

## Structural Study and Thermodynamics of the Fixation of Strontium on Polyantimonic Acid

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The mechanism of strontium fixation on hydrated antimony pentoxide (*Fd3m* space group) has been specified from thermodynamical interpretation of sorption isotherms and crystal structure. When the ionic fraction increases in the solid, two types of protons (protons in  $\text{H}_3\text{O}^+$  groups and protons bonded to framework oxygen) are successively exchanged. In acid media ( $\text{pH} < 3$ ) the uptake of  $\text{Sr}^{2+}$  is limited to 0.31 mole/mole, and  $\text{Sr}^{2+}$  is exclusively located in S(I) sites ( $x = y = z \sim 0.5$ ). In more basic media ( $\text{pH} > 3$ ),  $\text{Sr}^{2+}$  is retained in S(I) as long as the concentration in the solid is less than 0.31 mole/mole. Beyond this value S(II) sites ( $x = y = z = 0.300$ ) are occupied up to a total capacity of 1 mole/mole. Thermodynamical data were calculated for each of these exchange steps. © 1992 Academic Press, Inc.

### Introduction

Radioactive strontium is one of the major fission products in nuclear wastes after a cooling time of some years. It seems attractive to separate it from primary wastes in a way suitable for further storage in safe conditions. Fixation on an inorganic exchanger having a high affinity for strontium could be a promising way of separation. Among possible exchangers, hydrated antimony pentoxide (HAP) has already been pointed out as a potential product for the fixation of strontium (1-7). Many papers have been published on the synthesis, properties, and applications of HAP as well as on the kinetic and thermodynamic studies of cation exchange.

Depending on the preparative conditions, HAP may be amorphous, glassy, or crystalline (3, 8). Crystalline antimony acid may present a layered structure derived from the ilmenite type or two cubic forms; one has a  $\text{KSbO}_3$  type structure; the other is the pyrochlore form (*Fd3m*). A monoclinic form has also been described (9).

The water content depends on the preparation process and the formula of the pyrochlore form could be represented as  $\text{Sb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ , where  $n = 3$  to 4 (8). Three types of water molecules have been detected: water needed for the hydration of protons to  $\text{H}_3\text{O}^+$ , constitution water, and water weakly bound to the lattice (10, 11). For Baetsle and Huys (2), the four  $\text{H}_2\text{O}$  molecules which are associated with one  $\text{Sb}_2\text{O}_5$  group are constituents of the crystal structure. However, we have found

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in many papers that the composition of HAP corresponds to  $\text{Sb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  with  $n < 4$  (11–13).

Some authors have tried to correlate the ion-exchange properties and the structural features of HAP (2, 14). Concerning the exchange sites, there is a discrepancy between the results found in the literature (15–19).

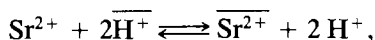
About the kinetics, it has been shown that the fixation of strontium on the pyrochlore form can be divided into two stages: a fast step related to a superficial fixation and a slow kinetics related to the diffusion in the tridimensional lattice (7).

Isotherms of the exchange of various metal ions with hydrogen ions have been studied on crystalline antimonite acid ( $\text{Sb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ) (2, 6, 20, 21). Generally, isotherms and Kielland plots were calculated using the theoretical capacity in spite of the discrepancy in the experimental capacity values. We have shown that the theoretical capacity of HAP is achieved only in basic medium (7).

In the present work we have tried to characterize more accurately the mechanism of strontium fixation on hydrated antimony pentoxide. For that purpose, we have determined the crystal structures of HAP (pyrochlore form) before and after strontium fixation, in connection with a thermodynamical interpretation of the sorption isotherms, using the real capacity values.

