Original paper

Synthesis and characterization of cadmium chlorapatite $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$

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Abstract. One of the most effective methods for the immobilization of toxic metals involves the use of minerals from the apatite supergroup. The formation of cadmium chlorapatite may lead to successful entrapping of cadmium; thus, it is important to examine the solubility constant to determine the stability of cadmium in the apatite structure. Cadmium chlorapatite was synthesized and characterized by X-ray diffraction, infrared spectroscopy, Raman spectroscopy, and scanning electron microscopy. The solubility constant ($\log K_{sp}$) of cadmium chlorapatite was -65.58. The Gibbs free energy of formation of cadmium chlorapatite reached -3950.48 kJ mol⁻¹. The solubility constant turned out to be low but was enough for cadmium chlorapatite to be considered a very stable compound.

Key-words: Apatite, Cadmium, Cadmium chlorapatite, Dissolution, Solubility constant

1. Introduction

Environment pollution by heavy metals has gained widespread attention because of their toxicity and non-biodegradability (Fu, Wang 2011). One of the critical polluting heavy metals originating from industries is cadmium (Wang et al. 2018). Cadmium is mainly derived from petroleum refining, electroplating and alloying, nickel-cadmium batteries, coal combustion, and plastic stabilizers (Chen et al. 2018). Cadmium can accumulate in living tissues and cause serious health issues like bone and kidney damage, cancer, renal disturbance, and hypertension (Shirkhanloo et al. 2016). The removal of cadmium from the

environment is important and various treatment methods such as precipitation, adsorption, ion exchange, and membrane filtration have been used to remove to achieve this (Deng et al. 2017; Lee et al. 2018; Wong et al. 2014). Immobilization by minerals such as apatite is a promising method for cadmium removal (Matusik et al. 2012).

Phosphate-bearing apatite is generally characterized by the formula $M_{10}(PO_4)_6X_2$ (M and X represent cations and anions, respectively) (Drouet 2015). One of the features of apatites is the ability to exchange cations and anions in the structure. Hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$) and fluoroapatite ($Ca_{10}(PO_4)_6F_2$) are the most common minerals in this apatite supergroup; however, chlorinated and bromated counterparts are also present. Calcium ions can be replaced by other cations such as magnesium, cobalt, lead, strontium, or cadmium (Wopenka, Pasteris 2005; Sternlieb et al. 2009). Moreover, tetrahedron PO_4 can be replaced by VO_4 or AsO_4 (Hara et al. 2006). The ability of apatites to exchange cations and anions is very useful in designing specific materials for reducing the mobility and bioavailability of heavy metals, such as cadmium, in polluted water, soils, and sediments (Viipsi et al. 2013).

Many studies addressed the interaction of cadmium with apatites, especially the sorption of cadmium by apatites (Klee, Engel 1970; Jeanjean et al. 1996; Corami et al. 2008; Matusik et al. 2012; Zhu et al. 2017). Possible mechanisms for the sorption process are ion exchange, superficial sorption, and precipitation (Jeanjean et al. 1996). Another studies demonstrated that one of the most effective methods to remove Pb(II) ions from the solution is precipitation of pyromorphite and mimetite, initiating the idea of immobilizing Cd in the apatite structure and examining its stability (Ma et al. 1993; Miretzky, Fernandez Cirelli 2008; Flis et al. 2011).

The purpose of this research was to synthesize cadmium chlorapatite, characterize the mineral and determine its solubility constant based on the results of dissolution experiments.

2. Materials and methods

2.1. Synthesis of cadmium chlorapatite $Cd_5(PO_4)_3Cl$

To synthesize cadmium chlorapatite ($Cd_5(PO_4)_3Cl$), 10 g of $CdCl_2 \cdot 1.5 H_2O$ and 0.4 g of K_2HPO_4 were grated in an agate mortar, mixed and placed in a platinum melting-pot. The sample was then placed in an oven preheated to 750°C for one hour. To separate the cooled alloy from the melting-pot, the latter was heated in a sand bath until the alloy dissolved and the reaction product was obtained in the form of macroscopically visible transparent needles, sized 3-4 mm, at the bottom of the pot. The obtained mineral was rinsed several times with redistilled water and then placed in an oven and dried at 60°C until the water evaporated completely.

