

PAPER • OPEN ACCESS

Mechanical properties and microstructure of nano-ZrO₂ reinforced cementitious composites

To cite this article: Shichao Lu *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **490** 022070

View the [article online](#) for updates and enhancements.

Mechanical properties and microstructure of nano-ZrO₂ reinforced cementitious composites

Shichao Lu, Xiaoyan Wang, Yangchuan Ke*

Nanochemistry Key Laboratory of China National Petroleum Corporation, College of Science, State Key Lab of Heavy Oil Processing, China University of Petroleum, Beijing, China

*Corresponding author e-mail: kyc06@sohu.com

Abstract. A series of nano-ZrO₂ reinforced cementitious composites were prepared through mixing prepared nano-ZrO₂ suspension with Class G oil well cement in rotary mixer. The rheological properties of cement slurry, the mechanical properties and microstructure of cementitious composites were studied. The results indicated that the addition of nano-ZrO₂ below 1 wt% meet the requirements of cementing construction. The early compressive strength of cement stone for 1 day was about 35.6 MPa~41.8 MPa when the amount of nano-ZrO₂ was 0.05 wt%~1 wt%. The elastic modulus of nano-ZrO₂ cement stone was 8.14 GPa under uniaxial stress state. Microstructure analysis revealed that nano-ZrO₂ could enhance the toughness of cement paste.

1. Introduction

In the field of petroleum engineering, with the continuous improvement of the requirements of modern cementing engineering, the existing cement-based materials have defects such as large brittleness and low strength, which limit the further application of cement-based materials [1]. The impact of these defects on engineering quality is more and more prominent, and it has been unable to meet the requirements of cementing engineering [2]. Therefore, the development of new cement-based materials is the key to solve this problem.

Nanomaterials [3], as one of the promising materials, have opened up broad application prospects in national defense [4], electronics [5], chemical industry [6], medicine [7] and other fields [8]. Based on the special properties of nanomaterials and the continuous development of cementing field, the introduction of nanomaterials into the cementing field has become a trend [9]. As to nano-SiO₂ [10], nano-TiO₂ [11], and so on, poor dispersion results in the formation of some defect sites in the nanocomposite and limits the efficiency in the matrix. Nano-ZrO₂ is an inorganic non-metallic material with corrosion resistance, high temperature resistance and wear resistance [12]. Due to its own nano-effect and phase change effect, it is of great significance to apply nano-ZrO₂ to enhance the fracture toughness of cement-based materials [13].

In this paper, the nano-ZrO₂ suspension with different additions was mixed into oil well cement. The mechanical property tests of nano-ZrO₂ cementitious composites were performed. The effects of different nano-ZrO₂ contents on the rheological properties and compressive strength of cement-based composites were investigated, and the uniaxial mechanical properties of cement-based composites specimens were carried out. Furthermore, the microstructure was characterized by means of scanning electron microscope. The strengthening and toughening mechanism of composites was also analyzed.



2. Materials and methods

2.1. Materials

Class G oil well cement were obtained from Sichuan Jiahua cement plant in China. Nano-ZrO₂ was purchased from Beijing DK Nano Technology Co., Ltd. Dispersing agent DRS-1S was supplied by China National Petroleum Corporation Drilling Research Institute. The experimental water was tap water.

2.2. Preparation and Characterization of nano-ZrO₂ reinforced cementitious composites

The cement composite samples were prepared through mixing prepared nano-ZrO₂ suspension with Class G oil well cement in rotary mixer. A water to cement ratio (w/c) of 0.44 was used in all samples. The sample preparation, rheological properties and compressive strength test used in this paper mainly referred to ASTM C349, ASTM C305, GB/T 10238-2015, GB/T 19139-2012 standards. Uniaxial mechanical experiments were performed by TAW-1000 microcomputer controlled electro-hydraulic servo cement triaxial pressure testing machine (Changchun Chaoyang Test Instrument Co., Ltd.). Three replications of each test were conducted and average values were reported. The microstructure of the cement composites was characterized by scanning electron microscope S-4800 (Hitachi, Japan).

