The Strength and Microstructure Properties of Oil Well Cement with Halloysite Nanotube

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Abstract. Halloysite nanotube has attracted more and more attention to reinforce cement for its excellent physical properties and chemical composition. In this study, effects of halloysite nanotube on compressive strength, flexural strength, micro-structure and hydration products of oil well cement were investigated. The results show that the compressive and flexural strength of cement with 3% halloysite nanotube was increased by 35.2% and 38.5%, and the porosity decreased by 14.95%, respectively. Based on the results of SEM and MIP, the following conclusions can be obtained. Halloysite nanotube promoted the hydration process because of its high surface area, filled in the pores of hardened cement paste for the nano size and expansion process, and formed cross-linking structure for the tube-like appearance, all of which lead to denser micro-structure and better strength performance of oil well cement eventually.

Keywords. Halloysite nanotube; Cement; Compressive strength; Flexural strength; Pore structure

1. Introduction

In the field of petroleum engineering, cementing is to pump slurries to seal the annular of formation and casing. Cementing is an important link between well drilling and petroleum exploration, and its quality directly affects the life and production efficiency of petroleum wells. With the development of petroleum engineering, cementing technology is facing more and more challenges. Below the ground, the environment is harsh, such as external forces, high temperature and high pressure, which may break the seal of the cement ring [1-3]. Cement composites have relative low flexural strength and bad toughness, which are unable withstand the harsh environment. Hence, the enhancement of mechanical properties of oil well cement is important and necessary. In the engineering process, enhancement materials are usually incorporated, such as fiber, latex powder, whisker, nano-materials, etc [4-6]. Halloysite nanotube has attracted more and more attention for its nano size, tube-like morphology and high surface area. The cost of halloysite nanotube is low and widespread in nature [7-8]. Physically, halloysite nanotube is a kind of long multi-walled tubules like carbon nanotube curly formed by halloysite nano-layers, which can be utilized to increase the mechanical properties of cement matrix. Halloysite nanotube has the chemical stoichiometry of Al₄[Si₄O₁₀][(OH)₄]·4H₂O. And the main structure unit of inner surface of halloysite nanotube is aluminium-oxygen octahedron while that of outer surface core is silicon-oxygen tetrahedron, which has similar properties with SiO₂. Halloysite nanotube may be both useful to enhance the mechanical properties of cementitious composites from a physical and chemical point of view [9-10]. In the present study, the strength properties of oil well cement with different dosage of halloysite nanotube were investigated. In addition, MIP, XRD and
SEM were utilized to explore the pore structure and hydration products.

2. Experimental

2.1. Materials
Class G oil well cement from Jiahua Co. Ltd., Sichuan province were used and chemical compositions of the cement are shown in table 1. Halloysite nanotube (HNT) was provided by Nanyu material Co. Ltd., Hebei province. The diameter of halloysite nanotube is 20-60 nm, and the length is 0.8-2 μm, of which the transmission electron microscope morphology is shown in figure 1. A kind of dispersant was used to ensure the fluidity of oil well cement pastes.

![Figure 1. TEM morphology of halloysite nanotube.](image)

Table 1. Chemical compositions of class G oil well cement.

| SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | K$_2$O | SO$_3$ | MnO$_2$ | Loss on ignition |
|--------|------------|------------|-----|-----|--------|--------|---------|-----------------|
| 22.6   | 3.38       | 4.81       | 65.4| 0.7 | 0.35   | 1.20   | 0.1     | 0.22            |

2.2. Preparation of Cement Slurries
Cement pastes were mixed based on the Chinese standard GB/T 19139-2012. Halloysite nanotube was firstly dry mixed for 20 min with oil well cement before preparing pastes. To explore the influence of halloysite nanotube on the properties of cement pastes, five cement samples containing 0, 1, 2, 3 and 4% halloysite nanotube were respectively prepared (table 2). The prepared cement pastes were cured in appropriate molds at 90 °C condition for different ages. The molds of 50.8*50.8*50.8 mm$^3$ and 40*40*160 mm$^3$ were used for compressive and flexural strength testing.

