Mechanical properties and microstructure of nano-ZrO$_2$ reinforced cementitious composites

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Abstract. A series of nano-ZrO$_2$ reinforced cementitious composites were prepared through mixing prepared nano-ZrO$_2$ 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-ZrO$_2$ 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-ZrO$_2$ was 0.05 wt%~1 wt%. The elastic modulus of nano-ZrO$_2$ cement stone was 8.14 GPa under uniaxial stress state. Microstructure analysis revealed that nano-ZrO$_2$ 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-SiO$_2$ [10], nano-TiO$_2$ [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-ZrO$_2$ 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-ZrO$_2$ to enhance the fracture toughness of cement-based materials [13].

In this paper, the nano-ZrO$_2$ suspension with different additions was mixed into oil well cement. The mechanical property tests of nano-ZrO$_2$ cementitious composites were performed. The effects of different nano-ZrO$_2$ 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.

| Number | Nano-ZrO₂ content (wt%) | Density (g/cm³) | Shear stress values | n | K (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-ZrO\textsubscript{2} on the early compressive strength of cement stone

The compressive strength test was carried out after the nano-ZrO\textsubscript{2} reinforced cementitious composites were cured at 80 °C for 1 day. The experimental results are displayed in Figure 1. With the increase of nano-ZrO\textsubscript{2}, the compressive strength of cement stone is slowly developed. The nano-ZrO\textsubscript{2} 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-ZrO\textsubscript{2} 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-ZrO\textsubscript{2} and cement stone matrix is insufficient.

![Figure 1. The compressive strength of cementitious stone containing nano-ZrO\textsubscript{2} after 1 day curing.](image)

3.3. Uniaxial mechanical properties of nano-ZrO\textsubscript{2} reinforced cementitious composites

The 1.0 wt% nano-ZrO\textsubscript{2} 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-ZrO\textsubscript{2} 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-ZrO\textsubscript{2} cement stone is also decreased, and the elastic deformation interval is not significantly different from that of pure cement. Because nano-ZrO\textsubscript{2} 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-ZrO\textsubscript{2} 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.](table)

| 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-ZrO$_2$ cement stone stress-strains curve; b. pure cement stone stress-strains curve; 
c. 1 wt% nano-ZrO$_2$ cement stone strain2-strain1 curve; d. pure cement stone strain2-strain1 curve)

3.4. The microstructure and mechanism of nano-ZrO$_2$ modified cementitious composites

The morphology of nano-ZrO$_2$ reinforced cementitious composites with a nano-ZrO$_2$ 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-ZrO$_2$ 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-ZrO$_2$ 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-ZrO$_2$ have a certain toughening effect on cement.

Figure 3. SEM photographs of the cement stone containing nano-ZrO$_2$. 
4. Conclusion

Nano-ZrO$_2$ 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-ZrO$_2$ has relatively little influence on the fluidity of cement slurry, and the addition of nano-ZrO$_2$ 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-ZrO$_2$ is 0.05 wt%–1 wt%, which is higher than that of pure cement. The elastic modulus of nano-ZrO$_2$ cement stone is 8.14 GPa and is 8.5% lower than pure cement stone under uniaxial stress state. Microscopic analysis reveals that nano-ZrO$_2$ 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.

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