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Study of kaolinite rock in coal bearing stratum, North China

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Abstract

The proved reserves of kaolinite in coal measures in China is very rich, most of which are excellent industrial materials and are associated with the Permo-Carboniferous strata of North China. There are three types of kaolinite rocks in the present research area: the first type (be called tonsteins) occurs in the roofs, partings and floors of coal seams, normally called tonsteins, which are thinner and widespread; the second type, usually 2~6 m thick, is not adjacent to coal seams, usually in the lower part of coal measures of Upper Permian, similar to the flint clay in North America; the third type is soft kaolin clay of 0.5~5 m in thickness and associated with surficial weathered coals. Results of XRD, IR, DTA and SEM studies show that the content of kaolinite minerals is in general more than 70% and up to 90%~100% in some good quality rocks. The elements of Mo, W, Zr, Hf, Th, Ag and Sb are very rich in kaolinite rocks in the study area, with their average contents being higher than those in the earth’s crust, basalt and granite. It is suggested that tonsteins formed from the in situ alteration of air fall volcanic ashes, second type of kaolinite have formed mainly on the adjacent landmass, but some crystallization of gels within the basin is not ruled out, the third type of kaolinite is related to weathering of coals.

Keywords: kaolinite; coal seams; North China

1. Introduction

The study of kaolin in coal-measures in China started from the early 1950s. Qingxuan Chen first found kaolinite in Inner Mongolia Daqingshan Carboniferous coal-bearing strata in 1950\textsuperscript{[1]}. Yonghe Shen (1959) formally proposed to use "kaolinite" as sedimentary rock types, which was mainly composed by kaolinite and other related minerals. Since the early 1980s, Zhi Zheng et al have investigated the kaolinite clay of Carboniferous-Permian coal measures in Shanxi, Inner Mongolia, Hebei, Shandong province, indicating that kaolinite usually existed in the upper part of sedimentary cycle, deposited vertically, which was formed in the hydrodynamic environment form powerful to weak. Yiping Zhou (1983) made an analysis of kaolinite tonstein in the Upper Permian Xuanwei formation coal in eastern Yunnan. We can draw a conclusion that the sedimentary alteration of volcanic ash may be the main formation mode of kaolinite tonstein, but not the only one. After studying kaolinite in Carboniferous-Permian coal measures in Datong of Shanxi, Qing Chang (1985) considered that the kaolinite within coal measures was formed by colloid removal and outside mainly formed by mechanical handling. Baohua Feng (1986) found that there are sanidine, zircon with sharp edges and corners, and small amounts of apatite in kaolinite rock through the study of Carboniferous-Permian coal-measures kaolin in western Shandong. Metallogenic materials of kaolinite

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rocks are mainly from volcanic ash which dropped in the peat swamp. In acid medium, alkali metal and alkaline earth metal elements in the volcanic glass and fine-grained aluminum silicate rocks are easily dissolved out, and kaolinite formed after desiliconization. Shaoxian Liang (1986) obtained the same conclusion by the research on the 5th tonstein kaolinite mudstone in Taiyuan coal seams of Tongchuan mining area, northern Shanxi. Changling Liu (1987) argued that Tonstein (tonstein clay stone) was mainly based on volcanic material, also mixed with different degree of land-doped source materials. These substances are broken down in the swamp water, after deposition of colloid chemistry, and further kaolinitization, re-crystallization, ordering in diagenesis and epigenesis. Qinfu Liu, Pengfei Zhang et al (1994) believed that the causes of kaolinite in coal measures have been affected by many factors based on previous studies, which contain both the normal causes of deposition, and of volcanic deposition, furthermore biological, organic matters and its derivatives are the important factors in its formation process that can not be ignored. Kaolinite in coal tonstein, especially the thin, horizontal distribution and stability, are more volcanogenic; and kaolinite between or outside the coal seam should have several causes, which need specific analysis. It is difficult to explain all types of kaolinite rocks by only one origin model. This paper mainly presents the resources, classification and origin models in Permo-Carboniferous coal measures in North China.