### Thermodynamics

The ion-exchange process can be represented by the equilibrium



where the symbols with overbars refer to the solid phase, and the symbols without overbars refer to the aqueous phase. The thermodynamic equilibrium constant is given by

$$K = K_c \frac{f_{\text{Sr}}}{f_{\text{H}}^2}, \quad (1)$$

where  $K_c$ , the corrected selectivity coefficient, equals

$$K_c = \frac{|\text{H}^+|^2 X_{\text{Sr}} \gamma_{\text{H}}^2}{|\text{Sr}^{2+}| X_{\text{H}}^2 \gamma_{\text{Sr}}}, \quad (2)$$

$|\text{H}^+|$  and  $|\text{Sr}^{2+}|$  are the molalities of the cations in the equilibrium solution,  $X_{\text{H}}$  and  $X_{\text{Sr}}$  are the equivalent fractions of  $\text{H}^+$  and  $\text{Sr}^{2+}$  in the solid phase, and  $\gamma_{\text{H}}$ ,  $\gamma_{\text{Sr}}$ , and  $f_{\text{H}}$ ,  $f_{\text{Sr}}$  are the ionic activity coefficients in the liquid and in the solid phases, respectively.

The values of the ionic activity coefficient ratio in solution are calculated from the Debye–Hückel equation for dilute solutions,

$$\log \frac{\gamma_{\text{H}}^2}{\gamma_{\text{Sr}}} = \frac{2S\sqrt{I}}{1 + 1.5\sqrt{I}}, \quad (3)$$

where

$$S = 1.8252 \times 10^6 \left( \frac{\rho}{\varepsilon^2 T^3} \right), \quad (4)$$

$\rho$  is the density of water,  $\varepsilon$  is the dielectric constant of water,  $T$  is the absolute temperature of the system, and  $I$  is the ionic strength of the solution.

The thermodynamic equilibrium constant can be evaluated by using a simplified form of the Gaines–Thomas equation (22), assuming that the water content in the different ionic forms of the exchanger is almost the same,

$$\ln K = (Z_{\text{H}} - Z_{\text{Sr}}) + \int_{X_{\text{Sr}}=0}^{X_{\text{Sr}}=1} \ln K_c dX_{\text{Sr}}, \quad (5)$$

where  $Z_{\text{H}}$  and  $Z_{\text{Sr}}$  are the valencies of the ions.

The activity coefficients  $f_{\text{Sr}}$  and  $f_{\text{H}}$  are then given by

$$\ln f_{\text{Sr}} = (X_{\text{Sr}} - 1) - (1 - X_{\text{Sr}}) \ln K_c - \int_1^{X_{\text{Sr}}} \ln K_c dX_{\text{Sr}} \quad (6)$$

$$\ln f_{\text{H}}^2 = X_{\text{Sr}}(1 + \ln K_{\text{c}}) - \int_0^{X_{\text{Sr}}} \ln K_{\text{c}} dX_{\text{Sr}} \quad (7)$$

The standard free energy is

$$\Delta G^\circ = -\frac{RT}{Z_{\text{Sr}}Z_{\text{H}}} \ln K \quad (8)$$

The standard enthalpy  $\Delta H^\circ$  will remain constant over the range of temperature studied.

The standard enthalpy is given by the Gibbs–Helmoltz relation:

$$\frac{\partial}{\partial T} \left( \frac{\Delta G^\circ}{T} \right) = -\frac{\Delta H^\circ}{T} \quad (9)$$

The standard entropy  $\Delta S^\circ$  is

$$\Delta S^\circ = \frac{(\Delta H^\circ - \Delta G^\circ)}{T} \quad (10)$$

## Experimental

### Materials

We have used HAP produced by Carlo Erba (Milan, Italy). Analyses performed by nuclear activation and thermogravimetric analysis lead to a  $\text{Sb}_2\text{O}_5 \cdot 2.54 \pm 0.02 \text{H}_2\text{O}$  composition. Characterization by X-ray diffraction shows that the sample is highly crystalline. Electron microscopy shows small crystals ( $< 0.2 \mu\text{m}$ ) aggregated in particles ( $1 \mu\text{m}$ ).

