Mechanical Properties and Structures of Oil-well Cement Stone Reinforced with Siliceous Whisker

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ABSTRACT

To fully utilize the siliceous whiskers and improve the mechanical properties of oil-well cement, the cement composites with different additions of siliceous whiskers were prepared, and analyzed by means of scanning electron microscopy (SEM), mechanical testing, X-ray diffraction (XRD), and infrared spectrum analysis. The results showed that the addition of 2% siliceous whiskers could slightly improve the compressive strength, and markedly increased the flexural and tensile strength as well as toughness; it also decreased the permeability and porosity of oil-well cement composites. Moreover, it was confirmed that the siliceous whisker could not affect the cement hydration process and hydration products. The improvement in mechanical properties and the more compact microstructure could be mainly resulted from enhancement mechanisms such as bridging, crack deflection, and pulling-out in cement matrix.

Keywords: Oil Well Cement, Mechanical Properties, Siliceous Whiskers, Enhancement Mechanism

INTRODUCTION

Usually, cementitious materials have a relatively high compressive strength, which is the most basic property of cement-based composites, but they are more sensitive to tensile stresses than compressive ones. The brittleness indexes such as flexibility, tensile strength, and the impact resistance of cement are relatively low. Therefore, making an enhancement in tensile strength and maintaining the higher toughness simultaneously is a challenge for possible applications of brittle oil-well cements as the basic materials in the petroleum industry [1]. Nowadays, various methods have been used to improve the strength and toughness of cement composites, of which the most effective one is blending with various reinforcing additives, including natural fibers [2], carbon fibers [3], steel fibers [4], carbon nanotubes [5], nanosized particles [6-7], synthetic fibers [8], and the hybrid combination of different types of reinforcing additives [9-11]. Recently, an important reinforcing additive, namely $CaCO_3$ whiskers, has been used as a unique strengthening and toughening enhancer in cement composites [12-13], which is effective to delay the formation and propagation of micro-cracks. It was also found out that $CaCO_3$ whiskers not only can slightly improve the compressive strength, but also can significantly

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promote the flexibility, load-deflecting curves, and work of fracture [13]. To the best of our knowledge, nevertheless, the abovementioned investigations have not considered the hydration products, structures, and the permeability or porosity of cement composites, which are factors affecting the properties of composites directly [13], and they discussed the mechanical properties alone.

The mechanical properties and microstructures of cement composites depend on the type, dispersity, and content of the reinforcing additives [3,6,15-16]; the adhesion strength between reinforcing additives and cement [4,11,17]; and the hybrid dosages of different reinforcing additives [3,9,18-20]. Siliceous whisker is a new kind of reinforcing material, which has a structure similar to diamond, having a high strength and modulus. Compared with the other reinforcing additives used in oil-well cement completely [1,10,21], siliceous whiskers belong to a sort of whiskers which have a definite slenderness ratio, but barely have defects. Thus, this kind of whiskers has perfect mechanical properties, such as high strength, high Young's modulus, and good resistance to temperature, which allow them to be used as reinforcing materials [22-24]. Generally, the current paper is to assess the most effective addition of siliceous whiskers into oil-well cement and to discuss the mechanical properties and the structures of the composites obtained.

EXPERIMENTAL PROCEDURES

Materials

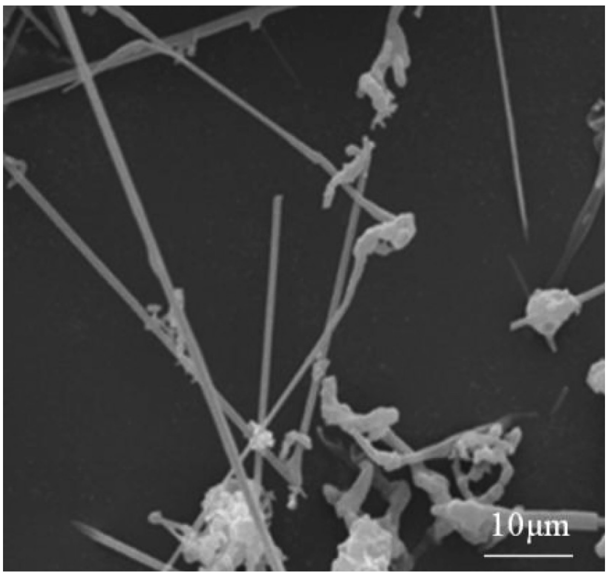
The siliceous whiskers used in this study were provided by Jiechuang Novel Materials Ltd. (Xuzhou, China), and its main properties are listed in Table 1. Other materials used included class G Portland cement (Sichuan Jiajiang Guijiu Special Cement Co., Ltd., China), the chemical composition of which is presented in Table 2. The fluid loss agent G33S and dispersant SXY-2 were commercially supplied. The SEM morphologies of siliceous whiskers are shown in Figures 1. As shown in Figure 1, siliceous whiskers is a kind of whisker with a diameter of 0.2~1.5 µm and a length of 10~100 µm.

