Chemical Engineering Journal 155 (2009) 580–585

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

# Sorption studies of $^{134}$Cs, $^{60}$Co and $^{152+154}$Eu on phosphoric acid activated silico-antimonate crystals in high acidic media

Ismail M. Ali*

*Nuclear Fuel Technology Department, Hot Labs. Centre, Atomic Energy Authority, P.C. 13759, Cairo, Egypt*

ARTICLE INFO

*Article history:*
Received 9 April 2009
Received in revised form 24 July 2009
Accepted 28 July 2009

*Keywords:*
Silico-antimonate
Phosphoric acid activation
Sorption kinetics

ABSTRACT

This work describes the sorption of $^{134}$Cs, $^{60}$Co and $^{152+154}$Eu by crystals of unmodified and phosphoric acid modified silico-antimonates (SiSb). Equilibrium and selectivity sequence for co-exiting metal ions under strongly acidic conditions of $HClO_4$, $H_2SO_4$, $HNO_3$ and HCl were investigated. The results showed that the silico-antimonate either in the high $Sb^{5+}$ content or in the phosphated form possesses acidic characters and shows cation-exchange properties more efficient in acidic media. Kinetic studies indicated that pseudo-second-order model gave better fitting parameters comparing to that of pseudo-first-order one. The thermodynamic parameters of the sorption processes revealed spontaneous and endothermic nature. High negativity of $\Delta G^\circ$ values for the modified SiSb confirms the positive role of phosphoric acid impregnation in the sorption process. The break-through capacities of the studied ions were further calculated from a column investigation.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

During the last few years, a wide application of inorganic ion exchangers in nuclear waste treatment has been investigated for fission and activation products elimination [1]. Most of the inorganic ion exchangers [2–4] such as lithium titanate, tin silicate, tin- and titanium-ferrocyanides, etc., exhibit very low ion exchange efficiency in the high acidic media. Considerable research has been carried out to study and develop acidic inorganic ion exchangers such as metal antimonates $M_xSb_yO_z{\cdot}wH_2O$ (M = Si, W, Ti, Mn, Sb) for the removal of $^{90}$Sr and other key radionuclides from nuclear waste effluents [5–7]. Ion exchange properties of titanium antimonate have been investigated to remove different radionuclides from acidic nuclear waste solutions and in the presence of strongly interfering calcium ions [8]. It was shown that the pyrochlore structure of antimonates could be tuned to the desired ion exchange selectivity by substituting various cations such as $W^{6+}$, $Nb^{5+}$ into the framework of the parent compound [9]. Recent investigations have shown that carbons obtained by phosphoric acid activation show not only developed porosity but also exhibit significant cation-exchange properties due to acidic surface groups [10]. This phenomenon received only occasional attention in the literature [11–13].

According to the literature, there are no studies describing the possible activation of antimonate surface with phosphoric acid. In this paper, an attempt has been tried to achieve reasonable separation and abstract the radionuclides of $^{134}$Cs, $^{60}$Co and $^{152+154}$Eu from strongly various acidic media. This aim can be achieved through preparing silico-antimonate with different Si/Sb ratios and after activation by phosphoric acid.

## 2. Materials and methods

All chemicals were of analytical grade and used without further purification. $^{134}$Cs and $^{152+154}$Eu isotopes were purchased from Amersham Life Science. $^{60}$Co was available by irradiating cobalt nitrate in the Egyptian Reactor Research 2 (ERR2).

