

## Removal Of Radiocobalt From Edta-Complexes Using Titanium Antimonate Sorbents

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### ABSTRACT

Two titanium antimonate materials were tested for the removal of radiocobalt from a solution containing complexing agent EDTA to simulate a nuclear power plant decontamination solution. The first material had a mixture of pyrochlore and rutile structures and it showed high removal (91 %) of radiocobalt was removed in the presence of EDTA. The second material, which had a mopungite structure, showed even higher (97 %) removal of radiocobalt. In addition, both materials had a very high radiocobalt uptake (> 99 %) in acidic solution when EDTA was absent. Results indicate that the titanium antimonate (TiSb) materials are highly promising for radiocobalt removal from nuclear decontamination solutions.

### INTRODUCTION

Complexing organic acids, e.g. ethylenediaminetetraacetic acid (EDTA) and oxalic acid are used regularly in nuclear sites to decontaminate facilities from of radionuclides, in order to decrease build-up of radioactivity and radiation dose to plant personnel. Due to its relatively long half life and strong gamma decay energy,  $^{60}\text{Co}$  is one of the major nuclides of interest for decontamination. Cation exchange resins are normally used at NPP's to remove  $^{60}\text{Co}$  from the primary circuit and other water streams but this method is not effective for  $^{60}\text{Co}$  complexed with EDTA. Highly selective inorganic ion exchange materials [1,2] have emerged recently for the removal of  $^{60}\text{Co}$  in nuclear industry but even these are rather ineffective to remove  $^{60}\text{Co}$  from the EDTA complex.

Titanium antimonate materials have been previously developed for the removal of ionic  $^{60}\text{Co}$  from acidic solutions [3] and it has been shown that the acidity of the titanium antimonate material can be increased by enhancing the amount of pentavalent antimony in the material, improving metal ion uptake in acidic solutions [4,5]. Very recently, these materials have been found effective for the removal of  $^{60}\text{Co}$  from EDTA and oxalate solutions [6]. This paper summarizes the key results of these earlier studies. Such summary should be useful and timely, considering that decommissioning and decontamination operations of nuclear facilities are increasing strongly in the near future.

### MATERIALS AND METHODS

Titanium antimonate materials were synthesized either under acidic conditions (TiSbA) or basic conditions (TiSbB) as described earlier [6]. The elemental composition of the materials (Table I) were determined by EDX (energy-dispersive X-ray spectroscopy) with Oxford INCA 350 microanalysis system connected to a Hitachi S-4800 field emission scanning electron microscope (FESEM) [6]. The crystal structures of materials were determined from the X-ray diffraction (XRD) patterns recorded with a Panalytical X'pert Pro MPD X-ray diffraction system. TiSbA was found to be a mixture of pyrochlore and rutile  $\text{TiO}_2$  structures while the TiSbB structure resembled that of mopungite [6].

Table I. Elemental composition of titanium antimonate materials

Element	% TiSbA	% TiSbB
O	73	71
Cl	3	0
Ti	12	5
Sb	12	14
Na	0	10

The sorption properties of the materials were studied using test solutions of 0.01 M NaNO<sub>3</sub> or Milli-Q water dosed with Co<sup>2+</sup> and EDTA concentrations varying between 0.2 µM and 200 µM. 20 mg of samples of sorbent materials were equilibrated with 10 ml of test solution for 1 or 4 days. Test solution pH was adjusted with varying amounts of HNO<sub>3</sub> or NaOH as necessary. The sorbent was removed from the solution by centrifugation (10 minutes at 3000 G). The solution was filtered with a 0.2 µm Acrodisc filter (PALL Life Sciences) and its equilibrium pH was measured with an Orion 3 star pH meter. Aliquots (5 ml) of solution were counted for <sup>57</sup>Co with an automatic gamma counter (Wallac 1480 Wizard™ 3).

The distribution coefficient ( $K_D$ ) was used to measure the distribution of <sup>57</sup>Co between the solution and the solid material at equilibrium, i.e.

$$K_D = \frac{C_s}{C_l} \quad (\text{Eq. 1})$$

where  $C_s$  (Bq/kg) and  $C_l$  (Bq/L) are the activity concentrations of <sup>57</sup>Co in the solid and solution respectively. Thus  $K_D$  can be used to estimate the processing capacity (L/kg) of the sorbent material under the prevailing conditions. It was calculated for <sup>57</sup>Co using equation (2):

$$K_D = \frac{(A_0 - A_{eq})}{A_{eq}} \times \frac{V}{m} \quad (\text{Eq. 2})$$

where  $A_0$  is the initial count rate of <sup>57</sup>Co in the solution,  $A_{eq}$  is the count rate of <sup>57</sup>Co at equilibrium and  $V/m$  is the solution volume to sorbent mass ratio (batch factor, ml g<sup>-1</sup>).

