

Research Article

Lab Study on the Effect of Cation Exchange Capacity on Slurry Performance in Slurry Shields

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Ion stabilizers can enhance the reinforcement slurry effect on the wall and stabilize the wall actively in slurry shields. This paper presents different cation exchange capacities obtained by changing the content of the ion stabilizer (1.5%, 2.0%, 2.5%, 3.0%, 3.5%, 4.0%, 4.5%, 5.0%, 5.5%, and 6.0%) in slurry associated with the basis of the existing slurry formula through the laboratory tests. In order to study the effect of the cation exchange capacity on the performance of slurry properties, the rheological properties of the slurry are analyzed and evaluated by the power law model. Results indicate that the cation exchange capacity of the slurry decreases first and then increases with the increase of the ion stabilizer content. When the content of the ion stabilizer is maintained at 3.50%, the cation exchange capacity reaches the minimum value of 2.92. The filtration volumes, pH values, and rheological parameters of the slurry also indicate an obvious linear change with the change of the cation exchange capacity. The minimum filtration volume is 9.70 mL/30 min when the ion stabilizer content reaches 3.50%. However, the pH value reaches the maximum, that is, 11.34 which is changed from 10, and the change could be considered as a constant value in the field work. When the cation exchange capacity increases, the continuity of polymer structure in the slurry decreases first and then increases, the flow index and consistency coefficient are located within a reasonable range, and the rheological properties of the slurry meet the design requirements of the standards.

1. Introduction

Slurry shields are TBM fitted with a full-face cutterhead which provides face support by pressurizing boring fluid inside the cutterhead chamber. The pressurized slurry system plays an important role in the stability of the excavation face associated with filter cake in slurry shields [1–4]. The slurry should be able to create an impermeable membrane at the ground interface. Once the ground interface becomes impermeable, the slurry can develop an adequate confinement pressure. Polymers, sands, vermiculites, even micro-organism, and other additives are usually added into the slurry to improve the performance of slurry in practical

construction engineerings [5–9]. Slurry shields in rock would generally require slurry with properties related mostly to its basic functions as lubrication, transport of cuttings. Slurry shields in soil would require slurry with properties related to primary functions, such as marsh funnel and plastic viscosity, pH, yield point, and filter cake properties. When slurry shields in mix ground conditions, it requires slurry with both primary functions and specific properties which are not simply the one applying to the worst soil conditions encountered at the face. There are new factors to consider, which exist only in mix face conditions, and cation exchange capacity of the slurry is one of them. The cation exchange capacity (CEC) is usually called methylene blue

capacity that is an important parameter representing the exchangeable ion quantity of the slurry such as ion stabilizer slurry fluid, which directly reflects the ion exchange capacity of the slurry fluid. It can be obtained according to the methylene blue titration test, a major international measurement method first proposed by the American Petroleum Society (API), and the total cation exchange capacity in the slurry fluid could be calculated. The bentonite-free slurry fluid formulation system composed of plant gum, poly-anionic cellulose, liquid ion stabilizer, graphite powder, and barite is selected on the basis of existing research because the bentonite itself has a certain cation exchange capacity, and the polymeric materials can meet the design requirements of viscosity, rheology, and filtration loss. Different cation exchange capacities are obtained by changing the content of the ion stabilizer in the slurry fluid, and the rheology performance of slurry is analyzed and evaluated by the power law model on the basis of the existing formula.