### *2.1. Synthesis of silico-antimonates*

SiSb were prepared by dropwise addition of 0.2 M aqueous solutions of $Na_2SiO_3$ to 0.2 M solutions of Sb-metal (dissolved in aqua regia) in 1:1, 1:2 and 2:1 volume ratios. Gel precipitates were appeared immediately with constant stirring rate at 60 ± 2 °C. Part of the gel product which was obtained from the reactants volume ratio1:2 was treated with 100 ml of 3 M $H_3PO_4$ at 75 °C for one weak. All the reaction products were aged for about two weeks in their mother solutions, decanted, washed with bidistilled water, centrifuged and dried by gentle heating (60 °C). The products were cracked by hot water followed by washing with 0.1 M $HNO_3$ to be free from $Cl^-$ ions and rewashed with bidistilled water to remove nitrate ions. Finally, the solids were dried at 70 °C in a drying oven, ground, sieved to mesh size 0.225–0.425 mm and stored at room temperature.

---

* Tel.: +20 2 0105787044; fax: +20 2 0244620784.
*E-mail address:* ismail_m_ali@yahoo.com.

1385-8947/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.07.050

### 2.2. Characterization of the products

The chemical compositions of the solid samples of the obtained SiSb were analyzed using the following techniques. X-ray fluorescence (XRF) was carried out using Phillips X-ray fluorescence model PW 2400 spectrometer. Powder X-ray diffraction was performed using a Shimadzu X-ray diffractometer, XD 610, with a nickel filter and Cu Kα radiation (1.54 Å) operating at 30 kV and 30 mA. Thermal analysis was measured using a Shimadzu DT-60 thermal analyzer, Japan, at a heating rate of 15°/min under a nitrogen atmosphere. The FTIR spectra were acquired in transmission applying KBr disc with a Bomem FTIR spectrometer.

### 2.3. Equilibrium studies

The distribution coefficient values ($K_d$) for the studied ions were determined using batch experiments by shaking 0.1 g of SiSb of different forms with 5 ml of $10^{-4}$ M solution of $XCl_n$ ($X = Cs^+$, $Co^{2+}$ and $Eu^{3+}$ ions) traced with the respective radioisotope (s). After equilibration (6 h) in a thermostatic shaker water bath at 30, 45 and 60 °C, the mixtures were centrifuged then 1 ml was withdrawn for radiometric assay by measuring the activity level of gamma-rays. A multichannel Analyzer Genie-2000 spectroscopy system (HPGe well type detector) CANBERRA, Inc., USA was used. The distribution coefficients were calculated from the relation:

$$k_d\,(\text{ml/g}) = \frac{A_o - A_{eq}}{A_{eq}}\frac{V}{m} \qquad (1)$$

where $A_o$ and $A_{eq}$ are the activities of the tracer in solution before and after equilibrium, respectively, and $V/m$ is the solution volume to adsorbent mass ratio (batch factor, 50 ml/g).

### 2.4. Column study

Dynamic conditions were conducted to separate radionuclides from their mixture as the following: a column of 0.5 cm internal diameter was packed with 1 g of SiSb (1:2) particles; the bed length (h) of the column was 2 cm and bed volume 1 ml. 500 ml of $10^{-4}$ M of multi-metal ions preconditioned with 3 M of $HNO_3$ as representing case of the studied acidic media was used for column saturation. The effluent flow rate was adjusted to be 0.8 bed volume/min. The break-through capacities (mg/g) of the studied ions were measured and calculated from the equation:

$$\text{break-through capacity} = \frac{V_{50\%} Z C_o}{W} \qquad (2)$$

where $V_{50\%}$ is the volume at which the ion uptake is 50%, $Z$ is the charge of the ion, $C_o$ is the initial concentration of each element and $W$ is the weight of the column bed (g). Statistical analyses were counted using analysis of variance (ANOVA) procedure [14].

