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Adsorption behavior of silica nanofluid on coal and its injection enhancement mechanism

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ADSORPTION BEHAVIOR OF SILICA NANOFLUID ON COAL AND ITS INJECTION ENHANCEMENT MECHANISM

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ABSTRACT: Coal seam water injection has proven effective in mitigating coal and gas outburst disasters in mines. However, its drawbacks, including the poor wettability of coal seams and the susceptibility to filtration loss of injected water, have led to low construction efficiency and uneven control outcomes. In this study, we propose a novel approach to address these issues by utilizing a water-based silica nanofluid to alter surface wettability. The four-stage deposition process of nanoparticles on the coal surface is identified, and the time-varying behaviour of modified coal wettability is revealed under the influence of key parameters, such as particle concentration. These findings provide a foundation for the application of nanofluids in modifying the wettability of reservoirs.

INTRODUCTION

Nanofluid, as a new type of fluid, has attracted lots of attention because of its excellent performance in changing rock wettability, which making it applicable in enhanced oil recovery (EOR) (Aghajanzadeh, et al., 2019). For the field of coalbed methane development, coal seam wettability is a very important parameter especially in coal seam water injection (A hydraulic measure to prevent coal and gas outburst). Therefore, the possibility of using nanofluid to improve the coal seam wettability for enhancing water injection effect becomes a very interesting topic.

In this work, water-based silica nanofluid, which has stable performance and is environmentally friendly, is selected as a wetting agent for coal seam water injection. Several variables are set to investigate the whole process of "particle adsorption-modification effect-injection enhancement mechanism" of nanofluid wetting agent, aiming to reveal the adsorption behavior of silica nanofluid on coal and its mechanism of injection enhancement through experiments.

SURFACE DEPOSITION CHARACTERISTICS OF SILICA NANOFLUIDS

Deposition patterns of nanofliuid droplets

The morphological evolution of droplets on solid surfaces is typically characterized by the contact line and contact angle. In this experiment, nanofluids come into contact with the coal surface, forming a stable droplet as the initial state. The concluding state is defined when moisture dissipates from the droplet until the angle between the droplet and coal surface falls below 10°, indicating complete nanoparticle precipitation. To mitigate individual differences, the time taken for droplet morphological evolution is normalized, yielding the morphological evolution law of silica droplets, as illustrated in **Figure 1**.

The coal sample exhibits favourable hydrophilicity towards nanofluid droplets, with a contact angle less than 90°. In contrast, deionized water droplets maintain symmetry throughout the evolution process, while nanofluid droplets display asymmetry. Notably, when the normalized time exceeds 0.6, particles gradually precipitate at both ends of the nanofluid droplets. This phenomenon is most pronounced in nanofluid droplets with a particle concentration of 1.5 wt%.

The nanoparticles precipitated from nanofluid droplets with four different particle concentrations adsorb and deposit on the coal sample surface, which can form different deposition patterns. Then, the scanning electron microscope (SEM) was adopted to observe the overall deposition patterns formed by the nanofluid droplets with four different particle concentrations. By doing so, the enlarged images of the deposition patterns are demonstrated in **Figure 2**.

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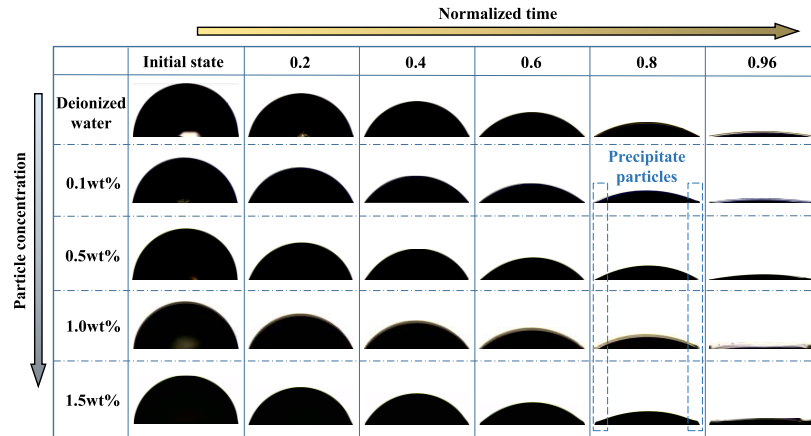
Figure 1: Evolution law of nanofluid and deionized water droplets morphology (Zou et al., 2023)