In formation evaluation, it is the contribution of cation exchange sites to the formation of electrical properties that is important or required to determine the clay types and dry clay parameters. In slurry shields, most studies are focused on the filter cake properties [10–13]. Because it is easy for slurry to penetrate into the stratum, causing a large amount of fluid loss when slurry shields cut through strong permeability stratum, resulting in poor filter cake on the excavation face, which is incapable of providing enough support required for the stability of the excavation surface [14–17]. Several factors control the formation of filter cake, such as the permeability of the rock and soil, the pressure, and properties of slurry (density, rheological properties, grain size distribution, etc.) [18–22]. Watanabe and Yamazaki and Wang and Zhu [23, 24] investigated the effects of density of slurry on the fluid loss in the highly permeable soils, and they found that the proportion of sand in the slurry played an important role in the fluid loss of slurry during the formation of filter cake. Cheng et al. [18] performed laboratory model tests on pure bentonite suspensions in medium coarse sands, and results indicated that the viscosity of suspensions had a significant influence on the filter cake properties. Fritz et al. [15] and Heinz [20] developed an apparatus for measuring the support pressure of slurry and performed the support pressure tests to evaluate the best combination of additives in slurries. Han et al. [19] evaluated the factors that control the formation of filter cake based on some laboratory tests; the results showed that the higher the viscosity of the slurry was, the easier for the filter cake to form, and the filter cake formed was thin and compactable. If there was less fluid loss in the process of formation of the filter cake, it indicated that the filter cake is easy to form. However, if there was less fluid loss after the filter cake formed, it indicated that the filter cake was compactable. Min et al. [25] investigated the processing of filter cake formed on the surface of coarse grained sandstone with high pressure, and the results indicated that the formation of filter cake was affected by the properties of slurry, especially particle size and density. Filz et al. [26] presented formed criteria of filter cake in sandy formation, and the results indicated that the percolation range had much more

effects on the strength of coarse granular soil due to the poor filter cake. Amorim et al. [27] investigated the influence of ionic strength on the apparent and plastic viscosities and water loss in sodium bentonite suspension with polymers, and the results could be concluded that the presence of salt and the increase of salinity in these suspensions strongly affect the plastic and apparent viscosities and water loss after polymers added. Liu and Santamarina [28] advanced a comprehensive filter cake growth model for water-based slurry implemented with robust, physically informed constitutive equations in their study, and they also obtained the results that environmental factors such as temperature, pH, ionic concentration, and cation contamination have a significant influence on filter cake properties. In this paper, further studies show the effect of ion exchange in slurry on its properties based on the current study mentioned above. Bentonite is composed of two tetrahedrally coordinated sheets of silicon ions surrounding an octahedrally coordinated sheet of aluminum ions, the isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} or Fe^{3+} for Al^{3+} in the octahedral layer results in a net negative surface charge on the layer, which makes it hold its physical and chemical properties, i.e., large specific surface area, cation exchange capacity, and adsorptive affinity for organic and inorganic ions [29, 30]. When the bentonite contained in the stratum dissolve in the slurry, the cations in the slurry (such as Ca^{2+} , Na^+ , and Mg^{2+}) will lead to chemical deterioration on the filter cake associated with slurry circulation, and the interaction between these charged ions can create an electrostatic field around them [31]. That is, the slurry will be converted from the well-suspended dispersion to the agglutination state and resulted in the increase of particle size. At the same time, the poor quality of the filter cake will appear and the slurry will lose its basic functions [32, 33]. In order to regulate the performance of slurry based on the micro- and macropoint, it is essential to study the effect of the cation exchange capacity on the performance of slurry. In this case, a dense, low permeability filter cake can be formed on the cutting face and improve the stability of the wall during excavation.

The ion stabilizer is one kind of advanced material and widely used to improve the physical and mechanical properties of stratum in many fields to meet the requirements of engineering technology, such as slope protection, water conservancy construction, road subgrade, and trenchless [34]. The ion stabilizer has strong practicability, stable performance, and low cost, as a new kind of chemical material. A proper amount of the ion stabilizer dissolves in the slurry fluid can form ionic solutions; that is, a liquid organic salt composed of cations and anions [35], which contains the basic properties of shield slurry. The ion stabilizer mainly forms high valence ions and water compounds with low water binding and high cohesive force in solution by ion exchange as an additive in the slurry fluid. The high valence cations in the solution are adsorbed by clay particles in the stratum, with neutralizing the negative charge on the surface of particles, reducing the repelling force between the clay particles, and effectively restraining the stratum hydration and expansion to improve the stability of the

excavation. The water compounds formed in the solution can effectively seal the cracks in the wall, reducing the invasion of filtrate, and improve the mechanical strength and impermeability of the rock and soil near the wall at the same time [36].