2.2. Dissolution experiments

Dissolution experiments were conducted at 25°C with an initial pH value of 2.5. The pH value of 0.05 M KNO_3 matrix solution was adjusted to the desired value using 0.1 M HNO_3 . The experiment was conducted in triplicate in unbuffered suspensions. To determine

that equilibration had been reached, samples of the reaction solutions were taken after 15 min and after 1, 2, 4, 25, 50, 93, 165, and 336 hours. The pH was allowed to drift freely after the initial value was set and the bottles containing the suspensions were always shaken after sampling. For each sample, the solids were allowed to settle before 5 mL of the supernatant was withdrawn without refilling with the solution afterwards. Equilibrium was deemed attained when the concentrations of Cd^{2+} , PO_4^{3-} in three consecutive samples were equal.

2.3. Methods

The composition of the synthesized samples was determined by X-ray powder diffraction using Philips APD PW 3020 X'Pert diffractometer with $\text{CuK}\alpha$ radiation and graphite monochromator. The measurements were done in a 2θ range of 5° to 65° with a 2θ step size of 0.05° . The spectra were interpreted using the XRAYAN software and Joint Committee on Powder Diffraction Standards (JCPDS) cards, 29-0254 and 30-0206. The Fourier-transform infrared (FTIR) spectra were obtained by a Nicolet 6700 spectrometer using the DRIFT technique (3% wt. sample/KBr) with 64 scans at 4 cm^{-1} . The FTIR spectra were analyzed by comparing them with the characteristic spectra of apatites described by Klee and Engel (1970). Raman spectra were obtained using the DXR Raman Microscope from (Thermo Scientific). The registration was carried out in the $100\text{--}3000\text{ cm}^{-1}$ range using a 780 nm laser. The positions and intensities of the bands were determined after decomposition of the spectra into component bands. Spectra decomposition was carried out by following the method proposed by Handke et al (1994). Air-dried, uncoated samples were examined by a variable pressure field emission scanning electron microscopy (SEM, FEI Quanta 200) equipped with an energy dispersive spectrometer for elemental microanalysis. PO_4^{3-} concentrations were determined colourimetrically (molybdene blue method; Lenoble et al. 2003) using a Hitachi 1600 spectrophotometer (Hitachi, Japan) at 870 nm wavelength. The molybdene blue method base, on formation of an antimonyl-phosphomolybdate complex, gives a blue species when reduced with ascorbic acid (Lenoble et al. 2003). The concentration of Cd^{2+} ions was determined by atomic absorption spectroscopy using a GBC SavantAA spectrometer. The concentration of Cl^- ions was calculated based on the stoichiometry of the compound as the dissolution was congruent. Solubility constant calculations were performed using the PHREEQC computer program and the MINTEQA.v4 thermodynamic database. The activities of ionic species were calculated from measured concentrations by conversion of the results from molarity to molality and application of the Davies equation or extended Debye-Hückel equation.

3. Results and discussion

3.1. Solid characterization

The X-ray pattern of the product of the synthesis reaction is shown in Figure 1. The product was identified as cadmium chloroapatite $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$ by comparing the peak positions with those of cadmium chloride phosphate reported in the JCPDS cards 29-0254 and 30-0206. All peaks were attributed to cadmium chloroapatite (CdClap) and there were

no other phases in the sample composition. Calculated unit cell parameters were: $a = 9.601(1) \text{ \AA}$ and $c = 6.395(1) \text{ \AA}$. These values agree well with the values of $a = 9.633 \text{ \AA}$ and $c = 6.484 \text{ \AA}$ reported for cadmium chloride phosphate (JCPDS cards 29-0254 and 30-0206).

