

Sorption of aqueous palladium onto synthetic hydroxyapatite

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Abstract The sorption of Pd(II) on hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) has been studied at 25 °C as a function of pH, in 0.01 M NaClO_4 , and 0.01 and 0.025 M $\text{Ca}(\text{ClO}_4)_2$ aqueous background electrolytes and Pd(II) concentration (9.3 to 47 μM), trying to minimize some types of reactions, such as solid dissolution of and metal precipitation. The radiotracer palladium, ^{109}Pd , obtained by neutron irradiation, has been used to calculate the palladium's distribution coefficients K_d between aqueous and

solid phase. A mathematical treatment of results has been made by ion-exchange theory in order to interpret palladium sorption onto treated solid. For this, we take into account the existence of active sites at the hydroxyapatite surface, and the aqueous solution chemistry of palladium as well as the effect of phosphate anions from solid dissolution. The results can be explained as evidence of sorption of the species PdOH^+ , and of a mixed hydroxo complex of Pd^{2+} like $(\text{XCaO}^-)\text{-PdOH}^+ \cdot n\text{H}_2\text{O}$ fixed onto $\{\equiv\text{Ca-OH}\}$ surface sites of the hydroxyapatite.

Keywords Palladium · Sorption · Hydroxyapatite · Surface sites · Ion-exchange theory

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Introduction

Chemistry of several B-metals in the +II oxidation state is of concern for nuclear waste management. Isotopes of ruthenium (Ru), rhodium (Rh) and palladium (Pd) fission products generated in nuclear spent fuel can have an important contribution to the high level waste long-term radiotoxicity. The beta emitting radionuclide palladium-107 is one of these long lived fission products with a half-life of 6.499×10^6 year [1]; its release from waste repositories to the biosphere could represent a long-term environmental hazard. Therefore, sorption studies of long-lived radioisotopes on possible materials for constituting the engineered barrier system (EBS) and surrounding natural rock are necessary to understand retardation of radionuclide release, and to optimize waste isolation. A variety of minerals have been evaluated for the waste form, the canister, waste package surround and as backfill materials [2, 3]. In this concept of multi-barrier disposal,

the mineral group apatite minerals is regarded as a possible additive to backfill materials [4] entering in the composition of engineered barriers or as matrices suitable for the immobilization of long-lived radionuclides in high-level radioactive waste disposals [5, 6]. Naturally occurring calcium hydroxyapatite (HAp) is member of the family of isomorphous inorganic substances and its ideal formula is $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. There has been, and continues to be, considerable interest in the cation-exchange properties of hydroxyapatite as a result of potential applications for the removal of environmentally undesirable elements from aqueous systems [7, 8]. The reports are abundant. Most of them have focused on the exchange of HAp with divalent cations as cadmium and strontium [8–10] because of the toxicities of these elements. The sorption of divalent cations has always been explained in terms of substitutions for cationic sites on apatite structure; the sorption of some actinides on synthetic hydroxyapatite has been fitted to the Langmuir isotherm model for simple adsorption [11–13]. To what extent an apatite, put in contact with an aqueous solution is able to retain these species, and can this be explained in terms of chemical equilibrium between these ions present in solution and functional groups at the surface? Can the retention of ions on hydroxyapatite be explained by the existence of surface sites? In a previous work, Badillo-Almaraz et al. [14] on the basis of depth profiling of cadmium ions obtained by nuclear microprobe analysis, considered that the sorption of this element on hydroxyapatite particles may be explained in terms of charge compensation on completely ionized phosphate sites at $\text{pH} > 5$. Wu et al. [15] arbitrarily assumed that calcium and phosphate sites are present at the apatite surface at the same concentrations, and supposed that they are amphoteric. However; Badillo-Almaraz [16] measured different concentrations for the calcium (60 mmol/100 g) and phosphate sites (37 mmol/100 g), consistently with the theoretical concentrations estimated by Kukura et al. [17] from crystallographic considerations.

In the present work, we are interested in studying the mechanisms involved in the uptake of palladium onto hydroxyapatite, since performance assessment requires sorption data over a wide range of chemical conditions for some long-lived radionuclide. To our best knowledge, no data have been reported for the sorption of palladium on hydroxyapatite and here we report sorption studies of palladium on synthetic HAp as a function of several parameters such as pH, effect of background electrolytes, and palladium concentration. In the interpretation of the sorption measurement, we take into account the existence of active sites at the hydroxyapatite surface, and the aqueous solution chemistry of palladium as well as the effect of phosphate anions from solid dissolution.

Materials and methods

Materials

Commercial hydroxyapatite (HAp) was purchased from Bio-Gel HTP, Bio-Rad. The solid was sieved to obtain a selected grain between 38 and 75 μm , purified and conditioned by equilibrations with 0.2 M $\text{Ca}(\text{ClO}_4)_2$ aqueous solutions in order to eliminate cationic impurities and to convert the surface to the homoionic Ca-form. The surface area of the hydroxyapatite sample, measured by the single-point BET (N_2) method, was 69 m^2/g . Conditioning and purification process have been described elsewhere [16]: HAp powder of 38–75 μm fractions was loaded into a Sigma chromatography column. After that, various quantities of 0.2 M $\text{Ca}(\text{ClO}_4)_2$ solutions were slowly introduced at the top of the column using a peristaltic pump to promote good contact between solid and liquid phases. The solid was then dried at 40 °C for 48 h after dehydration with methanol. It was characterized by X-ray diffraction methods (XRD): no significant change in the crystalline structure of the solids was detected after the purification process (data not shown).

