Microstructure Analysis of Attapulgite Clay Minerals

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Abstract. Land is the foundation of human being. However, with the rapid development of human society, soil is no longer clean, and soil remediation is imminent. Passivation of heavy metals in soils by passivates is a relatively economical, rapid and reasonable treatment measure. In this paper, the microstructure of attapulgite clay minerals and acid-modified attapulgite clay minerals are qualitatively and quantitatively analyzed by scanning electron microscopy. The results show that the attapulgite clay minerals have rough micro-surface, more synapses on the surface after modification, higher porosity, higher pore fractal dimension, larger probability entropy, and larger passivation potential of heavy metals.

1. Introduction

Soil is one of the basic elements of ecosystem, one of the most important natural resources of the country, the material basis for human survival and the main component of the ecological environment. However, with the rapid development of industrial and agricultural production, the rapid progress of human society, the discharge of "three wastes" in industrial production, the extensive use of chemical fertilizers and pesticides in agricultural production, and atmospheric deposition, etc. Diameter causes a large number of heavy metals to enter the soil of farmland. Heavy metal pollution has the characteristics of long-term, concealment and accumulation. It not only poses a serious threat to the quality of farmland and agricultural products, but also can enter the human body through the food chain and endanger human health. According to the survey, due to mining, metal smelting, industrial emissions and other reasons, the cultivated land area polluted by arsenic, cadmium, mercury, zinc, copper and other heavy metals in China is about 10 million ha, and the annual grain output polluted by heavy metals is about 10 million tons, resulting in huge economic losses and potential food safety hazards [3].

There are many remediation methods for heavy metal pollution, which can be divided into physical remediation, chemical remediation, biological remediation, combined remediation, etc. According to the remediation site, they can be divided into in situ remediation and heterotopic remediation. Usually, heavy metal contamination in soil often involves a large area. Ectopic remediation technology is relatively small and often cost too much. In-situ remediation technology is the trend technology of heavy
metal remediation in the future. Soil leaching can effectively remove heavy metals in in situ remediation technology, but the risk of secondary pollution is high; phytoremediation technology is safe, economical and effective, but its action time is long; in situ passivation technology adds one or more passivation remediation agents to contaminated soil, and adjusts the physical and chemical properties of soil, as well as adsorption, precipitation, ion exchange, humification, oxidation-reduction and a series of other passivation remediation agents. Reaction [4-5], changing the chemical form and occurrence state of heavy metals in soil, realizing the passivation/stabilization of heavy metals in soil, reducing their mobility and bioavailability in soil, thus preventing the migration and accumulation of heavy metals from soil through plant roots to above-ground parts of crops, in order to achieve the purpose of controlling polluted soil, is currently the remediation of moderately and mildly polluted soil. Better choice [6-8].

At present, in-situ passivation technology is mainly applied with passivates. Therefore, the selection of passivates with large pore size and large surface area is the key factor for heavy metal passivation. In this paper, attapulgite clay minerals are used as passivates, and their acid modification is carried out to analyse their microstructures. The purpose of this study is to explore the passivation mechanism from the microscopic point of view, in order to provide scientific theoretical support for the development of heavy metal remediation agents in soil.

2. Materials and methods

2.1. Test Material
Attapulgite clay mineral was used as passivation material and acid modified.

2.2. Test Method

2.2.1. Preparation of Modified Attapulgite Passivator. The modified attapulgite was modified by hydrochloric acid. The attapulgite clay of about 40g was put into a triangular bottle. Hydrochloric acid with a concentration of 0.05 mol/L at 80ml was added. The hydrochloric acid was oscillated at constant temperature for 2 hours. After cooling, the attapulgite was centrifugally washed until chloride-free ions existed. Then it was dried at 105°C and ground through 100 mesh sieves.

2.2.2. Microscopic Morphology Observation. FEI Q45 scanning electron microscopy was used to analyze the samples by SEM/EDS. The prepared samples were observed under environmental scanning mode. The observed samples were enlarged from 100 times to 30,000 times and photographed step by step. The micro-topographic maps of attapulgite and modified attapulgite were obtained.

