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Full Length Article

Preparation of carbamate-containing vaterite particles for strontium removal in wastewater treatment

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ABSTRACT

Submicron-sized particles of vaterite, containing carbamate-functionalised siloxane (V–Si), were prepared as the precipitant of radioactive strontium in the treatment of wastewater. The particles consisted Q2 of 10–22 nm-sized vaterite crystallites with preferred-orientation towards (00*l*) plane; a highly charged plane. The crystallites were suggested to be stabilised by the coordination of the siloxane through carQ3 bamate ($NH–COO^-$) groups. On being soaked in the aqueous strontium chloride solution, vaterite was dissolved from V–Si to facilitate the competitive precipitation of calcian-strontianite and calcite. The particles containing a large amount of silicon exhibited the highly-controlled dissolution; the formation of calcite was suppressed to increase the strontium contents in the resulting precipitates.

1. Introduction

Currently, the many benefits of nuclear science, such as nuclear power generation, are accompanied by drawbacks, such as the generation of various types of radioactive liquid waste (RLW). Strontium-90 (^{90}Sr) is the one of common radionuclides being contained in the RLW. To date, several inorganic materials have been examined for the decontamination of ^{90}Sr from the RLW by ion exchange [1–10] and chemical precipitation routes [11,12]. Carbonate precipitation methods have advantages of simplicity and cost effectiveness in terms of operation and applicability to large treatment volumes [11–14]. The efficiency of the methods is influenced by the separation of precipitates by membrane filtration process. The methods were explored to give an appropriate sizes, namely ~2 μm, to the precipitates for the ease of filtration, such as the co-precipitation on the surfaces of seed crystals [15,16]. These methods, however, lead to an undesirable increase in radioacQ4 tive secondary waste. To use the quasi-stable seed crystals, which uptake the strontium during their recrystallization, is assumed to be the solution for the volume reduction of wastes.

Vaterite is one of the polymorphs in calcium carbonates with minimum thermodynamic stability, dissolving in contact with aqueous solution. Therefore, it is potentially suitable for use as the reactive seed crystals. Tuning the solubility of vaterite is a key for achieving efficient strontium carbonate formation, since its rapid dissolution generally leads the recrystallization into calcite, which is the most thermodynamically stable polymorph. The authors previously developed a method for the preparation of siloxane-containing vaterite (V–Si) particles using a carbonation process [17–20]. In these V–Si particles, vaterite with 5–20 nm-sized lamellae is present, and it is enclosed by aminopropylsilane-derived siloxane. In contact with a buffer solution, the dissolution of vaterite was regulated by the hydrolysis of the siloxane.

We herein demonstrated the application of V–Si particles for the collection of strontium from aqueous environment. An aqueous solution of strontium chloride was used for the fundamental testing solution. Moreover, V–Si particles with a series of siloxane content were prepared: they provide an insight into the relationship between the chemical stability of vaterite and the efficiency of strontium carbonate formation.

2. Experiment

The V–Si particles were prepared via the following process. To methanol (200 mL) (Wako pure chemicals, Japan), deionised water (10 mL) and calcium hydroxide (15.5 g) (Kishida Chemical Co. Ltd., Japan) were added to give a calcium concentration of 1 mol L^{-1}. Aminopropyltrimethoxysilane (APTMS, Sigma–Aldrich,

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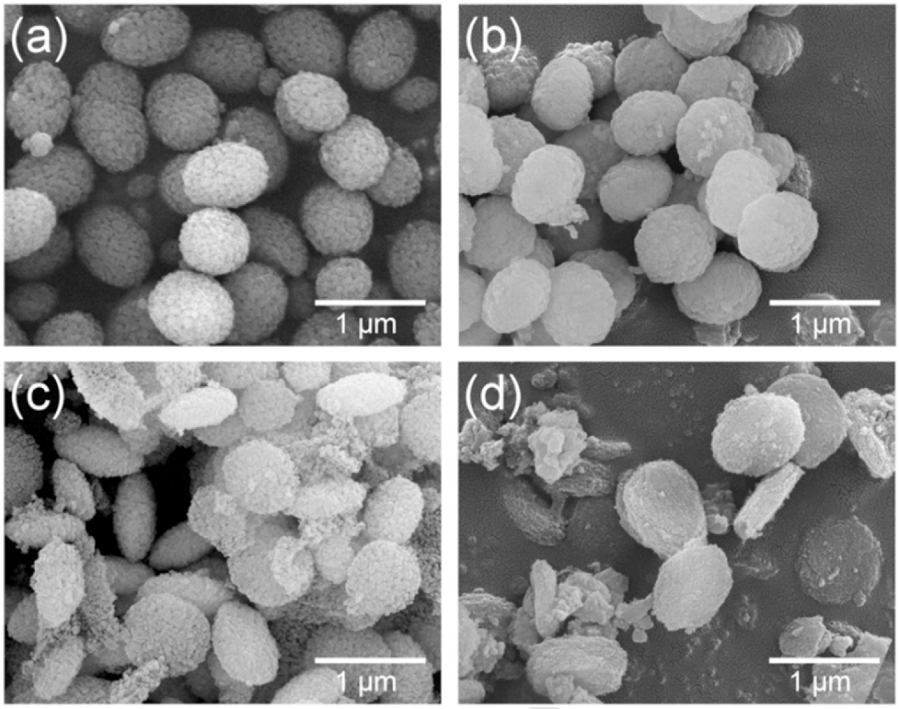

