratio was 0.4. In order to investigate the effect of SRA on the internal structure evolutions of hardened cement paste, one type of cement paste contained SRA which accounted for 2% of the binder, and another type was without SRA as the control hardened cement paste.

2.3 Test methods

The cement paste was cast in the 40 mm self-made cube moulds at room temperature. After one day, the hardened cement paste was demoulded, and moved into the standard curing room with the temperature of (20±2) °C, and the relative humidity above 95% for different curing ages. As for the nanoindentation test, the hardened cement paste was firstly intercepted, and then cut into small samples. One about 10 mm cube small sample was carefully selected to embed in epoxy resin in vacuum. After that, the sample was grinded and polished for the checkout the roughness of surface. If the surface roughness did not match the requirement, the work of grind and polish had to be repeated. Finally, the sample meeting the roughness requirement was cleaned by using an ultrasonic bath for the nanoindentation test. One representative area was selected from the sample which contained a square grid of 10×10 indentions. The distance between any two indentations was constant which was 20μm. Other information and details of the nanoindentation test such as loading and unloading systems as well as the calculated expression were found in the published literature [15]. As for the SEM test, the hardened cement paste was firstly broken into small samples with the size of about 5mm after 28 days curing, and then, the representative sample was selected and its surface was sprayed by gold for the SEM test to determine the microstructure variation.

3. Results and discussions

3.1 Nanoindentation characteristics

After the nanoindentation test, the test data mainly containing indentation depth *h* and indentation load *P* of 100 indentation points are recorded. Some irregular curves of *h* with the change of *P* are discarded, based on which the abnormal elastic modulus of phase is obtained. The different constituent phases of hardened cement paste have a certain range of elastic modulus. It is well agreed that the ranges of elastic modulus of porosity, LD C-S-H, HD C-S-H, CH and unhydrated particle correspond to less than 14GPa, 14-24GPa, 24-35GPa, 35-50GPa and greater than 50GPa, respectively. UHD C-S-H is ignored due to the high water-binder ratio. According to the criterion, the typical *P-h* curves of different constituent phase in the hardened cement paste are obtained, presented in Fig. 3.

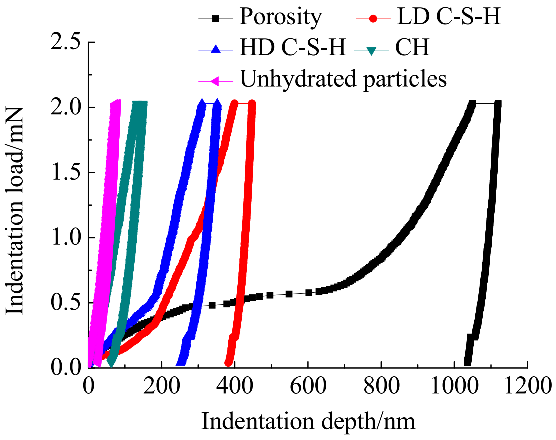
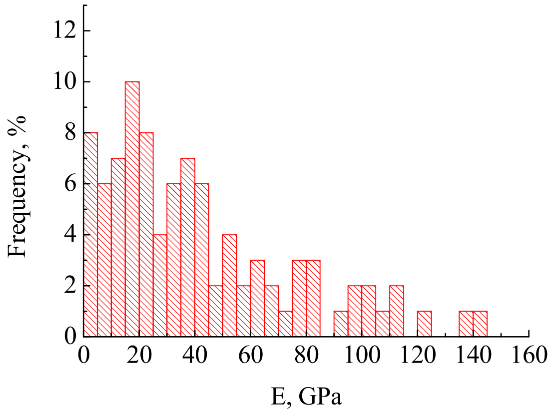
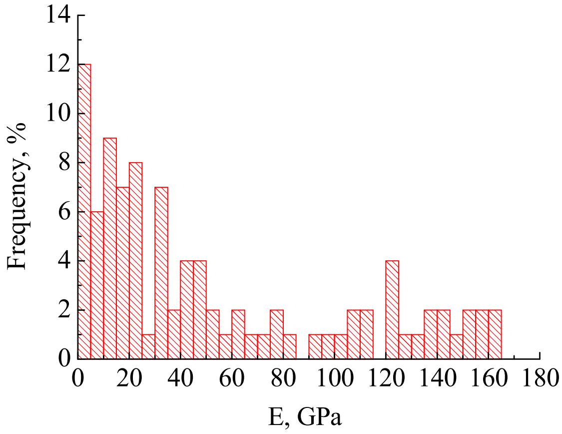


