



The influence of sulfonated asphalt on the mechanical properties and microstructure of oil well cement paste

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HIGHLIGHTS

- The level 2–3% of sulfonated asphalt improves the toughness of oil well cement paste.
- Sulfonated asphalt has some retarding effect on oil well slurry.
- The toughening mechanism of elastic asphalt particles is proposed.
- The mechanism depends on crack bending and deflection.

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ABSTRACT

In this work, sulfonated asphalt was chosen as an admixture, and the influence of the quantity (1%, 2%, 3%, 4% of the weight of the cement) of sulfonated asphalt on the mechanical properties of hardened cement slurry was studied. Moreover, the micro-morphology and porous structure characteristics were examined using the SEM and nitrogen adsorption-desorption method, respectively. Studies showed that the addition of asphalt had great potential to improve the tensile strength and toughness of cement paste. The tensile strength of cement paste with 3% sulfonated asphalt increased by 45% at 7 days and 17% at 28 days in comparison with that of specimens without sulfonated asphalt. In addition, 2–3% sulfonated asphalt levels were advantageous for improving the toughness of oil well cement paste. Asphalt particles caused crack bending and deflection as well as toughened oil well cement paste. The addition of 3% asphalt had a positive good effect on the pore size distribution in cement paste. The addition of asphalt decreased the compressive and flexural strength of cement paste at the same curing age. The content of 4% asphalt increased the pore size and caused deterioration of the mechanical properties of cement paste. It is necessary to balance the mechanical properties of cement paste and the amount of asphalt in the range 2–3% to be beneficial for this application.

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1. Introduction

Oil well cementing is the process of placing cement slurry in the annulus space between the well casing and the geological formations surrounding to the well bore, from the injection horizon to the surface [1]. The main purpose of primary cementing is to support and protect the casing and provide effective zonal isolation during the entire life span of the well. Due to the brittleness and poor resistance to the deformation of oil well cement paste in nature, well cement paste can lose its integrity due to the stresses induced by changes in pressure/temperature during operation and/or due to the external mechanical loading processes and lead

annular isolation to fail [2]. Improving the resistance to deformation and maintaining the mechanical integrity of the cement sheath throughout the life of the well are becoming increasingly important in modern cementing technology. Thus, excellent tensile strength, anti-crack properties, anti-impact toughness and flexural strength that is similar to the compressive strength of cement paste play important roles in providing zonal isolation.

The incorporation of admixtures is a solution to improve resistance to reforming and eliminate the brittleness of oil well cement paste. The incorporation of polymers especially contributes to increasing the flexural and tensile strength of cementitious composites [3]. The literature [4] shows that the effect of the application of a polymer on concrete has significantly progressed in the past 50 years. The application of polymers in cementing to

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strengthen the mechanical properties is attracting increasing scientific interest.

It is important to make better choices for polymer additives to enhance the toughness and tensile strengths of cementing systems to allow for better long-term zonal isolation. Asphalt is a polymer with saturated fraction, aromatic fraction, resin and asphaltene and has excellent flexibility, deformability and filling capacities. Early in the 19th century, asphalts were widely used in roads and water conservancy projects. In reviewing the literatures [5–10], it can be seen that increasingly modified asphalts, including cold asphalt products (emulsified asphalt and modified emulsified asphalt), were developed and widely used in road fields. The proper amount of emulsified asphalt mixed into concrete can improve the density of concrete and the anti-infiltration properties of the concrete swell and elasticity of concrete [11–12]. Zhenjun Wang et al. [13–14] studied the effects of asphalt emulsion, binders and curing ages on the workability of cement slurry and indirect tensile strength (IDT), dynamic stability (DS) and the dry shrinkage of a cement emulsified asphalt mixture. The results showed that higher emulsified asphalt content results in a higher increase of the IDT at a low temperature. Tyler Rutherford et al. [15] investigated the uniaxial compressive strength, indirect tensile quality, tensile strength ratio, dynamic modulus and phase angle, shrinkage and cement hydration heat of cement emulsified asphalt mortar (CEAM). They found that the A/C ratio showed a significant effect on the mechanical properties and cement hydration heat of CEAM. Moreover, Jian Ouyang et al. [16] studied the thixotropic behavior of fresh cement asphalt emulsion paste. Qiang Fu et al. [17] also explored the stress relaxation behavior of cement and asphalt mortar under different initial strain levels.