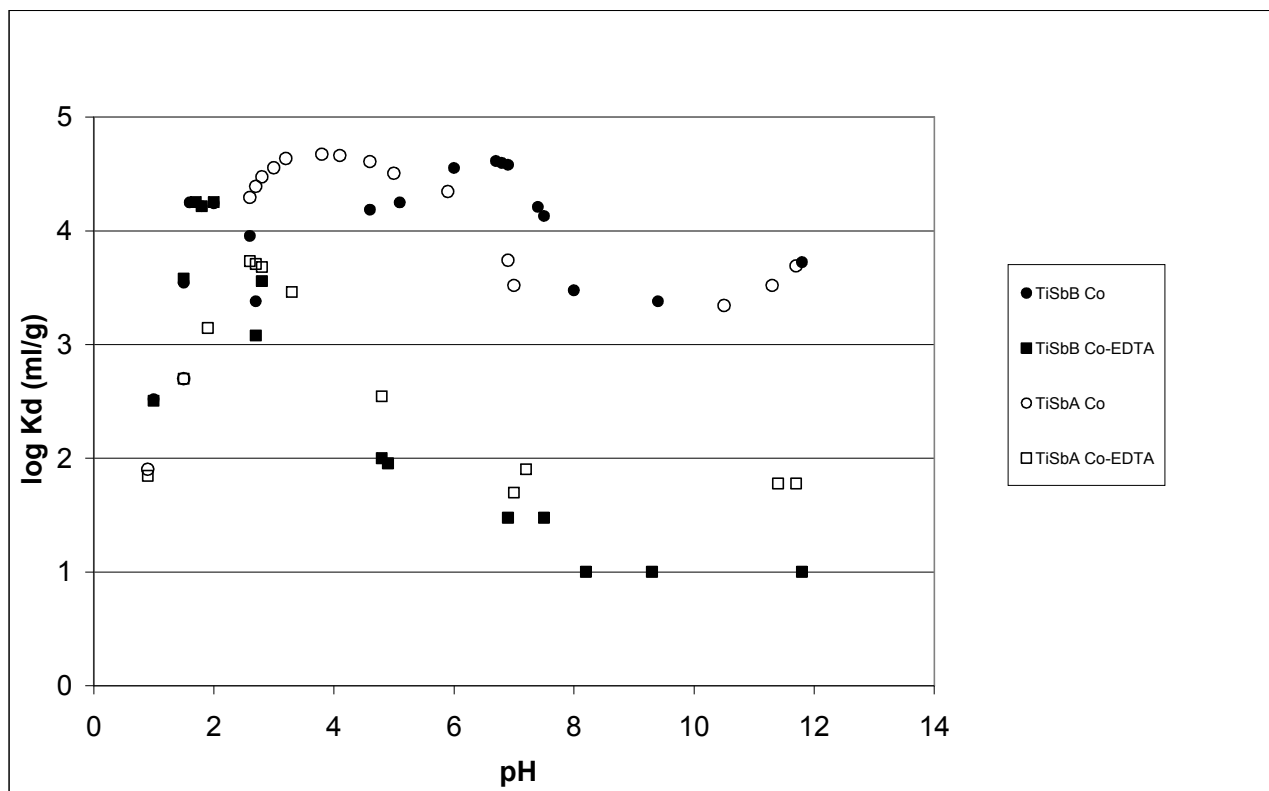


Fig.1. Uptake of  $^{57}\text{Co}$  from 10  $\mu\text{m}$  Co (Circles) Co-EDTA (squares)solutions in 0.01  $\text{NaNO}_3$  by TiSbA (open symbols) and TiSbB (filled symbols) as a function of solution pH

The sorption maximum of ionic cobalt in 0.01 M  $\text{NaNO}_3$  solution for TiSbA was located at pH 4 ( $K_D = 47000 \text{ mL/g}$ ) and for TiSbB at pH 7 ( $K_D = 38000 \text{ mL/g}$ )(Fig. 1). Thus acidic synthesis conditions led to better sorption properties at low pH values, whereas basic synthesis conditions led to a sorption maximum at higher pH.

When cobalt was complexed with EDTA, a drop in the  $K_D$  values could be seen compared to those obtained for ionic cobalt (Fig. 1). For TiSbA the maximum uptake for  $^{57}\text{Co}$  ( $K_D = 5400 \text{ mL/g}$ ) was at pH 2.6. For TiSbB, the uptake of  $^{57}\text{Co}$  was clearly higher ( $K_D = 18000 \text{ mL/g}$ ) and had the maximum at a somewhat lower pH (pH  $\approx 2$ ).

