

## **The Surface Properties of Aqueous Fluorapatite and Maghemite with Reference to the Dephosphorization of Magnetite**

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### **INTRODUCTION**

The Luossavaara-Kirunavaara AB (LKAB) in northern Sweden is one of the biggest suppliers in the world of high grade iron ore products. However, the Kiruna magnetite ore deposit contains an average of 1 wt% phosphorus (mainly fluorapatite), which is detrimental to the blast-furnace technology and the quality of the iron products. Consequently the apatite content has to be minimized. After magnetic separation the dephosphorization is performed by froth flotation of the apatite from magnetite fines using a fatty acid type collector (ATRAC) in combination with sodium silicate. The concentrated magnetite fines are then treated in a pelletizing plant.

The main difficulty during this reverse flotation process is the need to stabilize the phosphorus content in the magnetite concentrate at a satisfactory level of less than 0.025 wt% P with no residual collector coating on magnetite, which will trouble the formation of pellets. An increased dosage of collector would possibly reduce the phosphorus content in the magnetite concentrate but it may introduce a significant loss of production due to lower strength of the "green pellets" caused by the collector adsorbed at the magnetite surface. Thus the collector is used in small amounts to form less than a monomolecular layer on the apatite particle surfaces (starvation level).

Sodium silicate is used as a dispersant in optimum amounts i.e.  $300\text{-}500\text{ g t}^{-1}$  corresponding to  $2.4\cdot 10^{-4} - 4\cdot 10^{-4}\text{ mol dm}^{-3}$ . Small additions of water glass in the apatite flotation system possibly serve as a depressant and will also influence the particle dispersions. ATRAC-152 functions both as a collector and a frother but their mutual relationship and eventual synergistic effect as well as the mechanism of adsorption are not fully understood. The collector concentration together with the pH of the flotation pulp is an important key variable to control the flotation. For LKAB magnetite fines containing fluorapatite it has been reported that a pH about 8.5–9 is optimum for the flotation of apatite using a collector containing carbonyl functions. Obviously the success of the dephosphorization by flotation is heavily depending on the proper control of surfaces and interfaces in the mixture of several solid phases suspended in the aqueous solution through which the air bubbles are being dispersed. The apatite flotation from magnetite fines is depending on parameters like the hydrodynamics of the flotation pulp, pulp pH, temperature, collector concentration, level and speciation of ions (e.g.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) in the process water. Furthermore the possible mineral interactions in the flotation pulp which may be considered as a mixed mineral suspension have to be taken into account. Actually the different surface properties of fluorapatite and iron oxides with respect to surface hydration and surface charge (i.e.  $\text{pH}_{\text{pzc}}$ ), protolytic surface properties, surface site density and function, surface area, surface capacitance etc will strongly influence the separation.

As a part of the current research in the Agricola Research Centre (ARC) we have studied the protolytic surface properties and interactions in a mixed mineral suspension of fluorapatite and

maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) by means of potentiometric titrations in combination with SEM, Raman and  $^1\text{H}$   $^{31}\text{P}$  MAS NMR spectroscopy.

## **MATERIALS**

**Fluorapatite**. Synthetic fluorapatite was prepared according to Penel et al. (Penel, 1997). The surface area was determined using the BET ( $\text{N}_2$  adsorption) method to  $17.7 \pm 1.2 \text{ m}^2 \text{ g}^{-1}$ . The morphology and shape of the mineral particles were studied with SEM and they were found to occur as hexagonal rods.

- Hexagonal rods
- BET surface area  $17.7 \pm 1.2 \text{ m}^2 \text{ g}^{-1}$
- XRD, FT-IR and FT-Raman

Further identification and characterization were performed by means of XRD, FT-IR and Raman spectroscopy. The XRD diffractogram confirms that the product is well crystallized and that no phases beside fluorapatite are present, (Jarlbring 2005a).

