Research progress of clay transformation in drilling fluids

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Abstract. As an important slurry material for water-based drilling fluids, montmorillonite has been widely used in oil drilling because of its excellent properties such as expansibility, dispersion and suspension, slurry making, cation exchange and adsorption. However, at a certain temperature and pressure, montmorillonite will transform into illite, chlorite and other minerals, changing the properties of drilling fluids. In order to systematically summarize and sort out the current research status of montmorillonite transformation, this study focused on the research progress of montmorillonite transformation into other minerals under different temperature and pressure conditions, and summarized the transformation mechanism of montmorillonite. The montmorillonite is transformed into illite by adding K⁺ in the interlayer spacing and removing Si⁴⁺ by adding Al³⁺ to tetrahedron structure. The conversion of montmorillonite to chlorite by adding Fe²⁺, Mg²⁺ ions into the octahedron, and Si⁴⁺ in the tetrahedron is replaced by Al³⁺. The precipitated brucite layer is connected with the upper and lower layers.

1 Introduction

With the development of petroleum industry and the increasing demand for oil, the formation depth of oil and gas exploration is increasing, and the drilling scale of deep and ultra-deep wells is increasing progressively. For each oil well, the drilling fluid must be formulated with a variety of slurry materials and chemical treatment agents, or added to the drilling fluid in use, to adjust and maintain the drilling fluid performance at any time. With the continuous update of drilling fluid system, the variety of slurry raw materials and treatment agents is also increasing. At present, all kinds of new, efficient, non-toxic and multi-functional chemical treatment agents are actively developed. The performance, quality and technology of the products actually represent the development of drilling fluid technology.

The crystal chemical formula of montmorillonite is $E_x(H_2O)_{4}\{Al_{2-X},Mg\}_{2[}(Si,Al)_4O_{10}](OH)_2\}$, E is interlayer exchangeable cation, mainly Na⁺, Ca²⁺, followed by K, Li, etc. According to the type of the main cation between the layers, it is divided into sodium montmorillonite, calcium montmorillonite and other components. The amount of

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interlayer water depends on the type of cation between the layers and the humidity in the environment. The crystal structure of montmorillonite belongs to TOT type, and there are isomorphism substitutions in the structural unit. Because the charge is not neutralized, the structural unit has a certain number of cations and a large number of water molecules. Its excellent properties have been widely used in the petroleum industry.^[1]

The montmorillonite slurry is usually called bentonite, which is an important slurry material for water-based drilling fluids, especially the bentonite with sodium as the main exchangeable cation. Because it is composed of montmorillonite minerals with quite large layer as the main component, it is easy to disperse into very thin sheets in water, making it have a satisfactory viscosity and thixotropy. In addition, it improves the plastic viscosity, static and dynamic shear forces of the system to enhance the suspension and carrying capacity of drilling fluid against cuttings. At the same time, it can reduce the filtration loss, form the dense mud cake and enhance the wall-building ability.^[2] However, due to the presence of geothermal and pressure gradients during drilling, the deeper the borehole, the higher the temperature and pressure in the well. At a certain temperature and pressure, the drilling fluid degrades, crosslinks, ferments, and fails, which changes the properties of the drilling fluid. Under a certain temperature and pressure, montmorillonite is transformed into illite, chlorite and other minerals, which makes the performance of drilling fluid change dramatically, which is not easy to adjust and control.[3] Therefore, this study reviews the research and application progress of the transformation of montmorillonite into illite. chlorite and other minerals under different temperature and pressure conditions, and summarizes the transformation mechanism, in order to provide reference for the further development of montmorillonite in drilling slurry materials in the future.

2 Transformation from montmorillonite to Illite

Montmorillonite as the initial material simulates the transformation process to illite under high temperature and pressure conditions. According to the variation of morphology, the size of clay particles showes the change process of becoming smaller first and then getting larger with the increase of temperature and pressure. The morphology of clay mineral changes from lamellar to honeycomb-like structure gradually. Hence, in the transformation process from montmorillonite to illite, the formation of illite is based on the consumption of montmorillonite. The initial montmorillonite is constantly dissolved and transformed into illite. Fine-grained illite minerals grow near the montmorillonite and eventually form large-size illite crystals.^[4]

The transformation of montmorillonite to illite is affected by metal cations. The presence of K^+ is conducive to the transformation and accelerates the reaction. However, the presence of Na^+ , Ca^{2+} and Mg^{2+} inhibits the transformation. Besides, the presence of organic matter has an impact on the illitization of montmorillonite, but the influence of the presence of organic matter on the transformation process is not invariable. At the temperature from 150-250°C, the presence of organic matter promotes the illitritization of montmorillonite, however, under higher temperature, organic matter impedes the transformation. $^{[6]}$

In summary, the transformation process of illicitation of montmorillonite is as follows: illitization of montmorillonite is a process of addition K^+ in the interlayer spacing and silicon removal in tetrahedral structures. The content of Al^{3+} in silica tetrahedron of clay minerals increased gradually, while the content of Si^{4+} decreased gradually. With the increase of substitution of Si^{4+} by Al^{3+} in silica tetrahedron of montmorillonite, the amount of negative charges interlayer spacing also increases. Along with the removal of interlayer water and the entry of K^+ , a mixture of montmorillonite and illite is formed in this process.