Table 1: Properties of siliceous whiskers.

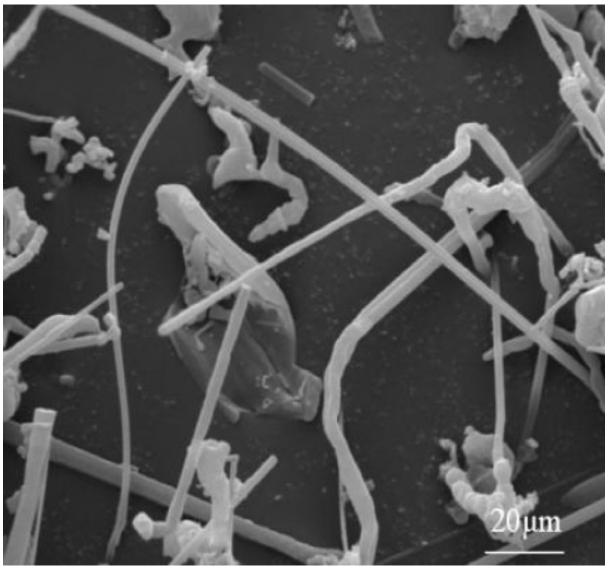
Species	Length (µm)	Diameter (µm)	Tensile Strength (GPa)	Bulk Density (g.cm^{-3})	Elastic Modulus (GPa)
Siliceous whiskers	15~80	0.3~1.4	20.58	3.2	48.02

Table 2: Chemical composition of class G oil-well cement as analyzed by X-ray fluorescence (XRF).

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	SO_3	MnO_2
Content (wt.%)	22.7	3.39	4.81	65.5	0.9	0.37	1.21	0.09



(a)



(b)

Figure 1: SEM micrographs of siliceous whiskers.

Specimen Preparation and Experimental Methods

Cement slurries were prepared and cured according to the standards of API recommended practice 10B [25]; also, cement, siliceous whiskers, fluid loss agent G33S, and dispersant SXY-2 were all mixed with the cement powders and were then stirred by a cement paste blender at a water/cement mass ratio (W/C) of 0.4. The detailed mixture proportion of the cement slurries is given in Table 3. The cement slurries were kept in standard curing molds at 100% relative humidity and at a temperature of 90 °C for 3, 7, 14, and 28 days. The cured rectangular specimens (50.8×50.8×50.8 mm^3) and cylindrical specimens (ϕ25.0×25.0 mm^3) were used to measure tensile and compressive properties at a crosshead speed of 600 N/s using electronic hydraulic testing machines (Haizhi Technology Co. Ltd., Beijing, China). In addition, the cured rectangular specimens (40.0×40.0×160.0 mm^3) were used to measure flexible strength with 3-point-bending using a motorized bending tester (Jianyi Instrument & Machinery Co. Ltd., Wuxi, China) at a span and a crosshead speed of 100 mm and 0.02 mm/min respectively. Furthermore, the cured rectangular specimens (ϕ25.0×40.0mm^3) kept in standard curing molds at 90 °C at 100% relative humidity for 7 days were used to measure the permeability using a particle volume or core gripper (Yiyong Technology Co. Ltd., Changzhou, China) at a pressure of 2 MPa; the pore size distribution of the cement was tested by mercury injection apparatus (Poremaster 60, Quantachrome Ins, USA). Moreover, the cured cylindrical samples (ϕ25.0×50.0mm^3) were used to measure the strain-stress curve by triaxial rock mechanics testing system (RTR-1000, GCTS Co., USA) according to the standards of GB/T 50266-99 at a constant loading rate of 2 KN/min and at a confining pressure of 20.7 MPa. There were 7 samples tested for each testing, and the standard deviation was expressed as the variation in the results.

