Study on the Performance of Fiber-Latex-Calcium Carbonate Whisker Gas Storage Cement

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Abstract. A cement slurry system was designed and optimized in order to meet the strict operation and production requirements of the gas storage well cementing. System formula was G cement +1.5% filtrate reducer +1% dispersant +0.5% defoamer +10% calcium carbonate whisker +8% polychloroprene latex +0.08% polypropylene fiber +0.09%PVA fiber + water. Evaluation experiments showed that the engineering properties of cement slurry system were well, such as good rheology, low water loss, no free liquid, wide adjusted range of thickening time, good anti channeling ability and good suspension stability. The experiment results of cement mechanical strength showed that the 7 days tensile strength of the cement specimen was increased 62.3% higher than that of the neat cement grout, while the 7 days compressive strength was increased 47% and the elastic modulus was reduced 41.7% compared to the standard peak. The micro-structure and morphology of gas storage cement specimens were observed and the mechanism of cement strength enhanced by fiber, latex and calcium carbonate whisker were studied that fiber and calcium carbonate whisker bridged the cracks, reduced cracked tip stress concentration, effectively prevented the development and diffusion of cracks, enhanced cement deformability and reduced the elastic modulus; polychloroprene latex formed latex film on the surface of cement particles and fiber, which improved the cementing strength and the interface micro-structure between fiber and cement, reduced the stress concentration caused by mutant materials, improve the toughness of cement stone greatly.

Keywords: gas storage; cement slurry; fiber; latex; calcium carbonate whisker.

1. Introduction

Underground gas storage is an artificial gas field or gas reservoir formed by re-injecting the natural gas produced by gas reservoir into the space where gas can be sealed, which has the function of regulating and stabilizing peak gas consumption and strategic energy reserve. The reciprocating injection-production operation environment of underground gas storage is complex and the conditions are harsh, and the pressure in the casing changes periodically. However, the conventional cement cementing toughness is poor, and the integrity of cement sheath is easy to be destroyed, which leads to the failure of gas storage well annular sealing, gas channeling and annular pressure, which will bring potential safety hazards and economic losses to the normal operation of the gas storage. Therefore, the cementing...
of gas storage wells requires higher performance of cementing slurry, which requires good gas channeling prevention performance and better deformation ability of cement sheath [1,2].

Researchers at home and abroad have done a lot of experimental research on improving the performance of gas storage cementing cement, mainly by adding fiber, composite materials, latex, silica sand and other additives into cement slurry to improve the cementing quality of gas storage. The research shows that calcium carbonate whiskers have small particle size and smooth surface, and can be well dispersed in cement matrix and effectively filled in the gaps between cement matrix [3,4]. Calcium carbonate whisker plays a role similar to fiber in the process of compressive failure of cement matrix, which improves the strength and toughness of cement paste by bridging, crack deflection and whisker or fiber pulling out, but the action range of fiber and whisker is different under different failure load degree and micro-crack size [5-7]. Many fluffy materials, i.e. small latex particles, are attached to the hydration products of latex cement paste. The latex particles are distributed between the cement matrix framework, which can not only increase the bonding strength of the interface, but also effectively inhibit the growth and extension of internal cracks in the cement paste. Therefore, it can reduce the brittleness of the cement paste and improve its pressure crushing capacity [8-10].

According to the performance requirements of cement slurry system for gas storage wells, the design and application of cement slurry system are studied in this paper. The cement slurry system for gas storage is designed with fiber, chloroprene latex, calcium carbonate whisker and other additives. The rheological properties, water loss, thickening time, settlement stability, mechanical properties and channeling resistance of the cement slurry system are evaluated as a whole; The elastic modulus, compressive strength, tensile strength and mechanical integrity of cement paste were tested and evaluated. The improvement mechanism and function of the cement slurry system were analyzed. The developed cement slurry system for gas storage well cementing has good comprehensive performance, which can meet the cementing requirements of gas storage, and provides technical reference for scientific and reasonable design of cement slurry system for gas storage well cementing.

2. Experiment

2.1. Experimental material

Experimental materials: cement (jiahua g oil well cement), polypropylene fiber (Shanghai yingjia industrial co., ltd.), polyvinyl alcohol fiber (Shanghai yingjia industrial co., ltd.), calcium carbonate whisker (Shanghai muhong chemical co., ltd.), neoprene latex (Jinan tuoda building materials co., ltd.), oil well cement defoamer G603, fluid loss reducer CG510S-P and dispersant SXY.