**Maghemite**. Synthetic maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) was prepared according to Garcell et al. (Garcell 1998) and Massart et al. (Massart 1987) with a few modifications. SEM measurements displayed that the particles were spherical with an average diameter of  $32 \pm 11 \text{ nm}$ . Further identification and characterization were performed by means of FT-IR and XRD. The surface area was determined by the BET method to  $89.7 \pm 6.3 \text{ m}^2 \text{ g}^{-1}$ . (Jarlbring 2005b)

- Spherical particles
- BET, surface area  $89.7 \pm 6.3 \text{ m}^2 \text{ g}^{-1}$
- Particle diameter  $30\text{-}50 \pm 10 \text{ nm}$
- XRD and FT-IR

## **EQUIPMENT**

### **Potentiometric Titrations**

During the potentiometric titrations an Ingold pH electrode was used. The reference electrode was a double junction Ag/AgCl electrode (Orion 900200 D/junction reference electrode. The titrant was added to the titration vessel applying an automatic system of precise EMF titrations, a PC was automatically controlling that the preset criteria were followed and then recording the potentials after each addition of titrant. The stirring was performed with a Mettler DV 70 propeller stirrer.

### **FT-IR Spectroscopy**

Spectra were recorded by using a Bruker IFS 66/v spectrometer equipped with an MCT detector. One hundred scans were combined and the resultant interferogram was Fourier transformed to obtain a resolution of  $2 \text{ cm}^{-1}$ . Samples for transmission measurements were put between calcium fluoride windows with a 6 micron spacer.

### **$^{31}\text{P}$ and $^1\text{H}$ MAS NMR**

Solid state magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were recorded using a Chemagnetics/Varian CMX-360 NMR spectrometer with a T3 4 mm MAS probe (Chemagnetics) and a magnetic field of 8.46 T. Both cross polarization (CP) and single-pulse experiments with proton decoupling were applied. The spectrometer software Spinsight 4.1 was used to process the recorded NMR spectra.

### **$^{31}\text{P}$ MAS NMR**

In the  $^{31}\text{P}$  MAS NMR single-pulse experiments, the  $90^\circ$  pulse was  $3 \mu\text{s}$  and the nutation frequency of the decoupling pulse was 60 kHz. The spinning frequencies were 4.2 and 12 kHz in the single-pulse

experiments. For the CP experiments the Hartmann-Hahn condition was fulfilled at the nutation frequencies of 50 kHz and 89 kHz for protons and phosphorus nuclei, respectively. 85 %  $\text{H}_3\text{PO}_4$  was used as an external standard and set to 0 ppm. The spinning frequency 4.2 kHz was chosen to avoid overlap of centre bands with spinning sidebands and to give the centre band in the NMR spectrum the highest intensity. CP experiments at different contact times (ct) in the interval 0.2-3.0 ms, were performed in order to estimate distance differences between protons and the phosphorus nuclei. A short  $^1\text{H}$  to  $^{31}\text{P}$  distance indicates that the actual phosphorus site is located near the protons and consequently, it is exposed at (or near) the surface where the protons and hydroxyl groups are adsorbed.

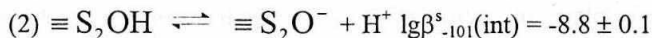
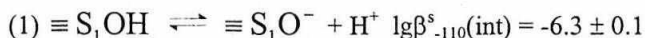
To avoid inconsistencies in the analysis due to the overlap of broad resonance lines the deconvolution routine in the spectrometer software Spinsight 4.1 was used to evaluate the integral intensity for each resonance line originating from phosphorus site. The deconvolution was first performed automatically by the software and then improved further manually for each spectrum to achieve optimum fit and reliability for the chemical shifts obtained of the same phosphorus sites but in different samples.

### **$^1\text{H}$ MAS NMR**

As external reference TMS was used (in a capillary glass-tube,  $\varnothing$  1 mm) and set to 0.0 ppm. The spinning frequency was 10 kHz and the spectra were recorded as single-pulse experiments, where  $90^\circ$  pulse, acquisition time and pulse delay were  $3\mu\text{s}$ , 40 ms and 15 s respectively. The spinning frequency is sufficient to partly average out the dipole-dipole interaction between protons on the mineral surface and to obtain partly resolved resonance peaks in the  $^1\text{H}$  MAS NMR spectra. In previous NMR studies of apatites and calcium phosphates even lower spinning frequencies ( $< 10$  kHz) have been implemented giving  $^1\text{H}$  MAS NMR spectra with a reasonable resolution. The recorded and Fourier transformed spectra were corrected on a background signal from the empty rotor, a broad resonance line originated from the plastic turbine and spacers in the 4 mm MAS rotors was subtracted after an appropriate normalization of the signal intensity.