Table 3: Composition of the prepared specimens.

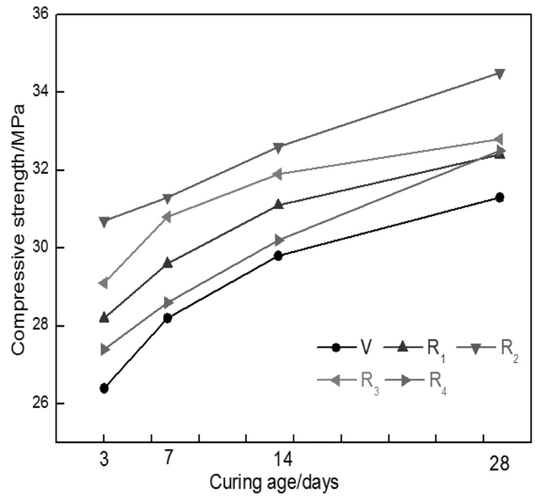
Specimens	Cement (g)	Siliceous whiskers (g)	G33S (g)	SXY-2 (g)	Water (g)
V	400	0	4	4	160
R_1	396	4			
R_2	392	8			
R_3	388	12			
R_4	384	16			

In addition, an X-ray diffraction meter (Shimadzu, XRD-7000, Japan) was used to study the diffraction behaviors of siliceous whiskers and the enhanced cement. The scanning electron microscope (SEM, JEOL JSM-6510LV, Japan) was used to observe the In addition, an X-ray diffraction meter (Shimadzu, XRD-7000, Japan) was used to study the diffraction behaviors of siliceous whiskers and the enhanced cement. The scanning electron microscope (SEM, JEOL JSM-6510LV, Japan) was used to observe the microstructure of the siliceous whiskers and the fracture surface of the specimens. Furthermore, the infrared absorption spectrometer (FI IR, Thermo Scientific, Nicolet 6700, America) was used to confirm compositional variation during the hydration process.

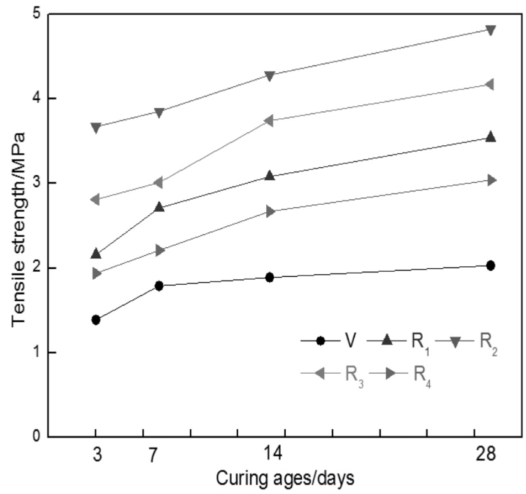
RESULTS AND DISCUSSION

Effect of Siliceous whiskers on the Mechanical Properties

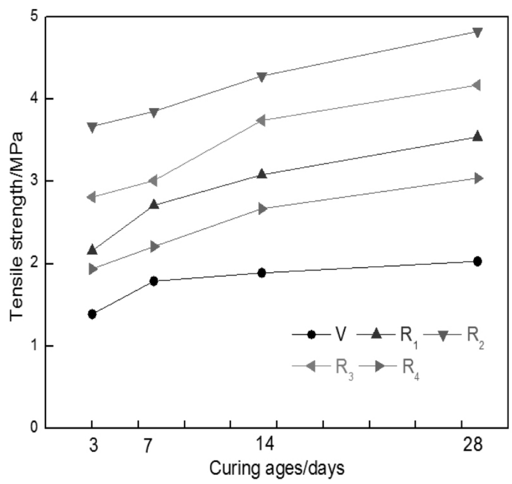
Figure 2 shows the mechanical properties of the cement stone; it can be seen that the mechanical properties of the cement composites are improved due to the addition of the siliceous whiskers, and they are increased with an increase in curing time. Compared with sample V (without siliceous whiskers), the compressive, tensile, and flexural strengths of sample R_2 respectively obtain an increment of 10.35%, 132.43%, and 30.39% after 28 days of curing by a 2% addition of siliceous whiskers, which is the most effective addition. The enhancement in the mechanical properties of the cement composites may result from the higher modulus of siliceous whiskers as well as the good adhesion between the whiskers and the cement composites [26].



a) Compressive Strength



b) Tensile Strength



c) Flexural Strength

Figure 2: Effect of adding siliceous whiskers on the cement mechanical properties.