### X-Ray Procedures

The crystal structures were determined from the diffraction line intensities collected on a Philips step-scan diffractometer fitted with a curved monochromator in the diffracted beam, a pulse-height analyzer, and a scintillation counter.  $\text{CoK}\alpha$  has been used with a scanning step of  $0.05^\circ 2\theta$  in the range  $15^\circ < 2\theta < 140^\circ$ .

The reliability factor

$$R = \frac{\sum |F_0 - KF_c|}{\sum |F_0|}$$

where  $K$  is the scale factor and  $F_0$  and  $F_c$  are the observed and calculated structure factors, was obtained after least-squares refinement of the crystallographic parameters (AFFINE program) (23). The structures were resolved from reflexions  $h k l$  such that  $h^2 + k^2 + l^2 < 108$ . Due to the limited set of available data, all the temperature factors of the atoms were not allowed to vary during the least-squares refinements. Interatomic distances were computed with the ORFFE program (24).

### Retention Capacity and Fixation Equilibria

Radioactive  $^{85}\text{Sr}$  was obtained by irradiating strontium nitrate in the neutron flux of a nuclear reactor using the facilities of the Pierre Sue Laboratory of Saclay. A known amount of sorbent was shaken with a solution containing the radioactive tracer. After a shaking time of 12 days the solid was separated from the solution by filtration. The quantity of element sorbed in the solid was determined by measuring the radioactivity of an aliquot of the solution.

The fixation equilibrium and capacity of retention were determined by varying the quantity of nonradioactive strontium introduced in the solution. A series of experiments was performed in nitric acid solutions, the pH ranging from 1 to 8.6 after equilibrium. Another series was performed by adding strontium hydroxyde, the pH ranging from 3 to 12.

## Results

### X-Ray Study

The HAP we have studied has a pyrochlore-type structure (space group  $Fd3m$ ) (25). The framework structure is well known: the octahedral anions ( $\text{O}^{2-}$ ) are in  $48f$  positions and the octahedral cations ( $\text{Sb}^{5+}$ ) in  $16c$  positions (26, 27). The pyrochlore unit skeleton consists of corner-shar-

TABLE I  
COMPOSITION OF INITIAL AND Sr<sup>2+</sup>-EXCHANGED POLYANTIMONIC ACID SAMPLES USED FOR THE CRYSTALLOGRAPHIC STUDIES

Samples	Composition per Sb <sub>2</sub> O <sub>6</sub>	Composition per unit cell	pH <sup>a</sup>
1 (Initial sample)	H <sub>2</sub> Sb <sub>2</sub> O <sub>6</sub> · 1.5H <sub>2</sub> O	H <sub>16</sub> Sb <sub>16</sub> O <sub>48</sub> · 12H <sub>2</sub> O	—
2 (Partial exchange)	Sr <sub>0.31</sub> H <sub>1.4</sub> Sb <sub>2</sub> O <sub>6</sub> · 1.1H <sub>2</sub> O	Sr <sub>2.4</sub> H <sub>11.2</sub> Sb <sub>16</sub> O <sub>48</sub> · 8.8H <sub>2</sub> O	1
3 (Partial exchange)	Sr <sub>0.275</sub> H <sub>1.45</sub> Sb <sub>2</sub> O <sub>6</sub> · 1.5H <sub>2</sub> O	Sr <sub>2.2</sub> H <sub>11.6</sub> Sb <sub>16</sub> O <sub>48</sub> · 12H <sub>2</sub> O	3.5
4 (Total exchange)	SrS <sub>2</sub> O <sub>6</sub> · 2.5H <sub>2</sub> O	Sr <sub>8</sub> Sb <sub>16</sub> O <sub>48</sub> · 20H <sub>2</sub> O	11.8

<sup>a</sup> pH of the solution at equilibrium.

ing (SbO<sub>6/2</sub>)<sup>-</sup> octahedra carrying an excess of negative charge (28). HAP has an open lattice structure: in the elementary cell we find eight cavities, each one connected to the neighboring cavities by four hexagonal windows (3 Å in diameter). The negative charge of the framework is compensated by the exchangeable cations. In order to know the localization and population of these cations we have determined the crystal structure before and after introduction of Sr<sup>2+</sup> cations. Table I reports the more important characteristics of the samples studied. The main crystallographic parameters, including the reliability factors *R*, are given in Table II. Interatomic distances and angles are reported in Table III.