### **RESULTS AND DISCUSSION**

The potentiometric titrations generate data to establish a model of the protolytic surface reactions of aqueous fluorapatite and maghemite separately as well in a mixture of minerals. The general fluorapatite model involves two different surface sites  $\text{S}_1$  and  $\text{S}_2$ , which are found to be deprotonated according to the following scheme (Jarlbring 2005a):



Then the potentiometric titrations produce data which make it possible to make thermodynamic models of protolytic surface reactions but this method can not supply a direct micro molecular information about the specific surface sites involved in the process. The evaluation of experimental data is founded on the measurements and analyses in solution which are supposed to reflect the surface activity. The description of the specific surface sites involved has to be based on more or less qualified assumptions and a sound chemical judgement.

In order to achieve more specific surface information on the molecular level the potentiometric titrations need to be combined with spectroscopic techniques preferably in situ i.e. including the interfacial water. The use of FT-IR (ATR) and Raman spectroscopy is well established and these techniques are frequently used but we have recently showed that MAS NMR spectroscopy can be a powerful tool to make more detailed evaluations of the surface sites involved in the proton adsorption and desorption reactions (Jarlbring 2006 and Sandström et al 2006)

Then the  $^{31}\text{P}$  CP MAS NMR studies have indicated that reaction at the surface site  $S_1$ , equation (1), on aqueous fluorapatite corresponds to the deprotonation of the surface phosphate sites  $\equiv \text{PO}_2\text{H} \rightleftharpoons \equiv \text{PO}_2^- + \text{H}^+$ ,  $\equiv \text{PO}_3\text{H}_2 \rightleftharpoons \equiv \text{PO}_3\text{H}^- + \text{H}^+$  and  $\equiv \text{PO}_3\text{H}^- \rightleftharpoons \equiv \text{PO}_3^{2-} + \text{H}^+$ . Obviously the deprotonation of the phosphorus sites will generate negative surface sites.

The reaction described by equation (2) refers to the protolytic reactions at the calcium surface sites, which can presumably be specified as  $\equiv \text{CaOH}_2^+ \rightleftharpoons \equiv \text{CaOH} + \text{H}^+$  and  $\equiv \text{CaOH} + \text{H}_2\text{O} \rightleftharpoons \equiv \text{Ca}(\text{OH})_2^- + \text{H}^+$ .

$\zeta$ -potential measurements of fluorapatite as a function pH indicate that the surface is negatively charged at  $\text{pH} > 5.5$ . In light of the results of potentiometric titrations in combination with MAS NMR we can conclude that the surface protolytic equilibria are explained by proton exchange with both calcium and phosphorus surface sites. The surface phosphate groups consist of neutral and negative species and the calcium sites involve positively charged  $\equiv \text{CaOH}_2^+$ , neutral  $\equiv \text{CaOH}$  as well as negatively charged  $\equiv \text{Ca}(\text{OH})_2^-$  in aqueous suspension. (Sandström et al 2006)

The fluorapatite surface is zwitterionic, where the positively charged  $\equiv \text{CaOH}_2^+$  sites are balanced by negatively charged  $\equiv \text{PO}_3\text{H}^-$  sites at  $\text{pH} \approx 5.5$ . At  $\text{pH} > 5.5$  the deprotonated phosphate groups will determine the surface charge and at  $\text{pH} < 5.5$  the protonated calcium sites will make the mineral surface positive before it starts to dissolve at low pH. (Wu 1991) We have visualized the surface speciation of aqueous fluorapatite as a function of pH in Fig.1. The different protolytic species are located at pH values where they approximately dominate and the corresponding  $\text{pK}_a$  values obtained from potentiometric titrations are indicated on the pH axes.