Obvious coffee-ring phenomenon (inhomogeneous deposition) could be observed on the edges of the deposition patterns formed by the nanofluid droplets with four different particle concentrations. This phenomenon is due to that the moisture of the edge of the droplets in the evolution process dissipates faster than that of the middle part of the droplets. This makes the capillary compensation flow formed inside the droplets flows from the center to the edge of droplets so as to make up for supplementing dissipated liquids, which allows the nanoparticles inside the droplets flow from the centre to the edge of the droplets to deposit (Deegan et al., 1997). Moreover, when the particle concentration is 0.1 wt%, the coffee ring of the deposition pattern for nanofluid droplets shows good continuity, with no evident fracture phenomenon occurred; when the particle concentration is 0.5 wt%, the fracturing phenomenon begins to occur in the coffee ring of the deposition pattern for nanofluid droplets; while when the particle concentrations are 1.0 wt% and 1.5 wt%, fractures can be obviously found in the coffee ring of the deposition pattern for nanofluid droplets, and a liquid bridge forms on the surface of nanoparticle aggregates. With further moisture dissipation, the liquid bridge connecting nanoparticle aggregates rupture instantly. This makes the nanoparticle aggregates subjected to the horizontal force arising from capillary force, causing circumferential force on the aggregates to increase stepwise to further be subjected to displacement (Yu et al., 2019).

Four-stage deposition process of nanofluid droplets

As shown in **Figure 3**, the variations in contact angle and contact line for nanofluid droplets with four different particle concentrations. It is evident that the changes in both the contact angle and contact line follow a similar pattern across the different particle concentrations. Specifically, the contact angle gradually decreases and exhibits a linear decline. Nevertheless, the decreasing amplitude of the contact line progressively intensifies with increasing normalized time, displaying an initial flattening change followed by a sharp decline.

Based on the variations in contact angle and contact line, the droplets undergo four distinct stages during the entire moisture dissipation-particle deposition process: the initial stage, contact angle dominance change, contact angle and line co-dominance change, and complete deposition. As illustrated in **Figure 4**, in the initial stage, nanoparticles within the nanofluid droplets are uniformly distributed. As moisture dissipates, the droplets progress into the angle dominance change stage. During this stage, the length of the contact line remains relatively constant, while the thickness and contact angle of the droplets gradually decrease. This results in the center zone of the droplets becoming thinner, and nanoparticles gradually accumulating towards the droplet's edge.