Nonframework electron density was found in two sites we have called S(I) and S(II) located in 32*e*. S(I) is very near the center of the hexagonal windows. We must point out that structure analysis gives only the electron density; two cations of a different nature located in the same site cannot be distinguished from each other. Assigning these sites to H<sub>3</sub>O<sup>+</sup> or Sr<sup>2+</sup> was based on the chemical analysis (Table I), but remains quite arbitrary when both cations occupy the same site. Thus, S(I) sites have been attributed nonambiguously to H<sub>2</sub>O or H<sub>3</sub>O<sup>+</sup> before the exchange process (sample 1). Taking into account the error

intervals, the found populations (Table II) agree with the thermogravimetric analysis (Table I). After the strontium fixation, sites S(I) and S(II) have been attributed in the refinement to Sr<sup>2+</sup> cations which have the highest electron density. We notice that the Sr<sup>2+</sup> population exceeds the values found in the exchange experiment, because H<sub>2</sub>O or H<sub>3</sub>O<sup>+</sup> is also located in the S(I) sites. As we have never found water in S(II) sites, we supposed that the population of Sr<sup>2+</sup> in the S(II) sites of sample 4 is the real concentration of this element in this site.

Table IV summarizes the cation distribution. In acid media (sample 2), Sr<sup>2+</sup> cations are all located in S(I) sites while in more basic media (samples 3 and 4) only the first introduced Sr<sup>2+</sup> cations are located in S(I) sites as long as the strontium population of these sites does not exceed 2.8 Sr<sup>2+</sup> per unit cell (sample 4). Beyond this value, S(II) sites are also occupied.

The calculated interatomic distances are reported in Table III. The strontium ionic radius being 1.32 Å, two Sr<sup>2+</sup> ions cannot be located in two S(I) sites adjacent to the same window (S(I)–S(I) = 0.71 Å) as in two S(II) sites of the same cavity (S(II)–S(II) = 2.19 Å). Sr<sup>2+</sup> ions can occupy S(I) and S(II) sites in the same cavity with S(I)–S(II) = 3.22 Å.

TABLE II  
CRYSTALLOGRAPHIC DATA FOR INITIAL AND EXCHANGED SAMPLES

Sites		Sample 1	Sample 2	Sample 3	Sample 4
Sb					
(16c)	$X = Y = Z$	0	0	0	0
	$P$	16	16	16	16
	OF	1	1	1	1
	$B$	0.9(2) <sup>a</sup>	1.0(3)	0.5(1)	2.0
O					
(48f)	$X$	0.339(7)	0.337(7)	0.336(5)	0.322(6)
	$Y = Z$	0.125	0.125	0.125	0.125
	$P$	48	48	48	48
	OF	1	1	1	1
	$B$	2.0	2.0	1.0(9)	1.9(7)
O <sup>b</sup> (I)					
(32e)	$X = Y = Z$	0.54(1)			
	$P$	14(5)			
	OF	0.44			
	$B$	2.0			
Sr(I)					
(32e)	$X = Y = Z$		0.509(7)	0.483(5)	0.520(5)
	$P$		4.8(5)	5.6(5)	5.95(8)
	OF		0.15	0.17	0.18
	$B$		2.0	2.0(9)	2.0
Sr(II)					
(32e)	$X = Y = Z$				0.300(6)
	$P$				5.2(4)
	OF				0.16
	$B$				1.9(9)
$R$		0.91	0.82	0.84	0.89
$a$		10.35(1)	10.34(1)	10.34(1)	10.34(1)

<sup>a</sup> Standard deviation on the last digit.