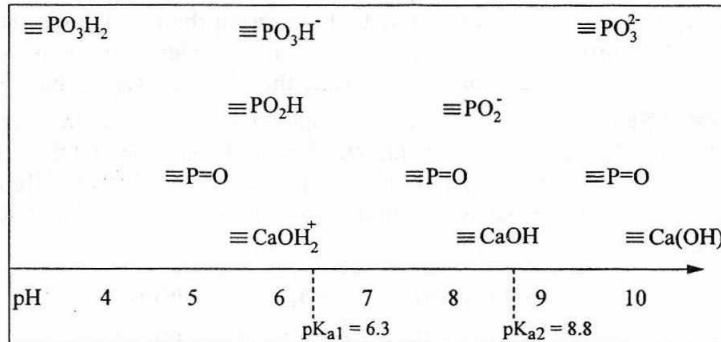
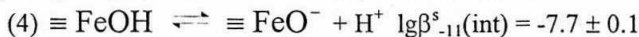


Fig. 1: The Dominating Surface Species in Aqueous Suspension of Fluorapatite as a Function of pH. The Speciation is based on the Results from Potentiometric Titrations in Combination with  $^1\text{H}$  and  $^{31}\text{P}$  Single-Pulse and  $^{31}\text{P}$  CP/MAS NMR Spectroscopy

The protolytic surface speciation of aqueous maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) was obtained from potentiometric titrations of maghemite suspensions. Maghemite was chosen (instead of magnetite) as a model substance of iron ore because it is expected to be more stable towards oxidation in aqueous suspensions. (Jarlbring et al 2005b). The reactions for protonation and deprotonation of the maghemite surface can be described by



With reference to this model  $pH_{pzc}$  is 6.6 (exp. 6.2) which indicates that the surface species  $\equiv FeOH$  dominates in the area  $5.5 < pH < 7.7$  and thus the maghemite surface is negatively charged in the flotation pulp at LKAB ( $pH$  8.5-9). A brief summary of the distribution of surface species on aqueous maghemite as a function of  $pH$  is given in figure 2.

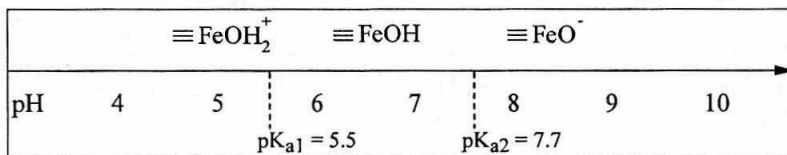
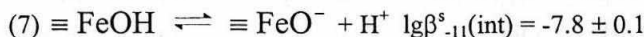


Fig. 2: The Dominating Surface Species in Aqueous Suspension of Maghemite As a Function of  $pH$ . The Speciation is Obtained From Potentiometric Titrations

The protolytic properties in a mixed mineral system of aqueous fluorapatite/maghemite are characterized by a reduced surface site density of fluorapatite, while the surface site density of maghemite remains less affected. This was clearly presented by the results from potentiometric titrations of mixed mineral suspensions (Jarlbring 2005c)



The evaluation of experimental titration data of the mixed mineral system indicated that the protolytic properties of the surface phosphorus sites are strongly affected by the interaction with the maghemite particles.

The proton exchange at these sites is drastically reduced and the surface reaction with reference to (1) is not longer necessary in the model to explain data. Comparing the reaction constants of the mixed mineral system with the corresponding results of the single mineral titrations it is obvious that reactions (5) and (7) are affected to a minor degree while the species  $\equiv FeOH_2^+$  has become noticeably less acidic. Furthermore SEM images from an X-ray mapping analyze of the fluorapatite surface after titration indicated that the maghemite particles are attached to the surface and they seem to block the some of the active surface sites (Jarlbring et al 2005 c). The interaction between fluorapatite and  $Fe^{2+}$  was further established by  $^{31}P$  CP MAS NMR studies of fluorapatite exposed to a solution of ferrous ions. (Sandström et al 2006)

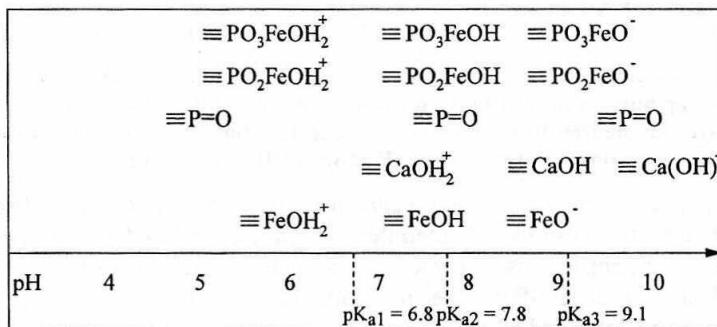


Fig. 3: The Approximate Location of Dominating Surface Species in a Mixture of Aqueous Fluorapatite and Maghemite. The Speciation is Based on Results From Potentiometric Titrations of a Mixture of Fluorapatite-Maghemite in Aqueous Suspension. Additional Information is Obtained From  $^1H$  and  $^{31}P$  MAS NMR, SEM Images and Raman Spectroscopy