Analytical-grade water was obtained from Millipore system. The chemicals used were NaClO_4 from Analytika, $\text{Ca}(\text{ClO}_4)_2$ and $\text{Pd}(\text{NO}_3)_2$ from Aldrich. All these compounds were employed without any pre-treatment. All solutions were prepared by weighting from previous chemicals and fresh water.

Solubility and aqueous species of Pd(II)

In this work, we study the interaction mechanisms of palladium with hydroxyapatite. The understanding of interface processes that may occur on solids in contact with aqueous solutions containing metals implies not only considering their speciation and solubility, but their interactions with natural solids such as apatites or clays. These processes consist in chemical retention (adsorption), diffusion into the solid (absorption) or surface precipitation. In order to understand the responsible mechanism of palladium retention, we have tried to minimize some types of reactions, such as dissolution of solid and precipitation of metal.

Due to method of palladium production (from stable palladium), it is difficult to work with palladium concentration under 9 μM total aqueous concentration. Whatever is ionic strength, this value is higher than the solubility limit of palladium in aqueous non-complexing medium as calculated from solubility products and hydrolysis constants reported in the literature [18, 19]. In aqueous media, palladium complexes are found only in the divalent oxidation state Pd(II). At 25 °C in non complexing aqueous

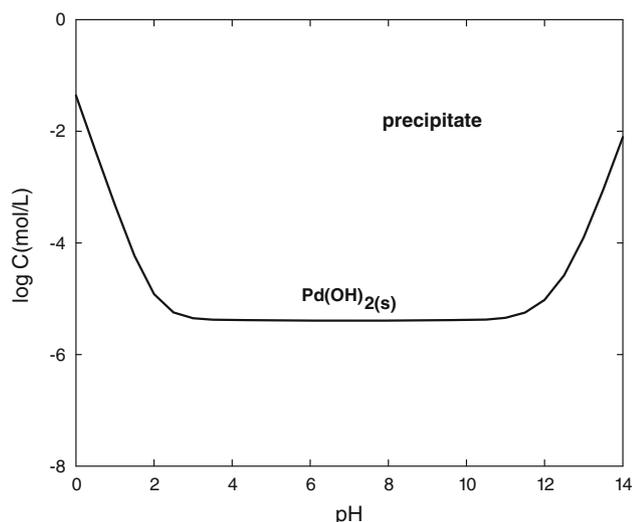


Fig. 1 pH dependence of the solubility of palladium hydroxide

solutions the solubility of $\text{Pd}(\text{OH})_2(\text{s})$ shows a strong pH dependence as a result of successive hydrolysis of $\text{Pd}^{2+}(\text{aq})$. The minimal solubility in the pH range 3–11, is at 4×10^{-6} M as shows in Fig. 1.

The sorption of Pd ions on HAp is obtained by the experimental conditions background electrolyte, pH of solution and concentration of palladium. To minimize interpretation uncertainties, all experiments have been carried out in perchlorate aqueous solutions since Pd^{2+} forms weak complexes with fluoride and perchlorate [20], and no data for palladium fluoride complexes have been reported to our knowledge.

In the present study, we first investigate the effect of palladium concentration of 4.7×10^{-5} M, 1.7×10^{-5} M and 9.3×10^{-6} M in 0.025 M background electrolyte $\text{Ca}(\text{ClO}_4)_2$ as a function of pH. Then, we study the sorption of Pd(II) on HAp of pH in the background electrolytes $\text{Ca}(\text{ClO}_4)_2$ 0.01 M and NaClO_4 0.01 M at palladium concentrations of 4.7×10^{-5} M again as a function of pH.

Sorption experiments

Because of the high sorptive capacity of hydroxyapatite for divalent elements [8–10], experiments with initial Pd(II) concentrations lower than 1×10^{-6} M results in equilibrium concentrations of Pd(II) near the detection limit.

Because of this, we designed a specific experimental methodology. Batch sorption experiments were carried out as a function of pH between about 6 and 11 in 50 mL Nalgene polycarbonate centrifuge tubes. 25 mL aliquots of 0.025 and 0.01 M $\text{Ca}(\text{ClO}_4)_2$ or 0.01 M NaClO_4 solutions were added to centrifuge tubes together with an aliquot of 500 μL taken from a suspension of 1 g/L of synthetic HAp in perchlorate solution under vigorously stirring. With this

procedure we obtain 0.020 g L^{-1} ratio at each tube. The pH of the suspensions was adjusted with dilute NaOH or HClO_4 solutions and measured with a combined pH electrode (Orion Co.). The outer reference cell of the combined glass electrode was filled with saturated $\text{NaCl}/\text{NaNO}_3$ solutions and calibrated with solutions of known $[\text{H}^+]$. The suspensions of synthetic HAp were shaken 24 h in rotary shaker set at 8 rpm at room temperature. The solid–liquid distribution coefficients K_d of palladium were obtained using the radiotracer technique. For that, the suspensions were spiked with ^{109}Pd tracer solution and shaken overnight. The samples were centrifuged before sampling the supernatant solutions and pH measurements. A preliminary study allowed us to verify that Pd is not significantly adsorbed onto polycarbonate tube walls.

