Micro Porosity of High Expansion Tuff and Its Application

Ming-xiong ZHENG¹,* and Fu-lai SUN²

¹Computing Center of Kunming University of Science and Technology, Yunnan, China
²College of land and resources of Kunming University of Science and Technology, Yunnan, China

*Corresponding author

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Abstracts. The pore size, distribution, connectivity and pore change of Lancang Lead Ore’s tuff were studied by means of SEM, AFM, nitrogen adsorption at low temperature and mercury injection at high pressure. And the pore research results were applied to the development of anti-collapse drilling fluid. The results show that the high expansion tuff of Lancang Lead Ore has the typical lamellar microstructure of clay. The pore diameter is most concentrated in the range of 1 - 20nm, the pore size is widely distributed, the throat is developed. It is known from pore research that chemical anti-sloughing can be used in the development of Lancang anti-collapse drilling fluid because of the similar size of tuff’s main pore and hydrate ions, and nano-plugging materials should be used as the main material when physical plugging materials are used, which explains why ordinary bentonite cannot prevent sloughing. And under the guidance, the application of alkaline soluble starch plus NaCl and KBr solution was successfully achieved.

Introduction

High expansion and easy collapse clay-rich tuff is widely distributed, especially in metal mines, tuff is ore-bearing, parent rock and surrounding rock in many areas and mines, and even prospecting marks[1] in many mines[1-4]. In engineering and mine resource survey drilling, high expansion tuff is often encountered, and tuff collapse has brought many difficult problems to construction projects and survey drilling, so it is necessary to study the mechanism of expansion and thus to carry out anti-collapse application.

Some scholars have done a lot of research on engineering treatment measures and theoretical basis of tuff. For example, J. A. Wolff studied the rheological behavior of wet tuff as early as 1981 [5], Yang Wendong studied the mechanical characteristics of excavation and support of soft tuff in Mirashan Tunnel in highway construction [6]. Tan Zhan studied the influence of soft tuff interlayer on the stability of the bank slope at the bridge site[7], Zhang Hailong carried out numerical simulation study on the generalized stress relaxation characteristics of Hejin tuff[8], Li Yongping studied the deformation control of high expansion tuff in the construction of Dapingzhang Copper Mine[9], Joseph S.Y. studied the liquid flow in tuff under unsaturated wet conditions and used several flow models to discuss it[10]. Michael M. studied the surface state of tuff before and after hydrolysis, and observed the particle size and pore size of tuff from the surface[11].

On the whole, these studies on tuff have their own clear purpose, there are relatively many engineering application studies, few take tuff’s expansion mechanism as the research object, and almost no studies combined collapse mechanism with tuff's collapse prevention drilling fluid. However, the probability of encountering tuff collapse during drilling is also high, it due to the large depth of coring drilling in mine exploration, which may lead to huge losses, such as two sticking accidents in deep exploration drilling of Lancang Laochang Lead Ore, with direct economic losses of 10 million yuan. Lancang Laochang Lead Ore’s tuff is a typical high-expansion collapse - prone tuff, which has a certain strength when it is dry and decomposes into sediment in a very short time when it meets water, and its decomposition speed is much faster than that of tuff in many other areas. This paper selects it as research sample.

In the study of tuff collapse prevention, it is necessary to understand the water transport process and the passage of the solution inside tuff. So, it is necessary to study the pore state and the pore...
change and its relationship with collapse prevention. Some research on chemical composition, mineral composition, cementation state, microstructure, chemical reaction and dispersion and collapse prevention of Lancang tuff has been done in earlier period [3]. Now, based on these studies, here, to further discuss the pore size and its application of tuff. To study the high expansion and high collapse tuff’s pore size, distribution, connectivity, formation and changes in water. And the pore results are applied to the development of collapse prevention drilling fluid.

The pores of Lancang tuff are small and developed. In order to accurately characterize the pore size distribution of tuff, appropriate analysis techniques and methods are needed. Maex K summarized and classified the pore characterization methods of porous media, and believed that there were mainly three kinds[11]: image analysis method, fluid injection method and non-invasive method.

**Pore Structure of Lancang Tuff**

The pore size, distribution and connectivity of Lancang lead tuff were studied by SEM(Figs.1-3), AFM(Fig.4), low temperature nitrogen adsorption (Figs.5-7) and high pressure mercury intrusion (Figs.8-10).