2. Materials and Methods

2.1. Materials. The test materials include ENI ion stabilizer, methylene blue titration materials and basic slurry fluid formulation materials consist of solvent (water), vegetable gum (CT), polyanion cellulose (PAC), graphite powder, and barite. The ENI ion stabilizer is mainly composed of petroleum sulfonated agent, modified sodium silicate, modified polymer surface active agent, and other materials, and it can decompose the clay mineral and nonclay particles in the stratum. It also can recrystallize the clay mineral particles and reduce the invasion of filtrate rely on making use of bonding and winding between polymer compounds and leaving the particles hydrophobic and dense. Its appearance is light yellow as shown in Figure 1. The positive charges in methylene blue solution are alkaline, which are unstable and able to react with most inorganic salts to produce compound salts. 0.01 mol/L methylene blue water solution, 3% hydrogen peroxide solution, and 2.5 mol/L dilute sulfuric acid solution were used as the methylene blue titration experiment materials in this study, as shown in Figure 2.

2.2. Methods. Different cation exchange capacities were obtained by changing the content of ion stabilizers in the slurry fluid based on the existing formula, and the designed addition of the ion stabilizer in the experiment was 1.5%, 2.0%, 2.5%, 3.0%, 3.5%, 4.0%, 4.5%, 5.0%, 5.5%, and 6.0% (Group 1–10). The same slurry fluid basic formula was used in each group in order to obtain the degree of influence of the ion stabilizer.

The slurry fluids with different ion stabilizer contents were prepared according to the API standard in the experiment. The slurry performance parameters of each group were measured by the ZNN-D6 digital display rotary viscometer, and the data were recorded. According to the standard analysis method, the rheological parameters of each group could be calculated with the data. The pH values of slurry were measured three times in each group by precision acidity and alkalinity tester, and then the average of these data was calculated. The tests of filtrate volume were carried out according to the API RP 13B-12009 standard, and the control pressure value was maintained at 0.69 MPa. The methylene blue titration tests were carried out three times for each group of slurry fluids according to the standard GB/T16783.1-2006, and the average CEC values were obtained. The mathematical formula for the calculation is as follows [37, 38]:

$$CEC = \frac{V_M}{V_D}, \quad (1)$$

where CEC is the cation exchange capacity of the slurry fluids (dimensionless unit), V_M is the consumption of methylene blue standard solution (mL), and V_D is the amount of slurry fluid samples (mL).

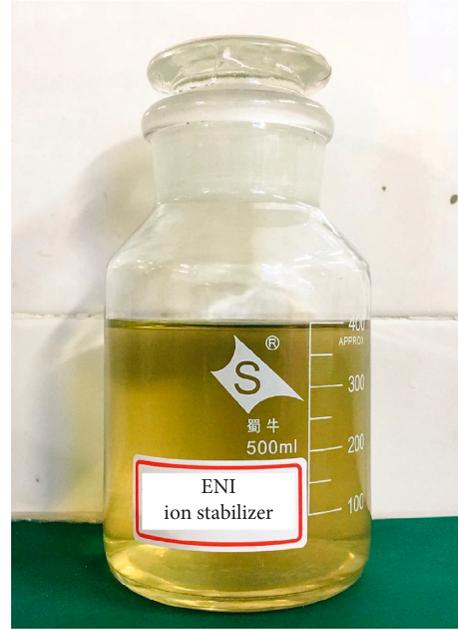


FIGURE 1: The actual picture of ENI ion stabilizer.



FIGURE 2: The reagent used for the methylene blue titration test.

3. Results and Discussions

All the pH test, methylene blue solution titration test (CEC), and filtrate test (FL_{API}) of slurry fluids were performed in the drilling fluid lab in Central South University, and the test results obtained are shown in Table 1.

3.1. Relationship between Cation Exchange Capacity of the Slurry Fluid and Its Content of Ionic Stabilizer. The relationship between the cation exchange capacity of the slurry fluid and its content of the ion stabilizer is indicated in Figure 3. The cation exchange capacity of the slurry fluid decreases first and then increases with the increase of the content of the ion stabilizer, and the cation exchange capacity of the slurry fluid is minimum when the stabilizer content is 3.5%.

TABLE 1: Experimental results of slurry fluids with different contents of ionic stabilizer.

