

Characterisation of the protolytic properties of synthetic carbonate free fluorapatite

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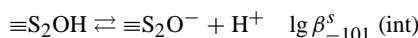
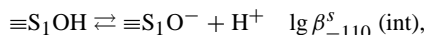
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Abstract

The acid/base surface properties of carbonate free fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) have been characterised using high precision potentiometric titrations and surface complex modelling. Synthetic carbonate free fluorapatite was prepared and characterised by SEM, XRD, FT-IR and FT-Raman. The specific surface area was determined to be $17.7 \pm 1.2 \text{ m}^2 \text{ g}^{-1}$ with BET (N_2 adsorption). The titrations were performed at $25 \pm 0.2 \text{ }^\circ\text{C}$, within the pH range 5.7–10.8, in 0.10 and 0.50 mol dm^{-3} NaNO_3 ionic media. Experimental data were interpreted using the constant capacitance model and the software FITEQL 4.0. The surface equilibria:



well describes the surface characteristics of synthetic fluorapatite. The equilibrium constants obtained were: $\lg \beta_{-110}^s \text{ (int)} = -6.33 \pm 0.05$ and $\lg \beta_{-101}^s \text{ (int)} = -8.82 \pm 0.06$ at $I = 0.10 \text{ mol dm}^{-3}$. At the ionic strength 0.50 mol dm^{-3} , the equilibrium constants were slightly shifted to: $\lg \beta_{-110}^s \text{ (int)} = -6.43 \pm 0.05$ and $\lg \beta_{-101}^s \text{ (int)} = -8.93 \pm 0.06$. The number of active surface sites, N_s , was calculated from titration data and was found to be 2.95 and 2.34 sites nm^{-2} for the ionic strengths 0.10 and 0.50 mol dm^{-3} , respectively. pH_{PZC} or the IEP was found to be 5.7 from Z-potential measurements.

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1. Introduction

Magnetite deposits of the “Kiruna-type”, containing significant quantities of apatite, are the base for several iron ores around the world. Some examples besides the original Kiruna deposit (Kiruna, Sweden) are in northern Chile (Nyström and Henríquez [1]) and in the Bafq district, Iran [2]. Since the phosphorus originating from the apatite is detrimental for most steel processes used today, it has to be separated from the magnetite. In Kiruna, this is performed by both magnetic separation and flotation of apatite with a collector of fatty acid type. To fully understand the adsorp-

tion step during the flotation, and to be able to achieve the optimal conditions, it is necessary to characterise the surface properties of both the value mineral (magnetite) and the gangue mineral (apatite), as well as the interactions between the surfaces of these minerals. This includes delineating the protolytic properties of fluorapatite and magnetite, and proton exchanges between the mineral surfaces. Magnetite surfaces are easily oxidised in contact with air, giving maghemite ($\gamma\text{-Fe}_2\text{O}_3$) as the primary oxidation product, Wesolowski et al. [3]. It is therefore also of great interest to characterise the surface properties of the maghemite phase. Knowledge of surface properties of the fluorapatite–hydroxoapatite system is also of great importance within dentistry and osteology, since apatite is the main mineral in both teeth and bones.

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Two earlier studies of the acid–base properties of fluorapatite surfaces were found [4,5]. In both, evaluation was performed using the surface complexation concept and the constant capacitance model. Wu et al. [4] studied a well-ground natural fluorapatite mineral with a specific surface area of $9.3 \text{ m}^2 \text{ g}^{-1}$. The concentration of active surface sites was estimated as $N_s = 12.3 \text{ sites nm}^{-2}$ using calculations based on crystallographic data. Perrone et al. [5] studied synthetically prepared carbonate fluorapatite with a specific surface area of $8.8 \pm 0.1 \text{ m}^2 \text{ g}^{-1}$ and a corresponding mineral compound (francolite) with the specific surface area $13.9 \pm 0.1 \text{ m}^2 \text{ g}^{-1}$. Based on titration data the concentration of active surface sites was estimated as $3.1 \text{ sites nm}^{-2}$.

The aim of this study is to increase the knowledge concerning the conditions for fluorapatite in the separation process from magnetite. As a first step the acid–base properties of synthetically prepared and well-characterised carbonate free fluorapatite are studied using potentiometric titrations and surface complex modelling. Synthetic mineral samples are used in order to obtain well-defined substances incorporating a minimum of impurities, as well as a high specific surface area. All results are based on experimental data achieved from potentiometric titrations. Compared to earlier works, the aim of this study is to make additional contributions to the knowledge about the protolytic properties of fluorapatite in general. To our knowledge, no earlier studies or surface complex models of carbonate free fluorapatite are presented. This work also forms a part of a larger project, which aims to simultaneously model flotation-like systems including magnetite and its oxidation products, together with apatite and flotation reagents.