2. Resources

Distribution: In China, coal resources has many ore-forming ages and widely distributed regions, mainly existing in the coal-bearing strata of the Late carboniferous, Permian, Late Triassic, Jurassic, Early cretaceous and the Quaternary. Almost all coal-bearing strata contain the industrial kaolinite rocks, with the horizon of ore production amounting to more than 40 layers. The Carboniferous-Permian age is the most important era for the coal-measure Kaolin (soil) mineralization. The number of ore deposits and reserve quantity is diminishing and quality gradually deteriorated along with the time going on. Kaolinite rock is widely distributed in 29 provinces, municipalities and autonomous regions (except Shanghai, Tibet and Taiwan). The high quality hard kaolinite (soil) is deposited in the following well-known deposits: Datong, Pinglu, Inner-Mongolia, Xinwen, Yixian, Shanxi Pubai, Tangshan, and Jiexiu. Shanxi are rich in knag soil; Henan, Shandong, Lianghuai regions in Anhui province and Pingxiang, Jiangxi are famous for coke gem type kaolinite rock; Yangquan of Shanxi province and Jiaozuo in Henan are abundant of soft clay; Maoming in Guangdong, Dongsheng in Inner Mongolia, Datong in Shanxi and other places have sandy kaolin deposits. Conclusions can be drawn that North China is China’s main production areas and the Carboniferous-Permian the metallogenic epoch of kaolin. In addition, there are better quality deposits of kaolin in the coal-bearing strata of Sichuan, Hubei, Guizhou, Xinjiang and northeast China. Vertically, most kaolinite is formed as the coal seam roof and floor, or has a certain distance from coal seams, or appears as knag soil type of soft kaolinite which exists in surface and underground shallow layer.

Reserves and quality: According to the estimation by Mining Bureau of the United States Ministry of the Interior, the reserves of kaolin is proven to be 12.157 billion tons all over the world. Proved reserves of 15 provinces in China has merely been 150 million tons and the estimated reserves is more than 1.2 billion tons. The symbiotic kaolinite rock (soil), in coal-bearing strata in China, is huge. But in the past coal geological exploration, the kaolinite was not considered as the main exploration targets. The precision exploration data couldn’t be given as the associated mineral resources mentioned in the geological report. Based on “The Research Report of Five Non-metallic Mineral Resources in Coal Measures” provided by the China Coal Processing and Utilization Association in 1990, proven reserves, prospective reserves, predicted reserves and total resources of coal measures kaolinite in 19 provinces, municipalities and autonomous regions in China are 1.673 billion tons, 5.529 billion tons, 11.086 billion tons, and 18.288 billion tons, respectively. In general, the size of coal-bearing kaolinite deposit in the Carboniferous-Permian is about billions of tons. In Zhungeer coal field of Inner Mongolia, the reserve of kaolinite is as much as 5.7 billion tons. The later the mineralogenetic epoch is, the less the deposit size and reserve are. The kaolinite deposit reserve in Tertiary coal is only one million tons. The well-known sandy kaolin deposits reserves in Maoming, Guangdong province is just 300 million tons. The mineral composition of coal kaolinite rock is mainly kaolinite, followed by a small amount of illite, montmorillonite, boehmite and rutile, hematite, siderite, chlorite, and so on, which generally contain a certain amount of organic carbon. The color of coal-bearing kaolinite (soil) is rather deep, mostly light gray or gray black. The chemical composition of many coal-bearing kaolinite (soil) is similar to that of the worldwide renowned high-quality kaolin. Therefore, a number of kaolinite rocks (soil) in coal measures are high-quality kaolin deposits. The ore grade of the coal-bearing kaolinite deposit reduced along with the time. The kaolinite content is almost more than 90% in Carboniferous-Permian coal-measures kaolinite rock in North
China. The content is up to nearly 100% in some mines such as Datong, Pinglu and Pubai. The coal measure kaolinite deposit has a large scale, with the reserves generally up to several million tons, someone up to thousand million or several billion tons. The production will be significant if the deposit is developed.

However, as the organic matter content is higher in coal measure kaolinite than that of non coal measure, some of them are of high level iron ore and titanium. The quartz, feldspar, rutile are scattered in kaolinite which contains some fine sand. In addition, the hard kaolinite is difficult to disperse in water influenced by diagenesis, and of no plasticity and cohesive property. These properties limited the application of kaolinite in coal measure. Therefore, the research should be strengthened in order to resolve the problems such as carbon removal, iron removal, titanium removal, flaking and whitening.