As the contact angle between the droplets and the coal sample surface decreases to a critical value, there is a sudden drop in the relative length of the contact line, marking the transition to the contact angle and line co-dominance change stage. In this stage, both the contact angle and the length of the contact line noticeably decrease. The droplets begin to shrink back towards the center, forming two distinct parts separated by the droplet edge. This process continues until the nanoparticles are entirely precipitated from the droplets, ultimately creating a deposition pattern on the coal sample surface, referred to as the complete deposition stage. It is noteworthy that the adsorption and deposition behavior of nanofluid droplets on the coal sample surface closely resembles the heating and evaporation behavior of droplets on a smooth surface.
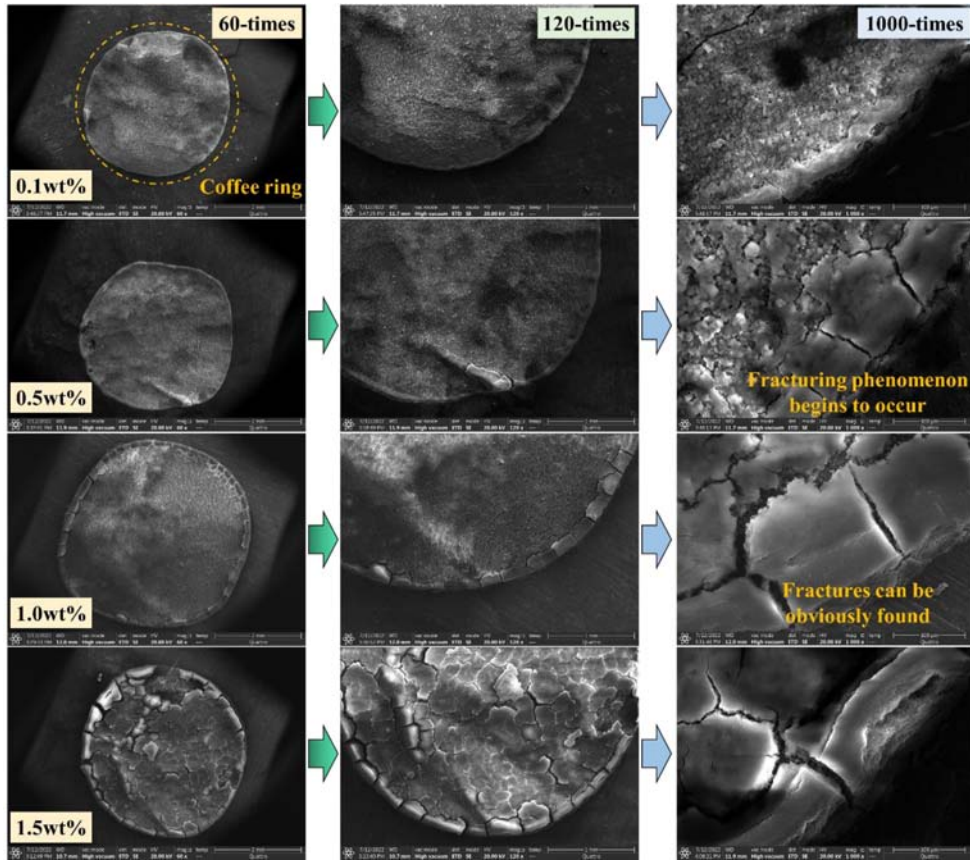
Figure 2: Deposition patterns of nanofluid droplets with different concentration (Zou et al., 2023)
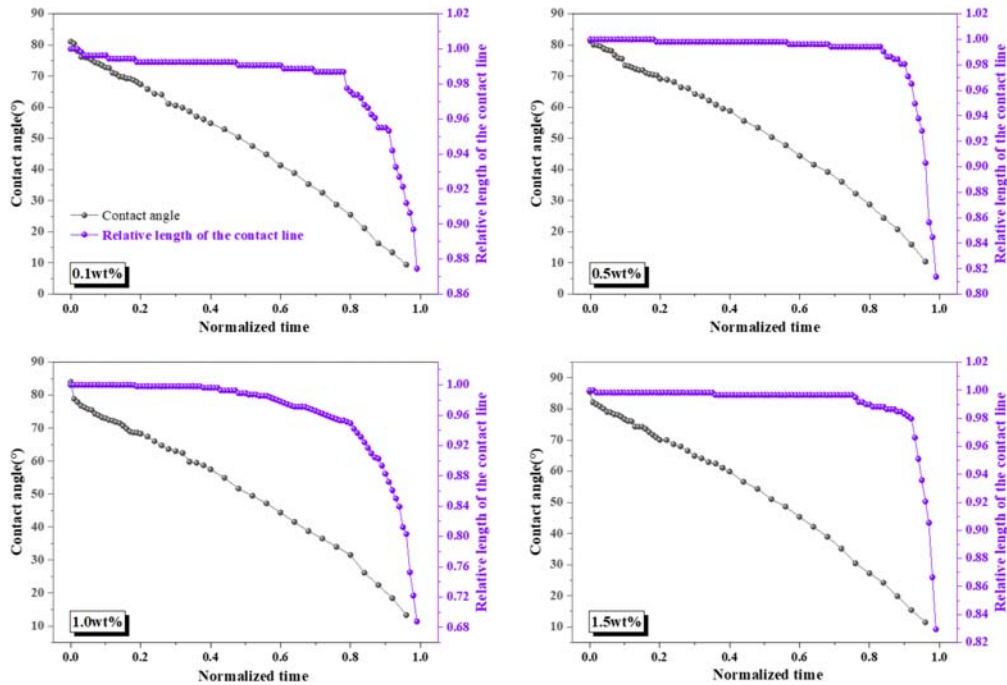

