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Experimental Study on Adsorption of Rare Earth Elements on Kaolinite and Halloysite

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1 Introduction

The weathered crust rare earth deposits is one of the most significant rare earth deposits, which are mostly distributed in southern China, especially in the south of Jiangxi province (Chi et al., 2007). The compositions of these deposits, which are weathered from igneous rocks such as granite through biological, physical or chemical processes in open systems (Chi et al., 2012), are quartz, feldspar, and mainly clay minerals (40%-70%, Chi et al., 2007). And the clay minerals in the deposits include halloysite (25%-50%), illite (5%-20%), kaolinite (5%-10%) and montmorillonite (< 1%) (Chi et al., 2007). Besides, not only the original rocks, but also the properties of clay minerals could influence the distributional patterns of the rare earth elements (Fan et al., 2015).

Halloysite and kaolinite are the most common clay minerals in the weathered crust rare earth deposits, both of which have the TO layered structure and similar chemical compositions. The chemical formula of halloysite is $\text{Al}_2[\text{Si}_4\text{O}_{10}](\text{OH})_2$, while the formula of kaolinite is $\text{Al}_2[\text{Si}_4\text{O}_{10}](\text{OH})_8$. Unlike kaolinite, the unit layers in halloysite are separated by a monolayer of water molecules. As a result, hydrated halloysite has a basal (d_{001}) spacing of 10 Å which is ~3 Å larger than that of kaolinite (E. Joussein et al., 2005). Because of the stronger bonds between the aluminosilicate layers, the water molecules can be driven off without changing the structure, easily and irreversibly (Hendricks S B et al., 1938). The particles of halloysite can adopt a variety of morphologies, commonly elongated tubule, when the kaolinite shows platy particle shapes (E. Joussein et al., 2005). Ma. & Eggleton (1999) suggested that the slightly

higher cation exchange capacity (CEC) for tubular halloysite than for other forms is due to cations present in the micro- and mesoporosity (halloysite tubes) as soluble salts. Besides the tubular shape can lead to its higher specific surface area (SSA) and porosity (Theng, 1995; Churchman et al., 1995; Levis & Deasy, 2002).

The aim of this article is to collect adsorption data of rare earth elements (REEs) by halloysite and kaolinite through simulation experiments to learn about the differentiation phenomenon of rare earth elements in the weathered crust rare earth ore, and whether kaolinite and halloysite play an important role in this process.

2 Methods

In this article, our samples are relatively pure halloysite and kaolinite. We mainly used X-ray diffraction, Scanning electron microscope, Raman spectra, Transmission electron microscope and other means to distinguish these two clay minerals, so that we can ensure the reliability of the samples. In addition, we also measured the point of zero charge (PZC) of these two minerals through potentiometric titration method (Zhang et al., 2012).

The key to our experiment is to simulate the processes of the adsorption. Considering the stability of the rare earth elements, our experimental system should be acidic. The REE sorption were measured at 25°C over pH = 2 and 4. In the first step, the solids were equilibrated with an 0.01mg/L REE-free solution (containing La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) until pH =4 was reached. After a 24-h of oscillation at 25°C, recording the pH of the solution at that time. Then the residual rare earth concentration of the solution after filtration, will be determined by inductively coupled plasma mass spectrometry (ICP-MS). Three experiments were performed in each group and the blank group was set up. After calculation, we can get the REEs adsorption

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capacity of halloysite and kaolinite.

In the next step, we set up another group, which we change the pH of the solution to 2 by adding HNO₃, and do the same step as the first one, so that we can compare the differences with the group of pH = 4.

In addition, the third step we do is to introduce 0.1mg/L and 1mg/L NaNO₃ and KNO₃ respectively into the solution over pH = 4 to explore the influence of metal cations on adsorption.

Results

pH is one of the most significant factor to affect the adsorption capacities of halloysite and kaolinite. When the pH is lower than the PZC (PZC_{halloysite}=2.9 and PZC_{kaolinite}=3.0), the adsorption capacities of halloysite and kaolinite are about more than 20 times lower than those in the solution with pH>3.5. The results also show that the REEs adsorption capacity of halloysite is 1.5 times higher than that of kaolinite when pH=4. The saturated REEs adsorption amount of halloysite can reach (mg/g): La 181.51; Ce 180.72; Pr 180.28; Nd 180.06; Sm 185.70; Eu 185.92; Gd 185.34; Tb 185.13; Dy 182.41; Ho 180.58; Er 181.98; Tm 179.04; Yb 177.56; Lu 179.04.

Metallic cations in the system also greatly affect the adsorption capacities of halloysite and kaolinite by competition adsorption. When Na⁺ and K⁺ cations are introduced into the solution, the saturated REEs adsorption amount are 10 times lower than before. However, kaolinite and halloysite do not show the characteristics of absorptive dissimilarity in the condition of Na⁺ addition. Only when there is K⁺ in the system both clay minerals show different absorption characteristics of REEs, in which the kaolinite adsorb MREEs and HREEs more, while halloysite shows the opposite way.

Discussion

When the pH is higher than the PZC, the surface charge of halloysite and kaolinite is a negative charge, while it shows the opposite way when the pH is lower than the PZC (Wei, 1992). And the positive charge can restrain the REEs adsorption capacity of these two minerals.

Halloysite shows higher specific surface area (SSA), cation exchange capacity (CEC) and porosity (Theng, 1995; Churchman et al., 1995; Levis & Deasy, 2002). These characteristics may enhance the adsorption capacity of halloysite and exhibit better adsorption ability than kaolinite.

The reason why Na⁺ and K⁺ affect the adsorption capacities of halloysite and kaolinite, could be understood as competition adsorption. Compared with the rare earth elements, Na⁺ and K⁺ have lower hydration energy, and can be adsorbed in the basal surface of the tetrahedral sheet more easily (E. Joussein et al., 2005). It may lead to the competition adsorption between these metallic cations and REEs.

The original rocks of the weathered crust rare earth ores are REE-riched granite. When the granite is weathered, the potash feldspar in granite would transform to halloysite and kaolinite and release potassium ions into the diagenetic environment at the same time. This natural environment is like the experimental conditions we simulated before, which contained K⁺ in the system. Halloysite-rich clays are reported to show a high selectivity for poorly hydrated cations, such as NH₄⁺, K⁺ and Cs⁺ (E. Joussein et al., 2005). The REEs adsorption characteristics of halloysite and kaolinite can be considered as the reason for REEs divergence. Thus, the K⁺ during the weathering of rocks may lead to the absorptive divergence of halloysite and kaolinite, and affect the distribution of REEs in the weathered crust rare earth deposits.

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