3. Results and Discussion

3.1. The influence of nano-ZrO₂ on the rheological properties of cement slurry

Nano-ZrO₂ and DRS-1S were pre-dispersed in the experiment to prepare nano-ZrO₂ suspension. The rheological properties of cement slurry system with different additions of nano-ZrO₂ were measured by the six-speed rotational viscometer at 25 °C. The results are shown in Table 1.

1[#]: Class G oil well cement + 0.2 wt% DRS-1S + 44% water cement ratio

2[#]: Class G oil well cement + 0.2 wt% DRS-1S + 0.025 wt% nano-ZrO₂ + 44% water cement ratio

3[#]: Class G oil well cement + 0.2 wt% DRS-1S + 0.05 wt% nano-ZrO₂ + 44% water cement ratio

4[#]: Class G oil well cement + 0.2 wt% DRS-1S + 0.10 wt% nano-ZrO₂ + 44% water cement ratio

5[#]: Class G oil well cement + 0.2 wt% DRS-1S + 0.50 wt% nano-ZrO₂ + 44% water cement ratio

6[#]: Class G oil well cement + 0.2 wt% DRS-1S + 1.0 wt% nano-ZrO₂ + 44% water cement ratio

Table 1. The influence of nano-ZrO₂ on the rheological properties of cement slurry.

Number	Nano-ZrO ₂ content (wt%)	Density (g/cm ³)	Shear stress values	<i>n</i>	<i>K</i> (Pa·s)
1 [#]	0.00	1.90	96/75/61/47/25/20	0.43	2.70
2 [#]	0.025	1.90	63/49/35/20/11/5	0.82	0.15
3 [#]	0.05	1.90	70/53/41/29/15/14	0.55	0.88
4 [#]	0.25	1.90	72/57/44/35/21/15	0.44	1.83
5 [#]	0.50	1.90	81/61//47/39/27/10	0.41	2.46
6 [#]	1.0	1.90	85/63/52/40/24/19	0.41	2.44

Note: *n* is the flow index, and *K* (Pa·s) is the consistency coefficient.

It can be seen from Table 1 that the effect of nano-ZrO₂ on the fluidity of the cement slurry is not obvious. With the increase of the amount of nano-ZrO₂, the flow index of the cement slurry decreases first and then basically remains constant, and the consistency coefficient increases slowly. The addition of nano-ZrO₂ is less than 1.0 wt%, which can meet the engineering performance of cement slurry. Nano-ZrO₂ is not involved in the hydration reaction during cement hydration process, but excessive nano-ZrO₂ tends to increase the amount of adsorbed water due to its high specific surface area, making the cement slurry thicker and rheological property worse.

3.2. The influence of nano-ZrO₂ on the early compressive strength of cement stone

The compressive strength test was carried out after the nano-ZrO₂ reinforced cementitious composites were cured at 80 °C for 1 day. The experimental results are displayed in Figure 1. With the increase of nano-ZrO₂, the compressive strength of cement stone is slowly developed. The nano-ZrO₂ content is 0.05 wt%~1 wt%, the compressive strength is about 35.6 MPa~41.8 MPa, and when the amount is 1 wt%, the compressive strength is increased by about 10% compared with pure cement. This indicates that nano-ZrO₂ has relatively little influence on the early compressive strength. It may be because in the early stage of cement hydration, the cement slurry is not hydrated sufficiently and the bonding force between nano-ZrO₂ and cement stone matrix is insufficient.