2.2.3. Quantitative Analysis of Microstructure. The pore image recognition and analysis system of PCAS developed by Dr. Liu Chun of Nanjing University was used to process the SEM image [9]. The software is a professional software for identification and quantitative analysis of pore and fracture systems. The specific steps are to binarize the image first (Fig. 1), then vectorise the binary image (Fig. 2). In the binarized image, white is particles, black is pores; in the vectorised image, black is pores, and other colors are particles. According to the automatic recognition and analysis function of the system, the vectorization results are automatically analysed. On the quantitative index of micro-structure, some related studies have put forward such quantitative indexes as the number of particles, the average area of particles, the average perimeter of particles, the equivalent edge length of particles, the coefficient of properties (roundness), the apparent void ratio, the fractal dimension of pore, etc. [10-12]. In this study, the probability entropy of the average shape coefficient of particles and the apparent void ratio are selected in combination with the automatic analysis function of PCAS. The fractal dimension of pore distribution and other indicators are used for quantitative analysis of particles and pore.
3. Results and discussion

3.1. Analysis of Microstructure and Morphology of Passivating Materials

Fig. 3 and Fig. 4 are scanning electron microscopic images of attapulgite clay minerals and acid modified attapulgite clay minerals respectively. From the graphs, the surface of both of them is rough, with sheet and strip structure. Natural attapulgite has montmorillonite, kaolinite, hydro mica and other carbonate minerals [13]. The micro-morphology of montmorillonite is mainly lamellar, while attapulgite is mainly strip. It is known that the passivation raw material contains a large amount of montmorillonite. After hydrochloric acid modification, attapulgite clay minerals have more complex surface morphology, more synapses and more specific surface area. Some studies have shown that in acid activation of palygorskite, when octahedral cations partially dissolve, most of the silicon-oxygen tetrahedrons are basically retained, so that the crystal structure of palygorskite can be maintained. Acid activation increases the Si-OH functional groups on the surface of palygorskite and changes the surface properties of palygorskite [14].
Figure 4. Scanning Electron Microscopic Images of Modified Attapulgite Clay Minerals

3.2. Quantitative Analysis of Microstructure of Passivating Materials

Table 1. Quantitative Analysis of Microstructure of Passivating Materials

| Passivating material | Region percentage (Porosity) | Pore porosity distribution fractal dimension | Probability Entropy |
|----------------------|------------------------------|--------------------------------------------|---------------------|
| Attapulgite          | 41.62%                       | 1.8198                                    | 0.9561              |
| Modified Attapulgite | 48.97%                       | 1.8805                                    | 0.9591              |

Table 1 is the quantitative analysis results of the microstructure of attapulgite and modified attapulgite. It can be seen from the table that the porosity of acid-modified attapulgite increases significantly, and the porosity increases by 17.66%. The pore morphology also has fractal characteristics. The fractal dimension can reflect the complexity of pore structure [15]. The higher the fractal dimension of pore distribution, the simpler the pore structure is. It can be seen that the fractal dimension of attapulgite pore is increased after modification, and the pore structure becomes more complex. Probability entropy is the regular degree of describing particles in soil. Its value usually ranges from 0 to 1. When probability entropy is 0, it shows that the direction of particle arrangement is the same. The larger the probability entropy is, the more random the particle arrangement is [16, 17]. The probability entropy of modified attapulgite is higher than that of original attapulgite, which indicates that some attapulgite materials are corroded more irregularly under the action of acid. Therefore, acid-modified attapulgite may increase the passivation of heavy metals and enhance the passivation effect.

4. Conclusion

The surface of attapulgite clay minerals is rough, lamellar and strip-like. After hydrochloric acid modification, the surface porosity increases by 17.66%, and the pore structure becomes more complex. The fractal dimension of the pore increases, the probability entropy gradually approaches to 1, and the particle arrangement becomes more irregular. Modified attapulgite clay minerals will be more effective in passivation of heavy metals. It is suggested that further experiments on passivation of heavy metals be carried out to clarify their passivation effects.
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