Effect of Siliceous Whiskers on the Permeability and Porosity

Table 4: Pore size distribution curves of specimens V and R_2.

Pore volume /Pore size distribution (%)	>200 nm	50-200 nm	20-50 nm	<20 nm
V	4.372/19.6	15.998/71.6	1.074/4.8	0.91/4.1
R_2	0.002/0.04	4.416/84.9	0.635/12.2	0.151/2.9

It is well known that cement composites are porous materials having a large number of pores and voids. The microstructure of cement composites is the key basic elements of the macro-properties. Generally, the more the pores and voids exist, the lower the mechanical properties of cement composites become. Table 4 shows the pore size distribution of the cement containing whiskers (R_2) and the pure cement (V). It is distinct that the addition of whiskers can improve the pore size distribution of cement composites, and the total pore volume and the pore size of the cement including whisker is significantly lower than the pure cement. The probability of the pore size bigger than 50 nm of the pure cement is 91.2% with a pore volume of 20.37 ml/g, while that of the cement composite containing whiskers decreased to 84.94% with a pore volume of 4.418 mL/g. This indicates that the modified cement contains fewer and smaller pores and voids, which is beneficial to mechanical properties.

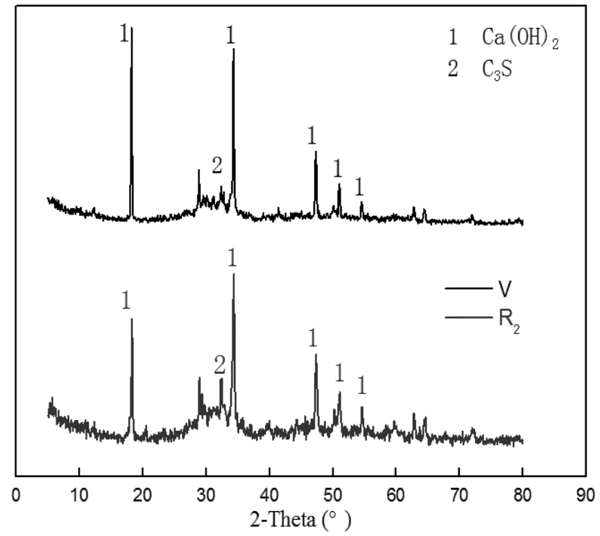
Table 5 shows the influence of siliceous whiskers on the permeability and porosity of the cement composites; the permeability and porosity of cement composites with whiskers is decreased nearly by 82.8% and 7.7% respectively compared to the pure cement, representing that siliceous whiskers can effectively enhance the microstructure and make more compact structures; this is also in accordance with the analysis of pore size distribution.

Table 5: Permeability and porosity of specimen V and specimen R_2.

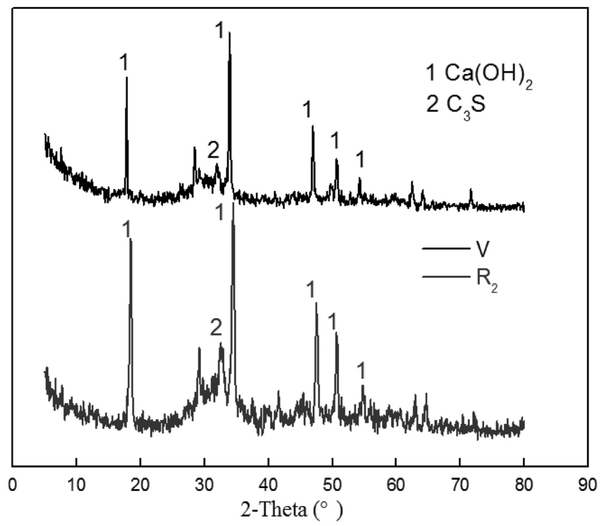
Specimens	Permeability (mD)	Porosity (%)
V	0.2533	83.78
R_2	0.0435	77.30