Fig.3 - Typical *P-h* curves of different constituent phases.



(a) Control hardened cement paste



(b) Hardened cement paste containing SRA

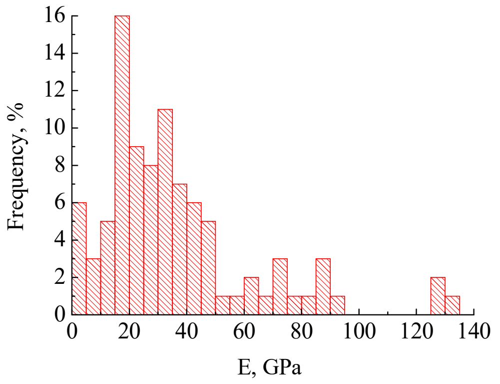
Fig.4 - Effect of SRA on frequency histogram of elastic modulus at 3 days.

According to the effective l *P-h* curves, elastic modulus of each indentation is obtained which corresponds to the single phase. The obtained elastic modulus of all effective

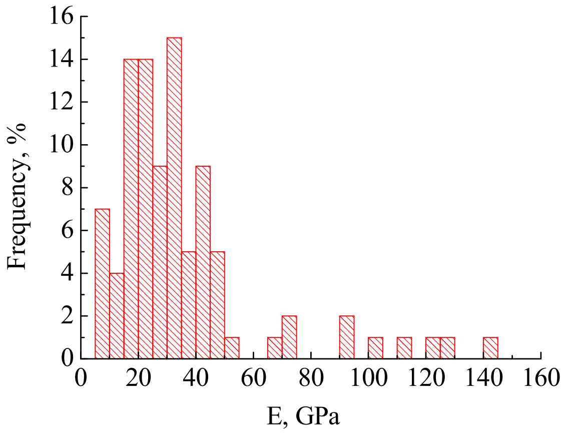
Table 2

Volume fractions of constituent phases in hardened cement paste (%)

Sample	Porosity	LD C-S-H	HD C-S-H	CH	Unhydrated particle
Control sample at 3 days	22.58	19.35	10.75	16.13	31.19
Sample containing SRA at 3 days	28.72	15.96	8.51	10.64	36.17
Control sample at 28 days	15.05	26.88	20.43	19.35	18.29
Sample containing SRA at 28 days	11.83	30.11	25.81	20.43	11.82



(a) Control hardened cement paste



(b) Hardened cement paste containing SRA

Fig.5 - Effect of SRA on frequency histogram of elastic modulus at 28 days.