The aqueous gamma activity after equilibration was provided by gamma-counting of a 2-mL sample of the clear supernatant, with the gamma detector HPGe and denoted A. Standard labelled solutions were also prepared with reference perchlorate solutions and spiked with ^{109}Pd , in order to obtain the initial aqueous activity denoted A° . Data from the equilibrium experiments were used to calculate distribution coefficients, K_d (mL/g) given by:

$$K_d = \frac{\overline{\text{Pd}}}{\text{Pd}} = \left(\frac{A^\circ}{A} - 1 \right) \cdot \frac{V}{m} \quad (1)$$

Equation 1 describes the distribution of Pd between the aqueous solution and the mineral surface, where $\overline{\text{Pd}}$ (mol/g) is the total concentration of Pd on the solid; V is the volume (mL) of solution, and m the mass (g) of solid. A° and A are the initial and final activities (Bq) of the solution respectively.

Results and discussion

Similar studies concerning the sorption of strontium on synthetic hydroxyapatite using batch method and radiotracer technique were reported by Lazić and Vuković [9]. Their experiments were performed in 200 cm^3 of $(1-11) \times 10^{-3} \text{ mol/dm}^3$ $\text{Sr}(\text{NO}_3)_2$ solution at pH 6.6, and 1 g of synthetic hydroxyapatite. The obtained isotherm evidenced an increase of adsorbed strontium with aqueous concentration, followed by leveling off of the curve. The authors fitted their experimental data quite well with the Langmuir model. However, they carried out their experiments at only one pH value and the sorption capacity of hydroxyapatite for Sr(II) could be higher than their final reported value of $1.5 \times 10^{-4} \text{ mol/g}$. Jeanjean et al. [10] studied the sorption of cadmium ions on hydroxyapatite as a function of pH. In our case, we also determined the palladium sorption as a function of pH and we tried to minimize palladium precipitation.

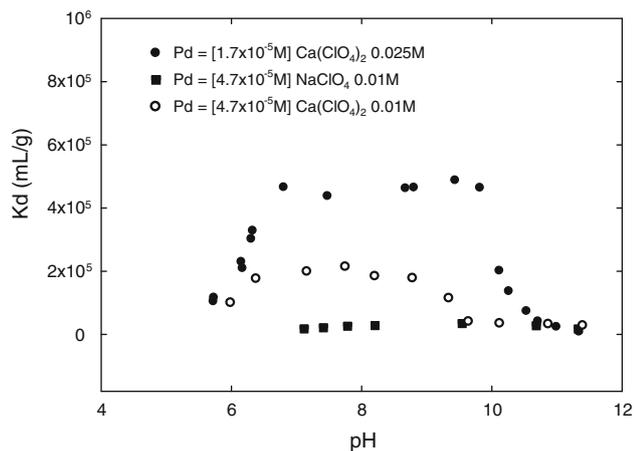


Fig. 2 Experimental distribution coefficient of palladium on HAp in perchlorate aqueous suspensions

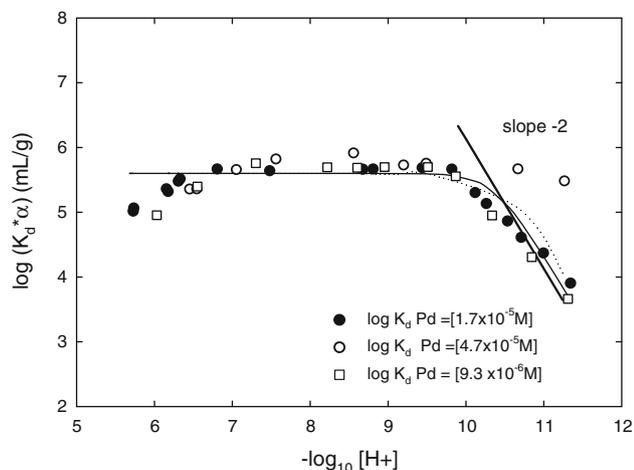


Fig. 3 Distribution coefficient of palladium on HAp in calcium perchlorate aqueous suspensions. $K_{dPd(OH)_2}$ (solid lines) were calculated with Eq. 10 from K_d experimental values and calculated Ringböm coefficient $\alpha_{Pd(OH)_2}$

Our experimental results in the Fig. 2 indicated the high affinity that palladium has for $=CaOH$ sites of hydroxyapatite. Distribution coefficients ranged from 99,800 to 460,200 mL/g with associated uncertainties from approximately 9 to 16.5%. Uncertainties are higher with the larger K_d due to measurement error in determining Pd(II) activities at very low values (very high sorption).