Calcium carbonate whisker belongs to aragonite type, which is white, fluffy, smooth and complete in appearance. It has good dispersibility and is a kind of reinforcing and toughening material with excellent performance. The basic physical properties of calcium carbonate whiskers selected in the experiment are shown in Table 1.

| Table 1. Basic physical properties of calcium carbonate whiskers |
|-----------------|---------------|-----------------|
| Appearance      | White powder  | Length/\(\mu m\) |
| Molecular weight| 100.09        | Diameter/\(\mu m\) |
| Mohs hardness   | 3             | Draw ratio       |
| Density/\(g/cm^3\) | 2.8          | PH value         |
| Moisture        | <0.3%        | Oil absorption/\(ml/g\) |

Polypropylene fiber and polyvinyl alcohol fiber are synthetic fibers, which have the advantages of high strength, good ductility and durability, and low market price, and are widely used as cement slurry modified materials. The two fibers used in the experiment are produced in Shanghai Yingjia Industrial Co., Ltd., and their basic performance parameters are shown in Table 2.
Table 2. Basic performance parameters of fiber

| Fiber category | Polypropylene fiber | Polyvinyl alcohol fiber |
|----------------|---------------------|-------------------------|
| Density/g/cm³  | 1.58                | 1.3                     |
| Tensile strength/MPa | 770                | 1600                    |
| Young's modulus of elasticity/MPa | 350                | 35                      |
| Acid-base impedance | High               | 17%-20%                 |

Chloroprene latex is a stable emulsion prepared by emulsion polymerization of chloroprene under the action of emulsifier, initiator and stabilizer, which has good interfacial adhesion and is often used as cement slurry modification material. The basic properties of neoprene latex used in the experiment are shown in Table 3.

Table 3. Basic performance parameters of neoprene latex

| Viscosity/Pa·s | Solid phase content/% | Density/g/cm³ | Storage stability |
|----------------|-----------------------|---------------|-------------------|
| 12             | 50                    | 1.09          | 90 days           |

The formula of compound cement slurry used in the experiment is shown in Table 4.

2.2. Experimental method

The application conditions of gas storage well cementing and its strict requirements on the performance of cement slurry system. According to the relevant standards of GB/T19139-2003 "Experimental Methods for Oil Well Cement" and "Technical Requirements for Tough Cement in Gas Storage Wells (Trial)", this paper carried out the gas storage well cementing experiment and performance test. When the admixture is added, the admixture is evenly and fully premixed with cement in advance, and then the cement slurry is prepared, and then the engineering performance of the cement slurry is tested, and the cement block is maintained according to the requirements of the mechanical performance test experiment. The compressive strength, tensile strength, elastic modulus and microstructure of the cement paste with specified curing time and temperature are tested for 7 days.

Table 4. Formula materials and dosage of cement slurry system in gas storage

| Numbering | Cement/g | Water/g | Fluid loss reducer/g | Dispersant/g | Defoaming agent/g | Calcium carbonate whisker/g | Neoprene latex/g | Polypropylene fiber/g | Polyvinyl alcohol fiber/g |
|-----------|----------|---------|----------------------|--------------|------------------|-----------------------------|-----------------|----------------------|--------------------------|
| S0        | 600      | 233     | 9                    | 0            | 0                | 0                           | 0               | 0                    | 0                        |
| S1        | 600      | 233     | 9                    | 6            | 3                | 60                          | 0               | 0.72                 | 1.08                     |
| S2        | 600      | 233     | 9                    | 6            | 3                | 60                          | 48              | 0.72                 | 1.08                     |

Note: The length of polypropylene fiber is 6mm and that of polyvinyl alcohol fiber is 9mm.

3. Test Results and Analysis of Cement Properties of Fiber-latex-calcium Carbonate Whisker Gas Storage

3.1. Test and analysis of conventional properties of cement slurry

The performance of cement slurry is an important factor to ensure the feasibility of cementing operation and cementing quality. Rheological properties, thickening time, water loss, free liquid and other properties will affect the pumping difficulty of cement slurry, construction safety factor, displacement efficiency of cement slurry, compactness of cement paste and anti-channeling performance. For this reason, the following performance tests have been made for the optimized cement slurry for gas storage, and the test results are shown in Table 5.
Table 5. Performance test of formulated cement paste

| Numbering | Mobility /cm | Fluidity index n (normal temperature) | API water loss/ml | Free liquid/ml |
|-----------|-------------|----------------------------------------|------------------|----------------|
| S0        | 22          | 0.77                                   | 33               | 1.6            |
| S1        | 21.9        | 0.73                                   | 22               | 0              |
| S2        | 20.4        | 0.81                                   | 24               | 0              |