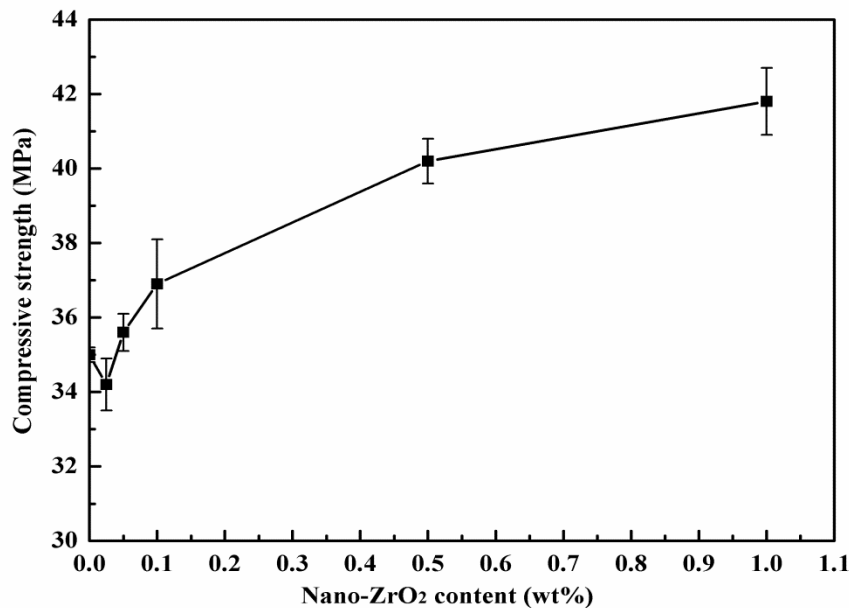


Figure 1. The compressive strength of cementitious stone containing nano-ZrO₂ after 1 day curing.

3.3. Uniaxial mechanical properties of nano-ZrO₂ reinforced cementitious composites

The 1.0 wt% nano-ZrO₂ cement stone sample (named as sample Z) was cured in a water bath at 80 °C for 2 days, and the uniaxial mechanical properties of the nano-modified cement stone were tested. The pure cement (named as sample P) was used as a comparative sample. The experimental results are shown in Table 2. The elastic modulus and Poisson's ratio in Table 2 are taken near the value of strain 1 of 2%, and in Figure 2, the stress-strain curve and the deformation curve of cement paste are given. The elastic modulus of nano-ZrO₂ cement stone under the uniaxial stress state is 8.14 GPa, which is 8.5% lower than that of pure cement. The peak strength of the nano-ZrO₂ cement stone is also decreased, and the elastic deformation interval is not significantly different from that of pure cement. Because nano-ZrO₂ has the effect of inducing cement hydration products, the hydrated product hydrated calcium silicate (C-S-H) gel is increased, thereby improving the plasticity of the cement stone, and dispersing a part of the energy when damaged, so as to achieve the toughening effect. Therefore, the nano-ZrO₂ acts as the toughening effect on the cement stone, and reduces the elastic modulus of the cement stone.

Table 2. Experimental results of uniaxial mechanical properties.

Sample	Lithology	Confining pressure (MPa)	Poisson's ratio	Elastic modulus (GPa)	Peak strength (MPa)
Z	Cement stone	0.1	0.28	8.14	35.4
P	Cement stone	0.1	0.21	8.90	35.9