3. Classification

In recent years, different scholars have put forward a number of classification program of coal-measures kaolinite rock, as the further study of coal-measures kaolinite rock, based on different factors, such as the material sources, creation environment, late reformation, and industrial value.

The classification of Tonstein which is accepted by the majority in overseas is proposed by Schuller (Williamson, 1970). The main types of kaolinite rock are crystalline type, granular type, compact type, false appearance and transitional type. Burger (1982) proposed a new one based on the description classification of Schuller, and combined with the main mineral composition of clay rocks. Bouroz (1962) put forward a classification about the causes, which has two main categories: pyroclastic kaolin tonstein and layered kaolin tonstein, as well as the other controversial types. The former formed in alteration of the original tuffaceous sediments, so it is very broad in lateral distribution equal-time layer. The latter formed by re-sedimentation of tuffaceous sediments and subsequent alteration, it may be diachronous, sometimes with limited lateral range. Barsley (1966) divided kaolin tonstein in Westphalia stage, North Stafford shire of United Kingdom into two types (kaolinite-A tonstein and kaolinite-B tonstein), which are similar with Bouroz’s (1962) categories respectively[3-4].

Yangjie Chen divided tonstein into three types: 1) Sedimentary type, including coal-measures kaolinite parting in layers and interlayer kaolin deposits. 2) Weathering type, containing weathering residual kaolin deposits and weathering leaching kaolin deposits. 3) Metamorphic kaolin deposits, due to spontaneous combustion, kaolinite rock turned into burnt rock baking by high temperature.

Based on occurrence horizon, properties and the causes, Shuwen Zhou (1990) divided tonstein into: 1) tonstein kaolinite deposits, including colloidal sedimentary type and volcanic causes type. 2) coal seam roof and floor of kaolinite rock (soil) deposits, including hard kaolinite rock and soft kaolinite rock. 3) Non-adjacent coal kaolinite (soil) deposits, including hard kaolinite, semi-hard-soft kaolinite rock and semi-soft kaolin.

According to the formation mechanism of North China platform coal measures kaolinite rock, Pengfei Zhang et al (1993) divided it into four types: condensed in-situ, reworked in-situ, clastic sedimentation and weathering in-situ. Qinfu Liu and Pengfei Zhang (1997) put forward the following types based on the relationship between kaolinite rock and coal seam for simple applications and concise purposes: 1) Kaolinite rock in coal seam and roof-bottom plate: occurred in the roof and floor of coal seam or in form of coal tonstein. Most of them are hard kaolinite rocks. Kaolinite tonstein has thin thickness, generally few centimeters to tens of centimeters (only a few mm thick), and the individual thickness over 1 m. The horizontal distribution is relatively stable and can be used as isochronous correlation layer. The thickness of the roof and floor kaolinite is larger, generally a few dozen centimeters to several meters, but the horizontal thickness changes a lot. This kind of kaolinite has darker colors, showing black gray-dark, dense block, conchoidal or sand-like fracture. 2) Non-adjacent coal kaolinite rock: existed in a certain distance from the coal seam, outputed independently, larger thickness, up to one meter to several meters, regional distribution relatively stable. Such as A layer kaolinite in Shandong, B layer in Huainan (formerly called bauxite, actually are kaolinite rock), North China and the G layer symbiotic bauxite symbiosis kaolin or kaolinite. Here kaolinite is aphanitic, often lenticular and oolitic structure, gray -light gray and conchoidal fracture. 3) Knag soil type soft kaolinite: appeared in the form of outcrop or in shallow underground associated with weathered coal. It is rich in organic matter and high plasticity, showing purple, brown, white and so on. The thickness reaches tens of centimeters to several meters. It is widely in China such as Tangshan, Jiexiu, Pinglu, ShuoXian, Qingshuihe, Zhungeer, and Laoshidan. Each rock type is very different from others in structure, property, causes and occurrence status[6-7].
4. Origin models

Based on the analysis of mineralogical, petrologic and geochemical evidences and the occurrence of the various types of kaolinite rocks, four origin models of kaolinite are put forward by Qinfu Liu and Pengfei Zhang (2006) as following:

1) Not adjacent to coal seams like bed-A kaolinite rock in west Shandong province: The bed-A kaolinite rock with pisolite and oolite in West Shandong Province being 5~8 m thick is located in the lower part of Shangshihezi Formation of upper Permian, and is not adjacent to coal seams. It shows regular changes from bottom to top in mineralogy and geochemistry: 1) The main clay minerals of bed-A kaolinite rock are kaolinite and berthierine. The content of kaolinite increases upwards whereas that of berthierine decreases. 2) The contents of SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$/FeO ratio increase and TiO$_2$, Sr/Ba ratio and WI (weathering index) decrease from bottom to top. 3) The REE changes ($\sum$REE from 186 to 23.68, LREE/HREE from 5.23 to 2.59, $\delta$Eu from 0.58 to 0.88) show that weathering and leaching were enhanced from bottom to top. 4) The development of seepage flow tube structures shows a meteoric fresh water leaching environment. All the evidences above show that kaolinite replaces berthierine during chemical weathering. Berthierine was deposited in coastal environment during starved-sediment period and was subsequently uplifted to ground subjected to surficial weathering.

2) The bed-B kaolinite rock in Huainan coalfield, Anhui province: This bed of kaolinite rock of 2~6 m in thickness being widespread and stable is located in the lower part of Xiashihezi Formation of upper Permian which was deposited in a lower delta plain environment. Bed-B kaolinite rock can be divided into four classes: micritic, silty, ferriferous, pelletoid and oolitic. Among them, the oolites and pellets which are complex aggregates of microcrystalline kaolinite and organic matters are very distinct in microstructure. Kaolinite content is as high as 95%~100%. Studies on sedimentology, geochemistry and paleontology show that the kaolinite was mainly derived from the weathered materials in source rocks which were transported and deposited in a lacustrine environment of the delta plain. The widespread red kaolinite-bearing mudrocks above or below this kaolinite rock bed indicate that rubefication was developed in parent rocks in the source area. Some crystals of kaolinite arranged in radiation around the grains were crystallized from alumino-silicon gel. The organo-clay complexes and the organo-Al(or Si) gel played an important role in the long distance transportation of the kaolinite-forming materials.

3) Tonsteins: More and more Tonsteins have been reported by many geologists all over the world over the past decades. They are generally considered as being volcanic origin. At present, there is a tendency among geologists to explain all the kaolinite rocks in coal seams by volcanic origin, however it is hard to imagine that some kaolinite rock beds up to 2~6 m thick can be formed this way. The authors, therefore, suggest that the process to form Tonsteins is complicated, involving many factors. The formation of Tonsteins depends on two important factors: one is the original kaolinite-forming materials and the other the transformation and crystallization of kaolinite in swamp environment at diagenetic stage. Two types of original materials can be transformed into kaolinite in swamp environment: one is the terrigenous clay and aluminosilicate minerals such as feldspar and biotite, and the other the volcanic ashes fallen into swamps. All the original materials which entered the swamp basin could be transformed and crystallized to form kaolinite with the leaching off alkaline or alkaline earth ions and silicon under the influence of organic acids.

4) The soft kaolin clay associated with weathered coals: This kind of kaolin clay contains high content carbon being soft, cryptocrystalline, well-plastic and with high Hinkley Index. It was crystallized from the low concentration of Si-Al sol which were formed by the dissolution of surrounded rocks adjacent to weathered coal under the influence of fulvic acid. It is the low concentration of Si-Al sol and low temperature and pressure in ground environment that result in the formation of well-ordered kaolinite through the slow and regular arrangement of Si and Al ions in crystallization.

5. Conclusion

1) Almost all coal measures contain the industrial kaolinite rocks which generally contain a certain amount of organic carbon in North China. The color of coal-bearing kaolinite (soil) is rather deep, mostly in light gray or gray black.

2) There are three types of kaolinite rocks associated with coal measures: The first occurs in the roofs, partings and floors of coal seams, normally called Tonsteins; the second one is not adjacent to the coal beds, similar to the...
flint clay in North America; the third type is soft kaolin clay associated with surficial weathered coals.

(3)There are four origin models of kaolinite associated coal seams: The first is chemical weathering origin model like the bed-A kaolinite rock in West Shandong Province; the second one is depositional origin model like the bed-B kaolinite rock in Huainan coalfield, Anhui Province; the third one is Tonstein origin model, it is formed by the alteration of volcanic ash fallen in the swamp environment. The fourth origin models is soft kaolin clay associated with weathered coals.

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