It can be seen from table 5 that the fluidity of S1 formula cement slurry after adding fibers is lower than that of S0 original slurry cement due to the hydrophilicity and random uniform distribution of fibers, and the fluidity of S2 formula after adding neoprene latex is slightly lower than that of S1 formula, but the fluidity of the three formulas is all greater than 18cm, which meets the requirements of site construction for the fluidity of cement slurry; The free liquid of formula S1 and S2 is zero and the water loss is less than 50ml, which meets the performance standard of cement matrix in gas storage. It can be seen from the thickening performance curves of cement slurry in fig. 1, fig. 2 and fig. 3 that the thickening curve of S2 formula cement slurry has right-angle characteristics, the initial consistency is less than 30Bc, the thickening transition time of cement slurry is less than 15 minutes, and the thickening transition time is short, which shows that the cementing strength of S2 formula cement slurry develops rapidly and can effectively avoid water channeling. Therefore, the cementing slurry of S2 formula gas storage can meet the construction standard.

![Figure 1. Thickening performance curve of S0 cement](image1)

![Figure 2. S1 thickening performance curve of S1 cement](image2)

![Figure 3. S2 thickening performance curve of cement slurry](image3)
3.2. Test and analysis of mechanical properties of cement paste

3.2.1. Stress-strain relationship of cement paste. In order to study the mechanical properties of cement paste under the actual working conditions of gas storage wells, triaxial stress-strain tests were carried out on cement paste modules cured at 60°C for 7 days with S0, S1 and S2 cement pastes under confining pressure of 20MPa. Figure 4, Figure 5 and Figure 6 show the stress-strain relationship of cement paste with different material ratio under triaxial confining pressure. As shown in fig. 4-6, the strain of S1 and S2 formula cements when reaching ultimate strength failure is greater than that of S0 virgin cement, and the 7-day strength of S1 and S2 formula cements is higher than that of S0 virgin cement. Comprehensive analysis shows that S2 formula cements have the best deformability.

![Figure 4. Triaxial stress-strain curve of S0 cement](image)

![Figure 5. S1 triaxial stress-strain curve of cement paste](image)

![Figure 6. S2 triaxial stress-strain curve of cement](image)
3.2.2. Test of mechanical properties parameters of cement paste. Test data of mechanical properties parameters of cement paste formulated by S0, S1 and S2 cured in 60°C water bath for 7 days are shown in Table 6.

Table 6. Mechanical performance parameters of cement paste

| Formula No. | 7d tensile strength/MPa | 7d compressive strength/MPa | Elastic modulus/GPa | Poisson's ratio |
|-------------|-------------------------|-----------------------------|---------------------|----------------|
| S0          | 2.61                    | 32.20                       | 7.152               | 0.179          |
| S1          | 3.92                    | 49.36                       | 3.945               | 0.185          |
| S2          | 4.23                    | 47.11                       | 3.790               | 0.189          |

Remarks: Curing temperature is 60°C, curing time is 7 days, and the experimental loading confining pressure is 20MPa.

According to the analysis of the data in Table 6, the strength performance of cement paste can be improved after adding fiber and calcium carbonate whisker into S1 formula cement slurry. After adding chloroprene latex into S2 formula, the tensile strength of cement paste is obviously improved. The 7d compressive strength of S2 formula cement paste is 47% higher than that of virgin cement paste, and the 7d tensile strength is 62.3% higher than that of virgin cement paste. This shows that adding a certain amount of fiber into cement slurry can effectively improve the strength of cement paste. After adding neoprene latex into S2 formula, the tensile strength of cement paste is further improved. Although the 7-day compressive strength of S2 formula cement paste is slightly lower than that of S1 formula cement paste, the toughness of S2 formula cement paste is the best, which can meet the toughness requirements of gas storage cement paste.

In the process of gas injection and production in gas storage, the cement sheath should have enough ability to resist the deformation and crack resistance of external forces in different directions. Based on the triaxial test data, the elastic modulus and Poisson's ratio of cement paste are calculated, and the results are shown in Table 6. The elastic modulus of S1 and S2 cement paste is greatly reduced compared with that of S0 virgin cement paste, while Poisson's ratio is improved. Especially, the elastic modulus of S2 cement paste is reduced by 47.1% compared with virgin cement paste after adding chloroprene latex. This shows that the combined action of neoprene latex, calcium carbonate whisker, polypropylene fiber and PVA fiber can not only improve the stress deformation ability of cement paste, but also enhance the strength of cement paste. When it is applied to gas storage wells, it can prolong the service life of cementing cement sheath and improve the service life of gas storage wells.

To sum up the experimental results, it can be concluded that S2 formula cement slurry system has excellent performance, which can meet various performance requirements of gas storage cementing and improve cementing quality. S2 cement slurry formula is: G grade cement +1.5% fluid loss additive +1% dispersant +0.5% defoamer +10% calcium carbonate whisker +8% neoprene latex +0.08% polypropylene fiber +0.09%PVA fiber+water.