Asphalts were widely used in the road transport field for the purpose of improving flexible pavement over the last years, but there are less relevant reports on asphalts applied in oilfields. In oil and gas engineering, sulfonated asphalts are used as a drilling fluid additive for water sensitive strata [18]. The literature [19] suggested that sulfonated asphalt could be effectively used in well drilling to improve the mud cake quality, blank off formation holes and cracks, decrease filter loss, increase the liquid phase viscosity, protect hydrocarbon reservoirs and regulate drilling fluid performance. Li Yong et al. [20] found that drilling fluid with sulfonated asphalt had a good anti-collapse effect and higher drilling efficiency. Suggestions were made for the use of sulfonated asphalt drilling fluid in geothermal well construction based on the field application experience, Wang Tiejun et al. [21] also found that polymer cation asphalt drilling fluid has a strong inhibition capacity, effectively fills tiny fissures in the strata and improves the mud lubricating function.

Although increasing reports of sulfonated asphalt being used to drilling fluids in oilfield are emerging, few studies have explored the suitability of asphalt to enhance the ability of oil well cement paste to resist deformation. In this work, sulfonated asphalt was chosen to serve as an admixture of oilfield cement considering the harsh wellbore environment (elevated temperature and pressure). The objective of this study was to investigate the effects of sulfonated asphalt on the mechanical properties and microstructure of oil well cement paste to explore whether asphalt will be applied as a reinforcing agent in cementing. Additionally, the relationship between the mechanical properties and microstructure was studied to explain the interaction mechanism between sulfonated asphalt and cement paste.

2. Materials and method

The properties of raw materials and the preparation of the specimens for testing are described as follows.

2.1. Raw materials

Class G high sulfate-resistant cement was produced by the Jiajiang cement plant in Sichuan province, China. The chemical and physical characterization of cement is presented in Tables 1 and 2, respectively. Sulfonated asphalt was provided by Licheng Chemical Co., Ltd. in Tianjin, China. The main properties of sulfonated asphalt were given in Table 3. Some additives were also used in the experiment. They are fluid loss additives (G33S) and dispersing agents (SXY-2) for oil well cement.

2.2. Experiment program

2.2.1. Specimen preparation

To investigate the mechanical properties and microstructures of oil well cement paste with the sulfonated asphalt, cement slurries were prepared and cured according to Chinese standard GB/T, 19139-2012. A water-cement ratio of 0.44 was adopted. Samples containing Class G oil well cement, water, fluid loss additives (G33S), dispersing agents (SXY-2) and sulfonated asphalt were created, as presented in Table 4. The cement slurries were prepared by adding the powder to water in a Waring blender at a speed of 4000 rpm for 15 s and 35 s at 12000 rpm. Fresh oil well slurries were cast into molds and cured in water baths at 90 °C for 1 day, 3 days, 7 days, 14 days and 28 days for aging, respectively. After reaching the predetermined ages, the samples were taken from the water, and the compressive strength, flexural strength, splitting tensile strength and the stress-strain curves were measured.

2.2.2. Alkali resistance of the sulfonated asphalt test

The indirect method was used to study the ability of sulfonated asphalt to resist alkaline erosion in the cement slurry. Sulfonated asphalts were soaked in a sodium hydroxide solution with a pH value of 13 (similar to the alkaline environment of cement slurry) for 28 days and were then filtrated, washed and dried, after which the infrared spectrum was obtained. A 6700-fourier transform infrared spectrometer (FT-IR) that was produced by the United States Nicolet Company and the potassium bromide tablet method were both adopted to analyze the sulfonated asphalt specimens

Table 1
Chemical characterization of cement.

Chemical characterization	Standard requirements (wt%) (Chinese GB10238-2005)	Sample (wt%)
MgO	≤6.0	1.42
SO ₃	≤3.0	2.52
Loss on ignition	≤3.0	1.03
Insoluble residue	≤0.75	0.55
Total alkali content (Na ₂ O equivalent)	≤0.75	0.43
C ₃ S	48–65	57.33
C ₃ A	≤3.0	2.34
2C ₃ A + C ₄ AF	≤24	18.21

Table 2
Physical characterization of cement.

Physical characterization	Standard requirements (China GB10238-2005)	Sample
Water/cement ratio	0.44	0.44
Free liquid	≤5.9	5.2
Initial consistency	≤30 B _c	9.0 B _c
Setting time at 52 °C	90–120 min	102 min
Compressive strength, 8 h at 38 °C	≥2.1 MPa	6.5 MPa
Compressive strength, 8 h at 60 °C	≥10.3 MPa	16.3 MPa

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