In figure 3 we have visualized and compiled all the available information from potentiometric titrations, SEM images, Raman spectroscopy as well as  $^1\text{H}$  and  $^{31}\text{P}$  MAS NMR as a simple picture showing the approximate distribution of dominating surface species in a mixture of fluorapatite-maghemite at  $4 < \text{pH} < 11$ .

The pH in the flotation pulp at LKAB is about 8.5 – 9. At this pH the surface of free iron ore particles are mainly negatively charged (maghemite and magnetite) as well as the phosphorus sites of fluorapatite. Most of the phosphate sites could possibly be blocked by interaction with iron ore particles or dissolved ferrous ions from these particles. The potentiometric titrations in combination with spectroscopic techniques have the potential to reveal new insight into the surface speciation in aqueous suspensions of fluorapatite as well as of fluorapatite/maghemite mixtures as a function of pH.

The interaction between the fluorapatite surface and ATRAC was studied by means of  $^1\text{H}$  MAS NMR. Three samples of fluorapatite were equilibrated for 2 h. at pH 5.0, 8.7 and 10.1 in an ATRAC solution with a concentration of approximately  $0.04 \text{ mg dm}^{-3}$ . After equilibration the solid samples were filtrated and dried in a desiccator before measuring in the NMR spectrometer. The single-pulse  $^1\text{H}$  MAS NMR spectra of fluorapatite/ATRAC powder samples are presented in figure 4.

The relative integral intensities of the resonance lines at 0.9 ppm and 3.8 ppm are dramatically increased in these samples compared to the  $^1\text{H}$  MAS NMR spectra of aqueous suspensions of pure fluorapatite.

Earlier  $^1\text{H}$  MAS NMR studies on apatite and calcium phosphates have assigned the resonance line at 0.9 ppm to protons in hydroxyl groups. These groups at aqueous fluorapatite surfaces are present mainly as  $\equiv \text{CaOH}$  sites at both neutral and slightly alkaline pH and then the resonance peak at 0.9 ppm is assigned to this group (Jarlbring et al 2006). As indicated above other possible calcium hydroxide surface groups are  $\equiv \text{CaOH}_2^+$  and  $\equiv \text{Ca}(\text{OH})_2^-$ . The resonance line at 1.3 ppm is increasing in alkaline suspensions in relation to other neutral or acidic samples and it is therefore assigned to the species  $\equiv \text{Ca}(\text{OH})_2^-$  (Sandström et al 2006).

The assignment of the  $\equiv \text{CaOH}_2^+$  sites is more uncertain. Presumably protons in these surface sites have chemical shifts close to 5 ppm (chemical shifts of protons in water molecules). It may be difficult to distinguish between protonated surface sites ( $\equiv \text{CaOH}_2^+$  or  $\equiv \text{PO}_x\text{H}$ ) and physisorbed water, which give rise to broad  $^1\text{H}$  NMR signal in the region 2 - 8 ppm.