4Mechanism Analysis of Cement Performance Enhancement in Fiber-latex-calcium Carbonate Whisker Gas Storage

By observing the microstructure and morphology of cement paste, the performance mechanism of gas storage cement reinforced by fiber, neoprene latex and calcium carbonate whisker was analyzed. Fig. 7 is a scanning electron microscope picture of the microstructure of cement paste with fiber-neoprene latex-calcium carbonate whisker S2 formula. in fig. 7, a is calcium carbonate whisker, b is fiber and c is neoprene latex.
By observing the microstructure of cement paste, it is found that whisker, fiber, latex and cement can grow well. When the cement paste is subjected to external load, the calcium carbonate whisker firstly reduces the stress concentration at the tip of micro-cracks in the cement paste by bridging action. With the increase of pressure, the whisker further inhibits the crack propagation through crack deflection until the external force reaches the ultimate tensile strength of the whisker. Whiskers are pulled out, and the process of whisker pulling out can also consume the crushing energy of cement paste to a certain extent, so that the role of whiskers in the pressure bearing process of cement paste ends. With the increase of pressure and crack size, fibers enhance the mechanical properties of cement paste in the same way of bridging, dispersing stress concentration and preventing crack development. During the hydration and hardening process of cement slurry, the colloidal particles precipitated from latex have certain elasticity and strength, which can effectively disperse and delay the spread of external forces. Various additives form complementary action in the process of pressure cyclic loading, which can prevent crack development at different stages and levels in the process of cement paste failure, change the brittle failure mode of virgin cement paste, and enhance the ductility of cement paste.

Use energy spectrometer to detect energy spectrum elements in S2 cement paste, as shown in Figure 8.

![Figure 7. S2 microstructure of formulated cement](image1)

![Figure 8. Analysis of surface elements of microstructure of S2 formula cement](image2)
According to the analysis in fig. 8, C, O, Si, Ca, Cl, Mg, Al and other elements are mainly attached to the fiber surface of cement paste extracted by fiber-neoprene latex-calcium carbonate whisker S2 formula, and the weight percentage of Si element shows that more cement hydrate is brought out during fiber extraction after latex is added. This shows that latex film formed on the surface of cement particles, fibers and whiskers can improve the microstructure of the interface between fibers and whiskers and cement matrix, relieve stress concentration caused by sudden change of materials, improve the interfacial bonding strength and increase the adhesive force between fibers and cement matrix surface. In addition, the cement attached to the fiber surface can increase the friction force between the cementation interfaces in the process of fiber pulling out, which makes the fiber difficult to pull out, thus consuming more crushing energy in the process of fiber pulling out and improving the strength and toughness of cement paste.

To sum up, fibers and calcium carbonate whiskers are uniformly and randomly distributed in cement matrix, which can effectively bridge multi-directional cracks in cement paste, disperse stress concentration at crack tip, prevent crack development, increase deformation ability of cement paste and reduce elastic modulus of cement paste. Chloroprene latex can form latex film on the surface of cement particles, whiskers and fibers, which can improve the interface microstructure of whiskers, fibers and cement matrix, improve the interfacial bonding strength, relieve the stress concentration caused by material mutation, and significantly improve the toughness of cement paste.

4. Summary
(1) The optimal formula of cement slurry system is: G grade cement +1.5% fluid loss additive +1% dispersant +0.5% defoamer +10% calcium carbonate whisker +8% neoprene latex +0.08% polypropylene fiber +0.09% PVA fiber + water.
(2) The cement slurry system of fiber-latex-calcium carbonate whisker gas storage has good engineering performance, large adjustable range of thickening time, good rheological property, low water loss, no free liquid and good anti-channeling ability. Compared with virgin cement paste, the 7-d tensile strength of cement paste in fiber-latex-calcium carbonate whisker gas storage increased by 62.3%, the 7-d compressive strength increased by 47%, and the elastic modulus decreased by 41.7%. The mechanical properties of cement can meet the cementing quality requirements of gas storage.
(3) The enhancement mechanism of cement performance in fiber-latex-calcium carbonate whisker gas storage is that fiber and calcium carbonate whisker can bridge cracks, disperse stress concentration at crack tip, prevent crack development, increase deformation ability of cement paste and reduce elastic modulus of cement paste. Latex forms a latex film on the surface of cement particles and fibers, which can improve the microstructure of the interface between fibers and cement matrix, increase the interfacial bonding strength, relieve the stress concentration caused by sudden change of materials, and significantly improve the toughness of cement paste.

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