



## KINETICS OF STRONTIUM SORPTION IN CALCIUM PHOSPHATE

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## ABSTRACT

Kinetics of strontium sorption by highly dispersed solids: tricalcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ , TCP) and hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ , HAP) were investigated. Analysis of sorption data was made taking into consideration composition and morphology of ultramicro particles. Conclusion is that the isomorphous strontium impurity is a structurally sensitive element for calcium phosphate. It was determined that the beginning of strontium desorption corresponds to the beginning of transformation of the TCP - HAP.  
Keywords: Waste management, Sorption,  $^{85}\text{Sr}$ , Hydroxyapatite

## INTRODUCTION

Calcium phosphate may be used for purification by sorption method of liquid radioactive waste containing strontium [1]. During precipitation amorphous tricalcium phosphate (TCP) is initially formed, which is a metastable form. This phase transforms in time into a stable hydroxyapatite (HAP) [2]. One of the most interesting questions in the process of sorption is the interaction of impurity with the metastable sorbent. While investigating these systems, complexities arise connected with the structure of the metastable solids.

The solids precipitated from highly supersaturated solutions are having extremely small particle sizes approx. 1 nm. Amorphous calcium phosphate ultramicro particle are having the size of some 1.5 nm and those of crystalline hydroxyapatite, some 3 nm [3]. Such small particle sizes are influencing the kinetics of sorption processes.

In this paper, TCP and HAP precipitated under previously described conditions /3,4/ were used as highly dispersed solid, so that we could use the existing data on composition and structure of ultramicro particles. Strontium, as isomorphous impurity of calcium phosphate was used as sorbate. Sorption kinetics data are necessary for optimisation of process of chemical treatment of liquid radioactive waste.

#### MATERIALS AND METHODS

TCP and HAP were precipitated from highly supersaturated solution. Chemical precipitation was done by reagent solution mixing in an efficient micro mixer and the synthesis method was previously described in detail /5/ on the example of barium carbonate and sulphate precipitation.

In this experiment 30 cm<sup>3</sup> of solution I and solution II was mixed. Solution I consisted of 12 mmole of Ca(NO<sub>3</sub>)<sub>2</sub> and 21.6 mmole of HNO<sub>3</sub>. In some cases a certain quantity  $m_0$  (mole) of Sr(NO<sub>3</sub>)<sub>2</sub> marked by <sup>85</sup>Sr was added. Solution II consisted of 7.2 mmole of K<sub>3</sub>PO<sub>4</sub> and approximately 22 mole of KOH. The ratio Ca/P = 1.667 in the initial solution corresponds to the stoichiometric composition of HAP.

Solution I and II was injected under pressure into the mixer and efficient mixing took place (Reynolds number = 2000) for 0.05 s. Under these conditions TCP was formed at initial supersaturation of 10<sup>8</sup>. From the mixer the suspension was flowing through the tube into the receiver for 0.03 s. In the receiver there was already a 0.3 dm<sup>3</sup> of KNO<sub>3</sub> solution, concentration 0.76 mole dm<sup>-3</sup> which was stirred by a magnetic stirrer (Reynolds number = 500). KNO<sub>3</sub> concentration in the receiver was equal to concentration of electrolytes in initial solution at the time of mixing in order to preserve the same ionic strength of solution during flowing of suspension from the mixer into the receiver.

In the preliminary experiment an exact KOH amount was determined which is to be added to the solution II so that the suspension after synthesis in the receiver would have a pH=10.8. Conditions for TCP formation and for its further transformation into HAP were maintained the same as in papers

/3,4/ which made it possible to obtain the solid phase with reproducible particle morphology.

Strontium sorption and desorption kinetics was investigated in order to determine time necessary for establishing equilibrium between the solid phase and solution.

In the first series of experiments  $^{85}\text{Sr}$  radionuclide was injected in the synthesis together with the  $\text{Ca}^{2+}$  ion, i.e. co-precipitation of impurity was performed. In this case it was assumed that the time between the beginning of precipitation and the contact between solid and impurity equals zero ( $t=0$ ). TCP in the receiver is diluted six times and a partial desorption of co-precipitated impurity may occur. Therefore, portions of suspension were taken at various time intervals, centrifugated and the Sr concentration in natant measured by radiochemical method. Results are shown on Figure 1.

In the second series of experiments the same  $^{85}\text{Sr}$  quantity was injected in the receiver in the  $\text{KNO}_3$  solution before the beginning of synthesis. This means that the impurity was coming in contact with TCP solid after approximately  $t=0.3$  s. Kinetics of solution composition change in this case is the kinetics of sorption of impurity (Figure 1).