To discard a potential Pd(II) precipitation, distribution coefficients for different initial Pd(II) concentrations were determined in the Fig. 3. Indeed, as palladium solubility (or equilibrium aqueous total concentration) is a thermodynamic constant for one set of experimental conditions (pH, temperature, ionic strength), the partition coefficient of palladium for two different initial concentrations have to

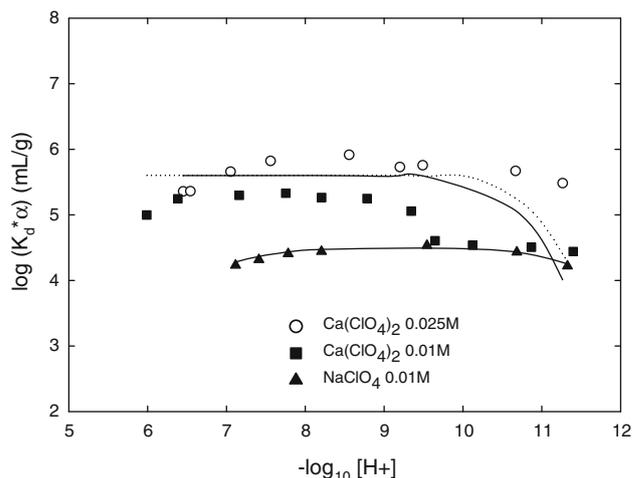


Fig. 4 Distribution coefficient of palladium on HAp at the same $[Pd(II)] = 4.7 \times 10^{-5}$ M. $K_{dPd(OH)_2}$ (solid lines) were calculated with Eq. 10 and Eq. 13 from K_d experimental values in several perchlorate aqueous suspensions and calculated Ringböm coefficient $\alpha_{Pd(OH)_2}$

have the same value in the same conditions. Figure 3 evidenced that distribution coefficients of Pd(II) are independent of the initial Pd concentration in $Ca(ClO_4)_2$ 0.025 M in the range corresponding to $7 < \log_{10}[H^+] < 10$. No influence of initial Pd concentration suggests partition behavior—not precipitation—Fig. 4 evidenced the influence of background electrolyte on distribution coefficients values at the same palladium concentration.

The distribution coefficients are highly pH dependent as illustrated by a plot of K_d versus pH (Fig. 2). At pH 6, the sorption of Pd(II) was the lowest with a K_d value of 103,000 mL/g in $Ca(ClO_4)_2$ or 17,000 mL/g in $NaClO_4$.

Moore et al., who have performed batch studies of Np(V) and Pu(IV) sorption in $NaClO_4$ non-complexing media [12, 13], have equally evidenced the high dependence of distribution coefficients as a function of pH ($6 < pH < 11$). A sorption isotherm is directly the consequence of aqueous speciation of different implied species. So in our study, we can suppose that distribution coefficients depend of palladium speciation, and eventually of phosphate speciation from solid dissolution. We have neglected that calcium could be implied in palladium sorption due to Coulombian repulsion. The K_d obtained is constant in the 7.0–10.0 pH range (Fig. 3), and it could be originated by constant Pd speciation in both phase.

According to Navibanets and Kalabina [18] and Van Middlesworth and Wood [23], the predominant species of palladium in the perchlorate—non complexing—media are $Pd(OH)_4^{2-}$, $Pd(OH)_3^-$, $Pd(OH)_2^0$, $PdOH^+$ and Pd^{2+} depending on pH and more precisely $Pd(OH)_2$ between pH 7 and 10 (Table 1) which is coherent with partition coefficient. Now concerning the phosphate species, the major free aqueous phosphate species does not change in the

Table 1 Thermodynamic data extrapolated to zero ionic strength by Davies used in this work for modeling the aqueous speciation and the sorption of aqueous Pd(II) onto hydroxyapatite [18, 23]

<i>K</i> name	Equilibrium	Log ₁₀ <i>K</i> ^o (<i>I</i> = 0 M)
*β ₁	Pd ²⁺ + H ₂ O _(l) ↔ PdOH ⁺ + H ⁺	-1.87
*β ₂	Pd ²⁺ + 2H ₂ O _(l) ↔ Pd(OH) _{2(l)} + 2H ⁺	-3.82
*β ₃	Pd ²⁺ + 3H ₂ O _(l) ↔ Pd(OH) ₃ ⁻ + 3H ⁺	-15.97
*β ₄	Pd ²⁺ + 4H ₂ O _(l) ↔ Pd(OH) ₄ ²⁻ + 4H ⁺	-29.20
*β ₅	Pd ²⁺ + HPO ₄ ²⁻ ↔ PdHPO ₄	3.36
*K _s	Pd ²⁺ + 2H ₂ O _(l) ↔ Pd(OH) _{2(s)} + 2H ⁺	1.57

7.0–12.1 $-\log_{10}[\text{H}^+]$ range: it is HPO_4^{2-} . The last hypothesis to verify is a potential palladium (II) complexation by phosphate species. But (Hydrogeno-) phosphate complexation of Pd(II) could very well predominate in the aqueous solution with no change in the Pd(II) aqueous speciation: for this reason such complexation might very well be undetected in our K_d measurements.