Figure 3: Corresponding relationship between contact line and contact angle of droplets (Zou et al., 2023)
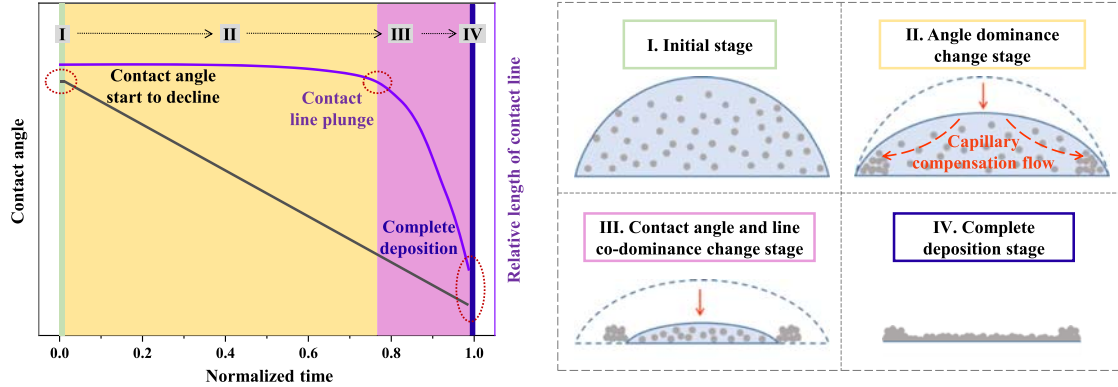
Figure 4: Four-stage deposition process of nanofluid droplets (Zou et al., 2023)

EFFECT OF SILICA NANOFLUID ON WATER CONTENT AND WETTABILITY

Variation in water content

The weight changes of the coal samples are depicted in **Figure 5**. The curves illustrate that the weight change patterns for the four coal samples treated with nanofluids at varying concentrations are similar, demonstrating a notable increase in mass after nanofluid treatment. Furthermore, a distinct reduction in mass is observed after sedimentation removal. Overall, the mass of the coal samples gradually decreases over time due to water evaporation. By the 13th day, the weight of each coal sample approaches its initial weight.
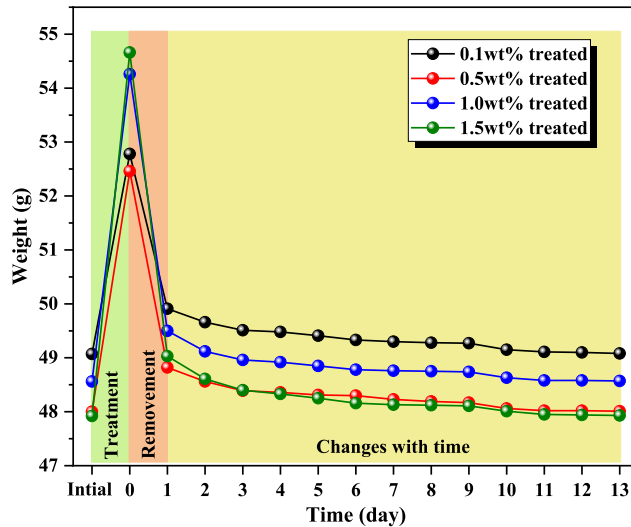

Figure 5: Changes in weight of coal samples (Zhang et al., 2022)

The total mass of sedimentation and water adsorbed after nanofluid treatments is presented in **Figure 6**. The results indicate distinct masses of adsorbed nanoparticles on the surface of coal samples treated with nanofluids at different concentrations. Notably, there is a characteristic trend wherein higher nanofluid concentrations correspond to greater masses of nanoparticle sedimentation adsorbed. This phenomenon can be attributed to the influence of concentration on nanofluid stability, as suggested by Zhang et al. (2021).