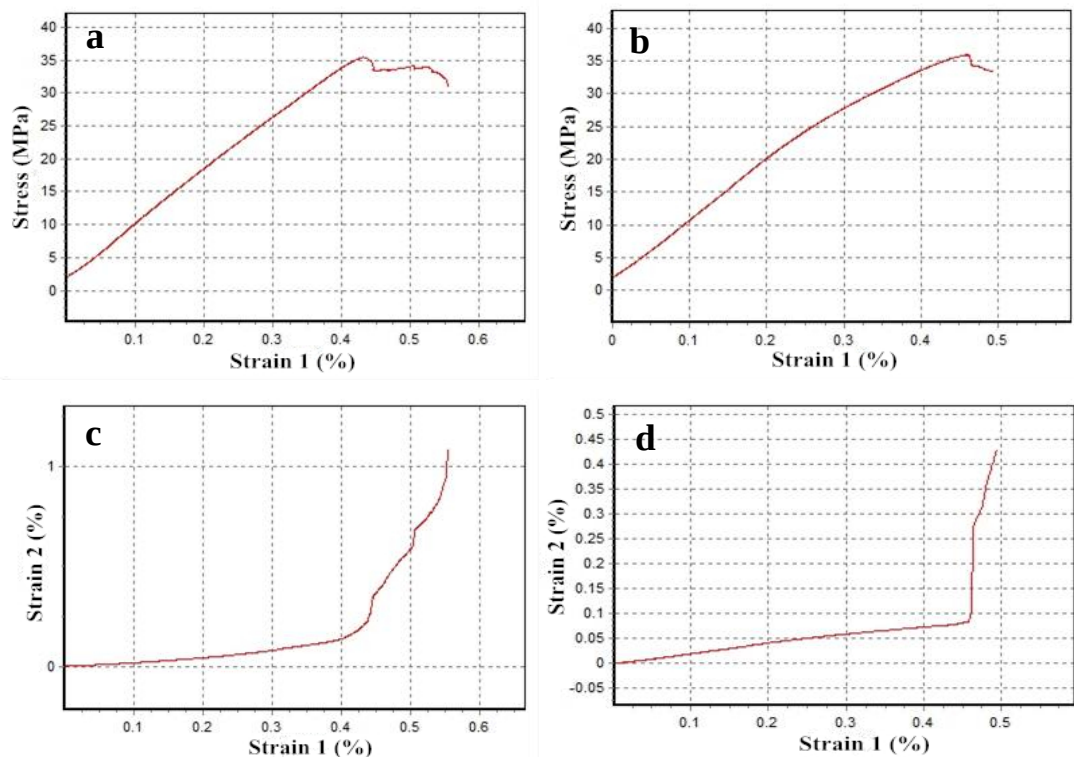


Figure 2. Images of uniaxial mechanical properties of cement stone.

- (a. 1 wt% nano-ZrO₂ cement stone stress-strains curve; b. pure cement stone stress-strains curve; c. 1 wt% nano-ZrO₂ cement stone strain2-strain1 curve; d. pure cement stone strain2-strain1 curve)

3.4. The microstructure and mechanism of nano-ZrO₂ modified cementitious composites

The morphology of nano-ZrO₂ reinforced cementitious composites with a nano-ZrO₂ addition of 1.0 wt% after 7 days curing are shown in Figure 3. From the picture, it can be seen that the hydration product grows very vigorously when 1.0 wt% nano-ZrO₂ is added, and the hydrated product C-S-H, which is strip-like and needle-like, is mostly intertwined into a network, forming a relatively complete hydrate system. Since the atom on the surface of the nano-ZrO₂ has high activity, it can induce the hydration product as the core to form more hydration products, thereby improving the compressive strength of the cementitious composites. At the same time, strip-like and needle-like hydration products can play a bridging role when damaged by external forces, which makes nano-ZrO₂ have a certain toughening effect on cement.

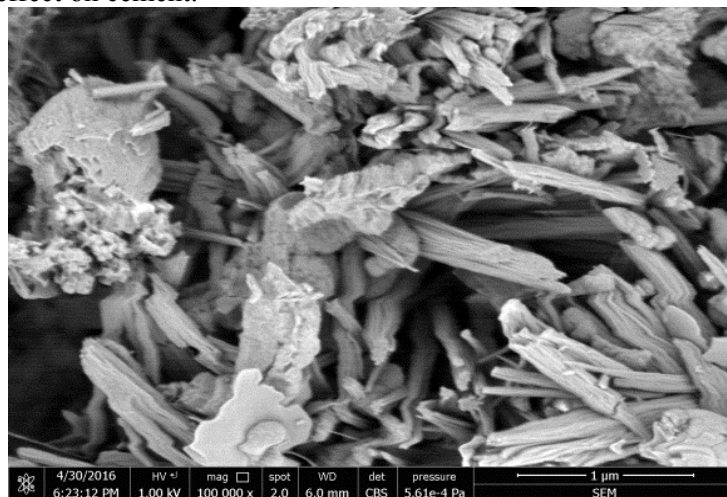


Figure 3. SEM photographs of the cement stone containing nano-ZrO₂.