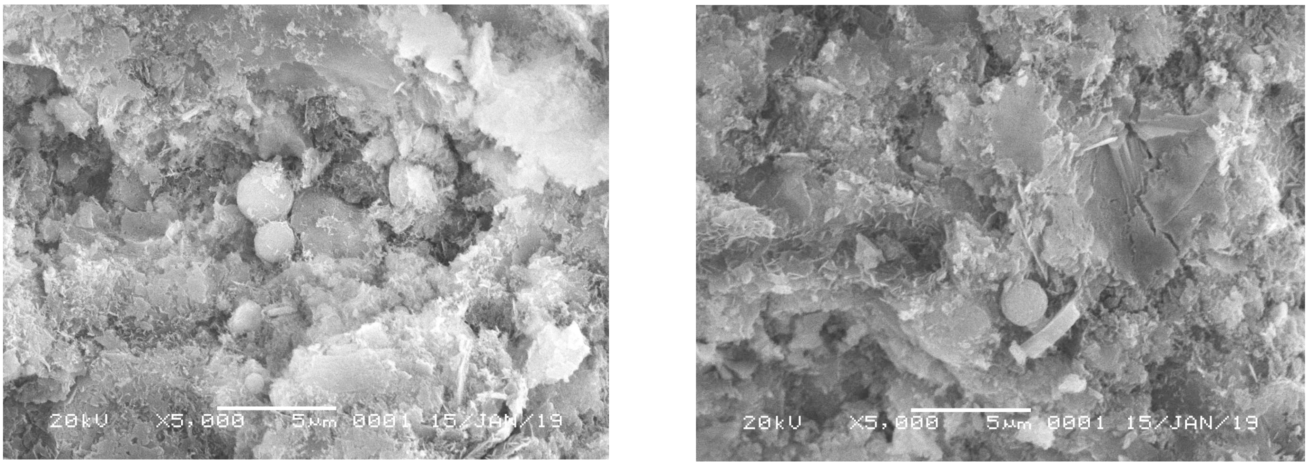
indentations is classified and analyzed, and the frequency histograms of elastic modulus of hardened cement paste containing SRA at 3 days and 28 days are presented in Fig.4 and Fig.5, respectively. The bin size of the histogram is constant, 5GPa. According to their own elastic modulus ranges of different constituent phases, the volume fractions of constituent phases in hardened cement paste containing SRA are determined by the results in Fig.4 and Fig.5, shown in Table 2.

It is observed that the volume fraction of unhydrated particles of the sample with SRA or without SRA at 3 days is maximum, followed by that of porosity, which indicates that the sample at 3 days has a low hydration degree. Compared with the control sample without SRA at 3 days, the sample with SRA has the higher volume fractions of porosity and unhydrated particles, and the lower volume fractions of LD C-S-H, HD C-S-H and CH. It is indicated that the utilization of SRA delays the hydration of cement paste at 3 days. In addition, the volume fraction of LD C-S-H is much greater than that of HD C-S-H of the sample regardless of SRA. The volume fractions of LD C-S-H in C-S-H (the sum of LD C-S-H and HD C-S-H) are similar between the samples with SRA and without SRA. Hence, C-S-H mainly exists in the form of LD C-S-H, and SRA has no obvious effect on the ratio of LD C-S-H to HD C-S-H at 3 days.

However, with the increase of curing ages, the volume fractions of constituent phases have great variations. Compared with the volume fractions of constituent phases of the samples at 3 days, the volume fractions of porosity and unhydrated particles are remarkably reduced of the samples at 28 days, and those of other constituent phases are increased, indicating that the hydration degree of the samples at 28 days is further increased. In addition, SRA reduces the volume fractions of porosity and unhydrated particles of the sample at 28 days, but increases the volume fractions of other constituent phases, which manifests that the utilization of SRA accelerates the hydration reaction of the sample and improves the internal structure. Meanwhile, LD C-S-H still accounts for the greater proportion of C-S-H of the samples at 28 days, and however, the volume fraction of HD C-S-H in C-S-H of the sample with SRA is slight greater than that of the control sample without SRA, manifesting that the utilization of SRA conduces to the increase of the ratio of HD C-S-H to LD C-S-H to improve the properties of cementitious materials containing SRA at 28 days.

3.2 SEM analysis

The microstructure of cementitious materials especially the dense condition has an important role in determining the variation of properties. The SEM technique is also one of effective methods for investigating the microstructure of cementitious materials [16, 17]. Hence, the SEM images of hardened cement paste without and with SRA at 28 days with the magnification of 5000× are determined, shown in Fig.6.