Moreover, coal samples treated with nanofluids of varying concentrations exhibit different water adsorption capacities. The water adsorption capacity of coal samples treated with 0.1wt% and 0.5wt% nanofluid is nearly identical. However, the water adsorption capacity of coal samples treated with 1.0wt% and 0.5wt% nanofluid is approximately 15% and 35% higher, respectively. Generally, there is a trend indicating that higher nanofluid concentrations result in greater water adsorption capacities for coal samples.
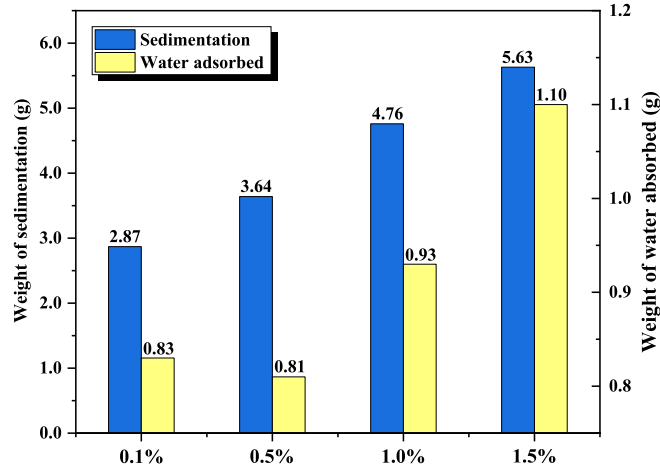
Figure 6: Total weight of sedimentation and water adsorbed (Zhang et al., 2022)

Variation in contact angle

The contact angle serves as a quantitative indicator of solid surface wettability, with lower values indicating better wettability. **Figure 7** illustrates the changes in contact angle for the coal samples. Initially, all four coal samples exhibited contact angles around 90°. Following treatment with 0.1wt%, 0.5wt%, 1.0wt%, and 1.5wt% water-based Silica nanofluid, the contact angles decreased to 39.52°, 36.94°, 31.95°, and 30.02°, respectively. Subsequently, the contact angles gradually stabilized over time, settling at 42.82° (0.1 wt%), 40.55° (0.5 wt%), 37.88° (1.0 wt%), and 34.43° (1.5 wt%).

These results indicate that water-based Silica nanofluid positively enhances the wettability of coal. However, the contact angles for coal samples treated with nanofluids of different concentrations vary. Specifically, the coal sample treated with 1.5wt% nanofluid exhibited the most favorable wettability among the four coal samples, while the coal sample treated with 0.1wt% nanofluid demonstrated the least improvement in wettability. Overall, the findings suggest that the wettability of the coal sample improves with increasing nanofluid concentration.
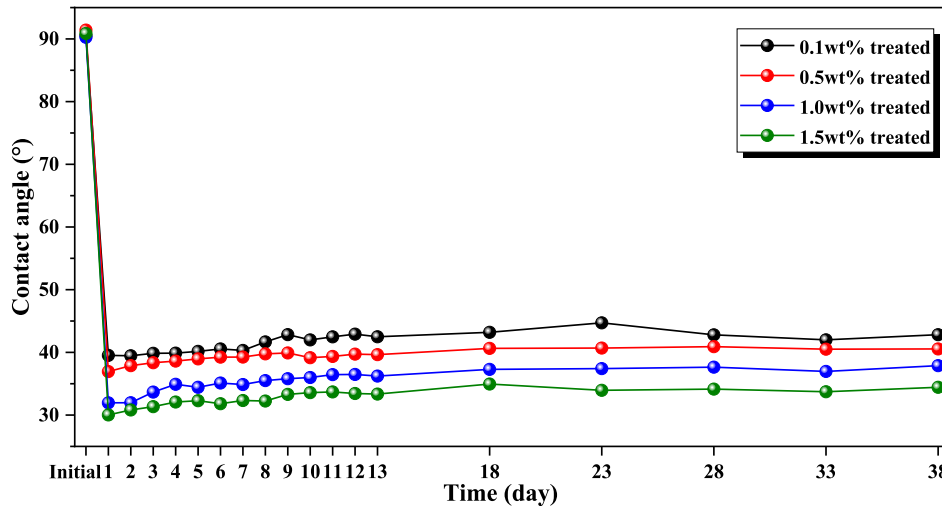

Figure 7: Change in contact angle of coal samples (Zhang et al., 2022)