4. Conclusion

Nano-ZrO₂ suspension with different content was added to the Class G oil well cement to carry out the rheological properties test of cement slurry and the mechanical properties experiment of cement stone. The rheological properties of cement slurry show that the addition of nano-ZrO₂ has relatively little influence on the fluidity of cement slurry, and the addition of nano-ZrO₂ below 1 wt% can meet the requirements of cementing construction. The mechanical properties experiment of cement stone indicate that the early compressive strength for 1 day is approximately 35.6 MPa~41.8 MPa when the amount of nano-ZrO₂ is 0.05 wt%~1 wt%, which is higher than that of pure cement. The elastic modulus of nano-ZrO₂ cement stone is 8.14 GPa and is 8.5% lower than pure cement stone under uniaxial stress state. Microscopic analysis reveals that nano-ZrO₂ can induce hydration products in cement slurry through nano-nucleation effect, promote the formation of hydrated products such as calcium silicate (C-S-H), and enhance the toughness of cement stone.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Grant No. 51674270), Major Project of the National Natural Science Foundation of China (No.51490650), National Science and Technology Major Project (2017ZX05009-003) and the Foundation for Innovative Research Groups of the National Natural Science Foundation of China (Grant: No. 51521063).

References

- [1] Joey Dacula Mangadlao, Pengfei Cao, Rigoberto C. Advincula. Smart cements and cement additives for oil and gas operations [J]. Journal of Petroleum Science and Engineering, 129 (2015) 63-76.
- [2] Yuanguang Yang, Bin Yuan, Qinliang Sun, Xin Tang, Xie Yingquan. Mechanical properties of EVA-modified cement for underground gas storage [J]. Journal of Natural Gas Science and Engineering, 27 (2015) 1846-1851.
- [3] Tianbin Wu, Yangchuan Ke. Preparation of silica-PS composite particles and their application in PET [J]. European Polymer Journal, 42 (2006) 274-285.
- [4] Ang Wei, Liuhua Pan, Wei Huang. Recent progress in the ZnO nanostructure-based sensors [J]. Materials Science and Engineering: B, 176 (2011) 1409-1421.
- [5] Wei Wu. Inorganic nanomaterials for printed electronics: a review [J]. Nanoscale, 9 (2017) 7342-7372.
- [6] Xu Hu, Yangchuan Ke, Yi Zhao, Shichao Lu, Chengcheng Yu, Fangfang Peng. Synthesis and characterization of a β -cyclodextrin modified polyacrylamide and its rheological properties by hybridizing with silica nanoparticles [J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 548 (2018) 10-18.
- [7] Shabir Hassan, Gyan Prakash, et al. Evolution and clinical translation of drug delivery nanomaterials [J]. Nano Today, 15 (2017) 91-106.
- [8] Michael K. Riley II, Wilfred Vermerris. Recent advances in nanomaterials for gene delivery--a review [J]. Nanomaterials, 7 (2017) 94.
- [9] Shilang Xu, Jintao Liu, Qinghua Li. Mechanical properties and microstructure of multi-walled carbon nanotube-reinforced cement paste [J]. Construction and Building Materials, 76 (2015) 16-23.
- [10] Sattawat Haruehansapong, Tawich Pulngern, Somchai Chucheeepsakul. Effect of the particle size of nanosilica on the compressive strength and the optimum replacement content of cement mortar containing nano-SiO₂ [J]. Construction and Building Materials, 50 (2014) 471- 477.
- [11] Bandu Madhukar Kale, Jakub Wiener, et al. Coating of cellulose-TiO₂ nanoparticles on cotton fabric for durable photocatalytic self-cleaning and stiffness [J]. Carbohydrate Polymers, 150 (2016) 107-113.
- [12] U Schulz, M Peters, Fr.-W Bach, G Tegeder. Graded coatings for thermal, wear and corrosion barriers [J]. Materials Science and Engineering: A, 362 (2003) 61-80.

- [13] Sarmad.I.Ibrahim, Alaa.A.Abdul Hameed, Farhad. M. Othman. Studying the Effect of Nano Additives and Coating on Some Properties of Cement Mortar Mixes [J]. Engineering and Technology Journal, 34 (2016) 553-566.