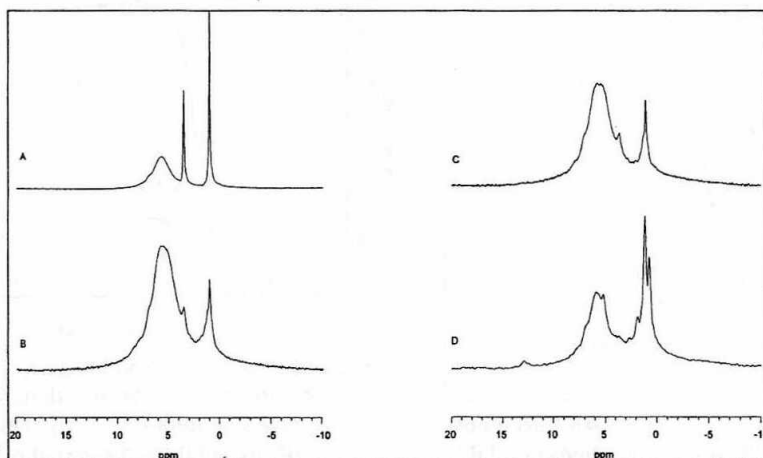


Fig. 4: Single Pulse  $^1\text{H}$  MAS NMR Spectra of Fluorapatite Equilibrated in ATRAC Solution at (A) pH 5.0, (B) pH 8.7, (C) pH 10.1 and (D) pH 8.5 with a Ten Fold ATRAC Concentration

The results visualized in figure 4 clearly indicate that the adsorption of ATRAC on fluorapatite in aqueous suspensions is strongly pH dependant. At pH 5 (fig. 4A) the resonance lines at 0.9 and 3.8 ppm are very pronounced and sharp, which indicate a strong adsorption at the calcium surface sites. This result is indirectly an indication that the resonance line at 3.8 ppm may be related to the  $\equiv\text{CaOH}_2^+$  sites. At higher pH (fig. 4 B and 4C) the adsorption seems to be decreased but the spectra indicate that the calcium surface sites are still involved in the adsorption process. When the added concentration of ATRAC is ten fold increased, the relative integral intensity of the resonance line at 0.9 ppm also increases while the peak at 3.8 ppm is becoming less pronounced (fig.4 D).

The froth flotation pulp at LKAB forms a closed system and the process water is recirculated.

This gives rise to a relatively high total concentration of calcium ions ( $3\text{-}4\cdot 10^{-3}$  mol  $\text{dm}^{-3}$ ) that could possibly influence the flotation process. To investigate how the calcium ion concentration may influence the adsorption of ATRAC we prepared two samples, one by adding 200  $\mu\text{l}$  of  $8.6$  mmol  $\text{dm}^{-3}$  (corresponding to a  $\text{Ca}^{2+}$  concentration of  $0.4\cdot 10^{-3}$  mol  $\text{dm}^{-3}$ )  $\text{Ca}(\text{NO}_3)_2$  solution to 0.15 g fluorapatite in aqueous suspension and the other by mixing 4.5 ml of a saturated  $\text{Ca}(\text{OH})_2$  solution with 0.15 g fluorapatite equilibrated with ATRAC. The filtrated solid samples were measured by  $^1\text{H}$  MAS NMR and the spectra obtained were very similar to pure fluorapatite indicating a drastically reduced adsorption of ATRAC. Consequently there is a competition for ATRAC between the  $\text{Ca}^{2+}$  ions in solution and the calcium sites at the fluorapatite surface. See figure 5 A and 5 B. The interaction between ATRAC and calcium ions was further investigated by FTIR spectroscopy by adding a solution of calcium nitrate in ethanol to a solution of ATRAC in the same solvent. The resulting precipitate was studied by infrared transmission spectroscopy as well as NIR-Raman spectroscopy. ATRAC obviously contains four carbonyl functions in addition to unsaturated carbons and hydroxyl groups. The most distinct infrared absorbance bands in the carbonyl stretching region of pure ATRAC appear at 1740 and 1711  $\text{cm}^{-1}$ . The latter band is shifted to 1723  $\text{cm}^{-1}$  in an ethanol solution. However, these two carbonyl functions are clearly affected by the presence of  $\text{Ca}^{2+}$  ions as shown in figure 6. The intensity at 1740  $\text{cm}^{-1}$  is reduced whereas the intensity at 1723  $\text{cm}^{-1}$  is increased upon mixing calcium nitrate and ATRAC in ethanol solution. This is a clear indication of the importance of the carbonyl functions in the interaction between ATRAC and the fluorapatite surface. In this context it could be mentioned that a calcium hydroxide solution in ethanol indicated an even stronger increase in