2.3. Testing of Strength and Microstructure
The compressive strength was measured by a domestic hydraulic testing machine. The flexural properties were tested by using a motorized 3-point-bending tester. Four repeated tests were done for each sample. Scanning electron microscopy (SEM, HITACHI SU8010, Japan) was utilized to see the microstructure of cement with halloysite nanotube. The SEM samples about 5mm×5mm×2mm size were prepared from fragments after the strength test. X-ray diffraction (XRD, BRUKER D8 ADVANCE, German) was used to compare the crystal phase composition of the halloysite nanotube cement samples with a scanning rate of 0.02s$^{-1}$ in a 2θ range of 10-60° after 28 days curing. Mercury intrusion porosimetry (MIP, QUANTA PoreMaster-60, USA) was utilized to measure the pore structure and pore size distribution of halloysite nanotube cement. The fragment sample of about 1 cm size should be vacuum dried before MIP test.
3. Results and Discussion

3.1. Flowability of HNT Cement
The purpose of the study is to determine the applicability of halloysite nanotube in oil well cement and the flowability of samples is firstly investigated. As seen in figure 2, results showed that flowability of samples containing halloysite nanotube decreased as the dosage of nanotube was increased. The probable reason for the results is that the halloysite nanotube possess high surface area which needed more water to lubricate the surface. 1-3% of the nanotubes can be applied in oil well cement as the flowability should be larger than 18 cm in order to meet the requirement of cement engineering.

![Figure 2. Flowability of blank, H1, H2, H3 and H4 samples](image)

**Table 2.** Mix recipe of blended cement samples (mass%).

| Sample | Cement | Water | Dispersant | HNT |
|--------|--------|-------|------------|-----|
| Blank(C) | 100 | 44 | 0.3 | 0 |
| H1 | 99 | 44 | 0.3 | 1 |
| H2 | 98 | 44 | 0.3 | 2 |
| H3 | 97 | 44 | 0.3 | 3 |
| H4 | 96 | 44 | 0.3 | 4 |

3.2. Strength Properties of HNT Cement
Figure 3 and table 3 show the compressive strength and flexural strength of the blank, H1, H2, H3 and H4 samples under the different aging time. The results show that the addition of 2-3% halloysite nanotube was more effective in enhancing the mechanical properties comparing blank samples. After curing 3, 7 and 28 days, the compressive strength of H3 was increased by 42%, 30.6% and 35.2%, and the flexural strength of H3 was increased by 53.1%, 34.5% and 38.5%, respectively. The above results indicate that incorporation of halloysite nanotube can improve the strength properties of oil well cement obviously. The main factors affecting the strength properties of oil well cement mainly include microstructure and crystal compositions. In the following parts, the enhancing mechanism of HNT would be discussed.
Figure 3. Compressive and flexural strength of the blank, H1, H2, H3 and H4 samples curing at 3, 7 and 28 days: (a) compressive strength; (b) flexural strength.

Table 3. Compressive and flexural strength of the blank, H1, H2, H3 and H4 samples curing at 3, 7 and 28 days.

| Sample | Compressive strength | Flexural strength |
|--------|----------------------|------------------|
|        | 3 days | 7 days | 28 days | 3 days | 7 days | 28 days |
| Blank(C) | 26.4±1.1 33.6±0.6 38.9±1.5 | 4.1±0.5 5.8±0.5 7.1±0.6 |
| H1     | 33.5±0.8 38.1±1.0 43.2±1.3 | 4.9±0.6 6.5±1.0 8.3±1.1 |
| H2     | 36.1±1.5 42.4±1.2 48.9±0.7 | 5.8±0.9 7.0±0.7 9.3±0.9 |
| H3     | 37.5±1.2 43.9±0.6 52.6±1.9 | 6.2±1.2 7.8±0.9 9.8±1.0 |
| H4     | 35.2±0.9 40.3±2.8 45.9±2.0 | 5.5±0.8 6.7±1.1 8.9±1.3 |

