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Removal of harmful constituents from geothermal water by selected anion clays

Yaowu Cao[a], Qinghai Guo[a,1], Yaqin Zhuang[a], Zhengyan Yu[a], Wei Guo[a], Canhai Zhang[b], Mingcheng Zhu[b], Qian Zhao[a], Tianlin Ren[a]

[a]*State Key Laboratory of Biogeology and Environmental Geology & School of Environmental Studies, China University of Geosciences, 430074 Wuhan, Hubei, P. R. China*

[b]*Huanghe Hydropower Development CO., LTD., State Power Investment Corporation, 810008 Xining, Qinghai, P. R. China*

Abstract

Four kinds of anion clays (hydrocalumite, hydrotalcite, iowaite and takovite) synthesized in this study were used for removing harmful constituents from the geothermal waters collected from three hydrothermal areas located in Qinghai Province, northwestern China. Iowaite performed better than the other anion clays in term of water dearsenication, while hydrotalcite exhibited higher efficiencies on removal of fluoride and sulphate. The increase in dosage of iowaite dramatically elevated the chloride concentrations of the treated geothermal waters as the enhanced release of original interlayer chloride in the iowaite duo to the anion exchange. Therefore, hydrotalcite is the optimal sorbent for uptake of undesirable constituents in Qinghai geothermal waters and is promising for wider use in treatment of geothermal waters in the future.

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Keywords: Anion clay; geothermal water; harmful constituent; sorption; Qinghai

1. Introduction

Sorption reactions at mineral-water interfaces have a profound impact on the solid-water treatment of harmful constituents and thus play an important role in controlling the mobility and fate of these species in aqueous environments. Anion clays (or layered double hydroxides) belong to the family of clay minerals, which have been widely applied in sorption reactions in view of their special lamellar microstructure. Although the use of these minerals in contaminant treatment is hampered by their limited natural distribution, the relatively simple and

* Corresponding author. Tel.: +86-13554116793; fax: +86-27-87436235.
E-mail address: qhguo2006@gmail.com

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economical synthesis at an industrial scale provides a possibility for their practical applications. In addition, taking into account of their tailor-made structures and chemical compositions, the option of the appropriate anion clays which adjust measures to local conditions is a central aspect of particular water treatment engineering.

Generally in high-temperature geothermal systems, as the longer time of fluid-rock interaction, the geothermal waters could dissolve large amounts of chemical species. According to our research, F, As and other harmful contents in geothermal waters of Qinghai province exceed the World Health Organization (WTO) guideline values by dozens of times. However, some geothermal areas in Qinghai province are close to residential areas and surface geothermal waters discharge into local rivers directly. Thus to investigate the effective environmental management is necessary for future geothermal resource utilization. We collected three geothermal water samples from three geothermal regions in the Qinghai province and parts of their chemical composition are shown in Table 1.

In this study, four kinds of anion clays are synthesized in the laboratory, such as hydrocalumite (HC), hydrotalcite (HT), iowaite (I) and takovite (T). Through sorption experiments, we can optimize the most appropriate sorbent to purify the Qinghai geothermal waters.

Table 1 Chemical composition of the water samples from the Qinghai province

Sample No.	pH	As (μg/L)	F (mg/L)	Cl (mg/L)	SO_4 (mg/L)
GH	7.3	92.81	5.16	715.31	241.15
GD	8.0	21.80	11.94	363.36	621.55
XH	7.2	16.48	7.36	222.66	472.95

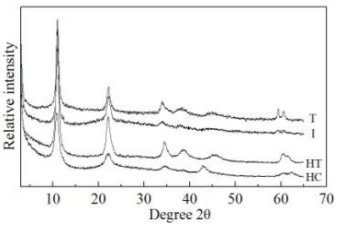

Fig. 1 XRD patterns of synthesized anion clays

2. Materials

2.1. Synthesis of sorbents and characteristic

The coprecipitation method[1] was used to synthesize the four anion clays in this study. The target products were mainly controlled by initial salt solutions. In the case of hydrotalcite ($Mg_6Al_2(OH)_{16}Cl_2{\cdot}4H_2O$) for example, salt solutions were prepared by mixing magnesium chloride and ferric chloride with the molar ratio of 3, which was added dropwise into a beaker along with a sodium hydroxide solution under substantial stir. The obtained suspension was then heated at 80°C to favour the crystallization. The solid products were filtered, washed and dried at 60°C. Likewise, hydrocalumite ($Ca_4Al_2(OH)_{12}Cl_2{\cdot}6H_2O$), iowaite ($Mg_6Fe_2(OH)_{16}Cl_2{\cdot}4H_2O$) and takovite ($Ni_6Al_2(OH)_{12}Cl_2{\cdot}4H_2O$) were prepared using this method.

The four solid samples were analyzed by X-ray Diffraction (XRD) using Cu Kα radiation (X'Pert PRO DY2198 diffractometer). The XRD patterns were collected from 5° to 65° with a 2θ step of 0.033°.

2.2. Sorption experiments and analysis

25 ml of three water samples were taken into 100 ml plastic bottles for sorption experiments. Three groups of sorbent dosages were prepared in equal molar mass of 0.082 mmol, 0.82 mmol and 4.08 mmol. After 24 h reaction time at room temperature, the solution samples were decanted and filtered through a 0.45 μm cellulose acetate membrane. The arsenic concentrations in the reacted solutions were analyzed by an AFS-2202 duel-channel atomic fluorescence spectrophotometer. The fluoride, chloride and sulphate concentrations were measured using DIONEX CO. ICS-900 ion chromatograph.

3. Results and discussion

3.1. Characteristic of solid phase

The XRD patterns of the solid phase are shown in Fig. 1. The reflections of the anion clays were in agreement with those reported in the literature[2], which indicated that the solid materials had a regular layered structure, and no characteristic peaks were from impurities.