Fig. 1. X-ray powder diffraction pattern of synthetic cadmium chlorapatite.

Figure 2 shows the infrared spectra of cadmium chlorapatite, with the analysis focused on mid-infrared spectra. The band at 3400 cm^{-1} is due to the adsorbed water and the rest of infrared spectra is poorly defined in the $4000\text{--}1400 \text{ cm}^{-1}$ region. The spectra indicates characteristic bands coming from P-O or O-P-O vibrations present in the $[\text{PO}_4]$ tetrahedra. These bands are attributed to the symmetric stretching vibrations ν_1 (939 cm^{-1}), asymmetric stretching vibrations ν_3 ($1057, 999 \text{ cm}^{-1}$), and asymmetric bending vibrations ν_4 ($600, 542 \text{ cm}^{-1}$). The weak band at 482 cm^{-1} may be originating from the symmetric bending vibrations ν_2 . The observed spectra are comparable with the spectra of CdClap, which were discovered by Klee and Engel (1970).

The Raman spectrum of CdClap is presented in Figure 3. The spectrum shows the bands due to the stretching mode of PO_4 , as in FTIR analysis. Symmetric stretching vibrations ν_1 (872 cm^{-1}) and asymmetric stretching vibrations ν_3 ($908, 933, 956, 980, 1021 \text{ cm}^{-1}$) are present, while the bands localized in the range of $340\text{--}540 \text{ cm}^{-1}$ are assigned to the bending mode.

Synthetic cadmium chlorapatite is presented in Figure 4. SEM images show that the precipitate is mainly composed of idiomorphic crystals in the form of hexagonal prisms with an average length of $300\text{--}400 \text{ }\mu\text{m}$, with some crystals eaching even 1.5 mm in length. The crystals are randomly distributed and have a smooth surface.

Fig. 2. Mid-IR spectrum of synthetic cadmium chlorapatite.

3.2. Dissolution experiments

Cadmium chlorapatite dissolution was most intensive during the first 50 hours of the experiment. Over time, the rate of release of phosphate ions and cadmium into the solution decreased (Figure 5). The initial pH of the solution was 2.5 and the final pH was 3.34.

The dissolution of cadmium chlorapatite was stoichiometric, i.e. the molar ratio of Cd, PO_4 and Cl ions in the tested solutions was approximately 5:3:1 (due to the mineral formula: $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$). The molar ratio Cd/ PO_4 in the equilibrium solution was 1.696 ± 0.11 . The results of the dissolution experiment are shown in Table 1.

Fig. 3. Raman spectrum of synthetic cadmium chlorapatite.

Fig. 4. Scanning electron microscopy images of cadmium chlorapatite.

TABLE 1

Results of the dissolution experiment for equilibrium state.

Sample	Temp. [°C]	Final pH	[Cd] (mmol/L)	[PO ₄] (mmol/L)	[Cl] (mmol/L)	Molar ratio Cd/PO ₄
1	25	3.34 ± 0.04	1.884±0.080	1.111±0.053	0.377± 0.011	1.696±0.11

Fig. 5. Concentrations of Cd and PO_4 in the $Cd_5(PO_4)_3Cl$ dissolution experiment with initial pH of 2.50 (equilibrium pH 3.34) and temperature 25°C.

Balance was achieved after two weeks of reaction (336 hours). To determine the state of equilibrium, it was necessary to check whether the differences between Cd and PO_4 concentrations in three consecutive samples were within the error limits. During the experiment, the pH value of the sample changed significantly. For equilibrium, it was 3.34.

In equilibrium, the solubility constant K_{sp} of cadmium chlorapatite is equal to the product of the ionic activity (IAP) which can be determined from the mineral dissolution reaction. For the following dissolution reaction of cadmium chlorapatite,

IAP can be written as:

$$\log IAP = 5\log\{Cd^{2+}\} + 3\log\{PO_4^{3-}\} + \log\{Cl^-\} \quad (2)$$

where brackets denote activities. The Cd^{2+} , PO_4^{3-} and Cl^- ion activities were calculated by the PHREEQC program using measured and equilibrated concentrations of Cd^{2+} , PO_4^{3-} , Cl^- ions and pH. The solubility constant was calculated based on the dependence of the equality of the solubility constant and the product of ionic activity. The results are presented in Table 2.