X-ray Diffraction Analysis of Siliceous Whiskers Enhanced Cement

Figure 3(a) and (b) show the comparison of X-ray diffraction between the virgin cement (V) and the cement containing siliceous whisker (R_2) cured for 7 days and 28 days respectively. The results demonstrated that there was no new kind of hydration in the cement with siliceous whiskers cured for 28 days, while the hydrations were most similar in Figure 3(a) when they cured for only 7 days. The crystal phase of specimen R_2 consists of calcium hydroxide (CH), ettringite (AFt) etc. As a result, siliceous whiskers have no effect on the hydration process and products of cement composites.



a) 7 days

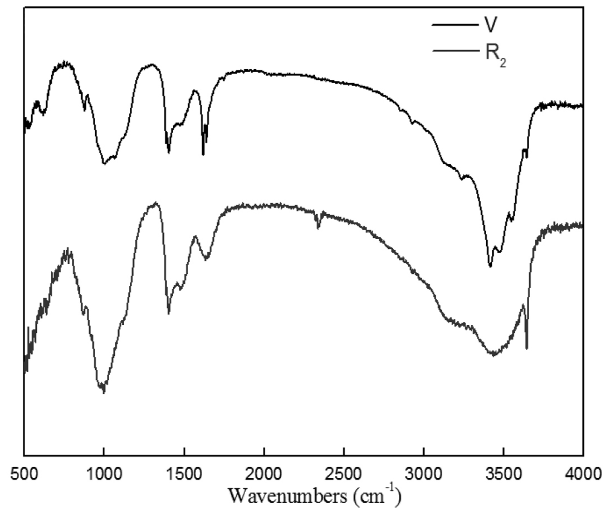


b) 28 days

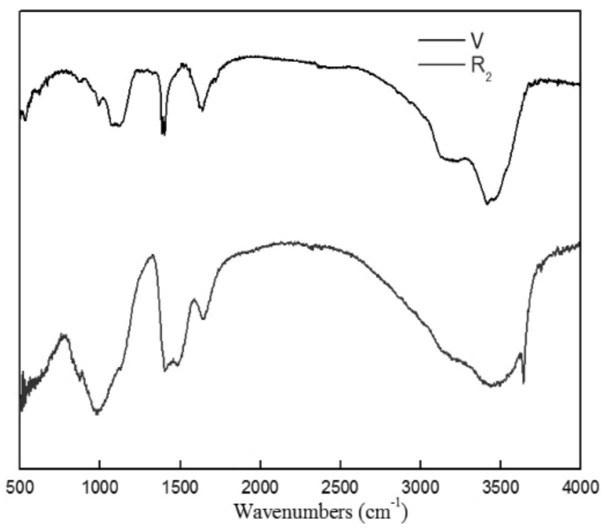
Figure 3: XRD pattern of specimen V and the specimen R_2.

Infrared Spectrum Analysis of Siliceous Whiskers Enhanced Cement

Infrared absorption spectrum (IR), also known as molecular vibration spectrum, has been broadly used in the chemical group and bond characterization based on the position of characteristic peaks. Therefore, the infrared spectrum analysis can be used in cement analysis due to the different vibration frequency of anionic groups.



a) 7 days



b) 28 days

Figure 4: IR spectra of specimen V and the specimen R_2.

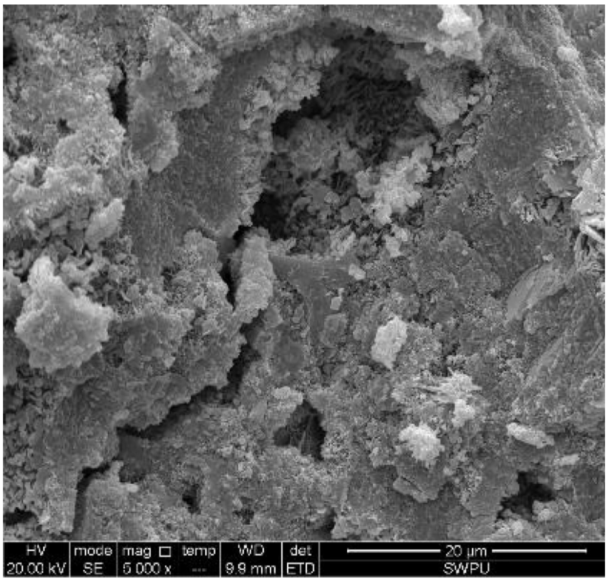
The infrared absorption spectra of the cement with whiskers (R_2) and the pure cement (V) curing for 7 and 28 days are displayed in Figure 4. The C-S-H gel is an amorphous crystal, resulting in different asymmetric stretching vibration displacements of