Furthermore, K_d increases with pH for values between 6 and 7; which is correlated to the change of phosphate speciation form HPO_4^{2-} (at pH > 7.21) to H_2PO_4^- (at pH < 7.21) and equally of palladium speciation from PdOH⁺ to Pd(OH)₂. And it decreases above $-\log_{10}[\text{H}^+]$ value 10. This observation cannot be explained by palladium or phosphate speciation. But in basic media, we can observe an exchange between sodium or calcium ions from background electrolytes and proton from =CaOH sites and so a competition between palladium species and background cations conducting to palladium desorption.

Moreover, the sorption of palladium appeared to be a little favored between pH 7 and 10 on increasing the concentration of the common ion calcium in solution whereas, in the presence of sodium, the sorption of palladium is decreased. This cannot be originated in sorption equilibria. However, indirect influences are possible in aqueous phase. Adding calcium in the system decreases hydroxyapatite solubility and so the aqueous concentration of phosphate. Another possible effect is incomplete knowledge of phosphate-palladium complexes. Unfortunately, no thermodynamic data have been reported concerning palladium phosphate compounds and complexes.

A mathematical treatment of results has been made by ion-exchange theory [21, 22] in order to interpret palladium sorption onto treated hydroxyapatite.

General considerations

Ion-exchange theory IET assumes that each phase (the aqueous solution and the solid with the interface) is neutral.

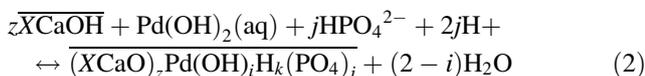
The system includes two totally no miscible and electrically neutral phases: a solid phase named ion exchanger, and a liquid phase—an aqueous solution who exchanges ions with the solid phase. The charges of the surface are exactly compensated by ions coming from the solution. Aqueous speciation is classically modeled with mass balance and the law of mass action using published equilibrium constants (Table 1). The surface of hydroxyapatite is assumed to have sorption sites $\{\equiv\text{Ca-OH}\}$ and $\{\equiv\text{Ca-PO}_2(\text{OH}_2)\}$ when pure hydroxyapatite is originally in contact with aqueous solutions; according to Badillo-Almaraz [16] the former are Brönsted acid weak sites and the latter are Brönsted acid strong sites, these sites can exchange their hydroxyl ions OH⁻ or protons H⁺. Even if the IET assumes several sorption sites, the hydroxyapatite has been treated with Ca(OH)₂ aqueous solutions in order to replace the surface phosphate groups with hydroxyl groups [16] and to simplify its surface. The following species are the results of ionic exchanges of aqueous cations Na²⁺ or Ca²⁺ with surface species $\{\equiv\text{Ca-OH}\}$. Using notations that include charge compensation, the following initial—i.e. before any Pd sorption—stoichiometries were taken into account at calcium sites: $\{\equiv\text{Ca-OH}\}$, $\{\equiv\text{Ca-O}^-, \text{Na}^+\}$ or $\{\equiv(\text{CaO}^-)_2, \text{Ca}^{2+}\}$.

We use simpler notations $\overline{\text{XCaOH}}$, $\overline{\text{XCaONa}}$ and $\overline{(\text{XCaO})_2\text{Ca}}$ where upper-lined is for inside the solid phase or at its surface, and X is an anion inside the solid phase—not at the surface: it cannot be exchanged—for electro-neutrality X is formally with charge -1, it represents HO⁻ or PO₄³⁻ bridging to other Ca²⁺ cations of the solid. This $\overline{\text{XCaOH}}$ notation takes into account the electro-neutrality of the surface—hence including the aqueous counter-ions neutralizing ionized surface—and the steric constraint that (only) $\overline{\text{X}^-}$ is blocked inside the solid. Starting with $\overline{\text{XCaOH}}$ it can exchange its $\overline{\text{H}^+}$ mono-cation with M^z cations ($z > 0$) from the aqueous solution giving $\overline{(\text{XCaO})_z\text{M}}$. $\overline{\text{XCaOH}}$ can also exchange its $\overline{\text{OH}^-}$ mono-anion with M^z anions ($z < 0$) from the aqueous solution giving $\overline{(\text{XCa})_{-z}\text{M}}$. According to Navibanets and Kalabina [18] and Van Middlesworth and Wood [23], the predominant species of palladium in the perchlorate media are Pd(OH)₄²⁻, Pd(OH)₃⁻, Pd(OH)₂⁰, PdOH⁺ and Pd²⁺ depending on pH. However, we wrote Pd(OH)₂(aq)—not Pd²⁺—because it is the major Pd aqueous species in most of our pH conditions with surface species $\{\equiv\text{Ca-OH}\}$. According to the aqueous chemistry of phosphate (Table 2), the major aqueous species does not change in the 7.0–12.1 $-\log_{10}[\text{H}^+]$ range: it is HPO_4^{2-} . If we observe our experimental results (Fig. 3), log K_d is constant in the 7.0–10.0 $\log_{10}[\text{H}^+]$ range, this plateau could be related with no change in the Pd(II) speciation in both phase. Moreover, log K_d increases with pH for values