![Figure 1. Microscopic Pore SEM.](image)

![Figure 2. Flaky Structure SEM.](image)

![Figure 3. latent pore SEM of montmorillonite.](image)

![Figure 4. AFM Profile Measurement of Tuff.](image)

![Figure 5. Nitrogen Adsorption Desorption Curve.](image)

![Figure 6. Nitrogen Pore Size Distribution Curve.](image)

![Figure 7. Partial Nitrogen Pore Size Distribution Curve.](image)

![Figure 8. Mercury Removal Mercury Curve of Tuff.](image)

![Figure 9. Pore Size Distribution Curve by Mercury Intrusion Test.](image)

![Figure 10. Partial Distribution Diagram.](image)
On the basis of other previous studies, SEM, AFM, low-temperature nitrogen adsorption and high-pressure mercury intrusion tests were carried out on tuff to comprehensively discuss the microscopic pore characteristics of tuff and draw the following conclusions:

Lancang lead ore high expansion tuff has typical lamellar microstructure, which is the reaction of clay microlayer. Lancang high-expansion collapse tuff is macroscopically compact but microscopically porous, with pore diameter ranging from tens to hundreds of nanometers, the most concentrated pore size ranging from 1 to 20 nm, porosity ranging from 12.26% to 13.32 %, and average pore diameter ranging from 27.8 to 29.6 nm. The pore size distribution is extensive, the throat is developed, the connectivity between pores is good, the micro-pore structure is diverse, and the pores are mainly intergranular pores.

**Variation and Expansion of Lancang Tuff’s Pores**

In order to study the changes of tuff pores, a comparative test of dry tuff, immersed tuff and tuff treated with anti-collapse formula solution was designed. After treatment with composite saturated brine anti-sloughing drilling fluid formula in which tuff does not collapse, it can be seen that the surface of tuff was covered with a gelatinous film, which prevents water from entering. When observed by SEM, the tuff surface is covered with a dry crystalline layer, which is of little significance to the study of pore expansion. Comparing the dry tuff SEM image of Fig. 11 with the tuff SEM images of Figs. 12 to 14 after a very short time of immersion treatment, it can be seen that the pore change of tuff is very obvious after encountering water. Through the comparison of many samples, three main reasons for the change of tuff’s water-bearing pores can be found.

First, the Lancang tuff which rich in clay has a large number of micro-sheet layer structures, the clay micro-sheet with asymmetric mineral crystal structure curls in water so that new pores are created from the surface to the inside. As shown in Fig. 12, the micro-sheet in the free space has a large curling amplitude after encountering water, the pore changes obviously, and new pore channels are created, thus facilitating the diffusion and entry of water. Crimping also increases the distance of micro layer, and with a large expansion force, tuff expands and its strength decreases. Curling force is one of the force sources of tuff’s disintegration in water or drilling fluid or other solutions. The Energy spectrum test shows that the curled microchips are mainly montmorillonite and kaolinite.

Second, the curl is not obvious but the water wedged between tuff sheets. From Fig.13, it can be seen that the pores are obviously loose and porous. The micro-sheets are not curled but the interval between the sheets is obviously larger, and the structure between tuff agglomerates is loose. This is due to the different material and different environmental conditions for the formation and evolution of clay in tuff. XRD tests show that clays in Lancang tuff could be more than 50%, mainly are montmorillonite and kaolinite, and contains illite, muscovite and phlogopite. Although not all the micro-sheets are curled, they all have strong hydrophilic and water absorbing ability, which makes tuff expand strongly and can lead to the destruction of the original rock structure.
Third, dissolution of soluble salts leads to decomposition of tuff. The material composition of Lancang lead ore tuff is very complex. X-ray fluorescence and other tests show that it contains more than ten kinds of metal elements. Chemical dissolution tests also show that it contains a variety of soluble salts. Tuff can dissolve quantities of K$^+$, Na$^+$, Ca$^{2+}$ and Mg$^{2+}$ in water. Previous studies show that dissolution of K$^+$ and Na$^+$ plays an important role in the collapse [3]. After water enters tuff, soluble salts partially dissolve. Dissolution of salts not only reduces the cementation strength, but also creates new pores, providing channels for further diffusion of water, and is also the cause of expansion and collapse.

Application of Pore Research in Development of Environmental Protection Anti-sloughing Drilling Fluid

The particularity of Lancang lead ore’s tuff determines the particularity of its anti-collapse drilling fluid. In the deep exploration drilling, there were two consecutive sticking accidents, the drilling tools could not be taken out, and the exploration plan was affected and the environmental impact might be brought.

It is necessary to find a kind of stable and feasible environment-friendly anti-sloughing drilling fluid, this requires some basic research. The conclusion of this paper about tuff pores is one of the research bases for the development of anti-collapse drilling fluid. On this basis, through a large number of tests, combined with the research of tuff expansion and collapse mechanism and anti-collapse mechanism, a collapse prevention drilling fluid formula was obtained by combining chemical collapse prevention with physical water resistance. The application of pore research in drilling fluid development is as follows:

From the area where the pore size is mainly concentrated, it can be seen that the hydrated ion size is close to the main pore size, which provides a basis for Lancang tuff to adopt chemical collapse prevention. Because clay is negatively charged, it adsorbs hydratable ions. When the main pore size is similar to that of hydratable ions, a certain chemical barrier can be formed. Fig. 15 is a comparative picture of Lancang tuff completely mudded in water within 1 minute. As shown in Fig. 16, tuff can remain stable in unsaturated KBr solution for 1 hour or several hours (tuff’s material composition is diverse and rock heterogeneity is very large), but some tuff structures in low concentration KBr solution are damaged after a long time (Fig. 17), and the obvious wet state inside the tuff can be observed after taken the tuff out. In high concentration or saturated NaCl and KBr mixed solution, tuff can remain very stable for a long time (Fig. 18). Even, after being soaked in high concentration or saturated NaCl and KBr mixed solution, taking it out and putting it into the water, the tuff can still keep stable for a certain period of time, experiments show that some tuff will not collapse again. Compared with the above water, low-concentration solution and high-concentration mixed solution, it can be seen that:

