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ScienceDirect
Colloids and Surfaces A: Physicochem. Eng. Aspects 307 (2007) 77–82
COLLOIDS AND SURFACES A
www.elsevier.com/locate/colsurfa

Diffusion mechanism of certain fission products in the particles of silico(IV)titanate

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Received 20 October 2006; received in revised form 10 April 2007; accepted 1 May 2007
Available online 5 May 2007

Abstract

The kinetics and mechanism of diffusion of Cs^+, Co^{2+} and Eu^{3+} in the H^+-form of silico(IV)titanate (SiTi) have been studied. The sorption conditions were set to study the particle diffusion mechanism only and is confirmed from straight lines of Bt versus $1/r^2$ plots. The values of diffusion coefficients, activation energy and entropy of activation were calculated and their significance was discussed. The data obtained have been compared with that reported for other organic and inorganic exchangers.

Keywords: Diffusion mechanism; Ion exchange; Silico(IV)titanate

1. Introduction

Radioactive liquid wastes are generally composed of major quantities of non-radioactive components contaminated with minor amounts of hazardous gamma emitting radionuclides such as ^{137}Cs, ^{60}Co, ^{154}Eu, ^{144}Ce, etc. Separation and concentration of these radioactive materials from large volumes of radioactive waste minimize the volume of the radioactive fraction that is to be safeguarded for long time. A main approach developed is to introduce efficient sorbent for different metal species for volume reduction.

Many inorganic ion exchangers have been shown to exhibit good thermal and radiation stabilities, and for this reason considerable interest in these materials have arisen in recent years, particularly in the atomic energy field [1–6]. Within this context, different types of inorganic ion exchange materials have been synthesized for the treatment of aqueous radioactive liquid wastes. Studies relating to the utilization and development of inorganic sorbents and their applications to the treatment of various streams have been carried out over a number of years [2–9]. Lehto and Harjula [2] reported that not many sorbents are effective for the separation of fission products from acidic liquid wastes and further they suggested the need to develop new inorganic sorbents to accomplish these tasks. In a previous work [10–13], we reported on the synthesis of several inorganic ion exchangers and evaluated their potential use for the removal of heavy metal ions and selected fission products from acidic streams.

A titanium silicate of ideal formula $Na_2Ti_2O_3(SiO_4)\cdot 2H_2O$ are a new class of ion exchangers that were jointly invented by researches at Sandia National Laboratories and Texas A&M University [3]. Crystalline silico(IV)titanate (CST) was synthesized as a highly crystalline powder from a mixture of titanium isopropoxide, tetraethylorthosilicate and NaOH under hydrothermal condition [4]. Anthony et al. [5,6] reported the synthesis of sodium titanium silicate (CST) by two different procedures. El-Naggar et al. [7] investigated the synthesis and characterization of amorphous silico(IV)titanate. In the course of the successful application of these ion exchange materials, our interest has been directed to study the diffusion mechanism of Cs^+, Co^{2+} and Eu^{3+} on the prepared semi-crystalline silico(VI)titanate under control of particle diffusion mechanism.

2. Experimental

All chemical used were of analytical reagent grade purity and used without further purification. The radioactive tracers $^{134}Cs^+$

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doi:10.1016/j.colsurfa.2007.05.004

and $^{60}Co^{2+}$ were delivered by Amersham Radiochemical Center, $^{152+154}Eu$ was locally prepared. In this respect, highly pure spectroscopic materials was used as Eu_2O_3 target and warped in an aluminium can and irradiated with neutrons for 48 h in the Egypt 2 MW research reactor at Inshas, using a neutron flux of $1.3 \times 10^{13}\,n\,cm^{-2}\,s^{-1}$.

2.1. Preparation of silico(IV)titanate

Silico(IV)titanate was prepared by dropwise addition of sodium metasilicate (1 M) to titanium tetrachloride (1 M) dissolved in 4 M HCl at Si/Ti molar ratio of 1.0 with continuous stirring in water bath at $60 \pm 1\,°C$. After complete addition, the mixture was hydrolyzed in distilled water at $60 \pm 1\,°C$ where a white precipitate of silico(IV)titanate was formed after the addition of 3 M KOH to the mixture reaction till pH ≈ 5.