Table 2 Thermodynamic data extrapolated to zero ionic strength with Davies equation used in this work for the aqueous speciation of calcium, phosphorus and hydroxyapatite [16]

<i>K</i> name	Equilibrium	Log ₁₀ <i>K</i> ^o (<i>I</i> = 0 M)
* <i>K</i> ₁	Ca ²⁺ + H ₂ O _(l) ↔ CaOH ⁺ + H ⁺	−12.70
* <i>K</i> ₂	Ca ²⁺ + PO ₄ ^{3−} ↔ CaPO ₄ [−]	6.49
* <i>K</i> ₃	Ca ²⁺ + H ⁺ + PO ₄ ^{3−} ↔ CaHPO ₄	14.97
* <i>K</i> ₄	Ca ²⁺ + 2H ⁺ + PO ₄ ^{3−} ↔ CaH ₂ PO ₄ ⁺	21.02
* <i>K</i> ₅	Ca ²⁺ + 2H ₂ O _(l) ↔ Ca(OH) _{2(s)} + 2H ⁺	22.63
* <i>K</i> ₅	H ₃ PO ₄ ↔ H ₂ PO ₄ [−] + H ⁺	−2.15
* <i>K</i> ₆	H ₂ PO ₄ [−] ↔ HPO ₄ ^{2−} + H ⁺	−7.21
* <i>K</i> ₇	HPO ₄ ^{2−} ↔ PO ₄ ^{3−} + H ⁺	−12.36
* <i>K</i> ₈	Ca ₁₀ (PO ₄) ₆ (OH) ₂ + 14H ⁺ = 10Ca ²⁺ + 6H ₂ PO ₄ [−] + 2H ₂ O	28.48

between 5 and 7; which is correlated to the change of phosphate speciation from HPO₄^{2−} (at pH > 7.21) to H₂PO₄[−] (at pH < 7.21). For this, the ionic exchange equilibrium with the predominating species is:



for $z = 2 - i + k - 3j > 0$. Its equilibrium constant is:

$$K_{+,i,j,k} = \frac{[(\overline{XCaO})_z Pd(OH)_i H_k(PO_4)_j]}{[\overline{XCaOH}]^z \cdot [Pd(OH)_2(aq)] \cdot [HPO_4^{2-}]^j \cdot [H^+]^{2j}} \quad (3)$$

And the distribution coefficient is:

$$K_{d+,i,j,k} = \frac{[(\overline{XCaO})_z Pd(OH)_i H_k(PO_4)_j]}{[Pd(OH)_2(aq)] \cdot \alpha_{Pd(OH)_2}} = \frac{K_{+,i,j,k} \cdot [\overline{XCaOH}]^z \cdot [HPO_4^{2-}]^j \cdot [H^+]^{2j}}{\alpha_{Pd(OH)_2}} \quad (4)$$

where $\alpha_{Pd(OH)_2} = [Pd(II)]_T / [Pd(OH)_2]$ is the classical Ringböm coefficient calculated from published thermodynamic data [18, 19]. $[Pd(II)]_T$ is the total aqueous concentration of palladium in which complexation of palladium with phosphates can be negligible in our conditions.

Thus, we have to determine the theoretical expression of partition coefficient of Pd(OH)₂ as a function of experimental conditions. No explicit electrostatic term is included in IET, as for mass action law in the bulk solution. Consequently, stoichiometric coefficients are obtained by classic slope analysis of log–log plots for IET, which is a way of checking the model [21, 22].

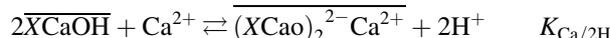
We can conclude that:

$$\log_{10} K_d \cdot \alpha_{Pd(OH)_2} = \log_{10} K_{i,j,k} + j \cdot \log_{10} [HPO_4^{2-}] + 2j \cdot \log_{10} [H^+] + z \cdot \log_{10} [\overline{XCaOH}] \quad (5)$$

In this expression, HPO₄^{2−} concentrations vary as a function of pH and nature or electrolyte concentrations and \overline{XCaOH} have to be evidenced by saturation experiments or physical observations.

Mass balance on exchange sites

In basic media, where hydroxyapatite surface can be negatively charged, sodium and calcium ions can be adsorbed onto surface. These sorption mechanisms have to be considered to determine \overline{XCaOH} concentration. The ionic exchange equilibria and the associated thermodynamic constants with the different species are:



The mass balance of the exchange sites can also be written as

$$C_e = [\overline{XCaOH}] + [\overline{XCaO}^- Na^+] + [(\overline{XCaO})_2^{2-} Ca^{2+}] = [\overline{XCaOH}] \cdot \left(1 + K_{Na/H} \frac{[Na^+]}{[H^+]} + K_{Ca/2H} \frac{[Ca^{2+}]}{[H^+]^2} \right) \quad (6)$$

where C_e is the total concentration of CaOH exchange sites.

