Study on the mechanism of the effect of changing \( \zeta \) potential of rock surface on rock-breaking efficiency

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Abstract. The relationship between \( \zeta \) potential of near surface of rock and rock-breaking efficiency in recent years were reviewed. Based on the microscale of crystal lattice, the influence of cataclysmic change of induced dipole on \( \zeta \) potential of near surface of rock core in the process of rock failure was investigated. The effect of changing potential on the hardness of near surface of rock was analyzed. The results indicated that \( \zeta \) potential of near surface of rock could be changed suddenly by induced dipole from the crystal lattice of rock core caused by microfracture extension. In addition, the rock-breaking efficiency could be improved by changing \( \zeta \) potential of rock surface. This study can be helpful for the design of novel additives for drilling fluids, and endow with economically and technically viable petroleum development and production processes.

1. Introduction
The rock-breaking efficiency and wellbore stability are of great importance to drilling engineering. Both of them have significant influence on the rate of penetration (ROP) [1-5]. The comprehensive effect of the transient of induced electric dipole, the variable motion of separated charges at the crack edge, and the relaxation of separated charges at fracture surfaces in the process of rock failure could generate self-potential. However, the mechanism of generation process, distribution and difference of self-potential, and the rock-breaking efficiency are not clear [6-10].

In this paper, the generation and mechanism of self-potential in the process of microfracture growth are analyzed in details. Meanwhile, the mechanism of the effect of changing self-potential on the hardness of near surface of rock is investigated.

2. The microscopic characterization of \( \zeta \) potential from microfracture extension
From the micro level, the stress is not enough to make the atomic nucleus of rock crystal rupture and change the chemical structure of rock crystal, but only to change the electronic potential in the periphery, so the original electric equilibrium state begin to change. The electron clouds are likely to be distorted under the influence of external environment disturbance, and thus affect the interaction force between solid particles. The comprehensive effect of interaction force is the deformation fracture of solids in the macroscopic.

The rupture process of rock under pressure is evaluated by Long et al [11]. The generation process and distribution of self-potential in the process of microfracture extension are investigated. At the beginning of rupture, due to microcracks, the charge separation in crack tips happens, and potential
begin to change, so the generation and equilibrium of positive and negative charges at the local region of fracture could be formed. Based on the imaging results of positive and negative high probability region, the direction of invisible cracks could be deduced. When the fracture can penetrate through the rock, the deduced position and direction of electric charges are basically the same as the actual fracture, which indicates that the electric charges have been generated in the fractures in the process of fracture. This is precisely the existence of the position of maximum resistivity variation.

3. The research status

3.1. Rehbinder effect
In the early 1840s, Rehbinder et al. proposed that the rate of rock breaking could be accelerated when some metal salts such as AlCl₃, NaCl or sodium soap were added into the drilling fluids [12]. These findings were no fluke; other studies had come to similar conclusions [13]. The micro-hardness of rock could be reduced when chemical additives were used, the rate of rock breaking could be accelerated greatly, and the drilling effect could be improved.

This traditional theory was further supported by the percussion drilling. However, due to different rock-breaking mode, it had been called into question in the process of drilling operation of artificial diamond.

3.2. IEP (isoelectric point) theory
In the mid-1980s, Westwood et al. proposed that the solution of hexyl alcohol and dodecyltrimethylammonium bromide (DATB) was used to test the hardness of quartz and granite [14]. The experimental results indicated that the pendulum hardness of rock was up to the maximum when ζ potential of rock or mineral was zero. The concentration of the solution of DTAB was chosen as 1×10⁻³ mol/L, ζ potential of quartz was zero, and the maximum ROP could be obtained. However, Westwood found that the results from several studies were contradictory to the above conclusions.

In the late 1980s, the conception of IEP (isoelectric point) theory was proposed by Engelmann et al [15, 16]. IEP theory indicated that the maximum surface tension of rock could be obtained in the equipotential point.

3.3. High ζ potential absolute value theory
It has been proved that the maximum surface microhardness of rock or mineral could be obtained when ζ potential is zero. The central question is whether or not the surface hardness of rock is the biggest, the maximum ROP could be achieved. Ge et al. found that ROP had been no change when pH value of aqueous solution was adjusted to 2 to change ζ potential of quartz to zero [17,18].

![Figure 1. The effect of the concentration of CTAC on ζ potential.](image-url)
Hexadecyl trimethyl ammonium chloride (CTAC), Teepol and Tween-80 were used to test the drillability of rock for diamond by Ge et al, respectively. The results indicated that the drillability of rock could be improved when the absolute value of $\xi$ potential of rock surface was increased. The improvement of the drillability of rock might be different for different surfactants. Due to different mineral composition and chemical component for rock, there were differences for the influence of rock drillability even if the surfactants were the same kind, as shown in Figure 1 and Figure 2.