<sup>b</sup> H<sub>2</sub>O or H<sub>3</sub>O<sup>+</sup>.

Note. Atomic coordinates,  $X$ ,  $Y$ ,  $Z$ ; population,  $P$ ; occupancy factors, OF; temperature factors,  $B$  (Å<sup>2</sup>); Reliability factor,  $R$ ; and unit cell parameter,  $a$  (Å).

It is interesting to observe that whatever the Sr<sup>2+</sup> exchange rate is, there is no variation of the unit cell parameter. However, the framework of the octahedra is fairly modified. We notice (Table III) a decrease of the Sb–O distance in the totally exchanged sample 4 compared to the unexchanged or partially exchanged samples.

#### Fixation Capacity

The thermodynamical treatment of the exchange equilibrium needs an accurate determination of the fixation capacity which is the basis for the calculation of the ionic

fraction in the solid. According to Baetsle (2) and Konecny (6), the theoretical capacity of 1 mole of strontium per mole of Sb<sub>2</sub>O<sub>5</sub> can be achieved. Our experiments (7) showed that this capacity is observed only at high pH. At low pH (pH < 3), even for the highest strontium concentrations in solution, a limit of only 0.31 mole/mole is achieved. Gill and Tandon (29) have also observed a maximum uptake far from the theoretical capacity at low pH. It seems therefore that, depending on the pH range, two distinct values of the capacity are to be considered.

TABLE III  
CRYSTALLOGRAPHIC DATA FOR INITIAL AND EXCHANGED HAP

	Sample 1	Sample 2	Sample 3	Sample 4
Sb-(6)O	2.05(3)	2.03(2)	2.03(2)	1.97(2)
O-(8)O	2.64(2)	2.65(2)	2.65(2)	2.70(2)
O-(4)O	3.13(7)	3.08(6)	3.08(4)	2.88(6)
S(I)-(3)O	2.42(9)	2.45(5)	2.45(6)	2.55(7)
S(I)-(3)O	2.70(9)	2.56(5)	2.57(6)	2.67(6)
S(II)-(3)O				2.57(7)
S(II)-(3)O				4.62(8)
S(I)-(1)S(I)	1.4 (2)	0.3 (1)	0.6 (1)	0.71(9)
S(I)-(3)S(I)	2.5 (2)	3.4 (1)	3.15(7)	3.07(9)
S(I)-(3)S(I)	3.75(4)	3.66(1)	3.67(1)	3.68(5)
S(II)-(3)S(II)				2.19(9)
S(II)-(6)S(II)				3.79(4)
S(II)-(3)S(II)				4.38(9)
S(I)-(3)S(II)				1.91(8)
S(I)-(3)S(II)				2.49(5)
S(I)-(1)S(II)				3.22(6)
S(I)-(1)S(II)				3.94(6)
O-Sb-O	99(1)	99(1)	99(1)	94(1)
O-Sb-O	80(1)	81(1)	81(1)	86(1)
O-O-O	53(1)	54(1)	54(1)	58(1)
O-O-O	72(1)	72(1)	71(1)	64(1)

Note. Interatomic distances (Å) and bond angles (°).

### Thermodynamical Treatment of the Exchange Equilibrium

According to the preceding considerations, we have calculated the variation of the logarithm of the corrected selectivity coefficient  $K_c$  in two steps. In the first step, when the concentration  $C_{Sr}$  in the solid does not exceed the reduced capacity achieved

at low pH, the ionic fraction  $X_{Sr}$  varies from 0 to 1, while  $C_{Sr}$  varies from 0 to 0.31 mole/mole. In the second step,  $X_{Sr}$  varies from 0 to 1 while  $C_{Sr}$  varies from 0.31 to 1 mole/mole. For comparison, we have also calculated  $\ln K_c$  in the whole domain of exchange,  $X_{Sr}$  varying from 0 to 1 while  $C_{Sr}$  varies from 0 to 1 mole/mole (Fig. 1).