Fig. 1. SEM images of samples: (a) V, (b) V–0.01Si, (c) V–0.05Si, and (d) V–0.1Si particles.

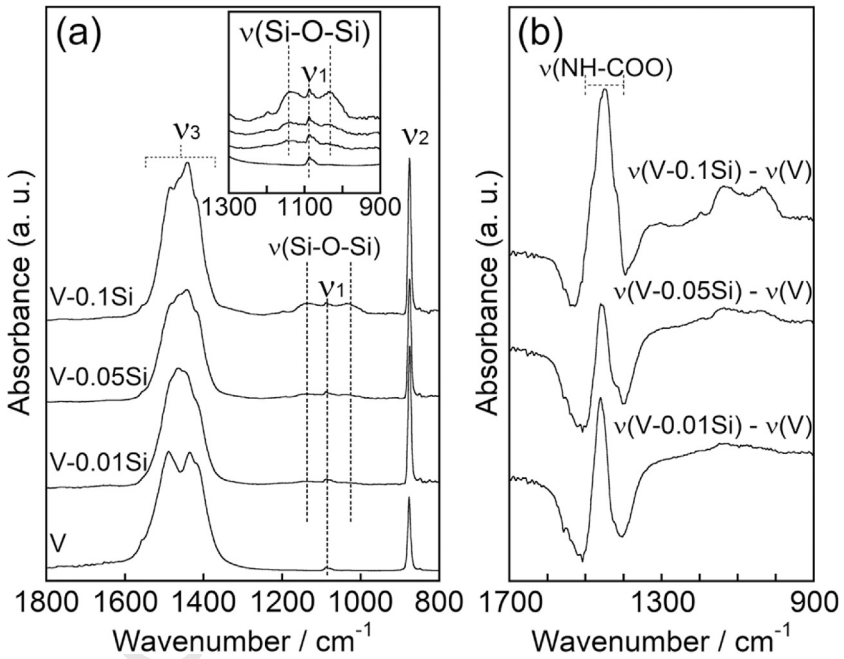

Fig. 2. (a) ATR-FTIR spectra of V and V–*x*Si particles, and (b) vaterite-subtracted differential infrared spectra of V–Si particles.

USA, reagent grade) was then added to the slurry, and the resulting APTMS concentration in the slurry was adjusted to 0.01–0.10 mol L^{-1}. The slurry was then placed in a water bath at 20 °C and stirred at 400 rpm using an overhead stirrer. Carbon dioxide gas was then introduced into the slurry at 2 L min^{-1} for 2 h, to give the opaque precursor gel. A portion of the gel (50 g) was added to methanol (450 mL) and the mixture was homogenised by ultrasonication for 10 min. This was followed by separation using centrifugation at 15,000 rpm for 10 min. Finally, the resulting solid was dried under vacuum and broken down with an agate mortar and pestle to form the desired particles. Hereafter, the samples will be referred to as V–*x*Si, where *x* represents the concentration (mmol L^{-1}) of APTMS in the precursor slurry. Pristine vaterite (V) particles were also prepared by omitting the addition of silane and the homogenization.

The elemental composition of each sample was estimated by dissolving the sample in hydrochloric acid and measuring the concentration by inductively coupled plasma optical emission spectrometry (Shimadzu, ICPS-7510: ICP-OES, n = 3). X-ray diffractometry (RIGAKU, SmartLab: XRD) and attenuated total reflectance

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