(a) Control hardened cement paste (b) Hardened cement paste containing SRA

Fig.6 - SEM images of hardened cement paste at 28 days.

It can be observed that the microstructure of hardened cement paste is mainly composed of unhydrated particles, various hydration products and pores with the different sizes as well as microcracks. SRA has a great effect on the microstructure of hardened cement paste at 28 days. As for the control hardened cement paste without SRA, some smooth and globular unhydrated fly ash can be still discovered, indicating the low hydration reaction, and some various hydration products with the different sizes and shapes mainly containing C-S-H and CH are overlapped to form the internal microstructure. However, there also exist capillary pores with the large sizes and air voids as well as microcracks, part of which are interconnected to form a passage. The internal microstructure of control hardened cement paste is divided into several separate pieces due to the passage. Compared with the control hardened cement paste, the hardened cement paste has a denser internal microstructure, which corresponds with the results of nanoindentation test. A little unhydrated fly ash is found, and a lot of hydration products are generated and overlapped each other. Some pores, air voids and microcracks are also discovered due to the high water-binder ratio, but their sizes are relatively small, especially which are disconnected and separate. Hence the denser internal microstructure is observed, indicating the utilization of SRA can improve the internal structure at 28 days.

4. Conclusions

In this work, the effect of SRA on the internal structure variation of hardened cement paste has experimentally been investigated by the combined use of nanoindentation and SEM techniques. The following conclusions can be obtained:

(1) C-S-H mainly exists in the form of LD C-S-H in the hardened cement paste from 3 days to 28 days. The utilization of SRA increases the volume fractions of porosity and unhydrated particles, but reduces the volume fractions of hydration products, and has no obvious effect on the ratio of LD C-S-H to HD C-S-H at 3 days. However, with the increase of curing age to 28 days, the utilization of SRA reduces the volume fractions of porosity and unhydrated particles, and increases the volume fractions of hydration products, and especially leads to the increase of the ratio of HD C-S-H to LD C-S-H.

(2) The utilization of SRA can improve the internal microstructure of hardened cement paste due to the accelerated hydration reaction at 28 days, which is in agreement with the results of nanoindentation test.

Acknowledgments:
The authors would like to acknowledge the Science and Technology Project of Fujian Education Department of China ((Grant No.JAT160531) for the financial support to the work present in this work.

REFERENCES

[1] F. Pelisser, A.B.S.S. Neto, H.L. La Rovere, R.C. de Andrade Pinto, Effect of the addition of synthetic fibers to concrete thin slabs on plastic shrinkage cracking, Construction and Building Materials, 2010, **24**(11), 2171.
[2] W. Sun, H. Chen, X. Luo, H. Qian, The effect of hybrid fibers and expansive agent on the shrinkage and permeability of high-performance concrete, Cement and Concrete Research, 2001, **31**(4), 595.
[3] D.Y. Yoo, N. Banthia, Y.S. Yoon, Effectiveness of shrinkage-reducing admixture in reducing autogenous shrinkage stress of ultra-high-performance fiber-reinforced concrete, Cement and Concrete Composites, 2015, **64**, 27.
[4] I. Mehdipour, K.H. Khayat, Effect of shrinkage reducing admixture on early expansion and strength evolution of calcium sulfoaluminate blended cement, Cement and Concrete Composites, 2018, **92**, 82.
[5] İ. Demir, Ö. Sevim, E. Tekin, The effects of shrinkage-reducing admixtures used in self-compacting concrete on its strength and durability, Construction and Building Materials, 2018, **172**, 153.
[6] P. Zhan, Z. He, Application of shrinkage reducing admixture in concrete: A review, Construction and Building Materials, 2019, **201**, 676.

[7] C. Medina, M. Frías, M.I.S. De Rojas, Microstructure and properties of recycled concretes using ceramic sanitary ware industry waste as coarse aggregate, Construction and Building Materials, 2012, **31**, 112.