Content (%)	PAC (%)	CT (%)	Graphite powder (%)	CEC	FL_{API} (mL)	pH
1.50				4.75	11.30	10.99
2.00				4.25	10.60	11.16
2.50				3.58	10.30	11.21
3.00				3.25	10.20	11.26
3.50	0.30	2.50	0.50	2.92	9.70	11.34
4.00				3.42	10.50	11.26
4.50				4.92	10.60	11.02
5.00				6.00	10.90	11.08
5.50				6.83	11.30	11.09
6.00				7.67	11.50	11.12

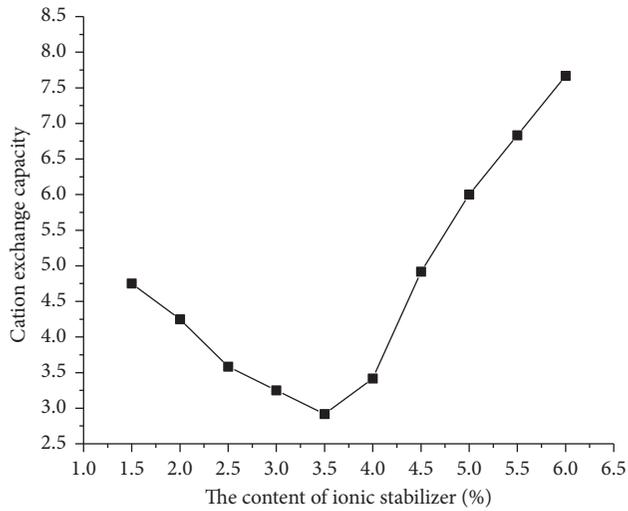


FIGURE 3: Curve of cation exchange capacity of the slurry fluid.

3.2. Effect of Cation Exchange Capacity on Filtrate and pH.

Figure 4 shows the relationship between the cation exchange capacity of the slurry fluid and the filtrate volume. As the cation exchange capacity of the slurry fluid increases, filtrate volume also increases with it. The residue deposits on a permeable stratum when the slurry is forced against the stratum under a pressure. Filtrate is the liquid that passes through the stratum, leaving the filter cake on the cutting surface. When the filter cake formed, it has an important effect on filtration, mainly including inherent resistance and adsorption resistance. The inherent resistance of the filter cake can be considered as a constant in this experiment, which is generally related to the concentration of the slurry fluid and the characteristics of the filter. The adsorption resistance is greatly influenced by the adsorption capacity, which increases as the ion exchange capacity of the slurry fluid increases. According to the calculation model of adsorption resistance, the adsorption differential pressure increases as the viscosity of the slurry fluid is constant, which indirectly leads to the increase of the filtrate volume of the slurry fluid.

Figure 5 shows the relationship between the cation exchange capacity and its pH values of the slurry fluid. The

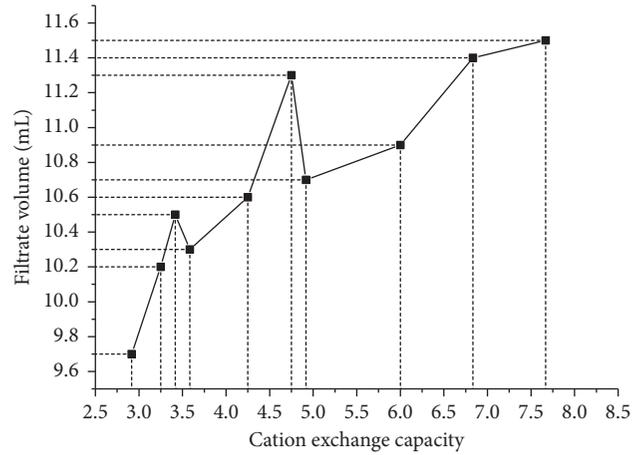


FIGURE 4: Curve of filtration volume.