The palladium sorption is negligible as compared to the exchange capacity of hydroxyapatite and compared to the other adsorbed species. Thus Eq. 5 can be modified as:

$$\begin{aligned} \log_{10} K_d \cdot \alpha_{Pd(OH)_2} &= \log_{10} K_{i,j,k} + j \log_{10} [HPO_4^{2-}] + 2j \log_{10} [H^+] \\ &+ z \log_{10} C_e - z \log \left(1 + K_{Na/H} \frac{[Na^+]}{[H^+]} + K_{Ca/2H} \frac{[Ca^{2+}]}{[H^+]^2} \right) \end{aligned} \quad (7)$$

HPO₄²⁻ concentration

Phosphate concentration in the solution depends on the dissolution of hydroxyapatite. It can be also calculated from the solubility product K_s of hydroxyapatite and acidity constants of phosphoric acid (K_a) (Table 2):

$$\log_{10}[\text{HPO}_4^{2-}] = \frac{1}{6}\log_{10} K_s + \log_{10} K_{a_2} + \frac{4}{3}\log_{10}[\text{H}^+] - \frac{5}{3}\log_{10}[\text{Ca}^{2+}] \quad (8)$$

Using this we obtain from Eq. 7 becomes:

$$\begin{aligned} & \log_{10} K_d \cdot \alpha_{\text{Pd}(\text{OH})_2} \\ &= C1 + \frac{10j}{3}\log_{10}[\text{H}^+] - \frac{5j}{3}\log_{10}[\text{Ca}^{2+}] \\ & \quad - z \log \left(1 + K_{\text{Na}/\text{H}} \frac{[\text{Na}^+]}{[\text{H}^+]} + K_{\text{Ca}/2\text{H}} \frac{[\text{Ca}^{2+}]}{[\text{H}^+]^2} \right) \end{aligned} \quad (9)$$

where

$$C1 = \log_{10} K_{i,j,k} + z \log_{10} C_e + \frac{i}{6}\log_{10} K_s + j \log_{10} K_{a_2}.$$

In Ca(ClO₄)₂ media and for the studied pH range, we can consider that the total aqueous concentration of calcium [Ca]_T is constant and equal to the sum of the Ca²⁺ and CaOH⁺ concentration. For pH < 11.5, [Ca²⁺] ~ [Ca]_T and Eq. 9 is valid:

$$\begin{aligned} \log_{10} K_d \cdot \alpha_{\text{Pd}(\text{OH})_2} &= C2 + \frac{10j}{3}\log_{10}[\text{H}^+] \\ & \quad - z \cdot \log_{10} \left(1 + K_{\text{Ca}/2\text{H}} \frac{[\text{Ca}]_T}{[\text{H}^+]^2} \right) \end{aligned} \quad (10)$$

with $C2 = C1 - \frac{5j}{3}\log_{10}[\text{Ca}]_T$.

So for pH values, where the calcium sorption onto hydroxyapatite can be negligible, $\log_{10} K_d \cdot \alpha_{\text{Pd}(\text{OH})_2}$ as a function of $-\log_{10}[\text{H}^+]$ shows a slope equal to $-10j/3$. For more basic media, where calcium onto surface site becomes more important, the same representation evidences a slope equal to $(-10j/3 - 2z)$.

But we cannot measure the exchange capacities and the equilibrium constants in order to have a set of equations and to solve them analytically for speciation in both phases, to identify the stoichiometries of the sorption equilibria. Our experimental results allow us only to determine sorption mechanisms and not all associated thermodynamic constants.

In NaClO₄ medium, the interpretation of experimental results is more difficult as regard of calcium concentration. Indeed, the total aqueous calcium concentration is depending of hydroxyapatite solubility:

$$K_s * K_{a_2}^6 = \frac{[\text{Ca}^{2+}]^{10} [\text{HPO}_4^{2-}]^6}{[\text{H}^+]^8} = \frac{[\text{Ca}]_T^{10} [\text{P}]_T^6}{[\text{H}^+]^8 \alpha_{\text{Ca}^{2+}}^{10} \alpha_{\text{HPO}_4^{2-}}^6} \quad (11)$$

where [Ca]_T and [P]_T are the total aqueous concentration of calcium and phosphate respectively. $\alpha_{\text{HPO}_4^{2-}}$ the Ringböm coefficient of HPO₄²⁻ defined as:

$$\alpha_{\text{HPO}_4^{2-}} = \frac{[\text{P}]_T}{[\text{HPO}_4^{2-}]}$$

If the calcium complexation by phosphate is not significant, the total aqueous concentration of calcium is about equal to Ca²⁺ concentration.