INJECTION ENHANCEMENT MECHANISM OF COAL SEAM WATER INJECTION

The changes in the sample surfaces are depicted in **Figure 8**. Following water treatment, there was a notable time-dependent alteration in the surface water content of samples #1 and #3. Upon nanofluid treatment, some of the silica nanofluid components, including silica nanoparticles and water, were initially adsorbed onto the surfaces of samples #2 and #4. Over time, the moisture content on the

surfaces of samples #2 and #4 gradually decreased, leading to the sedimentation of substantial amounts of silica particles. Eventually, the sedimentation on the surface of the samples was removed, revealing that a small quantity of silica nanoparticles remained adsorbed on the surface of the raw coal.
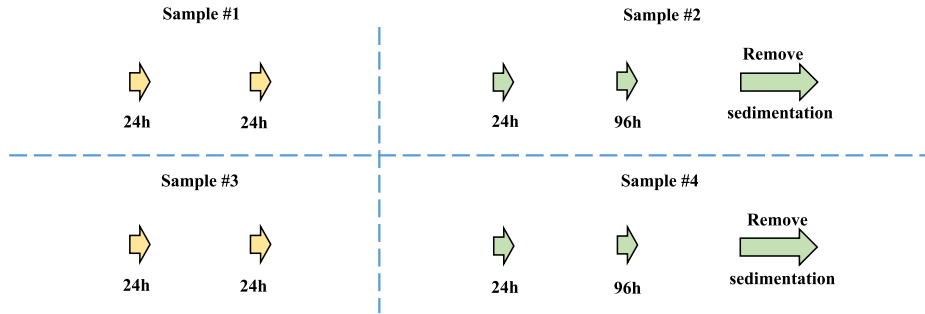
Figure 8: Changes in the surfaces of the coal samples (Zou et al., 2022)

The SEM images of the coal sample surfaces are presented in **Figure 9**. In **Figure 9(a)**, natural textures and fissures are visible on the surface of the raw coal, with no other attachments observed before treatment. **Figure 9(b)** shows that after treatment, Silica nanoparticles were adsorbed onto the surface of the raw coal. These particle accumulations, composed of multiple irregularly shaped and variably sized nanoparticles, formed due to the presence of numerous unsaturated bonds on the nanoparticle surfaces, resulting in a strong adsorption capacity. The interactions involving unsaturated bonds, hydrogen bonds, and molecular forces ultimately led to the adsorption of nanoparticles on the coal surface.
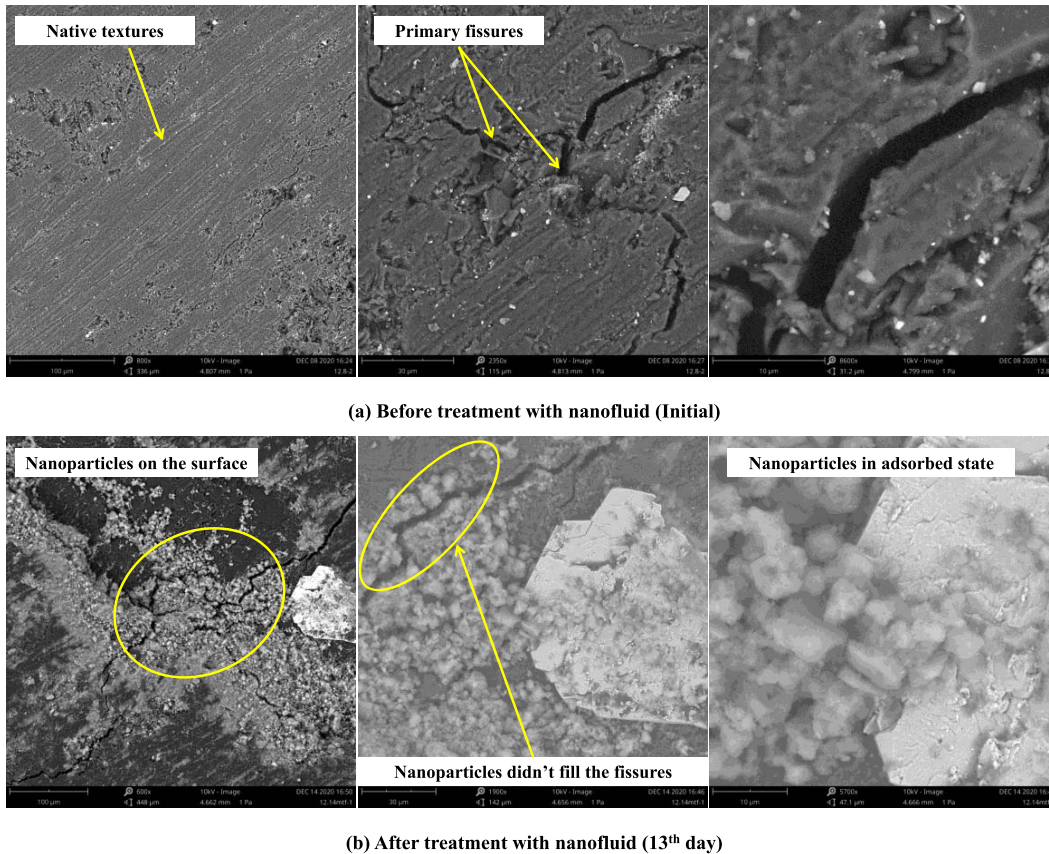
(a) Before treatment with nanofluid (Initial)