In the first step we observe a straight horizontal line, while the second step is characterized by a linear decrease of  $\ln K_c$ . When  $\ln K_c$  is calculated in the whole domain of 0 to 1 mole/mole, we observe a nonlinear variation.

Thermogravimetric analysis showed that water concentrations in the solid are similar before and after strontium fixation. So we have applied the simplified Eq. (5) in calculating the equilibrium constant  $K$ . The thermodynamic parameters derived from the ex-

TABLE IV  
CATION DISTRIBUTION BEFORE AND AFTER  
STRONTIUM FIXATION IN HAP

Sites	S(I)	S(II)
Sample 1	14(5) H <sub>2</sub> O or H <sub>3</sub> O <sup>+</sup>	—
Sample 2	2.4 Sr <sup>2+</sup> + 11(2) H <sub>2</sub> O or H <sub>3</sub> O <sup>+</sup>	—
Sample 3	2.2 Sr <sup>2+</sup> + 14(3) H <sub>2</sub> O or H <sub>3</sub> O <sup>+</sup>	—
Sample 4	2.8(4)Sr <sup>2+</sup> + 12(3) H <sub>2</sub> O	5.2(4) Sr <sup>2+</sup>

Note. Population per unit cell deduced from crystallographic and chemical analysis.

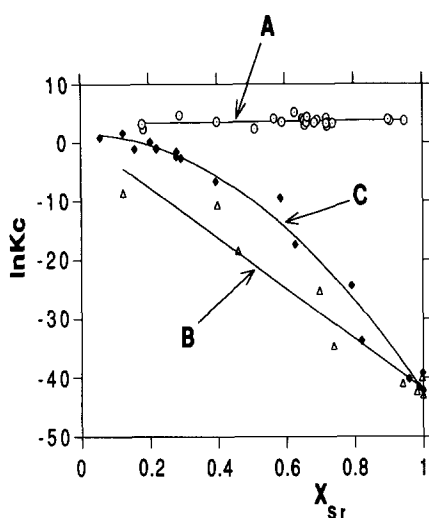


FIG. 1. Variation of the logarithm of the selectivity coefficient  $K_c$  of the  $\text{Sr}^{2+}/\text{H}^+$  exchange in HAP as a function of the ionic fraction  $X_{\text{Sr}}$  in the solid. (A)  $X_{\text{Sr}}$  variation of 0–1 for  $C_{\text{Sr}}$  variation in the solid of 0–0.31 mole/mole  $\text{Sb}_2\text{O}_5$ . (B)  $X_{\text{Sr}}$  variation of 0–1 for  $C_{\text{Sr}}$  variation of 0.31–1 mole/mole. (C)  $X_{\text{Sr}}$  variation of 0–1 for  $C_{\text{Sr}}$  variation of 0–1 mole/mole.

perimental data are given in Table V. These values will be discussed later. Figures 2a and 2b show the variation of the activity coefficients  $f$  of  $\text{H}^+$  and  $\text{Sr}^{2+}$  ions in the exchanger as a function of the exchange rate, calculated from Eqs. (6) and (7).

## Discussion

Structural considerations clearly indicate that  $\text{Sr}^{2+}$  ions occupy successively two