$$\begin{aligned} \log_{10}[\text{Ca}^{2+}] &= \frac{1}{16}\log_{10} K_s + \frac{3}{8}\log_{10} K_{a_2} + \frac{1}{2}\log_{10}[\text{H}^+] \\ & \quad - \frac{3}{8}\log_{10} \frac{3}{5} + \frac{3}{8}\log_{10} \alpha_{\text{HPO}_4^{2-}} \end{aligned} \quad (12)$$

Moreover the total calcium aqueous concentration in neutral and basic media, where calcium is susceptible to be sorbed onto hydroxyapatite is negligible. It can be also negligible in mass balance of surface sites. Equation 10 becomes:

$$\begin{aligned} \log_{10} K_d \cdot \alpha_{\text{Pd}(\text{OH})_2} &= C3 + \frac{5j}{2}\log_{10}[\text{H}^+] - \frac{5j}{8}\log_{10} \alpha_{\text{HPO}_4^{2-}} \\ & \quad - |z|^* \log_{10} \left(1 + K_{\text{Na}/\text{H}} \frac{[\text{Na}^+]}{[\text{H}^+]} \right) \end{aligned} \quad (13)$$

with $C3 = \log_{10} K_{i,j,k} + \frac{3j}{48}\log_{10} K_s + \frac{3j}{8}\log_{10} K_{a_2} + |z| \cdot \log_{10} C_e + \frac{5j}{8}\log_{10} \frac{3}{5}$. So, for pH where sodium sorption onto hydroxyapatite is negligible, $\log_{10} K_d \cdot \alpha_{\text{Pd}(\text{OH})_2}$ as a function of $-\log_{10}[\text{H}^+]$ evidences a slope equal to $-5j/2$. For more basic media, this graph evidences a slope equal to $-5j/2 + |z|$.

The theoretical value of $\log_{10} K_d \cdot \alpha_{\text{Pd}(\text{OH})_2} = \log_{10}(K_d \cdot \alpha_{\text{Pd}(\text{OH})_2})$ was calculated in according Eqs. 10 and 13. The logarithm of the distribution coefficient of palladium(II) was found to be constant in all cases as a function of $-\log_{10}[\text{H}^+]$ in the range studied to $6 \leq -\log_{10}[\text{H}^+] \leq 10$ and evidences a slope equal to $-10j/3$, from this we assumed $j = 0$; for more basic media, where calcium onto surface site becomes major, the same representation evidences a slope equal to $(-10j/3 - 2|z|)$, the logarithm of the distribution coefficient was found to linearly decrease with a slope equal to -2 as a function of $-\log_{10}[\text{H}^+]$ in the range studied to $10 \leq -\log_{10}[\text{H}^+] \leq 11.5$ since stoichiometric coefficient, z , could be determined equal to 1. This slope was interpreted as evidence for the sorption of Pd species with stoichiometry $(\text{XCaO}^-) - \text{PdOH}^+ \cdot n\text{H}_2\text{O}$. For this interpretation, it is assumed that the engaged sorption site was saturated with H⁺: {≡Ca-OH}. As a conclusion for this first study, the model is quite simple: a single sorption site and one sorbed species for modeling the sorption of Pd in a limited pH range 6–11.

(Hydrogen-) phosphate complexation of Pd(II) could very well predominate in the aqueous solution with no change in the Pd(II) aqueous speciation too: for this reason such complexation might very well be undetected in our K_d measurements. Note that these equilibria predict no direct influence of the total Pd concentration, neither of the Na^+ or Ca^{2+} concentrations. This cannot be originated in the above exchange equilibria. However, indirect influences are possible in both phases. Adding calcium in the system decreases the aqueous concentration of phosphate. Another possible effect is the existence of others complexes containing phosphate or others thermodynamic data for PdHPO_4 complexes. Unfortunately, no thermodynamic data have been reported concerning palladium phosphate compounds and complexes.

Conclusions

The aqueous sorption mechanism of Pd on hydroxyapatite has been studied in basis of radiotracer techniques, as a function of several physicochemical parameters such as of pH, effect of background electrolytes, and palladium concentration. The principal features of sorption isotherms are a strong dependence of pH solution, one hand for the dissolution-precipitation of hydroxyapatite and the other hand for the hydrolysis equilibria and potential complexation by the phosphates of palladium. Pd(II) can be sorbed on hydroxyapatite as cationic species $(\text{XCaO}^-) - \text{PdOH}^+ \cdot n\text{H}_2\text{O}$ in the $-\log_{10}[\text{H}^+]$ range 6–11. This sorption behaviour could be modeled for palladium (II) at low concentration in perchlorate solutions, by using ion exchange theory and considering the constants phosphate complexation of Pd^{2+} . Our experimental results allow us only to determine sorption mechanisms and not all associated thermodynamic constants.

In the literature, the Langmuir model has been used to accurately model sorption data of other radionuclides and heavy metals to hydroxyapatite including strontium [9, 11] and actinides [12, 13]. Unfortunately, a good fit of data to the Langmuir isotherm does not give any information about the mechanism of sorption because interactions after sorption to a surface are not accounted for in the equation. In this study of hydroxyapatite, sorption measurements of

phosphate and palladium concentrations are used to hypothesize the mechanisms of sorption.

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