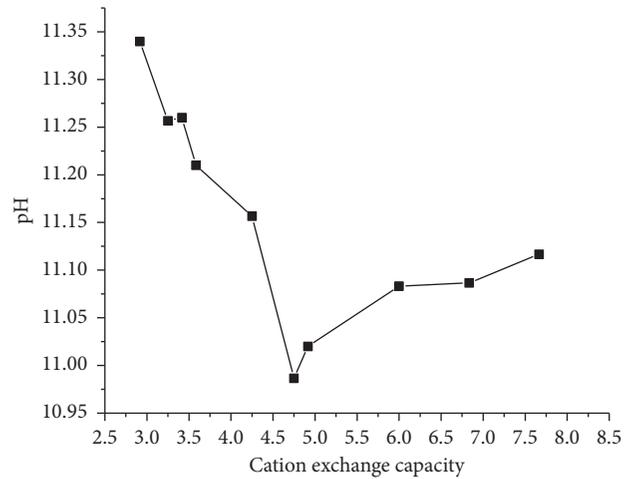


FIGURE 5: Curve of pH change in the slurry fluid.

pH value decreases first and then increases with the cation exchange capacity increasing. A solution with a concentration of hydrogen ions higher than 10^{-7} mol/L is acidic, and a solution with a lower concentration is alkaline, which indicates that hydrogen ions concentration in the slurry is less than 10^{-10} mol/L. So, it is easy to learn that the slurry fluid is still an alkaline solution of $\text{pH} > 10$ from the diagram. However, the change of pH is relatively small, which can be seen as a constant in practical engineering.

3.3. Effect of Cation Exchange Capacity of the Slurry Fluid on Its Rheological Properties. The rheology is the characteristics of slurry fluid flow and deformation under the action of external forces, which is generally expressed by different rheological models and parameters.

The rheological parameters of the slurry fluid are tested and calculated according to the API standard. The rheological model discrimination coefficient (F) under different cation exchange capacities is calculated by Equation (2), and the results are shown in Table 2.

TABLE 2: Rheological model discriminant coefficient (F).

CEC	2.92	3.25	3.42	3.58	4.25	4.75	4.92	6.00	6.83	7.67
F	0.56	0.54	0.46	0.48	0.55	0.56	0.33	0.47	0.49	0.39

$$F = \frac{\theta_{200} - \theta_{100}}{\theta_{300} - \theta_{100}}, \quad (2)$$

where F is the rheological model discriminant coefficient. When $F = 0.5 \pm 0.03$, it is defined as the Bingham model; otherwise, the power law model is applied. θ_N is the dial value of viscometer when the speed is N (mPa·s).

According to above discriminant coefficients, the slurry fluid could be defined as the power law model with different cation exchange capacities. Power law fluid is non-Newtonian model, which usually includes pseudoplastic fluid and expansion plastic fluid. The rheological properties of the slurry fluid can be characterized by rheological parameters such as the flow index, consistency coefficient, apparent viscosity, plastic viscosity, and static shear force, as shown in Table 3.

3.3.1. Power Law Model. The variation tendency of flow behavior index and consistency coefficient indicate a highly symmetrical relationship, as shown in Figure 6 and Figure 7, respectively. The amount of negative charges in the slurry fluid increases with the increase of the cation exchange capacity. The high valence cations in the slurry fluid can be hydrated and flocculated when the cation exchange capacity is less than 4.75, which inhibits the ion exchange in the ionic solution. The interaction between entanglement of polymer molecular chains and the adsorbent groups on the molecular chain is weakened in the slurry fluid, and the continuity of the formed polymer spatial structure is poor, which leads to the increase of the flow behavior index and the decrease of the consistency coefficient. When the cation exchange capacity reaches 4.75, the amount of coagulation in the slurry fluid is maximum. At the time, flow behavior index and consistency coefficient reach an interval maximum value and the filtration volume also fluctuates greatly. The cationic flocculation reaction in the slurry fluid reaches a dynamic equilibrium. The flow behavior index and consistency coefficient remain constant when the cation exchange capacity reaches 4.92. The dynamic equilibrium is upset after the cation exchange capacity exceeds 6.00. Because there are a lot of free high-valence cations in the slurry fluid due to the dissolution of coagulation, the ion exchange effect in the solution is enhanced, and as the coefficient of consistency increases sharply, the flow behavior index decreases. There are too many polymers with continuous spatial structure formed in the slurry fluid which reduces the slurry fluid dispersion and decreases the water retention property, resulting in the increase of filtrate volume. Normally, the smaller the flow index is, the better the shear dilution performance of the fluid is under the power law model. However, it is not the smaller, the better when it comes to the matter of the overall performance of slurry fluid. The filtrate value of slurry fluid is the largest when the flow behavior

index is the smallest, which is indicated in Figures 4 and 6. The flow behavior index and consistency coefficient are close to the median value which is convenient to adjust related parameters, and the filtrate volume is the smallest when the cation exchange capacity reaches the minimum value.