Si-O bond in $[SiO4]^{-4}$ such as the Si-O bond with a displacement range of 900-980 cm^{-1} and the Si-O-Si bond with a displacement range of 980-1000 cm^{-1}; the aggregations will also be $V_3[SiO_4]$ when displacement reaches 1100 to 1200 cm^{-1}. The strong and narrow sharp peaks at 3640 cm^{-1} corresponds to the characteristic spectral line of OH^{-1} in $Ca(OH)_2$; comparing with the pure cement, the peak of specimen R_2 is representing a weaker vibration of OH^{-1}, indicating less $Ca(OH)_2$ in the cement composites. Furthermore, the nearby larger absorption peak at 3640 cm^{-1} is the stretching vibration peak of hydroxyl in the water crystallization. It can be seen that there is no difference in the characteristic peaks representing anionic groups, which is in accordance with the XRD analysis.

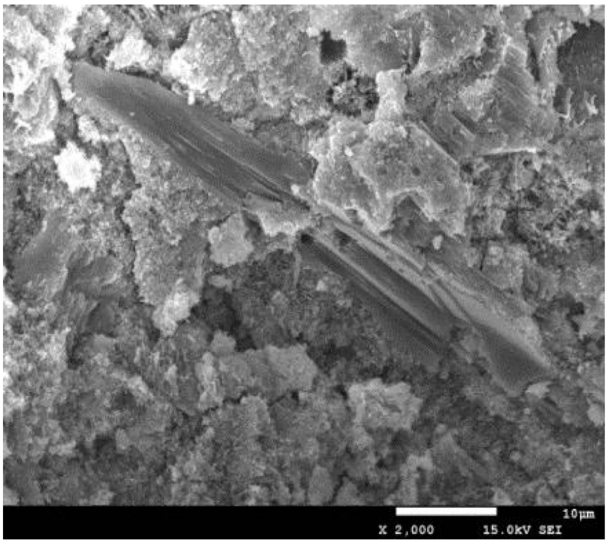
Siliceous Whiskers Enhancement Mechanism for the Mechanical Properties of Oil Well Cement

Fractured Surface Morphology

The structure of oil-well cement stone formed is connected with the hydration and its products during the hardening process. The scanning electronic microscope morphology of the composites with siliceous whiskers (R_2) and the virgin specimen (V) is shown in Figure 5. It can be seen that a more compact structure is formed due to the special structure of siliceous whiskers. There are fewer micro-cracks, which may be attributed not only to the small sized siliceous whiskers as the fillers of voids in the cement, but also to the lack of any clear gap between the cement matrix and siliceous whiskers.



a) specimen V

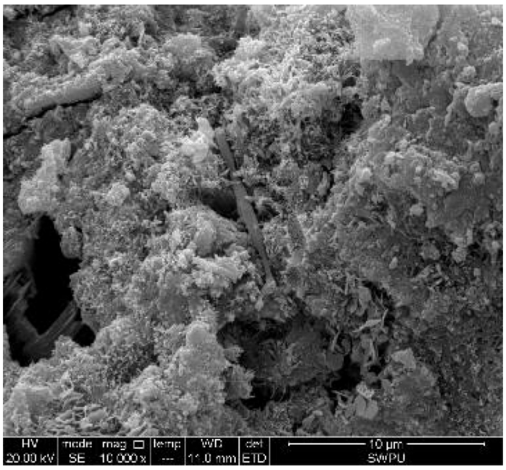


b) specimen R_2

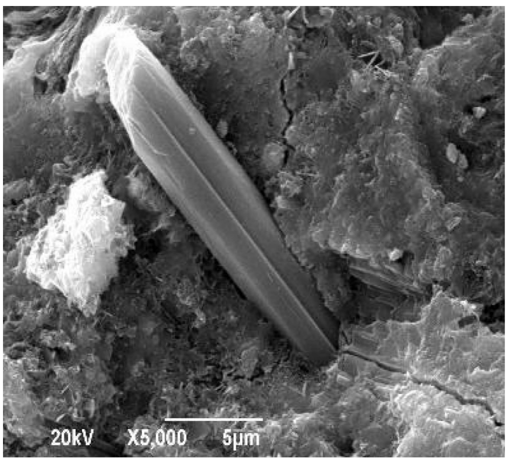
Figure 5: SEM micrographs of the fractured surfaces.