types of crystallographic sites as the ionic fraction increases in the solid. This result is in complete accordance with the values of the two observed exchange capacities and with the two types of selectivity coefficient variations. The nature of the exchanged protons of the polyantimonic acid may be deduced from the pH dependency of the exchange capacity and the presence of two types of protons in the solid: protons in  $\text{H}_3\text{O}^+$  groups and protons bonded to oxygen atoms belonging to the framework as it was shown by the IR adsorption spectra (16, 30). We can now propose a mechanism of fixation including two steps. In the first step, strontium ions are exchanged with the protons of the  $\text{H}_3\text{O}^+$  groups located near the center of the hexagonal windows. In acid solutions ( $\text{pH} < 3$ ) only this type of proton is exchanged and the uptake of  $\text{Sr}^{2+}$  is limited to 0.31 mole/mole, corresponding to 2.8  $\text{Sr}^{2+}$  per unit cell, which is also the maximum population of the S(I) sites in the studied solid (Table IV, sample 2). In more basic solutions ( $\text{pH} > 3$ ) strontium is also retained in these sites as long as the concentration in the solid is less than 0.31 mole/mole. In this first step,  $K_c$  values remain constant, indicating very reduced steric effects and weak interaction between occupied adjacent sites (Fig. 1). In fact, assuming that cations are statistically distributed in the crystallographic sites, only every two cages will be occupied by  $\text{Sr}^{2+}$ . The shortest distance between two occupied S(I) sites is then large ( $\text{S(I)}-\text{S(I)} = 6.1 \text{ \AA}$ ). In this first step, we can notice the high affinity of polyantimonic acid for  $\text{Sr}^{2+}$  ( $\Delta G^\circ < 0$ ). The reaction is endothermic and the positive value of  $\Delta S^\circ$  suggests that the degree of freedom of the metal ion increases most likely by dehydration of  $\text{Sr}^{2+}$  during its transfer from the aqueous phase to the solid phase and because of the high number of vacant sites.

In the second step,  $\text{Sr}^{2+}$  is exchanged with the protons of the OH groups of the framework. The exchange of these protons occurs

TABLE V  
THERMODYNAMIC CONSTANTS OF  $\text{Sr}^{2+}/\text{H}^+$   
EXCHANGE ON HAP

Thermodynamic constants	1 < pH < 2.6		3 < pH < 12
	60°C	22°C	22°C
$K^\circ$ (mole kg <sup>-1</sup> )	$8.7 \times 10^3$	12	$3.6 \times 10^{-11}$
$\Delta G^\circ$ (kcal mole <sup>-1</sup> )	-3.0	-0.72	7.1
$\Delta H^\circ$ (kcal mole <sup>-1</sup> )	19		—
$\Delta S^\circ$ (kcal mole <sup>-1</sup> K <sup>-1</sup> )	0.066	0.066	—

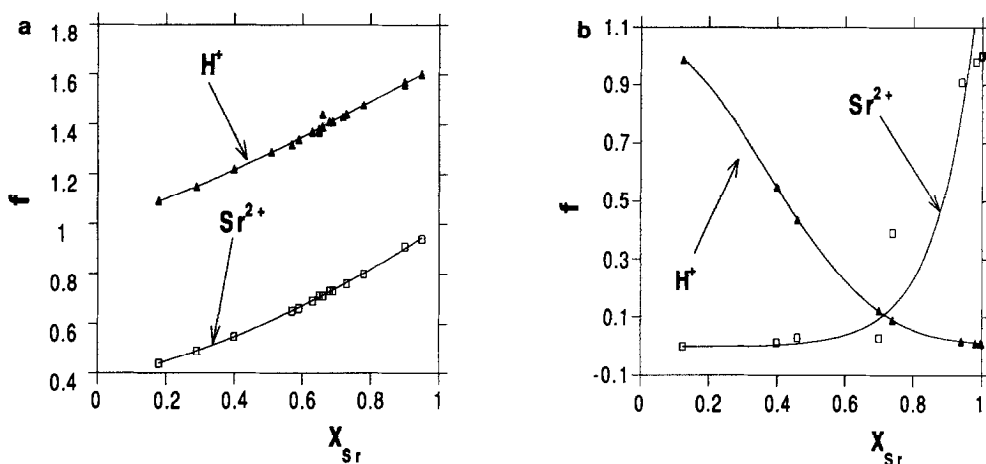
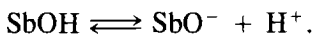


FIG. 2. (a) Variation of the activity coefficient  $f$  of  $Sr^{2+}$  and  $H^+$  as a function of ionic fraction  $X_{Sr}$  for  $C_{Sr}$  concentration in the solid of 0–0.31 mole/mole. (b) Variation of the activity coefficient  $f$  of  $Sr^{2+}$  and  $H^+$  in HAP as a function of ionic fraction  $X_{Sr}$  for  $C_{Sr}$  concentration in the solid of 0.31–1 mole/mole.