3.3.2. Effect of Cation Exchange Capacity of Slurry Fluid on Its Viscosities. The apparent viscosity, shear stress, and shear rate of the slurry fluid with different cation exchange capacities are calculated according to the data obtained from the viscometer and Equations (3)–(5) [39, 40], and shear rate obtained is the average value to improve the accuracy:

$$\mu_{AV} = \frac{\tau}{D}, \quad (3)$$

$$\tau = 0.511\theta_N, \quad (4)$$

$$D = \frac{21936.7646N}{13750.3615 - 901.2775m + 38.5114m^2 - m^3}, \quad (5)$$

where μ_{AV} is the apparent viscosity of slurry fluid (mPa·s), τ is the shear stress (Pa), θ_N is the dial reading of viscometer when the speed is N (mPa·s), D is the shear rate (s^{-1}), N is the speed of viscometer (r/min), m is the calculation constant, and $m = 1/n$, n is the flow behavior index of the slurry fluid.

Figure 8 shows the relationship between the cation exchange capacity and slurry viscosities. They all show a highly consistent trend, decreasing first and then increasing as the cation exchange capacity increases. Finally they show a gradually decreasing trend. When the cation exchange capacity is less than 4.75, with the increase of the flocculation degree in the slurry fluid, the ion exchange effect and the dispersion degree in the solution are weakened. At the same time, as the viscosity increases, the frictional resistance between the flocculant, the polymer and the liquid phase increases at the macroscopic scale. The flocculation amount reaches the maximum and the viscosities reach the peak value while the cation exchange capacity is 4.75. And the cationic flocculation reaction in the slurry fluid reaches a dynamic equilibrium. In this case, its viscosities remain relatively constant when the cation exchange capacity is between 4.92 and 6.00. Then, the dynamic equilibrium of flocculation is tipped when the cation exchange capacity exceeds 6, and the dispersity of the slurry fluid decreases, resulting in the decrease of viscosities.

Figure 9 shows the rheological curves of slurry fluids with different cation exchange capacities. It can be learned from Equation (3) that apparent viscosity is the ratio of shear stress to shear rate at a certain shear rate; that is, apparent viscosity is the slope of the line section of the curve in Figure 8. The diminished amplitude of the slope of the curve (i.e., apparent viscosity) is maximum with the increase of the shear rate when the cation exchange capacity is the smallest, indicating that the shear dilution ability of the slurry fluid is the strongest at this time.

3.3.3. Effect of Cation Exchange Capacity of Slurry Fluid on Its Static Shear Force. The static shear force is determined by

TABLE 3: Rheological parameters of slurry fluid with different cation exchange capacities.

CEC	Flow behavior index	Consistency coefficient (Pa·s ⁿ)	Apparent viscosity (mPa·s)	Plastic viscosity (mPa·s)	Initial shear force (Pa)	Final shear force (Pa)
2.92	0.64	0.31	25.33	18.14	0.81	1.32
3.25	0.64	0.28	22.63	16.17	0.72	0.84
3.42	0.64	0.29	23.33	16.69	0.58	0.49
3.58	0.68	0.21	23.12	17.35	0.76	0.63
4.25	0.68	0.23	24.08	18.02	0.85	0.94
4.75	0.70	0.19	24.66	18.99	0.99	0.89
4.92	0.65	0.26	22.62	16.31	1.12	1.26
6.00	0.65	0.25	21.53	15.54	1.35	1.26
6.83	0.53	0.50	19.50	12.05	1.23	0.82
7.67	0.52	0.51	18.61	11.30	0.54	0.18