After overnight standing, the product obtained after centrifugation (≈10^4 rpm) and filtration was washed with distilled water and dried at 50 °C. In order to remove the air trapped and adherent fine particles, the crude product was rewashed with near boiling distilled water ($70 \pm 1\,°C$), dried at 50 °C and finally washed with 1 M HNO_3 until free from chloride ions. After derided at 50 °C, the final product ground, sieved (0.12–0.44 mm) and finally air dried at room temperature.

To obtain an insight into the nature of structure of the prepared silico(IV)titanate, the powder X-ray diffraction patterns of prepared silico(IV)titanate was carried out at different heating temperatures (50–850 °C) as shown in Fig. 1. It was found that that silico(IV)titanate has semi-crystalline structure and the crystallinity of the prepared material improved with the increase of heating temperature from 50 to 850 °C.

2.2. Kinetics studies

The radius of the particle of the sieved fractions was determined by measuring the diameter of 100 particles with an optical microscope. The particles were assumed to be spherical and a mean equivalent radius was calculated. The reaction take place between the metal ions and the counter ions in the exchanger and the rates are controlled by particle diffusion mechanism only. Kinetics experiments were performed by using batch factor of V/m equals $50\,ml\,g^{-1}$, and 10^{-3} M metal chloride solution in a shaker thermostat adjusted at the desired temperatures. After the adjusted interval period, the solid was separated immediately from the solution and the extent of sorption was determined as the following:

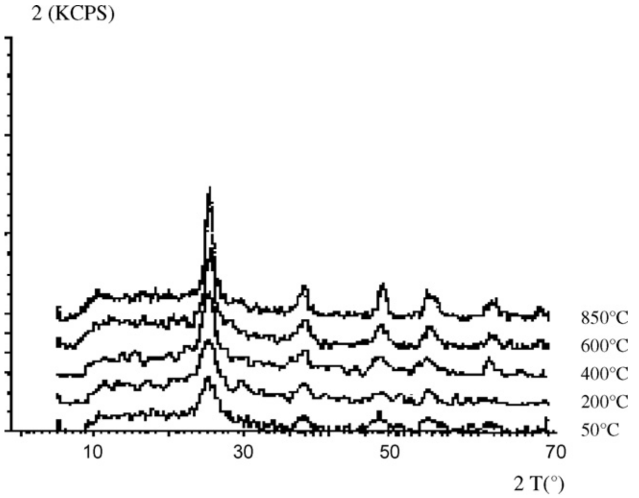

Fig. 1. X-ray diffraction patterns for the prepared silicotitanate (SiTi-II) at different drying temperatures.

$$\%\text{sorption} = \frac{A_i - A_f}{A_i} \times 100$$

where A_i and A_f are the initial and final concentration of the metal ions in solution.

2.3. Analysis

The radioactive nuclides used in this study ^{134}Cs, ^{60}Co and $^{152+154}Eu$ were measured radiometrically in both solid and liquid phases using NaI(TI) scintillation detector connected to an scalar SR7 obtained from Enterprises, USA. The counting rates of different samples were measured to give at least 10 times as that of the background. All tests were repeated two to three times and the total experimental error was about ±3%.

3. Results and discussion

3.1. Mathematical model

The experimental conditions of the present study were set for the partical diffusion mechanism only (as mentioned before in Section 2). The fractional attainment of equilibrium at time t, $F(t)$, was used and is expressed as:

$$F(t) = \frac{Q_t}{Q_\omega} = \frac{\text{Amount of exchange after time } t}{\text{Amount of exchange after infinite time}}$$

For the particle diffusion controlled kinetics, the expression developed by Boyed et al. [14] and improved by Reichenberg [15], Eq. (1), which is used in this work:

$$F = 1 - \frac{6}{\pi}\sum_{n=1}^{\infty}\frac{1}{n^2}\,e^{-n^2 Bt} \qquad (1)$$

and

$$B = \frac{\pi^2 D_i}{r^2} \qquad (2)$$

where B is a mathematical function, D_i the self-diffusion coefficient of the ions undergoing exchange within the exchanger, n is an integer number, r refers to the radius of the particles. When $F(t)$ is less than 0.4, Eq. (1) can be approximated in a simpler form:

$$F(t) = \frac{6}{R}\left(\frac{D_i t}{\pi}\right)^{1/2} \qquad (3)$$

which hold to a fairly good approximation. Therefore, a plot of $F(t)$ against the square root of the contact time must be give a