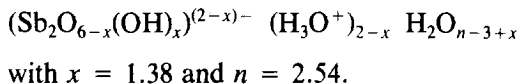
only when the pH is high enough to shift to the right the following equilibrium:



$Sr^{2+}$  ions occupy the S(II) sites until a total capacity of 1 mole/mole, including both sites, is reached. A negative value of the slope of the linear variation of  $\ln K_c$  versus  $X_{Sr}$  is observed during this exchange step, indicating a large steric effect. The linear variation of  $\ln K_c$  may be interpreted by the interaction between two  $Sr^{2+}$  ions located in adjacent sites (31). This effect leads to large variations of the activity coefficients versus  $X_{Sr}$  in the solid (Fig. 2b) compared to the first step (Fig. 2a). In this second step, we observe a positive standard free energy (Table V).

The decrease of the Sb–O distance in sample 4 may be interpreted by the total removal of the protons from the Sb–OH groups. The  $Sb_2O_6$  octahedra are more regular, leading to a decrease of the Sb–O distance, and to O–Sb–O and O–O–O angles approaching  $90^\circ$  and  $60^\circ$ , respectively.

According to these results, it is now possible to propose a chemical formula for the polyantimonic acid used in our experiments,



An important feature of our results, is the concordance between the number of S(I) and S(II) sites occupied by strontium and the two values of the exchange capacity. One could therefore conclude that the substitution of  $H_3O^+$  ions leads to placement of the  $Sr^{2+}$  ions in the same S(I) sites, while the substitution of  $H^+$  ions of the framework leads to placement of the  $Sr^{2+}$  in the S(II) sites. In fact the observed concordance could be a coincidence, as a rearrangement of  $Sr^{2+}$  ions may occur. The only method to control this fact is to repeat the same type of experiments on an antimonic acid with another  $x$  value and to compare the number of occupied sites to the capacity values.

## Conclusion

The use of a thermodynamical approach to the exchange together with a comprehensive structural study led to a better knowledge of the mechanism of the  $Sr^{2+}$  fixation on HAP. Two different protons are exchanged, leading to two different crystallo-



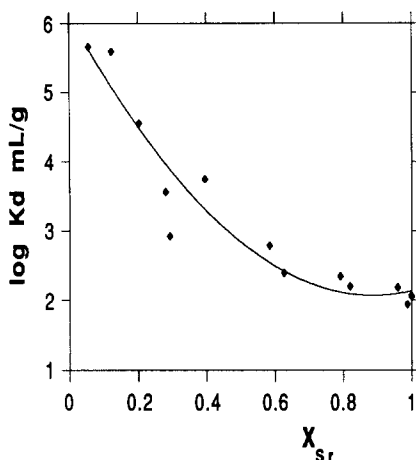


FIG. 3. Variation of the logarithm of the distribution coefficient  $K_d$  of  $Sr^{2+}$  on HAP as a function of ionic fraction  $X_{Sr}$  in the solid for  $C_{Sr}$  variation of 0–1 mole/mole  $Sb_2O_5$ .

graphic sites for  $Sr^{2+}$ . These results have some practical aspects for the retention of radioactive strontium from nuclear wastes. In acid waste solutions, only the reduced capacity of 0.31 mole/mole has to be considered. To achieve a higher concentration in the solid, the solution must be alkaline. However, in this case, the distribution coefficient  $K_d$  will fall off with the fixed concentration (Fig. 3), because of the decrease of the selectivity coefficient  $K_c$  leading to a less effective fixation. The kinetics of fixation is also an important parameter for practical use of the products. We have already shown that the working capacity has to be reduced due to the limited extent of the fast step of the fixation. In the future, it is probably possible to change these parameters by changing the preparation conditions, either in the same pyrochlore structure or in another symmetry obtained by altering the chemical composition.

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