(b) After treatment with nanofluid (13th day)

Figure 9: SEM images of the coal sample surface before and after treatment with nanofluid (Zou et al., 2022)

It is evident that the adsorption of nanoparticles on the surface of raw coal induced a change in the wettability of the coal sample. Therefore, the nanoparticles on the surface were identified as the primary contributors to the altered wettability of raw coal. The sedimentation and adsorption of nanoparticles on the surface of the raw coal resulted in an enhancement of the surface wettability of the coal samples.

The mechanism of wettability modification and injection enhancement of coal by water-based silica nanofluid is elucidated in **Figure 10**: during the nanofluid modification treatment, the nanofluid-modified coal sample adsorbs nano-silica dioxide particles. This adsorption results in the generation of Si-OH structures from these particles, serving as active sites that enhance the hydrophilicity of the nanofluid-modified coal sample. Consequently, this process increases the capillary force on water within the microfracture.
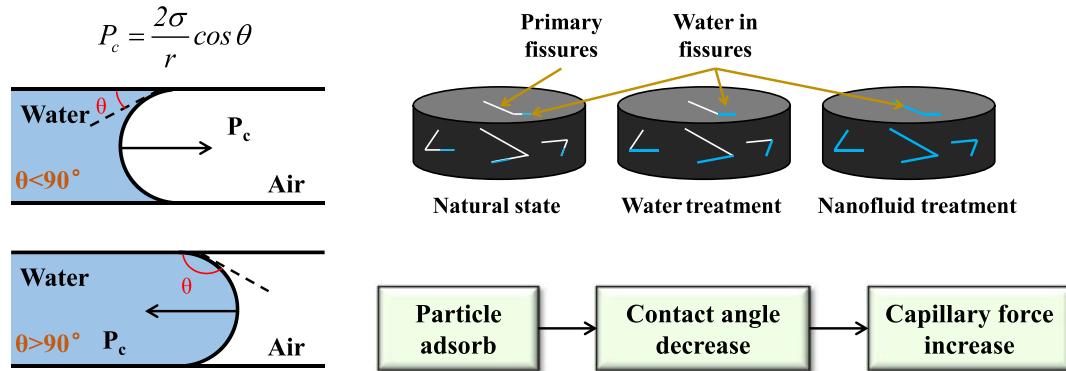
$$P_c = \frac{2\sigma}{r} cos\,\theta$$

Figure 10: Mechanism of injection-enhancement of coal by water-based silica nanofluid

CONCLUSIONS

Firstly, the adsorption-deposition behaviour of water-based silica nanofluid on coal surface is obtained: Water-based silica nanofluid droplets can be divided into initial stage, angle dominant change stage, line and angle co-dominant change stage and complete deposition stage throughout the process of water dissipation-particle deposition.

Secondly, the water adsorption capacity of coal samples treated with 0.1 wt% and 0.5 wt% nanofluid exhibits comparable levels. However, for coal samples treated with 0.5 wt% and 1.0 wt% nanofluid, the water adsorption capacity is approximately 15% and 35% higher, respectively, when compared to the former concentrations. Overall, it can be concluded that increasing the concentration of silica nanofluid enhances the water adsorption capacity of coal samples.

Thirdly, the mechanism of wettability-modification and injection-enhancement of coal by water-based silica nanofluid is revealed: the nanofluid-modified coal sample adsorbed the nano-silica dioxide particles during the nanofluid modification treatment, so that the Si-OH structure was generated from these particles as the active site, which enhanced the hydrophilicity of the nanofluid-modified coal sample and increased the capillary force on water in the microfracture.

ACKNOWLEDGMENTS

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