![Figure 2](image.png)

**Figure 2.** The effect of the concentration of CTAC on ROP.

4. **The mechanism analysis of $\xi$ potential changed suddenly by induced dipole**

A rock core is affected by the increasing external field force to generate microfracture. No microfracture is generated when the external field force is less than the critical collapsing force. However, microfractures are generated when the external field force is more than the critical collapsing force, and the crystal lattice of rock core could be damaged, so a large number of cations could be freed out from the crystal lattice. Given that some lattice sites lack particles, electron voids are generated in the crystal lattice. When these cations are freed out from the crystal lattice, the atomic nuclei of these free cations could be repelled by the positive electric field or attracted by the negative electric field, so the relative displacement between the nuclei and the electrons should be changed, resulting in ion deformation and generating induced dipole.

The additional gravity between the induced dipole and the nearest heterocharge ion is not enough to break the inherent vibration rule of ion, this ion could go back to the original position and prevent the ionic polarization under the influence of thermal motion. The crystal configuration of ions remains unchanged, and these ions in crystal lattice could prevent more electron voids from generation. In macroscopic view, the continuous extension of microfracture could be prevented. The effect of ion polarization on crystal configuration is shown in Figure 3.
Figure 3. The effect of ion polarization on crystal configuration.

The strength of induced dipole depends on two factors. The first factor is ionic polarization force. The strength of induced dipole is proportional to the intensity of electric field, as shown in Figure 4. As long as the crystal lattice is acted on by enough external electric field, fairly strong induced dipole could be generated whether cationic surfactant or anionic surfactant is used. This also explains why the experimental data are not conformed to the experimental results from IEP theory. The second factor is ionic deformability. The bigger the ions, the stronger the deformability. This result indicates that different mineral crystals have different surface hardness for the surfactant with the same ionic type.

Figure 4. The relationship between the strength of induced dipole and the strength of electric field.

If a new kind of additive for drilling fluids could permeate into the microfracture of rock core with higher penetration rate and larger osmotic volume in the initial stage of core failure, the chip hold down effect of bottom-hole rock could be reduced. As the drilling fluid additive has high ionic deformability and strong ionic polarization, the additional gravity generated from large enough induced dipole could damage the inherent vibration rule of ions and shorten the distance between ions, and the crystal could transform to the crystal configuration with low coordination number, as shown in Figure 5. When the crystal configuration changes, there are more electron void defects in the crystal lattice. In macroscopic view, the extension of microfracture could be continued to extend, and the rock-breaking efficiency could be improved.
5. The mechanism analysis of the effect of changing potential on near-surface hardness of rock
The adsorption between ionic surfactant and solid surface is mainly chemical adsorption. The transfer of surface charges could change the electron structure of near-surface area of solids, so the lattice displacement in near-surface area and ionization state of voids could be changed. The near-surface displacement with constant motion and mutual electrostatic reaction among various void defects could be affected. The near-surface displacement with constant motion and mutual electrostatic reaction among various void defects could be affected. The frictional resistance in intracell for motion displacement could be affected, too.

When $\xi$ potential is zero, the electron transfer between ionic surfactant and solid surface is the weakest, various mutual electrostatic reactions could be inhibited, and the displacement friction resistance of intracell could be increased. Therefore, the microhardness of solid surface is up to the maximum, and the rock breakage is very difficult. However, when $\xi$ potential is not zero, the electron transfer in near-surface area could be excited, various mutual electrostatic reactions could be increased, and the displacement friction resistance of intracell could be reduced, so the microhardness of solid surface could be reduced, and the rock breakage could be easily reached. As a result, these above physicochemical actions are closely related to the electron transfer action. Due to the absorption of surfactant ions, the electron transfer in solid surface could be changed, and the microhardness of solid surface could be affected effectively.

6. Conclusions
The $\xi$ potential of near surface of rock core can be changed suddenly by the induced dipole generated from the crystal lattice of rock core in the process of rock failure. The strength of induced dipole is depended on the polarization force and deformability of peripheral ions.

The influence of changing potential on the hardness of near surface of rock is investigated in detail. The results indicate that the electron transition could be ejected, the microhardness of near surface of rock could be reduced, and the rock-breaking efficiency could be improved when $\xi$ potential is changed and it is not zero.

A new kind of drilling fluid additives with high ion deformability and strong ion polarization could be applied in the drilling operation, so the configuration of crystal lattice of ions could be changed, the extension of microfracture could be accelerated, and the rock-breaking efficiency could be improved. This study will play a vital role in the drilling fluid design and drilling engineering.
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