With the extension of time, the content of illite increased in the mixture and finally completely transformed to illite.

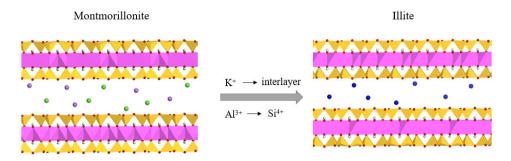


Fig.1. Schematic diagram to show structures involved in the transformation of montmorillonite to Illite interstratified minerals. (Color code: Ca, green; Si, yellow; H, white; Al, pink; K, purple; Na, blue; O, red.).

3 Transformation from montmorillonite to chlorite

The montmorillonite with low iron content with different molar ratios of Fe²⁺, Mg²⁺ and Al³⁺ ionic solutions were taken as the initial substances, respectively. Under different temperatures and pH conditions, it was observed that the flake montmorillonite dissolved obviously under SEM, and new chlorite appeared in the dissolved part.^[7] It has previously been found that a substance showing some properties of chlorite can be obtained by precipitating magnesium with ammonia in the presence of montmorillonite.^[8]

The conversion of montmorillonite under different conditions of temperature, pressure, fluid composition and reaction time was studied and the conditions of montmorillonite transformed to chlorite showed that a neutral to alkaline pH was needed for montmorillonite chloritization and the strong activity of Mg in this range may be the main factor for the formation of chlorite. [9] In addition, the types of cations in the octahedral structure of montmorillonite have a great influence on the types of chlorites. During the process of transformation of montmorillonite to chlorite, pH of the reaction system is decreased, and the change from basic to acidic is a process of releasing H ions. Therefore, The main reaction mechanism of transformation is dissolution and recrystallization, followed by solid transformation. [10]

In conclusion, the transformation of montmorillonite to chlorite is mainly the addition of Fe²⁺, Mg²⁺ and Al³⁺ ions in the octahedron. Si in the tetrahedron is replaced by Al, and the precipitated brucite layer is connected with the upper and lower layer by hydrogen bond.

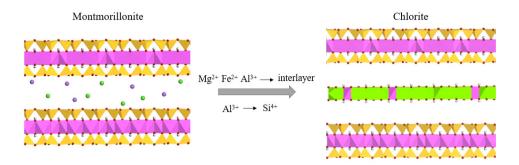


Fig. 2. Schematic diagram to show structures involved in the transformation of montmorillonite to chlorite interstratified minerals. (Color code: Ca, green; Si, yellow; H, white; Al, pink; Na, blue; O, red.).

4 Transformation from montmorillonite to other minerals

Montmorillonite can also be converted to other minerals, which is also affects the properties of drilling fluids. Some researches show that montmorillonite can be converted to kaolin and the transformation process of montmorillonite to kaolin is similar to that of illite. This sequence is characterized by kaolinite-montmorillonite and kaolinite-kaolinite-montmorillonite (repeated several times).^[11] A solid mechanism leading to the formation of kaolinite from montmorillonite is that the montmorillonite layer is transformed into a kaolinite layer by peeling off a tetrahedral slice and adjacent interlayer spacing.^[12]

The montmorillonite with the ionic solution containing Fe³⁺ and K⁺ change obviously, and transform from montmorillonite to glauconite. The pH has a significant effect on the results. The results show that the transformation to glauconite is significant in the acidic environment, while the transformation to illite occurs in the neutral and alkaline environment, indicating transformation to glauconite under the conditions of low temperature, low kinetic energy, weak acid to weak alkaline.^[13]

5 Conclusion and prospect

In this paper, the review and summarize the conversion of montmorillonite, the montmorillonite can be converted into illite, chlorite and other minerals, and into the transformation mechanism of illite and chlorite research overview, montmorillonite to illite, montmorillonite, patent is in between the layers to join the K⁺, tetrahedral structure with Al removal process of Si, montmorillonite to chlorite: When Fe²⁺, Mg²⁺ and Al³⁺ ions are added to the octahedron, Si in the tetrahedron is replaced by Al, and the precipitated brucite layer is connected with the upper and lower layers by hydrogen bonds. In addition, the montmorillonite was transformed into other mineral species. The conversion of montmorillonite can affect the properties of drilling fluids, and in severe cases, can lead to drilling operations that cannot be carried out normally. However, the drilling environment is becoming more and more complex, and the requirements for drilling fluid are becoming higher and higher. What changes of montmorillonite will occur under complicated conditions is unknown, and what is the transformation mechanism, and whether these changes can be converted into montmorillonite under certain conditions remains to be studied.

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