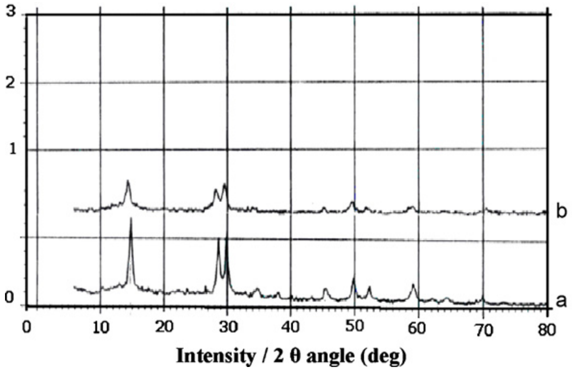

**Fig. 1.** XRD patterns of non-activated (a) and phosphoric acid activated (b) SiSb (1: 2).

## 3. Results and discussion

### 3.1. Structural and characterization of silico-antimonates

Conditions for the synthesis and elemental compositions of silico-antimonates are listed in Table 1. The IR, XRD and DTA-TG analyses were carried out to identify the physico-chemical properties of the materials. The FTIR spectra of SiSb (1:2) either that phosphoric acid activated or non-activated (Fig. not shown) indicate that the bands attributed to O–H bonding at 1642 and 3400 $cm^{-1}$ are the main peaks for all materials [7]. New spectral band at 1185 $cm^{-1}$ in the case of phosphoric acid activated SiSb was observed. This band is attributed to the phosphate group [8]. The presence of phosphate group was also quantitively confirmed from XRF measurements as given in Table 1.

The observed reflections and relative intensities in the XRD pattern of non-activated SiSb (1:2) (Fig. 1a) were consistent with cubic structure of antimony oxide [15]. However, material prepared at Si:Sb ratio of 1:2 then activated with phosphoric acid exhibited minor decrease for most peak intensities with no $2\theta$ changes (Fig. 1b). Accordingly, slightly distortion in the cubic structure seems to be occurred during the activation processing. Similar behavior was reported for most phosphate incorporated materials [16].

A simultaneous DTA/TG thermal analysis of silico-antimonate samples was carried out (curves not given). The data show that the dehydration reaction of SiSb (1:2) is appeared at two endothermic peaks (89 and 292 °C) which corresponding to a total water content of 10 mol. However, the dehydration reaction of phosphated SiSb (1:2) is appeared as two endothermic peaks at 94 and broad one at 300 °C with a total water content of 11 mol. Such behaviors may be indicating, higher thermal stability and water content of the activated silico-antimonate compared to the non-activated one. Therefore, in aqueous media it can be expected that the activated form of silico-antimonate has surface hydroxyl and phosphate groups which are more available to react with the positive metal ions.

**Table 1**
Synthesis and properties of silico-antimonates.

| Silico-antimonate[a] | 0.3 M Si:0.3 M Sb:3 M $H_3PO_4$ reactants volume, ml | Si/Sb mole ratio in product | Color | XRD | % Water content |
|---|---|---|---|---|---|
| SiSb(2:1) | 200:100:– | 0.41 | White | Crystalline | 19.50 |
| SiSb(1:1) | 100:100:– | 0.37 | White | Crystalline | 19.00 |
| SiSb(1:2) | 100:200:– | 0.29 | White | Crystalline | 19.20 |
| SiSb(1:2)/$H_3PO_4$ | 100:200:100 | 0.20 | White | Crystalline | 20.00 |

[a] Empirical formula of silico-antimonates by XRF (using oxides list); SiSb (2:1) $(Na_2O)_{0.3}(SiO_2)_{1.9}(Sb_2O_3)_{2.3}\cdot 11H_2O$; SiSb (1:1) $(Na_2O)_{0.3}(SiO_2)_{2.6}(Sb_2O_3)_{3.5}\cdot 15H_2O$; SiSb (1:2) $(Na_2O)_{0.3}(SiO_2)_{1.4}(Sb_2O_3)_{2.4}\cdot 10H_2O$; SiSb (1:2)/$H_3PO_4$ $(Na_2O)_{0.3}(SiO_2)_{1.0}(Sb_2O_3)_{2.4}(P_2O_5)_{0.15}\cdot 11H_2O$.

Download English Version:

https://daneshyari.com/en/article/151869

Download Persian Version:

https://daneshyari.com/article/151869

Daneshyari.com