## RESULTS

Kinetics of strontium sorption and desorption into calcium phosphate is shown in Figure 1. Sorption A was calculated on the basis of material balance:

$$A = (m_0 - cV) m_1^{-1}$$

where  $m_0$  (mole) is the mass of injected  $\text{Sr}^{2+}$  ion,  $c$  ( $\text{mole dm}^{-3}$ ) is concentration of  $\text{Sr}^{2+}$  ion in solution,  $V$  ( $\text{dm}^3$ ) is the suspension volume and  $m_1$  (mole) is the mass of  $(\text{PO}_4)^{3-}$  in solid. The value  $m_1$  practically is equal to the mass of  $(\text{PO}_4)^{3-}$  injected into the system because the remaining phosphate concentration in the solution amounts is approximately  $10^{-5}$   $\text{mole dm}^{-3}$ .

Figure 1 shows that TCP solid retains firmly impurities in the interval of  $0 < t < 100$  min. and in the interval  $100 < t < 300$  min. a partial rejection of impurity into solution occurs.

At  $t > 400$  min. equilibrium is established. Value of sorption and desorption is constant and coincides in both series within the experimental error.

#### DISCUSSION

Rejection of strontium from solid into solution at  $t < 300$  min. can not be explained by diffusion from particle bulk because the shape of kinetic curve does not in the least resemble the diffusion kinetics. It is possible to explain strontium behaviour taking into consideration transformation of TCP into HAP. TCP 5 min. after synthesis is X-ray amorphous /4, 6/. At  $100 < t < 300$  min. the lines characteristic for HAP appear and at  $t > 400$  solid phase becomes a well-crystallized HAP. Therefore, it may be concluded that strontium behaviour reflects TCP - HAP transformation i.e. strontium - the isomorphous impurity is a structurally sensitive element for calcium phosphate. This means that phase transformation induces partial rejection of strontium. Strontium "detects" beginning of transformation much earlier than other methods. X-ray analysis determine HAP after approximately 200 min. /6/. Kinetic changes of  $\text{Ca}^{2+}$  concentration in solution determines the beginning of transformation at 400 min. on the basis of induction period /7/.

In the experiment with  $t = 0.3$  s. sorption attains the same value as in experiment with  $t = 0$  but this process is slowed down by TCP - HAP transformation.

Comparison of these two kinetics shows that in the first case equilibrium is achieved for less than 100 min. while in the second case a much longer time is needed. It is possible to explain this difference by detailed knowledge of morphology of particles formed during this process.

Electrone microscopy has shown /4/ that the solid consists of aggregates in which ultramicro particles are visible (size approx. 1.5 nm.). In the case of  $t = 0$  ultramicro particles are formed in the presence of Sr and a fast establishment of equilibrium with solution is possible. In the second case particles are already formed so that Sr must migrate into

particle bulk in order to acquire equilibrium and therefore a much longer time is needed. Detailed analysis of these processes will be given in the paper submitted for press /4/.

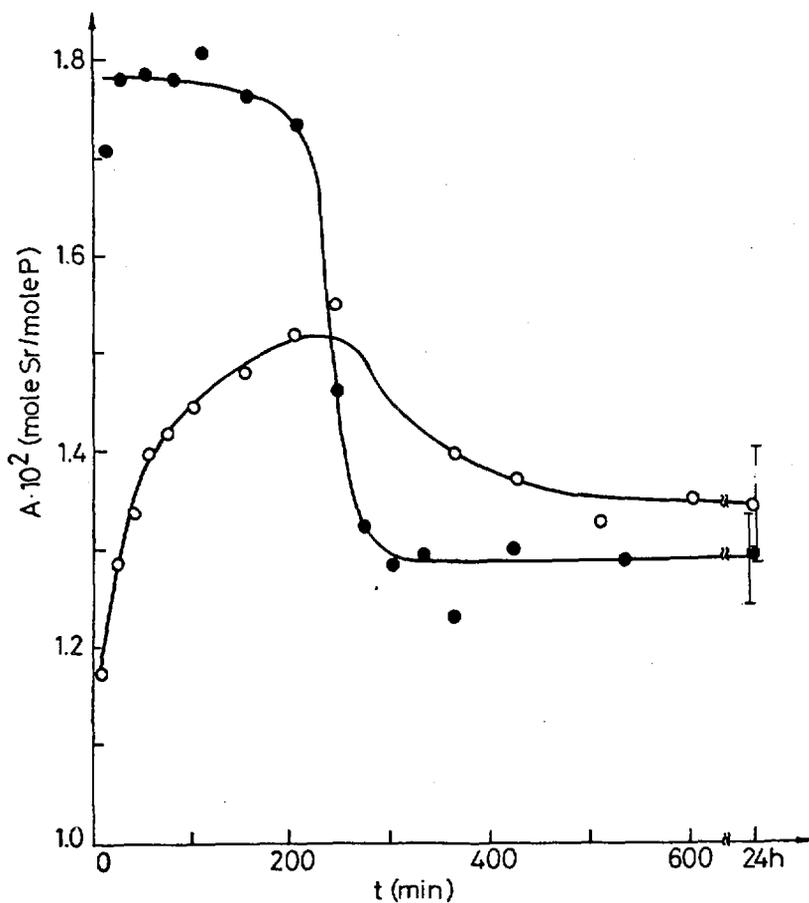


Figure 1. Kinetics of strontium sorption (o) and desorption (●) in calcium phosphate.

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