Enhancement Mechanism Analysis of Siliceous Whiskers

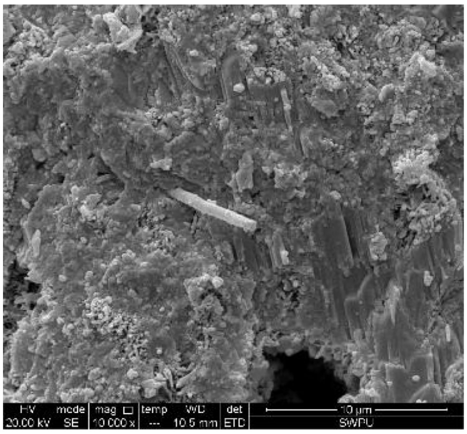
The reinforcing mechanism of siliceous whiskers on mechanical properties consists of bridging effects, crack deflection, and pull-out effects, which is detected in SEM photography of the cement with siliceous whiskers. Figure 6 shows the SEM photography of the cement with siliceous whiskers. It can be seen that the fracture failure of the cement materials is mostly caused by crack propagation, and the more the energy is consumed during crack propagation, the better the toughness of the cement become. The compact structure of siliceous whiskers cement matrix results in an extra function in cracking resistance and energy dissipation because of the smaller sized and more intensive siliceous whiskers. As shown, the micro-cracks are astricted by the siliceous whiskers which can bridge cracks in micro-cracks, expand cracking path, and increase the absorption and dissipation of energy during fracture, thereby forming an enhancement effect in cement matrix.



a) bridging



b) crack deflection



c) pull-out

Figure 6: SEM micrographs of the fractured surfaces of the enhanced cement.

In the initial stage of bearing external load, subjecting to low inner stress, some smaller micro-cracks are formed in the cement matrix. Because of the siliceous whiskers with a smaller size and good mechanical properties, the closure stress can be formed in the crack tip with crack bridging of the whiskers, which results in stress loading on the crack surface instead of stress concentration at the tip of the cracks [28]. Figure 6a shows the micro-cracks in the presence of whiskers; as the load increases, if the micro-cracks gradually grow into larger and even regional cracks, the siliceous whiskers larger in size at this point play a leading role in bridging cracks and effectively limiting the large-scale crack extension until the whiskers are destroyed.

The micro-cracks in the cement cannot develop in the original orientation when approaching the whisker with a smaller angle (<90°) because of the high modulus of whisker; as a result, the propagation direction of cracks would be transformed to spread along the interface between the whiskers and the cement matrix; with an increase in the path of crack propagation (Figure 6b), more loading energy is consumed, resulting in less damage in the microstructure of the cement.

The microscopic appearance of the fracture surface of the cement composites containing whiskers are shown in the Figure 6c. As analyzed above, whiskers can act as bridges to connect the both sides of cracks to decrease the crack extension; also, with an increase in load and bearing duration, some of the siliceous whiskers would be pulled out, which might facilitate better stress transfer from the cement matrix to the stronger whisker. Vast energy is also consumed due to the rubbing action between whiskers and cement. Moreover, the addition of whiskers can significantly improve the microstructure of the cement composites, and more energy will be consumed in crack extension, resulting in an effective enhancement of toughness and mechanical properties of the cement.

CONCLUSIONS

The current paper discussed the effect of siliceous whiskers on the mechanical properties and microstructures of oil well cement composites. The results show that there is a reinforcing effect of siliceous whiskers on mechanical properties; an improvement of 10.35%, 132.43%, and 30.39% was seen in compressive, flexibility, and tensile strengths respectively after 28 days of curing in the presence of 2% siliceous whiskers. Also, the analysis of the results reveal that siliceous whiskers plays a positive effect on permeability, porosity, and pore size distribution, and the microstructure of cement enhanced by whiskers becomes more compact; the permeability and porosity are decreased by 82.8% and 7.7% respectively. Meanwhile, the presence of whiskers can improve the loading damage process in the microstructure based on the reinforcement mechanisms such as bridging, pulling-out, crack deflecting, and more damage energy can be absorbed and dissipated. The improvement in the mechanical strength and microstructure of oil well cement composites may be significant for the cementing engineering and possible applications of siliceous whiskers.

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