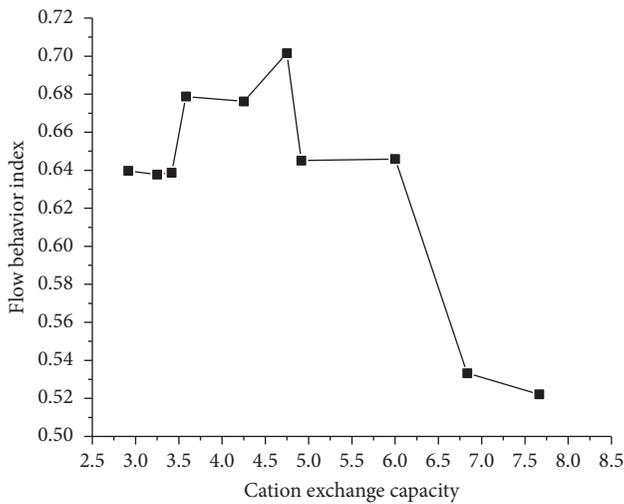


FIGURE 6: Curve of flow behavior index of slurry fluid.

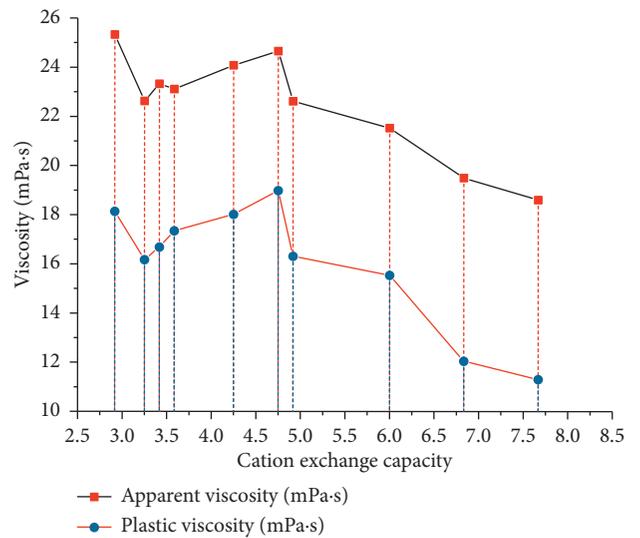


FIGURE 8: Curve of viscosities of the slurry fluid.

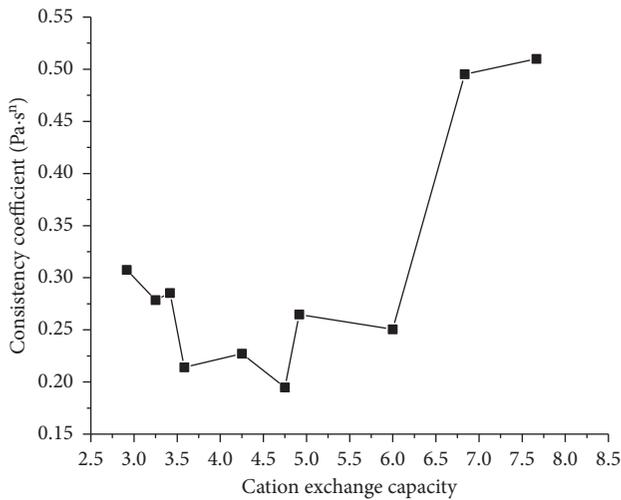


FIGURE 7: Curve of consistency coefficient of slurry fluid.

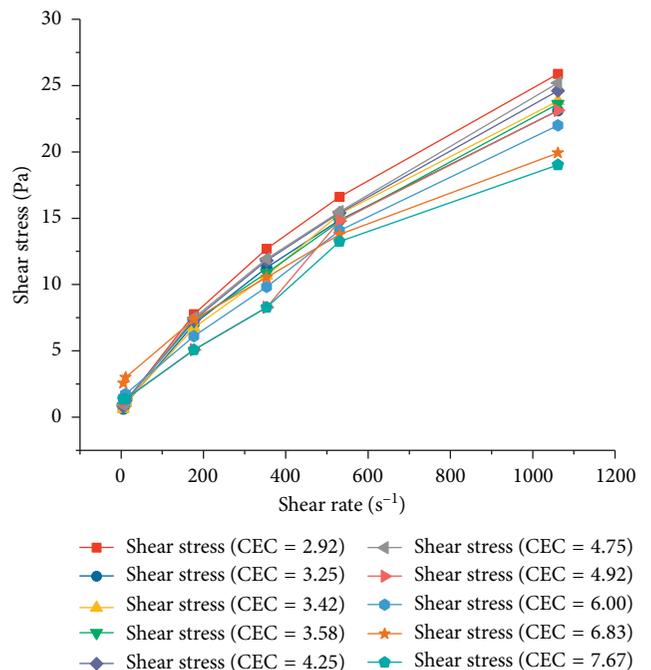


FIGURE 9: Rheological curves of slurry fluids.