2. Materials and methods

Synthetic fluorapatite was prepared according to the method described by Penel et al. [6]. A solution of $0.4 \text{ mol dm}^{-3} \text{ Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (solution A) was prepared by dissolving 94.47 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (MERCK) in 1000 cm^3 of Milli-Q water. Another solution, $0.24 \text{ mol dm}^{-3} (\text{NH}_4)_2\text{HPO}_4$ and $0.18 \text{ mol dm}^{-3} \text{ NH}_4\text{F}$ (solution B), was prepared by dissolving 31.69 g of $(\text{NH}_4)_2\text{HPO}_4$ (Riedel–de Haën) and 5.93 g of NH_4F (KEBO) in 1000 cm^3 of Milli-Q water. All chemicals used were of analytical grade. The solutions were prepared in glass vessels, the risk of interactions between F^- and the glass may be neglected due to the relatively high pH and the short contact time during preparation and synthesis. Solution A was added drop-wise into the boiling solution B for 1 h under stirring. A white “milky” precipitate was formed, pH was adjusted to approximately 9 by adding small portions of 25% NH_3 . The product was aged for 1 h at 80°C under stirring. When the precipitate had settled and cooled to room temperature, it was washed with CO_2 -free Milli-Q water and dialysed in Millipore 12-14000 D tubes until the conductivity reached a stable value around $10 \mu\text{S cm}^{-1}$. The product was dried

overnight at room temperature, and then stored in a desiccator containing silica gel as a drying agent.

2.1. Solutions

All solutions were prepared using boiled Milli-Q water and chemicals of analytical grade. A standard solution of dilute HNO_3 $0.500 \text{ mol dm}^{-3}$ was prepared from HNO_3 (MERCK) and standardized using TRIS (hydroxymethylaminomethane) (Trizma-base) with methyl red as indicator. From this standard solution, a $0.0100 \text{ mol dm}^{-3} \text{ HNO}_3$ solution was prepared. NaOH solutions were formed from a saturated solution of NaOH (MERCK) and standardized against the known $0.0100 \text{ mol dm}^{-3} \text{ HNO}_3$ solution. The total ionic strength of these two solutions was set to 0.10 mol dm^{-3} by the addition of NaNO_3 . A second pair of $0.0100 \text{ mol dm}^{-3}$ acid and base solutions was prepared at the ionic strength 0.50 mol dm^{-3} .

2.2. Equipment

During the potentiometric titrations a pH electrode (Ingold) and a reference electrode, a double-junction Ag/AgCl-electrode (Orion 900200 [®]D/junct. ref. electrode), were used. The titrant was added to the titration vessel by an automatic system for precise EMF titrations. A Mettler DV 70 stirrer was used.

2.3. XRD

Characterisation of the fluorapatite was done with XRD. The XRD analysis was performed using a SIEMENS D5000 X-ray diffractometer. The straight base line and the sharp peaks of the diffractogram (Fig. 1) confirm that the product is well crystallised. The diffractogram has no “extra peaks” compared to reference diffractogram JCPDS-15-0876 and the one published in [7] for fluorapatite, indicating that there are no other phases than fluorapatite present in the sample. The XRD diffractogram is almost identical to the

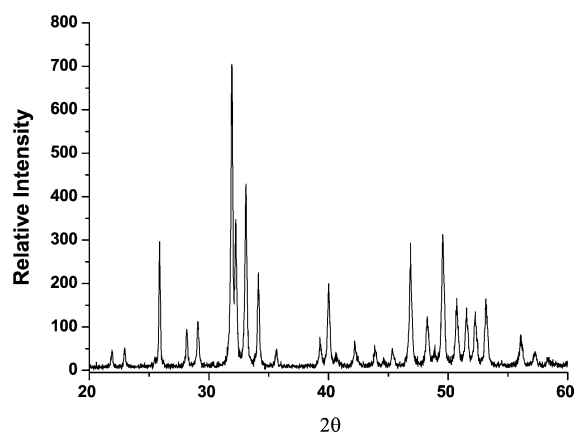


Fig. 1. XRD diffractogram of synthetic carbonate free fluorapatite.

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