[8]F. Sanchez, K. Sobolev, Nanotechnology in concrete-a review, Construction and Building Materials, 2010, 24(11), 2060.

[9] C. Hu, Z. Li, A review on the mechanical properties of cement-based materials measured by nanoindentation, Construction and Building Materials, 2015, **90**, 80.

[10] Z. Luo, W. Li, K. Wang, S.P. Shah, Research progress in advanced nanomechanical characterization of cement-based materials, Cement and Concrete Composites, 2018, **94**, 277.

[11] J.J. Chen, L. Sorelli, M. Vandamme, F.J. Ulm, G. Chanvillard, A Coupled nanoindentation/SEM-EDS study on low water/cement ratio Portland cement paste: evidence for C-S-H/Ca(OH)$_2$ nanocomposites, Journal of the American Ceramic Society, 2010, **93**(5), 1484.

[12] S. Barbhuiya, P.L. Chow, S. Memon, Microstructure, hydration and nanomechanical properties of concrete containing metakaoli, Construction and Building Materials, 2015, **95**, 696.

[13] Z. He, C. Qian, S. Du, M. Huang, Nanoindentation Characteristics of Cementitious Materials Containing Lithium Slag, Nanoscience and Nanotechnology Letters, 2017, **9**(2), 155.

[14] Z. He, C. Qian, S. Du, M. Huang, M. Xia, Nanoindentation characteristics of cement paste and interfacial transition zone in mortar with rice husk ash, Journal of Wuhan University of Technology-Materials Science Edition, 2017, **32**(2), 417.

[15] Z.H. He, C.X. Qian, Y. Zhang, F. Zhao, Y.B. Hu, Nanoindentation characteristics of cement with different mineral admixtures, Science China Technological Sciences, 2013, **56**(5), 1119.

[16] R.D. Moser, P.G. Allison, M.Q. Chandler, Characterization of impact damage in ultra-high performance concrete using spatially correlated nanoindentation/SEM/EDX, Journal of materials engineering and performance, 2013, **22**(12), 3902.

[17] W. Wilson, J.M. Rivera-Torres, L. Sorelli, A. Durán-Herrera, A. Tagnit-Hamou, The micromechanical signature of high-volume natural pozzolan concrete by combined statistical nanoindentation and SEM-EDS analyses, Cement and Concrete Research, 2017, **91**, 1.

***

MANIFESTĂRI ȘTIINȚIFICE / SCIENTIFIC EVENTS

The 2nd International Conference on Construction Materials for a Sustainable Future (CoMS_2020)

15-17 April 2020, Bled, Slovenia

The conference is organized by ZAG - the Slovenian National Building and Civil Engineering Institute alongside co-organizing institutions the University of Zagreb, Faculty of Civil Engineering, the University of Novi Sad, Faculty of Technical Science, and the BAM - Federal Institute for Materials Research and Testing.
The scope of the conference is to address the importance of sustainable development for our future wellbeing, given that the building and construction sector is one of the main contributors to climate change. Authors of scientific and technical papers researching these issues are invited to present their achievements.

The primary goals of the CoMS conference are to bring together scientists and experts in the field of construction materials and other areas of civil engineering, and give them the opportunity to present the results of their research, findings and innovations. The CoMS conference will focus on building stronger and more equitable partnerships in order to develop innovative, practical and durable solutions necessary for building a sustainable future.

Authors wishing to present their papers are kindly invited to submit an abstract in accordance with the following themes and topics:

- Innovations in materials and technologies
- Material – environment interaction
- Sustainable design, construction and maintenance
- Energy efficiency, recycling, and remediation
- Inspection, monitoring, assessment and repair
- Modelling from nano to structure
- Innovative components for a healthy, comfortable and sustainable environment
- Social and economic aspects of the building environment
- Digitalization and automation

Contact: http://coms.zag.si/

***