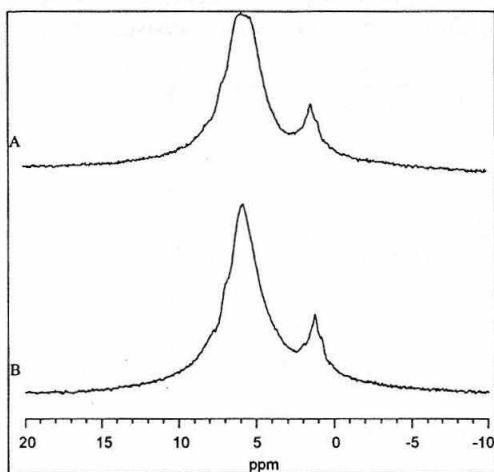


Fig. 5: Single-Pulse  $^1\text{H}$  MAS NMR Spectra of Fluorapatite Equilibrated in Solutions of ATRAC Including (A)  $8.6$  Mmol  $\text{Dm}^{-3}$   $\text{Ca}(\text{NO}_3)_2$  and (B) Saturated Solution of  $\text{Ca}(\text{OH})_2$

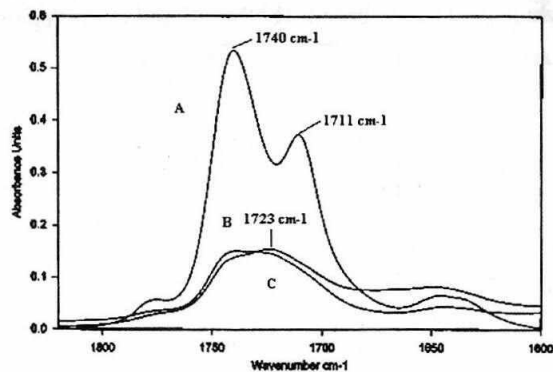
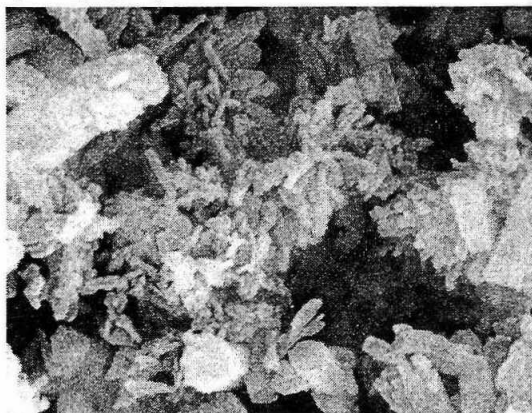
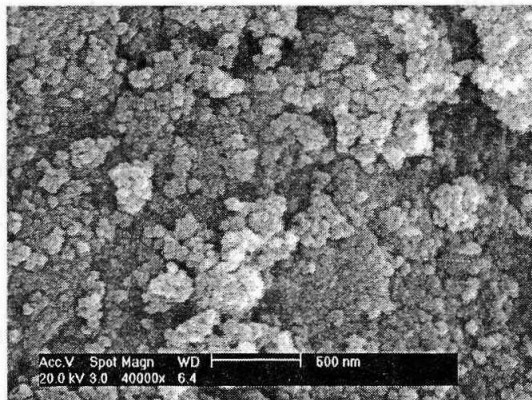


Fig. 6: Infrared Spectra of Pure ATRAC (Upper Spectrum A), ATRAC in Ethanol Solution (B), and the Precipitate Formed When a Calcium Nitrate Solution in Ethanol is Mixed with a Solution of ATRAC in the Same Solvent (C)

the intensity of the  $1723\text{ cm}^{-1}$  band although this increase could be partly attributed to the presence of hydroxyl groups.



**Illustration 1**



**Illustration 2**

## CONCLUSIONS

The combination of potentiometric titrations and spectroscopic techniques reveal valuable information about mineral surface speciation on a molecular level.

The protolytic properties of aqueous fluorapatite surfaces are controlled by a number of phosphorus sites and calcium hydroxyl species.

At the pH values present in the LKAB flotation process (pH 8.5 -9) the phosphate sites are negatively charged and characterized by the interaction with iron ore particles and/or ferrous ions from the pulp.

The ATRAC adsorption is markedly pH dependant and the interaction with the fluorapatite surface occurs at the calcium hydroxyl sites.

Excess calcium ions in the flotation pulp seem to form ATRAC complexes in solution and compete for the collector with the fluorapatite surface.

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