3.3. SEM of HNT Cement
The mechanical properties of cement are determined by the micro-structures, SEM of blank cement and cement with 3% HNT at different ages were shown and compared in figure 4. According to the results, the blank cement had loose structure, in which obvious pores can be seen. In addition, high amount of hydration products and net-work structure can be observed in H3 cement samples. It can be concluded that adding halloysite nanotubes can lead to a more compact microstructure of hardened cement paste and the probable reasons are drawn. At first, the nanosized halloysite nanotube can fill up many voids in hardened cement pastes [11]. Second, high activity of halloysite nanotube may improve the hydration process to generate more hydration products and SiO₂ and Al₂O₃ on the surface halloysite nanotube may exert pozzolanic effects to convert part of calcium hydroxide into hydrated calcium silicate [10]. Third, the halloysite nanotube acts as an inorganic reinforcing phase like fiber reinforcement to form net-work structure [12]. At last, expansion of halloysite nanotube may happen as there is some water contained between the layers of the tube and furtherly fill up in different size pores of hardened cement paste [10].
Figure 4. SEM of blank cement (a) and H3 cement (b) samples at 3, 7 and 28 days.

3.4. Pore Structure of HNT Cement

Pores in cement matrix are detrimental for its strength properties. The pore structures and parameters of the blank cement and cement reinforced with 3% HNT are shown in Table 4. According to the results, incorporation of 3% halloysite nanotube reduced the pore diameter and total pore volume of the pastes by 12.3% and 14.95% by comparing with the blank sample. These results are mainly attributed to the filling up because of the nanosize and expansion of halloysite nanotube, more amounts of hydration products due to the HNT promotion, network structure between tube-like halloysite and hydration products, which eventually improve strength performance of the cement improved.

| Sample     | Total intruded volume (mL/g) | Average pore diameter (nm) | Total porosity (%) | Total surface area (mL/g) |
|------------|------------------------------|----------------------------|--------------------|--------------------------|
| cement     | 0.2199                       | 19.5                       | 32.38              | 46.374                   |
| HNT cement | 0.2145                       | 17.1                       | 27.54              | 42.465                   |

4. Summary

(1) The strength properties of cement with halloysite nanotube improved obviously as the compressive and flexural strength was increased by 35.2% and 38.5% compared with blank sample, respectively.

(2) Denser structure of H3 cement can be observed according to the results of SEM, which may be explained by filling effects, high activity and inorganic fiber behavior of halloysite nanotube.

(3) The porosity of cement with halloysite nanotube is decreased by 14.95%, which may be explained by hollowed tubular shape and void filling up due to its nanosize and expansion of halloysite nanotube.

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References

[1] Dousti M R, Boluk Y, Bindiganavile V 2019 Constr Build. Mater. 205 456
[2] Velissarioua D, Katsiotisa N, Tsakiridisb P, Katsiotisc M, Pistofidisc N, Kolovosd K, Beazi M 2019 Constr Build. Mater 197 63
[3] Costa B L de S, de O Freitas J C, de A Meloa D M, da S Araujob R G, de O Cristina Y H 2019 Constr Build. Mater 197 331
[4] Eftekhari M, Mohammadi S, Khanmohammadi M 2018 Constr Build. Mater 175 134
[5] Li M, Zhou S, Guo X 2017 Constr Build. Mater 150 619
[6] Khana M, Cao M, Ali M 2018 Constr Build. Mater 192 742
[7] Luciana Guimaraes A N E, Gotthard S, Helio A 2010 J. Phys. Chem. C. 114 11358
[8] Zhao Y F, Abdullayev E, Vasiliev A, Lvov Y, Zhao Y, Abdullayev E, Vasiliev A 2013 Journal of Colloid and Interface Science 406 121
[9] Tironia A, Craverob F, Scianb A N, Irassara E F 2017 Applied Clay Science 147 11
[10] Nima F, Abang A, Ramazan D, Mohammed P A. 2013 Cem. Concr. Res. 48 97
[11] Albdirya MT, Yousifb F 2019 Composites Part B 160 94
[12] Y. Yang, Y. Deng, 2018 Constr Build. Mater 182 258-272