the number of structural chains and the strength of the single structure chain in the unit volume. The value of static shear force mainly reflects the suspension capacity of the slurry, so the larger the static shear force is, indicating the slurry structure more stable, the better its suspension capacity is.

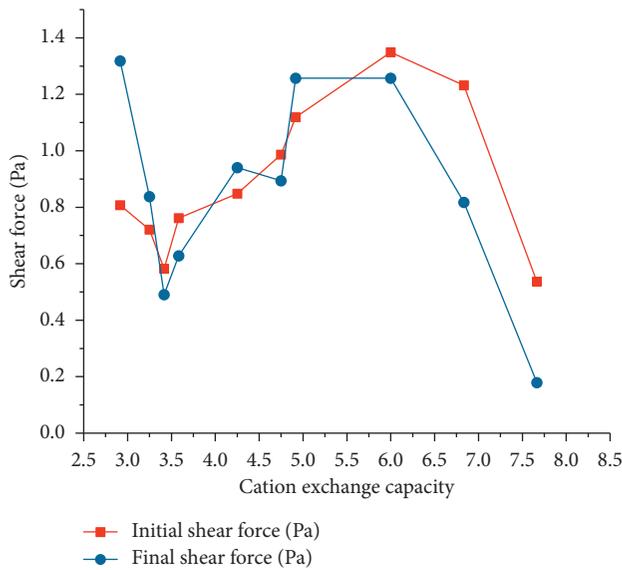


FIGURE 10: Curve of static shear force of slurry fluid.

The varying regularity with the cation exchange capacity is shown in Figure 10. The structure formation of the polymer space is hindered by the hydration and flocculation of high valence cation with the increase of the cation exchange capacity, and the static shear force of the slurry fluid drops sharply when the cation exchange capacity is less than 3.42. The floc and the polymer can form a complex with a certain spatial structure and strength with the flocculation reaction, which leads to the gradual increase of the static shear force when the cation exchange capacity is between 3.42 and 6.00. The dynamic equilibrium of the flocculation reaction is tipped after the cation exchange capacity exceeds 6.00. Then the structures of the complex begin to break down with the ion exchange enhanced in the solution. When the continuous polymer of excessive space structure is formed, it will result in diminish in dispersion of the slurry fluid, which makes the static shear force reduce abruptly.

4. Conclusions

Ion stabilizers can enhance the reinforcement slurry effect on the wall and stabilize the wall actively in slurry shields. This paper presents the effect on the slurry fluid from different cation exchange capacities.

The cation exchange capacity of the slurry fluid decreases first and then increases following the increase of the ion stabilizer content in the slurry fluid. And the filtration volume, pH value, and rheological parameters of the slurry fluid indicate a linear trend obviously as the cation exchange capacity increases.

With the increase of the cation exchange capacity, the continuity of the spatial structure formed by the polymer in the slurry fluid decreases first and then increases, which directly leads to the change of the flow behavior index. The viscosity and static shear force of the slurry fluid present a corresponding regular change with the continuity of the polymer spatial structure too.

The test results also indicate that the filtrate of the slurry fluid is minimum when the cation exchange capacity reaches the smallest. This is beneficial to restrain the hydration expansion of rock and soil, maintaining the stability of the excavation face. Slurry filtrate volume and rheological parameters such as viscosity, static shear, flow behavior index, and consistency coefficient are present with ideal values following with smallest value of the cation exchange capacity. The spatial structure of the polymer in the slurry fluid is relatively continuous, which is beneficial to cation transporting in the fluid system. These cations can neutralize the negative electricity of the clay in the cutting face and strengthen the stability of the wall. In this case, the overall performance of the slurry fluid reaches a relatively ideal state.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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