(1) Free water migrates and diffuses rapidly inside tuff.
(2) Tuff’s wetting inside indicates that hydrated ions pass through large pores in tuff.
(3) The adsorption of hydrated ions by tuff can prevent the solution from entering tuff pores.
(4) After soaking in mixed solution then soaking in water, tuff can still remain stable, it indicating that, besides ion adsorption, ion exchange has taken place between some tuff and solution ions, and ion exchange has a modifying effect on tuff.

During the physical anti-collapse process, pore study can provide guidance for the selection of particle size in the anti-collapse formula. From the pore analysis of tuff, it is known that the pore size is mainly concentrated in tens of nanometers and is widely distributed. Therefore, it should be mainly composed of nano materials of tens of nanometers in the anti-collapse drilling fluid. It can be explained that only dispersed plugging of bentonite can’t play the final anti-collapse role in the Lancang tuff anti-collapse experiment, but the plugging role of more delicate alkaline soluble starch is very obvious. The pore study provides an application basis for the use of alkaline soluble starch. After treatment with the anti-sloughing drilling fluid formula containing alkaline starch and saturated brine, the surface of tuff covered with a gelatinous film, which prevents water from entering. As shown in Fig. 19, in the solution which only with soluble starch, the solution viscosity
is small, the tuff’s collapse is slightly slower than in the water, but it still decomposition quickly, and complete decomposition within 5 minutes. After adding a small amount of NaOH to the soluble starch solution and stirring, the alkaline soluble starch becomes viscous quickly, and the milky white solution becomes transparent. The low pH and low concentration soluble starch can obviously hinder the decomposition and collapse of tuff, some tuff in Lancang lead ore can last for several hours without decomposition or local decomposition, but some tuff’s structure damaged after hours (Fig. 20), some tuff can remain stable for a long time. After increasing the pH value and increasing the soluble starch concentration, the stability of the tuff can be significantly improved (Fig. 21).

However, due to the particularity of Lancang tuff expansion and collapse, for reasons of safety, it is necessary to combine chemical and physical methods for comprehensive collapse prevention, which has excellent effect and can reduce the usage of soluble starch, NaCl and KBr. As shown in Fig. 22, tuff has excellent stability in alkaline soluble starch and NaCl and KBr mixed anti-sloughing drilling fluid, which is comparable to oil-based anti-sloughing drilling fluid (tuff does not swell and collapse in nonpolar oil), and even becomes harder than before due to the modification by ion exchange. This mixed anti-collapse solution is not only applicable to Lancang lead ore tuff, but also has the same effect on other high-expansion and easy-collapse tuffs.

In the karst areas with high altitude and where the drilling fluid is completely lost, the use of alkaline soluble starch is undoubtedly an environmentally friendly choice compared with other chemicals.
Summary and Outlook

Through the research, the following conclusions are drawn:

(1) Lancang lead ore high expansion tuff has typical lamellar microstructure of clay. Lancang high-expansion collapse tuff’s pore diameter most concentrated pore size ranging from 1 to 20 nm, porosity ranging from 12.26% to 13.32%, and average pore diameter ranging from 27.8 to 29.6 nm. The pore size distribution is extensive, the throat is developed, the connectivity between pores is good, the micro-pore structure is diverse, and the pores are mainly intergranular pores.

(2) The pore and strength of tuff change greatly when it absorbs water. The curling of tuff flakes, the wedging of water between tuff lamellae and the dissolution of soluble substances in tuff all lead to tuff expansion and structural damage, also resulting in a large number of new pores, all of these provide conditions for the further rapid diffusion of water into the interior.

(3) In this paper, pore research is applied to the study of anti-collapse drilling fluid. From the main pore size distribution, it can be seen that the collapse prevention of Lancang tuff can be started from the aspects of chemical collapse prevention and physical blockage prevention. The main pore diameter which can determine the decomposition of tuff is similar to the pore hydrate ion diameter, so chemical anti-collapse is very effective. The physical collapse prevention materials should refer to the pore size, with the materials capable of cementing blockage in the nano-particle size should be the main one. Under this guidance, through a large number of tests, stable and environment-friendly anti-sloughing drilling fluid was obtained.

Outlook: Current research shows that the tuff of Lancang lead mine does not expand and collapse in certain concentration of KCl and other solutions, but in most salt solutions, why does the pore expand or not expand? Therefore, in the depth of research, it is necessary to further study the molecular structure of minerals, to study the bonding situation, to find out the ultimate cause of pore change: the molecular interaction between water solution and tuff micro-minerals.

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