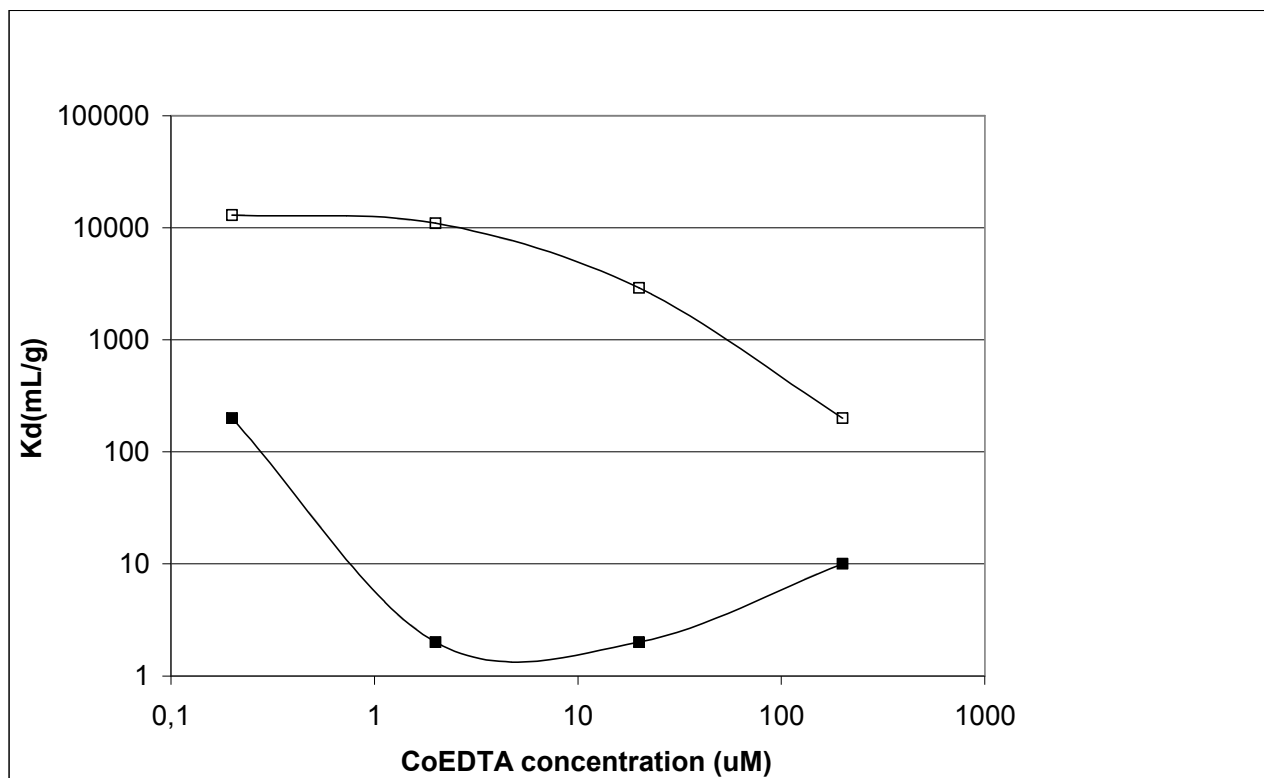


Fig. 2. Uptake of  $^{57}\text{Co}$  from Co-EDTA solutions of different concentration by TiSbA (open symbols) and TiSbB (filled symbols).

Further test were carried out to test the effect of Co-EDTA concentration on  $^{57}\text{Co}$  uptake (Fig. 2). For TiSbA, the uptake of  $^{57}\text{Co}$  was high ( $K_d < 10000 \text{ mL/g}$ ) when Co-EDTA concentration was less than 1  $\mu\text{mol/L}$  and  $K_d$  fell below 1000  $\text{mL/g}$  as the concentration approached 100  $\mu\text{mol/L}$ . Quite clearly, TiSbA is efficient for the removal of Co-EDTA at trace concentrations that typically prevail in radioactive decontamination solutions. Uptake of  $^{57}\text{Co}$  from Co-EDTA for TiSbB was much lower than for TiSbA. Mainly this is due to the native pH of the solutions. TiSbA produced a slightly acidic solution ( $\text{pH} \approx 3$ ) where the uptake of Co and Co-EDTA is high (see Fig. 1). In case of TiSbB, the native pH of solution was about 10 where the uptake conditions are highly favorable.

## CONCLUSIONS

Promising results were obtained with the two synthesized titanium antimonate (TiSb) materials for radiocobalt removal from various solutions simulating nuclear decontamination solutions. Sorption levels of cobalt were more than 99 % in the presence of only ionic  $\text{Co}^{2+}$ , and over 91-97 % in the presence of Co-EDTA complex for both materials.

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