TABLE 2
Calculated equilibrium activities.

Sample	Temp. [°C]	pH	$\log \{Cd^{2+}\}$	$\log \{PO_4^{3-}\}$	$\log \{Cl^-\}$	$\log IAP$
1	25	3.34	-2.865	-15.914	-3.510	-65.58±0.63

All compounds contain intrinsic energy, referred as Gibbs free energy. The Gibbs free energy of a system is defined as the enthalpy of the system minus the product of the temperature and entropy of the system and it may be used to predict the spontaneity of a process. A negative value indicates a spontaneous process, a positive value – a non-spontaneous process, and zero indicates that the system is at equilibrium (Huang, Gobran 2005). The relation between the reaction equilibrium constant (K_{sp}) and the change in Gibbs free energy of reaction (ΔG°_r) is given by the equation:

$$\Delta G^\circ_r = -RT \ln K_{sp} \quad (3)$$

where R is the gas constant ($8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the temperature (298.15 K). This gives a value for ΔG°_r of $374.310 \text{ kJ mol}^{-1}$. Calculation of the Gibbs free energy for the formation of cadmium chlorapatite is enabled by equation 4:

$$\Delta G^\circ_f(\text{CdClap}) = 5\Delta G^\circ_f(\text{Cd}^{2+}) + 3\Delta G^\circ_f(\text{PO}_4^{3-}) + \Delta G^\circ_f(\text{Cl}^-) + RT \ln K_{sp} \quad (4)$$

Based on the values provided by Robie et al. (1978): $\Delta G^\circ_f(\text{Cd}^{2+}) = -77.58$, $\Delta G^\circ_f(\text{PO}_4^{3-}) = -1019.00$ and $\Delta G^\circ_f(\text{Cl}^-) = -131.27 \text{ kJ mol}^{-1}$, and $\log K_{sp} = -65.58$ as experimentally determined above, Gibbs free energy of formation of CdClap may be calculated as $\Delta G^\circ_f(\text{CdClap}) = -3950.48 \text{ kJ mol}^{-1}$. The obtained $\log K_{sp}$ value is higher than the value reported by Eighmy et al. (1997), where $\log K_{sp}$ for cadmium chlorapatite was -49.66 . This difference is probably caused by the difference in methodology - the synthesis of cadmium chlorapatite at high temperatures may cause the formation of the mineral with slightly different properties than those of the natural mineral or those synthesized at low temperatures. The ΔG°_f value describes the amount of energy that is released or consumed when a phase is created from other phases. The mineral with lower energy is more stable. The solubility constant and the Gibbs free energy of formation of cadmium chlorapatite confirm its low solubility and high stability. Comparing the calculated solubility constant of cadmium chlorapatite with the K_{sp} of pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$), it can be seen that K_{sp} is higher for pyromorphite. $\log K_{sp}$ of pyromorphite is -79.6 (Flis et al., 2011) and $\log K_{sp}$ of cadmium chlorapatite is -65.58 . This proves that Cd substituted pyromorphite is less stable than Pb-pyromorphite. Precipitation of Pb-pyromorphite is one of the effective methods to remove lead ions from contaminated soils and solutions. The similarity between pyromorphite and cadmium chlorapatite allows the assumption that cadmium chlorapatite can be successfully used for the immobilization of Cd.

4. Conclusions

Cadmium chlorapatite is a mineral that is less stable and more soluble than chloride pyromorphite. However, its solubility constant is low enough for it to be considered a very stable compound. This is confirmed by the theories currently being researched on the use of apatites to remove cadmium impurities from soil and water. It seems that immobilization of cadmium in the structure of the stable apatite will allow for the effective immobilization of this toxic element.

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5. References

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